

A STUDY OF THE DIRECT AND SENSITIZED REACTIONS OF
1,3-CYCLOOCTADIENE AND 1,3,5-CYCLOHEPTADIENE IN
SOLUTION

Research Report by

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To Karen

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Abstract

A number of experiments were carried out in an attempt to determine the course of bicyclic isomerization in cycloheptatriene and 1,3-cycloöctadiene. Results, inconsistent with literature reports but showing definite consistency within the course of the experiments, led to the further examination of both the direct and benzophenone-sensitized reaction of the above compounds. Attempts were made at fractionation by preparative vapor chromatography. The fractions obtained were examined by NMR spectroscopy in the case of 1,3-cycloöctadiene. A crystalline product obtained from the sensitized reaction of cycloheptatriene was also partially characterized.

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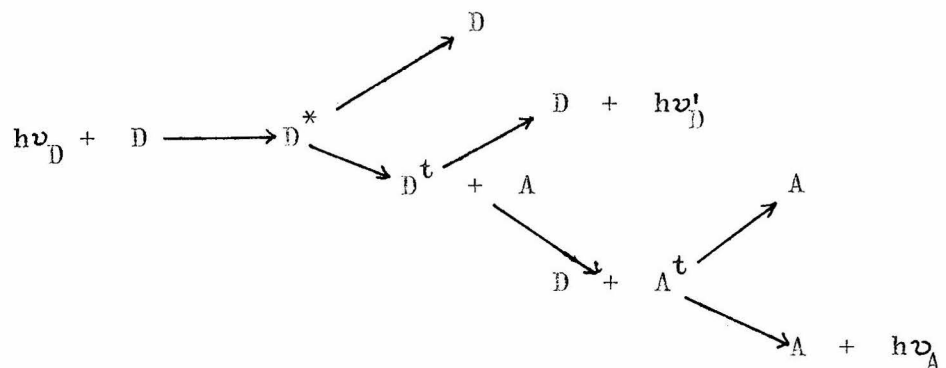
Historical

Though fluorescent phenomena and light-induced chemical reactions (i.e. photosynthesis) have been observed by man for many centuries, and reference to photochemical reactions may be found in the literature in the late 1800's, it was the work of Lewis, Lipkin, and Magel⁽¹⁾ which marked the era of organic photochemistry. With the further postulation of the phosphorescent state by Lewis and Kasha, its definition as a triplet state phenomenon, and its eventual recognition as a unique and universal molecular property^(2,3), full-scale investigation was underway. Many classes of organic molecules, from the simplest to the most complex and exotic, have since been studied⁽⁴⁾ by physical organic chemists, but mechanistic studies have proceeded primarily by standard kinetic techniques, which are sometimes inadequate when dealing with the extremely short-lived and energy-rich systems which characterize photochemical reactions.

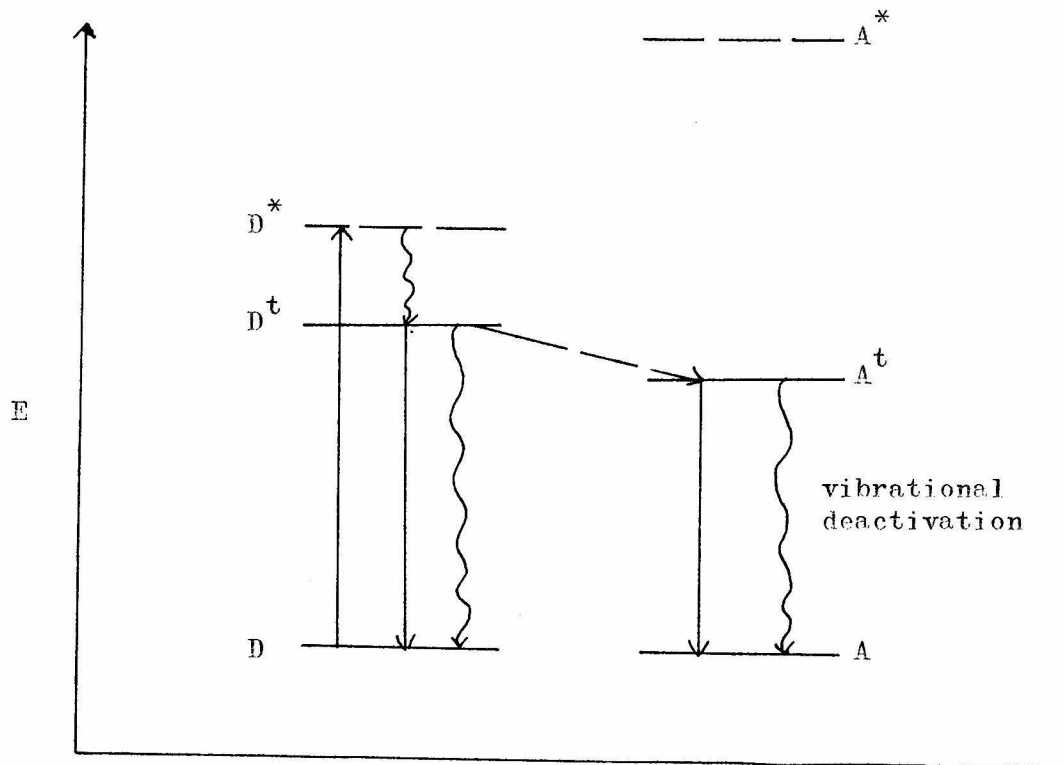
Terenin and Ermolaev⁽⁵⁾, with the discovery of intermolecular energy transfer and its assignment as a triplet process, provided the basis for the necessary investigative techniques. Their conclusions were based on the study of the observed phenomenon of induced phosphorescence in naphthalene in the presence of benzaldehyde at wavelengths of irradiation which would not ordinarily induce luminescence in naphthalene alone.

By photoelectric measurements it was shown that the mean life-time of the sensitizer (in this case, benzaldehyde) was shortened under such conditions, presumably by the process of radiationless transfer to the acceptor (naphthalene). Similar studies were made with other compounds as sensitizers and acceptors, with similar results. One of these studies, using benzil as the sensitizer and α -methylnaphthalene as acceptor, inadvertently provided the first direct data of relative triplet energies, when it was shown that α -methylnaphthalene did not affect the mean life-time of benzil but did reduce that of benzophenone.

On the basis of singlet and triplet state lifetimes, it was postulated that the observed energy transfer was indeed a triplet process. The proposed mechanism and a schematic representation of the process are given below.



(The possibility of a DA complex is ruled out since there is no change in the phosphorescent spectra of either D or A; in addition, there is no shortening of the mean life-time of the acceptor.)



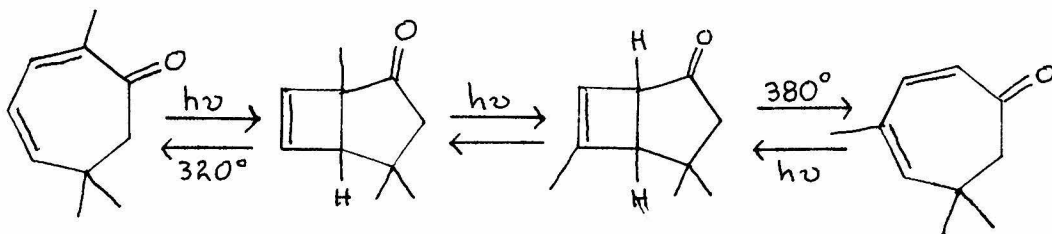
The fact that such sensitizers do indeed react photochemically by triplet state processes was examined more closely for the particular case of benzophenone by Hammond and Moore⁽⁶⁾. They showed that in the reaction benzophenone + benzohydrol + light = benzopinacol the rate of the reaction is diffusion-controlled. Since the maximum diffusion constant is about 5×10^7 /sec. and fluorescent rates are greater than 10^8 /sec., it was concluded that the triplet state of benzophenone was the active moiety, especially since no fluorescence could be detected for benzophenone and there was no isotope effect with deuterated benzohydrol.

Diverse mechanistic investigations have since been aided by the use of "sensitizer techniques." Notable

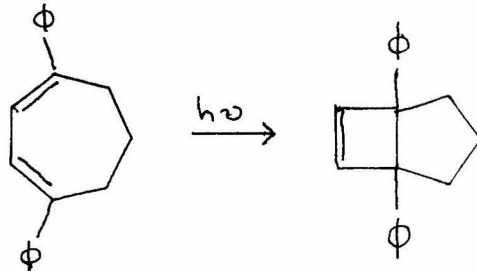
examples have been the studies of the dimerization of isoprene and of butadiene^(7,8) and the subsequent postulation of cis and trans triplets as stable, noninterconvertible, stereoisomeric states as reaction intermediates.⁽⁹⁾ Others in the field have also demonstrated the remarkable effect of the nature of the excited state upon the course of reaction, notably Zimmerman⁽¹⁰⁾ and Griffin⁽¹¹⁾ in their studies of cis-dibensoylethylene and Schenck in his study of coumarin dimerization⁽¹²⁾.

Conjugated Large Ring Systems

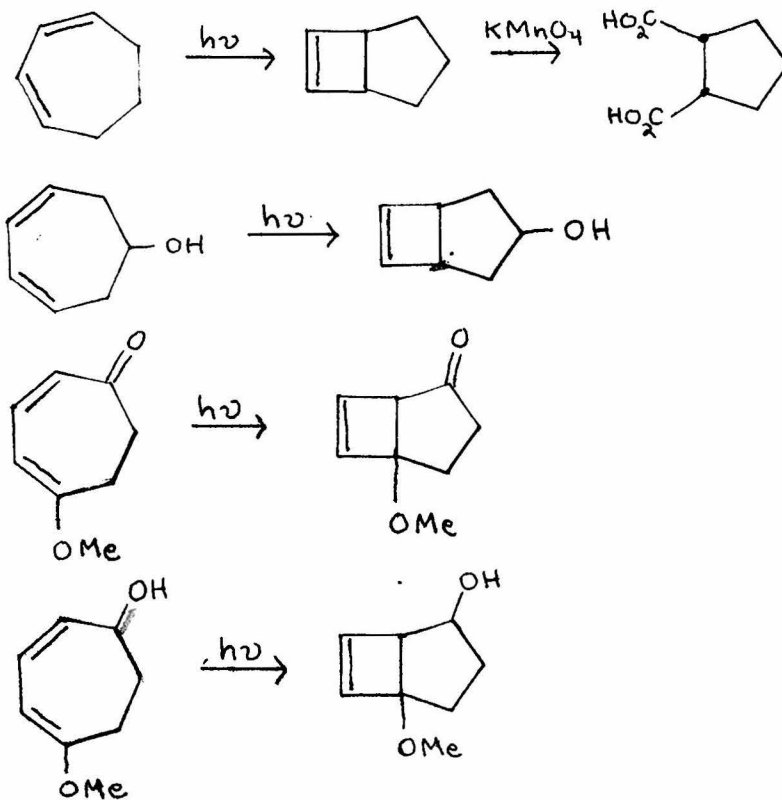
In the past few years photochemical studies of conjugated cycloheptyl and cycloöctyl compounds have been numerous. Due to the nature of these compounds, investigations were usually first begun with naturally-occurring representatives of the various series. Thus eucarvone, examined by Büchi and Burgess,⁽¹³⁾ seems to be the first cycloheptadiene to be investigated. Their conclusions as to the type of reaction to be expected have essentially been shown to be the case in nearly all other related compounds. The reaction is shown below.



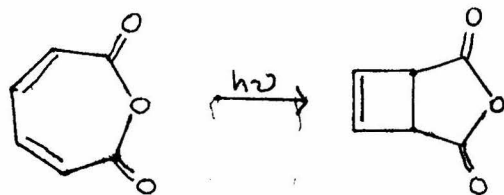
Many other examples of a similar ring closure in the cycloheptadienes can be cited. Rigaudy and Courtet⁽¹⁴⁾ have examined 1,4-diphenyl-1,3-cycloheptadiene;



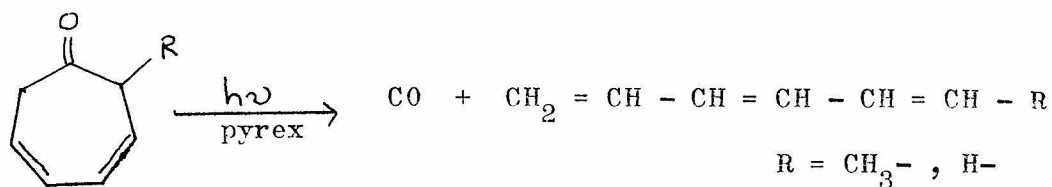
Chapman, Pasto, and coworkers⁽¹⁵⁾ have examined a whole series of cycloheptadienes;



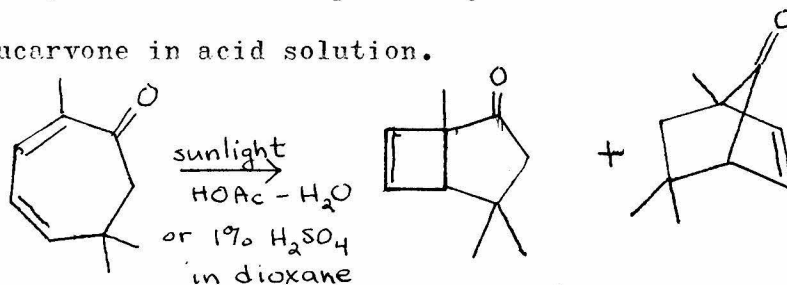
while Fonken⁽¹⁶⁾ has reported a similar isomerization in the related heterocyclic, muconic anhydride.



One exception, reported by Chapman and Borden⁽¹⁷⁾,

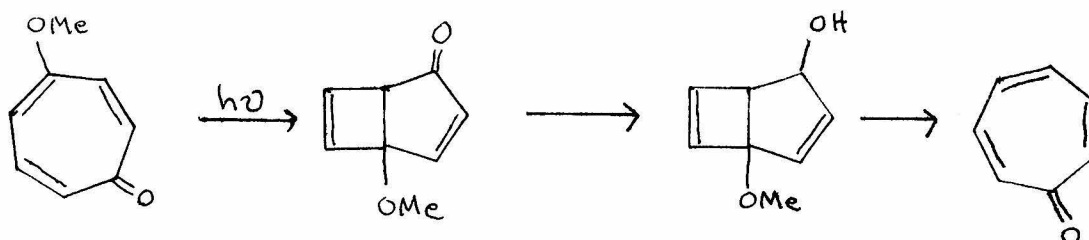


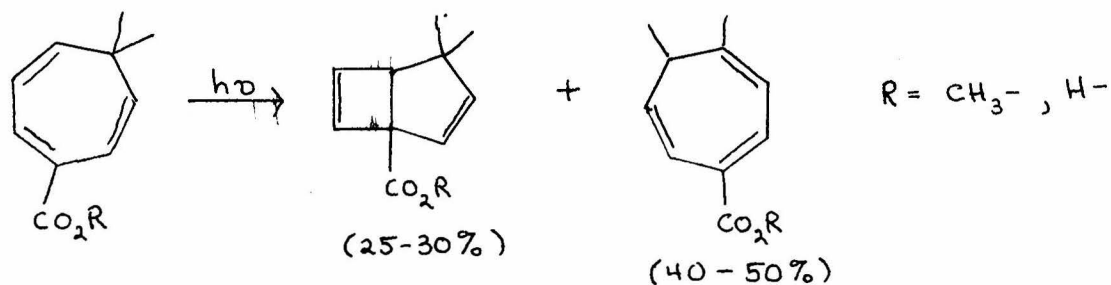
has been explained by the fact that initial excitation is an $n \rightarrow \pi^*$ transition of the carbonyl group with subsequent triplet carbonyl transfer to the diene system, rather than direct excitation of the diene system itself. Another exception has been reported by Hurst and Whitham⁽¹⁸⁾, involving eucarvone in acid solution.



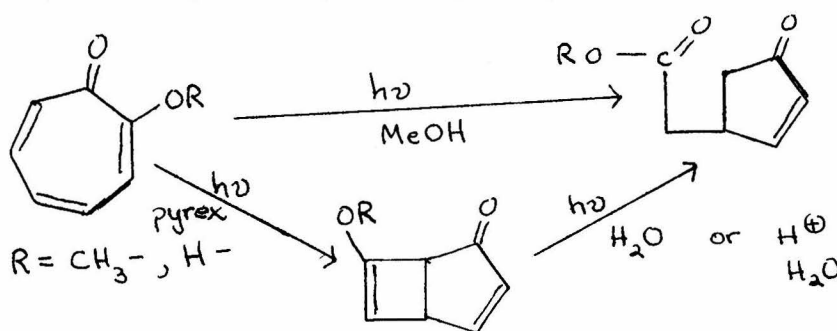
The necessity of the presence of H^+ for the reaction has led to its explanation as a solvolytic rather than photochemical mechanism and thus removed it from the realm of contradiction also.

Examination of the cycloheptatriene series has produced an analogous ring closure reaction as the expected end product of photochemical excitation. Chapman and coworkers^(19, 20) have reported on a series of reactions studied in their laboratories.

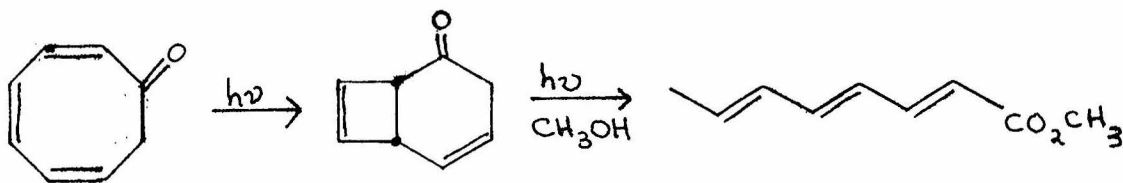
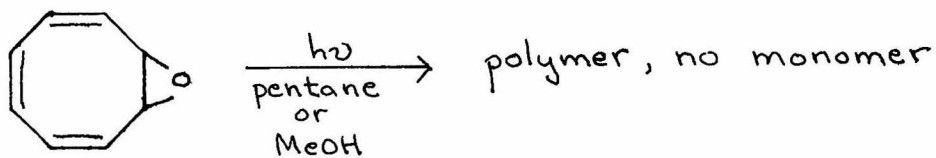




Once again it is a solvent effect which seems to account for the exception reported by Chapman⁽²¹⁾.

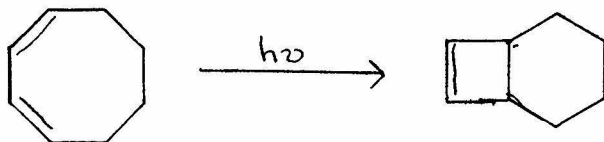


The few cyclooctyl compounds which have been reported show no such patterned response, as evidenced by the few examples cited below, reported by Büchi and Burgess.⁽²²⁾



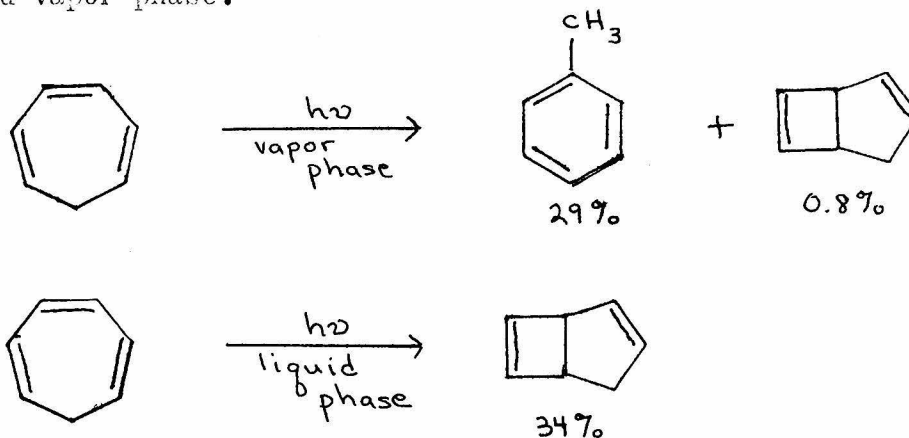
Results and Discussion

The two representatives of these large ring compounds which have had the most thorough examination seem to be 1,3-cyclooctadiene and 1,3,5-cycloheptatriene. The former has been studied extensively both by Dauben and Cargill⁽²³⁾ and Chappell and Clark⁽²⁴⁾. Both have concluded that the ring closure isomerization is the preferred photochemical path under normal conditions.

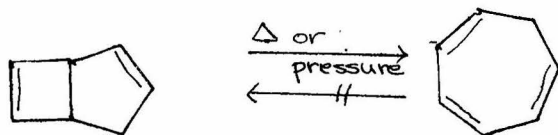


The closure product, bicyclo (4.2.0) oct-7-ene, has been characterized thoroughly by both groups, by NMR spectroscopy in the case of Chappell and Clark, and by periodate oxidation to the diacidic cyclohexane in the case of Dauben and Cargill.

Dauben and Cargill⁽²⁵⁾ have also examined the photoreaction of cycloheptatriene and characterized its ring closure isomer by NMR spectroscopy. Srinivasan⁽²⁶⁾ has also studied the reaction closely, in both the liquid and vapor phase.



Quantum yields and kinetic studies of the vapor phase reaction under various temperature and pressure conditions, as well as in the presence of inert gases, have led Srinivasan to postulate that toluene is formed from a high vibrational level of the electronic ground state, formed by the singlet decay of the excited electronic state. He further postulates that ring closure isomerization must then be due to triplet state reaction at ground vibrational levels since toluene formation is effectively halted in solution and the ground electronic state displays the following equilibrium at increased temperatures or, in the vapor phase, at increased pressure.



It was the original intention of this investigation to study the reactions of these two compounds in the presence of a triplet sensitizer to determine the validity of Srinivasan's postulation for the cycloheptatriene and to see if it could be extended to the somewhat analogous cyclooctadiene system. However, though much effort has been expended to find a set of conditions that will indeed yield a single product in either the sensitized or the unsensitized reaction of either compound, no such reaction has ever been observed in the course of these experiments. Whether this is the effect of naive

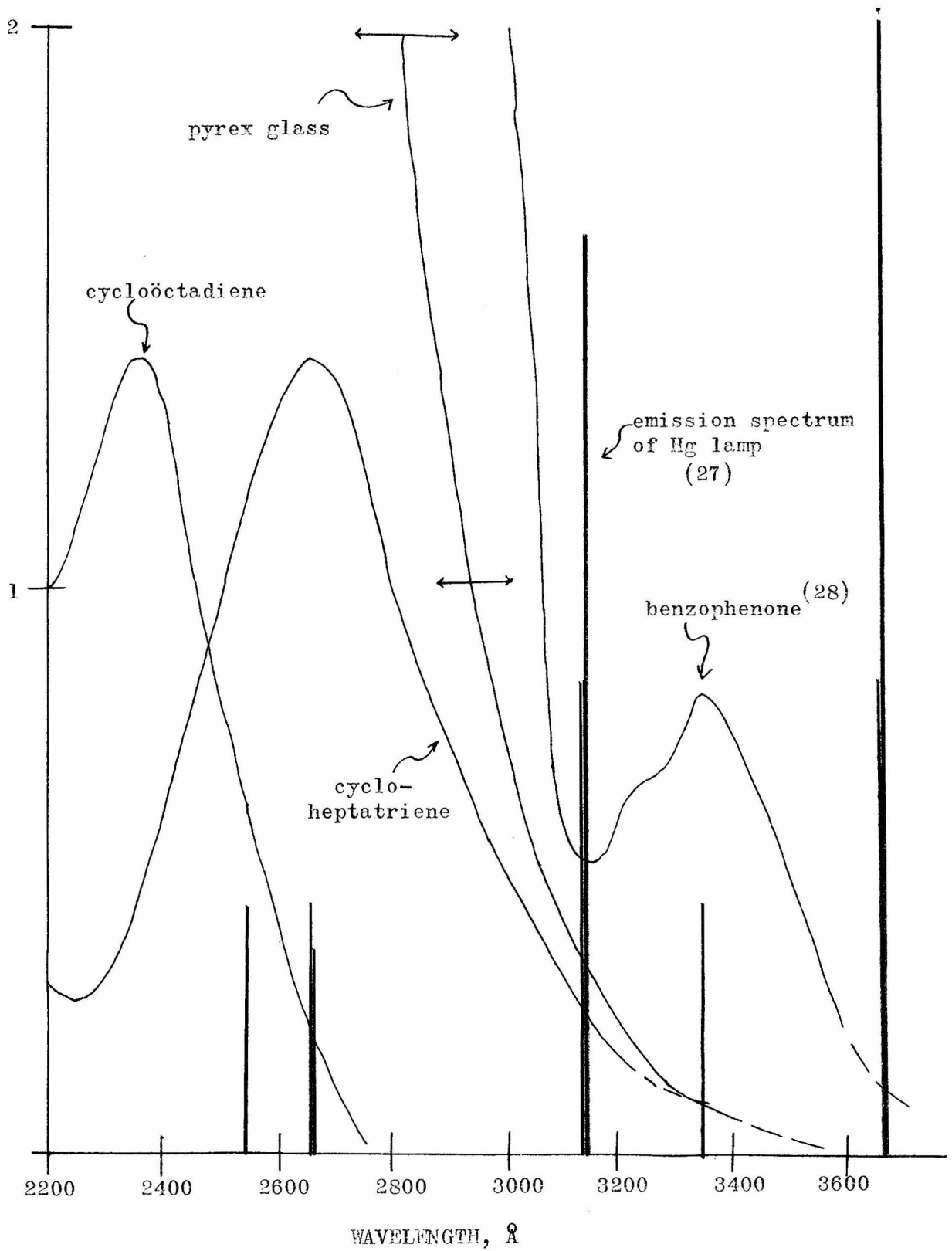
experimental techniques or the hand of God remains for the present an equally insoluble problem. Nevertheless results have been obtained, though at best inconclusive and at worst feeble they may be; such results, especially such results, are most conducive to discussion and speculation. In the light of burgeoning knowledge and belated wisdom I should like to attempt such a discussion in the following pages.

The diagram on the following page indicates the first and perhaps most serious sin committed during the experimental procedures described in a later section. Pyrex glass was used extensively throughout as a filter to prevent direct absorption by the acceptor compound. While it is readily observed that an efficient job was done by the pyrex in the case of the cycloöctadiene, it is just as obvious that it fell far short of expectation in the case of cycloheptatriene. The emission lines of major concern, 3125-3131.8 Å, fall in an area where absorption by sensitizer, filter, and acceptor are nearly equal. This fact must be remembered and seriously considered, especially when discussing results with an initially high acceptor concentration.

1,3-Cycloöctadiene

Although the data is very qualitative, examination of the results of the various öctadiene experiments show several very important facts. Table I shows that the

Effectiveness of Pyrex Glass as a Filtering Agent



diene system yields not one but several products upon irradiation. There is one major product in the direct reaction, as reported in the literature, but two minor products are also in evidence. It is these latter products, in almost equal amounts, which account for the bulk of the sensitized reaction, though still a fourth product is in evidence in large enough quantity to be considered of interest. The data of Table VI clearly supports this interpretation. The unsensitized reaction is clearly hindered by the filtering effects of the pyrex tubes in which the reaction was run, and only after prolonged photolysis was conversion effected, on the order of 10%. There was little effect on the sensitized reaction, however. All samples show approximately the same conversion, irregardless of exposure time. It seems clear that two distinct processes are in evidence, a sensitized and a direct. If the former is indeed a sensitized reaction it is almost surely a triplet process. The direct reaction must be explained by some other means.

The results of expt. #5 add further weight to these conclusions. There is no evidence of a direct reaction, though exposure times were about the same in this experiment as in expt. #4. This can only be explained by the fact that there were further barriers to irradiation, namely the 30-35 cm. between the light

source and the tubes. The intensity falls off as the square of the distance, which could easily account for the results of Table IX; the light was filtered twice by pyrex and its intensity was a fraction of its original 450 watts. Taken as a whole, the results in Table X show once again that the sensitized reaction does exist, as evidenced by the rapid conversion even at low intensities and short periods of exposure. The same major products are in evidence; the examination of the data on the basis of concentration can give some idea as to the processes which control their production.

It is evident that at very low concentrations, 0.1%, conversion to nearly equal amounts of D_4 and D_5 is the major process. The consistency with which these products appear, only together and in nearly equal amounts, would lead one to speculate that they might be isomeric forms of the same product. The similarity of retention times on the vapor chromatograph also suggests this possibility.

At medium concentrations, 1%, the above conversion to the proposed isomeric substances is still of major importance, though a competing process, which has as its end product an insoluble crystalline substance, also assumes considerable stature. At higher concentrations, 10%, there is evidence of inhibition of the above processes and the introduction of still another product, which was

first observed in expt. #1. At still higher concentrations this same process is in evidence also.

The results of expt. #6, run at medium concentration, once again prompt images of an isomeric process. Tube (Da) provides the only contradictory information in the whole series, and rather defies explanation. It is possible that the loss of considerable solvent and the presence of oxygen had a marked effect upon the course of the reaction, which was run in quartz. It is equally likely that two solvent peaks could have been produced during the injection of the sample into the vapor chromatograph. If that were the case, all compounds would then be designated by one lower number and the familiar direct reaction would be in evidence once again, for the diene was determined by its retention time to indeed be diene while the other compounds were assigned on the basis of pattern more than retention.

The attempts at characterization of these products by preparative vapor chromatography and subsequent NMR analysis have proved to be of limited but not negative value. In all preparations, diene has been recovered in sufficient purity to identify it by comparison with known spectra and spectral values. Figure I is an NMR spectrum of cyclooctadiene as used in the majority of these experiments. The similarity to the spectra of Figures IV and VII are unmistakable. Thus a valuable reference point

FIGURE I

1,3-Cyclooctadiene

Neat sample

External standard

Filter bandwidth: 4 cps

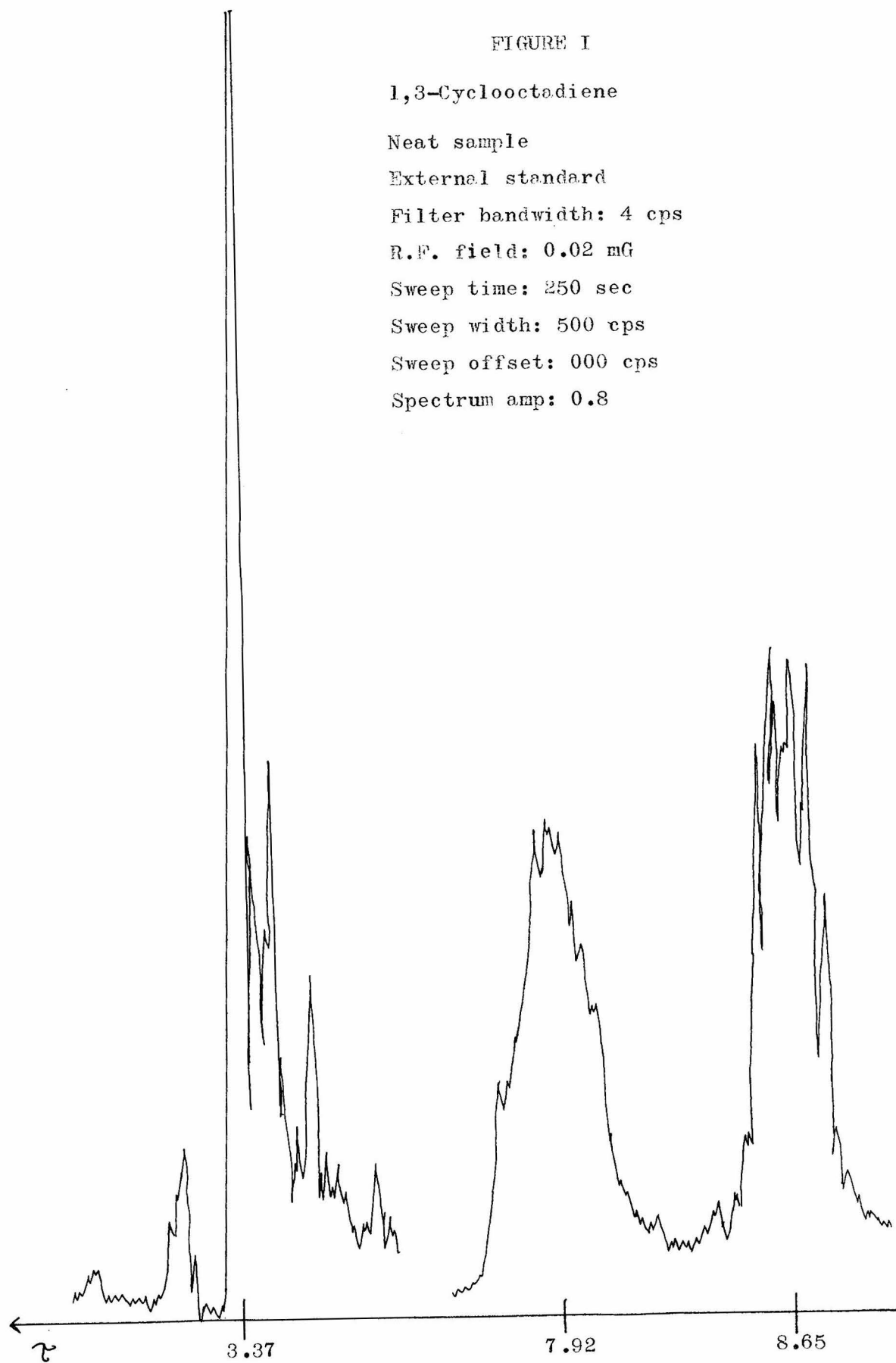
R.F. field: 0.02 mG

Sweep time: 250 sec

Sweep width: 500 cps

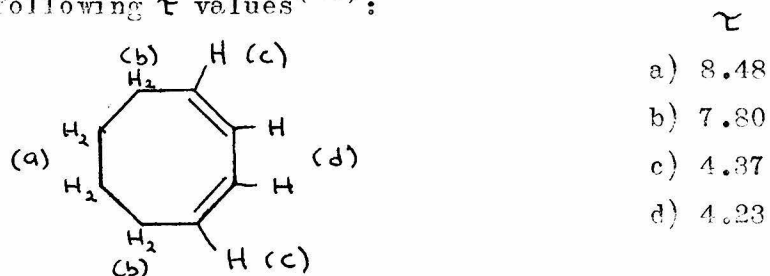
Sweep offset: 000 cps

Spectrum amp: 0.8



in the chromatographic trace has been established in each case. Such a point is necessary since the large nature of the preparative samples used have a tendency to overload the chromatographic columns and substantially deform and lengthen characteristic peak contours and compound retention times.

The analysis of the direct reaction in expt. #6 is greatly hindered by the difficulty in assigning the various fractions to those shown in other analyses by vapor chromatography. If this matter is disregarded for a few moments, the situation may become clearer. The original molecule has been analyzed and the various hydrogens assigned the following τ values⁽²⁹⁾:



These values agree very well with our assigned values, being about 0.1 p.p.m. higher; this is probably due to our use of an external standard, and should be a consistent statistical error in all τ values given.

The study of Chappell and Clark⁽²⁴⁾ has provided us with NMR analysis of the ring closure isomer predicted as the major product of the direct reaction.



If we examine Figure III with this data in mind, and also remembering that fractions one and two were not very well separated by the chromatographic column and that there will be remnants of the spectrum in Figure II also, a little headway can be made. The marked similarity of the two spectra become even more evident upon closer examination, and if intensities are ignored. Let us thus ignore the band at 7.85 in Figure III on the basis of intensities between the two spectra. In a similar manner ignore the bands at 3.80 and 7.10 in Figure II. Though it would now seem possible to analyze them successfully, that task defies my limited abilities, even with Jackman⁽²⁹⁾ in hand. All that I can say with some surety is that neither is the ring closure isomer; the first fraction is also very probably saturated. As for the fifth fraction, while its spectrum is of possibly great interest, that which is presented is of little use.

Analysis of the sensitized reaction's spectra will not be of much higher calibre. Once again the first fraction as represented by Figure VI is of little more than curiosity value. The analysis of the third fraction can once more be simplified by eliminating the

band at 4.09 as an obvious remnant from the starting material, which it matches very closely in retention time. Fraction five is also little more than a curiosity at the present time. It is said that it is the wise man who knows his limitations; this, unfortunately, has brought me to mine.

1,3,5-Cycloheptatriene

The data for cycloheptatriene is even more qualitative in nature, especially due to the unfortunately direct absorption during a seemingly sensitized photolysis. Nevertheless certain patterns of reaction still emerge, which can provide us with at least some basic ideas about the nature of the triene reaction.

The data in Tables II and III show that the direct reaction has one major product, but that if the reaction is run through quartz, as done in the literature, several other products seem to occur also, possibly due to the increased photons available through quartz. The remaining data on the direct reaction, taken mostly through pyrex, is difficult to make any type of case for. In all cases, conversion is at best very slight, usually less than 1%, giving several minor products seemingly indiscriminately, though Tables V and VII suggest the desirability of a path leading to the formation of T_3 . Concentration ranges seem to have little effect upon the outcome of this reaction. Table XI shows some degree of

consistency with these results even through quartz, though the major product is now T_4 . Such inconsistency might be explained on the basis of difficulty in assigning retention times to the various trace compounds which give evidence of their existence only very unwillingly. In such cases it is order of separation by the column more than retention time which provides the basis for classification. Any modification, from contamination of the microsyringe with acetone during injection to a wandering of the base line, could lead to the introduction or the suppression of an unexpected compound in the pattern. Thus, with such a limited amount of conversion as was the case in most samples, such inaccuracy might be accountable and expected.

In the sensitized reaction, however, yields are much higher and straightforward, consistent evidence for such a sensitized pathway is obvious. Table IV shows two major products, of nearly equal amount, which dominate the reaction and seem to appear in greater quantity with increased photolysis. A similar result can be seen in the data of Table V. It is difficult to assess the possibility that T_3 also is a product of the reaction, for this might just as easily be due to the direct reaction taking place simultaneously. Relative rates of reaction would seem to indicate that this was not the case, however, and that this third product did indeed play a role in the sensitized mechanism.

The effect of concentration, summarized in

Table VIII, is clearly in evidence. At approximately 0.1% T_4 and T_5 are produced in nearly equal amounts, though at longer exposures the production of T_5 dominates. The difference over time might be explained on the basis of contribution by the direct reaction of T_5 , which it preferentially produces. There is also a crystalline product which may be the main product of the reaction at these concentrations, since it is in evidence in macroscopic quantities even at these low concentrations and after very short exposure times.

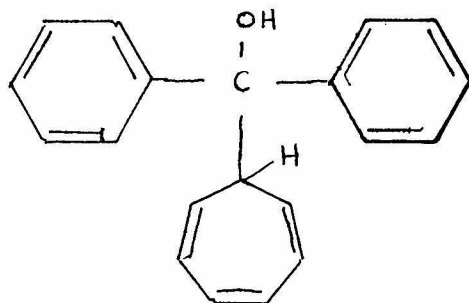
At median concentrations, 1.0%, there is at first competition in the production of T_3 at short exposure times, but eventually the pattern of product distribution becomes the same as at lower concentrations, with evidence of the same precipitate formation and nearly equimolar production of T_4 and T_5 .

At higher concentrations, 10% or more, product distribution resembles that of the direct reaction very closely, T_3 being the main result with T_5 (but no T_4) also being produced.

Results consistent with these were also obtained from the last two experiments done, both at medium concentrations. Table XI shows the now familiar distribution of products, even in the presence of oxygen. Expt. #8 gave small conversion, probably due to the reduction of benzophenone concentration, to any volatile products, but the crystalline solid was in

evidence to a large enough extent to permit an attempt at characterization.

The melting point, or rather sublimation point of the solid precludes the products which readily come to mind, such as benzohydrol, m.p. 68-69°C., benzophenone itself, m.p. 49°C., or even benzopinacol, which decomposes at 186°C., leaving a black, charry residue rather than cleanly subliming. The infrared spectrum, which is summarized in Table XIII, seems to provide support for the following proposed structure,⁽³⁰⁾



though a carbon-hydrogen analysis and NMR spectrum will be necessary for positive identification. Though there was some initial trouble in finding a solvent for the compound, it seems likely that chloroform will prove to be of use, both for purification procedures and NMR spectroscopy.

ExperimentalBenzophenone

Benzophenone - Matheson, Coleman, and Bell reagent grade - was recrystallized from diethyl ether; m.p. 48-49°C. It was used in the first four experiments. The reagent benzophenone, m.p. 48-49°C., was used without further purification for the remainder of the experiments.

2-Acetonaphthone

2-acetonaphthone, Eastman Kodak White Label, was recrystallized from hot ligroin; m.p. 53°C.

9-Fluorenone

9-fluorenone - Matheson, Coleman, and Bell reagent grade - was recrystallized from hot ligroin; m.p. 83-84°C.

Diethyl Ether

Diethyl ether, Mallinkrodt anhydrous reagent, grade (to meet A.C.S. standards) was used without further purification, always freshly opened.

Isopentane

Isopentane, Phillips Petroleum Company reagent (99%) was used without further purification.

Pentane (normal)

Normal pentane, Phillips Petroleum Company reagent (99%) was used without further purification.

Carbon Tetrachloride

Carbon tetrachloride - Matheson, Coleman, and

Bell spectroquality reagent - was used without further purification; approximately 1% tetramethylsilane was dissolved in this reagent for use as an internal NMR standard (prepared by Dr. Charles Stout).

1,3-Cycloöctadiene

1,3-cycloöctadiene, Aldrich Chemical Company reagent grade, was used without further purification, always freshly opened. For experiment #5 the 1,3-cycloöctadiene was further purified by distillation at $33-36^{\circ}/40-42$ mm. Vapor chromatography at high sensitivity showed one impurity, less than 0.3% by volume.

1,3,5-Cycloheptatriene

1,3,5-cycloheptatriene, Columbia Organic Chemicals or K & K Laboratories practical grade (98%), was used without further purification, always freshly opened. For experiment #5 Columbia Organic Chemicals technical grade (85%) was purified by distillation at $23-28^{\circ}/39-42$ mm. Vapor chromatography at high sensitivity showed two impurities, of less than 0.1% total volume.

Ultraviolet Spectra of 1,3-Cycloöctadiene and 1,3,5-Cycloheptatriene

A 1.77mg. sample of 1,3,5-cycloheptatriene (triene) was diluted to volume in a 5-ml. volumetric flask with spectroquality methanol, then examined on the Beckman DU Spectrophotometer to obtain approximate values for the absorption maximum and extinction coefficient at

this concentration ($1.92 \times 10^{-3} \text{M}$). The solution was then diluted fivefold with methanol ($3.84 \times 10^{-4} \text{M}$) and the continuous ultraviolet absorption spectrum obtained by analysis on a Carey Model 14B. Analysis yielded $\lambda_{\text{max}} 2670 \text{ \AA}$, absorbance 1.36. A similar procedure was followed in the analysis of 1.76 mg. 1,3-cyclooctadiene (diene). Analysis of the final concentration ($3.26 \times 10^{-4} \text{M}$) on the Carey Model 14B yielded $\lambda_{\text{max}} 2340 \text{ \AA}$, absorbance 1.39.

Ultraviolet Spectrum of Pyrex Glass Test Tubes

Two 13 x 100 mm. pyrex test tubes were sealed containing air. Ultraviolet spectra were taken on the Carey 14B with air as a reference, yielding absorbance > 2 at $\lambda \geq 2830 \pm 70 \text{ \AA}$, absorbance > 1 at $\lambda \geq 2930 \pm 50 \text{ \AA}$.

Sensitized Reactions of 1,3,5-Cycloheptatriene and 1,3-Cyclooctadiene

Experiment #1

Sample preparation: A 1.059 g. sample of diene was added with a microsyringe to each of two 10-ml. volumetric flasks. To one flask was added 0.545 g. benzophenone. Both flasks were then diluted to volume with diethyl ether, giving solution (A) 0.1 M in diene and solution (B) 0.1 M in diene and 0.3 M in benzophenone. Photolysis samples were prepared in 13 x 100 mm. test tubes constricted at the neck, of approximately 2 ml. volume, from solution (A) in both pyrex (A_p) and quartz (A_q) and from solution (B) in pyrex only (B_p). These tubes were then frozen at liquid

nitrogen temperatures, evacuated to 10^{-3} mm., and sealed under this pressure. (A similar degassing cycle was used for all succeeding sample tubes unless otherwise stated.) A 0.1 M solution (C) of triene was also prepared, using 0.887 g. triene diluted with diethyl ether to volume in a 10-ml. volumetric flask. Photolysis samples were prepared as above, one in quartz (C_q) and two in pyrex, (C_{p1}) and (C_{p2}).

Sample irradiation: (A_p) and (C_{p1}) were refrigerated as zero-time reference blanks. The remaining tubes were taped to the surface of an Hanovia quartz immersion apparatus containing a 400-watt Hanovia high pressure mercury arc lamp and photolyzed for approximately 113 hrs.

Sample analysis: Product distribution was determined by vapor chromatography on a William Instrument Company Aerograph and a Loenco Model 15. A 5 ft. by 1/4 in. column (Z) packed with 15% by weight Carbowax-20M on C22 firebrick, 40-80 mesh, was used for these analyses. The results are summarized in Tables I-II.

Experiment #2

To each of two 5-ml. volumetric flasks was added 0.443 g. triene with a microsyringe. To one flask, 0.545 g. benzophenone was also added. Both flasks were then diluted to volume with diethyl ether, giving solution (D) 0.1 M in triene and solution (E) 0.1 M in triene and 0.6 M in benzophenone. Approximately 2 ml. samples were prepared

TABLE I

Product Distribution, Diene; expt. #1 (Page 24)

Product #	Product designation	(A _p) [*]	(A _q)	(B _p)
1	D ₁		trace	trace
2	D ₂		trace	minor
3	D ₃		major	minor
4	D ₄		minor	major
5	D ₅		minor	major
6	diene		----	trace
7	D ₆		----	medium

TABLE II

Product Distribution, Triene; expt. #1 (Page 24)

Product #	Product designation	(C _{p1})	(C _{p2})	(C _q)
1	T ₁	trace	----	trace
2	T ₂	----	----	trace
3	T ₃	----	major	major
4	T ₄	----	----	medium
5	T ₅	----	----	medium
6	toluene	----	----	trace
7	triene	major	trace	minor
8	T ₆	trace	----	trace

TABLE III

Product Distribution, Triene; expt. #2 (Page 25)^{*}

Sample	T ₁	T ₂	T ₃	T ₄	T ₅	Toluene	Triene	T ₆
(D ₁)	trace	---	major	---	---	---	minor	trace

^{*} No analyses for (A_p), (D₂), or (E₁)

in 13 x 100 mm. pyrex test tubes, (D_1), (D_2), and (E_1), degassed, then taped to the outside of a 400-watt Hanovia immersion apparatus, quartz, for photolysis, approximately 68 hrs. Analyses were by vapor chromatography on column (Z), as above. Table III is a summary of the results.

Experiment #3

Solutions (F), 0.1 M in triene, and (G), 0.1 M in triene and 0.6 M in benzophenone were prepared as in experiment #2 above. 1 ml. aliquots were placed in 13 x 100 mm. pyrex tubes - (F_{1-3}) and (G_{1-4}) - and degassed, the freezing cycle being repeated twice before sealing. Tubes (F_1) and (G_1) were kept refrigerated as zero-time reference blanks. The remaining tubes were taped to the outside of a 200-watt Hanovia quartz immersion apparatus fitted with a pyrex filter and photolyzed. (F_2) and (G_2) were removed after approximately $14\frac{1}{2}$ hrs.; the remaining tubes were exposed an additional 24 hrs. ($38\frac{1}{2}$ hrs. total). Vapor chromatography on column (Z) was used for analysis; the data is summarized in Table IV.

Experiment #4

Sample preparation: Solutions (H), 0.1 M in triene, and (J), 0.1 M in triene and 0.6 M in benzophenone were also prepared as in experiment #2 above. Solutions (K), 0.1 M in diene, and (I), 0.1 M in diene and 0.6 M in benzophenone, were prepared analogously, using 0.530 g. diene. Photolysis samples of approximately 1.5 ml. volume were prepared in pyrex tubes and degassed - (H_{1-2}), (J_{1-2}), (K_{1-3}), and

TABLE IV

Product Distribution, Triene; expt. #3 (Page 27)

Sample	T ₁	T ₂	T ₃	T ₄	T ₅	Toluene	Triene	T ₆
(F ₁)	----	----	----	----	----	----	major	----
(F ₂)	----	medium	minor	minor	trace	----	very major	trace
(F ₃)	----	minor	----	minor	trace	----	very major	----
(G ₁)	----	----	----	----	----	----	major	----
(G ₂)	----	trace	trace	major	major	----	trace	----
(G ₃)	trace	minor	minor	very major	very major	trace	minor	trace
(G ₄)	medium	minor	minor	very major	very major	trace	minor	trace

(F₁) and (G₁) are zero-time references

(G₃) and (G₄) were prepared identically

(L₁₋₃). Tubes (H₁) and (K₁) were refrigerated as zero-time references. The remaining tubes were taped to a 400-watt pyrex Hanovia apparatus, which was then submerged in a 3 liter beaker filled with water at room temperature.

Sample irradiation: Photolysis was carried out over a 42½ hr. period; the water bath temperature was checked periodically, remaining at 27^o ± 1^oC. (L₁) was removed after 16 hrs. exposure; (K₂), (L₂), and (J₁) were removed after 20 hrs.; the remaining tubes were exposed the entire 42½ hrs.

Sample analysis: Analyses were made on a Loence Model 70 Hi-Flex Programmer vapor chromatograph. Matching 8 ft. by 1/8 in. columns (Y) were packed with 35% by weight Carbowax-20M on C22 firebrick, 40-80 mesh, approximately 7.4 ml. of packing per column, then flushed with 10-12 p.s.i. of nitrogen gas for 2½ hrs. for use in the analyses. The Programmer was used isothermally at 65^oC. with 25 p.s.i. helium flow. The injector temperature was 46^oC.; the detector temperature was 110^oC., the detector filament current 110 ma. Results are summarized in Tables V-VI.

The Effect of Acceptor Concentration in the Sensitized Reaction; Experiment #5

Sample preparation: Neat samples of diene and triene were prepared in capillary tubes, pyrex, sealed off at one end. The tubes were filled with a microsyringe, inserting 88.8 mg. and 88.2 mg. of triene and diene respectively into each of two tubes. One tube of each compound was then

TABLE V

Product Distribution, Triene; expt. #4 (Page 27)

Sample	T ₁	T ₂	T ₃	T ₄	T ₅	Toluene	Triene	T ₆
(H ₁)	----	----	----	----	----	----	major	trace
(H ₂)	22*	3	70	-----	----	trace	1780	trace
(J ₁)	300	300	300	800	800	200	12000+	1000+
(J ₂)	300	300	1600	2000	2000	trace	1560	1000+

TABLE VI

Product Distribution, Diene; expt. #4 (Page 27)

Sample	D ₁	D ₂	D ₃	D ₄	D ₅	Diene	D ₆
(K ₁)	----	----	----	----	----	major	trace
(K ₂)	trace	trace	trace	----	trace	very major	trace
(K ₃)	90	30	3000+	20	10	30000+	300
(L ₁)	100	250	250	2600	3000	----	750
(L ₂)	40	100	trace	2375	2300	----	3000+
(L ₃)	120	250	trace	2425	2375	----	1700+

* Values are meaningful for comparison only within the same sample.

saturated with benzophenone. The neat triene tube (A), the saturated triene tube (A_s), the neat diene tube (F), and the saturated diene tube (F_s) were degassed and sealed. 10-ml. volumetric flasks, each containing 1.090 ± 0.003 g. benzophenone (0.6 M), were used in the preparation of the remainder of the sensitized solutions; the flasks were filled to volume with diethyl ether after addition of the acceptor. Measurement and addition were accomplished by use of micro-syringes and pipettes. By weight, solution (B) contained 11.1 mg. (0.15%) triene, solution (C) 111.0 mg. (1.51%), and solution (D) 1.110 g. (14.7%); solution (G) contained 9.3 mg. (0.12%) diene, solution (H) 93.5 mg. (1.26%), and solution (J) 935.0 mg. (12.4%). Four 1.5-ml. samples of each solution were transferred to constricted 13 x 100 mm. pyrex tubes - (B,C,D,G,H,J₁₋₄) - degassed, and sealed. The fourth sample of each solution was refrigerated for future reference. Finally, comparison solutions of diene and triene were prepared directly, measured by microsyringe into constricted pyrex tubes containing 1 ml. diethyl ether. By weight, sample (E_1) contained 1.1 mg. (0.14%) triene, sample (E_2) 11.1 mg. (1.52%), and sample (E_3) 111.0 mg. (13.5%); sample (K_1) contained 0.9 mg. (0.14%) diene, sample (K_2) 9.3 mg. (1.25%), and sample (K_3) 93.5 mg. (11.6%). These tubes were also degassed and sealed.

Sample irradiation: The tubes were photolyzed by

TABLE VII

Product Distribution, Unsensitized Triene; expt. #5 (Page 29)

Sample	T ₁	T ₂	T ₃	T ₄	T ₅	Toluene	Triene	T ₆
(E ₁)	trace	trace	trace	trace	trace	----	major	trace
(E ₂)	trace	50	50	trace	trace	trace	10000+	trace
(E ₃)	trace	40	225	50	trace	trace	15000+	trace
(A)	----	trace	950	trace	260	110	80000+	trace

TABLE VIII

Product Distribution, Sensitized Triene; expt. #5 (Page 29)

Sample	T ₁	T ₂	T ₃	T ₄	T ₅	Toluene	Triene	T ₆
(B ₁)*	200	115	trace	650	650	----	1000	trace
(C ₁)	200	75	300	30	90	60	18000+	trace
(D ₁)	180	20	2100	30	580	360	60000+	trace
(B ₂)*	850	2050	trace	280	460	trace	trace	trace
(C ₂)	250	340	560	850	900	140	3220	trace
(D ₂)	trace	trace	2000	trace	600	400	60000+	trace
(B ₃)*	100	450	100	1900	2400	----	----	----
(C ₃)*	75	100	100	1250	1550	100	1100	trace
(D ₃)	trace	----	580	----	100	75	50000+	trace
(A _s)	----	trace	930	trace	200	125	100000+	----

* Denotes yellowish-white precipitate, crystalline, among products at this concentration

TABLE IX

Product Distribution, Unsensitized Diene; expt. #5 (Page 29)

Sample	D ₁	D ₂	D ₃	D ₄	D ₅	Diene	D ₆	D ₇
(K ₁)	trace	trace	trace	----	----	major	----	----
(K ₂)	trace	trace	trace	----	----	major	----	----
(K ₃)	----	----	----	----	----	major	----	----
(F)	----	----	trace	trace	----	major (90000+)	trace	900

TABLE X

Product Distribution, Sensitized Diene; expt. #5 (Page 29)

Sample	D ₁	D ₂	D ₃	D ₄	D ₅	Diene	D ₆	D ₇
(G ₁)	100	100	trace	1400	1350	----	----	----
(H ₁)*	250	230	90	290	280	1470	200	400
(J ₁)	130	----	130	130	trace	27000	6400	800
(G ₂)	600	----	----	2400	2475	----	----	----
(H ₂)*	100	500	----	1900	2100	----	----	----
(J ₂)	trace	----	trace	----	----	4800	2000	300
(G ₃)	200	350	trace	3000	2950	----	----	----
(H ₃)*	400	550	trace	2300	2600	----	----	----
(J ₃)	trace	----	----	320	----	12000+	6000	680
(F _s)	----	----	----	trace	----	50000+	8000	800

* Denotes yellowish-white precipitate, crystalline, among products at this concentration

a 450-watt Hanovia pyrex immersion apparatus placed at the center of the merry-go-round, a double concentric circle of tube holders immersed in a thermally-regulated water bath and rotated by an electric motor. The temperature was kept at $27^{\circ} \pm 0.5^{\circ}\text{C}$. throughout the entire 36 hrs. of the photolysis. Tubes (B,C,D,G,H,J₁) were removed after 13 hrs.; tubes (B,C,D,G,H,J₂) were removed after 25 hrs.; tubes (B,C,D,G,H,J₃), (E₁₋₃), (K₁₋₃), (A,F,A_S,F_S) were removed after the full 36 hrs.

Sample analysis: Analyses were done on the Loenco Programmer vapor chromatograph, using columns (Y). The Programmer was used isothermally at 64°C . with 25 p.s.i. helium flow. The injector temperature was 52°C .; the detector temperature was 113°C ., the detector filament current 110 ma. The results are summarized in Tables VII-X.

Large Volume Preparative Procedures

Experiment #6

Solutions of both diene and triene were prepared on a large scale, to provide product yields suitable for isolation and characterization. Components were mixed in 100-ml. graduated cylinders. A solution of triene and an analogous solution of diene were prepared in quartz tubes in a manner similar to that of Schenk⁽³¹⁾. 10-ml. graduated cylinders were used for solute measurement and addition. Solution (Ta) contained 1.29 g. (1.5 ml.) triene in 100 ml. diethyl ether; solution (Da) contained 1.52 g. (1.7 ml.) diene in 100 ml. ether. The solutions were

poured into quartz tubes, bubbled with nitrogen gas for approximately 10 minutes, then corked. Double volumes of (Ta) and (Da) were then prepared, and poured into 250-ml. quartz tubes to which constricted pyrex necks had been added. The triene tube (Ta2) was stoppered; the diene tube (Da2V) was degassed and sealed. Double volume solutions were again prepared, two of triene, one of diene, with 10.90 g. benzophenone added to each. The solutions were poured into 250-ml. pyrex tubes; this technique in all cases led to substantial ether loss by evaporation. Tube (Ts0) was stoppered, tubes (TsV) and (DsV) degassed and sealed. All tubes were photolysed on a 450-watt quartz Hanovia immersion apparatus immersed in a water bath which was kept at approximately 27°C. (Ts0) was exposed for 113 hrs.; (TsV) was exposed for 225 hrs.; all other tubes were exposed for 245 hrs. During the photolysis stoppered tubes lost substantial amounts of ether, as much as 1/2 by volume in some cases. Qualitative yields and product distribution were obtained by analysis on the Programmer vapor chromatograph fitted with columns (Y). The detector temperature was 130°C., the detector filament current 110 ma.; the injector temperature was 110°C. Results of the analyses are summarized in Tables XI-XII.

The products were then concentrated and purified in the following manner: ether was stripped off, first at atmospheric pressure and room temperature, finally

TABLE XI

Product Distribution, Triene; expt. #6 (Page 34)

Sample	T ₁	T ₂	T ₃	T ₄	T ₅	Toluene	Triene	T ₆
(Ta)	trace	minor	minor	medium	trace	trace	major	----
(Ta2)	trace	minor	trace	medium	trace	----	major	----
(Ts0)	trace	180	225	2150	2300	100	1900	----
(TsV)	100	100	800	7000	7000	500	9000	trace

TABLE XII

Product Distribution, Diene; expt. #6 (Page 34)

Sample	D ₁	D ₂	D ₃	D ₄	D ₅	Diene	D ₆	D ₇
(Da)	major	trace	trace	minor	trace	medium	trace	----
(Da2V)	75	35	----	900	trace	1500	trace	----
(DsV)	trace	100	trace	1600	1600	----	----	----

at 250 mm. and pot temperature of 40°C. till copious precipitate formed. The material was then filtered and the solution examined by v.p.c., which showed product distributions to be unchanged. The material was then chromatographed on an alumina column, 5 in. x 3/4 in., and eluted with three 10-ml. washings of 30-60° ligroin; the ligroin was then removed under reduced pressure. Mixed samples of the degassed and stoppered unsensitized reaction tubes indicated that there was little effect on products or distribution due to the introduction of oxygen; therefore tubes (Ta) and (Ta2) were combined into (Tu) and (Da) and (Da2V) were combined into (Du).

Preparative vapor chromatography was attempted upon the tube contents (Du), using the Loenco Model 15 and column (Z). An 0.1 ml. sample was injected into the machine and the various fractions were collected in capillary tubes at isopropanol-dry ice slurry temperatures. These fractions were then analyzed on a Varian A-60 spectrometer used without modification. Standard Varian Analytical Sample Tubes (4.28 mm. I.D.) were used for all spectra taken. Each capillary tube was washed with 0.1 ml. spectroquality carbon tetrachloride, transferred by microsyringe to an NMR tube, diluted with two more washings of the capillary tube (0.05 ml.), then diluted further with CCl_4 till the NMR tube was filled to at least 32 mm. with solution. Tetramethylsilane was used as an external reference. Magnetic shielding values are expressed by

FIGURE II

First fraction,
expt. #6 (Page 34)

Retention time 34 minutes

Solvent CCl_4

External standard

Filter bandwidth: 1 cps

R.F. field: 0.06 mG

Sweep time: 250 sec

Sweep width: 500 cps

Sweep offset: 000 cps

Spectrum amp: 10

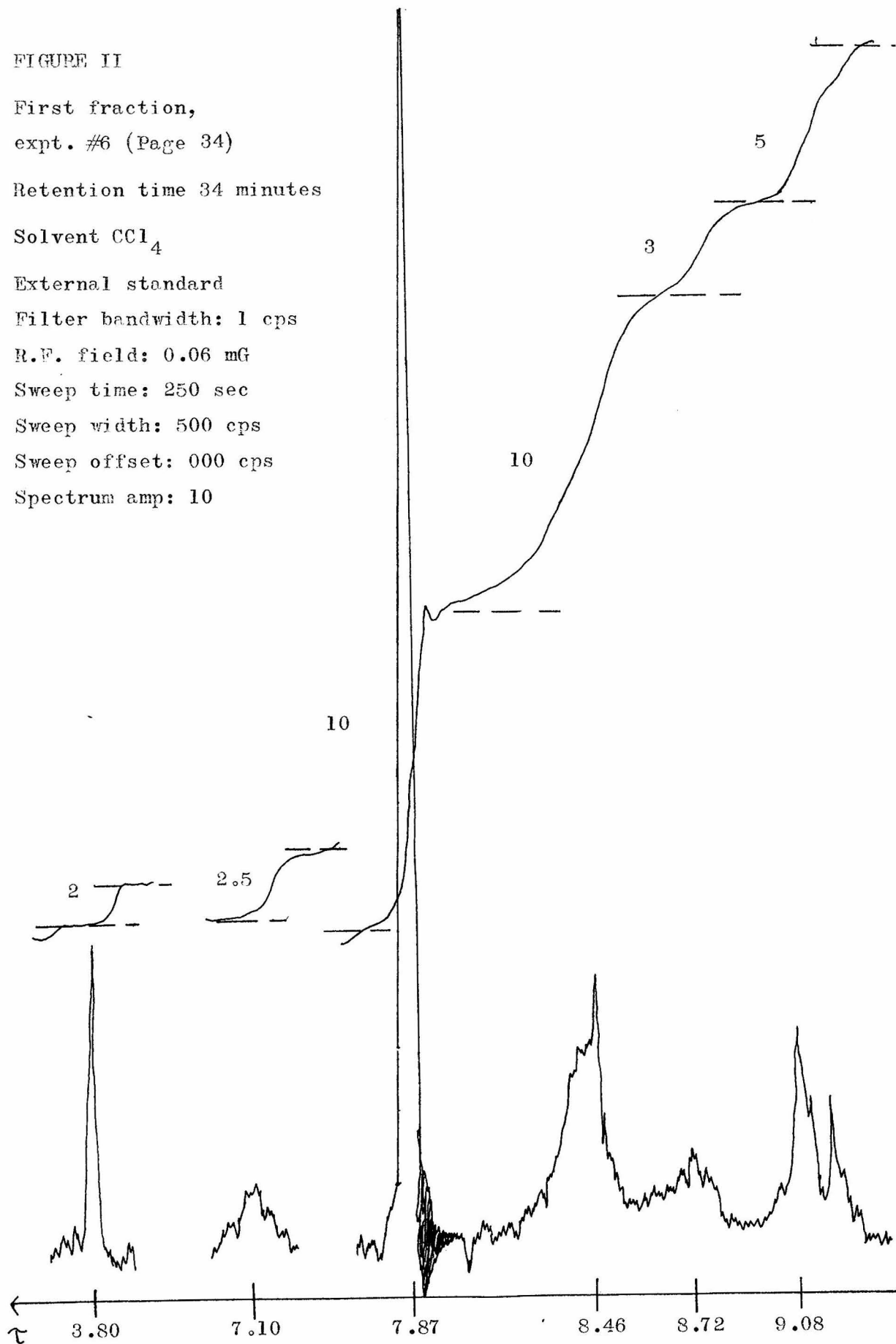


FIGURE III

Second fraction, experiment #6 (Page 34)

Retention time 48 minutes

Solvent CCl_4

External standard

Filter bandwidth: 1 cps

R.F. field: 0.06 mG

Sweep time: 250 sec

Sweep width: 500 cps

Sweep offset: 000 cps

Spectrum amp: 10

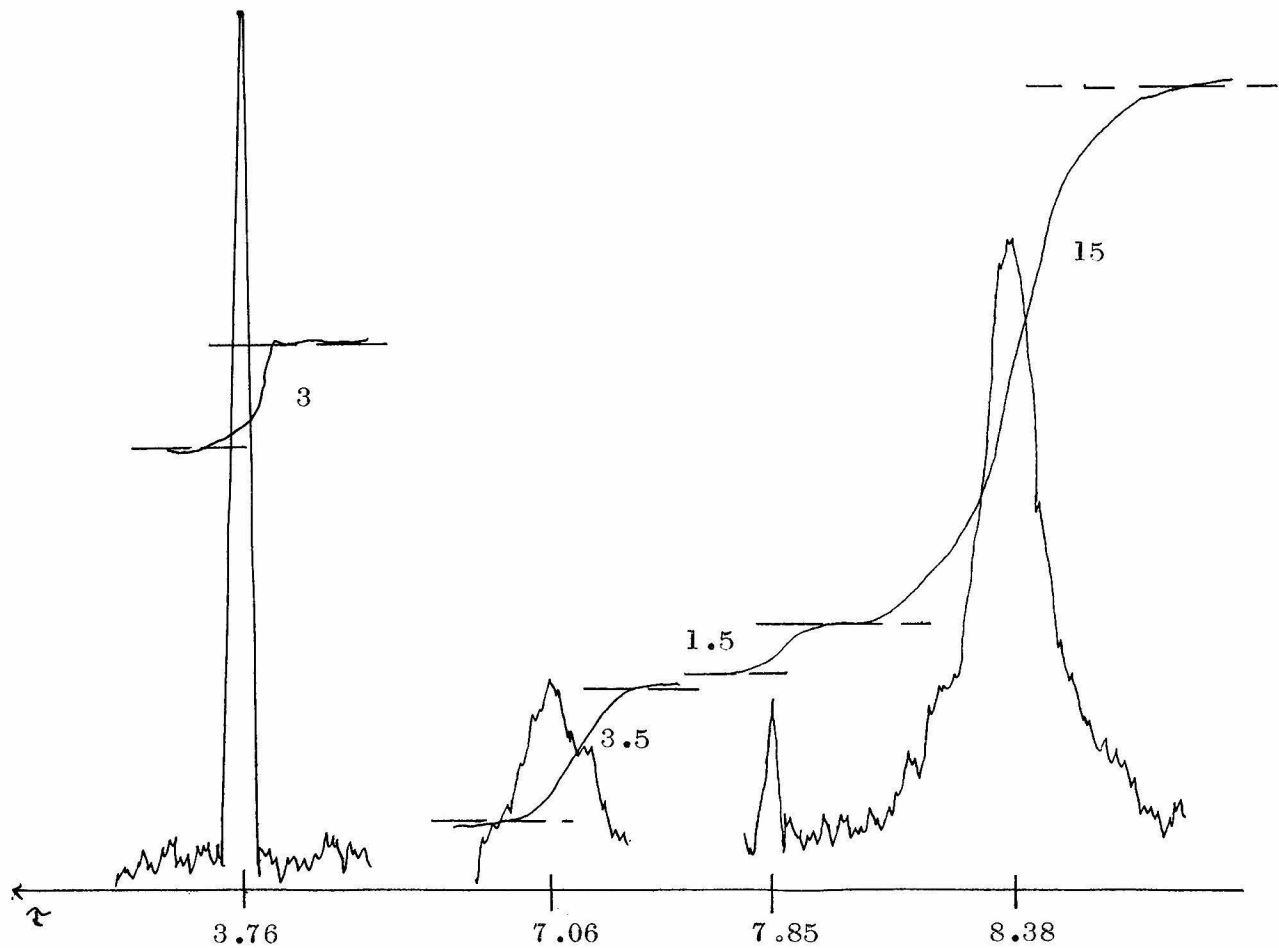


FIGURE IV

Third fraction, expt. #6 (Page 34)

Retention time 80 minutes

Solvent CCl_4

External standard

Filter bandwidth: 1 cps

R.F. field: 0.06 mG

Sweep time: 250 sec

Sweep width: 500 cps

Sweep offset: 000 cps

Spectrum amp: 10

Integral amp: 40

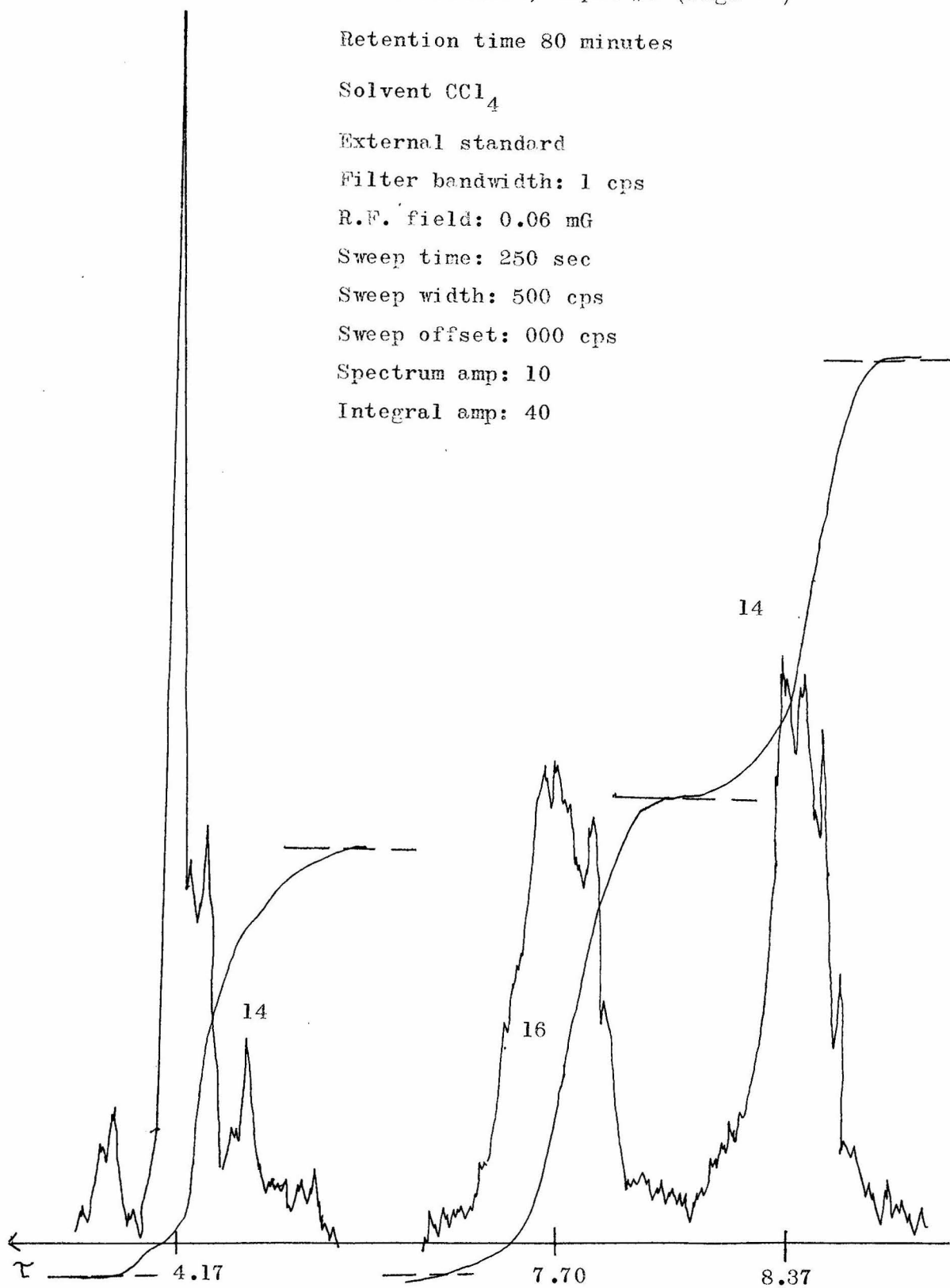


FIGURE V

Fifth fraction, expt. #6 (Page 34)

Retention time 144 minutes

Solvent CCl_4

External standard.

Filter bandwidth: 0.2 cps

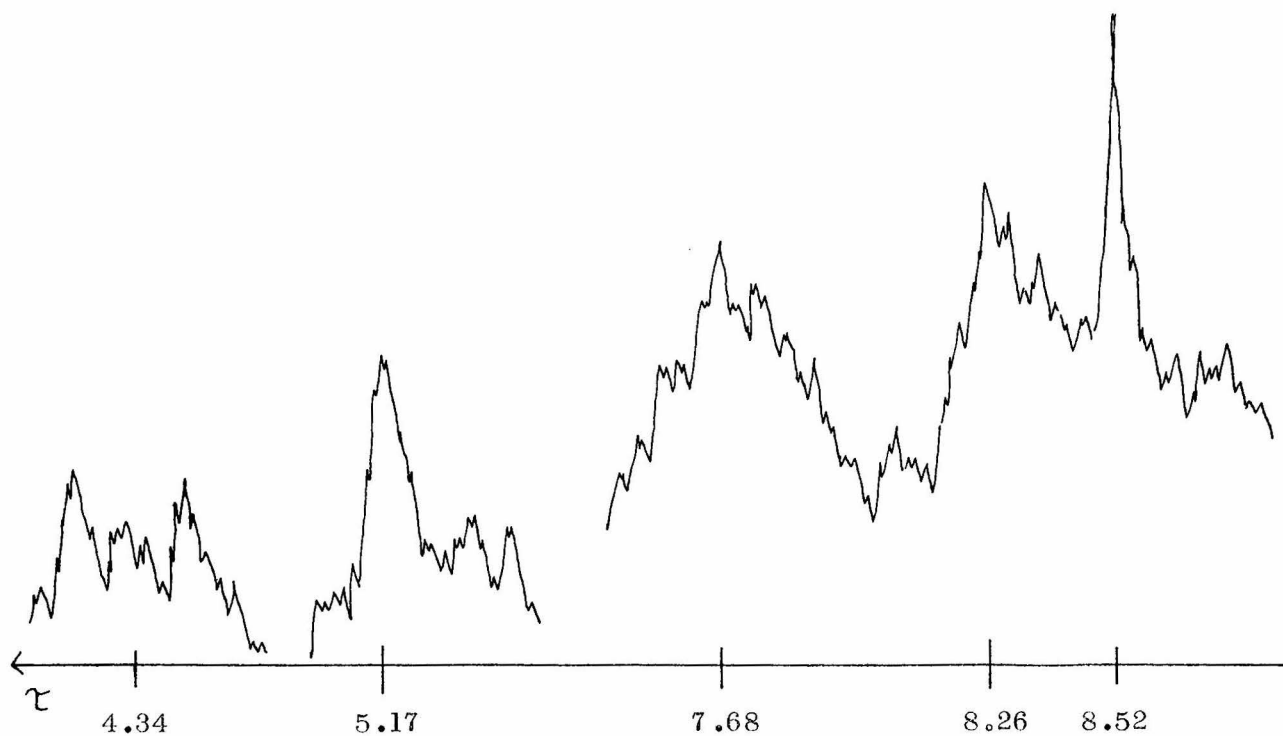
R.F. field: 0.1 mG

Sweep time: 250 sec

Sweep width: 500 cps

Sweep offset: 000 cps

Spectrum amp: 80



τ values as defined by Tiers⁽²⁹⁾. Spectra are represented in Figures II-V.

Preparative Procedure in Neat Diene; Experiment #7

Using a 10-ml. syringe, a 5-ml. sample of diene was inserted into a constricted 13 x 100 mm. pyrex test tube. The diene was then saturated with benzophenone at room temperature. The tube was degassed, the cycle being repeated twice before sealing, then taped to the outside of a pyrex Hanovia 450-watt immersion apparatus and photolysed approximately 100 hrs., immersed in a water bath at $27^{\circ} \pm 1^{\circ}\text{C}$.

A column (W) was prepared for the purpose of separating the components after photolyzation, 20 ft. x 1/4 in., packed with 35% by weight Carbowax-20M on C22 firebrick, 40-80 mesh. Five samples, ranging from 0.035-0.045 ml., were injected with a microsyringe and the four fractions collected from each in capillary tubes at dry ice-isopropanol temperatures. The column temperature was 104°C . and the helium flow 25 p.s.i.

The corresponding fractions from each run were combined by rinsing the contents of each with 0.1 ml. of CCl_4 , containing approximately 1% tetramethylsilane, into a common Varian NMR tube. Where necessary, the tubes were further diluted till they contained over 32 mm. solution. These fractions were then analyzed on the Varian A-60, using the tetramethylsilane included in the solvent as an internal standard. Spectra are represented in Figures VI-IX.

FIGURE VI

First fraction, expt. #7 (Page 42)

Retention time $29\frac{1}{2}$ minutes

Solvent CCl_4

Tetramethylsilane internal standard

Sweep time: 250 cps

Sweep width: 500 cps

Sweep offset: 000 cps

Spectrum amp: 20

R.F. field: 0.16 mG

Filter bandwidth: 4 cps

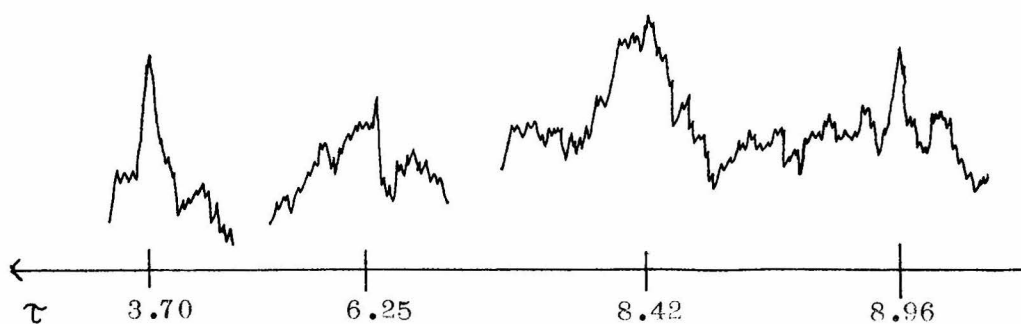


FIGURE VII

Second fraction, expt. #7 (Page 42)

Retention time $48\frac{1}{2}$ minutes

Solvent CCl_4

Tetramethylsilane internal standard

Sweep time: 250 sec Sweep width: 500 cps

Sweep offset: 000 cps Spectrum amp: 25

R.F. field: 0.14 mG Filter bandwidth: 1 cps

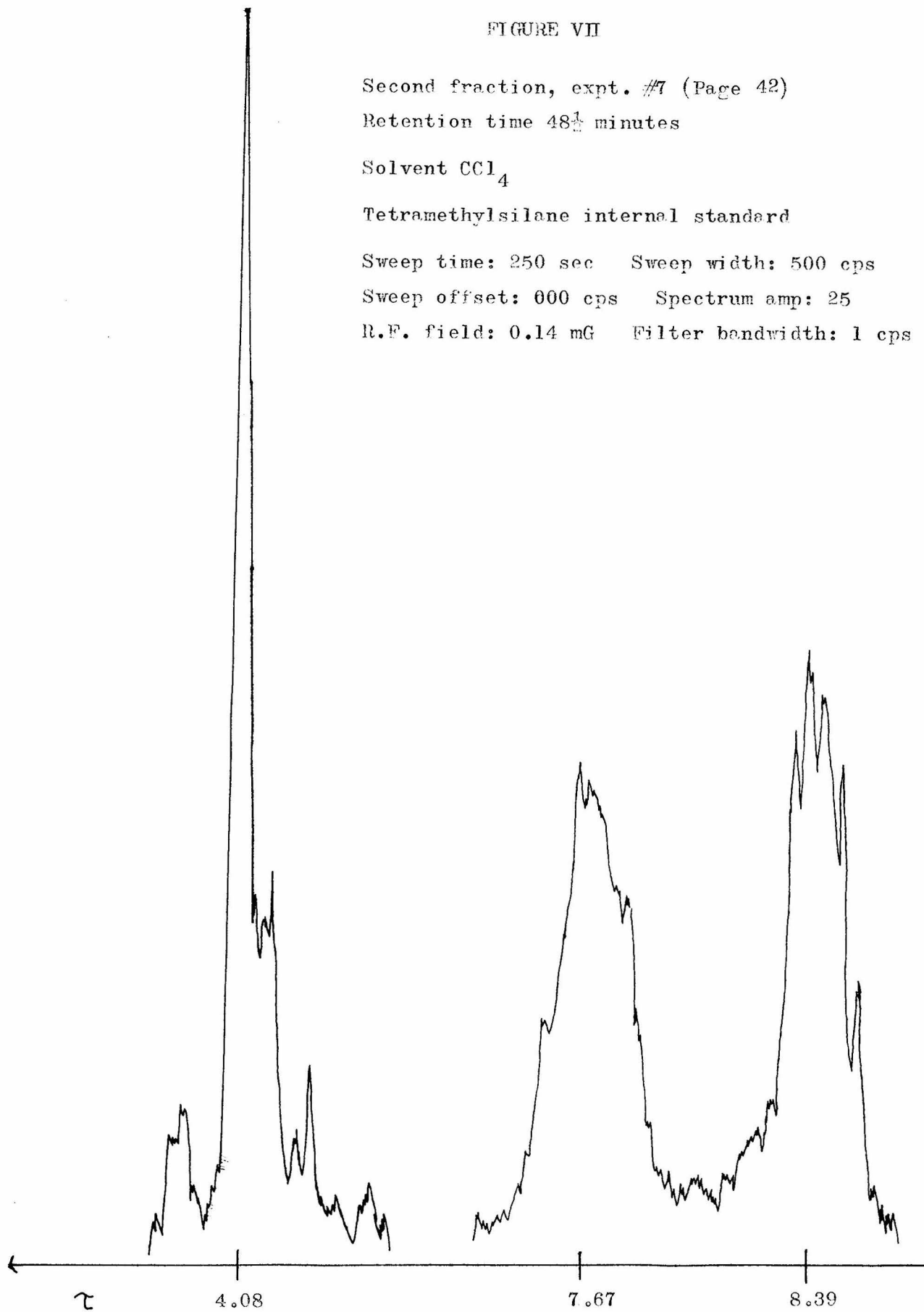


FIGURE VIII

Third fraction, expt. #7 (Page 42)

Retention time 54 minutes

Solvent CCl_4

Tetramethylsilane internal standard

Sweep time: 250 sec Sweep width: 500 cps

Sweep offset: 000 cps Spectrum amp: 50

R.F. field: 0.20 mG Filter bandwidth: 1 cps

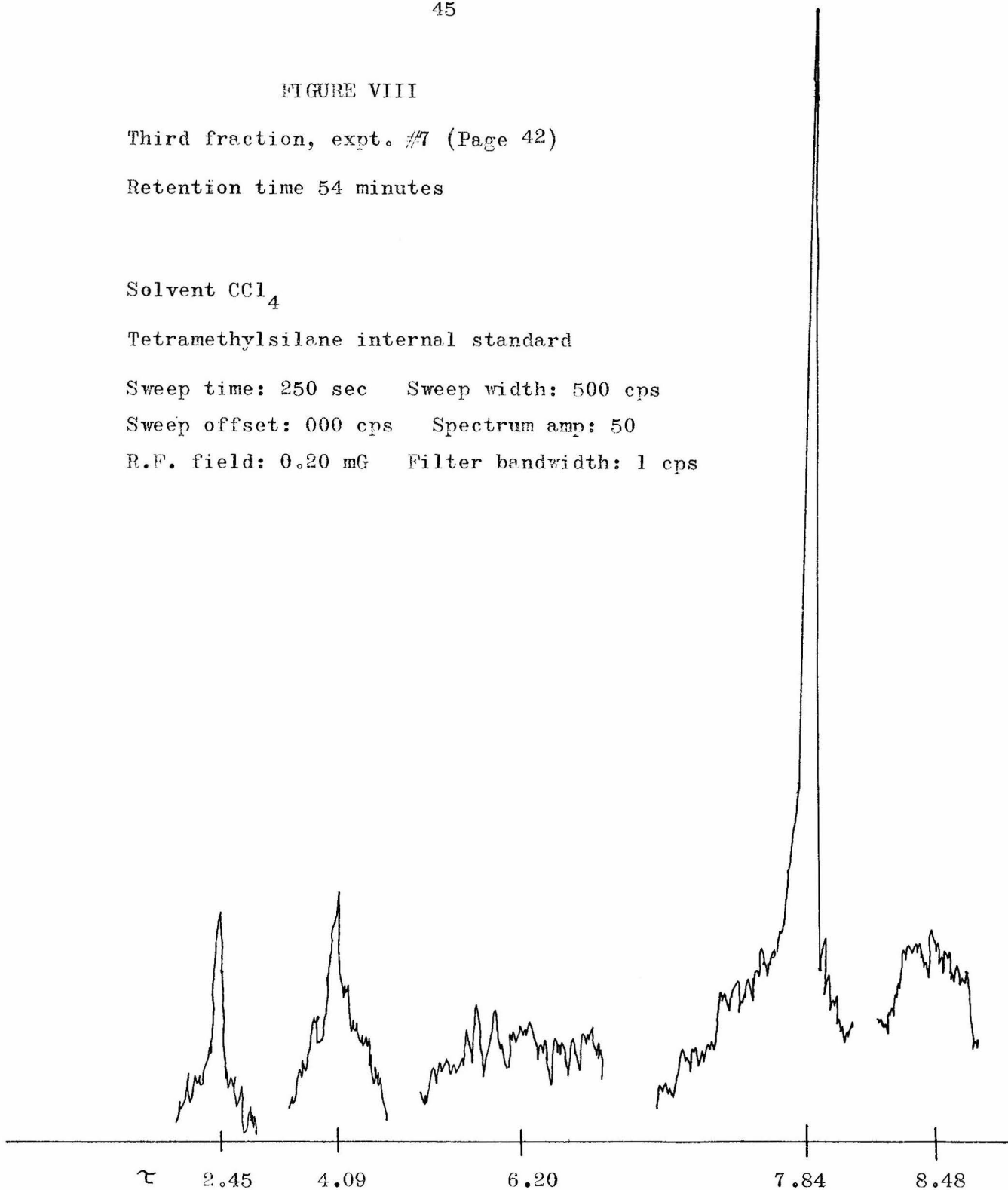


FIGURE IX

Fourth fraction, expt. #7 (Page 42)

Retention time $73\frac{1}{2}$ minutes

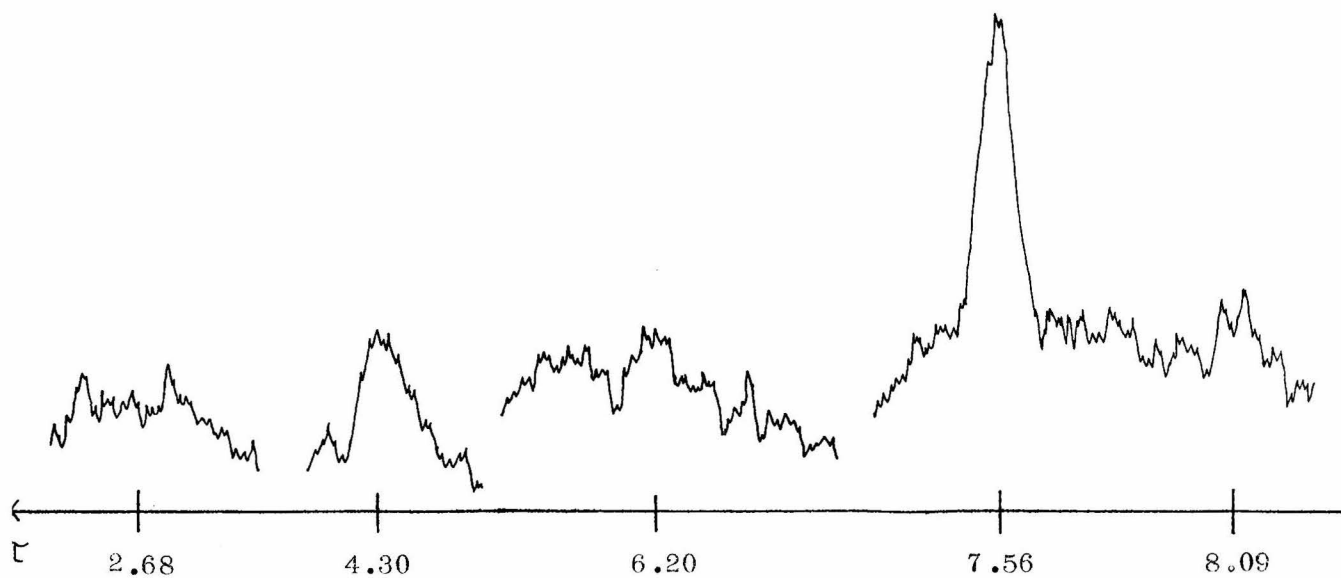
Solvent CCl_4

Tetramethylsilane internal standard

Sweep time: 250 sec Sweep width: 500 cps

Sweep offset: 000 cps Spectrum amp: 80

R.F. field: 0.16 mG Filter bandwidth: 0.2 cps



Preparative Triene Procedure; Experiment #8

To a 100-ml. volumetric flask was added 1 g. benzophenone and 5 ml. (3.550 g.) triene; the flask was then filled to volume with isopentane, giving a solution 0.055 M in benzophenone and 0.039 M in triene. Seven tubes were prepared from 13 mm. O.D. pyrex tubing by rounding the bottoms and constricting the necks, giving a total length of approximately 40 cm. to each. 10-15 ml. of the solution was transferred to each tube (T_{1-7}) by 10-ml. syringe. The samples were then degassed and sealed. They were photolyzed on a 450-watt quartz Hanovia immersion apparatus, immersed in a water bath at 24-28°C., for 182 hrs; an opaque yellow material formed on the inside of the tubes, closest to the lamp, so the tubes were rotated with respect to the lamp after approximately 100 hrs. In addition, large colorless crystals formed throughout the tubes.

The contents of (T_1) were separated by decanting, the solution poured off, leaving both the yellow solid and the clear crystals behind. The yellow solid was scraped from the side of the tube, and attempts made at dissolving it; it was insoluble in pentane, acetone, dioxane, and dimethyl sulfoxide, though the latter solvent removed the yellowish color and left the crystals white. The solid was stable above 200°C. and insoluble in concentrated nitric acid.

(T_2) was similarly decanted. The colorless crystals were washed in isopentane, then dried with air.

A single crystal was further dried by crushing on filter paper; a melting point was taken on a Bausch & Lomb polarizing microscope equipped with a Variac-controlled electric heating stage and a Thomas Temperature Thermistor. There was a marked change in crystalline form to long, thin needles beginning at 150°C. and continuing till 185-195°C., at which point the crystals sublimed.

Several more crystals were washed with isopentane and air dried. 1.5 mg. were then ground to a fine powder in a mortar and pestle. Several hundred milligrams of anhydrous potassium bromide were then added, and the powders mixed thoroughly. A stiff cardboard slide with a 1.5 cm. hole in its center was placed on a polished die, and the center cavity just filled with the powder mixture. The slide and powder were covered with the other half of the die and compressed in an hydraulic press at 30,000 p.s.i. for approximately one minute. This formed the powder into a translucent glass suitable for infrared examination. A spectrum was taken on the Beckman Model IR7 spectrophotometer, using air as reference with the double beam. Results of the analysis are summarized in Table XIII.

The solution from (T₁) was analysed on the Programmer with columns (Y); conversion to volatile products was negligible - estimates from the remaining triene showed it to be much less than 5%.

TABLE XIII

Infrared Analysis of Crystalline Product from Expt. #8 (Page 47)

Frequency in cm.^{-1}	Intensity % absorption	Character of peak
650	30	sharp
680	13	shoulder
693	47	shoulder
703	77	very sharp
745	59	very sharp
758	57	very sharp
		} doublet
845	19	blunt
915	12	broad
957	18	sharp
1005	28	shoulder
1028	57	sharp
1045	48	sharp
		} doublet
1165	32	broad
1270	27	blunt
1340	30	broad, skewed
1448	58	very sharp
1497	46	very sharp
1600	18	sharp
3060	27	sharp
3590	45	blunt

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