COMPETITIVE REACTIONS OF NUCLEOPHILES SOLVOLYSES OF CYCLOPROPYLCARBINYL AND CYCLOBUTYL METHANESULFONATES IN THE PRESENCE OF NaBH.

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Abstract—Cyclopropylcarbinyl (I) and cyclobutyl (II) mesylates were solvolysed in aqueous diglyme with or without added NaBH₄ under a variety of conditions. The reaction products were isolated and analyzed by VPC. A mixture containing cyclopropylcarbinyl, cyclobutyl and minor quantities of homoallyl products, was obtained in all cases. The proportion of the unsaturated compound was greater in hydrocarbon than in carbinol products, the composition of the mixture depending upon reaction conditions and the starting mesylate. Thus, solvolysis of both I and II yielded cyclopropylcarbinol and cyclobutanol in a ratio of nearly 1:1, while in the hydrocarbon products methylcyclopropane predominated over cyclobutane by a factor of 3 in the reactions of I and by a factor of 2 in the reactions of II. It was shown that a direct displacement reaction of the BH_4^- ion on the primary mesylate I is not competitive with the solvolysis and cannot therefore be responsible for the above results. It was found that a better yield in hydrocarbons was obtained with I and II than with (1-methylcyclopropyl)carbinyl (III) and 1-methylcyclobutyl (IV) mesylates. The unexpected fact that the BH₄⁻ ion competes more efficiently with water for intermediates formed in solvolyses of I and II than for those of III and IV was confirmed by determination of competition factors of N_3^- ion vs water. In all cases, intermediates formed from I and II showed more discrimination in their reactions with reagents differing in nucleophylicity than did those formed from III and IV.

The results indicate that the attack of the nucleophile occurs mostly on the ion pair formed in the rate determining step. The latter reaction is apparently subject to reactivity relationships typical for a direct displacement reaction and not characteristic for free carbonium ions. These facts should be borne in mind when conclusions concerning the structure of carbonium ions are drawn from the composition and structure of solvolysis products.

It is concluded that the ion pairs trapped by $NaBH_4$ have different structures, depending upon the starting isomeric mesylate. It is shown that the formation of an equilibrating mixture of classical ions or ion pairs as intermediates in these reactions cannot account for experimental results.

SOLVOLYSIS in the presence of NaBH₄ has been used by several authors to investigate the structure and the nature of carbonium ion intermediates.¹⁻³ The underlying principle of such work is that the intermediate formed in the rate determining step will be "trapped" by BH₄⁻ ion before being diverted to usual solvolysis products.

In a previous paper² we described a detailed examination of the reaction of (1-methylcyclopropyl) carbinyl (III) and 1-methyl-cycloputyl (IV) mesylates with NaBH₄ under solvolytic conditions.

It was observed, inter alia, that the solvolysis of III and IV with added NaBH₄ gives rise to some gem-dimethylcyclopropane together with methylcyclobutane while the only carbinol product detected was 1-methylcyclobutanol. This observation was interpreted as being due to unequal charge distribution on different C atoms in the supposedly nonclassical intermediate and to the smaller selectivity of the stronger nucleophile BH₄⁻, as compared to water, between possible reaction sites. It was



pointed out that equilibrating classical ions cannot account for the results and that the "classical" hypothesis leads to wrong predictions with respect to the product distribution.

In this paper we wish to report the results of a similar study on the parent, unsubstituted cyclopropylcarbinyl-cyclobutyl system. From the available data,⁴ the sulfonate esters I and II should yield upon solvolysis a mixture of products consisting of cyclobutyl, cyclopropylcarbinyl and minor amounts of homoallyl derivatives. According to principles described² some predictions about the outcome of this work could be made (see Discussion). Thus, if the intermediate in the solvolysis is a nonclassical structure from which all products arise, then *more* of the minor olefinic product should be formed in the reaction with the stronger nucleophile BH_4^- ion than with water. However, if the intermediate consists of rapidly equilibrating classical ions, then the reverse result can be predicted.

RESULTS

Kinetic measurements. The rate of formation of methanesulfonic acid in solvolysis of mesylates I and II in aqueous diglyme was determined by automatic titration using a pH-stat. The calculated rate constants are given in Table 1.

Starting ^e Material	Exp. No.	% aq. Diglyme	t°C	$k \cdot 10^4 \sec^{-1b}$
N	1	60	20.0	26.08 ± 0.11
	2°	60	20 ·0	49·60 ± 0·13
	3	80	20-0	1.13 ± 0.02
	4	60	4 0·0	250
	5	66·67	40-0	108
	64	66·67	40 •0	196
OMs	7	60	40-0	2·73 ± 0·01

TABLE 1. RATES OF LIBERATION OF METHANESULFONIC ACID IN SOLVOLYSIS OF CYCLOPROPYLCARBINYL AND CYCLOBUTYL MESYLATES IN AQUEOUS DIGLYMF

" The concentration of mesylates was approximately 0.01 molar.

^b Average rate constants from 3-4 values calculated each from 10-20 points between 5-80% reaction completion. Uncertainties are standard errors.

' With 1 mole/l LiCl.

"With 0.5 mole/l NaN₃.

The phenomenon of internal rearrangement was observed in solvolysis of mesylate I⁵. Thus, in Exp. No. 4, after the first reaction a subsequent, much slower, acid forming reaction was observed. The rate of this slow solvolysis $(2.6 \cdot 10^{-4} \text{ sec}^{-1})$ was found to be practically the same as the solvolysis rate of the mesylate II. The two "infinity titers" for the fast and the slow reaction were estimated and it was calculated that 89.6% of the initial mesylate I undergoes solvolysis directly to products and methane-sulfonic acid, while 10.4% rearranges to mesylate II which is about 100 times less reactive. Therefore, the titrimetric rate constants given in Table 1, Exp. Nos 1–6, represent the sum of solvolysis rate constants and internal rearrangements rate constants. (k solvolysis of I in Experiment 4 was calculated to be $224 \cdot 10^{-4} \text{ sec}^{-1}$). The large difference in reactivity between mesylates I and II can be used, by stopping the reaction after an appropriate time interval, to study the solvolytic behavior of I without interference by II.

Solvolyses in aqueous diglyme. Both mesylates I and II were solvolysed under stirring in 60% aqueous diglyme at 40.0° in the presence of a small excess of finely ground CaCO₃. After about 7 solvolysis halflives the products were salted out by addition of K_2CO_3 , freed from most of the solvent by distillation and then analysed quantitatively by VPC. The presence of three isomeric carbinols was detected : cyclopropylcarbinol, cyclobutanol and allylcarbinol. These compounds were identified by comparison of their VPC retention times with those of authentic samples. Their presence in solvolysis products could be detected also by NMR spectroscopy. No other products were found. The results of these experiments are summarized in Table 2. It appears from Table 2 that the composition of the mixture produced depends on the starting mesylate. The differences observed are small but are reproducible and are believed to be real. It could be shown by NMR that neither mesylate contained more than 0.5% of unesterified parent carbinol. A rearrangement subsequent to the formation of solvolysis products seems improbable because of the presence of

Table 2. Solvolysis products of cyclopropylcarbinyl and cyclobutyl mesylates in 60 % aqubous diglyme at 40.0°

				Products [*]	
Mesylate*	Exp. No.	LiCl mole/l) −сн₂он	OH	СН₂ОН
	1	0	53·5 ± 0·3	43·7 ± 0·3	2·7 ± 0·1
	2	1	54·1 ± 0·2	43·2 ± 0·2	2·7 ± 0·1
	3	0	47·7 ± 0·1	49·3 ± 0·2	2·9 ± 0·3

Initial concentrations 0.25 mole/l.

^b Average values of 2-3 independent experiments with 3-4 VPC analyses of each products mixture. Uncertainties are standard errors.

CaCO₃ which neutralizes the acid formed in the reaction. The salting out of carbinols into the diglyme layer by means of K_2CO_3 is practically quantitative and a subsequent fractionation of carbinols during distillation seems likewise improbable because of the high b.p. of the last fraction (diglyme b.p. 160°) as compared to b.ps of the carbinols (113°, 121° and 123°).

The observed difference (5%) in the relative amount of cyclopropylcarbinol in the products mixture from solvolysis of I and II could be due to a competitive displacement of water on the primary mesylate I. This possibly seems unlikely because of the results of Exp. No. 2 (Table 2) and Exp. No. 2 (Table 1). While the addition of 1 mole/1 LiCl accelerates the solvolysis rate of I by a factor of 1.9 the direct displacement reaction rate of water on I should be unaffected by the presence of this salt. This should result in a lower relative amount of cyclopropylcarbinol in the products mixture of Exp. 2 (Table 2) as compared to products mixture from Exp. No. 1 (Table 2). In fact, no significant difference between the two mixtures was observed.

Solvolyses in aqueous diglyme in the presence of NaBH₄. Both mesylates I and II were solvolyzed at 40-0° in aqueous diglyme in the presence of NaBH₄. The following parameters were varied: water content of the solvent, initial concentrations of the mesylate and of NaBH₄, and reaction time. Volatile hydrocarbon products were flushed with gaseous N₂ into a trap cooled with liquid air. After distillation on a vacuum line, the products were weighed and analysed by VPC.

In all experiments it was possible to detect the presence of three hydrocarbons which were identified by comparison of their retention times with those of authentic TABLE 3. SOLVOLYSIS PRODUCTS OF CYCLOPROPYLCARBINYL AND CYCLOBUTYL MESYLATES IN AQUEOUS DIGLYME IN PRESENCE OF ADDED NaBH4

		1%			Peartion		Proc	ducts	
Mesylate	Exp. No.	Aqueous diglyme	[ROMs] moi	[NaBH4] lc/l	time	% RH	∕сн, %	~	СН3 %
	-	જ	0-25	-		34·6 ± 0·6	70-5 ± 0-1	24·3 ± 0·1	5.18 ± 0.02
2	6	8	0-25	1	5	39-7 ± 0 - 9	70.4 ± 0.1	24·3 ± 0·1	5·24 ± 0·02
CH ² OMs	ę	99	0-25	1	210	41.7 ± 0.7	70.0 ± 0.2	24.4 ± 0.1	5-69 ± 0-06
7	4	99	0-25	2-25	0-25	45.4 ± 1.2	$70-9 \pm 0.2$	24-4 ± 0-1	4·75 ± 0·02
	Ś	8	0-25	2:25	10	60-8 ± 0-8	70.7 ± 0.1	244 ± 0-2	4-95 ± 0-01
	9	80	0-125	1	120	57-9 ± 1-6	74-9 ± 0-2	20-3 ± 0-1	4-83 ± 0-07
	7	8	0-25	1	R	19.9 ± 1.3	61.3 ± 0.1	32 ·1 ± 0·1	6-56 ± 0-01
	œ	8	0-25	1	210	$31 \cdot 1 \pm 0.3$	60.7 ± 0.1	32·2 ± 0·1	7.05 ± 0.05
sM0	6	8	0-25	2:25	Ś	9.6 ± 0.4	61.0 ± 0.1	33·2 ± 0·1	5-84 ± 0-05
	10	8	0-25	2:25	210	51-2 ± 1-4	59-8 ± 0-1	340±01	6·16 ± 0·05
]	II .	80	0-125	1	210	19.0 ± 1.9	61.0 ± 0.2	32·3 ± 0·1	6-67 ± 0-03

• Average values of 2-3 independent experiments with 3-4 VPC analyses of each products mixture. Uncertainties are standard errors.

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Competitive reactions of nucleophiles

samples, as methylcyclopropane, cyclobutane and 1-butene. Comparison of NMR and IR spectra with those of authentic samples confirmed the presence of these hydrocarbons in the mixtures produced. No elimination products could be detected. The results are summarized in Table 3.

In Exp. Nos. 2 and 8 (Table 3), after isolation of hydrocarbons, K_2CO_3 was added to the remaining reaction mixture and the carbinol products isolated as described previously. A VPC analysis of the products yielded results identical to those of Exp. Nos 1 and 3 (Table 2). Several features of the results obtained should be pointed out.

The composition of the mixtures produced is nearly independent of reaction time. This indicates that the hydrocarbon products are isolated quantitatively as they are formed.

The composition of the mixtures is dependent upon the starting mesylate. Thus, under similar reaction conditions (Exp. Nos 1, 2, 3, 7, 8), methylcyclopropane, cyclobutane and 1-butene are obtained from I in the ratio 13.5:4.7:1 and from II in the ratio 8.7:4.6:1. The possibility that these differences are due to a direct displacement of BH₄⁻ on the primary mesylate I can be excluded because a 2.25-fold increase in concentration of NaBH₄ did not result in any measurable increase in the relative amount of methylcyclopropane product in solvolysis of I (Exp. Nos 4 and 5).*

During solvolysis of cyclopropylcarbinyl mesylate the possibility of the formation of homoallyl mesylate through internal rearrangement⁵ should be taken into account. The latter compound could give 1-butene by direct displacement and thus increase the amount of this hydrocarbon in the products. However, the rate of displacement should be comparable to that on cyclopropylcarbinyl mesylate (both are primary esters), i.e. quite slow in comparison with the solvolysis rate. Therefore, the formation of 1-butene by direct displacement should be quite negligible especially in the beginning of the reaction. Small, but constant increase in the proportion of 1-butene in the "trapping" products of both mesylates when the reaction times were long (Exp. Nos 3, 8 and 10) could be due to internal rearrangement followed by direct displacement.

Competition factors. In hydrolysis of a sulfonate ester in the presence of added nucleophile water and the nucleophile can compete for the intermediate ion.⁶ If the concentrations of both water and added nucleophile are large compared to the initial concentration of the sulfonate then the following equation is valid:

$$\frac{k_{y}}{k_{0}} = \frac{[\text{RY}] [\text{H}_{2}\text{O}]}{[\text{ROH}] [\text{Y}^{-}]}$$

where k_y and k_0 represent rate constants for the attack of the intermediate ion by added nucleophile and by water respectively, and [RY] and [ROH] reaction products concentrations. The ratio k_y/k_0 is the competition factor of the intermediate for the nucleophile with respect to water.^{7,8} From the data in Table 3, knowing the yield in hydrocarbons [RY] the concentrations of NaBH₄[Y⁻] and of water it is possible to calculate the competition factors of intermediates in solvolysis of cyclopropylcarbinyl mesylate and of cyclobutyl mesylate for the BH₄⁻ ion.

^{*} Solvolysis of I is 23 times slower in 80% than in 60% aqueous diglyme (Table 4). If direct displacement were important, then a large excess of methylcyclopropane should be observed in Products of Exp. No. 6 (Table 3), which is not the case.

			Desetion		Products ⁴	
Mesylate	[ROMs] mole/l	[NaBH ₄] mole/l	time min	RH %	CH ₃ %	CH ₃ %
CH ₃ CH ₂ OMs	0-25	1	5	24·9 ± 0·1	15·5 ± 0·2	84·5 ± 0·2
CH ₃ OMs	0-25	1	5	21·5 ± 1·7	3·1 ± 0·1	96·8 ± 0·1

Table 4. Solvolysis products of (1-methylcyclopropyl)carbinyl and 1-methylcyclobutyl mesylates in 60% aqubous dislyme at 40.0° in presence of added NaBH₄

* Average values for 2-3 independent experiments and 3-4 VPC analyses of each mixture produced. Uncertainties are standard errors.

This work was initiated by the observation that a better yield in hydrocarbons was obtained in solvolysis with added NaBH₄ of I and II than in an analogous solvolysis of (1-methylcyclopropyl) carbinyl and 1-methylcyclobutyl mesylates. To confirm this observation, both latter mesylates were prepared and solvolysed in presence of NaBH₄⁻ under conditions identical with those used in the present work. The results are given in Table 4.

Competition factors were then calculated for all 4 mesylates and are given in Table 5. A difficulty arose when it was observed that the concentration of $NaBH_4$

b f = -1-4- f	[NaBH4] mole/l	$k_{\rm BH_4}^{-}/k_{\rm H_2O}^{b}$	
Mesylate	initial	final	lower	upper
	1 2·25	0·48 1·39	14·6 15·3	30-4 34-8
OMs	1 2∙25	0·18 0·64	10-0 10-3	56·7 36·4
	1	0-36	6-4	17.8
	1	0-48	6-1	12.7

Table 5. Competition factors of intermediates pormed in solvolysis of some mesylates in 60 % aqubous diglyme for BH_4^- with respect to water

" [ROMs] = 0.25 mole/l.

^b Calculated from the initial (lower) and final (upper) concentrations of BH₄⁻ according to Eq. 1. was not constant through the reaction but decreased significantly because of reaction with water caused by the liberated methanesulphonic acid. Therefore, initial and final concentrations of NaBH₄ were determined and two competition factors calculated for each mesylate, representing the lower and the upper limit of the true competition factor. The results seem to indicate that in fact, competition factors of the unsubstituted mesylates are higher than those of either methyl-substituted analogues. It appeared necessary to confirm these results in a more clearcut manner. Therefore all four mesylates were solvolysed in a 0.5 molar solution of NaN₃ in 66.67% aqueous diglyme.

Table 6. Competition factors of intermediates pormed in solvolysis of some mesulates in 66.67% aqueous diglyme for N_3^- with respect to water

Mesylate	$k_{N_3}^{-}/k_{H_3O}^{b,c}$
	31-4 ± 1-0
OMs	28·2 ± 0·4
	12.3 ± 0.5
CH ₃ OM ₈	150 ± 10

" [ROMs] = 0.01 - 0.02 mole/1.

 $[NaN_3] = 0.5 \text{ mole/l.}$

^b Calculated according to Eq. 1. Uncertainties are standard errors.

^c A direct displacement process contribution to the competition factors is negligible. Solvolysis of I in a 0.5 molar solution of NaN₃ in aqueous diglyme is only 1.9 times faster than in absence of salt (Table 1, Exp. Nos. 5 and 6).

After approximately 7 solvolysis halflives, the acid formed was titrated. The yield in carbinol ROH and of azides RY produced could then be calculated from the titer and the initial amount of the mesylate. From these data and according to Eq 1 competition factors for N_3^- were calculated in all four cases and are given in Table 6. The results fully confirm those obtained with BH_4^- as a nucleophile.

DISCUSSION

Competition factors. A principle in carbonium ion chemistry which seems to be widely accepted can be stated as follows: The less stable a carbonium ion is, the more reactive it is and the less selective it is between reagents differing in nucleophilicity.^{8,9}

In this respect only a perfunctory examination of Tables 5 and 6 reveals the surprising results that the intermediate produced in the solvolysis of *secondary* cyclobutyl mesylate displays a selectivity between water and azide ion (or BH_4^-) which is about *twice* as large as the selectivity shown by the intermediate produced in solvolysis of *tertiary* 1-methylcyclobutyl mesylate!

The same pattern is observed with the corresponding cyclopropylcarbinyl derivatives. A more systematic investigation, the results of which will be published elsewhere, revealed that the behaviour of the cyclopropylcarbinyl-cyclobutyl system was not, in this respect exceptional.

There is now ample evidence in the literature that solvolysis products arise rather from the attack of the nucleophile on the ion pair than on the free carbonium ion.^{10, 11} The latter seems to be the case even in solvents of good solvating properties and with compounds which can give relatively stable carbonium ions. Thus Hill¹² found that the k_{N5}/k_{H20} competition factor of the intermediate in solvolysis of trityl halide depends upon the nature of the halide used. Clearly, if products were formed only from the free carbonium ion, no influence of the nature of the leaving group on the composition of the mixture produced could be observed. Brown and Bell³ found that the hydrocarbon yield in solvolysis of benzhydryl halides in aqueous diglyme with added NaBH₄ depends upon the nature of the leaving group. This dependence is even more pronounced with phenylethyl halides.

If it is assumed that nucleophiles attack ion pairs rather than free carbonium ions then the results of our work are put into proper perspective.

There are two factors which should have a major importance in determining the selectivity of ion pairs between nucleophiles. The first one, already discussed, is the stability of the cation part of the ion pair. However, the reaction of an ion pair with a nucleophile resembles a direct displacement reaction and should be subject in some measure to reactivity relationships observed in S_N2 reactions. From this standpoint, "secondary" ion pairs should display a larger degree of discrimination between reagents of differing in nucleophilicity than intermediates derived from tertiary systems. Apparently, this latter factor is in cases examined, more important than the former which results in higher competition factors in reactions of unsubstituted mesylates I and II as compared to their methyl-substituted analogues III and IV. Sneen et al. have investigated solvolyses of 2-octyl sulfonates and have found that they proceed by way of undissociated ion pairs from which products are formed through complete inversion of configuration.¹¹ Depending upon reaction conditions. they found that either the formation or the destruction of such an ion pair could be rate determining. The rate of the solvolysis of 2-octyl mesylate in 25% aqueous dioxan is determined by the formation of the ion pair. Nevertheless, the $k_{NT}/k_{H_{2}O}$ competition factor was found to be exceptionally high. It was proposed that a high competition factor could be used as a diagnostic for reaction at an ion pair stage.¹³ Our conclusions are based upon this criterion.

The question which remains to be answered is whether the formation or the destruction of the ion pairs is in our case rate determining. An examination of the data points to the former interpretation. Thus, both mesylates I and II yield similar mixtures of products upon solvolysis. Therefore, the ion pairs from which the products arise must have similar structures. If the formation of these ion pairs were not rate determining there would be no explanation for the 100-fold difference in solvolytic reactivity between the mesylates I and II. Moreover, the addition of NaN_3 accelerates the solvolysis of I by a small factor as expected from salt effects (Table 1, Exp. Nos 5, 6).

Mixtures of products—mesylates I and II. In our previous work² we have concluded, on grounds of selectivity principles,⁹ and products distribution, that the intermediate(s) in solvolysis of III and IV cannot be formulated as an equilibrating mixture of classical carbonium ions and that they must possess nonclassical structures. An analogous analysis can be performed on results of the present investigation.

In solvolysis in aqueous diglyme of both I and II, allylcarbinol is formed in about 3% yield together with the major products cyclopropylcarbinol and cyclobutanol (Table 2). In terms of a nonclassical ion intermediate (e.g. a bicyclobutonium ion*) these results mean that the nucleophile can attack the carbonium ion at three different sites and that the attack on the C atom giving rise to homoallylic products represents the reaction path of relatively highest activation energy (Scheme 1). Addition of a strong nucleophile, such as BH_4^- should reduce the highest energy barrier more than the other two.



This mechanism predicts that a larger amount of 1-butene will be found in the hydrocarbon products than of allylcarbinol in the carbinol products. If the intermediate is to be formulated as a mixture of rapidly equilibrating classical ions, then a reverse prediction concerning the change in the mixture produced with an increase in the nucleophilicity of the reagent should be made. Namely, if it is assumed that cyclopropylcarbinyl and cyclobutyl ions are more stable than allylcarbinyl ion, then the former should be also more selective and display a more distinct preference for BH_4^- than the latter.

The experimental results, as seen from Tables 2 and 3, bear out the former prediction. The proportion of unsaturated products is about twice as great in the hydrocarbon mixture than in the carbinol mixture.

However, this approach based upon reactivity relationships prevailing with carbonium ions is oversimplified. In hydrolysis of either cyclopropylcarbinyl or cyclobutyl mesylate, cyclopropylcarbinol and cyclobutanol are formed in a ratio of nearly 1:1 (Table 2). According to previous arguments, this ratio should not be much affected

* A discussion of the exact structure of the nonclassical intermediate is beyond the scope of this work. A bicyclobutonium ion structure is assumed but the above arguments would be identical for any structure that can yield cyclopropylcarbinyl, cyclobutyl and allylcarbinyl products in a one step reaction. by a change in the nucleophilicity of the reagent. In fact a ratio of 2:1 of methylcyclopropane to cyclobutane is found in the reaction of II and of 3:1 in the reaction of I (Table 3).

It appears that ion pair phenomena must be responsible for such results. In the displacement reaction of BH_4^- on the ion pair, the reaction path yielding the "primary" product, methylcyclopropane, seems to be favoured over the one yielding the "secondary" product cyclobutane for the same reasons that make primary derivatives more prone to direct displacement reactions than secondary derivatives.

Thus, the larger competition factors observed with I and II relative to III and IV and the preponderance of "primary" methylcyclopropane in the hydrocarbon mixture produced seem to be due to the same cause: to reactivity relationships typical of direct displacement reactions shown by ion pair intermediates.

Finally, it should be pointed out that the intermediates (ion pairs) formed from I and II have *different* though similar structures. Even in hydrolysis, the composition of the mixture seems to depend upon the starting mesylate. This dependence is much more pronounced in the reaction with BH_4^- . Also, competition factors (Table 6) differ significantly. As far as we are aware, this is the first observation of this kind in the cyclopropylcarbinyl-cyclobutyl system.

Classical ions. Taking into account ion pair phenomena, can the results of this work be interpreted in terms of equilibrating classical ions?

The composition of the products, especially if BH_4^- is present, depends upon the starting mesylate. Hence, the composition of the mixture of equilibrating ion pairs must also depend upon the starting mesylate. This is possible only if the reaction with the nucleophile occurs before the complete thermodynamic equilibrium is obtained. In this respect, the higher proportion of rearranged homoallylic products in the reaction with BH_4^- than with water cannot be explained.

Mixtures of products-mesylates III and IV. In our previous work² it was observed that solvolyses of III and IV in the presence of NaBH₄ gave mixtures in which some gem-dimethylcyclopropane was present. The relative amount of the latter product was always more important in reactions of III than of IV (see Table 4). The results obtained when the relative amount of water in the solvent and the concentration of added NaBH₄ were varied seemed to indicate that the reaction of the primary mesylate III with NaBH₄ proceeded by two competitive mechanisms (S_N1 and S_N2). In the present work, the possibility of a direct displacement of BH_4^- on the primary mesylate I has been excluded. Therefore, it seems highly unlikely that the latter mechanism would be operative with III under identical reaction conditions as with I. In view of present findings, the only reasonable interpretation of our former results seems to be that the solvolysis of III and IV proceed by way of ion pairs which can yield the reaction products directly. These ion pairs are subject to reactivity relationships typical of direct displacement reactions. Also, taking into account differences in mixtures produced (Table 4) and competition factors (Tables 5 and 6) it can be concluded that the intermediates reacting with nucleophiles have similar but different structures, depending upon the starting mesylate III and IV.

CONCLUSION

We can now summarize the results of this work:

(1) The solvolysis of cyclopropylcarbinyl and cyclobutyl mesylates proceeds by way of charge delocalized, nonclassical intermediates.

(2) These intermediates are ion pairs and not free carbonium ions. The ion pair produced from I has a similar but different structure from the ion pair produced from II.

(3) The reaction of these ion pairs with nucleophiles is subject to reactivity relationships typical of direct displacement reactions. Therefore, the composition of the mixtures produced cannot be taken as indicative of the relative amount of charge on different C atoms in the intermediate.

(4) Solvolysis products of (1-methylcyclopropyl)carbinyl and 1-methylcyclobutyl mesylate also arise at least in part, from ion pairs with similar (and non-classical) but different structures.

Sneen¹³ has advised caution about the representation of reactions of *simple* secondary systems as proceeding through free carbonium ion intermediates. We can now extend this warning to some systems which undergo solvolysis through stabilized non-classical intermediates. Even in cases where formally tertiary carbonium ions can be formed (III and IV), ion pair phenomena reflect on the products formation step. Ion pairs do not behave like free carbonium ions in their reactions with nucleophiles. Therefore, any conclusions about the structure and the nature of carbonium ions which are based upon the composition of solvolysis products can be made only with utmost caution.

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; NMR spectra: Varian A-60A Spectrometer. VPC: Aerograph Autoprep A-700 with Disc Integrator 201-3. Carrier gas $H_2 \cdot NaBH_4$ was commercial material obtained from Fluka AG, Buchs, Switzerland, diglyme was purified according to the published procedure. All other reagents were analytical grade.

Methanesulfonates I and II were prepared according to the published procedure.² According to "infinity" titers and NMR spectra they were 90–97% pure. The impurities were pyridine and methylene chloride. The maximum possible amount of unesterified parent carbinol present in the ester was determined to be 0.2–0.5%. Methanesulfonates III and IV were analogous to those prepared earlier.²

Rate measurements were performed as described previously.² Approximately 15 mg (0.1 mmole) of the mesylate was solvolysed in 12 ml aqueous diglyme at constant temp and the rate of acid formation followed with an automatic recording titrator (Radiometer, Copenhagen, TTT 11).

Product studies

A. Hydrolysis. Either I or II (1.5 g, 10 mmoles) was added to a vigorously stirred suspension of CaCO₃ (0.55 g, 10% excess) in 60% aqueous diglyme at 40.0°. The stirring was continued for 3 min and 5 hr respectively (about 7 solvolysis halflives). After cooling to room temp K_2CO_3 was added, the diglyme layer separated and dried overnight with MgSO₄ and K_2SO_4 . The products were separated from most of the solvent by distillation through a 60 cm glass column up to the temp of 160°. VPC analysis of the produced mixture was performed using a combination of a nonpolar column (20 × 0.4 cm, 15% silicone oil SE-30 on Chromosorb P 45/60) followed by a polar column (60 × 0.4 cm, 15% glycerol on Chromosorb P 45/60) at 75° and gas flow of 150 ml/min.

B. Reaction with NaBH₄. To a stirred soln of NaBH₄ (1·22 g, 32 mmoles) in 60% aqueous diglyme (32 ml) at 40·0°, 1·2 g (8 mmoles) of the corresponding mesylate was added. Stirring was continued and the reaction products flushed continuously into a trap cooled with liquid air by means of N₂. The hydrocarbon products were distilled on a vacuum-line. After weighing, the distillate was analysed by VPC using a silicone column (20 ft $\times \frac{3}{8}$ in; 20% SE-30 on Chromosorb P 60/80) at 35° and a gas flow of 150

mi/min. The reactions of mesylates III and IV were performed analogously except that the reaction mixture was heated to 60° after solvolysis and flushed with N₂ at that temp for 1 hr.

Competition factors

Azide ion. About 45 mg (0.3 mmole) of the mesylate I or II was weighed to a precision of ± 0.1 mg and introduced together with the weighing container into 15 ml of a 0.5 molar soln of NaN₃ in 66.67% aqueous diglyme at 40.0°. After closing the reaction flask, stirring was started and continued for about 7 solvolysis halflives. After cooling, the liberated hydrazoic acid was titrated potentiometrically in 10.0 ml of the reaction soln. Another sample of the mesylate from the same batch was solvolyzed for 7 halflives in the same solvent without added NaN₃ and the amount of liberated methanesulfonic acid determined by titration.

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