SOME FLUORINATED CYCLOBUTENES AND THEIR DERIVATIVES

Thesis by

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To the memory of

Thomas Dale Stewart

ABSTRACT

Cyclobutene structures were established for the cycloaddition products of 1-ethynylcyclohex-1-ene with trifluorochloroethylene or difluorodichloroethylene. The orientations of the addends were in accord with theories developed previously.

Hydrolysis of the fluorinated cyclobutenes with sulfuric acid gave halogen-substituted cyclohexenylcyclobutenones as well as cyclohex-1-enylcyclobutadienoquinone. Some halide displacement reactions of the adducts were found to give, in general, products corresponding to reaction by $SN2'$ mechanisms. 1, 1, 2-Trifluoro-2-chloro-3-(cyclohex-1-enyl)-cyclobutene gave Diels-Alder adducts with maleic anhydride and dicarbethoxyacetylene. 1, 1-Difluoro-2, 4-dichloro-3-(cyclohex-1-enyl)-cyclobutene with triethylamine underwent dehydrohalogenation and afforded, by means of an unusual rearrangement, 2-fluoro-1, 3-dichloro-5, 6, 7, 8-tetrahydronaphthalene.

The nuclear magnetic resonance (NMR) spectra of the fluorinated cyclobutenes and cyclobutenones showed spectra which were anomalous in terms of simple NMR theory but which could be explained by assumption of cross-ring spin-spin coupling between hydrogen and fluorine.

TABLE OF CONTENTS

TABLE OF CONTENTS (Cont.)

TABLE OF CONTENTS (Cont.)

TABLE OF CONTENTS (Cont.)

CHAPTER I

GENERAL INTRODUCTION

DISCUSSION

During studies of the preparation of tetrafluoroethylene by pyrolysis of difluorochloromethane, Benning, Downing, McHarness and Park (1, 2) first discovered octafluorocyclobutane as a side product. Shortly thereafter, in 1946, Harmon showed that octafluorocyclobutane resulted from the thermal dimerization of tetrafluoroethylene. Further he found that trifluorochloroethylene and difluorodichloroethylene thermally dimerized to cyclobutanes and to these cyclobutanes he assigned head-to-head orientation of the initial monomers, for example eq. 1.

(1) $$2\ CF_2{=}CFCl \longrightarrow \begin{matrix} CF_2\text{-}CFCl \\ | \quad | \\ CF_2\text{-}CFCl \end{matrix}$$

The ability of tetrafluoroethylene to form four-membered ring compounds was subsequently exploited by Coffman, Barrick, Cramer, and Raasch (3-10). These workers studied the cycloaddition* of tetrafluoroethylene with ethylene, substituted alkenes, dienes, and enynes. In general they found the ease of cycloaddition of tetrafluoroethylene was in the order enynes and dienes > alkenes conjugated with an activating oxygen or nitrogen function > 1-alkenes > non-terminal alkenes. Some examples of the reactions studied

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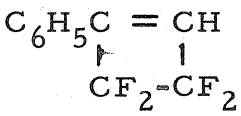
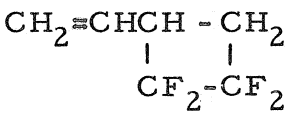
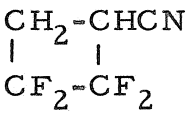
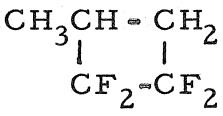
*"Cycloaddition" is taken to be a thermal ring-forming reaction involving alkenes or alkynes. In all of the cases of interest to the present thesis, substituted cyclobutanes or cyclobutenes result from addition of an alkene to an alkene or an alkene to an alkyne.

are shown in eqs. 2-5.

(2) $C_6H_5C{\equiv}CH + CF_2{=}CF_2 \longrightarrow$ 

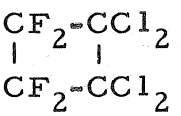
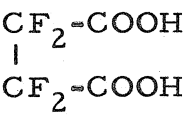
(3) $CH_2{=}CHCH{=}CH_2 + CF_2{=}CF_2 \longrightarrow$ 

(4) $CH_2{=}CHCN + CF_2{=}CF_2 \longrightarrow$ 

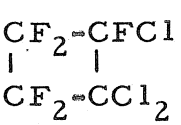
(5) $CH_3CH{=}CH_2 + CF_2{=}CF_2 \longrightarrow$ 

The reaction of eq. 4 was also studied by Barney and Cairns (11).

Concurrent with Harmon's initial work (3, 14), Henne and Ruh studied the dimerizations of trifluorochloroethylene, eq. 1, and difluorodichloroethylene, eq. 6 (12). Henne and Zimmerschied (13) unambiguously demonstrated that the addends came together in the head-to-head orientation by opening the cyclobutane ring to form tetrafluorosuccinic acid.

(6) $2CF_2{=}CCl_2 \longrightarrow$  $\longrightarrow$ 

Kropa and Padbury showed that the cycloaddition of trifluorochloroethylene to difluorodichloroethylene resulted in a product with adjacent CF_2 groups, eq. 7 (15, 16).

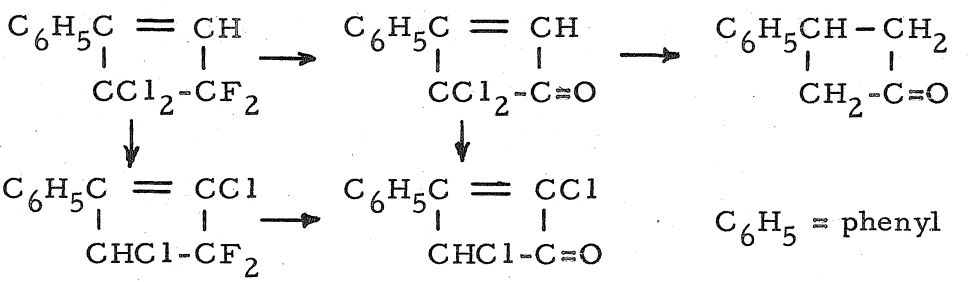
(7) $CF_2{=}CFCl + CF_2{=}CCl_2 \longrightarrow$ 

Later work by various workers (17-19) confirmed the cycloadditions of the fluorochloroalkenes described in eq. 1, 6, and 7.

An investigation of the cycloadditions of difluorodichloroethylene was carried out by Burch (20). He clearly showed that methyl acrylate, methyl methacrylate, acrylonitrile, 2, 3-dimethylbutadiene, and chloroprene each gave but one product when they underwent cycloaddition with difluorodichloroethylene. Further, he obtained considerable evidence that cyclobutanes were formed. He showed the chloroprene adduct to be 1, 1, 2-trichloro-3, 3-difluoro-1-ethenylcyclobutane. Burch did not firmly establish the orientations of the other cycloaddition products, but in general he recognized the now accepted pattern of orientations as will be discussed later.

The general difficulty in obtaining large quantities (100 g. or more) of substituted cyclobutanes or cyclobutenes by classical methods of synthesis led Roberts, Kline, and Simmons to investigate the cycloaddition of difluorodichloroethylene to phenylacetylene (21). They found that a single cyclobutene was formed and established its structure as 1, 1-difluoro-2, 2-dichloro-3-phenylcyclobutene. A study of this cyclobutene showed that it could be converted to several new and interesting phenylcyclobutenes and phenylcyclobutenones, eq. 8.

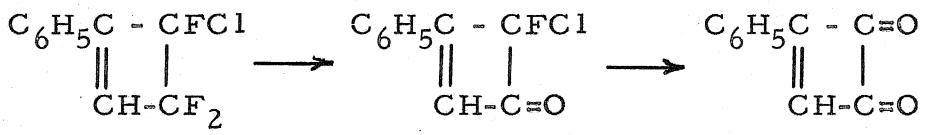
(8)



Subsequent studies by Roberts and coworkers (21-29) of the derivatives from 1, 1-difluoro-2, 2-dichloro-3-phenylcyclobutene have elucidated the chemistry of the cyclobutene and cyclobutenone ring systems considerably. A review of much of this work has been published (24).

Cycloaddition of trifluorochloroethylene to phenylacetylene was found by Smutny and Roberts (30) to result in 1, 1, 2-trifluoro-2-chloro-3-phenylcyclobutene. This trifluorochlorocyclobutene was converted into a very unusual compound, phenylcyclobutadienoquinone, eq. 9.

(9)



An X-ray diffraction study of phenylcyclobutadienoquinone supports the correctness of the structure established by chemical evidence (34). From the heat of combustion and estimation of the phenyl-ring and four-ring interaction energy, the resonance energy of the cyclobutadieneoquinone system was calculated to be 3-6 kcal. (32).

The wide variety and unusual nature of the products derived from cycloaddition adducts of phenylacetylene and the ease with which large amounts of substituted cyclobutenes are obtained, suggested that another series of compounds be studied where the phenyl group was replaced by an appropriate alkenyl or alkyl group. For the purpose of studying the cyclobutadienoquinone system and

obtaining the resonance energy of that system, the parent molecule would be desired; however, attempts to synthesize cyclobutadienoquinone from the cycloaddition adduct of ethyl propiolate and trifluorochloroethylene failed (32).

The commercial availability of 1-ethynylcyclohexan-1-ol and the ease of its conversion to 1-ethynylcyclohex-1-ene made a study of the cyclohexenylcyclobutene system a logical choice. Further, the formation of cyclohexylcyclobutadienoquinone might be possible and more information could be obtained on the cyclobutadienoquinone system.

This thesis reports the formation of new fluorochlorocyclohexenylcyclobutenes and the reactions of these derivatives. A general discussion of cycloaddition has been presented as well as a nuclear magnetic resonance study that establishes cross-ring spin-spin coupling between hydrogen and fluorine in substituted cyclobutenes (33).

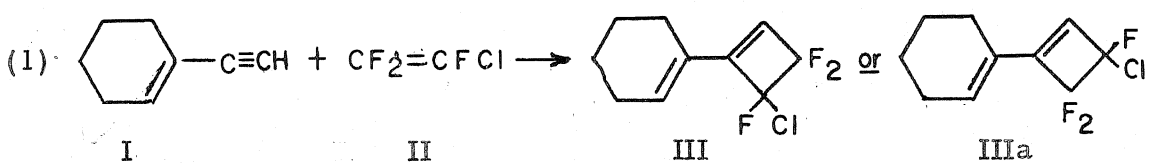
CHAPTER II

FORMATION OF SUBSTITUTED CYCLOBUTANES AND CYCLOBUTENES BY CYCLOADDITION

RESULTS AND DISCUSSION

The Cycloaddition Products from 1-Ethynylcyclohex-1-ene and Fluorochloroethylenes.

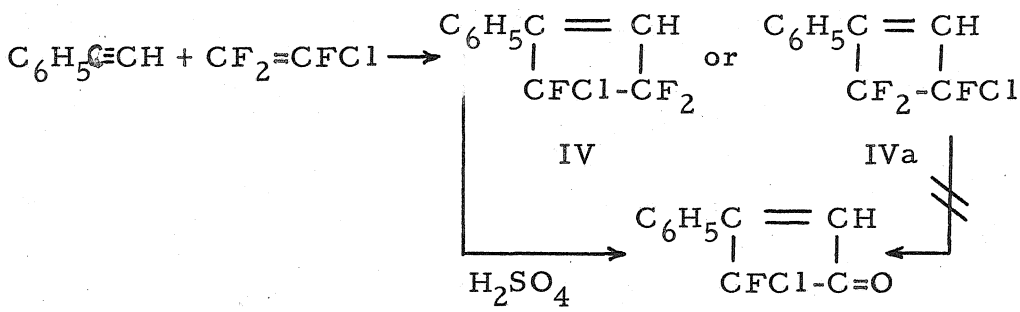
When 1-ethynylcyclohex-1-ene (I) and trifluorochloroethylene (II) were heated in sealed tubes at 95° for 20 hours, a single cycloaddition product was formed, which was assigned the structure 1, 1, 2-trifluoro-2-chloro-3-(cyclohex-1-enyl)-cyclobutene (III) on the basis of its elemental analysis, infrared, ultraviolet, and nuclear magnetic resonance (NMR) spectra, chemical reactions, and by analogy with the structure assigned to the adduct from phenylacetylene and trifluorochloroethylene (30).



I II III IIIa

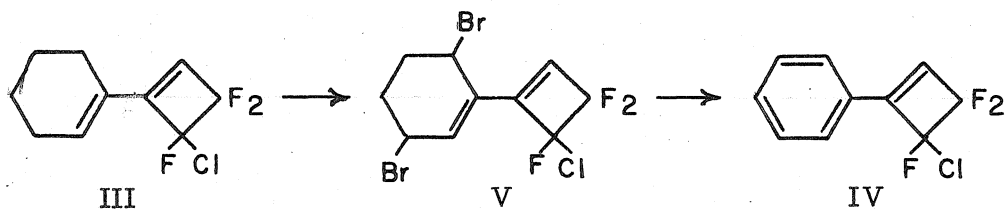
The structural assignment for the latter adduct as 1, 1, 2-trifluoro-2-chloro-3-phenylcyclobutene (IV) was made by Smutny and Roberts (30, 31) who had hydrolyzed IV with sulfuric acid to 2-fluoro-2-chloro-3-phenylcyclobutenone whose ultraviolet absorption maximum at 2795 Å. required that a fully conjugated structure be assigned. However, the possible structure IVa for the initial adduct was not completely ruled out.

(2)



It was assumed that trifluorochloroethylene added to phenylacetylene and 1-ethynylcyclohex-1-ene in the same direction. It was of interest to prove this assumption. When III (or IIIa) was heated under reflux in carbon tetrachloride with two moles of N-bromosuccinimide, a dibromide was isolated which was assigned the structure, 1, 1, 2-trifluoro-2-chloro-(3, 6-dibromocyclohex-1-enyl)-cyclobutene (V). Dehydrobromination of V with two moles of potassium hydroxide in t-butyl alcohol resulted in a product which was shown by comparison of the refractive indices and the infrared, ultraviolet and NMR spectra to be identical with the adduct from phenylacetylene and trifluorochloroethylene.

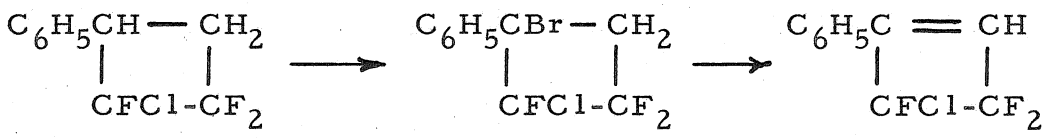
(3)



The conversion of III to IV, eq. 3, shows that the orientation of trifluorochloroethylene cycloadditions was the same for phenylacetylene and 1-ethynylcyclohex-1-ene.

Cycloaddition of trifluorochloroethylene and styrene was found by Silversmith, Kitahara, Caserio, and Roberts (25) to give a cyclobutane whose structure was unambiguously established as

1, 1, 2-trifluoro-2-chloro-3-phenylcyclobutane (VI) by its analysis, chemical reactions and proton NMR spectrum (25, 33). The reaction between VI and one mole of N-bromosuccinimide resulted in formation of 1, 1, 2-trifluoro-2-chloro-3-bromophenylcyclobutane (VII) which was easily dehydrobrominated to IV.

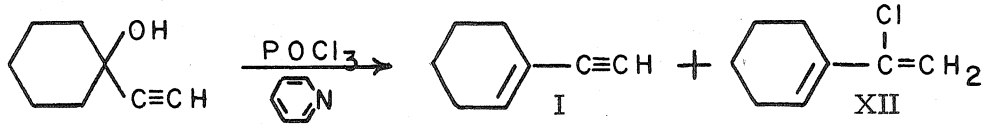
(4) 

VI VII IV

It should be clear that trifluorochloroethylene adds to styrene, phenylacetylene, and 1-ethynylcyclohex-1-ene to give four-ring compounds with the gem-difluoro group across the ring from the phenyl or cyclohexenyl group.

When I was heated at 95° for 24 hours with difluorodichloroethylene (VIII), a solid adduct (IX) was formed. The structure of IX was established as 1, 1-difluoro-2, 2-dichloro-3-(cyclohex-1-enyl)-cyclobutene by elemental analysis, chemical tests, and infrared, ultraviolet, and NMR spectra as well as by conversion to 1, 1-difluoro-2, 2-dichloro-3-phenylcyclobutene (X) and thence to 2, 2-dichloro-3-phenylcyclobutenone (XI) (21).

The preparation of 1-ethynylcyclohex-1-ene from 1-ethynylcyclohexan-1-ol by the method of Hamlet, Henbest and Jones (35) often resulted in the isolation of a side product, 1-(1-chloroethenyl)-cyclohex-1-ene (XII), eq. 5.

(5) 

I XII

The cycloaddition of XII with II at 130° resulted in 1, 1, 2-trifluoro-2, 3-dichloro-3-(cyclohex-1-enyl)-cyclobutane (XIII) as shown by its chemical and physical properties and by dehydrochlorination to III, eq. 6.

(6) $C_6H_9C(Cl)=CH_2$ (XII) $\longrightarrow$ $C_6H_9C(Cl)\text{-}CH_2$ / $CFCl\text{-}CF_2$ (XIII) $\longrightarrow$ $C_6H_9C=CH$ / $CFCl\text{-}CF_2$ (III)

C_6H_9 = Cyclohex-1-enyl

Discussion of Orientation and Mechanism in the Cycloaddition Reaction.

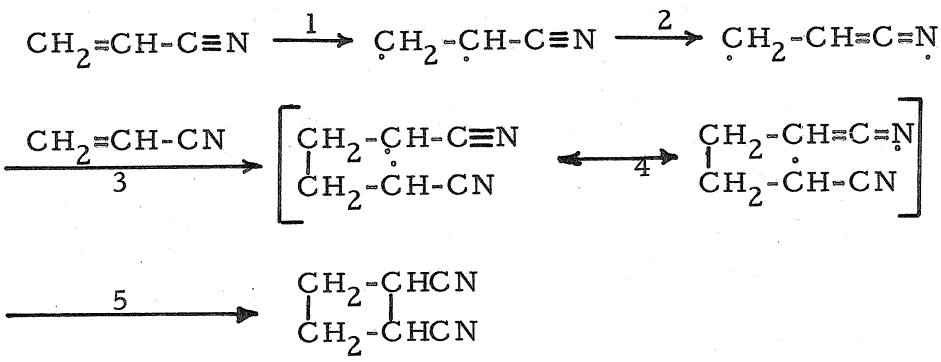
In the preceding cycloaddition reactions, only one of the two possible products was formed as shown by the examples in eqs. 1 and 2 where III and IV were formed, respectively; IIIa and IVa were not detected. Earlier workers also reported that only one of the two possible adducts was formed when unsymmetrical reagents were used as addends (12-20). The head-to-head dimerizations of trifluorochloroethylene (II) and difluorodichloroethylene (VIII) were mentioned earlier in the General Introduction. For example, dimerization of difluorodichloroethylene results in 1, 1, 2, 2-tetrafluoro-3, 3, 4, 4-tetrachlorocyclobutane and not its isomer, 1, 1, 3, 3-tetrafluoro-2, 2, 4, 4-tetrachlorocyclobutane.

(7) $2CF_2=CCl_2 \longrightarrow$ $CF_2\text{-}CCl_2$ / $CF_2\text{-}CCl_2$ Not $CF_2\text{-}CCl_2$ / $CCl_2\text{-}CF_2$

No explanation has yet been published for the orientation that results in the cycloaddition of fluorochloroethylenes with themselves or for the cycloadditions of phenylacetylene or styrene with either trifluorochloroethylene or difluorodichloroethylene.

An explanation for the formation of 1, 2-dicyanocyclobutane by the dimerization of acrylonitrile was offered by Coyner and Hillman (36) and is shown schematically in eq. 8.

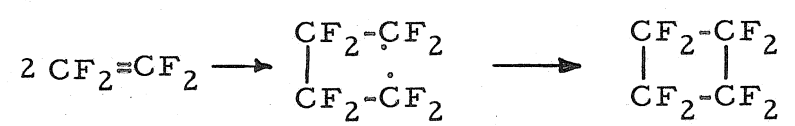
(8)



They suggested the first step (step 1) of the dimerization was "splitting of one electron pair of the double-bond" of acrylonitrile and that the resulting diradical was stabilized by resonance (process 2). A carbon-carbon bond between β-carbon atoms of two acrylonitrile molecules then formed (step 3) and the resulting new diradical was stabilized by resonance (process 4). Cycloaddition was completed by formation of a single bond between α-carbons (step 5).

A diradical intermediate was also postulated in the formation of octafluorocyclobutane from tetrafluoroethylene by Lewis and Naylor (37), eq. 9.

(9)



Recent work by Hazeldine (38) and Miller and Koch (39, 40) has established the direction of free-radical attack on the double bond of fluoroalkenes. From this work the relative stabilities of two possible radicals such as $RCF_2CFCl\cdot$ and $RCFClCF_2\cdot$ can be

inferred. Equations showing the preferred point of attack by a free radical, R°, on a double bond for a few selected fluoroalkenes are given in Table I.

Table I

Direction of Radical Attack (R°) on Fluoroalkenes (38-40)

$CH_2=CHF \longrightarrow RCH_2\dot{C}HF$

$CH_2=CHCl \longrightarrow RCH_2\dot{C}HCl$

$CF_2=CFCF_3 \longrightarrow RCF_2\dot{C}FCF_3$

$CF_2=CFCl \longrightarrow RCF_2\dot{C}FCl$

$CH_2=CF_2 \longrightarrow RCH_2\dot{C}F_2$

$CH_2=CHCN \longrightarrow RCH_2\dot{C}HCN$

$CH_2=CHCOOCH_3 \longrightarrow RCH_2\dot{C}HCOOCH_3$

The theory of resonance predicts that when a free radical (R°) attacks phenylacetylene, styrene, or 1-ethynylcyclohex-1-ene at the triple bond ~~that~~ the corresponding radicals formed would be $C_6H_5\dot{C}=CHR$, $C_6H_5\dot{C}HCH_2R$, and $C_6H_9\dot{C}=CHR$. This prediction is confirmed by chemical evidence such as the anti-Markownikoff addition of hydrogen bromide to styrene in the presence of a peroxide (41).

If the mechanism proposed by Coyner and Hillman is generalized, and if the experimentally observed direction of radical attack on fluoroalkenes is taken together with the direction of radical attack predicted by resonance theory on phenylacetylene, styrene, and 1-ethynylcyclohex-1-ene, then it is possible to predict the orientation of addends for the cycloadditions shown in eqs. 1, 2, and 6.

The structure of the carbon four-membered ring compound formed from two addends in the cycloaddition reaction can be predicted by writing a diradical transition state using the more stable of the possible radicals for each addend. The formation of 1, 1, 2-trifluoro-2-chloro-3-(cyclohex-1-enyl)-cyclobutene is shown as an example, eq. 10.

(10) $C_6H_9C{\equiv}CH + CF_2{=}CFCl \rightarrow [C_6H_9\dot{C}{=}CH \;|\; F\dot{C}Cl\text{-}CF_2] \rightarrow C_6H_9C{=}CH \;|\; FCCl\text{-}CF_2$

I II III

C_6H_9 = cyclohex-1-enyl

In eq. 10, four possible diradicals would have to be considered.

$R\dot{C}{=}CH \;|\; F\dot{C}Cl\text{-}CF_2$ IIIa‡

$R\dot{C}{=}CH \;|\; \dot{C}F_2\text{-}CFCl$ IIIb‡

$RC{=}\dot{C}H \;|\; \dot{C}F_2\text{-}CFCl$ IIIc‡

$RC{=}\dot{C}H \;|\; FCCl\text{-}\dot{C}F_2$ IIId‡

Of the possibilities IIIa‡ corresponds to the diradical intermediate that would be expected from a mutual radical attack of the addends (Table I and discussion above). IIIa‡ would be predicted as the diradical of the lowest energy. The diradicals IIIb‡ and IIIc‡ are expected to be less favorable while diradical IIId‡ corresponds to the worst possible combination. The observed cycloadditions of trifluorochloroethylene and difluorodichloroethylene with themselves and with phenylacetylene, styrene, and 1-ethynylcyclohex-1-ene give the products predicted by forming the diradical intermediate

from mutual radical attack by the addends.

The principle for predicting products from cycloadditions includes the cycloadditions of difluorodichloroethylene observed by Burch (20) and these are predicted in Table II.

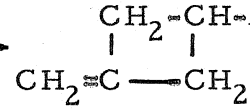
Table II

Predicted Products from Cycloaddition of Difluorodichloroethylene with Various Addends (20)

Addend	Predicted Product
Methyl acrylate	$\overbrace{CCl_2CF_2CH_2CHCO_2CH_3}$
Methyl methacrylate	$\overbrace{CCl_2CF_2CH_2C(CH_3)CO_2CH_3}$
Acrylonitrile	$\overbrace{CCl_2CF_2CH_2CHCN}$
2, 3-Dimethylbutadiene	$\overbrace{CCl_2CF_2CH_2C(CH_3)C(CH_3)=CH_2}$
Chloroprene	$\overbrace{CCl_2CF_2CH_2C(Cl)CH=CH_2}$ *

*Another adduct, $CCl_2CF_2CH_2CH\,C(Cl)=CH_2$, could be formed. Chloroprene and tetrafluoroethylene formed two products by addition across either bond. Cycloaddition across the chlorovinyl double bond was favored by a factor of five (4).

Cycloaddition of allene with numerous activated alkenes has been reported by Cripps, Williams, and Sharkey (42) to give substituted 3-alkylidenecyclobutanes, eq. 11.

(11) $CH_2=C=CH_2 + CH_2=CH-A \longrightarrow$ 

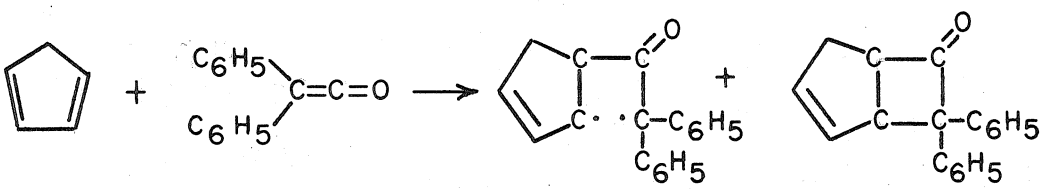
A = CN, CO_2R, COOH, CHO, Aryl

The products formed in eq. 10 are those predicted by resonance theory (41) and the diradical mechanism; allene and acrylonitrile are used as examples in eq. 12.

(12) $CH_2{=}C{=}CH_2 + CH_2{=}CHCN \longrightarrow CH_2{=}C(CH_2{-}\dot{C}HCN){-}CH_2 \longrightarrow CH_2{=}C(CH_2{-}CHCN){-}CH_2$

The thermal dimerization of allene to 1, 2-dimethylenecyclobutane (43) is also in agreement with a diradical mechanism.

Staudinger initially investigated the addition of diphenylketene to cyclopentadiene and to styrene and derivatives thereof (44-47). His work was repeated by later workers who also studied the addition of diphenylketene to 1, 3-hexadiene, cyclohexene, and cyclopentene (48-51). The products from cyclopentadiene and 1, 3-hexadiene are the ones predicted by assuming a radical attack on the carbonyl carbon of diphenylketene, eq. 13.

(13) 

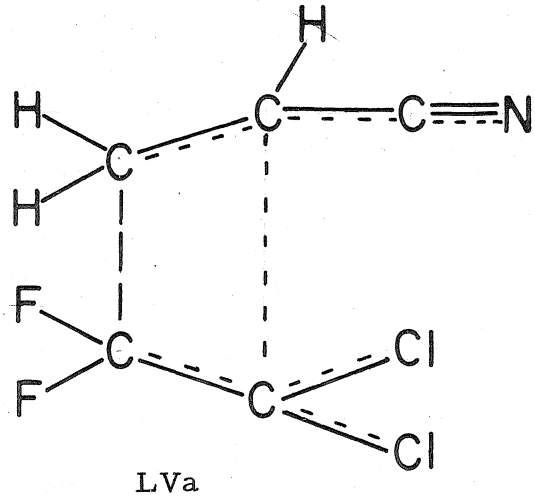
The structure of the adduct from styrene and diphenylketene also agrees with the structure predicted by an intermediate diradical (51). Additions of dimethylketene and ketene to conjugated dienes and substituted alkenes has been reported (47, 52). Structures for the adducts were not established but can be predicted on the basis of an intermediate diradical.

Dimerizations of substituted ketenes do not give products that would be predicted by a diradical mechanism, presumably because the reaction mechanism is ionic. It seems reasonable to assume that substituted ketenes can undergo additions by either an

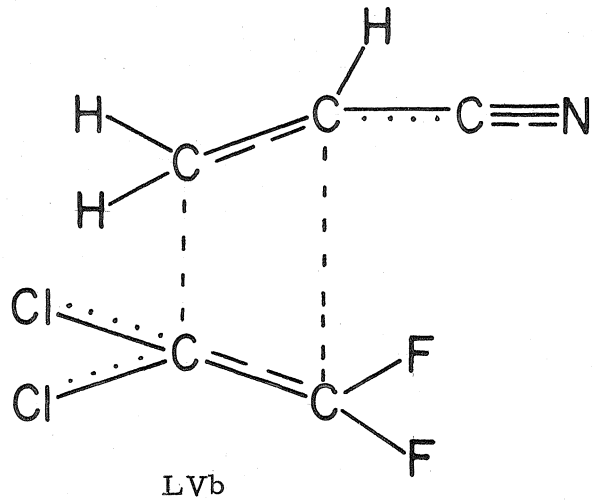
ionic controlled or a radical controlled path depending on the polarizability and radical nature of the other addend.

In addition to the fluoroalkenes discussed earlier, perfluoropropene (53, 61), perfluoroacrylonitrile (54), 1, 3-perfluorobutadiene (55), and α, β, β-trifluorostyrene (56) have been reported to dimerize thermally to cyclobutanes. Presumably these would all have head-to-head orientation of the monomer in the final cyclobutane. A few non-fluorinated alkenes have been reported to dimerize to cyclobutanes. The thermal dimerization of butadiene (57), vinylacetylene (58), divinylacetylene (59), and styrene (60) are believed to give cyclobutanes with head-to-head orientations of the monomers.

Throughout the preceding discussion a diradical intermediate in cycloadditions was assumed. In actuality, there is no reason to require a bona fide diradical intermediate of the type indicated in eqs. 8-10, 12, and 13. However, a diradical mechanism does lead to accurate predictions of the course of the reaction. Alternatively and preferably the reaction can be conceived as a four-center reaction that involves making both bonds of the four-membered ring at once but, however, <u>not</u> necessarily symmetrically. Indeed, it has been reported that addition of radical inhibitors to a cycloaddition reaction mixture has no inhibiting effect on the formation of desired product(s) (4, 12, 21). Consider the cycloaddition of acrylonitrile and difluorodichloroethylene. Two of the several possible unsymmetrical transition states are shown as LVa and LVb. In LVa, the bond between the methylene and difluoromethylene carbons is considered to be formed to a greater extent than the bond between the



LVa



LVb

dichloromethylene and the cyanomethylene carbons. This arrangement is expected to be more favorable than LVb (or the other possible unsymmetrical transition states) since together the dichloro- and cyanomethylene carbons should be better able to tolerate a mutually low bond order (and concomitant free valences) if the resonance arguments cited before with regard to the diradical mechanism are valid.

A kinetic study of the dimerizations of trifluorochloroethylene (II) and difluorodichloroethylene (VIII) showed the cycloadditions to be second order. The activation energies were 26 kcal. (64). A point of particular interest and significance was that the dimerization of II led to a 5:1 ratio of cis- to trans- 1,2-dichlorohexafluorocyclobutanes. A 1:1 cis- to trans- ratio would be predicted on a statistical basis*. Steric interaction between the chlorine atoms in the cis-configuration, would be a destabilizing influence. Van der Waals attractions are too small by a factor of 10 to account for the predominance of the cis-isomer (62). A difference of about 1 kcal. is

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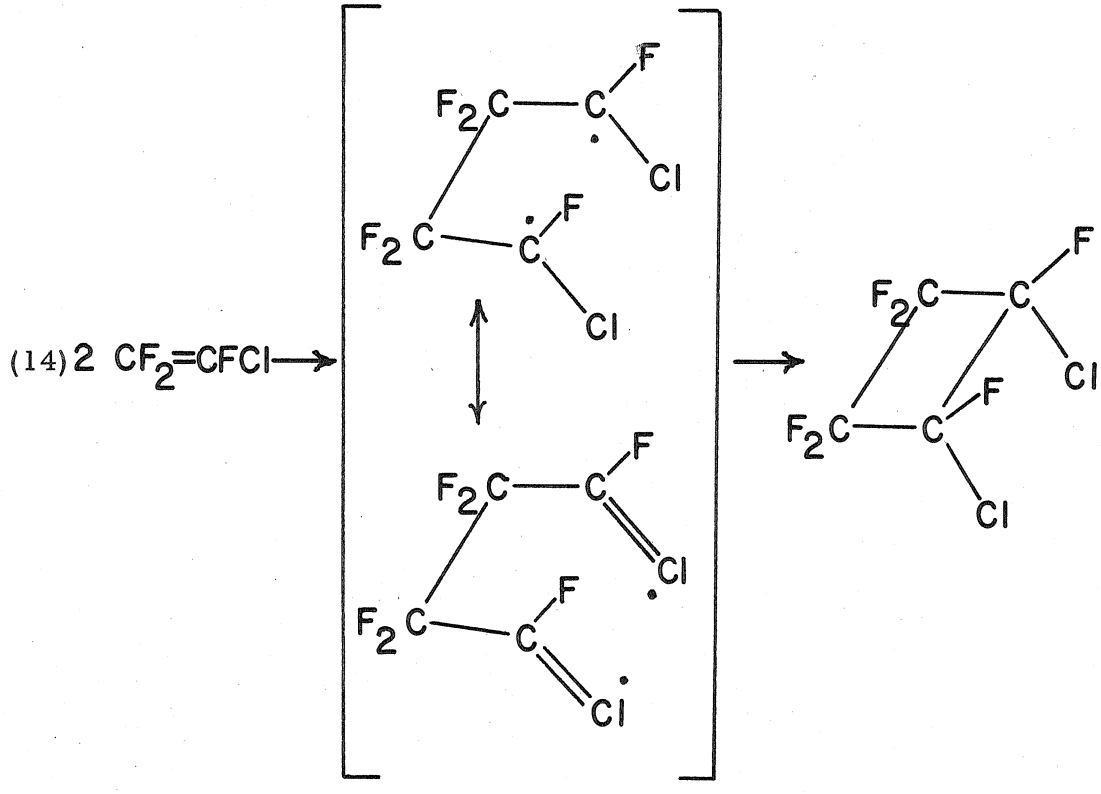
*An error in calculation of predicted cis- to trans- ratio was made in the published work which gave 2:1 rather than 1:1 (64).

required in the activation energies for the formation of cis- and trans- dimers to account for the observed 5:1 ratio in favor of the cis-dimer.

If diradical resonance forms for the dimerization transition states are written, one can see the possibility for bonding between the d-shell electrons of two chlorines; such bonding, of course, would cause the cis configuration to be favored, eq. 14 (67)*.



A still more generalized view of cycloadditions has been offered by Roberts (63). He suggests that many cycloadditions may depend on the formation of an intermediate quasi six-membered ring. When applied to the system of eq. 13, four carbons and two chlorines can be regarded as becoming bonded by four electrons in six molecular orbitals, two of the six orbitals being d-orbitals of chlorine as shown in Fig. 1.

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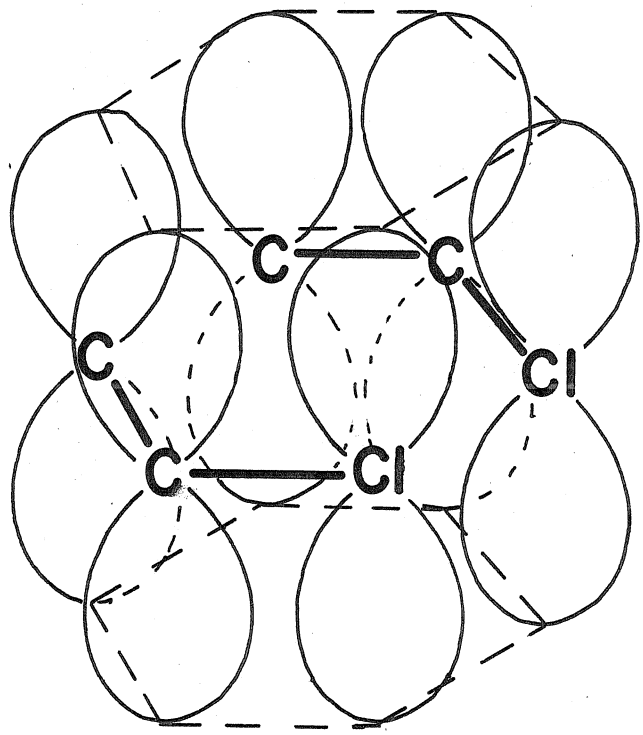
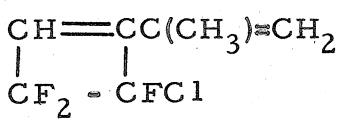
*A similar explanation has been offered for the configuration of the dimerization product of chloroprene (67).

Fig. 1

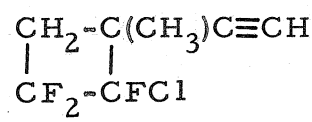


Cycloaddition Reactions of Isopropenylacetylene.

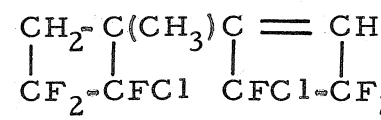
From the cycloaddition of isopropenylacetylene and trifluorochloroethylene, three products were isolated. The infrared spectra, chemical analyses and application of the rule for cycloaddition permit the assignment of structures for the new adducts as 1, 1, 2-trifluoro-2-chloro-3-isopropenylcyclobutene (XV), 1, 1, 2-trifluoro-2-chloro-3-ethynyl-3-methylcyclobutane (XVI) and 1, 1, 2-trifluoro-2-chloro-3-methyl-3-(3, 3, 4-trifluoro-4-chloro-cyclobut-1-enyl)-cyclobutane (XVII).



XV



XVI



XVII

EXPERIMENTAL

All melting and boiling points are uncorrected. Analyses are by Dr. A. Elek, Los Angeles, California. Infrared and ultraviolet spectra are considered in Chapter III of this thesis, and nuclear magnetic resonance spectra in Chapter IV.

1-Ethynylcyclohex-1-ene (I). - The procedure of Hamlet, Henbest, and Jones was modified to increase the scale of the reaction (35). From 813 g. (6.56 moles) of 1-ethynylcyclohexan-1-ol* was obtained 393 g. (5.80 moles, 57.7%) of I, b.p. 54-59° (29-31 mm.) $n^{25}D$ 1.4938. A higher boiling material, b.p. 80-92°(29-31 mm.) $n^{25}D$ 1.5182, amounted to 100 g. and was identified as 1-(1-chloroethenyl)-cyclohex-1-ene (XII) (65).

In second and third runs, from 800 to 805 g. (6.45 and 6.50 moles) of 1-ethynylcyclohexanol were obtained 540 and 614 g. (5.08 moles, 79% and 5.80 moles, 89%) of I, b.p. 50-60° (30-40 mm.). In the second run, 32 g. of XII was obtained, b.p. 80-95° (23-30 mm.); no XII was isolated in the third run.

1-Ethynylcyclohex-1-ene has a characteristic ultraviolet absorption maximum at 2235 Å.

1,1,2-Trifluoro-2-chloro-3-(cyclohex-1-enyl)-cyclobutene (IV). - The most satisfactory conditions for obtaining IV are described. To each of four heavy-walled Pyrex tubes (19x25x615 mm.) was added 25.0 ml. (22.0 g., 0.208 mole) of 1-ethynylcyclohex-1-ene. The tubes were cooled in a Dry Ice-isopropyl alcohol bath and

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*A generous sample was kindly furnished by the Air Reduction Co.

trifluorochloroethylene (II) passed in. A volume of gas was condensed, sufficient to form 25 ml. of liquid II, $\underline{d} \approx 1.5$ (37 g., 0.32 mole). The tubes were sealed, allowed to warm to room temperature and then heated over a 4-hour period to 95°. After 20 hours at 95°, the tubes were cooled in Dry Ice, vented, and the contents poured into a beaker to degas. Crude III was distilled through a Claisen head equipped with a short air condenser. The purified III amounted to 149 g. (79%), b.p. 71-73° (1 mm.), $\underline{n}^{25}D$ 1.4808. When cooled in ice, the product cyrstallized to sharp white needles, m.p. 11-13°.

In other preparations the yield of III was found to vary between 72 and 88%. Large-scale runs in a 1-liter stainless-steel Parr bomb gave high yields but on the third run the head gasket of the bomb ruptured. The ensuing expansion of hot gases (probably hydrogen fluoride was most important) eroded the bomb head and cylinder to a depth of 2 mm. rendering the bomb unusable. All subsequent preparations of III were carried out in sealed Pyrex tubes.

The analytical sample of III was purified by redistillation through a 30-cm. Vigreux column, b.p. 68.5-70.0° (1 mm.), $\underline{n}^{25}D$ 1.4800, $\underline{d}^{25}_4$ 1.268. The ultraviolet absorption spectrum of III in cyclohexane solution showed λ_{max} 2415 Å., ϵ 18,500. The infrared absorption at 3095 and 3040 $cm.^{-1}$ and double-bond absorption at 1643 and 1594 $cm.^{-1}$. The proton nuclear magnetic resonance (NMR) spectrum of III was in agreement with the assigned structure (33). Bromine and potassium permanganate solutions were

decolorized by III. When III was added to ethanolic silver nitrate or sodium iodide in acetone, no precipitate formed.

Anal. Calcd. for $C_{10}H_{10}F_3Cl$: C, 53.94; H, 4.53; Cl, 15.93. Found: C, 53.89; H, 4.57; Cl, 15.82.

1,1,2-Trifluoro-2-chloro-3-phenylcyclobutene (IV). - From 80.0 g. (0.784 mole) of commercially available phenylacetylene (Farchan Research Laboratories) and 92 g. (0.79 mole) of trifluorochloroethylene was prepared 149 g. (0.683 mole, 87%) of IV, b.p. 79-82°(3 mm.), $n^{25}D$ 1.5101, by the method of Smutny and Roberts (30).

Because commercial phenylacetylene was suspected to contain styrene as an impurity, another preparation of IV was made from phenlyacetylene purified by the method of Johnson and McEwen (66). From 22.0 g. of commercial phenylacetylene ($n^{25}D$ 1.5462) was prepared 36.2 g. (83%) of bis-phenylethynylmercury, m.p. 124.6-125.1° (lit. (66) 124.5-125°). In a 250-ml. round-bottomed flask, 36.2 g. (0.090 mole) of the mercury derivative was heated with 40 g. (0.61 mole) of potassium cyanide dissolved in 100 ml. of distilled water. Phenylacetylene was steam distilled, as generated, over a 7-hour period and separated from water by pentane extraction. The pentane solution was dried over magnesium sulfate, the solvent distilled, and the residual liquid distilled under reduced pressure. The purified phenylacetylene amounted to 13.0 g., b.p. 60.5-61.0° (40 mm.), $n^{25}D$ 1.5449. Comparison of the infrared spectra of commercial and purified phenylacetylene showed marked differences in the fingerprint region which could be accounted for

by about 10% styrene in the commercial material. Purified phenylacetylene (6.5 g.) gave 9.0 g. of 1,1,2-trifluoro-2-chloro-3-phenylcyclobutene (IV), b.p. 74° (1.5 mm.), $n^{25}D$ 1.5128. Comparison of the infrared spectra of IV prepared from the two purities of phenylacetylene showed differences in the fingerprint region that could be accounted for by the presence of 1,1,2-trifluoro-2-chloro-3-phenylcyclobutane (25) in IV prepared from commercial phenylacetylene.

Conversion of 1,1,2-Trifluoro-2-chloro-3-(cyclohex-1-enyl)-cyclobutene (III) to 1,1,2-Trifluoro-2-chloro-3-phenylcyclobutene (IV). - To a 200-ml. round-bottomed flask was added 24.0 g. (0.135 mole) of N-bromosuccinimide, 15.0 g. (0.0673 mole) of III, 0.3 g. of benzoyl peroxide and 100 ml. of carbon tetrachloride, previously distilled from phosphorus pentoxide. The reaction mixture was heated under reflux for 22 hours. Succinimide was removed by filtration and the solvent was flash distilled. The residual liquid was distilled through a 30-cm. Vigreux column. The product was collected in the b.p. range 123-127° (2 mm.). It amounted to 12.5 g. (49%), and was assigned the structure, 1,1,2-trifluoro-2-chloro-3-(3,6-dibromocyclohex-1-enyl)-cyclobutene (V). A center cut, $n^{25}D$ 1.5534, was submitted for analysis.

Anal. Calcd. for $C_{10}H_8F_3ClBr_2$: C, 31.57; H, 2.12. Found: C, 33.57; H, 2.12.

In a 100-ml. round-bottomed flask equipped with a magnetic stirrer was prepared a solution of 1.67 g. (87%, 0.0258 mole) of potassium hydroxide in 50 ml. of t-butyl alcohol. To this was added 4.92 g. (0.0129 mole) of V; a precipitate formed immediately. The reaction mixture was stirred for 1.5 hours, filtered and the t-butyl

alcohol distilled at reduced pressure. A reddish-brown oil remained which was dissolved in chloroform, washed with water, and dried over calcium chloride. After the solvent was flash distilled, the residue was distilled and collected in two parts, b.p. 65-66° (0.7-0.9 mm.). The fractions amounted to 3.0 g. (60%), $n^{25}D$ 1.5140 and 1.5134, respectively. The infrared spectrum of the distillate was identical with the spectrum of IV prepared from purified phenylacetylene.

1,1-Difluoro-2,2-dichloro-3-(cyclohex-1-enyl)-cyclobutene (IX). - The preparation of IX was identical to that of 1,1,2-trifluoro-2-chloro-3-(cyclohex-1-enyl)-cyclobutene with the exception that difluorodichloroethylene (VIII) replaced trifluorochloroethylene. From 88 g. (0.830 mole) of acid-washed redistilled 1-ethynylcyclohex-1-ene was prepared 180 g. (0.754 mole, 91%) of IX, b.p. 87-90° (2 mm.). An infrared lamp was used to heat the air condenser to prevent IX from crystallizing during distillation. IX crystallized from ethanol as long white needles, m.p. 44-45°.

In other runs, yields from 62-91% were obtained. Temperature control was found to be critical; when 100° was exceeded, the yield of IX was greatly diminished. Addition of 0.5 g. of hydroquinone to some reaction tubes did not detectably affect the yield. In some cases, IX was obtained as an oil, $n^{25}D$ 1.5090-1.5100, which eventually crystallized.

An analytical sample of IX, m.p. 44.9-45.4°, was obtained after six recrystallizations from ethanol. The infrared spectrum of IX in a potassium bromide disk and in carbon tetrachloride solution showed double-bond absorption at 1654 and 1590 $cm.^{-1}$. The

ultraviolet absorption spectrum had λ_{max} 2450 Å., ϵ 18,400. The proton and fluorine NMR. spectra of IX were in agreement with the assigned structure. Solutions of bromine and potassium permanganate were decolorized by IX. A white precipitate formed slowly when IX was treated with ethanolic silver nitrate; no precipitate formed with sodium iodide in acetone.

Anal. Calcd. for $C_{10}H_{10}F_2Cl_2$: C, 50.23; H, 4.22; Cl, 29.66. Found: C, 50.32; H, 4.39; Cl, 29.56.

1,1-Difluoro-2,2-dichloro-3-phenylcyclobutene (X). - From 6.5 g. of purified phenylacetylene was prepared 5.0 g. of X, b.p. 92° (2 mm.), $n^{25}D$ 1.5428, by the method of Roberts, Kline, and Simmons (21).

Conversion of 1,1-Difluoro-2,2-dichloro-3-(cyclohex-1-enyl)-cyclobutene (IX) to 1,1-Difluoro-2,2-dichloro-3-phenylcyclobutene (X). - To a 250-ml. round-bottomed flask was added 25.0 g. (0.105 mole) of IX, 38.6 g. (0.210 mole) of N-bromosuccinimide, 0.7 g. of benzoyl peroxide, and 100 ml. of dry carbon tetrachloride. The reaction mixture was heated under reflux for 14 hours. Succinimide was removed by filtration and the solvent distilled. The residue was distilled through a 30-cm. Vigreux column. Two fractions amounting to 4.1 and 9.7 g. believed to contain the desired product, 1,1-difluoro-2,2-dichloro-3-(3,6-dibromocyclohex-1-enyl)-cyclobutene (XIX) were collected, b.p. 124.5-134.0° (2.2-3.3 mm.), $n^{25}D$ 1.5670, and b.p. 132° (2.2 mm.), $n^{25}D$ 1.5722, respectively. The infrared spectra of the two fractions showed double-bond absorptions at 1640 and 1590 $cm.^{-1}$.

In a 200-ml. round-bottomed flask was prepared a solution of 1.50 g. (87%, 0.0233 mole) of potassium hydroxide in 100 ml. of t-butyl alcohol. To the magnetically stirred solution was added 8.5 g. of XIX. An immediate precipitate formed. The reaction mixture was heated for 2 hours under reflux and poured into water. The organic phase was separated with pentane, washed repeatedly with water, and dried over magnesium sulfate. The pentane was flash distilled and the residual liquid carefully distilled through a 30-cm. Vigreux column.

Fract.	B.p., °C.	Pressure, mm. Hg	Bath, °C.	Wt., g.	$n^{25}D$
1	90.5-93.0	1.6	134-139	0.35	1.5505
2	93.94	1.6	139-145	0.88	1.5542
3	94-97	1.6	145-146	1.40	1.5611
4	95	1.6-1.7	146-151	0.96	1.5702

The infrared spectrum of each fraction of the distillate was taken and the spectra compared with the spectrum for authentic 1, 1-difluoro-2, 2-dichloro-3-phenylcyclobutene (X). All absorption bands for X were present in fractions 1-3 but additional bands of increasing strength appeared with increasing refractive index ($n^{25}D$ 1.5436 for X). The ultraviolet spectrum of fraction 2 had λ_{max} 2580 Å. for a 0.0216 g. sample dissolved in 100 ml. of cyclohexane, optical density 1.53, cell thickness 1 mm., ϵ 16,700 for assumed molecular weight 235. The ultraviolet spectrum of X in cyclohexane solution had λ_{max} 2570 Å., ϵ 18,400. Comparison of ultraviolet spectra showed a difference in the shape of the absorption curves. The

proton NMR spectrum of fraction 2 had three peaks at -26, +26, and 58 c.p.s. relative to benzene. The areas were in the approximate ratio of 10:1:1, respectively. Comparison with the proton NMR spectrum of pure X showed the peaks at -26 and +26 c.p.s. corresponded to X and led to the conclusion that fraction 2 was a mixture of X and an unknown compound, probably 1,1-difluoro-2-chloro-4-bromo-3-phenylcyclobut-2-ene.

To prove conclusively the formation of X, fractions 1 and 2 were combined in a 10-cm. Pyrex test tube. To the tube was added 2.0 g. of 97.1% sulfuric acid and the mixture heated on a steam bath for 11 minutes and poured over ice. A brown solid formed which was separated but could not be crystallized from ethanol. The ethanol solution was poured into water and the brown solid taken up in carbon disulfide. The carbon disulfide solution was dried over calcium chloride and passed through a 2 x 10-cm. column packed with 100-mesh acid-washed alumina. Ultraviolet light was used to illuminate the column and the elution of a narrow band with carbon disulfide was followed. Evaporation of the solvent from the eluted band left a white solid which was crystallized twice from hexane and gave pure white needles, m.p. 80.2-80.5°. The sample did not depress the melting point of an authentic sample of 2,2-dichloro-3-phenylcyclobutenone (XI), m.p. 79.8-80.3°, prepared earlier by D. Knutsen (68). The infrared spectrum of XI prepared from IX was identical with the infrared spectrum of authentic XI.

1,1,2-Trifluoro-2,3-dichloro-3-(cyclohex-1-enyl)-cyclobutane (XIII). - To a heavy-walled Pyrex tube was added 20.0 g. of 1-(1-chloroethenyl)-cyclohex-1-ene (XII). The tube was cooled

in a Dry Ice-acetone bath and an equivalent volume (30 g.) of trifluorochloroethylene condensed in. The tube was sealed, heated at 125° for 18 hours, cooled, vented, and the contents distilled. A low boiling fraction amounted to approximately 10 g. of starting XII, b.p. 51-53° (2 mm.). The product amounted to 10 g. (20%) of pale yellow liquid, b.p. 91-94° (2 mm.), $n^{25}D$ 1.4737, and was assigned the structure 1,1,2-trifluoro-2,3-dichloro-3-(cyclohex-1-enyl)-cyclobutene (XIII).

Anal. Calcd. for $C_{10}H_{11}F_3Cl_2$: C, 46.35; H, 4.28; Cl, 27.37. Found: C, 46.47; H, 4.35; Cl, 27.17.

The infrared spectrum of XIII showed a single double-bond absorption at 1666 $cm.^{-1}$ and did not show an ultraviolet absorption maximum above 2200 Å. Solutions of bromine and potassium permanganate were decolorized by XIII. An instantaneous precipitate formed when XIII was treated with ethanolic silver nitrate. Sodium iodide in acetone did not react with XIII. Microhydrogenation of XIII over a platinum catalyst in ethanol resulted in uptake of 1 mole of hydrogen. Hydrogenolysis of chlorine occurred as shown by titration of the filtered solution with 0.9 eq. of base and precipitation of silver chloride from the final ethanol solution.

Conversion of 1,1,2-Trifluoro-2,3-dichloro-3-(cyclohex-1-enyl)-cyclobutane (XIII) to 1,1,2-Trifluoro-2-chloro-3-(cyclohex-1-enyl)-cyclobutene (III). - In a 100-ml. round-bottomed flask was prepared a solution of 1.17 g. (0.0209 mole) of potassium hydroxide in 20 ml. of t-butyl alcohol. To the solution was added 4.96 g. (0.0192 mole) of XIII and the solution heated under reflux

for two hours. Potassium chloride was removed by filtration and the solvent distilled under reduced pressure. The residual liquid was taken up in 10 ml. of pentane, washed with water, dried over magnesium sulfate and the solution distilled through a 30-cm. Vigreux column. A forerun was discarded and the rest of the distillate was collected as a single fraction which amounted to 2.0 g., b.p. 78-80° (1-2 mm.), $\underline{n}^{25}$D 1.4810. Comparison of the infrared, ultraviolet and proton NMR spectra of the product with corresponding spectra of authentic III, $\underline{n}^{25}$D 1.4800, identified the product as III.

Cycloaddition of Isopropenylacetylene (XIV) and Trifluorochloroethylene (II). - To four heavy-walled Pyrex tubes (19 x 25 x 615 mm.), cooled in Dry Ice, was added 53.2 g. of XIV (75 ml., 0.81 mole) and 110 g. (75 ml., 0.9 mole) of II. The tubes were sealed, heated at 95° for 20 hours, cooled in Dry Ice, vented, and the contents poured into a distilling flask. The low-boiling material was removed under water aspirator pressure. The residual liquid was distilled under reduced pressure through a 30-cm. Vigreux column.

Fraction	B.p., °C.	Pressure, mm. Hg	Bath, °C.	Wt., g.	$\underline{n}^{25}$D
Forerun	-44	35.3	65	2.0	1.4038
1	44-49	35.3-36	64-73	30.0	1.4039
2	43	35.2	73-80	1.6	1.4035
3	-63	35-37	80	0.9	1.4122
4	63-65	35-37	80-82	22.5	1.4288
5	60-62	32-34	82-110	4.7	1.4295
6	51	1	--	0.5	1.4252
7	51-53	1	110-135	9.4	1.4206
8	53-84	1	135-180	0.5	--
9	84-100	1	180	0.1	1.4742

Fraction 1 was assigned the structure 1, 1, 2-trifluoro-2-chloro-3-methyl-3-ethynylcyclobutane (XVI) from its infrared spectrum which showed a strong, sharp acetylenic carbon-hydrogen absorption at 3290 $cm.^{-1}$ and a weak triple-bond absorption at 2100 $cm.^{-1}$.

Anal. Calcd. for $C_7H_6F_3Cl$: C, 46.05; H, 3.31; Cl, 19.42. Found: C, 45.91; H, 3.42; Cl, 19.38.

Fractions 4 and 5 were believed to be 1, 1, 2-trifluoro-2-chloro-3-isopropenylcyclobutene (XV) because of their infrared spectra which showed double-bond absorption at 1588 and 1635 $cm.^{-1}$, and vinyl carbon-hydrogen absorption at 3090 $cm.^{-1}$. The fluorine and proton NMR spectra were in agreement with the assigned structure, XV.

Anal. Calcd. for $C_7H_6F_3Cl$: C, 46.05; H, 3.31; Cl, 19.42. Found: C, 45.93; H, 3.24; Cl, 19.37.

Fraction 7 was not submitted for analysis. It was assigned the structure, 1, 1, 2-trifluoro-2-chloro-3-methyl-3-(3, 3, 4-trifluoro-4-chlorocyclobutenyl)-cyclobutane (XVII) from its boiling point and refractive index and by analogy to the cycloaddition of vinylacetylene and tetrafluoroethylene (4).

CHAPTER III

REACTIONS AND PROPERTIES OF CYCLOHEXENYLCYCLOBUTENES AND THEIR DERIVATIVES

RESULTS AND DISCUSSION

New Cyclobutenones Formed by Hydrolysis of Cycloaddition Adducts of 1-Ethynylcyclohex-1-ene

It was found that 1, 1, 2-trifluoro-2-chloro-3-(cyclohex-1-enyl)-cyclobutene (III) and 1, 1-difluoro-2, 2-dichloro-3-(cyclohex-1-enyl)-cyclobutene (IX) could be hydrolyzed by sulfuric acid to ketones in a manner similar to the hydrolyses of fluorochlorophenylcyclobutenes (21, 30, 31). Because the structures of III and IX were well established, it was possible to assign structures to the derived ketones by examination of their physical and chemical properties and comparison of these properties with those for the phenyl substituted analogs, ~~the latter~~ whose structures have been proved (21, 25, 30). In Table I, the frequencies of double-bond and carbonyl infrared absorptions and the wave lengths of ultraviolet absorption maxima are given for several phenyl- and cyclohexenylcyclobutenones. The nuclear magnetic resonance (NMR) spectra are given in Chapter IV of this thesis.

When III was treated with concentrated sulfuric acid for about 0.5 hours at less than 50°, a white crystalline monoketone was obtained, 2-fluoro-2-chloro-3-(cyclohex-1-enyl)-cyclobutenone (XXIII). Sulfuric acid hydrolysis of III at 60° gave a maximum yield of 37% of cyclohex-1-enylcyclobutadienoquinone* (XXIV), a yellow crystalline solid, which formed a mono-2, 4-dinitrophenylhydrazone derivative.

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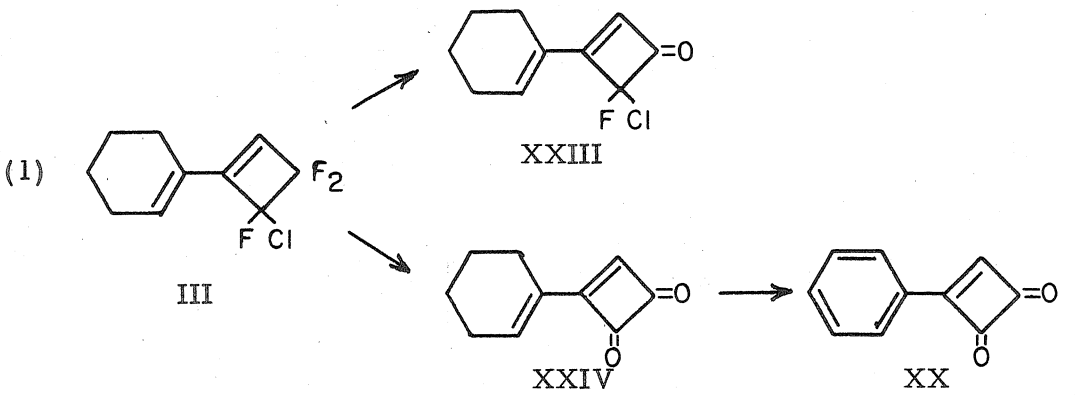
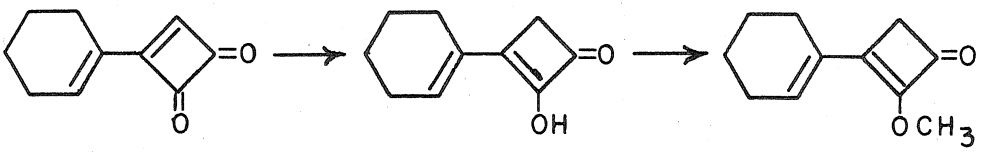
*More properly, 3-(Cyclohex-1-enyl)-cyclobuten-1, 2-dione.



An accompanying product was XXIII which could be separated from XXIV by crystallization, sublimation, or chromotography. Bromination of XXIV unexpectedly yielded some phenylcyclobutadienoquinone (XX), and this reaction proves the carbon-skeleton structure of XXIV.

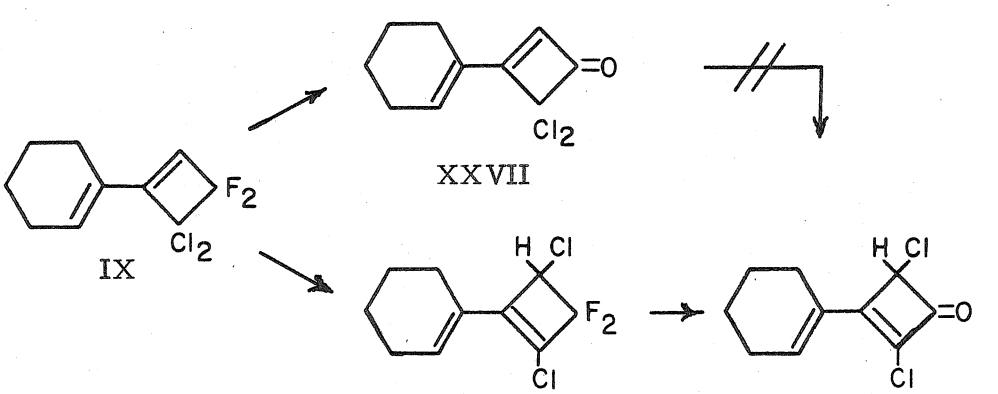
One reason for synthesizing XXIV was to convert it to cyclohexylcyclobutadienoquinone, a study of which could yield considerable information on the resonance energy and stability of the cyclobutadienoquinone ring. Hydrogenation of XXIV over a platinum catalyst did result in the uptake of one mole of hydrogen; however, the product did not have the desired structural features and was assigned the structure, 2-hydroxy-3-(cyclohex-1-enyl)-cyclobut-2-en-1-one (XXV). Compound XXV was extremely unstable to oxygen and an analytical sample was only obtained by careful purification procedures. Compound XXV formed an unstable 2, 4-dinitrophenylhydrazone derivative, gave a positive enol test with ferric chloride, and was methylated by diazomethane to yield crystalline 2-methoxy-3-(cyclohex-1-enyl)-cyclobut-2-en-1-one (XXVI). Evidence that the hydroxyl group reacted was obtained from the infrared spectra

of XXV and XXVI.

(2) 

XXIV XXV XXVI

Hydrolysis of 1, 1-difluoro-2, 2-dichloro-3-(cyclohex-1-enyl)-cyclobutene (IX) with concentrated sulfuric acid at 60-70° gave 2, 2-dichloro-3-(cyclohex-1-enyl)-cyclobutenone (XXVII). Efforts to convert XXVII to 2, 4-dichloro-3-(cyclohex-1-enyl)-cyclobutenone (XXVIII) failed. Rearrangement of IX with triethylamine gave 1, 1-difluoro-2, 4-dichloro-3-(cyclohex-1-enyl)-cyclobutene (XXIX). When XXIX was hydrolyzed at 95° with concentrated sulfuric acid, an uncrystallizable pale yellow liquid was isolated, which was assigned the structure XXVIII from its physical and chemical properties.

(3) 

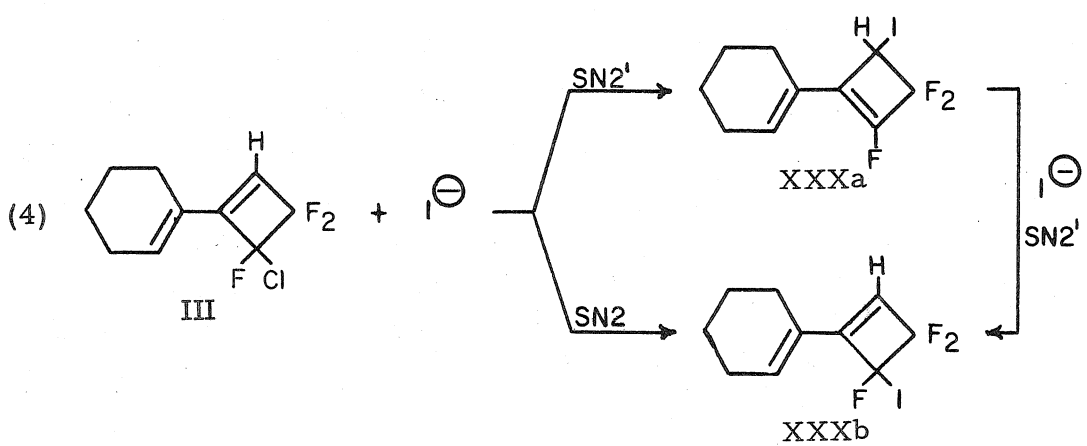
IX XXVII XXIX XXVIII

Displacement Reactions of Some Fluorochloro-(cyclohex-1-enyl)-cyclobutenes

The displacement reactions of 1, 1, 2-trifluoro-2-chloro-3-(cyclohex-1-enyl)-cyclobutene (III), 1, 1-difluoro-2, 2-dichloro-3-(cyclohex-1-enyl)-cyclobutene (IX), and 1, 1-difluoro-2, 4-dichloro-

3-(cyclohex-1-enyl)-cyclobutene (XXIX) with sodium iodide in acetone, sodium ethoxide in ethanol, and silver nitrate in ethanol were studied. In general, it was found that displacements occurred similar to those observed for phenylcyclobutenes (27, 73).

Compound III reacted slowly with either refluxing sodium ethoxide in ethanol or sodium iodide in acetone. With silver nitrate in ethanol, only starting material (III) was recovered after extended heating under reflux; an insignificant amount of silver chloride precipitated. The iodide displacement products were 1, 1, 2-trifluoro-4-iodo-3-(cyclohex-1-enyl)-cyclobut-2-ene (XXXa) and 1, 1, 2-trifluoro-2-iodo-3-(cyclohex-1-enyl)-cyclobutene (XXXb); a single ethoxide product was isolated, 1, 1, 2-trifluoro-4-ethoxy-3-(cyclohex-1-enyl)-cyclobut-2-ene (XXXI).

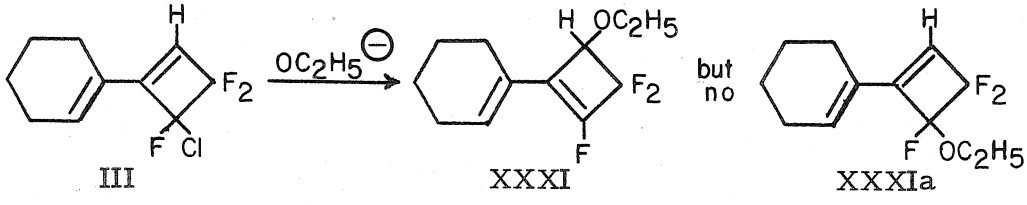


The formation of XXXa by an SN2' mechanism is probable. With XXXb two paths for formation are reasonable. First, direct displacement by SN2 mechanism would give the product. Recent work by Caserio (28) showed that optically active 2-chloro-4-bromo-3-phenylcyclobut-2-en-1-one was racemized by lithium bromide in acetone. In addition, optically active 2-chloro-2-fluoro-3-phenylcyclobuten-1-one was racemized by lithium chloride in acetone.

The most likely mechanism for these racemizations would seem to be an SN2 mechanism. From this, the formation of XXXb would be considered to be by an SN2 mechanism. On the other hand, a study of displacement reactions of perfluoroallylic halides by Miller and Fainberg (71) showed that the displacements occurred by $SN2'$ mechanism rather than by SN2 mechanism. On the basis of this work, the formation of XXXb by two $SN2'$ displacements is deemed more favorable than a direct SN2 displacement. A vinyl carbon substituted by fluorine is particularly labile to nucleophilic attack provided an appropriate allylic substituent can be eliminated by an $SN2'$ reaction.

In the displacement reaction of ethoxide ion with III, the only product isolated was the one corresponding to an $SN2'$ mechanism.

(5)

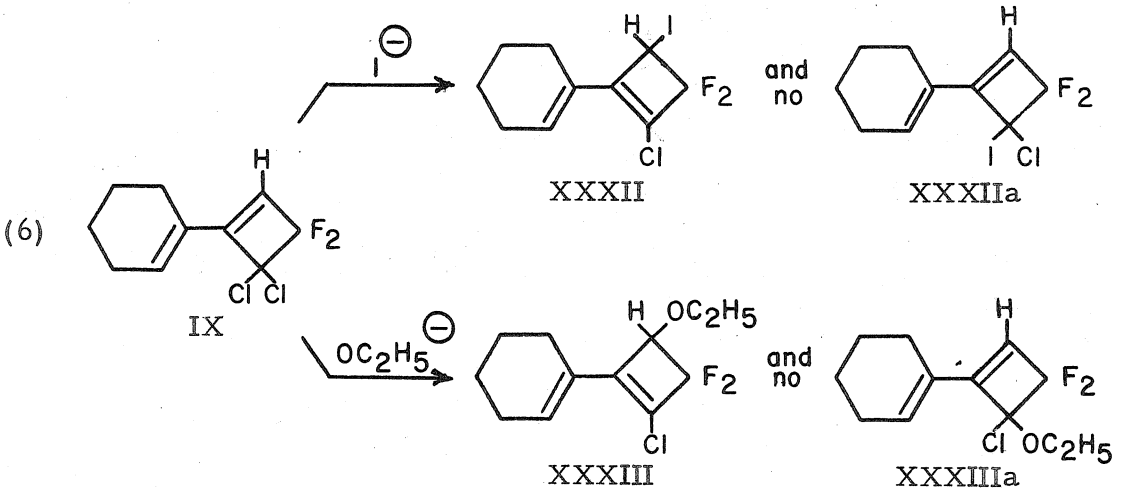


III XXXI XXXIa

By analogy to the iodide ion reaction, XXXIa would also be expected. During distillation of XXXI, a black polymer that amounted to about one-half of the initial starting material was formed. It is conceivable that the fluoroether, XXXIa, was indeed formed and that it decomposed when distillation was attempted. However, another possibility was elimination of hydrogen fluoride from XXXI to give a cyclobutadiene derivative which then polymerized.

The displacement reactions of 1, 1-difluoro-2, 2-dichloro-3-phenylcyclobutene (X) with sodium iodide in acetone and sodium

ethoxide in ethanol were studied previously (27, 73). With iodide or ethoxide ion, X gave products corresponding to reaction by an $SN2'$ mechanism. With the cyclohexenyl analog of X (IX), similar reactions occurred in good yield. No evidence for products formed by an SN2 mechanism was found.

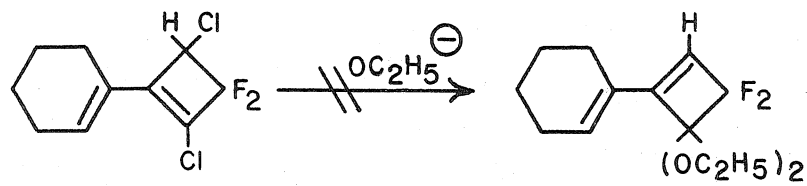


Formation of 1, 1-difluoro-2-chloro-4-iodo-3-(cyclohex-1-enyl)-cyclobut-2-ene (XXXII) and 1, 1-difluoro-2-chloro-4-ethoxy-3-(cyclohex-1-enyl)-cyclobut-2-ene (XXXIII) without formation of their isomers, 2-chloro-2-iodo- and 2-chloro-2-ethoxy- cyclobutenes (XXXIIa and XXXIIIa), was in agreement with the character of displacements observed on X. Furthermore, the formation of only XXXII and XXXIII would be expected from Miller and Fainberg's work which showed that a vinyl carbon substituted with chlorine was not attacked by a nucleophilic reagent to displace an allylic substituent. Chlorovinyl compounds differed markedly from fluorovinyl compounds in this respect.

When 1, 1-difluoro-2, 2-dichloro-3-(cyclohex-1-enyl)-cyclobutene (IX) was heated with a catalytic amount of triethylamine, a rearrangement occurred to form 1, 1-difluoro-2, 4-

dichloro-3-(cyclohex-1-enyl)-cyclobutene (XXIX). The latter did not react with sodium iodide in acetone or silver nitrate in ethanol even after extended heating under reflux. Starting material was recovered. With sodium ethoxide in ethanol, at either room or refluxing temperature, XXIX gave several products none of which was identified. One product was found to be fluorine-free and retained two chlorine atoms. It was suspected to be formed by opening of the cyclobutene ring, but this remains unproved. It had been hoped that IX would be converted to 1, 1-difluoro-2, 2-diethoxy-3-(cyclohex-1-enyl)-cyclobutene by a reaction analogous to the conversion of 1, 1-difluoro-2, 4-dichloro-3-phenylcyclobutene to 1, 1-difluoro-2, 2-diethoxy-3-phenylcyclobutene, observed earlier by Kitahara (27).

(7)

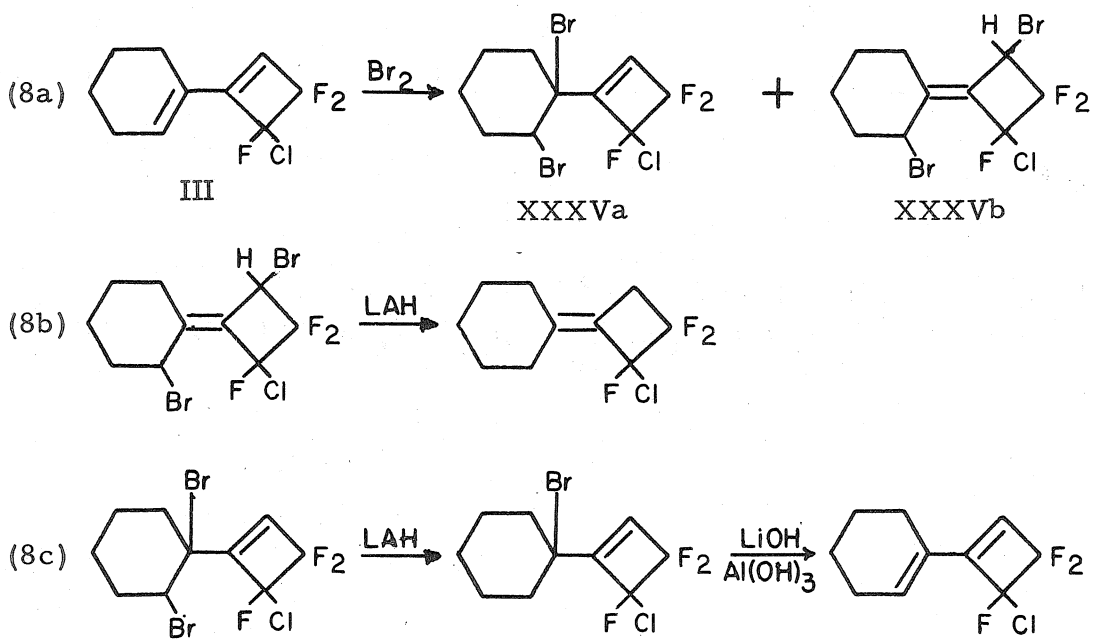


XXIX

Reactions of 1, 1, 2-Trifluoro-2-chloro-3-(cyclohex-1-enyl)-cyclobutene (III) and Some Derivatives.

Bromine added smoothly to III at room temperature to give a mixture of dibromides (XXXV). The proton NMR spectrum of XXXV showed a doublet vinyl-hydrogen peak which was assigned as a cyclobutene vinyl hydrogen on the basis of cross-ring coupling with fluorine (Chapter IV). One of the bromination products was then assigned as 1, 1, 2-trifluoro-2-chloro-3-(1, 2-dibromocyclohexyl)-cyclobutene (XXXVa) resulting from addition of bromine across the

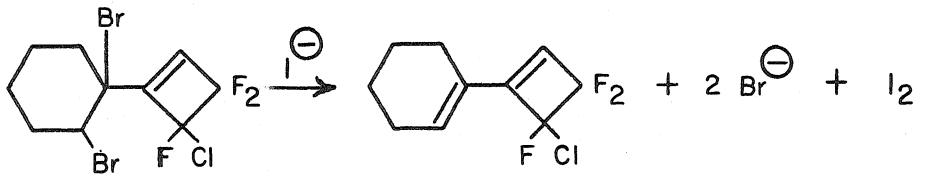
cyclohexenyl double bond. The small area of the doublet peak in the NMR spectrum suggested that XXXVa was a minor product. No other proton absorption occurred in the NMR spectrum at a field that would correspond to additional vinyl hydrogens. Two peaks of large area compared to the doublet were observed at fields corresponding to hydrogens attached to halogen substituted carbons. These peaks were nearly of equal area and were assigned as the tertiary hydrogens in the product that would result from 1, 4-bromination of III, 1, 1, 2-trifluoro-2-chloro-4-bromo-3-(2-bromocyclohexylidenyl)-cyclobutane (XXXVb). The major product of the bromination was therefore believed to be XXXVb. The absence of a singlet proton resonance absorption in the region of the NMR spectrum expected for a vinyl cyclohexenyl type hydrogen, suggested strongly that bromination across the cyclobutene double bond occurred to only a slight extent, if at all.



The infrared spectrum of XXXV was in agreement with the NMR assignments, particularly the observation of a strong absorption at 1700 cm.$^{-1}$ which was assigned as the di-exocyclic double bond of XXXVb. When XXXV was treated with lithium aluminum hydride (LAH), a mixture was obtained which contained III as shown by the infrared spectrum of the mixture. The reduction products could not be separated by distillation. It was concluded the reactions proceeded as shown in eq. 8.

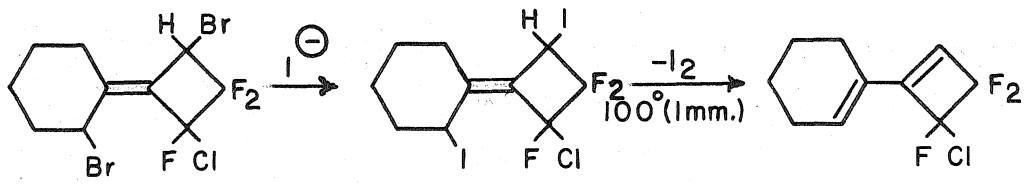
When XXXV was treated with sodium iodide and the products distilled, a forerun of III was obtained, and then III and XXXV distilled together as the temperature was raised. During the distillation, iodine vapors were observed in the column. The reactions of eq. 9 are suggested to explain the observations.

(9a)



XXXVa III

(9b)

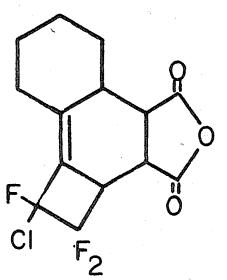


XXXVb

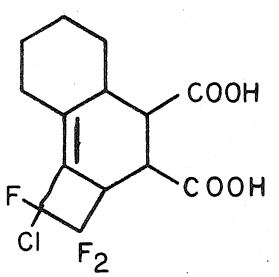
Hydrogenation of III at 60 p.s.i. hydrogen pressure was extremely slow in ethanol over a platinum catalyst at room temperature. After 42 hours, only a small percent reaction had occurred; III was recovered. A small amount of product distilled at a lower boiling point than III but it could not be purified. Hydrogenolysis of chlorine had occurred as shown by the presence

of chloride ion in the aqueous phase during the work-up. Several attempts to rearrange III with triethylamine to 1, 1, 2-trifluoro-4-chloro-3-(cyclohex-1-enyl)-cyclobut-2-ene failed. III was aromatized to IV (Chapter II).

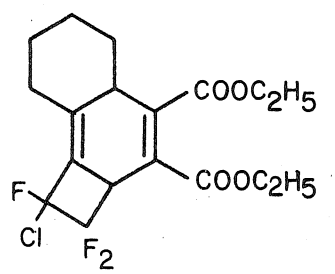
When III was heated under reflux in toluene with either maleic anhydride or dicarbethoxyacetylene, the Diels-Alder adducts were formed which were considered to be 1, 2-dicarboxyanhydro-3, 4-(1, 1, 2-trifluoro-2-chloroethano)-1, 2, 3, 5, 6, 7, 8, 9-octahydronaphthalene (XXXVI) and 1, 2-dicarbethoxy-3, 4-(1, 1, 2-trifluoro-2-chloroethano)-3, 5, 6, 7, 8, 9-hexahydronaphthalene (XXXVIII), respectively. The maleic anhydride adduct (XXXVI) was purified and characterized as the corresponding diacid (XXXVII).



XXXVI

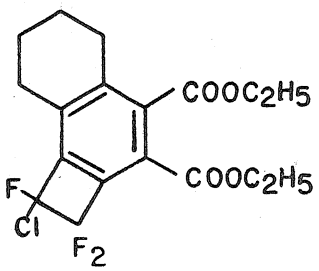


XXXVII

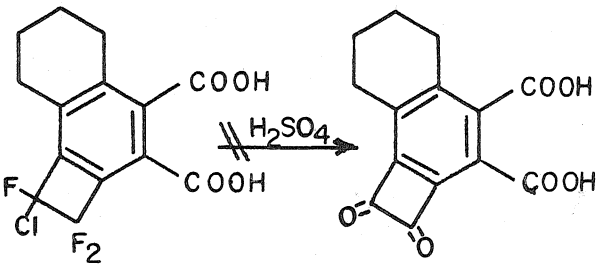


XXXVIII

Addition of one mole of bromine to XXXVIII, dehydrobromination with potassium t-butoxide, and saponification of the resultant product with 6 N sodium hydroxide, resulted in formation of 1, 2-dicarboxy-3, 4-(1, 1, 2-trifluoro-2-chloroethano)-5, 6, 7, 8-tetrahydronaphthalene (XL). Attempted hydrolysis of XL to a diketone failed.



XXXIX



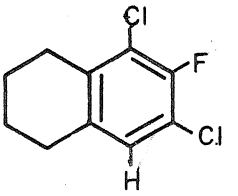
XL

Evidence for aromatization of XXXVII with platinum and palladium-on-charcoal catalyst in cyclohexene solvent was obtained. Formation of the aromatized diethylester (XXXIX) was based on spectral evidence only. No sample of the diester was obtained sufficiently pure for analysis.

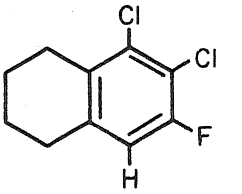
Reactions of 1, 1-Difluoro-2, 4-dichloro-3-(cyclohex-1-enyl)-cyclobutene (XXIX).

Earlier it was mentioned that XXIX did not undergo the expected reaction with sodium ethoxide (eq. 7), but gave instead a fluorine-free product. The unexpected result of the ethoxide reaction has again been mentioned because of a more unexpected reaction of XXIX with triethylamine. Synthesis of XXIX was carried out by heating IX in a sealed tube with a catalytic amount of triethylamine at 140-150°. On some occasions incomplete rearrangement occurred. To insure that rearrangement of IX to XXIX was complete, IX was heated at 180° for 36 hours with triethylamine in a sealed tube. When the tube was vented, a large volume of hydrogen halide was evolved. A white solid was isolated which accounted for 41% of starting IX. Infrared and ultraviolet spectra as well as inertness to bromine and permanganate solutions were

in agreement with the tetrahydronapthalene structures, XLI or XLII.



XLI

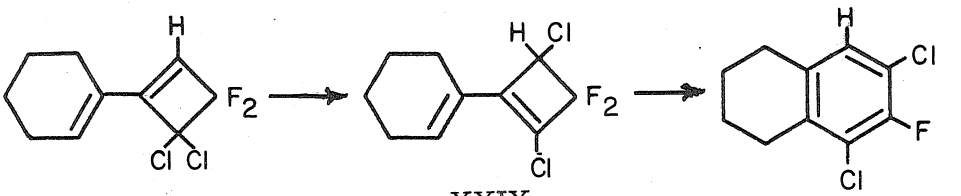


XLII

The proton and fluorine NMR spectra were also in agreement with either structure. The most important feature of the NMR spectra was J_{HF} 10 c.p.s. Earlier work by Gutowsky, Holm and Saika on hydrogen-fluorine coupling in the benzene system showed J_{HF} = 6.2-10.1, 6.2-8.3, 0.0-2.2 c.p.s. for ortho, meta, and para couplings, respectively. The possible para arrangement of hydrogen and fluorine was therefore reasonably excluded and only XLI or XLII needed to be considered.

It was suspected that the tetrahydronapthalene derivative was formed from XXIX rather than from IX as in eq. 10. This was confirmed by conversion of XXIX to a product identical in its properties to the original tetrahydronapthalene derivative. The structure XLI was therefore assigned to the tetrahydronapthalene derivative because it was considered unlikely that a second chlorine rearrangement would occur as would be necessary to attain the structure XLII.

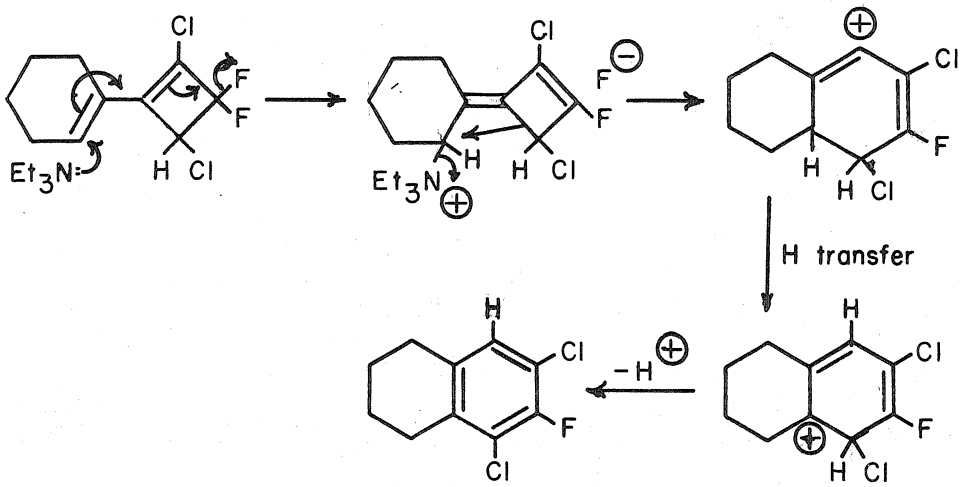
(10)



IX XXIX XLI

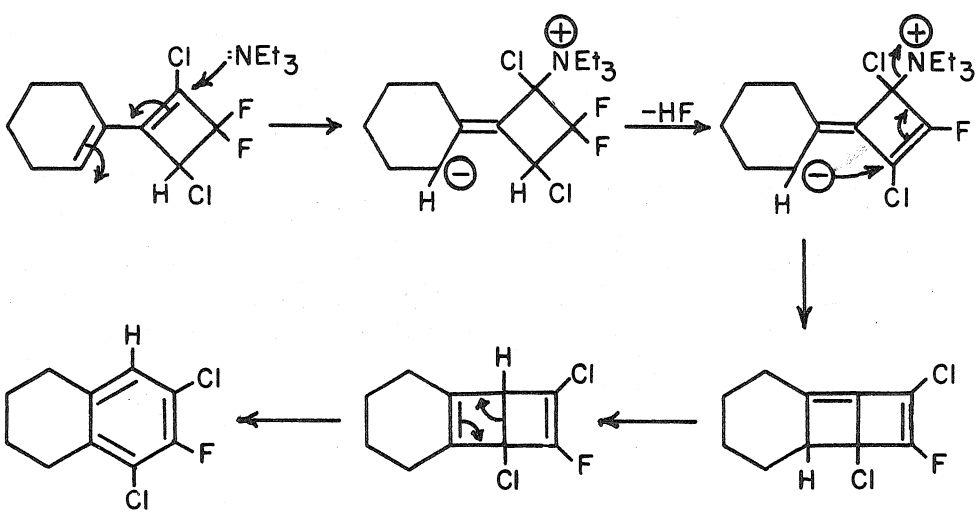
In considering possible mechanisms for the reaction, a carbonium ion mechanism such as in eq. 11 was discarded because of the unlikely vinylcarbonium ions required and because of the lack of suitable ionizing solvent.

(11)



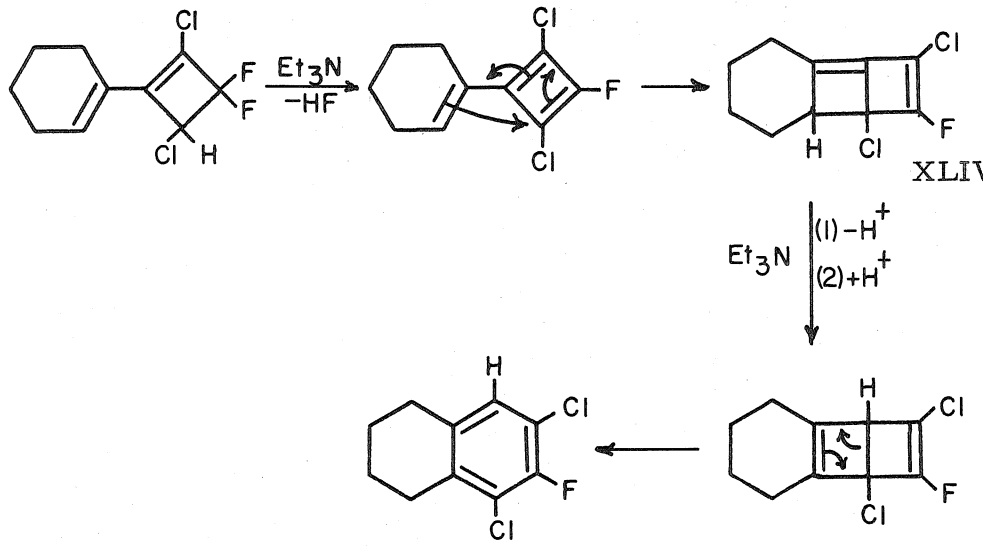
An ionic-type mechanism not involving carbonium ions such as that shown in eq. 12 must also be considered.

(12)



XLIV

The most likely mechanism, as suggested by Roberts (63), involves formation of a cyclobutadiene intermediate, eq. 13.

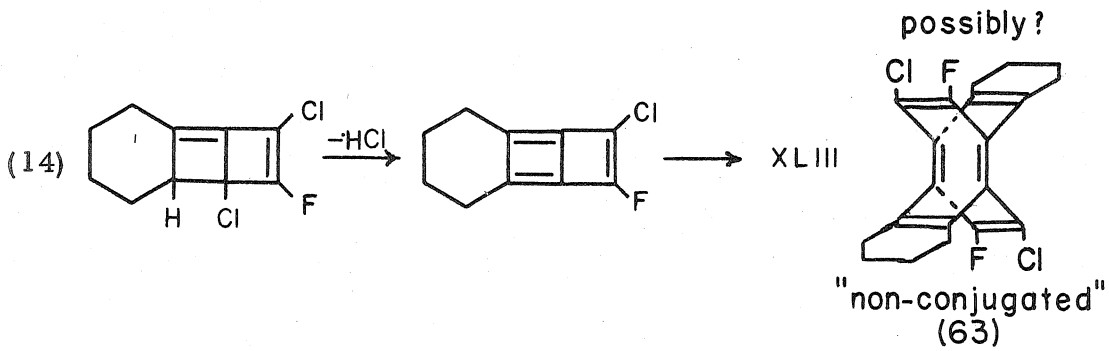


Presumably the mechanism of eq. 13 could be differentiated experimentally from mechanisms of the type shown in eqs. 11 and 12. With 1, 1,- difluoro-2, 4-dichloro-3-(cyclohex-1-enyl)-cyclobut-2-ene-4-C^{14}, a reaction by a mechanism involving a cyclobutadiene intermediate (eq. 13) would result in equal C^{14}-activity at the 2 and 4 carbons in 3-fluoro-2, 4-dichloro-5, 6, 7, 8-tetrahydronaphthalene. On the other hand, with mechanisms of the type shown in eqs. 11 and 12, C^{14}-activity would appear in the product at only the 2 position.

In another attempted rearrangement of IX to XXIX, the reaction was carried out at 1 atmosphere, 150°. Some XXIX was isolated as well as a high boiling, viscous liquid, probably a dimer (XLIII). Analysis showed $C_{10}H_{11}FCl$ ($C_{20}H_{22}F_2Cl_2$). The hydrogen analysis was too high to fit any reasonable empirical formula. $C_{20}H_{18}F_2Cl_2$ was considered as probable.

The dimer did not contain conjugated double bonds as shown by the lack of an ultraviolet absorption maximum between 2200-4000 Å. It decolorized bromine and permanganate solutions and showed absorption in the infrared spectrum at 1740 and 1725 $cm.^{-1}$. The proton NMR spectrum of the dimer was relatively uninformative; the high viscosity of the dimer resulted in broadening of the spectrum. The presence of cyclohexyl type protons was clearly indicated. It could not be determined if proton absorption occurred in the vinyl or tertiary hydrogen region of the NMR spectrum.

No suitable structure for XLIII was derived. If the intermediate (XLIV) shown in eqs. 12 and 13 is formed, elimination of hydrogen chloride from it would give XLV, from which a dimer (or dimers) could be formed, eq. 14.



A molecular orbital calculation for bicyclo [2.2.0] 1,3,5-hexatriene gave a delocalization energy of 1.66β and a predicted singlet ground state (27). The proposed intermediate XLV contains this same ring system and might also be expected to be stable and, under the reaction conditions that resulted in dimerization, be an intermediate in the dimerization.

Spectral Correlations for Substituted Cyclobutenes and Cyclobutenones.

In Tables I and II, some infrared spectral absorption data are given for the substituted cyclobutenes and cyclobutenones studied as well as ultraviolet absorption characteristics. In identifying new compounds synthesized in this study, frequent comparisons of infrared spectra in the carbonyl and double-bond regions were made and certain correlations found. The identification and assignment of cyclohex-1-enyl and cyclobutenyl double bonds were made primarily on the basis of comparison with their corresponding phenyl analogs. It was assumed that the cyclobutene double bond would absorb at about the same frequency in cyclohex-1-enyl- and phenylcyclobutenes. In Table I each of the phenylcyclobutenes shows double-bond absorption at 1620-1650 $cm.^{-1}$. Each of the cyclohexenyl cyclobutenes shows an absorption at 1634-1645 $cm.^{-1}$; this was assigned to the cyclobutene double bond. (The exceptions are the fluorovinyl derivatives, XXXa and XXXI. Fluorovinyl double bonds commonly show marked shifts to higher frequencies (72).) The double bond occurring at 1590-1608 $cm.^{-1}$ was then assigned as the cyclohexenyl double-bond absorption. The intensity of absorption was generally strong for both double bonds. Confirmatory evidence for the assignments was found in the infrared absorption spectrum of the isopropenyl cyclobutene, XV, which showed double bonds at 1588 and 1635 $cm.^{-1}$. The intensity of the 1588 $cm.^{-1}$ absorption was about three times that for the 1635 $cm.^{-1}$ absorption. A terminal vinyl group would be expected to show enhanced absorptivity (72).

Table I

Comparison of the Infrared and Ultraviolet Spectra of Cyclohex-1-enyl- and Phenylcyclobutenes

Compound	Infrared Absorptions* Vinyl C-H	4-ring C=C	6-ring C=C	Phenyl Ring	Very strong C-F absorption	Solvent	Ultraviolet Absorptions* λ_{max}	ϵ_{max}
$C_6H_5\overline{C=CHCF_2CFCl}$ IV	-	1621	-	1600 1575 1495	1330, 1221, 1127, 1110, 1107	-	2550 2140	16,500 11,900
$C_6H_9\overline{C=CHCF_2CFCl}$ III	3095 3040	1643	1594	-	1311, 1308, 1121, 1109, 1106	-	2425	18,500
$C_6H_5\overline{C=CHCF_2CCl_2}$ X	-	1637	-	1600 1580 1492	1300, 1280, 1160, 1110	-	2570	18,400
$C_6H_9\overline{C=CHCF_2CCl_2}$ IX	-	1645	1590	-	1300, 1280, 1132, 1117	CCl_4	2450	18,400
$C_6H_5\overline{C=CClCF_2CHCl}$ LI	-	1620	-	1600 1580 1492	1300, 1280, 1175, 1135, 1087	CCl_4	-	-
$C_6H_9\overline{C=CClCF_2CHCl}$ XXIX	3030	1640	1608	-	1300, 1280, 1175	-	2495	19,200
$C_6H_9\overline{C=CClCF_2CHI}$ XXXII	3020	1634	1600	-	1290, 1130, 1177	-	2515	16,700

*Infrared absorptions in $cm.^{-1}$; ultraviolet absorptions in $\mathring{A}$. All ultraviolet spectra observed with cyclohexane solvent.

Table I (cont.)

Infrared Absorptions*

Compound	Vinyl C-H	4-ring C=C	6-ring C=C	Phenyl Ring	Very strong C-F absorption	Solvent	Ultraviolet Absorptions* λ_{max}	ϵ_{max}
$C_6H_5\overbrace{C=CC1CF_2C}HOC_2H_5$ XXII	-	1648	-	1605 1580 1500	1340, 1295	-	-	-
$C_6H_9\overbrace{C=CC1CF_2C}HOC_2H_5$ XXXIII	3030	1638	1608	-	1400, 1365, 1328, 1305, 1280, 1250	-	2475	13,900
$C_6H_9\overbrace{C=CFCF_2C}HI$		1700	1630	-	Many between 1150-1400	-	2400	14,000
$C_6H_9\overbrace{C=CH\ CF_2C}FI$ XXXa, XXXb	-	1640	1590					
$C_6H_9\overbrace{C=CFCF_2C}HOC_2H_5$ XXXI	-	1695	1635	-	Many between 1150-1400	-	-	-

*Infrared absorptions in $cm.^{-1}$; ultraviolet absorptions in $\mathring{A}$. All ultraviolet spectra observed with cyclohexane solvent.

Table II

Comparison of the Infrared and Ultraviolet Spectra of Cyclohex-1-enyl- and Phenylcyclobutenones

Compound	Infrared Absorptions* Vinyl C-H	4-ring C=O	4-ring C=C	6-ring C=C	Phenyl Ring	Other IR Data	Ultraviolet Absorptions* λ_{max}	ϵ_{max}
$C_6H_5\overline{C=CHCOCFCl}$ XLVI	3080	1782	1555	-	1601 1580 1489	KBr disc	2795 2980** 2165 2215	24,800 12,900** 10,700 9,900
$C_6H_9\overline{C=CHCOCFCl}$ XXIII	3067	1776	1548	1616	-	KBr disc	2730	28,000
$C_6H_5\overline{C=CHCOCO}$ XX	3080	1785	1554	-	1600 1580 1485	KBr disc	2825 2960	23,000 14,200
$C_6H_9\overline{C=CHCOCO}$ XXIV	3030 3090	1780	1538	1620	-	KBr disc	2720	20,200
$C_6H_5\overline{C=C(OH)COCH_2}$ XXI	-	1745	1653	-	1600 1575	$CHCl_3$ sol. OH 3200	3120 2330 2250	17,900 7,500 8,500
$C_6H_9\overline{C=C(OH)COCH_2}$ XXV	3030	1738	1638	1613	-	CCl_4 sol. OH 3210	3000	9,750
$C_6H_5\overline{C=C(OC_2H_5)COCH_2}$ XXII	3060	1755	1635	-	-	CCl_4 sol.	3120 2330; 2250 2190	17,800 7300; 8640 8,530

Table II (cont.)

Infrared Absorptions *

Compound	Vinyl C-H	4-ring C=O	4-ring C=C	6-ring C=C	Phenyl Ring	Other IR Data	Ultraviolet Absorptions* λ_{max}	ϵ_{max}
$C_6H_9\overline{C=C(OCH_3)COCH_2}$ XXVI	3020	1751	1628	1610	-	CCl_4 sol.	2975	16,800
$C_6H_5\overline{C=CHCOCCl_2}$ XI	-	1780	1553	-	1601 1580 1488	-	2830 3025 2225	24,700 13,200 8,820
$C_6H_9\overline{C=CHCOCCl_2}$ XXVII	3030 3080	1787	1548	1625	-	-	2730	22,400
$C_6H_5\overline{C=CClCOCHCl}$ XLVII	3020	1765 1790	?1580-1600?		?1580-1600? 1500	CCl_4 sol. CS_2 sol.	2905 2980 3115	25,300 25,500 15,500
$C_6H_9\overline{C=CClCOCHCl}$ XXVIII	3030	1785	1560	1610	-	t-CH 1490	2840 2900**	21,700 21,100**

*Infrared adsorptions in $cm.^{-1}$; ultraviolet adsorptions in $\mathring{A}$. All ultraviolet spectra observed in cyclohexane solvent.

**Shoulder

The 1635 $cm.^{-1}$ absorption was therefore assigned as that of the cyclobutene double bond and the 1588 $cm.^{-1}$ absorption as that of the isopropenyl double bond.

The preceding assignments from Table I seem logical and clear. Inspection of the cyclobutene double-bond absorption of the non-vinyl substituted phenylcyclobutenones shows cyclobutene absorption at 1553-1555 $cm.^{-1}$. In the corresponding cyclohexenyl cyclobutenes the range is 1538-1548 $cm.^{-1}$. For XXIX (vinyl chloride) the absorption is at 1560 $cm.^{-1}$. The assigned cyclohexenyl double bond is in the range 1610-1625 $cm.^{-1}$. The absorption assigned to the cyclobutenone double bond occurs at a very low frequency for double-bond absorption. The reason for the low frequency of absorption is probably that the cyclobutenone ring system is highly conjugated, a conclusion that is consistent with the observed dipole moments, which will be discussed later.

Each of the cyclobutenones substituted by an alkoxy or hydroxy group on the cyclobutene vinyl carbon shows cyclobutene double-bond absorption at 1628-1653 $cm.^{-1}$. The cyclobutene double-bond absorption frequency for the cyclohexenylcyclobutenones is lower in each case than the frequency for the corresponding phenylcyclobutenones. From the wide range of frequencies found for cyclobutene double bond absorption, it is apparent that the frequency of absorption depends on the kind of cyclobutene substitution either in conjugation with the double bond or directly on the double bond. A correlation in the carbonyl absorptions is apparent. The cyclobutenones without vinyl cyclobutene substitution

at the 2-carbon absorb between 1776 and 1790 $cm.^{-1}$. The cyclobutenones substituted by hydroxy or alkoxy groups at the vinyl 2-carbon of the cyclobutene ring absorb at lower frequencies, 1738-1755 $cm.^{-1}$.

The preceding correlations are given in Table III.

Table III

Infrared Correlations of Substituted Cyclobutenes and Cyclobutenones

	C_4 C=C $cm.^{-1}$	C_6 C=C $cm.^{-1}$	C_4 C=O $cm.^{-1}$
Phenylcyclobutenes	1620-1650		
Cyclohexenylcyclobutenes	1634-1645	1590-1608	
Phenylcyclobutenones*	1553-1555		1780-1790
Cyclohexenyl-cyclobutenones*	1538-1548	1610-1625	1776-1787
Phenylcyclobutenones**	1635-1653		1745-1755
Cyclohexenyl-cyclobutenones**	1628-1638	1610-1613	1738-1751

*No vinyl cyclobutene substitution at the 2-carbon

**Hydroxy or alkoxy substitution on vinyl 2-carbon in cyclobutene ring

The ultraviolet absorption spectra of cyclohexenyl- and phenylcyclobutenones, not having alkoxy, hydroxy, or chloro substitution on the cyclobutene double bond, show a narrow range of absorption maxima. For the phenylcyclobutenones, XLVI, XX and XI, the ultraviolet spectra show λ_{max} 2795-2830 $\mathring{A}$., ϵ 24,700-28,000; for the cyclohexenyl-cyclobutenones, XXIII, XXIV, and XXVII, λ_{max} 2720-2730 $\mathring{A}$., ϵ 22,400-28,000.

The 2,4-dichlorocyclobutenones absorb at longer wave lengths, phenyl λ_{max} 2905, 2980 and 3115 Å., ϵ 25,300, 25,500 and 15,500; cyclohexenyl λ_{max} 2840 and 2900 Å., ϵ 21,700 and 21,100.

The cyclobutenones, substituted by alkoxy or hydroxy group at the vinyl cyclobutene 2-carbon, absorb at still longer wave lengths. Phenyl derivatives XXI and XXII have λ_{max} 3120 Å., ϵ 17,800 and 17,900; cyclohexenyl derivatives XXV and XXVI have λ_{max} 3000 and 2975 Å., ϵ 9,750* and 16,800. A generalization from the ultraviolet spectra is that cyclohexenyl cyclobutenones absorb at about a 100 Å. shorter wave length than the phenylcyclobutenones.

The ultraviolet absorption spectra of fluorinated cyclobutenes (cf. Table I) also show that the maxima around 2500 Å., fall at shorter wave lengths for the cyclohexenyl derivatives than for the phenyl derivatives. In general, the maxima for cyclohexenyl derivatives fall between 2400 and 2500 Å., and those for the phenyl derivatives between 2550 and 2600 Å. The surprising feature is that the absorptions occur at such long wave lengths. Comparison with styrene (2440 Å.) and butadiene (2170 Å.) shows that the absorption maxima of the difluorophenylcyclobutenes and difluorocyclohexenylcyclobutenes occur from 100-300 Å. longer wave length than would be expected. The observed extinction coefficients for the compounds under discussion are about the same.

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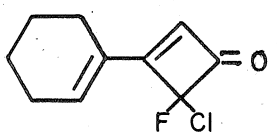
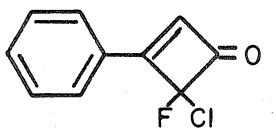
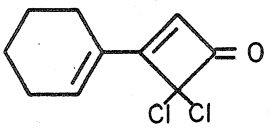
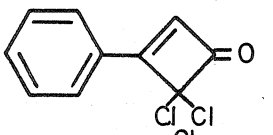
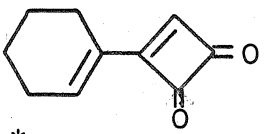
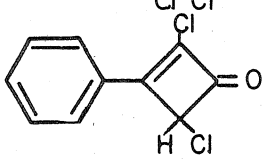
*Probable error in measurement of concentration.

It seems reasonable that the increased wave length of absorption is due to the gem-difluoro group, possibly through the interaction of p-orbitals of fluorine with the π-orbitals of the cyclobutene double bond. In the absence of the ultraviolet spectrum for phenylcyclobutene this must remain speculation.

The dipole moments of six substituted cyclobutenones are given in Table IV.

Table IV

Dipole Moments of Some Phenyl- and Cyclohexenyl-Substituted Cyclobutenones and Cyclobutendiones*

Compound		Dipole Moment, D.	Compound		Dipole Moment, D.
	XXIII	5.46		XLVI	5.16
	XXVII	5.46		XI	5.17
	XIV	5.62		XLVII	4.75

*Dipole moments were kindly measured by Dr. R. M. Badger and his students, California Institute of Technology.

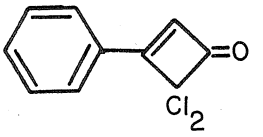
Examination of the structure of XLVII shows the cross-ring chlorines should lie in a plane at right angles to the direction of an approximate axis diagonally across the cyclobutene ring and passing through the carbonyl group; near coplanarity of the rings and a square four-membered ring was assumed. The dipole moments associated with the two carbon-chlorine bonds are not the same and differ by about 0.5 D. Because they do not form a 180°

angle, there will be a net moment due to the two chlorines of about 1.5 D. assuming a tetrahedral bond angle at the tertiary chlorine and 1.5 and 2.0 D. for the two kinds of carbon-chlorine bonds. Application of the Pythagorean theorem gives a net dipole moment for the phenylcyclobutenone system of $\sqrt{(4.75)^2-(1.5)^2} = 4.5$ D.

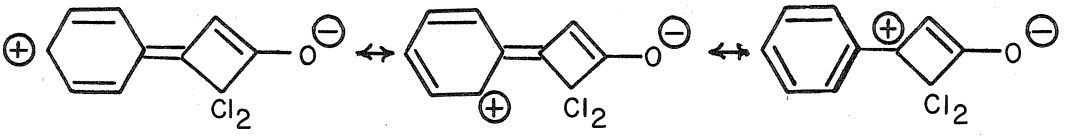
The two chlorines of XI should give a net dipole moment of $2(2.0 \sin 35^\circ)$ where the carbon-chlorine bond is assigned a value of 2.0 D. For the phenylcyclobutenone system a moment is calculated of $\sqrt{(5.17)^2-4(2.0 \sin 35^\circ)^2} = 4.65$ D. From XI and XLVII a dipole moment of 4.6 D. can be associated with the phenylcyclobutenone system.

The lack of symmetry of the cyclohexenyl group means that the plane of the dichloromethylene group in XXVII is almost certainly not at right angles to the direction of the cyclohexenylcyclobutenone dipole moment contribution. The deviation is probably relatively small and will be ignored. Applying the Pythagorean theorem to XXVII, a dipole moment of $\sqrt{(5.46)^2-4(2.0 \sin 35^\circ)^2} = 4.95$ D. is calculated for the cyclohexenylcyclobutenone system. A value of 4.9 D. is assigned to maintain the observed 0.3 D. difference (Table IV) between phenyl and cyclohexenyl systems.

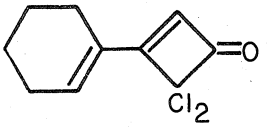
From the small difference in dipole moments for cyclohexenylcyclobutenones and phenylcyclobutenones it is concluded that in the normal states for these ketones there is probably more conjugation in the cyclohexenylcyclobutenones than in the phenyl ketones. Moreover the magnitude of any charge distribution must be somewhat larger for the cyclohexenyl system since the conjugated system is physically shorter.



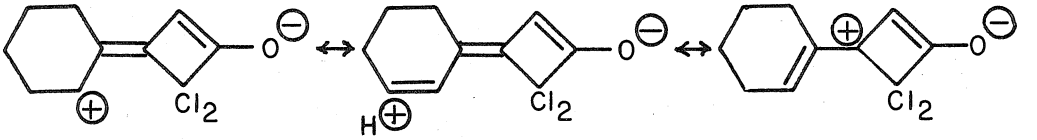
XI



XIa XIb XIc



XXVII

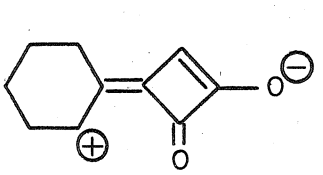


XXVIIa XXVIIb XXVIIc

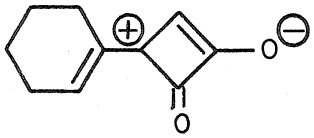
The sum of resonance forms XIa and XIb will give a system longer than the system XXVIIa. The possibility of hyperconjugation of XXVII permits the writing of resonance form XXVIIb which will lengthen the system over which charge for XXVII is distributed. However, one can probably conclude that the cyclohexenyl system interacts more strongly with the cyclobutenone ring than the phenyl system provided it is assumed that the relative contributions of XIc and XXVIIc to the respective resonance hybrids are about the same.

For cyclohex-1-enylcyclobutadienoquinone (XXIV) the amount of cross conjugation is of interest. Assuming geometry

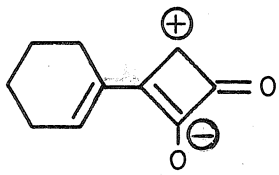
similar to that found in the phenylcyclobutadienoquinone system (34) and taking the assigned moment of the cyclohexenylcyclobutenone system as 4.9 D., a value of 2.7 $\pm$ 0.5 D. is found for the dipole moment contribution of the cross-conjugated carbonyl in XXIV. This is barely less than the 2.9 D. found for acrolein and barely greater than the 2.5 D. found for propionaldehyde (41). For XXIV, then, the resonance contributions to the normal state could conceivably include XXIVb and XXIVc in addition to the expected XXIVa.



XXIVa



XXIVb



XXIVc

EXPERIMENTAL

All melting and boiling points are uncorrected. Nuclear magnetic resonance spectra are given in Chapter IV, this thesis. Analyses were by Dr. A. Elek, Los Angeles, California. Dipole moments were measured through the courtesy of Dr. R. M. Badger, California Institute of Technology.

1,1,2-Trifluoro-2-chloro-3-(cyclohex-1-enyl)-cyclobutenone (XXIII). - In a 500-ml. filter flask were mixed 130 ml. of 96% sulfuric acid and 24.8 g. of 1,1,2-trifluoro-2-chloro-3-(cyclohex-1-enyl)-cyclobutene (III). The reactants were stirred magnetically for 35 minutes without application of heat. An exothermic reaction occurred and a maximum temperature of 40° was attained after about 20 minutes. Hydrogen fluoride was evolved and removed with a water aspirator. The dark-red solution was poured into 1500 ml. of an ice-water slurry. A cream-colored precipitate formed which, when filtered and dried in an evacuated desiccator, amounted to 22.4 g. of crude XXIII (100%). A hot hexane solution of the crude XXIII was treated with Norite, filtered through Celite and set aside to crystallize. The first crop of crystals amounted to 15.3 g. of pale yellow XXIII. A hexane solution of the first crop was passed through a 3.6 x 15-cm. column packed with acid-washed alumina. The eluted solution gave a first crop of white crystals that amounted to 6.0 g. of XXIII, m.p. 46.7-47.3°. Bromine and permanganate solutions were decolorized by XXIII. Silver nitrate in ethanol and sodium iodide in acetone did not give precipitates with XXIII at room temperature. Microhydrogenation of XXIII over platinum resulted in uptake of 1 mole

of hydrogen and generation of hydrogen chloride. The infrared spectrum of XXIII showed double-bond absorptions at 1548 and 1616 $cm.^{-1}$ and carbonyl absorption at 1776 $cm.^{-1}$. The ultraviolet spectrum in cyclohexane solution had λ_{max} 2730 Å., ϵ 28,000. The proton and fluorine NMR spectra were in agreement with the structure assigned for XXIII as was the dipole moment, 5.46 D.

Anal. Calcd. for $C_{10}H_{10}OFCl$: C, 59.84; H, 5.03; Cl, 17.68. Found: C, 59.72; H, 5.11; Cl, 17.58.

The 2,4-dinitrophenylhydrazone derivative of XXIII was obtained as red needles from ethyl acetate-acetonitrile, m.p. 198.5-198.6°.

Anal. Calcd. for $C_{16}H_{14}O_4N_4FCl$: C, 50.47; H, 3.71; N, 14.71. Found: C, 50.43; H, 3.77; N, 14.62.

Cyclohex-1-enylcyclobutadienoquinone (XXIV). - A large number of preparations of XXIV were made; the best conditions are described. In a 250-ml. Pyrex beaker equipped with a tantalum wire stirrer were mixed 75 ml. of 97.1% sulfuric acid and 24-28 g. of III. A deep-red solution formed followed by an exothermic reaction. The temperature of the reactants rose over a period of 10-15 minutes to 40-45°. Evolution of acidic gases occurred about 5 minutes after mixing. (When the reaction was quenched after 15 minutes, only XXIII was isolated.) When the temperature of reactants began to fall, an oil bath at 60-65° was placed under the reaction vessel and heating continued for 20-30 minutes. During this time the reaction temperature rose to 57-62° and evolution of acidic gases became vigorous. (When the reaction temperatures in excess of 70° were used, the yield of XXIV was greatly diminished.) The

dark-red solution was poured slowly into 1500 ml. of an ice-water slurry. A yellow-brown precipitate formed which was filtered, washed repeatedly with large volumes of water and dissolved in hot hexane; a black insoluble oil remained. When the hexane solution cooled, from 3-5 g. (23-41%) of dull yellow XXIV crystallized, m.p. 70-75°. Recrystallizations alternately from 95% ethanol (1 g. XXIV/5 ml. ethanol) and hot hexane gave bright yellow XXIV which remained stable over several months, m.p. 77-78°. An analytical sample was obtained by sublimation at 50° (1 mm.), m.p. 77.8-78.4°. Unrecrystallized XXIV decomposed on attempted sublimation or on standing at room temperature several days. A modified work-up used methylene chloride as solvent. The resulting solution was washed repeatedly with sodium bicarbonate solution. When the methylene chloride was evaporated and the crude product crystallized, XXIV was obtained that was more stable, but the yield was not improved.

Varying amounts of XXIII were isolated from mother liquors, accounting for up to 60-65% of starting III. In one run a yellow solid (1.0 g.), not identified, m.p. 230-240°, was isolated from the hexane insoluble residue. The structure assigned to XXIV was in agreement with its physical properties and analysis.

Anal. Calcd. for $C_{10}H_{10}O_2$: C, 74.06; H, 6.22. Found: C, 73.89; H, 6.24.

The infrared absorption spectrum of XXIV showed double-bond absorptions at 1538 and 1620 $cm.^{-1}$ and carbonyl absorption at 1780 $cm.^{-1}$. The ultraviolet absorption spectrum observed in cyclohexane had λ_{max} 2720 Å., ϵ 20,200. The dipole moment was

found to be 5.62 D. Solutions of bromine and potassium permanganate were decolorized by XXIV.

When 1 g. (0.0062 mole) of XXIV was treated with 1.05 g. (0.0062 mole) of bromine in acetic acid at 50°, hydrogen bromide was evolved. Some XXIV was recovered; phenylcyclobutadienoquinone (10 mg.) was also isolated and identified by melting point 140-145° and by comparison of infrared and ultraviolet spectra with spectra for authentic XXIV, m.p. 150-151°. The 2,4-dinitrophenylhydrazone (2,4-DNP) of XXIV was obtained as red needles, m.p. 260° (dec.). Analysis showed it to be a mono-2,4-DNP derivative.

Anal. Calcd. for $C_{16}H_{14}O_5N_4$: C, 56.14; H, 4.12; N, 23.37. Found: C, 56.72; H, 4.30; N, 22.96.

2-Hydroxy-3-(cyclohex-1-enyl)-cyclobut-2-en-1-one (XXV). - In a 200-ml. citrate bottle was placed 0.2 g. of platinum oxide and 10 ml. of 95% ethanol. The catalyst was activated, and 3.0 g. (0.185 mole) of cyclohex-1-enylcyclobutadienoquinone in 50 ml. of 95% ethanol was added. The bottle was flushed three times with hydrogen and then shaken overnight under 60 p.s.i. of hydrogen on a Parr hydrogenation apparatus.

The isolation and purification of the product ~~was~~ were done in a cold room at 2° as follows. First the catalyst was removed by filtration, and 200 ml. of water added to the filtrate. The resulting white solid was separated by centrifugation. (In early runs the product was filtered and dried; the yield was 90-100% of crude XXV.) Six recrystallizations from 50% ethanol-water with separation by centrifugation, resulted in formation of long, sharp,

white needles, m.p. 151-152° (dec.), 154° (dec.) on a melting block. Crystals were filtered only in the final separation, dried at 1 mm. over phosphorus pentoxide, and stored under nitrogen. When exposed to air at room temperature, XXV became yellow-orange and changed in odor from an extremely pleasant odor to a sharp odor reminiscent of buturic acid.

The infrared spectrum of XXV showed strong absorptions at 1613, 1638, 1745, and 3200 $cm.^{-1}$ which were assigned, respectively, as two double-bond, carbonyl, and oxygen-hydrogen absorptions. The ultraviolet absorption spectrum in cyclohexane had λ_{max} 3000 Å., ϵ 9,750. The proton NMR spectrum was in agreement with the structure assigned for XXV. Solutions of bromine and potassium permanganate were decolorized by XXV. With a ferric chloride solution an intense green-black solution formed. A 2,4-DNP derivative was formed, m.p. 250-251° (dec.).

Anal. Calcd. for $C_{10}H_{12}O_2$: C, 73.14; H, 7.37.
Found: C, 73.06; H, 7.30.

A 1-g. sample of cyclohex-1-enylcyclobutadienoquinone was found to adsorb quantitatively one mole of hydrogen at 1 atm. over platinum catalyst in ethanol. The product was found to be XXV by comparison of the m.p. and infrared spectra of samples from the 60 p.s.i. hydrogenation and the quantitative hydrogenation. Oxidation of XXV apparently occurred by addition of one molecule of oxygen to XXV as shown by the analysis of a sample exposed to oxygen.

Anal. Calcd. for $C_{10}H_{12}O_3$: C, 66.67; H, 6.67.
Found: C, 65.85; H, 7.00.

Based on exactly ten carbons in the skeleton, an empirical formula $C_{10.0}H_{12.6}O_{3.12}$ was calculated. When a sample of XXV was allowed to stand in cyclohexane solution, the ultraviolet spectra showed a change in absorption from λ_{max} 3000 Å., ϵ 9,750 to λ_{max} 2310 Å., ϵ 6000.

2-Methoxy-3-(cyclohex-1-enyl)-cyclobut-2-en-1-one (XXVI). - The reaction of 0.2 g. of XXV with diazomethane by the method of Caserio, Roberts, Neeman, and Johnson (69), gave a solid which when recrystallized from ethanol-water amounted to 50 mg., m.p. 125-130°. The infrared spectrum of the solid showed double-bond absorptions at 1610 and 1628 $cm.^{-1}$ and a carbonyl absorption at 1780 $cm.^{-1}$. The 3200 $cm.^{-1}$ absorption of XXV had disappeared. The ultraviolet absorption spectrum showed λ_{max} 2975 Å., ϵ 16,800. The proton NMR spectrum was in agreement with the structure assigned for XXVI. Solutions of bromine and potassium permanganate were decolorized by XXVI. A 2,4-dinitrophenylhydrazine solution gave a precipitate when XXVI was added. A sample of XXVI was submitted for analysis without taking precautions to avoid oxygen.

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 73.71; H, 8.44. Calcd. for $C_{11}H_{14}O_3$: C, 68.0; H, 7.20. Found: C, 65.88; H, 7.17. A calculation on the basis of an 11-carbon skeleton gave $C_{11.0}H_{14.35}O_{3.38}$.

The analysis found is not in agreement with the structure assigned, XXVI. It is considered probable that XXVI was in hand for the results reported prior to analysis since the material had only limited exposure to air. The analytical sample was exposed to air over a considerable period during attempted purification before the analysis. It is believed that XXVI reacted with oxygen in a manner

similar to its precursor, XXV. The initial analysis of XXV was similar to that of XXVI. The limited availability of XXV and XXVI did not permit another analysis.

2,2-Dichloro-3-(cyclohex-1-enyl)-cyclobutenone(XXVII). - In a filter flask equipped with a magnetic stirrer were mixed 25 g. (0.105 mole) of 1,1-difluoro-2,2-dichloro-3-(cyclohex-1-enyl)-cyclobutene and 200 ml. of 96% sulfuric acid. The reactants were heated at 65° for 40 minutes under water aspirator pressure and poured into one liter of an ice-water slurry. The resulting yellow precipitate was filtered, washed repeatedly with water until the washes had pH 3, and dried at room temperature and 1 mm. The crude product amounted to 15 g. (66%) and was crystallized from 200 ml. of hot hexane. The first crop amounted to 10.0 g. which was recrystallized from hexane as white rhombohedrons, m.p. 86.0-86.5°.

The infrared spectrum of XXVII showed double-bond absorptions at 1548 and 1625 $cm.^{-1}$ and carbonyl absorption at 1787 $cm.^{-1}$. The ultraviolet absorption spectrum had λ_{max} 2730 Å., ϵ 22,400. The dipole moment was found to be 5.46 D. The proton NMR spectrum was in agreement with the assigned structure. Bromine and potassium permanganate solutions were decolorized by XXVII. No precipitate was formed with either ethanolic silver nitrate or with sodium iodide in acetone at room temperature.

Anal. Calcd. for $C_{10}H_{10}OCl_2$: C, 55.30; H, 4.65; Cl, 32.68. Found: C, 55.26; H, 4.74; Cl, 32.75.

The 2,4-dinitrophenylhydrazone of XXVII crystallized as red needles from ethyl acetate, m.p. 201-202°.

Anal. Calcd. for $C_{16}H_{14}O_4N_2Cl_2$: C, 48.38; H, 3.55. Found: C, 45.67; H, 3.40.

1,1-Difluoro-2,4-dichloro-3-(cyclohex-1-enyl)-cyclobutene (XXIX). - In a sealed Pyrex tube, 1 ml. of triethylamine and 60 g. of 1,1-difluoro-2,2-dichloro-3-(cyclohex-1-enyl)-cyclobutene were heated at 150-160° for 16 hours. The resultant dark-brown liquid was washed with water and distilled through a 30-cm. Vigreux column. Purified XXIX amounted to 55 g. (93%), $n^{25}D$ 1.5188, d^{25}_4 1.300.

Anal. Calcd. for $C_{10}H_{10}F_2Cl_2$: C, 50.32; H, 4.22; Cl, 29.66. Found: C, 50.24; H, 4.19; Cl, 29.70.

The infrared spectrum of XXIX showed double-bond absorptions at 1608 and 1640 $cm.^{-1}$. The ultraviolet absorption spectrum had λ_{max} 2550 and 2180 Å., ϵ 16,500 and 11,900, respectively. Solutions of bromine and potassium permanganate were decolorized by XXIX.

2,4-Dichloro-3-(cyclohex-1-enyl)-cyclobutenone (XXVIII). - Attempts to prepare XXVIII from 2,2-dichloro-3-(cyclohex-1-enyl)-cyclobutenone (XXVII) (triethylamine or chloride ion catalysts) failed. XXVIII was prepared through the reaction of 4.2 g. of XXIX with 10 ml. of 97.1% sulfuric acid at 95° for 5 minutes. An oil formed when the dark-red reaction solution was poured into an ice-water slurry. The oil was separated with methylene chloride, washed with bicarbonate solution, dried over calcium chloride, and the solvent removed with an air stream. A pale yellow oil remained which was dissolved in a minimal amount of benzene and passed through a 2 x 10-cm. column packed with silicic acid-Celite.

Elution with hexane followed by 50% hexane-benzene resulted in separation of XXVIII and XXIX; however, XXVIII remained a liquid. Attempted sublimation of XXVIII was unsuccessful; XXVIII was then distilled, b.p. 95-100° (3-4 mm.), $n^{25}D$ 1.6053.

The infrared spectrum of XXIX showed double-bond absorptions at 1560 and 1610 $cm.^{-1}$ and carbonyl absorption at 1785 $cm.^{-1}$. The ultraviolet absorption spectrum had λ_{max} 2840 Å., ϵ 21,700 and a shoulder at 2900 Å., ϵ 21,100. Solutions of bromine and potassium permanganate were decolorized by XXIX. No precipitate was formed with either ethanolic silver nitrate or sodium iodide in acetone. No analysis was obtained for XXIX. The 2,4-dinitrophenylhydrazone was obtained as red needles after three recrystallizations from ethyl acetate, m.p. 204-206°.

Anal. Calcd. for $C_{16}H_{14}O_4N_2Cl_2$: C, 48.38; H, 3.55; N, 14.11; Cl, 17.85. Found: C, 48.54; H, 3.79; N, 14.70; Cl, 18.10.

1,1,2-Trifluoro-2-chloro-3-(cyclohex-1-enyl)-cyclobutene (III) with Sodium Iodide in Acetone. - In a 100-ml. round-bottomed flask, 50 ml. of a saturated solution of sodium iodide in acetone was heated under reflux for 8 days with 12.5 g. (0.0564 mole) of III. A white precipitate was separated; the filtered solid gave a precipitate with silver ion which was soluble in conc. ammonium hydroxide solution. The acetone was distilled from the filtrate and the residue extracted twice with hexane. The hexane solution was dried over calcium chloride; the solution slowly became violet on standing. After filtration and distillation of solvent, the pressure was reduced and the residue distilled through a 30-cm. Vigreux column.

Fraction	B. p., °C.	Pressure, mm. Hg	Bath, °C.	Wt., g.	$n^{25}D$	Appearance
Forerun	-77	2.5	-127	0.8	1.4822	pale yellow
1	77-79	2.5-2.9	127-135	2.7	1.4830	pale yellow
2	79	2.8-3.0	135-138	1.5	1.4851	pale yellow
3	80-85	3.0	138-143	1.0	1.4908	yellow
4	85-94	3.0	143-145	0.9	1.5232	yellow orange
5	94-95	3.0	145-150	1.9	1.5336	yellow orange
6	95-98	3.0	150-167	1.2	1.5338	orange red

As judged by their infrared spectra, fractions 1-3 consisted primarily of III; fractions 5 and 6 were free of III. On the basis of infrared absorptions at 1695, 1647, 1635, and 1590 $cm.^{-1}$, the ultraviolet absorption λ_{max} 2395 Å., ϵ 14,000, and the proton and fluorine NMR spectra, fractions 5 and 6 were believed to be a mixture of 1,1,2-trifluoro-4-iodo-3-(cyclohex-1-enyl)-cyclobut-2-ene (XXXa) and 1,1,2-trifluoro-2-iodo-3-(cyclohex-1-enyl)-cyclobutene (XXXb). On standing in air, XXX became dark violet and decomposed.

1,1,2-Trifluoro-2-chloro-3-(cyclohex-1-enyl)-cyclobutene (III) with Sodium Ethoxide in Ethanol. - In a 200-ml. round-bottomed flask, sodium (1.86 g., 0.0810 mole) was dissolved in 50 ml. of absolute ethanol. To the solution was added 18.0 g. (0.0810 mole) of III. The reactants were heated under reflux for 16 hours; a substantial precipitate formed. The reaction mixture was poured into water and the organic phase separated with methylene chloride. The solution was dried over calcium chloride and distilled through a 30-cm. Vigreux column.

Fraction	B.p., °C.	Pressure, mm. Hg	Bath, °C.	Wt., g.	$\underline{n}^{25}D$
Forerun	71-75.5	1.7-1.9	108-110	0.3	1.4726
1	75.5-76.0	1.8-1.9	110-108	2.8	1.4712
2	74.5	1.4-1.6	108-106	3.2	1.4684
3	74.0-76.0	1.6-1.7	106-118	2.5	1.4669
4	--	1.7	--	0.8	1.4644
Residue (black, shiny solid)				6	

The infrared and nuclear magnetic resonance spectra indicated the various fractions consisted of a mixture of III ($\underline{n}^{25}D$ 1.4800) and 1,1,2-trifluoro-4-ethoxy-3-(cyclohex-1-enyl)-cyclobut-2-ene (XXXI). Small amounts of III and XXXI were separated by passing a hexane solution through a 3.6 x 15-cm. column packed with silicic acid. Unfortunately III eluted first. The best sample of XXXI obtained had $\underline{n}^{25}D$ 1.4579 and appeared to be free of III as judged by its proton NMR spectrum; however, some III was indicated by the infrared spectrum. The ultraviolet absorption spectrum showed λ_{max} 2475 Å., ϵ 13,900. A satisfactory analysis was not obtained.

1,1-Difluoro-2,2-dichloro-3-(cyclohex-1-enyl)-cyclobutene (IX) with Sodium Iodide in Acetone. - In a 200-ml. round-bottomed flask, 12.37 g. (0.0517 mole) of IX and 22.7 g. (0.152 mole) of sodium iodide in 100-ml. of reagent grade acetone were heated under reflux for 8 days. A white precipitate identified as sodium chloride (3.0 g., 100%) was separated; the filtrate was poured into water. The organic phase was separated with five 20-ml. portions of methylene chloride. The solution was washed successively with 200-ml. of distilled water, two 100-ml. portions of 10% potassium iodide solution, and 100-ml. of water. It was dried over calcium chloride

and magnesium sulfate, and distilled to remove solvent. The residual red liquid was distilled through a 30-cm. Vigreux column under reduced pressure.

Fraction	B.p., °C.	Pressure, mm. Hg	Bath, °C.	Wt., g.	$n^{25}D$
Forerun	-108.5	1.0-1.4	-145	--	--
1	109-111	1.0-1.4	145-148	2.51	1.5725
2	111	1.0-1.4	148-150	4.50	1.5737
3	111-112	1.0-1.4	150-155	3.79	1.5744
4	112 -	1.0-1.4	155-165	--	1.5745

) The yellow distillate, 1,1-difluoro-2-chloro-4-iodo-3-(cyclohex-1-enyl)-cyclobut-2-ene (XXXII), amounted to 10.8 g. (0.0324 mole, 63%).

The infrared spectrum of XXXII showed double-bond absorptions at 1600 and 1634 $cm.^{-1}$. The ultraviolet spectrum in cyclohexane had λ_{max} 2515 Å., ϵ 16,700. The proton and fluorine NMR spectra were in agreement with the structure for XXXII. Solutions of bromine and potassium permanganate were decolorized by XXXII. With ethanolic silver nitrate a pale-yellow, ammonium hydroxide-insoluble precipitate formed. XXXII slowly turned violet in air but remained pale yellow under nitrogen.

Anal. Calcd. for $C_{10}H_{10}F_2ClI$: C, 36.01; H, 3.02; total silver halide from 11.31 mg., 12.95 mg. Found: C, 36.20; H, 3.20; total silver halide from 11.310 mg., 12.13 mg.

1,1-Difluoro-2,2-dichloro-3-(cyclohex-1-enyl)-cyclobutene (IX) with Ethanolic Potassium Hydroxide Solution. - In a 200-ml. round-bottomed flask, 4.3 g. (87%, 3.7 g., 0.066 mole) of potassium hydroxide was dissolved in 50 ml. of absolute ethanol. To this

was added 11.9 g. (0.050 mole) of IX, and the resultant solution was heated under reflux for 3 hours. A precipitate, identified as potassium chloride, was separated by filtration and amounted to 3.1 g. (83%). The filtrate was poured into 100 ml. of water, acidified with hydrochloric acid to pH 4, and the organic phase was separated with five 20-ml. portions of methylene chloride. The solution was washed successively with two 40-ml. portions of 5% sodium bicarbonate solution and 100-ml. of water, dried over magnesium sulfate, and the solvent distilled. The residual liquid was distilled under reduced pressure through a 30-cm. Vigreux column.

Fraction	B.p., °C.	Pressure, mm. Hg	Bath, °C.	Wt., g.	$n^{25}D$
Forerun	81-85.5	1.0	115-119	1.0	1.5152
1	88.5-88.0	1.0	119-118	-	1.5010
2	88.0-87.0	1.0	118-120	4.6	1.4969
3	87.0	1.0	120	-	1.4937
4	87-66	1.0-1.3	120-144	0.3	1.4920
5	-126	1.0-1.3	144-162	0.2	1.5162
6	126-	-	162-180	0.7	1.5765
7	130	1.0-1.1	180-235	0.5	1.5728

The forerun was identified as mostly IX by comparison of infrared spectra. Fractions 1-3 showed decreasing amounts of IX as determined by the disappearance of double-bond absorptions in the infrared spectra at 1590 and 1645 $cm.^{-1}$. The formation of the product was followed by appearance of double-bond absorptions at 1608 and 1638 $cm.^{-1}$. Fraction 4 was found to be free of IX and

was assigned the structure, 1,1-difluoro-2-chloro-4-ethoxy-3-(cyclohex-1-enyl)-cyclobut-2-ene (XXXIII). The ultraviolet absorption in cyclohexane had λ_{max} 2475 Å., ϵ 13,900. This absorption and the proton and fluorine NMR spectra were in agreement with the structure assigned for XXXIII. Solutions of bromine and potassium permanganate were decolorized by XXXIII. Solutions of silver nitrate in ethanol and sodium iodide in acetone did not give precipitates.

Anal. Calcd. for $C_{12}H_{15}OF_2Cl$: C, 57.95; H, 6.08; Cl, 14.25. Found: C, 57.78; H, 6.23; Cl, 14.33.

Fractions 1-3 (4.6 g.) were combined and distilled through a 40-cm. spinning band column with a heated jacket at 80°. By using a reflux ratio 15-20:1 and a take-off of 1-2 drops/min., a 1.3 g. sample of XXXIII was obtained, b.p. 87.5° (1.0-1.1 mm.), $n^{25}D$ 1.4921. The lowest refractive index obtained was 1.4917 at total take-off. A pot residue of about 0.5 g. of black tar remained, indicating XXXIII or some impurity had decomposed.

From the infrared and proton NMR spectra, fractions 6 and 7 were mixtures; carbonyl absorption was evident in the infrared spectra. No fluorine peaks could be found when the fluorine NMR spectrum of fraction 6 was observed under the same conditions in which a 50% solution of a compound containing one fluorine per molecule, molecular weight 226, gave a readily detectable signal. Fractions 6 and 7 were not further investigated.

1,1-Difluoro-2,2-dichloro-3-(cyclohex-1-enyl)-cyclobutene (IX) with Ethanolic Silver Nitrate Solution. - In a 200-ml. round-bottomed flask equipped with a magnetic stirrer, 9.00 g. (0.0530 mole) of finely-ground silver nitrate, 10.4 g. (0.0435 mole) of IX,

and 100-ml. of absolute ethanol were heated under reflux for six days. The procedure for isolation of 1,1-difluoro-2-chloro-4-ethoxy-3-(cyclohex-1-enyl)-cyclobutene (XXXII) was similar to the procedure used in isolation of XXXII in the ethoxide reaction. The crude pale-yellow product was distilled through a 30-cm. Vigreux column. Three fractions of the distillate, b.p. 95-96° (1.7-1.9 mm.), $\underline{n}^{25}D$ 1.4992-1.5032, amounted to 0.7 g. The fractions were identified as mixtures of IX and XXXII by comparison of their infrared and NMR spectra with those for mixtures of authentic IX and XXXII. During the work-up, 3.8 g. (0.0262 mole, 60%) of silver chloride was isolated. The distillate did not approach the theoretical 6.4 g. of XXXII. A residue of non-distillable black polymer amounted to about 5 g.

Bromination of 1,1,2-Trifluoro-2-chloro-3-(cyclohex-1-enyl)-cyclobut-2-ene (III). - To a solution of 24.5 g. (0.11 mole) of III in 50 ml. of carbon tetrachloride was added dropwise over a 24-hour period a solution of 18.8 g. (0.118 mole) of bromine in 150 ml. of carbon tetrachloride. The resulting solution was washed with 200 ml. of sodium bicarbonate solution and 200 ml. of water and the solvent distilled. The crude product amounted to 37.5 g. (89%) and was distilled through a 30-cm. Vigreux column and, with the exception of the forerun, the boiling points and refractive indices of fractions varied continually, b.p. 97-108°(1.0 mm.), $\underline{n}^{25}D$ 1.5262-1.5327. The distilled product was believed to be a mixture of dibromides of III (XXXV).

Anal. Calcd. for $C_{10}H_{10}F_3ClBr_2$: C, 31.40; H, 2.64; total silver halide from 12.505 mg., 16.9 mg. Found: C, 32.00; H, 2.83; total silver halide from 12.505 mg., 15.185 mg.

The infrared spectrum of XXXV showed that the double-bond absorptions of III at 1643 and 1594 $cm.^{-1}$ had disappeared and were replaced by a strong absorption at 1690 $cm.^{-1}$ and weaker absorptions at 1589, 1640, and 1613 $cm.^{-1}$. Three carbon-hydrogen absorptions between 1400 and 1460 $cm.^{-1}$ were replaced by two absorptions.

The proton NMR spectrum of XXXV showed a doublet at -7 and -15 c.p.s. (relative to benzene) which was assigned as a cyclobutene vinyl hydrogen split by a cross-ring fluorine (see Chapter IV). There were also two peaks of equal areas at +42 and +56 c.p.s. which were assigned as two tertiary hydrogens attached to a bromine substituted carbon. The sum of the areas for tertiary hydrogens was greater than that for the vinyl hydrogens. On the basis of the infrared and NMR spectra, XXXV was believed to be a mixture of 1,1,2-trifluoro-2-chloro-(1,2-dibromocyclohexyl)-cyclobutene (XXXVa) and 1,1,2-trifluoro-2-chloro-4-bromo-3-(2-bromocyclohexylidenyl)-cyclobutene (XXXVb) with XXXVb in a larger amount.

When 10.0 g. of XXXV was treated with 40 g. of sodium iodide in acetone, an immediate precipitate formed and the solution became dark red. The reaction mixture was stirred for one hour at room temperature, poured into water, and the organic phase separated with methylene chloride. The dark-red methylene chloride

solution was washed with 200 ml. of water, two 200-ml. portions of concentrated sodium thiosulfate solution, 100 ml. of water, and the pale yellow solution dried over magnesium sulfate. The product was distilled through a 30-cm. Vigreux column under reduced pressure.

Fraction	B.p., °C.	Pressure, mm. Hg	Bath, °C.	Wt., g.	$n^{25}D$
Forerun	-65°	2	-110	0.5	1.4853
1	65-90 (Violet Vapors)	2	110-160	2	Dark red
2	90-135 (Violet Vapors)	2	160-170	2	Dark red
3	135-139	2	170	2	1.5304 Pale Red

Violet vapors of iodine were clearly visible during distillation of fractions 2 and 3. The dark red color of fractions 2 and 3 disappeared when the fractions were washed with a sodium thiosulfate solution. The infrared spectrum of the forerun showed it to be mostly III. Fractions 1 and 2 were mixtures of III and XXXV, and fraction 3 was only XXXV. Careful comparison of the infrared spectra of starting XXXV and fraction 3 showed a marked reduction of the intensity of absorptions at 1589, 1640, and 1613 $cm.^{-1}$ in the spectrum for fraction 3.

When 15.8 g. of XXXV was stirred over a one-hour period with a solution of 0.80 g. lithium aluminum hydride in dry reagent ether, a white precipitate formed. The reaction product was separated by distillation, b.p. 73-87° (1.4-1.5 mm.), $n^{25}D$ 1.4851-1.4999 and found by infrared analysis to be a mixture of III and some

other product that showed strong infrared absorption at 1700 $cm.^{-1}$. The unknown product was believed to be 1, 1, 2-trifluoro-2-chloro-3-cyclohexylidenylcyclobutane.

1, 2-Dicarboxyanhydro- (XXXVI) and 1, 2-Dicarboxy-3, 4-(1, 1, 2-trifluoro-2-chloroethano)-1, 2, 3, 5, 6, 7, 8, 9-octahydronaphthalene (XXXVII). - In a 250-ml. round-bottomed flask, 19.7 g. (0.201 mole) of maleic anhydride, 44.7 g. (0.201 mole) of III and 125 ml. of toluene were heated under reflux for 40 hours. The solvent was slowly distilled; a yellow oil remained. The oil was dissolved in 100 ml. of toluene. The solution was heated 3 days on a steam bath, poured into a large crystallizing dish, and the toluene allowed to evaporate. A solid product remained which was dissolved in hot dioxane, hexane added slowly to the cloud point, and the solution set aside. Three crops of crystals were obtained in this manner which amounted to 7.45 g. (m.p. 233-234° dec.), 8.0 g. (m.p. 230-234° dec.), and 12.7 g. (m.p. 225-232° dec.), total 28.2 g. (42%). No additional crystals could be obtained from the mother liquor which was then set aside for several months; eventually 15-20 g. of additional adduct crystallized.

Anal. Calcd. for $C_{14}H_{12}F_3ClO_3$: C, 52.43; H, 3.77; Cl, 11.05. Found: C, 52.20; H, 3.92; Cl, 11.15.

Recrystallization of XXXVI from hot ethanol gave white crystals, m.p. 238.6-238.8°. XXXVI did not give a positive ferric chloride test but gave a positive ferric hydroxamate test for an anhydride. Bromine was decolorized by XXXVI, very slowly at first, but as additional bromine was added it was decolorized instantaneously and hydrogen bromide was evolved vigorously.

A neutralization equivalent of XXXVI was measured in 95% ethanol to the green endpoint of bromthymol blue. Titrations were with base standardized against potassium acid phthalate under the same conditions, neut. equiv. 169, theor. neut. equiv. for XXXVI 160.

A 3.0 g. sample of XXXVI in 100 ml. of ethanol was neutralized with 100 ml. of 0.103 N sodium hydroxide. Acidification with 400 ml. of 0.275 M sulfuric acid gave a white precipitate which was recrystallized from 50% ethanol-water, m.p. 246-248°. An analysis checked for XXXVII.

Anal. Calcd. for $C_{14}H_{14}O_4F_3Cl$: C, 49.64; H, 4.16; Cl, 10.46. Found: C, 48.99; H, 4.08; Cl, 10.84.

A sample of XXXVII was heated at 78° (1 mm.) for 48 hours, m.p. 237-238°; the analysis was correct for XXXVII.

Anal. Calcd. for $C_{14}H_{14}O_4F_3Cl$: C, 49.64; H, 4.16; Cl, 10.46. Found: C, 49.71; H, 4.43; Cl, 10.96.

Another ferric hydroxamate test on maleic anhydride, XXXVI and XXXVII showed maleic anhydride pos., XXXVI neg., and XXXVII neg., respectively.

An apparent discrepancy was resolved when it was realized that XXXVI used in this second ferric hydroxamate test for an anhydride had been crystallized from ethanol-water. The initial characterization of XXXVI was on material crystallized from dioxane-hexane. This material was authentic anhydride and remained as an anhydride after crystallization from absolute ethanol. Then the bulk of XXXVI was recrystallized from hot ethanol-water. Apparently

hydrolysis occurred to form XXXVII. Until discovery of this latter fact by comparison with the diacid XXXVII obtained by a deliberate hydrolysis, the accidental hydrolysis was not realized. The last two analyses given above and electron diffraction powder photographs confirmed that the alleged XXXVI was truly XXXVII.

1,2-Dicarbethoxy-3,4-(1,1,2-trifluoro-2-chloroethano)-3,5,6,7,8,9-tetrahydronaphthalene (XXXVIII). - In a 50-ml. round-bottomed flask, 10.0 g. (0.0585 mole, $n^{25}D$ 1.4405) of dicarbethoxyacetylene, 13.0 g. (0.0585 mole, $n^{25}D$ 1.4807) of III, and 15 ml. of toluene were heated under reflux for 44 hours. After the toluene was removed by distillation, the residue was distilled under reduced pressure through a 30-cm. Vigreux column.

Fraction	B.p., °C.	Pressure, mm. Hg	Bath temp., °C.	Wt., g.	$n^{25}D$
Forerun	-78	2-3	-150	0.73	1.4757
1	74-90	2-3	150-207	0.70	--
2	90-180	2-3	207-220	0.50	--
3	180-186	2-3	220-224	5.0	1.5080
4	186-190	2-3	224-240	3.8	1.5120

Analysis of the product was in agreement with the assigned structure, XXXVIII.

Anal. Calcd. for $C_{18}H_{20}O_4F_3Cl$: C, 55.04; H, 5.13; Cl, 9.03. Found: C, 54.84; H, 5.13; Cl, 9.10.

Solutions of bromine and potassium permanganate were decolorized by XXXVIII. With sodium iodide in acetone or ethanolic silver nitrate no precipitate formed. However, when XXXVIII was added to a potassium t-butoxide solution, heat was evolved and a precipitate formed.

The infrared spectrum showed weak absorption in the double-bond region, 1596 and 1600 cm.$^{-1}$. The ultraviolet spectrum showed λ_{max} 2925, 2840, and 2150 Å. The proton NMR spectrum was very unsatisfactory because of the high viscosity of XXXVIII which caused the proton peaks to be broadened. Dilution of XXXVII with carbon disulfide caused the peaks to resolve somewhat but the loss of signal strength resulting from dilution prevented additional information from being obtained. The presence of fluorine in XXXVIII was confirmed by the fluorine NMR spectrum.

In a 50-ml. round-bottomed flask with a side-arm, 1.7 g. of XXXVIII, 1.0 g. of 10% palladium-on-charcoal catalyst, 0.3 g. platinum oxide, and 10 ml. of reagent grade cyclohexene were heated under reflux for 4 days, during which period hydrogen gas was slowly bubbled through. The mixture was filtered and the solvent evaporated. The residue was allowed to stand at 1 mm. pressure for 24 hours; it was believed to be mostly (?) 1,2-dicarbethoxy-3,4-(1,1,2-trifluoro-2-chloroethano)-5,6,7,8-tetrahydronaphthalene (XXXIX), on the basis of its infrared and ultraviolet spectra. The infrared absorption spectrum for XXXVIII showed bands at 1630 (m) and 1596 (w) cm.$^{-1}$ in the double-bond region; XXXIX showed aromatic absorption at 1613 (vw), 1600 (m), and 1507 (vw) cm.$^{-1}$. The ultraviolet spectra showed λ_{max} 2925 and 2840 Å. for XXXVIII and λ_{max} 2925, 2780, 2715, 2680, and 2620 Å. for XXXIX.

1,2-Dicarboxy-3,4-(1,1,2-trifluoro-2-chloroethano)-5,6,7,8-tetrahydronaphthalene (XL). - To a carbon tetrachloride solution of 6.55 g. (0.0167 mole) of XXXVIII in a 200-ml. flask was added dropwise 2.94 g. (0.0184 mole) of bromine in 50 ml. of carbon

tetrachloride. After the bromine was decolorized, 60 ml. (0.0362 mole) of a 0.604 molar potassium t-butoxide solution was added dropwise; a precipitate formed instantly with each drop, and heat was evolved.

The reaction mixture was poured into 200 ml. of water and 100 ml. of methylene chloride added. After separation from the aqueous phase, the organic phase was dried over magnesium sulfate and set aside to permit the solvent to evaporate. The liquid residue was heated overnight under reflux with 15-ml. of 6 N sodium hydroxide. The homogeneous solution was acidified and extracted with four 50-ml. portions of ether; the dark-red ethereal solution was extracted with three 30-ml. portions of 1 N sodium hydroxide until colorless. The sodium hydroxide solution was acidified and extracted with methylene chloride. A red oil did not dissolve and this was dissolved in ether. From the ethylene chloride extract was obtained 1.37 g. of yellow solid, m.p. 65-72°; 0.3 g. of this was recrystallized from carbon tetrachloride and had m.p. 167-169°.

Anal. Calcd. for $C_{14}H_{10}O_4F_3Cl$: C, 50.24; H, 3.01; Cl, 10.59. Found: C, 50.33; H, 3.21; Cl, 10.51.

From the ethereal solution was obtained 0.5 g. of an orange solid, m.p. 120-130°. The infrared spectrum of this material was identical to the infrared spectrum of XL which had m.p. 167-169°. A neutralization equivalent of XL (m.p. 120-130°) was obtained, neut. equiv. 164, theor. neut. equiv. for XL 167. The ultraviolet spectrum of XL showed λ_{max} 2590 and 2520 Å., ϵ not measured due to low solubility of XL in cyclohexane.

2-Fluoro-1, 3-dichloro-5, 6, 7, 8-tetrahydronaphthalene (XLI). - A sealed heavy-walled Pyrex tube containing 30 g. of IX and 1 ml. of triethylamine was heated for 24 hours at 105° and then for 36 hours at 180°. The tube was cooled in ice and vented; a large volume of hydrogen halide escaped. The black tar in the tube was dissolved in benzene and washed with water until the washes were neutral. The benzene solution was concentrated to 50 ml.; 250 ml. of hot hexane was added, and the resultant precipitate was separated. The precipitate was extracted three times with 250-ml. portions of hot hexane. Evaporation of hexane resulted in 4 g. of a solid which when crystallized five times from ethanol amounted to 0.24 g. of white crystals, m.p. 68.1-68.4° (XLI). By repeated extractions of crude reaction product and concentration of mother liquors, 10 g. of XLI was eventually obtained (41%). The infrared spectrum of XLI showed strong absorption at 1600, 1577 and 1565 $cm.^{-1}$. The ultraviolet spectrum observed in cyclohexane showed λ_{max} 2740, 2800, and 2835 Å., ϵ_{max}, respectively 1350, 1270 and 1520 which are typical for a tetrahydronaphthalene derivative (70). XLI did not decolorize bromine or permanganate solutions and did not give precipitates with silver nitrate or sodium iodide solutions. A Rast determination gave mol. wt. 227, calcd. 203.

The proton NMR spectrum was observed in toluene and in cyclohexane and showed four peaks at 16, 26, 196, and 236 c.p.s. relative to benzene, peak ratios 0.5:0.5:4.0:4.0. The fluorine NMR spectrum showed two sharp peaks separated by 10 c.p.s. The proton peaks at 16 and 26 c.p.s. were then assigned as an aromatic hydrogen coupled with a single fluorine atom.

Anal. Calcd. For $C_{10}H_9F Cl_2$: C, 54.82; H, 4.14; Cl, 32.27. Found: C, 54.88; H, 4.78; Cl, 33.54.

A Dimer (XLIII) of 1, 1-Difluoro-2, 4-dichloro-3-(cyclohex-1-enyl)-cyclobutene (XXIX). - In an attempt to prepare XXIX from IX, about 150 g. of IX was heated with 2 g. of triethylamine at 150° in a 200-ml. round-bottomed flask equipped with a reflux condenser. Distillation resulted in a low boiling fraction (65 g. of XXIX), b.p. 80-120° (2 mm.), an intermediate fraction (15 g.), b.p. 120-170°, and a high boiling fraction (40 g.), b.p. 170° (2mm.). The high boiling material was redistilled and a center cut taken, b.p. 151° (1-2 mm.), $n^{25}D$ 1.5485. The infrared absorption spectrum in chloroform showed double-bond absorption at 1725 and 1740 $cm.^{-1}$, possible vinyl-hydrogen absorption at 3010 $cm.^{-1}$; the spectrum contained fewer absorption bands than the spectrum of XXIX. The ultraviolet absorption spectrum in cyclohexane did not show a maximum between 2200-4000 Å.

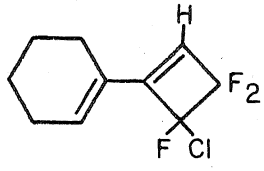
Anal. Calcd. for $C_{20}H_{16}F_2Cl_2$: C, 65.7; H, 4.39; Cl, 19.15; F, 10.4. Found: C, 64.47; H, 5.82; Cl, 19.66; F, 10.05 (by difference).

CHAPTER IV

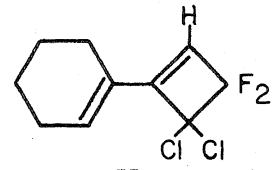
NUCLEAR MAGNETIC RESONANCE SPECTRA OF SUBSTITUTED CYCLOBUTENES

RESULTS AND DISCUSSION

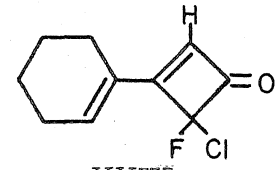
In the study of the cycloaddition adducts of 1-ethynylcyclohex-1-ene, it was of importance to assign the correct structures to the addition products. In the early stages, nuclear magnetic resonance (NMR) spectroscopy was called upon to confirm the structures assigned for III, IX, and XXIII.



III

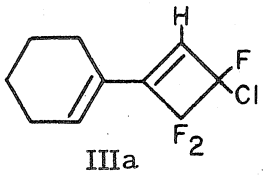


IX

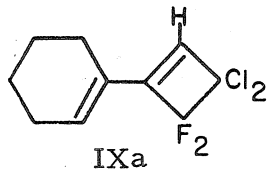


XXIII

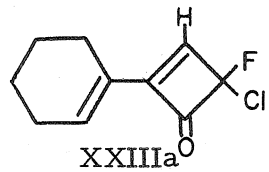
On the basis of simple NMR theory, it had been expected that the proton NMR spectra for the adducts with the structures III and IX would show the cyclobutene-ring vinyl hydrogen in III and IX split by spin-spin interaction involving the gem-difluoro group into a quartet and triplet, respectively. Similarly, no splitting of the cyclobutene-ring vinyl hydrogen for an adduct with structure XXIII would be expected. Surprisingly, NMR spectral evidence suggested that the structures assigned above were wrong. The proton NMR spectra showed the cyclobutene-ring vinyl hydrogen in III, IX, and XXIII to be a doublet, singlet, and doublet, respectively. This NMR evidence strongly suggested that the structures were instead IIIa, IXa, and XXIIIa.



IIIa

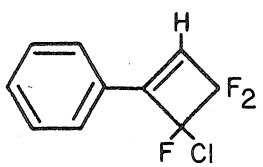


IXa

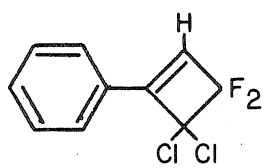


XXIIIa

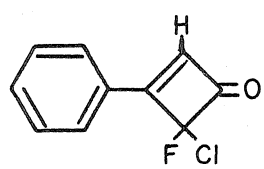
Since the phenyl analogs of the compounds in question had been synthesized earlier (see Chapter II), the proton NMR spectra of these compounds were observed. Here, a parallel situation obtained, the spectra showing the cyclobutene-ring vinyl proton in each to be a doublet, singlet, and doublet, respectively, for IV, X, and XLVI.



IV



X

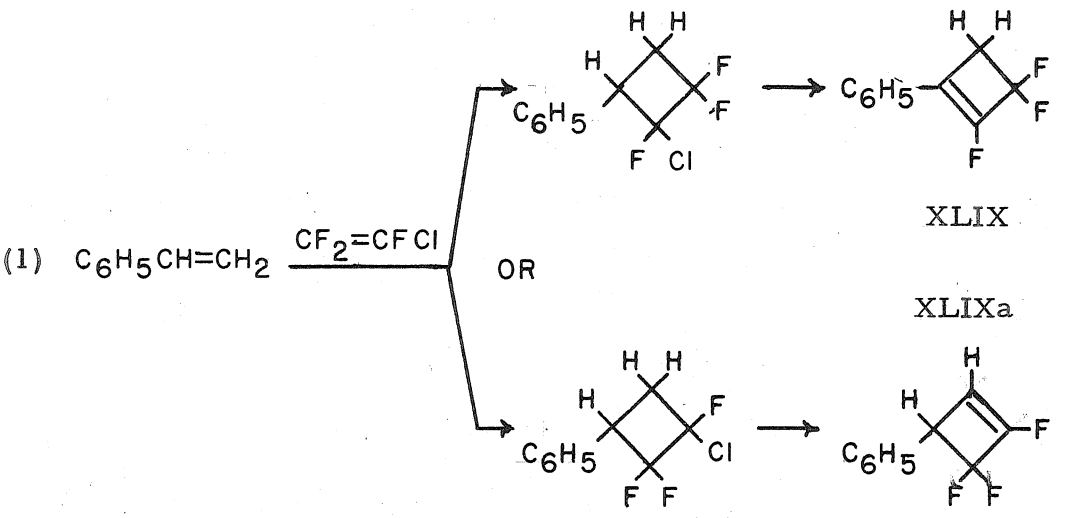


XLVI

However, for these phenylcyclobutenes, the chemical evidence overwhelmingly indicated that the structures IV, X, and XLVI were correct and that the isomers corresponding to IIIa, IXa, and XXIIIa were not formed. Furthermore, III and IX had been converted to IV and X (Chapter II), respectively. These conversions showed that the structures assigned to III, IX, and XXIII were correct despite the NMR evidence.

To explain the observed spectra, the idea that the spin-spin coupling constants for hydrogen and fluorine, J_{HF}, would decrease monotonically with the number of chemical bonds was discarded. Instead, it was concluded that cross-ring coupling existed between hydrogen and fluorine and that this cross-ring coupling

was greater by a factor of about ten than the coupling between hydrogen and fluorine on adjacent carbon atoms. This conclusion was confirmed by a NMR study of the dehydrochlorination product of the cycloaddition adduct from styrene and trifluorochloroethylene, eq. 1.



Two cycloaddition adducts are possible (eq. 1) which when dehydrochlorinated would give either XLIX or XLIXa. For XLIX two kinds of protons should be observed in the proton NMR spectrum and the ratio of peak areas expected would be 5:2. For strong cross-ring coupling, the smallest peak would be split into a doublet; otherwise a triplet would be expected for coupling with the adjacent gem-difluoro group. For XLIXa three peaks would be expected with a ratio of areas of 5:1:1. When the spectrum of the dehydrohalogenation product was taken, two kinds of protons were observed with peak ratios of 5:2. And the smaller peak was indeed a doublet, J_{HF} 12 c.p.s. The fluorine NMR spectrum of XLIX showed two kinds of fluorine, ratio of areas 2:1. The smaller peak was split into a triplet by the cross-ring methylene group with

J_{HF} 12 c.p.s., and this triplet was further split by the adjacent gem-difluoro group into a smaller triplet with J_{FF} 4 c.p.s. The NMR spectra for XLIX confirmed that cross-ring coupling between hydrogen and fluorine occurs in fluorinated cyclobutenes. The preliminary results for the preceding discussion were published (33).

Cross-ring coupling has since been found in other cyclobutenes. The magnitude of cross-ring hydrogen-fluorine coupling was initially reported as 8-12 c.p.s. (33); subsequent work shows a range of 8-21 c.p.s. After cross-ring coupling between hydrogen and fluorine was established, it was possible to make rapidly assignments to the peaks observed in the proton NMR spectrum of new cyclohexenylcyclobutenes and cyclohexenylcyclobutenones. The ability to identify the cyclobutene-ring protons by cross-ring coupling combined with chemical shift correlations was used in the study of the displacement reactions reported earlier (Chapter III).

The range of chemical shifts for various kinds of hydrogen on the cyclobutene ring for a large number of compounds ~~have~~ has been determined. In the cyclobutene series of Table I, the cyclobutene vinyl proton resonances occurred in the narrow range 20-32 c.p.s.* (δ_{H_2O} -1.30 to -1.00); for the fully conjugated monoketones of Table II, the cyclobutene vinyl proton resonances occurred in the range -16.4 to +17 c.p.s. (δ_{H_2O} -2.21 to -1.37). The absorption of the cyclobutene vinyl proton in the cross-conjugated ketone (LIII) and in the diones XX and XXIV fell at much lower fields, -72 to -122 c.p.s. (δ_{H_2O} -4.85 to -3.60). The much larger range over

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*All shifts reported in c.p.s. are at 40 mc. relative to benzene. δ_{H_2O} values are shifts in parts per million relative to water.

Table I

Nuclear Magnetic Resonance Absorption Spectra of Fluorinated Cyclobutenes [a]

Compound [b]	Peaks Obs. [c]	δ [d]	RA [e]	M [f]	J_{HF} [g]	Proton Assignment	Fluorine Spectrum or Solvent Used
$C_6H_5\overline{C{=}CHCF_2CF_2}$ XLVIII	-14	-2.15	5			Phenyl	2 peaks each multiply split
	8, 20, 32	-1.30	1	3	12	C_4 Vinyl	
$C_6H_5\overline{C{=}CHCF_2CFCl}$ IV	-14	-2.15	5			Phenyl	4 split peaks characteristic of substitution
	18, 26(22)	-1.25	1	2	8	C_4 Vinyl	
$C_6H_9\overline{C{=}CHCF_2CFCl}$ III	6	-1.65	1			C_6 Vinyl	4 split peaks characteristic of substitution
	21.3, 30.7(26)	-1.15	1	2	9.4	C_4 Vinyl	
	198, 215	3.15, 3.58	4:4			Cyclohexyl	
$C_6H_5\overline{C{=}CHCF_2CCl_2}$ X	-26	-2.45	5			Phenyl	1 peak; doublet
	26	-1.15	1	3	<2	C_4 Vinyl	J_{HF} 1-2 c.p.s.
$C_6H_9\overline{C{=}CHCF_2CCl_2}$ IX	-4.5	-1.90	1			C_6 Vinyl	1 peak; doublet
	32	-1.00	1			C_4 Vinyl	J_{HF} 1-2 c.p.s.
	194, 206	3.05, 3.35	4:4			Cyclohexyl	
$C_6H_5\overline{C{=}CFCF_2CH_2}$ [m] XLIX	-10	-2.05	5			Phenyl	Triplet-triplet vinyl F
	196, 208(202)	-3.25	2	2	12	C_4CH_2	J_{HF} 12; J_{FF} 4 c.p.s.
				3	2		CF_2 quartet J_{FF} 4 c.p.s.
$C_6H_5\overline{C{=}CClCF_2CH_2}$ [h] L	-20	-1.30	5			Phenyl	1 peak; weakly split triplet
	160	2.20	2			C_4CH_2	
$C_6H_5\overline{C{=}CClCF_2CHCl}$ [i] LI	-28	-2.50	5			Phenyl	
	61	-0.27	1			C_4 tertiary	
$C_6H_9\overline{C{=}CClCF_2CHCl}$ XXIX	6	-1.65	1			C_6 Vinyl	4 peaks separated 0.7, 0.6, 0.7 cm. $J_{FF} >$ chem. shift; ı ||| ı
	57, 63(60)	-0.30	1	2	6	C_4 Vinyl	
	179, 206	2.68, 3.35	4:4			Cyclohexyl	

Table I (cont.)

Compound[b]	Peaks Obs.[c]	δ[d]	RA[e]	M[f]	J_{HF}[g]	Proton Assignment	Fluorine Spectrum or Solvent Used
$C_6H_9\overline{C{=}CClCF_2CHI}$ XXXII	2	-1.75	1			C_6 Vinyl	4 peaks separated
	49	-0.57	1			C_4 Tertiary	4.2, 3.7, 4.2 cm.
	170, 198	2.45, 3.15	4:4			Cyclohexyl	J_{FF} > chem. shift
$C_6H_5\overline{C{=}CClCF_2CHOC_2H_5}$[ik] LVI	-23	-2.38	5			Phenyl	
	84	0.30	1		(J_{HH})	C_4 Tertiary	
	129, 230	1.43, 3.95	2:3	4, 3	8, 8	OCH_2CH_3	
$C_6H_9\overline{C{=}CClCF_2CHOC_2H_5}$ XXXIII	12	-1.50	1			C_6 Vinyl	4 peaks separated
	83	0.21	1		(J_{HH})	C_4 Tertiary	4.5, 8.0, 4.5 cm.
	123, 223	1.28, 3.78	2:3	4, 3	8, 8	OCH_2CH_3	Chem. shift > J_{FF}
	191, 209	2.98, 3.43	4:4			Cyclohexyl	
$C_6H_9\overline{C{=}CFCF_2CHOC_2H_5}$ XXXI	20	-1.30	1			C_6 Vinyl	
	78, 99(88.5)	0.41	1	2	21	C_4 Tertiary	
	124, 231	1.30, 3.98	2:3	4, 3	8, 8	OCH_2CH_3	
	188, 211	2.90, 3.48	4:4		(J_{HH})	Cyclohexyl	
$C_6H_9\overline{C{=}CHCF_2CFI}$ XXXb	6	-1.65	0.4			C_6 Vinyl	
	19, 25(22)	-1.25	0.4	2	6	C_4 Vinyl	
plus	165, 184	2.33, 2.80	4:4			Cyclohexyl	
$C_6H_9\overline{C{=}CFCF_2CHI}$ XXXa	-13	-1.45	0.6			C_6 Vinyl	
	56, 72(64)	-0.20	0.6	2, 3	16, 2	C_4 Tertiary	
$C_3H_5\overline{C{=}CHCF_2CFCl}$ XV	26.2, 33.8(30)	-1.05	1	2	7.8	C_4 Vinyl	
	44.4, 53.6(49)	-0.57	2	2	9.1	Vinyl CH_2	
	212	3.70	3		(J_{HH})	Methyl	

Table I (cont.)

(a) Measured using 5-mm. o.d. tubes of pure liquids, melted solid, or solutions as specified with Varian Associates High Resolution Spectrometer (V-4300) at 40 mc. and 12-in. magnet equipped with Super Stabilizer.

(b) C_6H_5 = phenyl; C_6H_9 = cyclohexenyl; C_3H_5 = isopropenyl.

(c) In c.p.s. at 40 mc. relative to benzene.

(d) In parts per million $\pm$ 0.06, referred to water.

(e) RA = Ratio of Areas, estimated visually in most cases; however, in some cases paper cut outs were weighed accurately.

(f) M = Multiplicity.

(g) Hydrogen-fluorine spin-spin coupling constant in c.p.s.

(h) Sample kindly furnished by Mr. S. Manatt.

(i) Sample kindly furnished by Dr. Y. Kitahara.

(j) Sample kindly furnished by Dr. E. Silversmith.

(k) Spectrum observed by Dr. J. D. Roberts. The approximate chemical shifts are accurate internally but may be translated along the field by up to 15 c.p.s. at 40 mc.

(l) Sample kindly furnished by the du Pont Co.

(m) Sample kindly furnished by Dr. R. Krall.

Table II

Nuclear Magnetic Absorption Spectra of Substituted Cyclobutenones[a]

Compound[b]	Peaks Obs.[c]	δ[d]	RA[e]	M[f]	J_{HF}[g]	Proton Assignment	Fluorine Spectrum or Solvent Used
$C_6H_5\overline{C{=}CHCOCF_2}$ LII	-21.7	-2.34	5			Phenyl	Doublet
	-28.7, -16.4, -4.1	-2.21	1	3	12.3	C_4 Vinyl	J_{HF} 12.1 c.p.s.
$C_6H_5\overline{C{=}CHCOCFCl}$ XLVI	-19					Phenyl	Doublet
	2, 11 (6.5)	-1.64	1	2	9	C_4 Vinyl	J_{HF} 9.2 c.p.s.
$C_6H_5\overline{C{=}CHCOCFCl}$ XXIII	-20	-2.30	1			C_6 Vinyl	Doublet
	-6, 4(-1)	-1.83	1	2	8.6	C_4 Vinyl	J_{HF} 8.6 c.p.s.
	175, 202	2.58, 3.25	4:4			Cyclohexyl	
$C_6H_5\overline{C{=}CHCF_2CO}$[i] LIII	-30, -19.6	-2.55, -2.29	5			Phenyl	Acetone
	-72	-3.60	1			C_4 Vinyl	
$C_6H_5\overline{C{=}CHCOCCl_2}$ XI	-36	-2.70	5			Phenyl	
	5	-1.92	1			C_4 Vinyl	
$C_6H_9\overline{C{=}CHCOCCl_2}$ XXVII	-13	-2.13	1			C_6 Vinyl	
	17	-1.37	1			C_4 Vinyl	
	174, 199	2.55, 3.10	4:4			Cyclohexyl	
$C_6H_5\overline{C{=}CC1COCHCl}$[k] XLVII	-20	-2.30	5			Phenyl	Acetone
	60	0.30	1			C_4 Tertiary	
$C_6H_9\overline{C{=}CC1COCHCl}$ XXVIII	-13	-2.13	1			C_6 Vinyl	
	45	-0.73	1			C_4 Tertiary	
	173, 204	2.53, 3.30	4:4			Cyclohexyl	
$C_6H_5\overline{C{=}CHCOCO}$[k] XX	-112	-4.85				C_4 Vinyl	Dimethyl sulfate
	-10	-2.05				Phenyl	

Table II (cont.)

Compound[b]	Peaks Obs.[c]	δ[d]	RA[e]	M[f]	J_{HF}[g]	Proton Assignment	Fluorine Spectrum or Solvent Used
$C_6H_9\overline{C{=}CHCOCO}$ XXIV	-103	-4.38	1			C_4 Vinyl	Deuterochloroform
	-35	-2.68	1			C_6 Vinyl	
	178, 202	2.65, 3.25	4:4			Cyclohexyl	
$C_6H_5\overline{C{=}C(OH)COCH_2}$[jk] XXI	-108	-4.50				Enol	Acetone
	-13	-2.12				Phenyl	
	190	-2.95				C_4 CH_2	
$C_6H_9\overline{C{=}C(OH)COCH_2}$ XXV	-82	-3.84	1			Enol	Deuterochloroform
	-21	-1.27	1			C_6 Vinyl	
	153	2.03	2			C_4 CH_2	
	176, 205	2.60, 3.33	4:4			Cyclohexyl	
$C_6H_5\overline{C{=}C(OC_2H_5)COCH_2}$[jk] XXII	-12	-2.10	5			Phenyl	
	106, 230	0.85, 3.95	2, 3			OC_2H_5	
	163	2.28	2			C_4 CH_2	
$C_6H_9\overline{C{=}C(OCH_3)COCH_2}$ XXVI	14	-1.45	1			C_6 Vinyl	Deuterochloroform
	97	0.63	3			OCH_3	
	145	1.83	2			C_4 CH_2	
	166, 197	2.35, 3.13	4:4			Cyclohexyl	

Table II (cont.)

(a) Measured using 5-mm. o.d. tubes of pure liquids, melted solid, or solutions as specified with Varian Associates High Resolution Spectrometer (V-4300) at 40 mc. and 12-in. magnet equipped with Super Stabilizer.

(b) C_6H_5 = phenyl; C_6H_9 = cyclohexenyl; C_3H_5 = isopropenyl.

(c) In c.p.s. at 40 mc. relative to benzene.

(d) In parts per million $\pm$ 0.06, referred to water.

(e) RA = Ratio of Areas, estimated visually in most cases; however, in some cases paper cut outs were weighed accurately.

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(g) Hydrogen-fluorine spin-spin coupling constant in c.p.s.

(h) Sample kindly furnished by Mr. S. Manatt.

(i) Sample kindly furnished by Dr. Y. Kitahara.

(j) Sample kindly furnished by Dr. E. Silversmith.

(k) Spectrum observed by Dr. J. D. Roberts. The approximate chemical shifts are accurate internally but may be translated along the field by up to 15 c.p.s. at 40 mc.

(l) Sample kindly furnished by the du Pont Co.

(m) Sample kindly furnished by Dr. R. Krall.

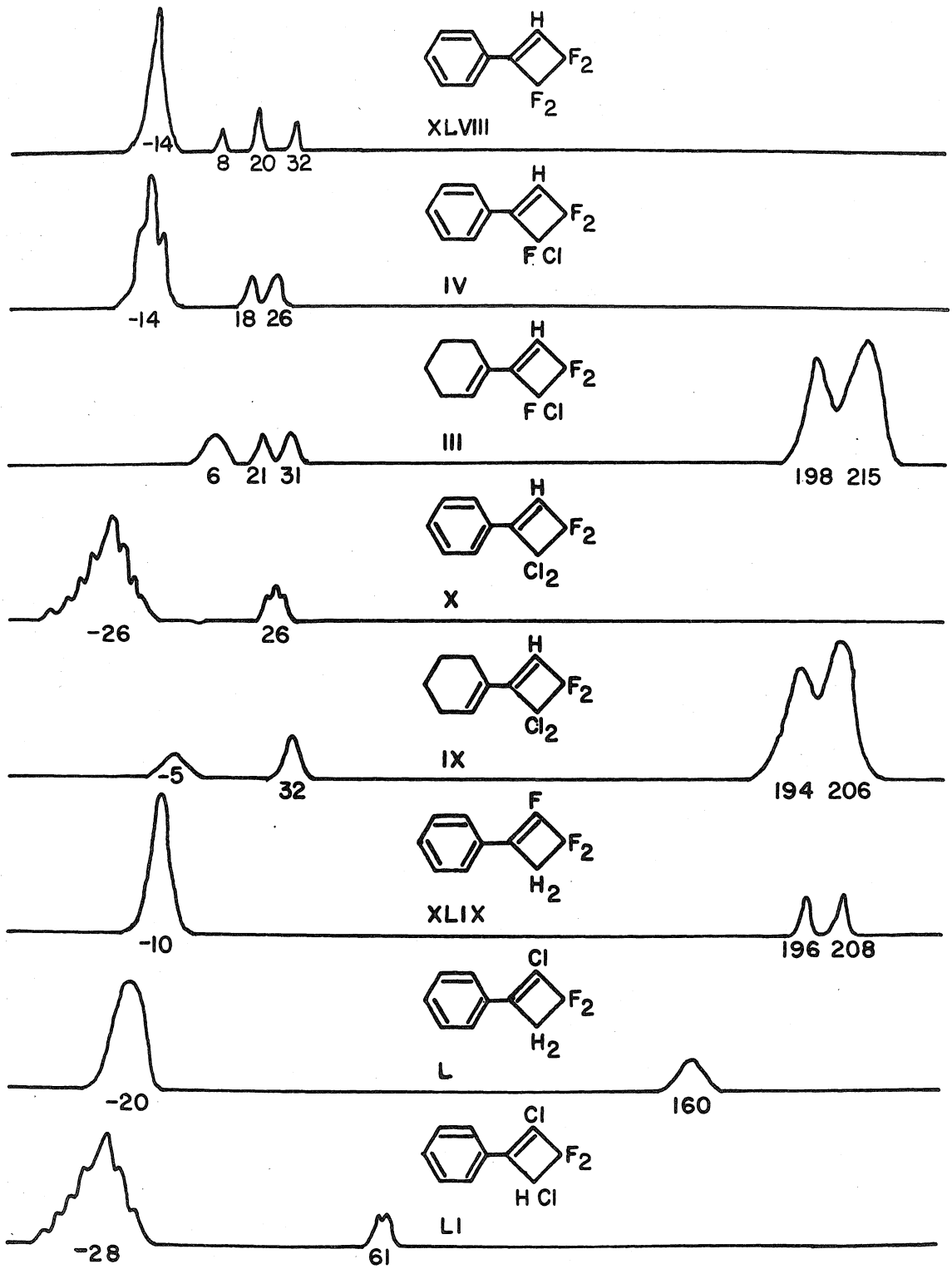


Fig. 1. - Proton NMR spectra of fluorinated phenyl- and cyclohex-1-enylcyclobutenes. Chemical shifts given in c.p.s. at 40 mc. relative to benzene. Ratio of peak areas approximately as observed. See Table I and EXPERIMENTAL for additional information.

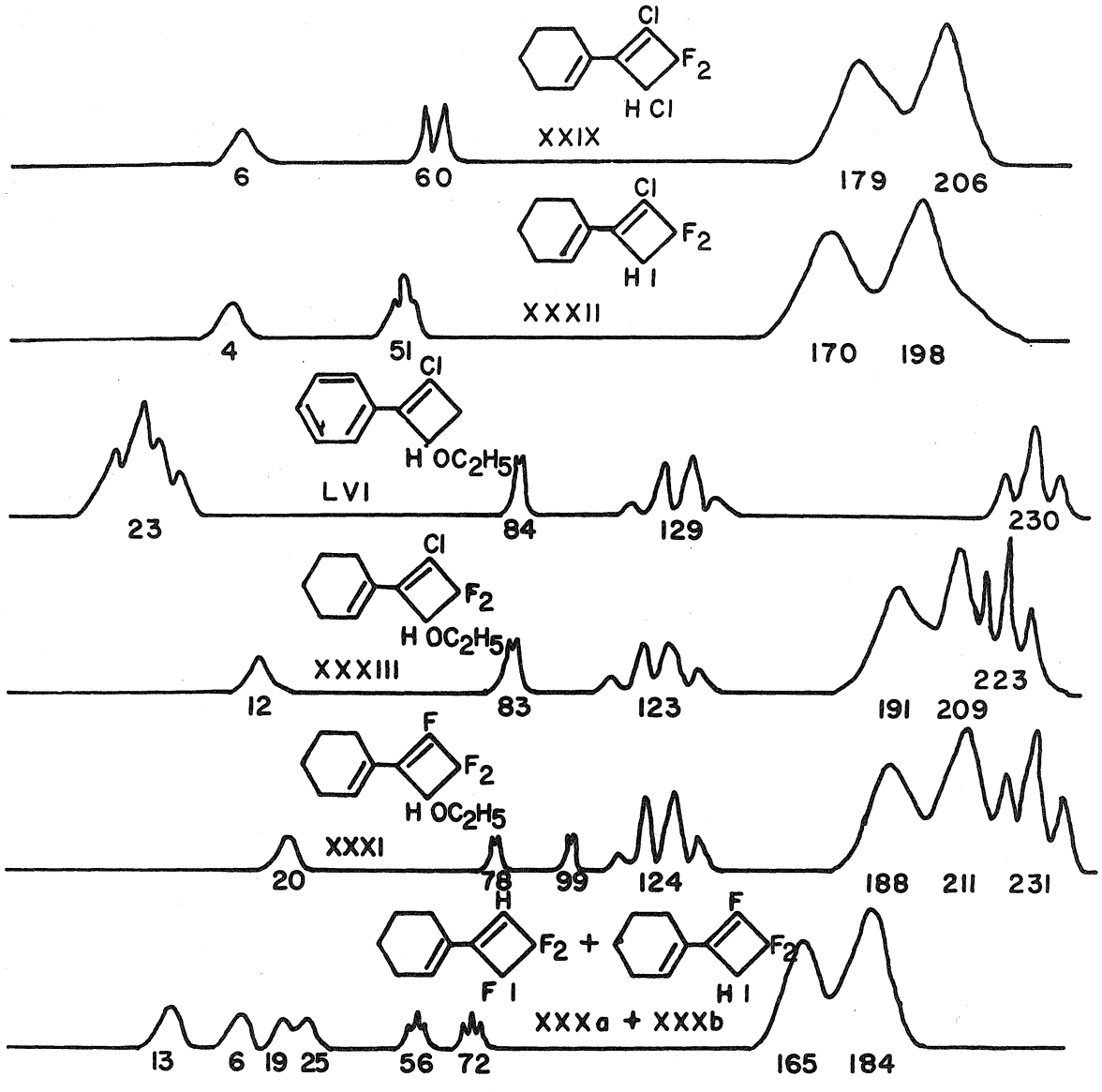


Fig. 1 (cont.). - Proton NMR spectra of fluorinated phenyl- and cyclohex-1-enylcyclobutenes.

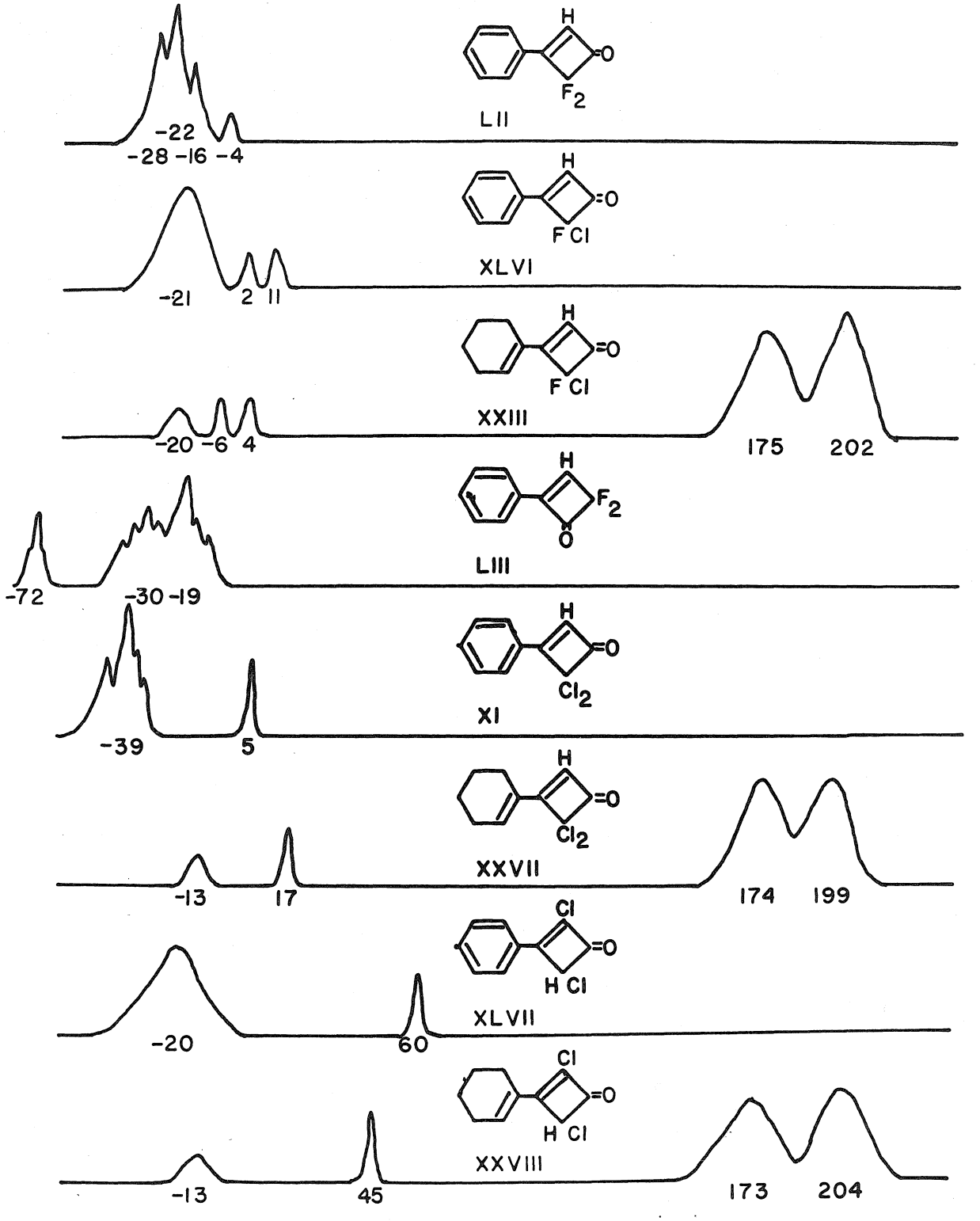


Fig. 2. - Proton NMR spectra of phenyl- and cyclohexenyl-cyclobutenones and cyclobutendiones. Chemical shifts given in c.p.s. at 40 mc. relative to benzene. Ratio of peak areas approximately as observed. See Table II and EXPERIMENTAL for additional information.

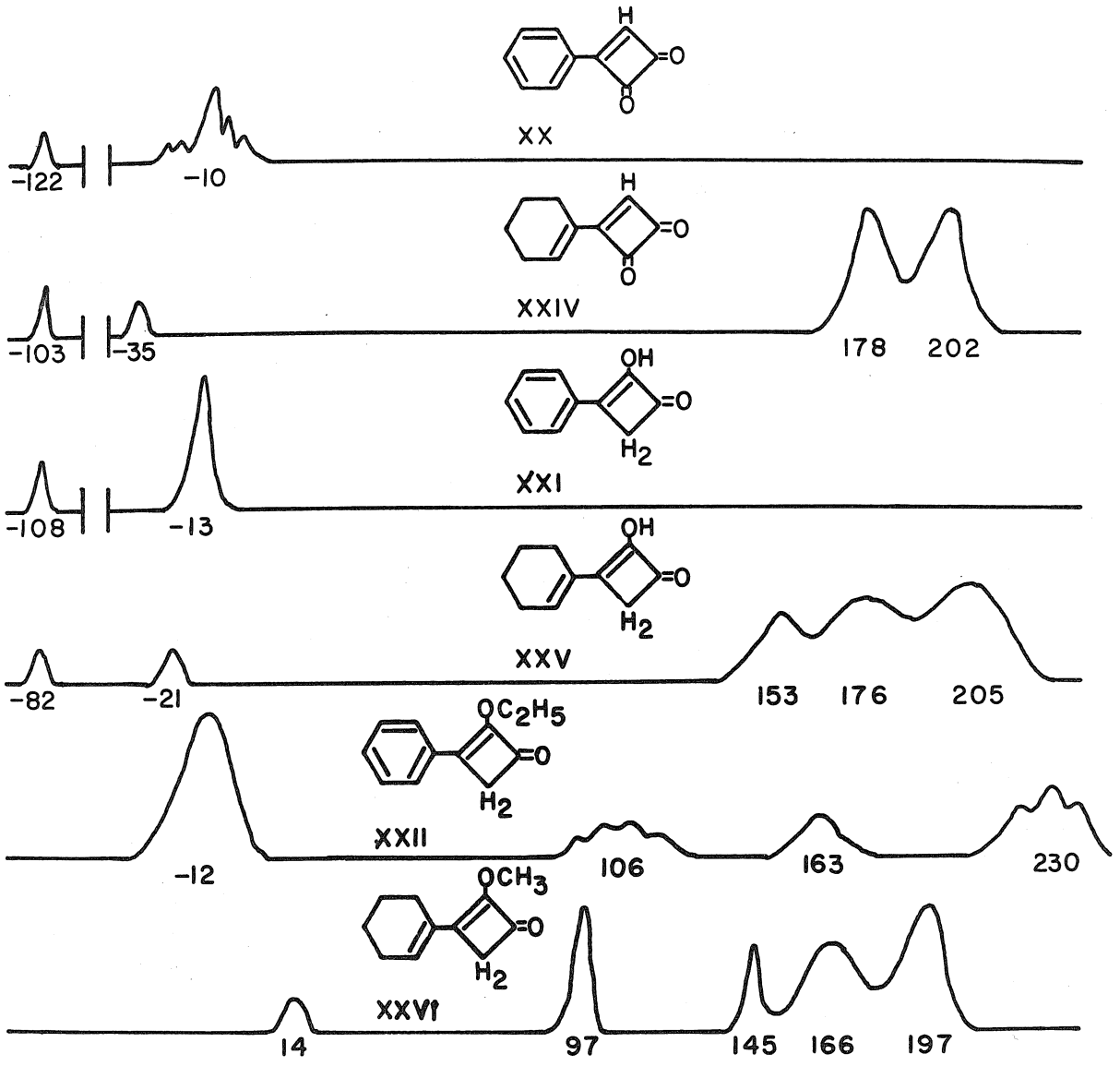


Fig. 2 (cont.) - Proton NMR spectra of phenyl- and cyclohexenyl-cyclobutenones and cyclobutendiones.

which the vinyl proton resonances in the cyclobutenones ~~was~~ were observed is probably a result of the different solvents necessary as well as the differences in chemical environment. A tertiary hydrogen attached to a cyclobutene-ring carbon bearing a halogen atom or an ethoxy group was found to give absorption in the NMR spectrum in the range 45-89 c.p.s. (δ_{H_2O} -0.73 to 0.41).

During the studies reported earlier (Chapter III), the correlations given in the preceding paragraph were repeatedly called upon to help assign structures to new products such as XXVIII, XXIX, XXXI, XXXII, and XXXIII.

As an example of the use of the preceding described correlations, it was possible to analyze the reaction mixture resulting from the reaction of 1, 1, 2-trifluoro-2-chloro-3-(cyclohex-1-enyl)-cyclobutene with sodium iodide in acetone (Chapter III). From the NMR spectrum of the reaction mixture it was concluded that 1, 1, 2-trifluoro-4-iodo-3-(cyclohex-1-enyl)-cyclobut-2-ene (XXXa) and 1, 1, 2-trifluoro-2-iodo-3-(cyclohex-1-enyl)-cyclobutene (XXXb) were formed in about a 3:2 ratio. In Fig. 3 the absorptions at -13 and 6 c.p.s. were assigned as the cyclohexenyl vinyl hydrogens of XXXa and XXXb, respectively. The doublet at 19 and 25 c.p.s. was assigned as the cyclobutene vinyl hydrogen of XXXb and has J_{HF} 6 c.p.s. for cross-ring coupling. The doublet at 56 and 72 c.p.s. was assigned as the cyclobutene tertiary hydrogen of XXXa and has J_{HF} 16 c.p.s. for cross-ring coupling and J_{HF} 2 c.p.s. for the weak coupling with the adjacent gem-difluoro group. The large peaks at 165 and 184 c.p.s. were assigned as the cyclohexenyl

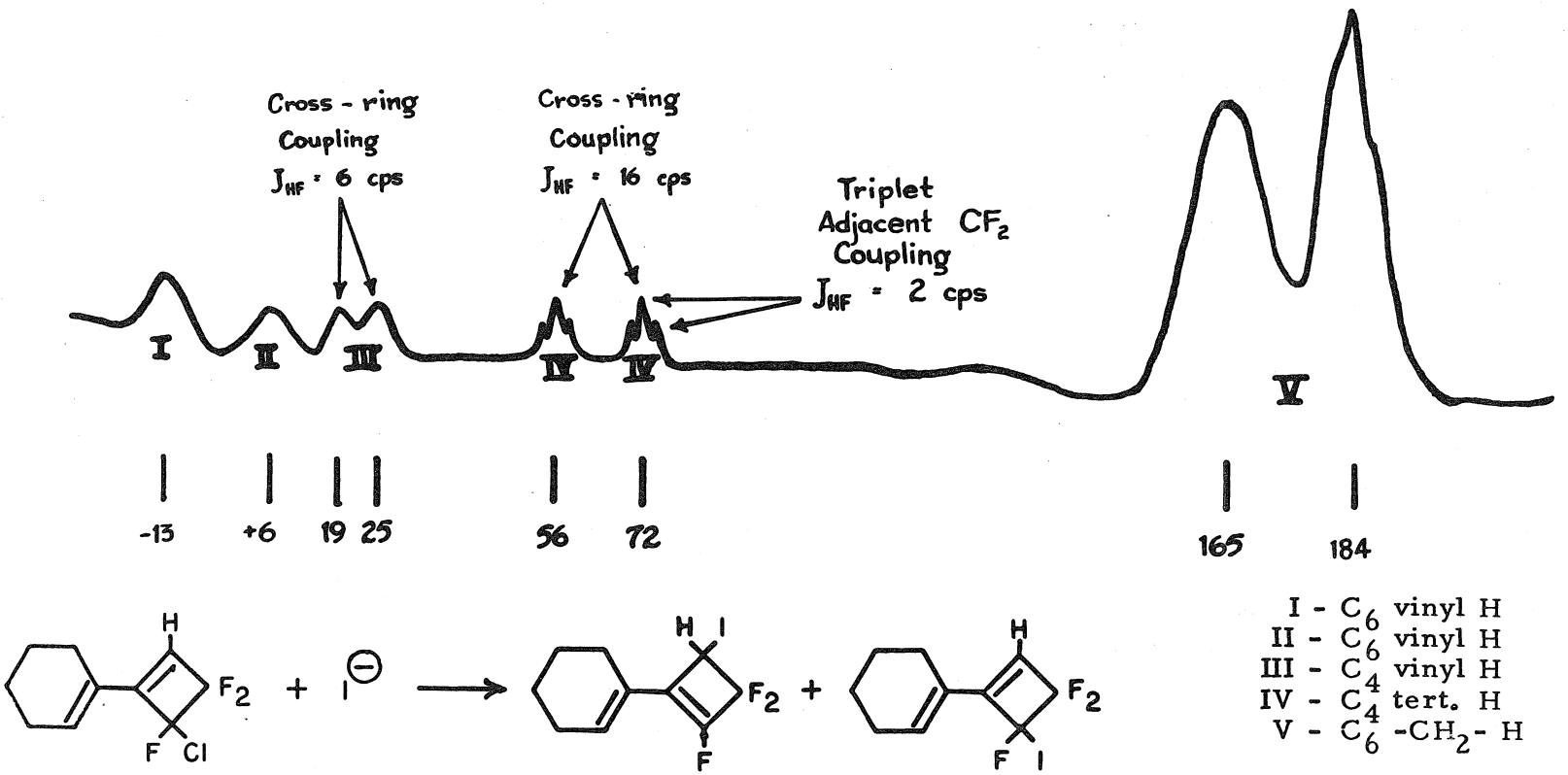
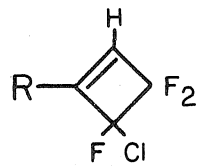


Fig. 3. - Proton NMR spectrum of the displacement products from the reaction of 1, 1, 2-trifluoro-2-chloro-3-(cyclohex-1-enyl)-cyclobutene with sodium iodide in acetone. Chemical shifts are in c.p.s. at 40 mc. relative to benzene.

methylene hydrogens.

The fluorine NMR spectra for most compounds could be understood on the basis of simple NMR theory, modified by cross-ring coupling, for example IX, X, XXII, XXIX, XXXII, and XXXIII. Only one type of compound gave spectra that could not be explained. The compounds were 3-substituted-1, 1, 2-trifluoro-2-chlorocyclobutenes, III, IV, and XV.



R = { Cyclohex-1-enyl (III); Phenyl (IV); Isopropenyl (XV)

In Fig. 4 traces are shown of the fluorine NMR spectra for the three compounds. The gross features are the same for each; four main peaks, three of which are doublets and the other peak a quintet which might be further split. The relative chemical shifts and splittings are indicated in Fig. 4. If the smallest doublet that appears at highest field in each of the spectra were not present, then the spectra could be explained on the basis of simple NMR theory. The small doublet was present in the spectra of each of the three compounds. The area of doublet was relatively about the same in each spectrum. The presence of the small doublets cannot be explained as due to an impurity in the samples used for observing the spectra and must be considered as an integral part of the spectra. The spectra remain unexplained but are of value because they should permit ready identification of the particular ring system in as yet unsynthesized trifluorochloroethylene adducts of conjugated enynes. Indeed, the fluorine NMR spectrum for XV was used to confirm the structural assignment.

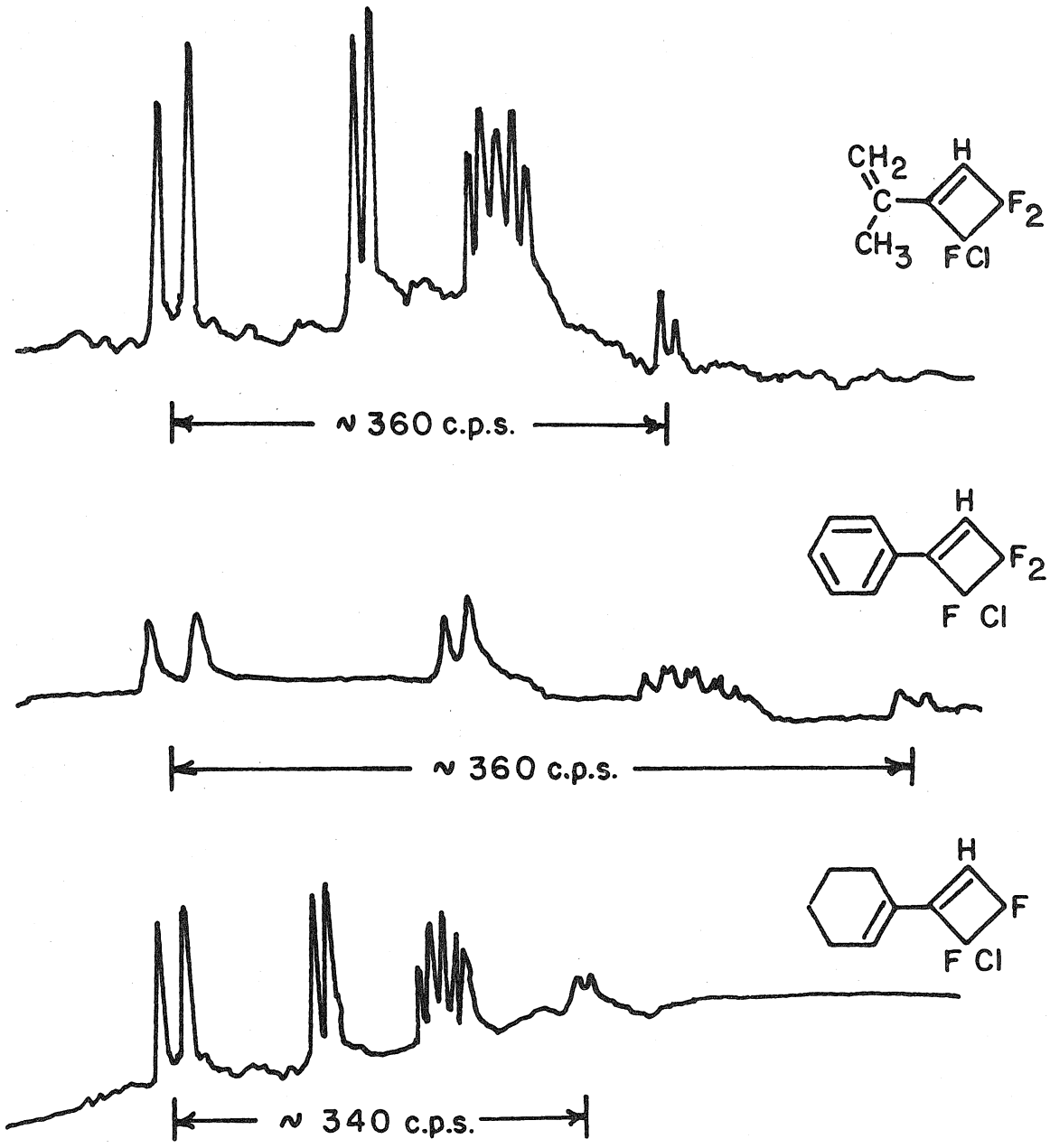


Fig. 4. - Fluorine NMR spectra for 3-substituted-1, 1, 2-trifluoro-2-chlorocyclobutenes. Relative scale in c.p.s. at 40 mc.

EXPERIMENTAL

The proton and fluorine nuclear magnetic resonance (NMR) spectra were observed with Varian Associates High Resolution Spectrometer (V-4300) at 40 mc. and 12-in. magnet equipped with Super Stabilizer. The samples were contained in 5-mm. o.d. tubes and except as noted in Tables I and II, were of pure liquids or melted solids. Proton chemical shifts were observed by changing from sample to ethanol or benzene during a continuous magnetic sweep. For convenience, pure benzene was used as the primary reference, 0 c.p.s. at 40 mc.; the center of CH_2 and CH_3 peaks of ethanol were observed at 134.3 and 237.0 c.p.s. Values for chemical shifts could be reproduced to 2.0 c.p.s. by this method. For the CH_2-CH_3 splitting, J_{HH} 7.4 c.p.s. was used and this value used to obtain splittings in other compounds. Some chemical shifts were obtained with the use of an audio oscillator, in particular the splittings in fluorine NMR spectra were often observed this way. The triplet CF_3 peak in the fluorine NMR spectrum of trifluoroethanol, J_{HF} 9.2 c.p.s. as established with an audio oscillator, was also used to measure splittings in fluorine NMR spectra of other compounds. Preparation of the compounds was described earlier.* Where compounds were furnished by other workers an indication is made in Tables I and II. Certain spectra used in Tables I and II and Figs. 1 and 2 were observed by other workers and were included to permit comparison of chemical shifts; appropriate notes are made in the tables and figures indicating these spectra.

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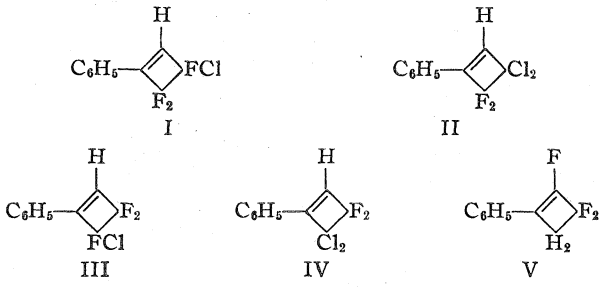
*See Chapters II and III of this thesis.

[Reprinted from the Journal of the American Chemical Society, **79**, 1008 (1957).]

ANOMALOUS SPIN-SPIN SPLITTING IN NUCLEAR MAGNETIC RESONANCE SPECTRA OF CYCLOBUTENES[1]

Sir:

A spectacular failure of F–F spin–spin coupling constants, A_{ij}, to decrease monotonically with the number of chemical bonds separating nuclei i and j has been deduced from the nuclear magnetic resonance (n.m.r.) spectrum of perfluorodimethylethylamine.[2] The current importance attached to the use of n.m.r spectra as a tool for establishment of organic structures prompts us to report a number of similarly anomalous H–F spin–spin coupling constants in cyclobutene derivatives. The present examples are particularly significant in that many of the compounds investigated are (or are derived from) cyclo-addition products of acetylenes with chlorofluoroethylenes[3] and would have been assigned quite plausible but incorrect structures on the basis of their n.m.r. spectra alone. Thus, the splitting of the vinyl hydrogen line of the adduct of phenylacetylene with trifluorochloroethylene into a doublet (A_{ij} = 8 c.p.s.) while the corresponding line of the adduct of phenylacetylene and 1,1-difluoro-2,2-dichloroethylene is not split by greater than 1–2 c.p.s. perforce suggests these substances to have structures I and II, respectively, even though chemical evidence[3] strongly favors III and IV. The only reasonable alternative is to



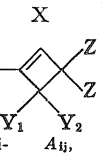
have the cross-ring H–F splitting (separation by *four* bonds) be substantially greater than the adjacent H–F splitting (separation by *three* bonds). This behavior has been observed repeatedly and twelve examples are listed in Table I which indicate the cross-ring H–F coupling to range from 8–12 c.p.s. and the adjacent H–F coupling to be less than 1–2 c.p.s. Compound V is particularly significant since the method of synthesis (trifluorochloroethylene with styrene followed by dehydrochlorination) and n.m.r. chemical shift data require the assigned structure to be correct and yet the methylene hydrogen absorption is only split into a doublet (12 c.p.s.) by the fluorine across the ring.

The need for caution in assigning structures on the basis of magnitude of spin–spin coupling constants for unusual cyclic compounds should be obvious.

Acknowledgment.—We are indebted to Drs. Y. Kitahara, R. E. Krall, E. F. Silversmith, E. J. Smutny, and Mr. S. Manatt for samples of many of the substances in Table I, and also to Mr. A. Bottini for discussions and assistance.

TABLE I

CYCLOBUTENE RING PROTON N.M.R. ABSORPTION[a] FOR R



Compound	R	X	Y_1	Y_2	Z	δ[b]	Multiplicity	A_{ij}, c.p.s.
IV	C_6H_5	H	Cl	Cl	F	−1.15	..	<1–2
III	C_6H_5	H	F	Cl	F	−1.25	2	8
	C_6H_5	H	F	F	F	−1.30	3	12
c	C_6H_9[d]	H	Cl	Cl	F	−1.00	..	<1–2
c	C_6H_9[d]	H	F	Cl	F	−1.15	2	9.4
V[e]	C_6H_5	F	H	H	F	+3.25	2[e]	12[e]
c	C_6H_5	Cl	H	H	F	+2.20	..	<1–2
	C_6H_5	Cl	H	Cl	F	−0.28	..	<1–2
c	C_6H_5	H	F	Cl	=O	−1.64	2[f]	9.2[f]
c	C_6H_9[d]	H	F	Cl	=O	−1.83	2[f]	8.6[f]
c	C_6H_5	H	F	F	=O	−2.21	3	12.3[f]
c	C_6H_5	H	=O		F	−3.60	..	<1–2

[a] Measured using 5-mm. o.d. tubes of pure liquids or solids in 50% acetone solution with Varian Associates High Resolution Spectrometer (V-4300) at 40 mc. and 12-in. magnet equipped with Super Stabilizer. [b] In parts per million, ±0.06, referred to water. [c] Preparation to be described in later papers. [d] C_6H_9 is 1-cyclohexenyl. [e] Fluorine spectrum shows triplet vinyl F-absorption, A_{ij} = 12 c.p.s. [f] Fluorine spectrum shows doublet with A_{ij} same as for proton.

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RECEIVED JANUARY 24, 1957

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PROPOSITIONS

1. Several syntheses of sulfur tetroxide are known, but in all cases reported, sulfur trioxide was a probable impurity. It is proposed that the oxidation of potassium persulfate with fluorine or ozone be studied as a synthesis of pure sulfur tetroxide (1-3).

2. Sulfur tetroxide has been proposed as an intermediate in the persulfate ion oxidations of water and isopropyl alcohol. An investigation of the kinetics of the reaction of sulfur tetroxide with water, methyl alcohol, and isopropyl alcohol is proposed (4-6).

3. Nuclear magnetic resonance spectra of fluorinated cyclobutenes show anomalous cross-ring spin-spin coupling between hydrogen and fluorine. A nuclear magnetic resonance study of fluorinated cyclopentenes is proposed to determine the amount of 1-3 spin-spin coupling between hydrogen and fluorine (7).

4. A possible cyclobutadiene intermediate has been suggested in the conversion of 1, 1-difluoro-2, 4-dichloro-3-(cyclohex-1-enyl)-cyclobut-2-ene (XXIX) to 2-fluoro-1, 3-dichloro-5, 6, 7, 8-tetrahydronaphthalene (XLI). It is proposed the reaction be studied using XXIX labeled at the 2- or 4-carbon with ^{14}C to determine if the ^{14}C-distribution in XLI is consistent with the proposed mechanism (8).

5. More than one possibility exists for the elimination of hydrogen halide from 1, 2-dicarbethoxy-3, 4-(1, 1, 2-trifluoro-2-chloroethano)-3, 5, 6, 7, 8, 9-hexahydronaphthalene (XXXVIII). Of high probability is the elimination of hydrogen chloride, possibly by a stereospecific 1, 4-elimination (E2?). An investigation of the elimination reactions of XXXVIII is proposed.

6. It has been suggested that electronic interactions in the transition state were responsible for predominance of the cis isomer in the dimer formed from trifluorochloroethylene. It is proposed that the dimerizations of trifluorobromoethylene and trifluoroethylene be investigated and that the dimerizations of acrylonitrile and trifluorochloroethylene be reinvestigated to determine (or redetermine) the configuration of the cycloaddition products. An investigation of the products from cycloaddition of chloroprene and fluoroprene with trifluorochloroethylene is also proposed (9).

7. Diazomethane and diphenyldiazomethane add to nitroolefins of the type $RCH{=}CHNO_2$ in opposite directions to give pyrazolines. It is proposed that an ionic mechanism might be demonstrated by the study of the products from the reaction of a nitroolefin with dimethyldiazomethane and with bis-trifluoromethyldiazomethane (10).

8. It is proposed that the products from the hyriodic acid reductions of 4-hydroxy-3, 4-diphenyl-2-cyclopenten-1-one and 4-hydroxy-3, 4-diphenyl-2, 5-dimethyl-2-cyclopenten-1-one be investigated by nuclear magnetic resonance spectroscopy to determine which of the alternate structures discussed in reference 11 for each case is correct.

9. Para-xylylene has been classified as a pseudodiradical because of its high reactivity to iodine and ease of polymerization. Theoretical calculations predict it to exist in a singlet ground state. Hexane solutions of para-xylylene have a half-life of 21 hours at -78° and when warmed to room temperature give a precipitate of polymer. An electron paramagnetic study of hexane solutions of para-xylylene at -78° and continuously on warming to room temperature is proposed to determine if there is a detectable diradical contribution to the

molecule at -78° or at any time prior to polymerization at a higher temperature (12).

10. The synthesis of gem-difluoro compounds usually requires relatively high temperatures and strong fluorinating agents. An investigation of the reactions of ketones with phosphorus pentafluoride is proposed as a milder, alternate synthesis of gem-difluoro compounds. If successful, a subsequent study of the reactions of phosphorus pentafluoride with other organic compounds such as alcohols and aldehydes would be logical.

11. The synthesis of many monofluoro aliphatic compounds requires relatively strong reaction conditions. The diazotization of alkyl amines in hydrogen fluoride might be a mild route to the corresponding alkyl fluorides or diazotization might give several products by reactions similar to those that occur when aliphatic amines are diazotized in water. It is known that diazotization of aromatic amines in hydrogen fluoride leads to the corresponding aromatic fluorides (13). An investigation of the diazotization of aliphatic amines in liquid hydrogen fluoride is proposed to determine the course of the reaction.

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