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THE "BICYCLOBUTONIUM ION"

REACTION OF (1-METHYLCYCLOPROPYL)CARBINYL AND 1-METHYL CYCLOBUTYL METHANESULFONATES WITH SODIUM BOROHYDRIDE UNDER SOLVOLYTIC CONDITIONS

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Abstract—The reaction of both, (1-methylcyclopropyl)carbinyl mesylate and 1-methylcyclobutyl mesylate, with $NaBH_4$ in aqueous diglyme affords a mixture of 1,1-dimethylcyclopropane and methylcyclobutane in addition to 1-methylcyclobutanol. The hydrolysis of both mesylates resulted in the formation of only one product, i.e. 1-methylcyclobutanol. The results obtained when the amounts of BH_4^- and water were varied indicate that the reaction of the primary mesylate with $NaBH_4$ proceeds by two competitive mechanisms (S_N1 and S_N2). The results are rationalized in terms of nonclassical ions and the inadequacy of the equilibrating classical ion pair hypothesis is discussed. The suggestion is made that the described method might be of use in some cases for distinguishing between classical and nonclassical carbonium ions.

The nonclassical carbonium ion concept was introduced by Winstein[1a] and Roberts[1b] in the early 1950's as an attractive description of cationic intermediates formed in some Wagner-Meerwein type rearrangement reactions. The recent strong criticism of this hypothesis[2] initiated numerous investigations aimed to provide an unequivocal answer to the question whether the first formed intermediates are appropriately described by a resonance stabilized "non-classical structure" or if a set of rapidly equilibrating classical ions can better account for the experimental observations.[3]

As an example the formation of a nonclassical "bicyclobutonium ion" has been proposed as the simplest explanation for the unusual behaviour of cyclopropylcarbinyl, cyclobutyl and homoallyl derivatives.[1c]

Our approach to this problem has been focused on rate studies of specifically deuterated cyclopropylcarbinyl and cyclobutyl derivatives.[4] Although accumulated evidence and reports in the literature[5] provide strong evidence in favour of the

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* Taken in part from the Master Thesis of Z.M., University of Zagreb (1965).

[1a] S. Winstein and D. S. Trifan, *J. Amer. Chem. Soc.* **71**, 2953 (1949); **74**, 1154 (1952); [b] J. D. Roberts and R. H. Mazur, *Ibid.* **73**, 2509 (1951); R. H. Mazur, W. N. White, D. A. Semenov, C. C. Lee, M. S. Silver and J. D. Roberts, *Ibid.* **81**, 4390 (1959). See also Ref. 5.

[2] H. C. Brown, *The Transition State*, Special Publ. No. 16; pp. 140–158. Chemical Society, London (1962). H. C. Brown and F. J. Chloupek, *J. Amer. Chem. Soc.* **85**, 2322 (1963); H. C. Brown and H. M. Bell, *Ibid.* **85**, 2324 (1963); H. C. Brown, F. J. Chloupek and Min-Hon Rei, *Ibid.* **86**, 1246, 1247, 1248 (1964).

[3] For discussion of the "phenonium" ion problem see H. C. Brown, K. J. Morgan and F. J. Chloupek, *J. Amer. Chem. Soc.* **87**, 2137 (1965).

[4a] S. Borčić, M. Nikoletić and D. E. Sunko, *J. Amer. Chem. Soc.* **84**, 1615 (1962); [b] M. Nikoletić, S. Borčić and D. E. Sunko, *Proc. Nat'l. Acad. Sci.* (U.S.) **52**, 893 (1964); [c] M. Nikoletić, S. Borčić, and D. E. Sunko, *Tetrahedron.*

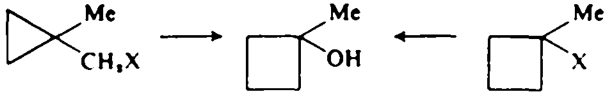
[5a] E. F. Cox, M. C. Caserio, M. S. Silver and J. D. Roberts, *J. Amer. Chem. Soc.* **83**, 2719 (1961), and previous papers; [b] K. L. Servis and J. D. Roberts, *Ibid.* **86**, 3773 (1964); [c] K. L. Servis and J. D. Roberts, *Ibid.* **87**, 1331 (1965).

non-classical structure, full interpretation of the known results is still not possible owing to the lack of knowledge of all the factors involved.

Important information concerning the structure of the cationic intermediates in solvolysis of cyclopropylcarbinyl, cyclobutyl and allylcarbinyl derivatives has been *inter alia* obtained by investigating the composition of the products resulting from solvolytic and/or the amine-nitrous acid deamination reaction.[1b,6,7] Although the nitrous acid deamination of aliphatic and alicyclic amines is generally accepted as a convenient means for the study of carbonium ions, the intermediates produced appear to be less solvated ("hot") and of greater energy content than those formed under solvolytic conditions. This and other complicating factors, e.g. S_N2 substitution on the diazonium ion, restrict the usefulness of correlations of product composition from the deamination reaction with those from solvolysis studies.

The borohydride trapping technique first described by Brown and Bell[8] has been recently applied by both Brown[9] and Winstein[10] in their studies of solvolysis of representative 2-norbornyl, anti-norbornen-7-yl and norbornadien-7-yl derivatives. In spite of the fact that the results obtained in some experiments have been diversely interpreted, the borohydride technique provides means for the study of cationic intermediates formed under solvolytic conditions. Therefore, the products formed in the solvolysis of (1-methylcyclopropyl)carbinyl and 1-methylcyclobutyl methanesulfonates in aqueous diglyme in the presence of sodium borohydride has been investigated.

Among the many studied cyclopropylcarbinyl and cyclobutyl derivatives, the 1-ring methyl substituted compounds deserve particular attention. The methyl substitution causes only a small rate enhancement[11] and the substitution of hydrogen for deuterium in the methyl produces abnormally small secondary isotope effects.[4b,c] Contrary to the nonsubstituted compounds, the deamination reaction of the corresponding amines I and II ($X = NH_2$) did not yield a mixture of products but resulted in the exclusive formation of 1-methylcyclobutanol.[5a] In addition, the solvolysis of I ($X = OMs, Cl$) in ethanol proceeds with an internal rearrangement to the corresponding 1-methylcyclobutyl derivatives.[4b,c,11b]



1 2

RESULTS

Materials. The methanesulfonates I and II ($X = OSO_2Me$) were prepared from the corresponding alcohols,[4c] the purity of which as determined by VPC was better than 98%. 1-Methylcyclobutanol contained less than 0·2% of (1-methylcyclopropyl)-carbinol. (1-Methylcyclopropyl)carbinol was free from the cyclobutyl isomer. The

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[6] E. Renk and J. D. Roberts, *J. Amer. Chem. Soc.* **83**, 878 (1961).

[7] J. D. Roberts and V. C. Chambers, *J. Amer. Chem. Soc.* **73**, 5034 (1951).

[8] H. C. Brown and H. M. Bell, *J. Org. Chem.* **27**, 1928 (1962).

[9] H. C. Brown and H. M. Bell, *J. Amer. Chem. Soc.* **85**, 2324 (1963); see also H. C. Brown and H. M. Bell, *Ibid.* **86**, 5006, 5007 (1964).

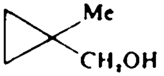
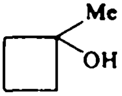
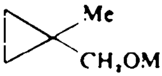
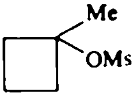
[10] S. Winstein, A. H. Lewin and K. C. Pande, *J. Amer. Chem. Soc.* **85**, 2324 (1963).

[11a] D. D. Roberts, *J. Org. Chem.* **29**, 294 (1964); see also Ref. 4*a*,*b* and 5*a*; [b] M. Nikoletić, S. Borčić and D. E. Sunko, *Pure and Appl. Chem.* **8**, 441 (1964); see also Ref. 4*c*.

NMR spectra of the methanesulfonate I revealed the presence of 2·4–4·5% of I (X = OH) and less than 0·8% of II (X = OMs) while II (X = OMs) contained less than 0·25% I (X = OMs).

Solvolysis in water. In order to ascertain that during solvolysis both mesylates yield only cyclobutyl derivatives, they were hydrolysed in water at 20·0°, in the presence of a 10% excess $CaCO_3$, and the products analysed by VPC (Experimental). The results are given in Table 1. By VPC analysis of a known mixture of pure alcohols I and II (X = OH), it was found that not more than 0·2% of one component could escape detection. Thus, the solvolysis of (1-methylcyclopropyl)carbinyl mesylate yields only the rearranged alcohol while the solvolysis of II proceeds without rearrangement.

TABLE 1. HYDROLYSIS PRODUCTS OF (1-METHYLCYCLOPROPYL) CARBINYL AND 1-METHYLCYCLOBUTYL METHANESULFONATES 20.0° [a]

Compound	ROMs in H_2O		Products in %	
	0·25M	2·4–4·5[b]		95·5–97·6
	0·25M	0		100

[a] Determined by VPC on a 2 m. UCON-LB-550-X column at 110° with He as carrier gas. The figures give the range of values obtained from 5 experiments.

[b] Present in the starting material.

Borohydride trapping. Two series of experiments were performed using as solvent 75% and 87·5% aqueous diglyme, respectively. The amount of sodium borohydride was varied between 0·25M and 2·0M. The concentrations of the respective mesylates were either 0·25M or 0·125M. The volatile products consisted of hydrocarbons and the yields were determined by weighing the material collected in liquid air cooled traps. Each sample of hydrocarbons was analyzed by VPC with two different columns (silicone DC 200 and UCON LB-550-X). The retention times were compared with the data obtained with samples of pure 1,1-dimethylcyclopropane and methylcyclobutane under identical conditions and were reproducible within 2%. The product composition was determined from the VPC data by the method of Wagner and Weber.[12]* The comparison of IR spectra taken in the gas phase of the obtained mixture of hydrocarbons with the spectra of known mixtures confirmed the results obtained by VPC.

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[12] I. F. Wagner and J. H. Weber, *Ind. Eng. Chem., Chem. Eng. Data Ser.* 3, 220 (1948).

* They found that, for binary mixtures, the actual ratio between the mol fractions of the two components and the ratio of plane areas obtained by integration is constant. Since the value of this constant can be determined experimentally using known mixtures of the respective compounds this method is much more accurate for quantitative work than the normalization procedure.

Mixtures containing as little as 1·7% of 1,1-dimethylcyclopropane in methylcyclobutane still gave detectable bands at 3086 and 1015 cm^{-1} characteristic for cyclopropane derivatives. Only 0·2% of one hydrocarbon in the trapped mixture could escape detection.

The results from the trapping experiments are summarized in Table 2.

The residual diglyme solution (Experimental) was analysed by VPC. The alcohols were recovered in about 75% yield. The non volatile products from the reaction of (1-methylcyclopropyl)carbinyl mesylate contained about 1% of the unrearranged alcohol. The only other component was 1-methylcyclobutanol. 1-Methylcyclobutyl mesylate yielded only 1-methylcyclobutanol. These results are in agreement with those obtained in the hydrolysis as described previously.

In all experiments 1,1-dimethylcyclopropane was detected in the hydrocarbon fraction obtained from both I and II. A better yield of hydrocarbon was obtained in the reaction of the cyclopropyl derivative than with the cyclobutyl derivative. Since the product composition obtained from the two isomeric mesylates was different, i.e. I yielded more 1,1-dimethylcyclopropane than II, two different mechanisms may be operative.

It is known that the reaction of primary and secondary alkyl halides and alkyl sulfonates with complex hydrides in aprotic solvents proceeds by direct displacement[8,13] while tertiary derivatives under similar conditions predominantly eliminate.[14] The reactivity decreases in the same order. On the other hand the solvolytic reactivities show an inverse order. Consequently, it can be assumed that the tertiary mesylate will react with $NaBH_4$ under solvolytic conditions exclusively by an S_N1 mechanism, while the primary derivative might exhibit both mechanisms. Starting from the assumption that the solvolytic reaction proceeds with both derivatives via the same intermediate, the amount of 1,1-dimethylcyclopropane formed from the cyclobutyl derivative can be used as a measure for the contribution of the S_N1 mechanism in the reaction of the primary mesylate. It was therefore of interest to determine whether the experimental results obtained with different amounts of nucleophiles are consistent with this interpretation.

The following reactions (Scheme 1) account for all products formed from I in the reaction with $NaBH_4$ under solvolytic conditions:

Path A. An S_N1 reaction leading to the bicyclobutonium ion III which subsequently reacts either with BH_4^- (path D) to give the isomeric hydrocarbons IV and V, or with the solvent (path C), yielding 1-methylcyclobutanol VI.

Path B. A direct S_N2 displacement on the primary carbon atom of I affords IV.

The molar fractions (X) of I undergoing the displacement reaction by the two mechanisms are given in Eqs (1) and (2).*

$$S_N1 \qquad X_A = X_C + X_D \qquad (1)$$

$$S_N2 \qquad X_B = (1 - X_C) - X_D \qquad (2)$$

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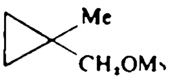
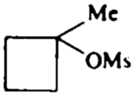
* The subscripts refer to the different paths shown in Scheme 1.

[13] E. L. Eliel, *J. Amer. Chem. Soc.* 71, 3970 (1949); G. K. Helmkamp and B. F. Rickborn, *J. Org. Chem.* 22, 479 (1957).

[14] N. G. Gaylord, *Reduction with Complex Metal Hydrides* p. 889. Interscience, New York (1956).

TABLE 2. DEPENDENCE OF PRODUCT COMPOSITION UPON REACTION CONDITIONS

Compound ROMs	Exper. No.	ROMs mole/l	$NaBH_4$ mole/l	% aq. diglyme	$\frac{NaBH_4}{ROMs}$	$\frac{NaBH_4}{H_2O}$	Products in %* 1-Methyl cyclobutanol X_O	Hydrocarbons 4 + 5 $X_B + X_D$	Ratio 4/5 f	X_B
	1	0·25	0·50	2	0·036	0·036	91·4	8·6	27/73	2·2
	2	0·25	1·00	75	4	0·072	75	25	22/78	5·2
	3	0·25	2·00	75	8	0·144	60	40	20/80	7·6
	4	0·125	0·25	87·5	2	0·036	91	9	50/50	4·5
	5	0·125	1·00	87·5	8	0·144	68	32	39/61	12·0
	6	0·25	0·50	75	2	0·036	92	8	1·7/98·3	
	7	0·25	2·00	75	8	0·144	71	29	1·7/98·3	

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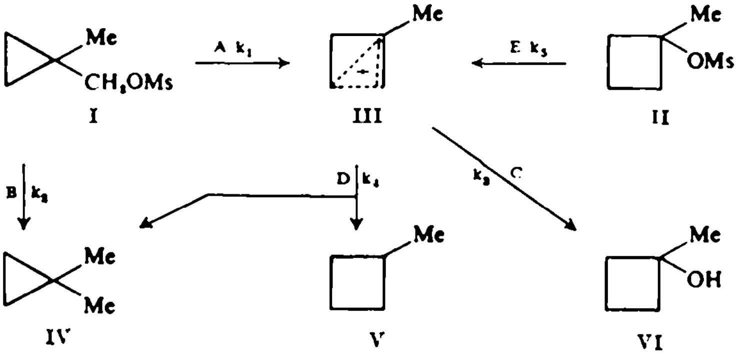
* Mean values from 3–5 runs of each set of experiments.

Scheme 1



From the amount of IV resulting from trapping of the carbonium ion III in the solvolysis of II—path E—the Eq (3) for the molar ratios (f) of hydrocarbons 4 and 5 formed from I can be written as:

$$f = \frac{X_{(4)}}{X_{(5)}} = \frac{X_B + 0{\cdot}017X_D}{0{\cdot}983X_D} \tag{3}$$

The value of (f) can be obtained by VPC analysis of the trapped hydrocarbons.

From Eqs (2) and (3) the molar fraction of hydrocarbons formed from III by path D can be calculated:

$$X_D = \frac{1 - X_C}{0{\cdot}983(f + 1)} \tag{4}$$

Thus, from the experimentally obtained values of (f) and $1 - X_C$ (i.e. the total yield of hydrocarbons) it is possible to calculate the relative contributions of different reaction paths in dependence to the changing ratio of sodium borohydride to water. The results are presented in Figs. 1 and 2.

The increase of X_B (direct displacement) with increasing ratio of ($NaBH_4$):(ROMs) when the amount of water in diglyme was kept constant (Table 2, Exp. No. 1–3) and also if its amount was decreased by keeping ($NaBH_4$):(ROMs) constant (Table 2, Exp. 1,4 and 2,5) can be considered as a strong indication that the primary mesylate indeed reacts with $NaBH_4$ by the two competing mechanisms. The larger increments for the S_N1 reaction in comparison to the S_N2 process (Fig. 1) can be ascribed to the salt effect.[8,10]

Reaction rates. In the solvolysis of (1-methylcyclopropyl)carbinyl mesylate and 1-methylcyclobutyl mesylate in 75% aqueous diglyme at 20° the first order rate constants were calculated from the plots log (a — x)/a *vs* time. The first compound showed an upward drift of the rate constant because of a concurrent internal rearrangement to the more reactive 1-methylcyclobutyl mesylate. Therefore the initial rate was determined from the slope of the titration curve and the ionization rate constant ($k = k_{\text{initial}} + k_{\text{rearrangement}}$) calculated according to the method of Young *et al.*[15] The observation of an internal rearrangement is in accord with the mechanism shown in Scheme 1 postulating a common intermediate for the solvolysis of both

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[15] W. G. Young, S. Winstein and H. L. Goering, *J. Amer. Chem. Soc.* 73, 1958 (1951).

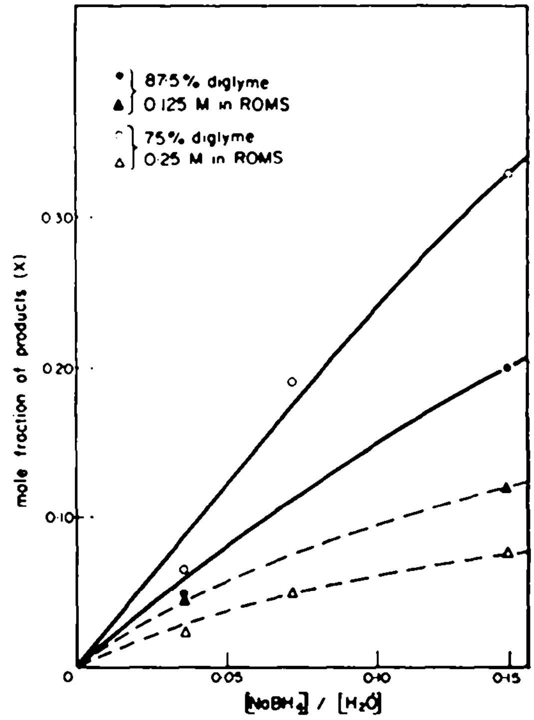


FIG. 1. Yield of hydrocarbons. Full line: path A–D(S_N1). Dotted line: path B(S_N2)

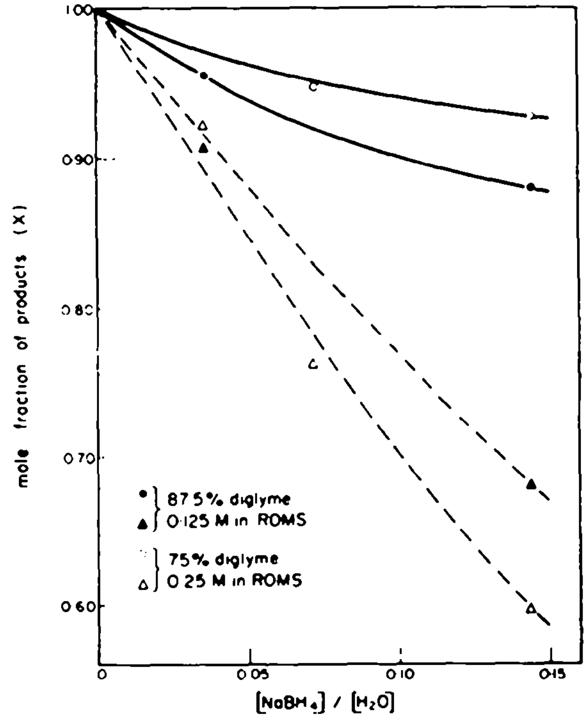
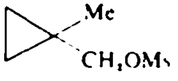
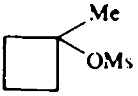


FIG. 2. Yield of products via path A(S_N1). Full line: hydrocarbons + 1-methylcyclobutanol. Dotted line: 1-methylcyclobutanol

TABLE 3

Mesylate	$k_{\text{initial}} \cdot 10^3\ \text{sec}^{-1}$	$k \cdot 10^3\ \text{sec}^{-1}$	$k_r \cdot 10^3\ \text{sec}^{-1}$
	1.013 ± 0.008	1.464 ± 0.009	0.451 ± 0.003
		2.896 ± 0.017	

mesylates I and II. 1-Methylcyclobutyl mesylate solvolysed under same conditions with a clean first order kinetic. The results are given in Table 3.

Competition factor. The competition factor k_4/k_3 for the reaction of BH_4^- and H_2O with the intermediate ion III can be calculated:

$$\frac{k_4}{k_3} = \frac{X_D}{X_C}\frac{(H_2O)}{(BH_4^-)}$$

Taking the experimentally determined initial and final values for (BH_4^-) (2·00M and 1·35M resp., in the reaction of mesylate I in 75% diglyme at 20°) it was found that the rate of attack of BH_4^- is 5·5 to 8·1 times higher than the rate of reaction of the cationic intermediate with water.

DISCUSSION

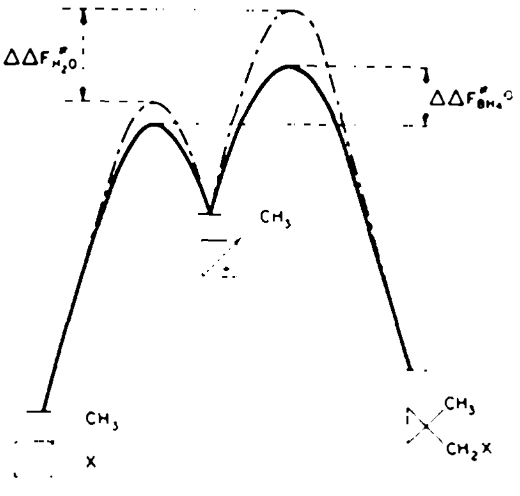
The results presented in this paper can be summarized as follows:

(1) The only detectable hydrolysis product of either 1-methylcyclobutyl mesylate or (1-methylcyclopropyl)carbinyl mesylate was 1-methylcyclobutanol.

(2) The solvolysis of 1-methylcyclobutyl mesylate in the presence of $NaBH_4$ results in the formation of small but measurable amounts of *gem*-dimethylcyclopropane.

(3) The solvolysis of (1-methylcyclopropyl)carbinyl mesylate in the presence of $NaBH_4$ results in the formation of considerable amounts of *gem*-dimethylcyclopropane.

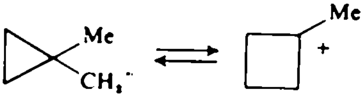
Scheme 2



The results obtained when the amounts of the respective reactants were varied are consistent with the different mechanistic pathways as presented in Scheme 1.

In terms of bicyclobutonium ion-like intermediates, all these observations can be rationalized as follows (Scheme 2). Due to unequal charge distribution at carbon atoms 1 and 2 of the non-classical ion III the $\Delta\Delta F^{\neq}_{H_2O}$ for the reaction with water is sufficiently large to allow the observation of only one product, i.e. 1-methylcyclobutanol. Addition of borohydride as a stronger nucleophile reduces the difference between the two energy barriers to an estimated value of 2·4 kcal/mole [$\Delta\Delta F^{\neq}_{BH_4} = 2{\cdot}3\ RT \log (98{\cdot}3/1{\cdot}7)$] leading to the formation of two hydrocarbons IV and V by the attack of BH_4^- on either position 2 or 1.

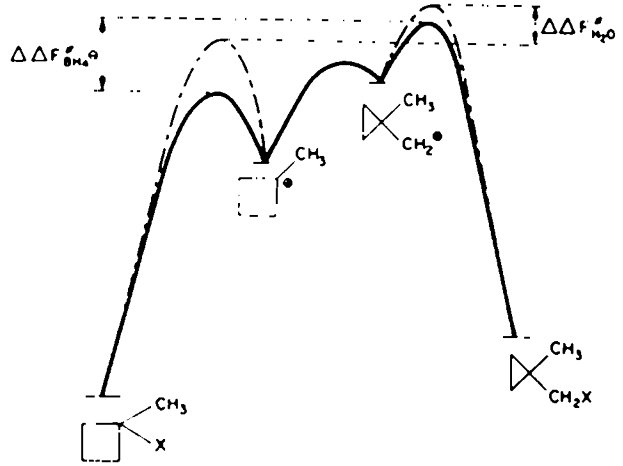
As an alternative hypothesis the formation in the rate determining step of a rapidly equilibrating pair of classical ions has been proposed. One could argue that the



borohydride, being a stronger nucleophile might trap the first formed classical ion before complete equilibration is reached.[16] If this were the case, the hydrolysis of 1-methylcyclobutyl mesylate in the presence of added $NaBH_4$ should yield a smaller amount of the rearranged material than in the absence of this nucleophile. The exclusive formation of 1-methylcyclobutanol in the latter case and the formation of *gem*-dimethylcyclopropane in the former contradict such predictions.

Since the results of this work indicate that $NaBH_4$ reacts only a few times faster with the intermediate ion (ions) than water, it is very dubious that in our case $NaBH_4$ is an effective agent for trapping the first formed intermediate in a presumably equilibrating mixture of classical ions. This is not surprising since these carbonium ions are highly reactive species and therefore do not display a pronounced degree of discrimination between different nucleophiles.

Scheme 3



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[16] H. C. Brown, Private communication

The inadequacy of "The equilibrating ions hypothesis" can be easily understood from Scheme 3 which is made on the following assumptions:

(1) The more stable a carbonium ion, the less reactive it will be towards nucleophiles.

(2) The decrease in stability of a carbonium ion is paralleled by a decrease of its selectivity between reagents of different nucleophilicity.[17]

(3) In the particular equilibrating mixture, the tertiary carbonium ion is more stable than the primary.

As illustrated in Scheme 3, these assumptions again lead to the wrong prediction, namely that in the solvolysis of 1-methylcyclobutyl mesylate the equilibrating pair of classical ions should yield *less* of the cyclopropylcarbinyl product with borohydride than with water. Clearly, either some of the aforementioned assumptions[17] are incorrect, or the proposed mechanism is not valid. The first two assumptions can hardly be challenged being generally accepted principles in organic chemistry.[17,18] One might argue that the third assumption is incorrect and should be reversed. This would make (1-methylcyclopropyl)carbinyl cation for at least 2·4 kcal/mole more stable than 1-methylcyclobutyl cation. Since tertiary carbonium ions are usually about 11 kcal more stable than the primary ones and cyclobutane is about 2 kcal less strained than cyclopropane, (1-methylcyclopropyl)carbinyl cation should be stabilized relative to other primary carbonium ions by some 16 kcal/mole. It would certainly be of interest to find a reasonable theoretical explanation for this conclusion.[19]

Finally, the method outlined in this paper could in principle be used for distinguishing between a non-classical ion and an equilibrating mixture of classical ions. When, in classical formulation, the discrete carbonium ions *are of different energy*, a competition experiment between two nucleophiles might provide an answer as to the nature of the solvolysis intermediate.

Note Added in Proof—This prediction has recently been confirmed. L. S. Spurlock and P. E. Newallis [*Tetrahedron Letters* 303 (1966)] report on products obtained in thermal isomerization by cyclopropylcarbinyl-SCN (apparently an ionization process). In addition to cyclopropylcarbinyl-NCS (75% of the products mixture) the following rearranged products were obtained: cyclobutyl-NCS (5%), homoallyl-NCS (2%), cyclobutyl-SCN (12%) and homoallyl-SCN (6%). All products were stable under reaction conditions.

During the isomerization of the thiocyanate an ion pair is formed in which the anionic part is "ambident", i.e. it can attack back the carbonium ion (ions) by either

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[17] C. G. Swain, C. B. Scott and R. H. Lohmann, *J. Amer. Chem. Soc.* 75, 136 (1953); see also Streitwieser *Solv Displacement Reactions* p. 55. McGraw-Hill, New York (1962).

[18] For an excellent discussion of the principles involved see L. M. Stock and H. C. Brown, "*A Quantitative Treatment of Directive Effects in Aromatic Substitution*", Advances of Physical Organic Chemistry (Edited by V. Gold) Academic Press, London and New York (1963).

An interesting example of an analogous rationalization of experimental results by means of the above "selectivity principles" is given on page 48. In Friedel-Crafts alkylation of toluene the more reactive (approximating) i-propyl cation is less selective than the more stable t-butyl cation. The former yields 28·5% of m-i-propyltoluene while the latter gives only 7% of m-t-butyltoluene.

[19] It should be pointed out that, considering Scheme 2, the fact that $NaBH_4$ reacts with the intermediate ion only about 3 times as fast as water is consistent with a lowering of the $\Delta\Delta F^{\neq}$ for the two reaction paths of that ion from at least some 3·5 kcal/mole with water to 2·4 kcal/mole with the borohydride ion. The same cannot be said for a mechanism based upon Scheme 3.

the sulfur or the nitrogen side. The reactivity ratio k_S/k_N in carbonium ion reactions has been found to be between 2 and 9. In fact, thermal isomerization of thiocyanates represents a competition experiment between two nucleophiles discussed above.

If the heating of cyclopropylcarbinyl-SCN produces an intermediate "bicyclobutonium" ion then energy profiles analogous to those in Scheme 2 are valid. There are three possible reaction paths of increasing $\Delta F^{\neq}$ yielding cyclopropylcarbinyl, cyclobutyl and homoallyl isothiocyanates respectively. Alternatively, the carbonium ion can react with the more nucleophilic side of the anion yielding thiocyanates. A mechanism based on these assumptions predicts *more* rearranged products and a *higher* ratio of homoallyl to cyclobutyl products in the reaction with the more nucleophilic sulfur-side of the anion. This prediction is clearly confirmed by experimental results. An alternative mechanism postulating a rapidly equilibrating mixture of classical cyclopropylcarbinyl, cyclobutyl and homoallyl cations as intermediates would require a Scheme of energy profiles analogous to Scheme 3. Assuming a decreasing stability of the carbonium ions in the order cyclopropylcarbinyl, cyclobutyl and homoallyl, such a mechanism predicts *less* rearrangement and a *lower* ratio of homoallyl to cyclobutyl products in the thiocyanate forming reactions than in isocyanate forming reactions, which is contrary to observation.

EXPERIMENTAL

IR spectra: Perkin–Elmer 221 Spectrophotometer with grating optics for the region 4000–1409 cm^{-1} and NaCl prism for the range 1409–650 cm^{-1}. VPC analyses: Perkin–Elmer 154-D Vapor Fractometer using He or N as the carrier gas. The instrument was calibrated with pure samples of known composition. $NaBH_4$ was commercial material obtained from Fluka AG. Diglyme was purified according ot the published procedure.[20] All other reagents were analytical grade. NMR spectra were recorded at 60 Mc with a Varian A-60 Spectrometer.

1,1-*Dimethylcyclopropane*. The hydrocarbon was prepared from 1,3-dibromo-2,2-dimethylpropane following the procedure of Shortridge *et al.*[21] The material was purified by distillation on the vacuum line and contained about 3% of impurities (VPC). The IR spectrum (Fig. 3) was identical with that published[22] and has characteristic bands at 3086, 1436 (very sharp), 1015, 934 and 845 cm^{-1}.

Methylcyclobutane.[23] Methylenecyclobutane was catalytically hydrogenated without solvent at 0–5° over Adams catalyst. The product contained about 8% of impurities (VPC). The IR spectrum showed characteristic absorption bands at 2984, 2970, 2960 and 2880 cm^{-1} (Fig. 4). B.p. 35–36°/753 mm.

(1-*Methylcyclopropyl*)*carbinol*. The carbinol obtained by LAH reduction of methyl (1-methylcyclopropane) carboxylate[24] contained a small amount of ester as the only impurity (VPC).

The methanesulfonate was prepared in 68% yield by reacting the carbinol in CH_2Cl_2 in the presence of pyridine with the theoretical amount of methanesulfonyl chloride.[24] Viscous oil, $n_D^{20} = 1{\cdot}4481$ The NMR spectrum of the mesylate showed the presence of 2·4–4·5% of unesterified carbinol, and less than 0·8% of 1-methylcyclobutyl mesylate.

1-*Methylcyclobutanol*. (1-Methylcyclopropyl)carbinol was isomerized by heating with HCl according to the isomerization of cyclopropylcarbinol.[25] No detectable amounts (i.e. not more than 0·2%) of the starting carbinol could be detected by NMR and VPC in the purified product (b.p. 118–120°/760, $n_D^{20} = 1{\cdot}4341$); yield 55%.

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[20] H. C. Brown, E. J. Mead and B. C. Subba Rao, *J. Amer. Chem. Soc.* 77, 6209 (1955).

[21] R. W. Shortridge, R. A. Craig, K. W. Greenlee, J. M. Derfer and C. E. Boord, *J. Amer. Chem. Soc.* 70, 946 (1948).

[22a] J. M. Derfer, E. E. Pickett and C. E. Boord, *J. Amer. Chem. Soc.* 71, 2482 (1949); [b] F. F. Cleveland, M. J. Murray and W. S. Gallaway, *J. Chem. Phys.* 15, 744 (1947).

[23] D. E. Applequist and J. D. Roberts, *J. Amer. Chem. Soc.* 78, 4020 (1956).

[24] S. Siegel and C. G. Bergstrom, *J. Amer. Chem. Soc.* 72, 3815 (1950).

[25] M. C. Caserio, W. H. Graham and J. D. Roberts, *Tetrahedron* 11, 171 (1960).

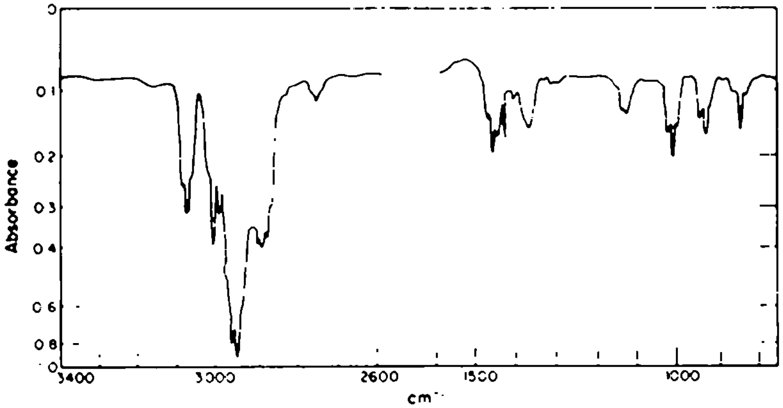

Fig. 3. IR spectrum of *gem*-dimethylcyclopropane (l = 10 cm, p = 25 mm)

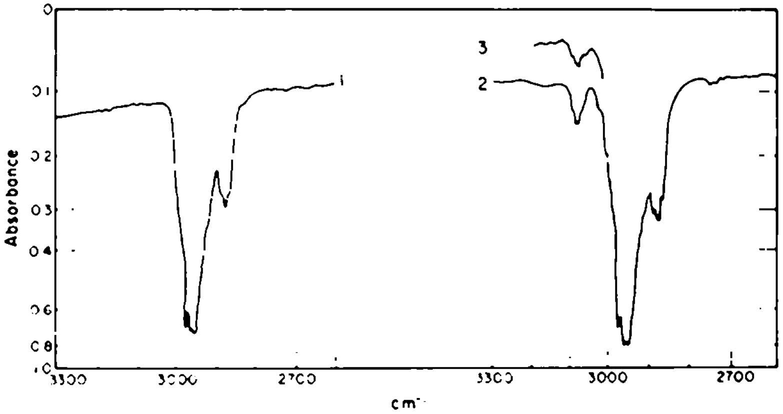

Fig. 4. IR spectra of I pure methylcyclobutane and in mixture with II 20% and 1·7% *gem*-dimethylcyclopropane. Spectrum III recorded at 242 mm press

The *methanesulfonate* was prepared in the manner described above in 54% yield. Yellowish oil $n_{\mathrm{D}}^{[illegible]}$ = 1·4575. From the infinity titer, NMR and IR spectra the product contained less than 0·25% of solvolyzable impurities in addition to some pyridine.

Product studies

(A) *Hydrolysis.* Either II or III (1·55 g., 9·42 mmoles) was added to a vigorously stirred suspension of $CaCO_3$ (0·52 g, 5·2 mmoles, 10% excess) in water (38 ml) at 20°. The stirring was continued for 2½ hr, the reaction mixture filtered and the ppt washed with pentane. The aqueous soln was continuously extracted with pentane for 12 hr, the combined extracts dried over $MgSO_4$ and the solvent removed by distillation through a 50 cm glass column. The residual oil was analyzed by VPC using a 2 m (UCON LB-550-X) column operated at 110° and with He as carrier gass at 4 psi. inlet press. The retention times of (1-methylcyclopropyl) carbinol and 1-methylcyclobutanol were 12·5 and 8·7 min respectively.

(B) *Reaction with sodium borohydride.* A sample of the corresponding mesylate (1·32 g, 8·0 mmoles) was added to a stirred soln of $NaBH_4$ (2·42 g, 64 mmoles) in 75% aqueous diglyme (32 ml) over a period of 1 min. The reaction mixture was kept at 20° and stirred for 1½ hr. The temp was then gradually raised to 45° and kept at 45° for 1½ hr. The volatile products were flushed with N and collected in two small traps cooled with liquid air, purified by distillation on the vacuum line and the yield determined by weighing. The hydrocarbon analysed by VPC with N as carrier gas at 4·95 psi inlet press and C-column (DC 200 silicone oil) operated at 40°. The retention times for 1,1-dimethylcyclopropane and methylcyclobutane were 7·5 and 11·6 min, respectively. With N at 2·6 psi and

R-column (40°) the respective retention times were 4·3 and 6·4 min. The IR spectra of the hydrocarbon mixture were recorded in the gas phase. 1,1-Dimethylcyclopropane obtained in admixture with methylcyclobutane from 1-methylcylcobutyl mesylate could be easily detected by the characteristic bands at 3086 and 1015 cm^{-1} when the gas press in the cell was increased to 242 mm Hg. (Fig. 4).

To the residual reaction mixture enough solid NaOH was added to affect the separation of diglyme, which was dried over $MgSO_4$ and separately distilled through a 50 cm column having a total condensation partial-take-off adapter. The fraction collected below the b.p. of diglyme contained the respective carbinols and about 10% diglyme. It was freed from diglyme by preparative gas chromatography. The recovery was usually better than 75%. VPC analyses were performed under same conditions as described for the hydrolysis products.

Rate studies

The procedure used for the kinetic runs was the one described previously.[44] For one measurement approximately 36 mg of the mesylate was solvolyzed in 12 ml 75% aqueous diglyme at 20·0°, and the rate followed with an automatic recording titrator (Radiometer, Copenhagen, TTT1). The rate constants were determined as described under Results.

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