THE NORBORNENYL-NORTRICYCLYL RADICAL SYSTEM

Chemistry 80
Thesis

submitted as partial fulfillment
of the requirements for the
Bachelor of Science Degree by

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Acknowledgements

I am grateful to Thomas A. Halgren for his supervision and timely suggestions. Also to Henry H. Suzukawa who assisted me in this research.

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ABSTRACT

The reduction of nortricyclyl and endo-norbornenyl bromides by tri-n-butyltine hydride has been used for the generation of the norbornenyl-nortricyclyl radical system. Utilizing the tri-n-butyltin hydride to also trap the radicals before full equilibration, a linear correlation of the ratio of product nortricyclene/ product norbornene to the hydrogen donor concentration has been obtained. Observation of this predicted linear relationship, and also of the predicted reciprocal correspondence of the intercepts associated withe linear plots obtained by initiating the radical system from the nortricyclyl bromide and from the endo-norbornenyl bromide, indicate that only classical norbornenyl and nortricyclyl radicals need be invoked. However, the existence of a product forming "nonclassical" species can not yet be ruled out.

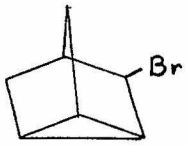
Several investigation have been reported which attempted to determine if the "nonclassical" free radical analogous to the "nonclassical" carbonium ion appeared as a reaction intermediate in the norbornenyl-nortricyclyl system. The norbornenyl radicals have been generated by the decarbonylation of norborn-2-en-5-yl carboxaldehyde[1]; from the norborn-2-en-5-yl carboxy radical[2,3]; by the addition of thiols to norbornadiene[4-6]; along with arenesulfonyl halides[7], and other substances[4]. The conclusion of these studies has been that delocalization

of the unpaired electron by participation of the neighboring double bond does not contribute to the nature of the free radical intermediate. However, in none of these investigations has the radical intermediates been generated from both norbornenyl and nortricyclyl derivatives.

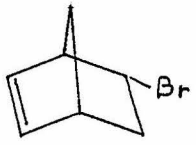
An independent investigation using tri-n-butyltin hydride to generate the norbornenyl-nortricyclyl radicals was inconclusive, and the results did not provide an answer to whether a single "nonclassical" intermediate or a pair of classical radicals were involved in the reaction mechanism. No effective trapping of the radicals was reported in this investigation.

DISCUSSION

The generation of the nortricyclyl-norbornenyl radical system by the decomposition of the t-butyl peresters has been found to be unsatisfactory and was abandoned in favor of the reduction of 2-nortricylcyl bromide (1) and endo- norborn-2-en-5-yl bromide (2) by organo-tin hydrides.



(1)



(2)

A free radical mechanism for the latter reaction has been verified by Kuivila.[9] The reduction process has the advantage of no side products which interfere in VPC analysis, a considerably lower reaction temperature, and

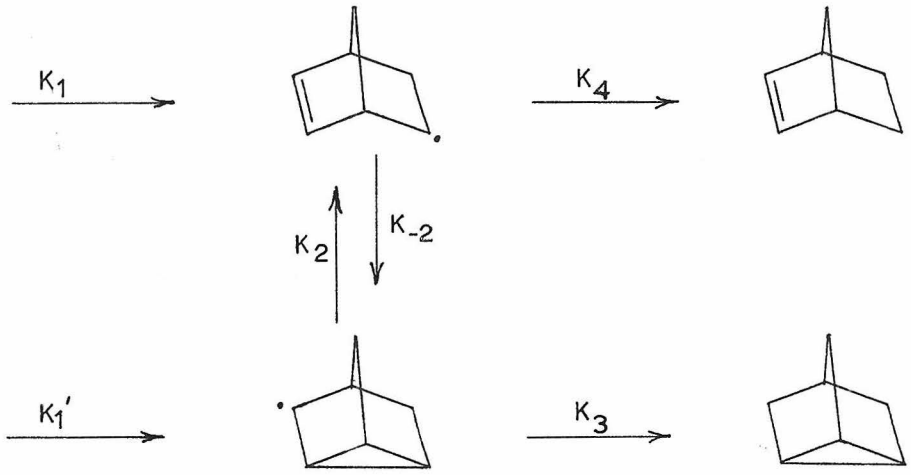
a virtually quantitative product yield.

Tri-n-butyltin hydride was subsequently tried. Reactions run at room temperature indicate that the tri-n-butyltin hydride is not as active in chain transfer as originally hoped, but there is definitely a trapping of the radicals before equilibration as evidenced by the changing of the norbornene to nortricyclene ratio as a function of hydrogen donor concentration.

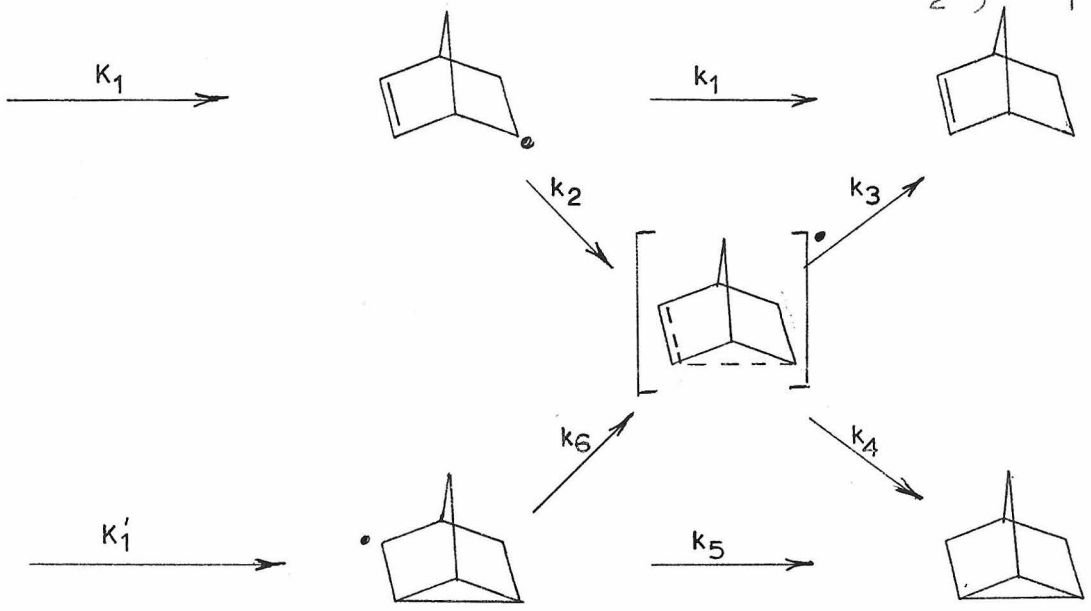
Two sets of three tubes of varying hydrogen donor concentration were reacted at room temperature for the nortricyclyl bromide using n-decane as a solvent. Five such tubes were reacted for the endo-norbronenyl bromide under similar conditions. To minimize concentration effects due to reaction of the hydrogen donor, a minimum ratio of 15:1 was maintained between the tri-n-butyltin hydride concentration and the respective bromides.

For the nortricyclyl bromide, a plot of product nortricyclene/ product norbornene vs. tri-n-butyltin hydride concentration should result in a straight line, if only classical radicals are formed. However, this alone is not proof of solely a classical intermediate, for any mechanism involving the irreversible formation of a nonclassical species leads to the same prediction. Similarly, for the norbronenyl bromide, a plot of product norbornene/ product nortricyclene vs. tri-n-butyltin hydride concentration should result in a straight line, also with the same qualification. The intercepts obtained from both linear plots should have a reciprocal relationship. Quantitatively, the

interconversion of classical nortricyclyl and norbornenyl radicals predicts that the slope of the linear plot should be equal to k_3/k_{-2} and the intercept equal to k_2k_3/k_1k_{-2} when starting from the nortricyclyl bromide, and equal to k_1/k_2 and k_1k_{-2}/k_2k_3 respectively when starting from the norbornenyl bromide.



In the case of the irreversible formation of a "nonclassical" radical, the intercept relationship still holds while the slope relationship holds only if $k_2k_5 = k_1k_6$.



These two limiting mechanisms lead to quite different predictions for the extent of deuterium label-equilibration which would be expected under the reaction conditions, if labeled starting material were employed. For the classical radical mechanism, the ratio of unrearranged to rearranged material, neglecting secondary isotope effects, is $1+2(k_3/k_{-2})(SnH)(1+k_1k_{-2}/k_2k_3) + 2(k_3/k_{-2})^2(SnH)^2(k_1k_{-2}/k_2k_3)$ and the limiting "nonclassical mechanism would predict no label rearrangement. Only nominal work was done to use this prediction.*

In both the norbornenyl and nortircyclyl bromide cases, a definite linear relation appeared, with slope .062 and .038 for the norbornenyl and nortricyclyl bromide cases respectively. The intercepts of 1.37 for the norbornenyl case and .735 for the nortricyclyl case observe the predicted reciprocal relationship. Thus the predicted behavior for the two proposed mechanisms is observed. However, the slopes of .062 and .038 indicate that only one radical per ten or twenty is being trapped before interconversion. Thus in an attempt to increase the capture ratio, the reaction was run at lower temperatures. An attempt was made to run the reaction at -30° C. but the temperature appeared too low to sustain the chain reaction. Even after one week of exposure to sunlight at this temperature, no reaction was observed. The temperature was raised to -10° C. where the reaction proceeded in a period of four days. From this evidence, a reaction run of five

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* an unsuccessful attempt to prepare 2,3,3 -d norborn-5-en-2-yl bromide was made.

tubes containing different hydrogen donor concentrations was prepared using the nortricyclyl bromide. This series was reacted at 0° C. for three days. The data (fig. 2b) shows almost a two-fold increase in the trapping ratio. A similar series of five tubes was run for the norbornenyl bromide (fig 2a) and a corresponding increase in the trapping ratio was again observed. However, the correlative properites predicted by theory have not been realized. That is, the results of the one experiment predict the values for the second to within 15-20%. This can easily be accounted for by the general scatter of the data, and further work should be done to unambiguously determine the slopes. However, the general agreement is heartening.

In an attempt to further increase the trapping, the more active hydrogen donor, di-n-butyltin hydride was used. In the case of the nortricyclyl bromide, another five-fold increase in trapping was observed, but for the norbornenyl bromide, the reaction resulted in destruction of the product norbornene, probably by addition of the di-n-butyltin radical to the double bond.

From independent experiments, it has been determined that under normal circumstances, no care need be taken in mixing the reactants to achieve an homogeneous mixture before reaction is underway. This is due to an incubation period of roughly 18 hours when sealed under vacuum at .03 mm Hg, before any rapid chain reaction occurs. A proposed explanation for this incubation period is that the small amount of oxygen still remaining in the tube re-

act with the tri-n-butyltin radicals to inhibit propogation. Thus, until all the oxygen is removed, chain reaction does not occur. This explanation has been verified to some extent by another experiment where the tube was sealed at .0005 mm Hg; the incubation period for this tube was roughly one hour.

Also for the tri-n-butyltin hydride, it has been established that addition of the hydride radical to the olefinic bond of norbornene is not significant under the reaction conditions, but occurs slowly upon exposure to direct sunlight.

Such results are not the case for di-n-butyltin hydride. Norbornene in neat hydride in a degassed nmr tube is destroyed to the extent of about 70% in a 24 hour period. Fortunately, the rate of the reduction reaction is on the order of 1 to 2 hours, but the incubation period is uncertain, and considerable work is needed to determine conditions under which reaction times would be uniform.

DATA

All the analysis was done by injecting the reacted mixture directly into a Perkin Elmer 800 flame VPC, using 10% Ucor Polar on Chromosorb W, or 10% Tricresyl Phosphate on Chromosorb W. An internal standard was used to calculate absolute yields on all reaction runs.

Table 1. Products from Bromide Reduction with Tri-n-butyltin Hydride

Bromide	Temp.	Tin Hydride Conc. M.	Percent Yield		Ratio[a]
Norbornenyl[b]	0° C.	.976	60.0	42.0	1.43
		1.81	60.4	39.2	1.54
		2.53	58.7	38.7	1.56
		3.18	60.3	36.6	1.65
		3.91	64.0	36.8	1.74
Nortricyclyl[c]	0° C.	.976	-	-	.811
		1.81	39.0	34.2	.872
		2.53	46.4	40.6	.881
		3.18	52.1	49.3	.942
		3.91	46.4	47.2	1.016

Table 2. Products from Bromide Reduction with Di-n-butyltin Hydride

Bromide	Temp.	Tin Hydride Conc. M.	Percent Yield		Ratio[a]
Norbornenyl[b]	0° C.	.886	58.7	37.5	1.57
		1.81	53.8	33.6	1.60
		2.73	48.1	29.7	1.62
		3.67	40.3	25.5	1.58
		4.77	41.5	23.4	1.77
Nortricyclyl[c]	0° C.	1.15	45.5	53.5	1.18
		2.16	38.0	58.4	1.54
		3.40	30.7	61.4	2.01
		3.85	28.2	63.5	2.25
		4.70	27.9	67.0	2.41

[a] Norbornene/nortricyclene for nortricyclyl bromide; nortricyclene/norbornene for norbornenyl bromide
[b] Hexamethyl ethane used as standard
[c] N-nonane used as standard

For reactions run at room temperature, only the ratio as obtained from VPC integration was used to plot preliminary data.

If, the results of the reaction of di-n-butyltin hydride and the norbornenyl bromide are modified by assuming that the norbornene formed in the reaction was destroyed

by the hydride and in actuality 99% theoretical yield was obtained, the following results are obtained.

Yield corrected norbornene	Yield nortricyclene	Ratio
61.5	37.5	1.64
65.4	33.6	1.95
69.3	29.7	2.34
73.6	25.4	2.88
75.6	23.4	3.23

If these results are plotted (fig 3) their correlation with the predicted line from the nortricyclyl bromide case is surprising.

EXPERIMENTAL

Determination of the Reaction Initiation Period

A special two-chamber container was made with one chamber consisting of an NMR tube. 0.16 ml of nortricyclyl bromide was place in one chamber and 0.52 ml of tri-n-butyltin hydride in the other. Two such tubes were prepared. The tubes were sealed under vacuum and mixed while just above their freezing points. The first tube was sealed at .03 mm Hg and the second at .0005 mm Hg. The contents were then transferred to the NMR tube and the tube was sealed. The reaction was followed by using NMR to observe the decrease of the nortricyclyl bromide by a corresponding decrease of a singlet peak at $\delta = 4.5$ corresponding to the hydrogen α to the bromine, while also observing the appearance of the olefinic protons of norbornene at $\delta = 6.0$

Determination of Possible Addition of Tri-n-butyltin Hydride to Norbornene

A 10:1 and 20:1 ratio of tri-n-butyltin hydride to norbornene were prepared and sealed in NMR tubes at .03 mm Hg. The extent of reaction was followed for three days by means of NMR. Nortricyclyl bromide was used as an external standard for the integration of the olefinic protons.

.Reaction Runs At Room Temperature.

Set #1, Three tubes with the following proportions of reactants were sealed at .03 mm Hg after two degassings.

Nortricyclyl bromide	.08 ml	.08 ml	.08 ml
Tri-n-butyltin hydride	.54 ml	1.08 ml	2.16 ml
Decane	1.62 ml	1.08 ml	.00 ml
Hexane (standard)	.02 ml	.02 ml	.02 ml

Set #2, Three tubes were sealed at .03 mm Hg after two degassings each containing the following proportions of reactants.

Nortricyclyl bromide	.02 ml	.02 ml	.02 ml
Tri-n-butyltin hydride	1.08 ml	.54 ml	.27 ml
Decane	.00 ml	.54 ml	.81 ml
Hexane (standard)	.005 ml	.005 ml	.005 ml

Set #3, Five tubes were sealed at .003 mm Hg after two degassings each containing the following proportions of reactants.

Endo-norbornenyl bromide N-nonane mixture*	.02ml	.02ml	.02ml	.02ml	.02ml
Tri-n-butyltin hydride	1.08ml	.88ml	.70ml	.50ml	.27ml
Decane	.00ml	.20ml	.38ml	.58ml	.81ml

*Mixture contains .4228 g. n-nonane, and 1.9752 g. endo-norbornenyl bromide.

These tubes were left to react at room temperature for thirty-six hours.

.Reaction Runs at 0° C.

Five tubes with the following proportions of reactants were sealed at .01 mm Hg after three degassings.

Nortricyclyl bromide-n-nonance mixture*	.02ml	.02ml	.02ml	.02ml	.02ml
Tri-n-butyltin hydride	1.08ml	.88ml	.70ml	.50ml	.27ml
Decane	.00ml	.10ml	.38ml	.58ml	.81ml

*Mixture contains .4357 g. n-nonane and 2.9200 g. nortricyclyl bromide.

Reaction tubes were places in a constant temperature bath at 0.0° C. for 96 hours.

Five similar tubes were made for the norbornenyl bromide.

Endo-norbornenyl bromide-n-nonane hexamethyl ethane[a] mixture*	.02ml	.02ml	.02ml	.02ml	.02ml
Tri-n-butyltin hydride	1.08ml	.88ml	.70ml.	.50ml	.27ml
Decane	.00ml	.20ml	.38ml	.58ml	.81ml

[a]Hexamethyl ethane was found to be a more satisfactory standard having a retention time slightly less than the norbornene.

*Mixture consisted of .1208 g. hexamethyl ethane, .0917 g. n-nonane, and .4112 g. endo-norbornenyl bromide.

Di-n-butyltin dihydride was similarly used to trap the radicals at 0° C. In the nortricyclyl bromide case, a solution of .1233g n-nonane, .3705 g. nortricyclyl bromide and .0971 g. hexamethyl ethane was prepared. .)2 ml of this solution was reacted in the following decane-di-n-butyltin dihydride mixtures.

Decane	.00ml	.20ml	.38ml	.58ml	.81ml
Di-n-butyltin dihydride	1.08ml	.88ml	.70ml	.50ml	.27ml

All the tubes were sealed at .08mm Hg and the reaction was allowed to stand at 0.0° C. for two hours. The tubes were then stored at -85° C. and analyzed starting with tube #1.

For the endo-norbornenyl bromide, a solution containing .0738 g n-nonane, .3292 g endo-norbornenyl bromide, and .0995 g hexamethyl ethane was prepared, and .02 ml was injected into tubes containing the following mixtures of decane and di-n-butyltin dihydride.

Decane	.00ml	.25ml	.46ml	.67ml	.88ml
Endo-norbornenyl Bromide	1.08ml	.83ml	.62ml	.41ml	.20ml

These tubes were sealed at .08mm Hg and allowed to react at 0.0° C. for four hours, and stored at -85° C. overnight before analysis.

The analysis of reaction products was done by injecting the reaction mixture directly into a Perkin Elmer 800 flame VPC using 10% Ucon Polar or 10% Tricresyl Phosphate on Chromosorb W.

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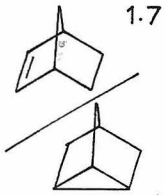
LEAST SQUARES CALCULATION
REACTION TEMPERATURE
0.0° C

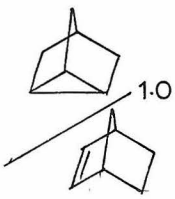
NORBORNENYL BROMIDE (fig 2a)



predicts for nortricyclyl case

slope = 0.0753
intercept 0.746

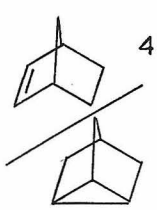
NORTRICYCLYL BROMIDE (fig 2b)



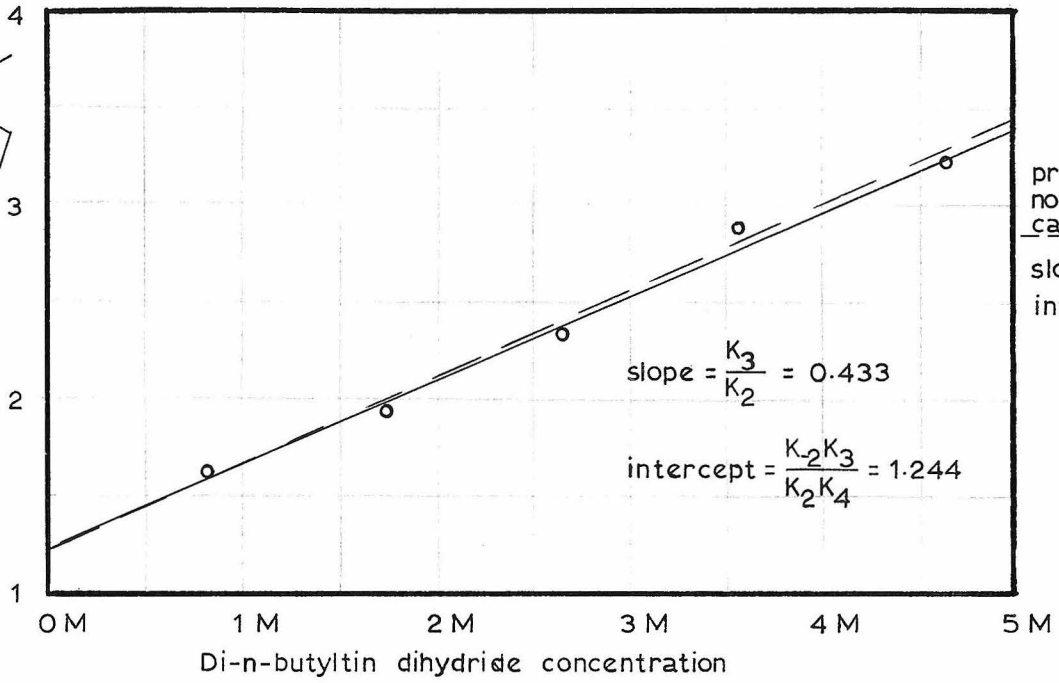
predicts for norbornenyl case

slope = 0.0887
intercept = 1.343

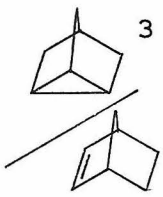
LEAST SQUARES CALCULATION
REACTION TEMPERATURE
0.0° C



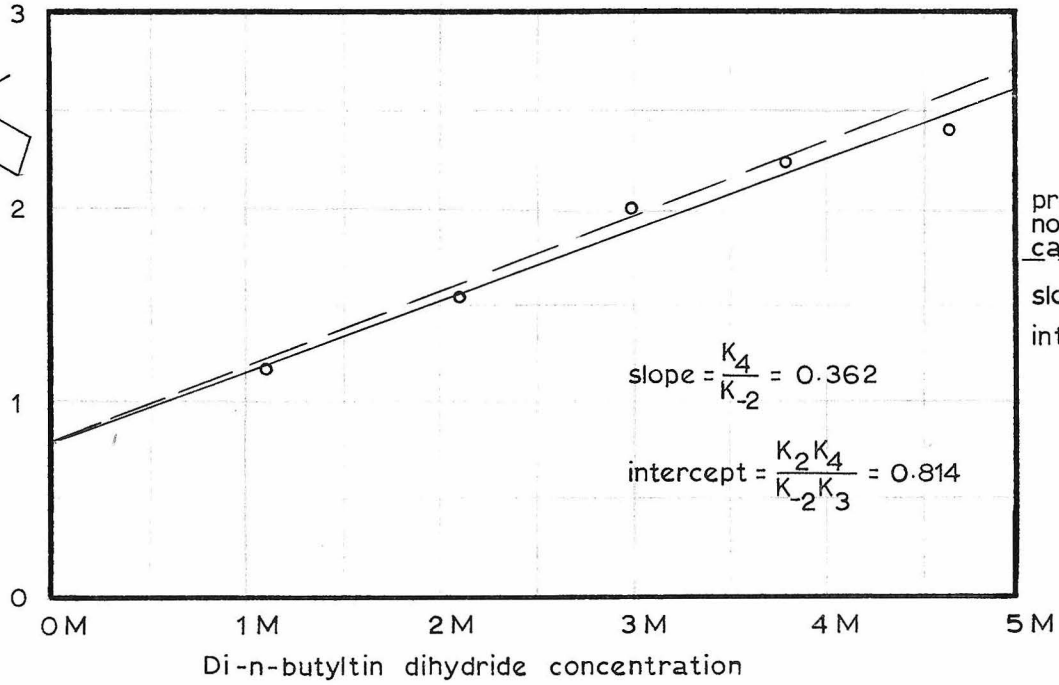
NORBORNENYL BROMIDE



predicts for nortricyclyl case
slope = 0.382
intercept = 0.804



NORTRICYCLYL BROMIDE

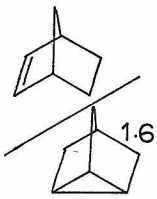


predicts for norbornenyl case
slope = 0.444
intercept = 1.228

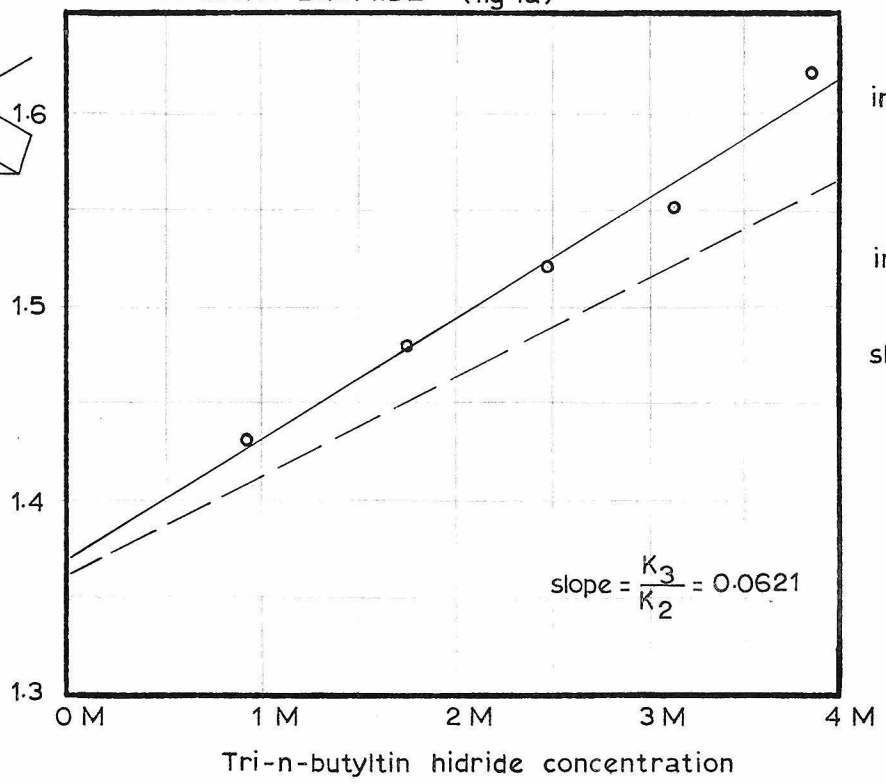
FIG. 3

LEAST SQUARES CALCULATION

REACTION TEMPERATURE
25 - 28° C



NORBORNENYL BROMIDE (fig 1a)



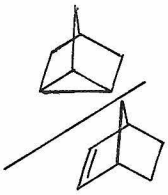
experimental

intercept = $\frac{K_{-2}K_3}{K_2K_4}$ = 1.369

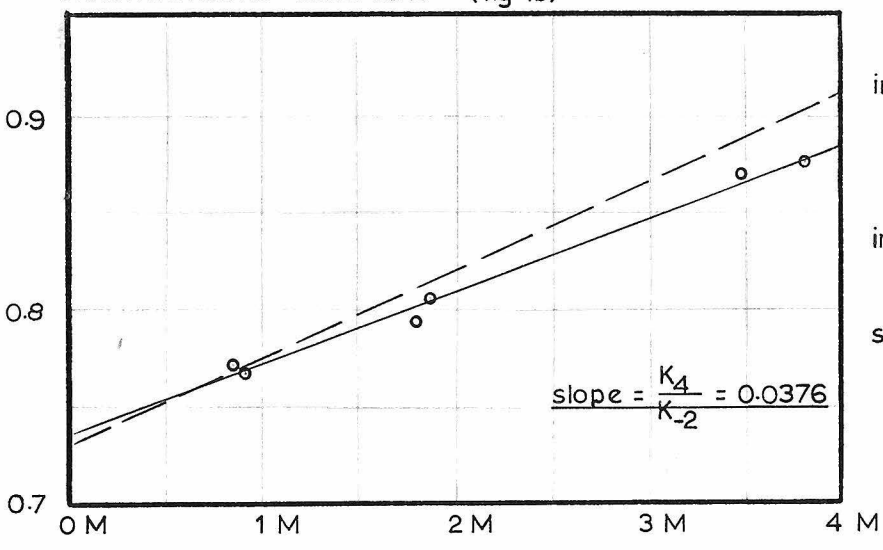
predicts for nortricyclyl case

intercept = $\frac{K_2K_4}{K_{-2}K_3}$ = 0.730

slope = = 0.453×10^{-1}



NORTRICYCLYL BROMIDE (fig 1b)



experimental

intercept = $\frac{K_2K_4}{K_{-2}K_3}$ = 0.735

predicts for norbornenyl case

intercept = $\frac{K_{-2}K_3}{K_2K_4}$ = 1.360

slope = $\frac{K_3}{K_2}$ = 0.512×10^{-1}