The Mechanism of the Free Radical Reduction of the Norbornyl-nortricyclyl System

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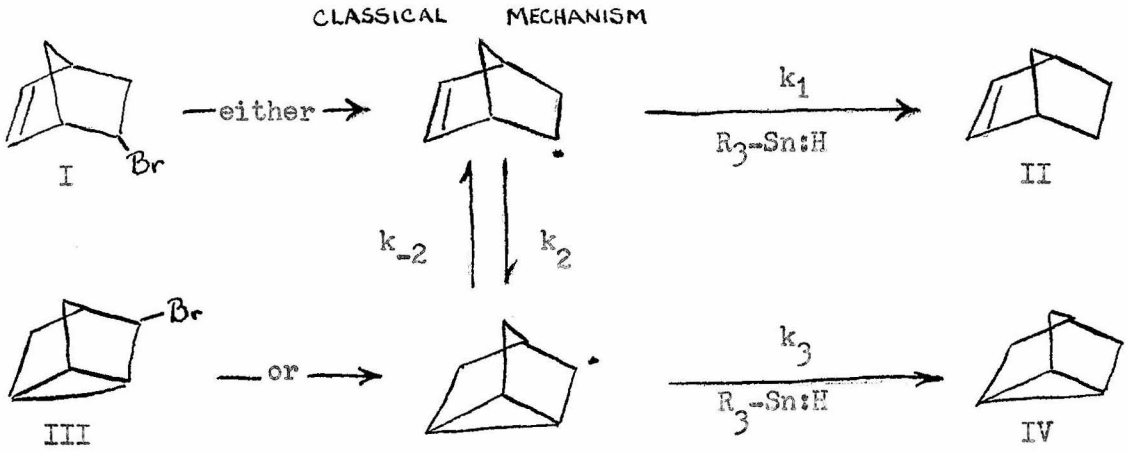
Assumption of a classical mechanism in the free radical reduction of norbornenyl or nortricycl bromide leads to measurable predictions about the relation between the ratio of the two products and the concentration of the hydrogen donor. Experimental work, using vpc analysis to determine the ratio of the products from the reaction of these bromides with tri-n-butyl tin and di-n-butyl tin hydride, shows that these predictions are fulfilled. It is concluded therefore, that such a classical mechanism is possible and that this mechanism is most probably the proper one for this reaction.

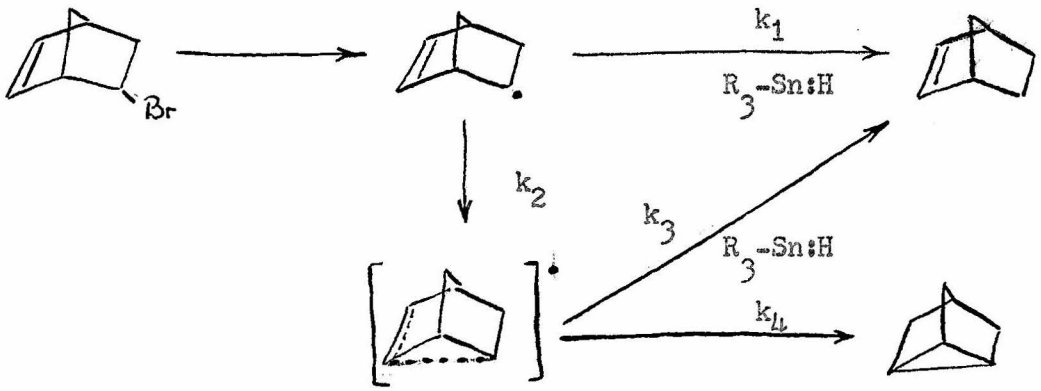
The free radical reduction of endo-dehydronorbornyl bromide [I] with tri-n-butyl tin hydride produces two products: norbornylene [II] and nortricyclene [IV] . The mechanism of this reduction is of some interest because the appearance of the nortricyclene indicates that the mechanism must include the conversion of one radical intermediate into another. Interconversion between classical norbornyl and nortricycl radicals seems logical, but the discovery of the non-classical carbonium ion in the norbornyl-nortricycl system raises the possibility that a corresponding non-classical free radical may also exist.



Assuming a mechanism of interconversion between the classical norbornyl and nortricyclyl radicals leads to some very definite, readily measured predictions. In the reduction of nortricyclyl bromide, the ratio of the yield of nortricyclene over the yield of norbornylene

should vary directly with the concentration of the hydrogen donor. A plot of this ratio against the hydrogen donor concentration would have a slope equat to $B = k_3/k_{-2}$ and an intercept $A = k_2k_3/k_1k_{-2}$. When norbornyl bromide is used as the starting material, a similar plot of the ratio of yield norbornylene over yield nortricyclene should yield a line with slope B/A and intercept 1/A. Thus, by merely assuming that the mechanism is correct, the data from the slope and intercept for one of these compounds should predict the results that would be obtained from the other.

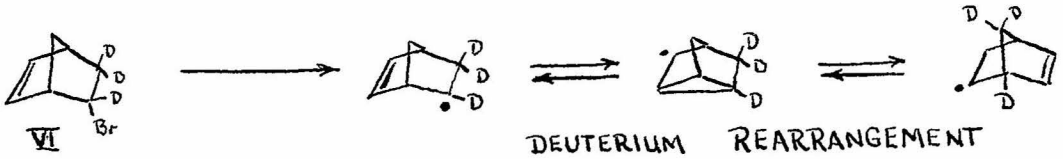
Unfortunately, while the possibility of interchange between classical radicals can be ruled out by a failure to satisfy these conditions, compliance with the predictions does not rule out the possibility of a non-classical mechanism. The following mechanism, and the corresponding one for nortricyclyl bromide,



also predicts such a straight line plot, and the slopes and intercepts will correspond if only $k_2k_6 = k_1k_7$, where k_6 and k_7 apply to the nortricyclyl radical and are analogous to k_1 and k_2 respectively.

Halgren[1] has suggested the use of labeled starting materials as a means of differentiating between a classical and a non-classical

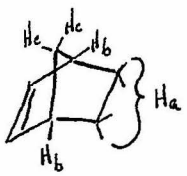
mechanism. Specifically, if a deuterium substituted norbornyl bromide [VI] is reduced by the classical mechanism, the positions of the deuterium will be rearranged:



Neglecting isotope effects, the ratio of unrearranged to rearranged norbornylene yielded should be:

$$1 + 2B[R_3\text{-}Sn\text{:}H](1 + 1/A) + 2B^2[R_3\text{-}Sn\text{:}H]/A \quad .$$

The non-classical mechanism would predict no deuterium rearrangement. Thus any envolvement of a non-classical mechanism would produce an amount of deuterium rearrangement somewhat less than predicted for the classical case. Comparing the experimental data with the two extreme cases would provide a fair estimate of the amount of possible non-classical participation. The number of protons predicted for the various positions of norbornylene as a result of these mechanisms are:



POSITION	Classical Radicals	Non-classical Mechanism
H_a	2.08	1.00
H_b	1.64	2.00
H_c	1.28	2.00

Experimental

A measurement of the slope and intercept relationships mentioned above was conducted. Preliminary work showed that the best results could be obtained through the reaction of a bromide with tributyl tin hydride. Testing the validity of the predictions would determine the

possibility of excluding a classical mechanism from consideration.

Nortricyclyl bromide, in substantial quantities, was obtained from previous work.[2] Analysis upon the vpc and by nmr indicated that the sample was adequately pure. The sample was used as recieved, without further purification.

Vinyl bromide was necessary for the production of norbornyl bromide. About 300 grams of 1,2-dibromoethane was dropped slowly into a solution of KOH in ethanol. The resulting gases were collected with a dry ice trap and kept at dry ice temperatures. When the dibromoethane had all been added, the mixture was refluxed for two hours. The liquid found in the collection flask proved to be vinyl bromide. The yield was about 35%.

This low yield proved to be disastrous to our attempts at making a deuterium substituted norbornyl bromide. Costs limited the supply of substituted dibromoethane to ten grams, yet no way could be found to increase the yield. Different bases were tested on unsubstituted dibromoethane, among them KOH in ethylene glycol, KO-t-Bu in t-BuOH, and LiCl in DMF, yet the yields did not increase. Subsequently, the deuterium substituted norbornyl bromide was not produced.

Norbornyl bromide was obtained from a diels-alder reaction of the vinyl bromide and freshly cracked cyclopentadiene.[3] 21.1 ml of vinyl bromide was sealed into a tube with 16.5 ml of cyclopentadiene and left overnight at 180° C. The resulting brownish liquid was distilled at 15 mm Hg pressure, collecting the product at between 91° and 95°C. The product was a colorless liquid containing a mixture of the endo and exo isomers of norbornyl bromide. These isomers were separated with a 12 foot carbowax column on the preparatory vpc.

Nmr and vpc analysis revealed that the resulting portions were pure endo and pure exo. The endo isomer was used in all subsequent work.

Reaction tubes were prepared with fixed quantities of one of the bromides and a varying amount of tri-n-butyl tin hydride. The volume was made constant through addition of the appropriate amount of decane. The tubes were then degassed, sealed, and given sufficient time to react. When the reaction was complete, the tubes were opened and the contents analysed on the vpc. Tricresyl phosphate was used for the column as it produced adequate separation of the two products with a retention time of about ten minutes at temperatures between 55° and 100° C.

Initially, the tubes were allowed to stand for two days at room temperature before analysis. However, it was found that the tin hydrides, especially the dibutyl tin hydride, had a tendency to attack the norbornyl species through a hydrostannation reaction. This tendency was minimized by lowering the temperature of the reaction to 0° C and allowing a week for the reaction to complete. The hydrostannation reaction could be controlled yet further through extensive degassing, as oxygen was found to initiate the hydrostannation while inhibiting the desired reduction reaction.

The lower temperature had other desirable side effects; lowering the temperature made the trapping of the radicals more competitive with the interchange equalibrium and thus increased the slope of the plot. As larger slopes are easier to determine experimentally than are small ones, this provided greater accuracy for the work. To take further advantage of this tendency, a stronger hydrogen donor, dibutyl tin hydride, was used to make the slope even steeper. Great care had

to be taken to keep the reaction at 0° C, however, as the hydrostannation reaction proceeded rapidly at room temperatures with this hydride.

Nmr spectra were made of endo-norbornylene with a large number of solvents. From these spectra, the position of the proton peaks for the various hydrogen atoms on the norbornylene was determined. Unfortunately, this data was not used as the synthesis of the deuterium substituted norbornyl bromide was unsuccessful.

Results and Conclusions

The results of the reaction series of the reduction of the bromides are plotted in figures 1, 2, and 3. The ratio of the products is plotted along the y-axis, while the concentration of the hydrogen donor is plotted down the x-axis. The solid black line indicates the experimental slope as determined from the data; the dashed line is the slope predicted by the data obtained from the other bromide. The experimental data corresponds nicely with the predicted values in all cases. In fact, as the temperature was lowered and a more active hydrogen donor used to increase the accuracy of the measurement, the agreement came within about 1%. (figure 3)

The close agreement between experimental data and our expectations demonstrates the possibility of a classical mechanism. While this finding does not exclude the possibility of a non-classical mechanism, the non-classical mechanism is somewhat more complex than the hypothesized classical mechanism, thus making the classical mechanism more logical. An exact statement will not be made, however, until the exact extent, if any, of non-classical contribution is known. The method outlined by Halgren looks promising if the materials needed can ever be obtained. While the accuracy of nmr analysis is not high enough to completely

exclude the posibility of any non-classical contributions, it will be adequate for determining any significant contribution. Until such a study is made, it can only be said that the classical mechanism for this reduction is not only logical, but is also highly possible.

Footnotes

1. Thomas A. Halgren, Graduate Teaching Assistant, California Institute of Technology. This work was conducted by Ted T. Fujimoto and myself under Tom's guidance and financed by the NSF.

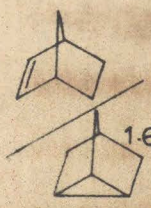
2. From the Crellin Labratories, California Institute of Technology, Dr. Robert's group.

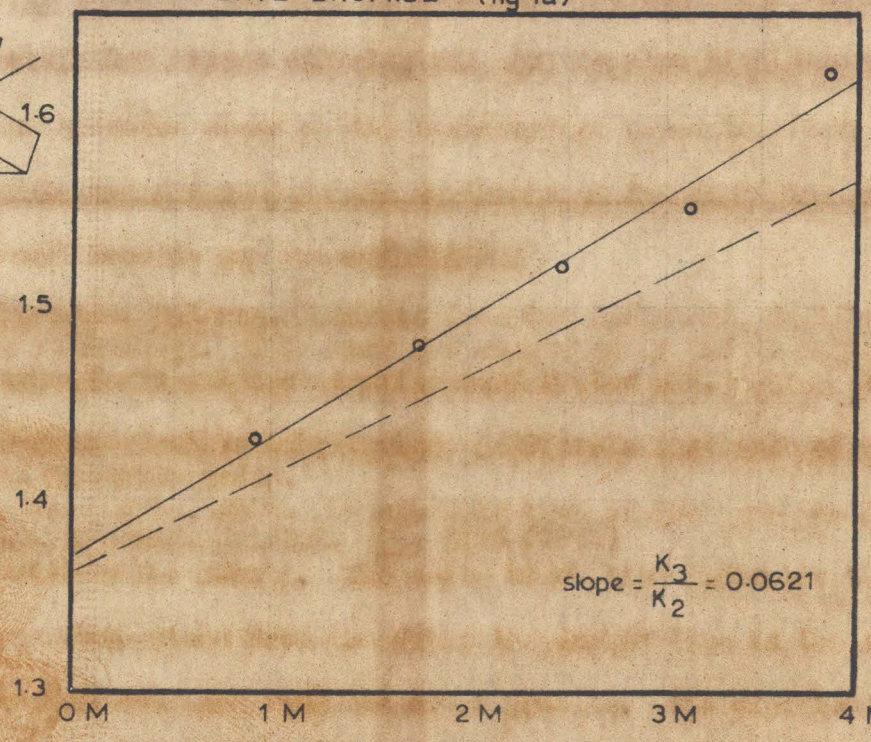
3. J.D. Roberts, J.A.C.S. 72, 3116 (1950)

LEAST SQUARES CALCULATION

REACTION TEMPERATURE
25 - 28° C

NORBORNENYL BROMIDE (fig 1a)





<u>experimental</u>

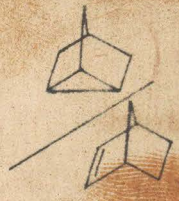
intercept = $\frac{K_{-2}K_3}{K_2K_4}$ = 1.369

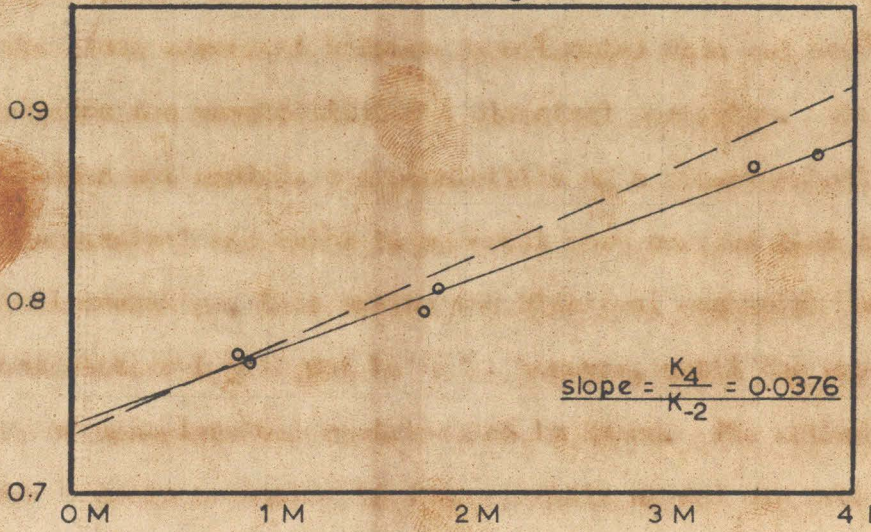
predicts for nortricyclyl <u>case</u>

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

slope = = 0.453×10^{-1}

NORTRICYCLYL BROMIDE (fig 1b)





<u>experimental</u>

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

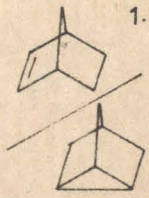
predicts for norbornenyl <u>case</u>

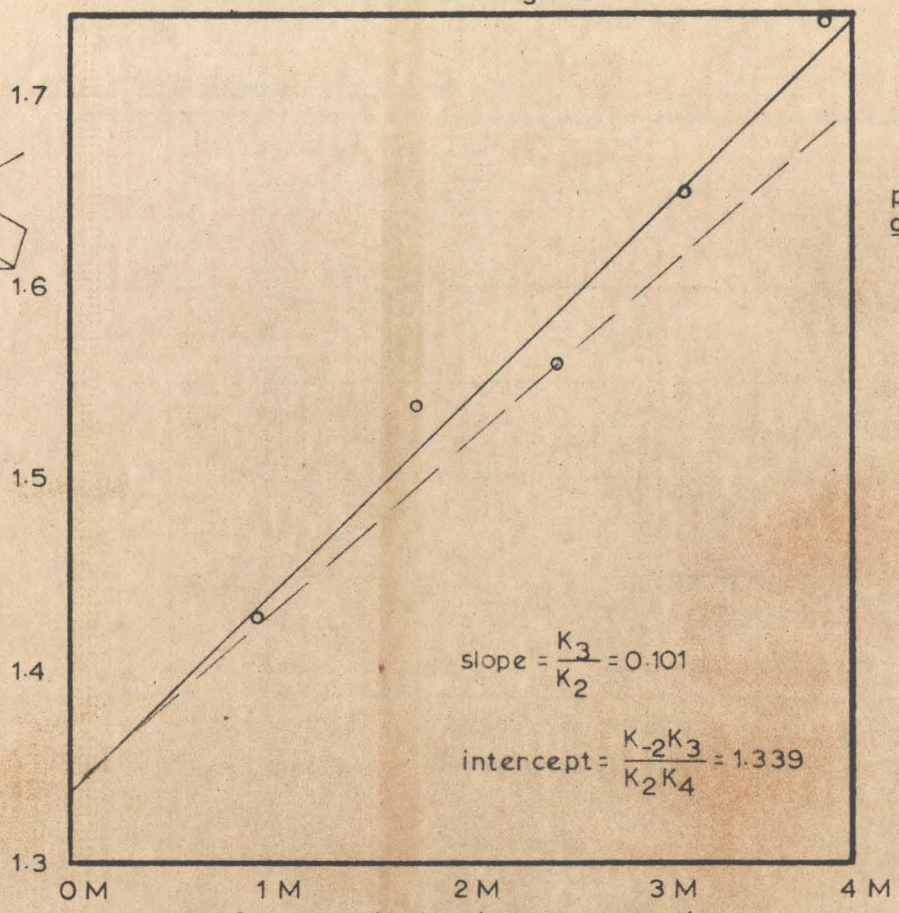
intercept = $\frac{K_{-2}K_3}{K_2K_4}$ = 1.360

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

LEAST SQUARES CALCULATION
REACTION TEMPERATURE
0.0° C

NORBORNENYL BROMIDE (fig 2a)

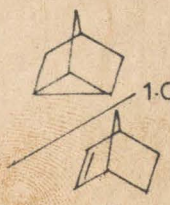


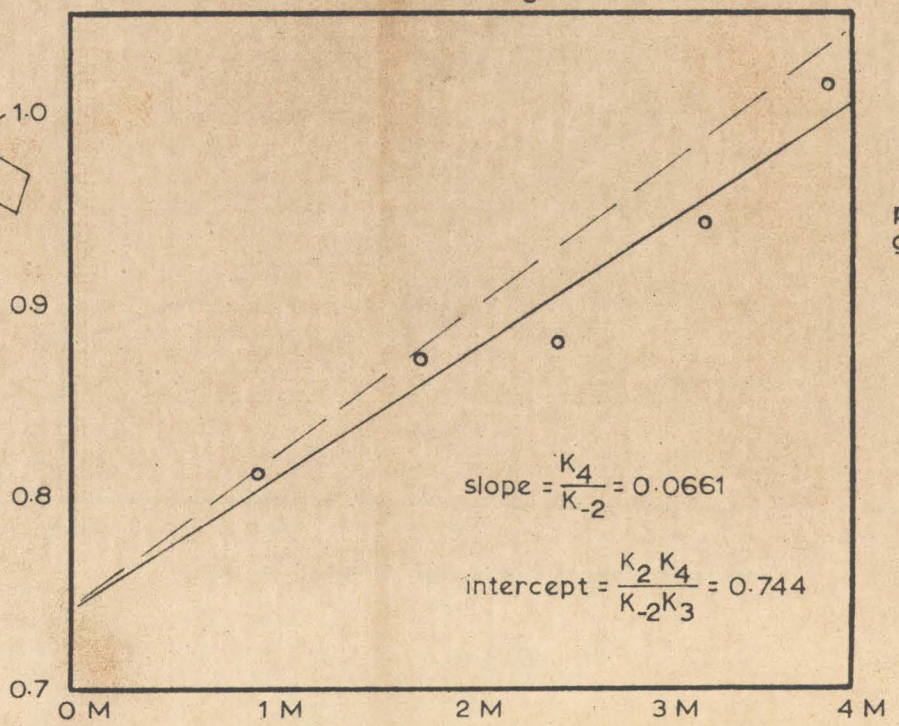


predicts for nortricyclyl case

slope = 0.0753
intercept 0.746

NORTRICYCLYL BROMIDE (fig 2b)

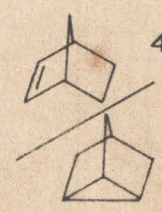




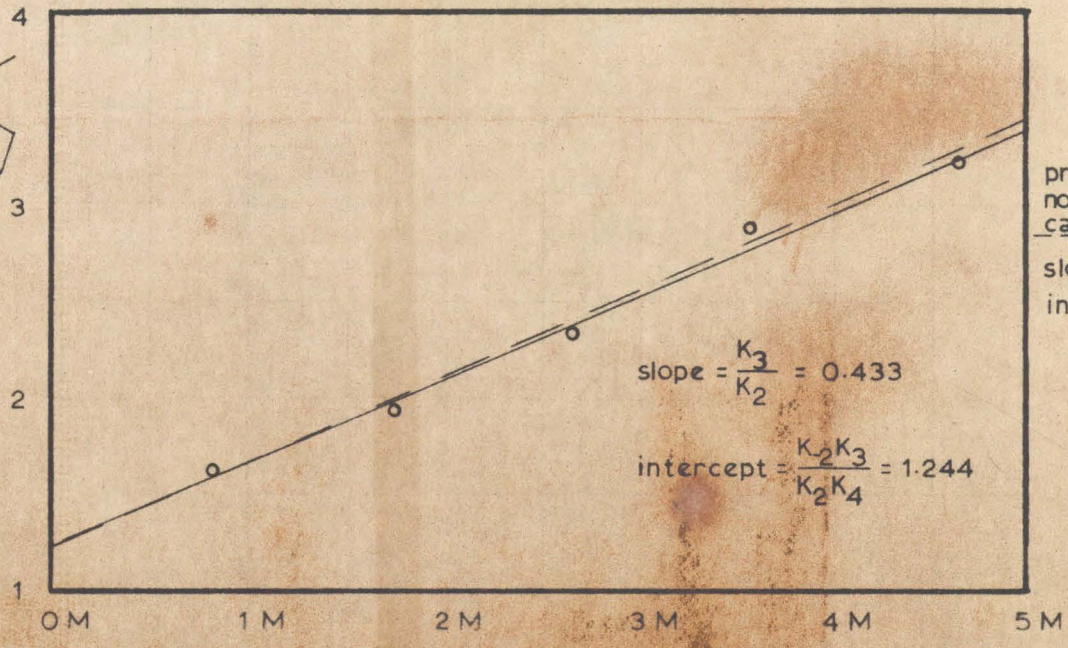
predicts for norbornenyl case

slope = 0.0887
intercept = 1.343

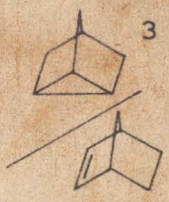
LEAST SQUARES CALCULATION
REACTION TEMPERATURE
0.0° C



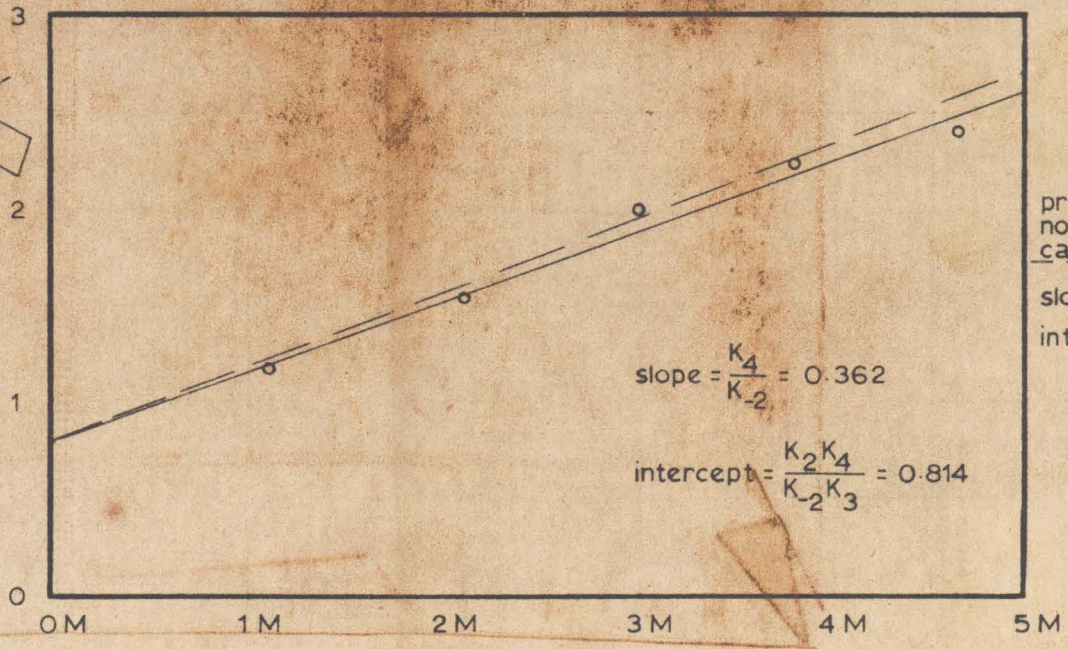
NORBORNENYL BROMIDE



predicts for nortricyclyl case
slope = 0.382
intercept = 0.804



NORTRICYCLYL BROMIDE



predicts for norbornenyl case
slope = 0.444
intercept = 1.228

FIG. 3