[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE UNIVERSITY]

The Solvolysis of *p*-Nitrobenzoates of Certain Cyclopropylcarbinols[1,2]

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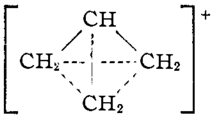
The *p*-nitrobenzoates of carbinols Ia–Va were prepared and solvolyzed in various concentrations of aqueous or methanolic dioxane at several temperatures. The relative first-order rates (Vb = 1) in 80% aqueous dioxane at 60° were: IVb, 60.7; IIIb, 246; Ib, 23,500; IIb, 124,000. Alkyl–oxygen fission was demonstrated, and a second cyclopropyl group on the carbonium carbon atom was nearly as effective as the first in enhancing the solvolysis rate. The solvolysis products were the original carbinols (or their methyl ethers); no elimination or rearrangement to cyclobutanols or allylcarbinols was observed. In several instances, "internal return" to a non-solvolyzing *p*-nitrobenzoate (shown to be the isomeric allylcarbinyl ester VII in the case of IIIb) occurred, the ratio of rearrangement to solvolysis increasing with decreasing ionizing power of the solvent. But rearrangement of IIIb → VII was not thermal, nor was the extent of rearrangement a direct function of the solvolysis rate. Rates, products and energetics can be interpreted in terms of an ion-pair mechanism which includes stabilizing the positive charge in the carbonium ion by ***each*** cyclopropyl group. Attempts to prepare tricyclopropylcarbinyl *p*-nitrobenzoate lead to 1,1-dicyclopropyl-4-chloro-1-butene (VIII) which, with aqueous potassium carbonate, was reconverted to tricyclopropylcarbinol.

Studies of physical properties, particularly spectra, place the cyclopropyl group between a vinyl and a saturated group with regard to ability to conjugate with adjacent unsaturation.[4] But the solvolysis of cyclopropylcarbinyl derivatives is exceptional,[5] proceeding at a greater rate than the corresponding allyl compounds

$$\triangleright\!-CH_2X > CH_2{=}CHCH_2X >> CH_3CH_2CH_2X$$

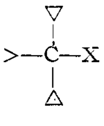
This acceleration is particularly striking in rigid systems, such as the i-steroids.[6] The positive charge which remains on carbon when X^- ionizes from the above systems is apparently better accommodated by the cyclopropyl than by the vinyl group. The rates cannot be explained by considering cyclopropyl as a less polarizable analog of the vinyl group (as has been done in interpretations of spectra). Special features have been ascribed to the carbonium ion intermediate which, in the extreme case of the reaction of cyclopropylcarbinylamine with nitrous acid,[7] is pictured with the three



methylene carbons equivalent. Often,[6,8–10] but not always,[10,11] rearrangement to allylcarbinyl or cyclobutyl derivatives occurs during solvolysis of cyclopropylcarbinyl compounds under ionizing conditions.

It was our purpose to examine some tertiary systems of this type (heretofore only primary and secondary systems had been studied) with regard both to rates and products. Compounds with more than one cyclopropyl group on the carbonium carbon atom were thought to be of particular interest for several reasons. If the driving force in these rapid solvolyses is release of strain in the three-membered ring, then one such ring should be sufficient to ensure rate enhancement, and one might predict no large effect from additional cyclopropyl substitution. Indeed, the electron-withdrawing inductive effect of the cyclopropyl group compared with other alkyl groups[1d] might decrease the rate of an S_N1[5] process. Alternatively, if resonance structures were possible which would allow distribution of the positive charge over several cyclopropane rings, a considerable rate increase might be observed, much as in the benzyl, benzhydryl, triphenylmethyl series. Certain similarities between phenyl and cyclopropyl groups[12] lend plausibility to this view.

To determine which of these alternatives prevailed, the *p*-nitrobenzoates of dicyclopropylisopropylcarbinol (Ia), di-(2-methylcyclopropyl)-isopropylcarbinol (IIa), diisopropylcyclopropylcarbinol (IIIa) and dicyclopropylcarbinol (IVa) were



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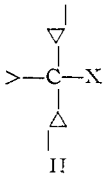

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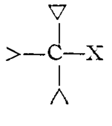

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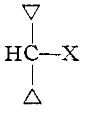

IV

a, X = OH; b, X = $-O\overset{O}{\overset{\|}{C}}C_6H_4$–*p*-$NO_2$; c, X = OCH_3

prepared, and the solvolysis rates and products in aqueous dioxane determined. The products were also determined in methanolic dioxane. For com-

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[1] Part V of a series on Cyclopropane Chemistry. For previous papers see (a) H. Hart and O. E. Curtis, Jr., THIS JOURNAL, **78**, 112 (1956); (b) H. Hart and J. M. Sandri, *Chemistry & Industry*, 1014 (1956); (c) H. Hart and O. E. Curtis, Jr., THIS JOURNAL, **79**, 931 (1957); (d) T. L. Brown, J. M. Sandri and H. Hart, *J. Phys. Chem.*, **61**, 698 (1957).

[2] Presented in part at a Symposium on the Chemistry of Three-membered Rings, American Chemical Society Meeting, Miami, Fla., April, 1957.

[3] From the Ph.D. thesis of Joseph Mario Sandri, Michigan State University, 1956; American Viscose Corporation Fellow, 1954–1955.

[4] For a review, see E. Vogel, *Fortschr. Chem. Forsch.*, **3**, 431 (1955). We refer especially to electron-donating ability, as in cyclopropyl ketones, esters, aromatics, etc.

[5] See A. Streitwieser, Jr., *Chem. Revs.*, **56**, 571 (1956), for a discussion and review.

[6] For a recent case, see E. M. Kosower and S. Winstein, THIS JOURNAL, **76**, 4347, 4354 (1956).

[7] J. D. Roberts and R. H. Mazur, *ibid.*, **73**, 3542 (1951).

[8] J. D. Roberts and R. H. Mazur, *ibid.*, **73**, 2509 (1951).

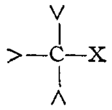
[9] J. D. Roberts and V. C. Chambers, *ibid.*, **73**, 5034 (1951).

[10] C. G. Bergstrom and S. Siegel, *ibid.*, **74**, 145 (1952).

[11] R. G. Pearson and S. H. Langer, *ibid.*, **75**, 1065 (1953).

[12] See ref. 8 with regard to solvolysis rates. But similarities do not appear to be restricted to ionic reactions. Hydrogen *atoms* are nearly as difficult to remove from cyclopropane as from benzene (A. F. Trotman-Dickenson and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 329 (1951); J. R. McNesby and A. S. Gordon, THIS JOURNAL, **79**, 825 (1957)). Other evidence with regard to peroxide decompositions reinforces this analogy (H. Hart and D. P. Wyman, unpublished results).

parison, triisopropylcarbinyl p-nitrobenzoate (Vb) also was studied.[13] Attempts to prepare the p-nitrobenzoate of tricyclopropylcarbinol[1b] (VI) were unsuccessful, but some of the chemistry of this alcohol is described.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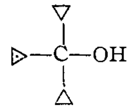

VI

Results

The Reaction Rates.—The solvolysis rates were determined in aqueous dioxane by titrating the liberated p-nitrobenzoic acid (PNBA). The rate constants and derived thermodynamic functions[14] are listed in Table I. In most instances, the ester was quantitatively solvolyzed to PNBA, but in certain cases less than the theoretical amount of acid was produced, due to a competing rearrangement discussed more fully below. The rate constants in Table I were calculated by two different methods for these two alternatives.

When solvolysis was complete, strict first-order kinetics were observed; plots of log $(V_f - V)$ *vs.* time (where V_f was the volume of standard sodium hydroxide required to neutralize the theoretical quantity of PNBA in a 5-ml. aliquot and V was the volume of the base required at time t) were linear, the reactions being followed nearly to completion. For those cases where no other rate constant is given in Table I, the values of k were determined from the slopes of these lines[15] (see Fig. 1).

Rearrangement was first detected during the solvolysis of diisopropylcyclopropylcarbinyl p-nitrobenzoate (IIIb) in 80% aqueous dioxane at 80°, when a plot of log $(V_f - V)$ *vs.* t started out nearly linear, but soon curved rather sharply and leveled off after 64.4% of the theoretical amount of PNBA had been produced (see Fig. 1). If the observed value for volume of base required to titrate the total PNBA *actually produced* in a 5-ml. aliquot was designated V_f', then a plot of log $(V_f' - V)$ *vs.* t was linear (Fig. 1). This implied that the original ester reacted by two paths, both kinetically first order, but only one of which produced PNBA. For these cases k, the over-all rate constant for reaction of ester, was calculated from the slopes of these lines. The fraction of original ester which rearranged to isomeric ester, $f_r = 1 - V_f'/V_f$, is also listed in Table I. That these kinetically determined values were valid was verified by product isolation.

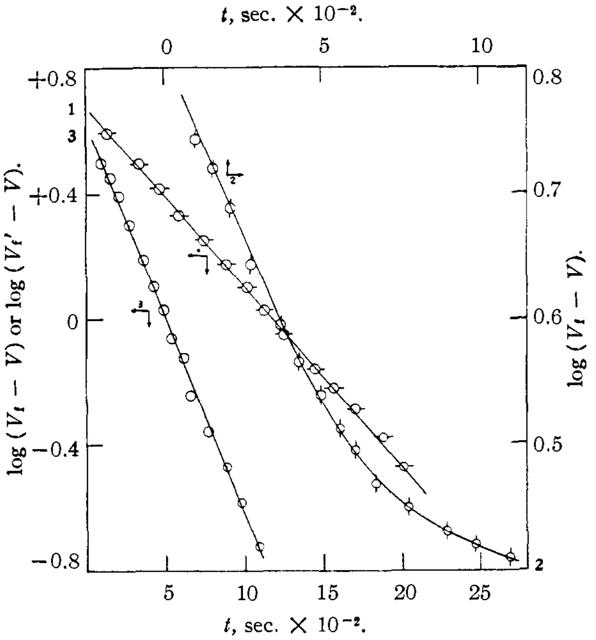
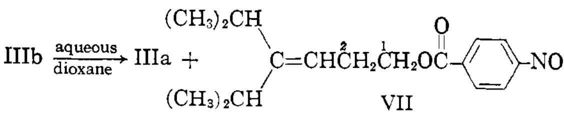


Fig. 1.—Plots of log $(V_f - V)$ or log $(V_f' - V)$ *vs.* t: curve 1, Ib in 80% aqueous dioxane at 25° (solvolysis was complete); curve 2, IIIb in 80% aqueous dioxane at 80°, plotted as log $(V_f - V)$ *vs.* t (35.6% rearrangement, 64.4% solvolysis); curve 3, the same data as curve 2, plotted as log $(V_f' - V)$ *vs.* t.

The Products.—The alcohol produced from each ester was unrearranged (*i.e.*, a cyclopropylcarbinol), as shown by identity of its infrared spectrum with that of authentic carbinol. This was true regardless of the extent of solvolysis (*vs.* rearrangement). For example, from Ib in 80% aqueous dioxane at 25° there was isolated a 95% yield of Ia; no evidence for olefin or isomeric alcohol was obtained. A high yield (81%) of the corresponding methyl ether Ic was isolated from methanolic dioxane under the same conditions; the infrared spectrum was indistinguishable from that of authentic ether prepared by reaction of methyl iodide with the corresponding potassium alcoholate.

$$\mathrm{Ib} \xrightarrow[\text{dioxane, 25°}]{\text{80\% methanolic}} \mathrm{Ic} \xleftarrow[\text{2, CH}_3\text{I}]{\text{1, K}} \mathrm{Ia}$$

The other product obtained when less than the theoretical amount of PNBA was formed was examined in detail with IIIb, and shown to be the isomeric ester, 4-isopropyl-5-methyl-3-hexenyl p-nitrobenzoate (VII). Its structure was proved by reduction with lithium borohydride to 4-isopropyl-5-methyl-3-hexenol (74%) and p-nitrobenzyl alcohol (81%). The unsaturated alcohol gave a good yield of diisopropyl ketone on permanganate oxidation. This fixed the position of the double bond, but the ester function might have been at C_1 or C_2. Rearrangements from cyclopropylcarbinyl to allylcarbinyl systems are well known; furthermore, if the ester function were at C_2 it would be allylic; VII did not produce any PNBA even after boiling for 26 hours in 70% aqueous dioxane;



$$\mathrm{IIIb} \xrightarrow[\text{dioxane}]{\text{aqueous}} \mathrm{IIIa} + ((\mathrm{CH_3})_2\mathrm{CH})_2\mathrm{C{=}CH\overset{2}{C}H_2\overset{1}{C}H_2OC({=}O)C_6H_4NO_2}\quad \text{VII}$$

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[13] *Cf.* P. D. Bartlett and M. Stiles, THIS JOURNAL, **77**, 2806 (1955).

[14] The heat of activation was determined from the usual linear Arrhenius plot, by subtracting RT from the energy of activation. The activation entropy was calculated from the Eyring equation $\Delta S^{\ddagger} = 2.303\,R \log (kh/k'T) + \Delta H^{\ddagger}/T$, where k is the rate constant, h is Planck's constant and k' is the Boltzmann constant.

[15] Since, in those instances where rearrangement was unimportant, the points fell beautifully on straight lines for the entire course of the reaction, it was felt unnecessary to go beyond the differential form of the rate equation to calculate k's.

TABLE I

SOLVOLYSIS RESULTS

Ester	Wt. % dioxane	Temp., °C.	$k \times 10^4$, sec.$^{-1}$	$fr \times 100$[a]	$\Delta H^\ddagger$[a]	$\Delta S^\ddagger$[a]
Ib	95	60	5.84	8.4		
			5.53	7.4		
	90	25	1.61			
			1.59			
		40	6.60		17.3	-17.8
			6.77			
		50	16.7			
			16.8			
	85	25	5.44			
			5.47			
	80	7	1.52			
			1.54			
		16	5.01			
			4.78			
			4.55[b]		19.3	− 7.1
			4.73[c]			
		25	13.2			
			13.0			
			13.5			
			13.5			
IIb	90	16	2.71	7.4		
			2.88	8.0		
		25	7.02	7.8	16.9	−16.3
			7.16	8.2		
		35	17.8	9.4		
			18.4	10.5		
			18.6	10.3		
	80	7	8.01			
			8.09			
IIIb	90	60	0.73	71.8		
			0.74	72.1		
	85	60	2.12	59.9		
			2.05	60.0		
		70	5.69	59.2	22.2	− 9.1
			5.79	59.8		
		80	14.6	62.6		
			14.9	60.8		
	80	60	5.00	35.2		
			4.65	35.5		
			4.47[d]	32.2		
			4.65[e]	37.4		
			5.09	36.1		
			4.27	34.4		
			4.49[f]	34.7		
			4.90[f]	36.3		
		70	12.0	35.0	20.8	−11.6
			11.7	35.3		
		80	30.2	35.8		
			28.9	35.6		
	70	40	1.64	4.4		
			1.57	3.8		
		50	5.21	4.4	20.7	-- 9.7
			5.02	4.6		
			4.58[g]			
			4.66[h]			
		60	14.5	5.7		
			14.8	5.5		
IVb	85	80	2.62			
			2.73			
	80	60	1.10			
			1.21			
		70	2.86		20.5	−15.4
			2.98			
		80	7.06			
			7.04			
Vb	80	60	0.020			
			.018			
		70	.068		30.4	+ 6.2
			.068			
		80	.277			
			.265			
	70	60	.076			
			.075			
		70	.250		27.2	− 0.6
			.259			
		80	.832			
			.798			

[a] For the method of calculating these quantities, see the section on Results. [b] The solvolysis solution (0.009368 *M* in ester) was also 0.009525 *M* in sodium hydroxide initially. The rate was followed by titration with standard hydrochloric acid. [c] Initially 0.008845 *M* in ester and 0.009525 *M* in sodium hydroxide; see note *b*. [d] The ester was dissolved in anhydrous dioxane and maintained at 60° for 3 days after which sufficient water was added to make the solution 80% dioxane, and rate measurements were begun immediately. [e] Same as note *d*, except sample was stored 5 days at 60°. [f] Rates determined by the inverse procedure (see Experimental). [g] 0.009296 *M* ester and 0.009410 *M* NaOH initially; see note *b*. [h] 0.009068 *M* ester and 0.009410 *M* NaOH initially; see note *b*.

the structure is therefore most certainly as shown.

The isomeric *p*-nitrobenzoates from Ib and IIb were not isolated, but the rearrangement probably followed the same pattern; IIb may give two isomeric homoallylic *p*-nitrobenzoates, depending upon the direction of ring opening.

Discussion

The cyclopropylcarbinyl *p*-nitrobenzoates studied must have solvolyzed with unimolecular alkyl–oxygen fission, supported by the following evidence. The kinetics were cleanly first order, independent of added hydroxide ion (see experiments with Ib at 16° and with IIIb at 60° in 80% dioxane, Table I), and unaffected by PNBA produced during the reaction (see Fig. 1). For a given ester, the rate was increased greatly by increasing the ionizing power of the solvent (compare Ib at 25° in 90, 85 and 80% dioxane, Table I). Finally, methanolysis gave the methyl ether and PNBA, rather than alcohol and methyl ester.[16]

The reactions were followed in only one manner, that is, titrimetrically. For this reason, it is not possible to assess quantitatively the importance of "internal return" from ion-pairs separated to varying degrees by solvent molecules,[17] but it is clear from the gross aspects of the reaction that this phenomenon is involved. The results are best interpreted in terms of ionization to an R^+PNB^- ion-pair which may return either to the original or rearranged ester, or solvolyze. As the separation of ion-pair counterparts increases, return to ester becomes less important, and reaction with solvent molecules to produce solvolysis products (alcohol or ether) predominates. The degree to which ion-

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(16) See C. K. Ingold "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 763, 764 and 780, for a discussion of this criterion applied to alkyl–oxygen fission.

(17) For a detailed discussion and leading references, see S. Winstein and G. C. Robinson, THIS JOURNAL, **80**, 169 (1958), and S. Winstein and A. H. Fainberg, *ibid.*, **80**, 459 (1958).

pair counterparts become separated will be a function of the solvent polarity and of the structure of the R group. All the data presented in this paper are consistent with, and best explained in terms of, this mechanism.

The dependence of the rearrangement/solvolysis ratio (f_r) on solvent is shown in Table II. The percentage of rearrangement fell off rapidly with increasing water content of the solvent until, in 70% dioxane, the reaction was almost entirely solvolysis (94.4%). But in the same percentage of *methanolic* dioxane, 66% of the original ester rearranged to the isomeric ester VII, demonstrating the considerably weaker ionizing power of methanol *vs.* water. In absolute methanol, however, the product resulted exclusively from solvolysis.

TABLE II

PERCENTAGE REARRANGEMENT OF DIISOPROPYLCYCLOPROPYLCARBINYL *p*-NITROBENZOATE (IIIb) IN SEVERAL SOLVENTS AT 60°

Solvent	$r^a \times 100$
90% aq. dioxane	72.0
85%	60.0
80%	35.2
70%	5.6
70% meth. dioxane[b]	66.0
100% methanol[c]	0.0
100% dioxane	[d]

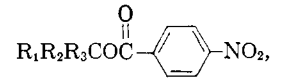
[a] Defined in section on Results. [b] Complete in 16 hours. [c] Product was solely the methyl ether IIIc; complete in 12 hours reflux. [d] No rearrangement (or solvolysis) after 3 days.

That the isomerization was not thermal but required some ionization is shown by the results in absolute dioxane. Even after five days at 60°, no isomerization occurred; when such a solution was diluted to 80% aqueous dioxane, solvolysis and isomerization proceeded smoothly, the same values of f_r being obtained as with fresh solutions (see Table I).

Before discussing the structural influences of *R* on the fraction of rearrangement, it will be instructive to consider briefly their effect on the over-all rates. The relative rates, for the limited number of structural changes studied thus far, are indicated in Table III. Those tertiary esters with two cyclopropyl groups are the fastest solvolyzing aliphatic *p*-nitrobenzoates yet reported. Indeed the secondary ester IVb solvolyzed as rapidly as tri-*t*-butylcarbinyl *p*-nitrobenzoate.[13] From the series Vb, IIIb, Ib it is apparent that as isopropyl groups were successively replaced by cyclopropyl, the rate increased, *with the second cyclopropyl group causing a rate enhancement nearly equal to that of the first.*

TABLE III

RELATIVE SOLVOLYSIS RATES OF SEVERAL *p*-NITROBENZOATES IN 80% AQUEOUS DIOXANE, 60°

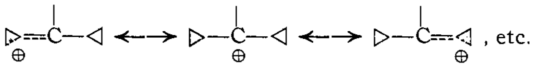


Ester	*R*₁	*R*₂ = *R*₃	Rel. rate
Vb	*i*-Pr	*i*-Pr	1[a]
IVb	H	Cyclo-Pr	60.7
IIIb	Cyclo-Pr	*i*-Pr	246[b]
Ib	*i*-Pr	Cyclo-Pr	23,500[c]
IIb	*i*-Pr	2-Me-cyclo-Pr	124,000[d]

[a] The referee raised some doubt about the suitability of Vb as a reference standard, arguing that this ester may undergo very rapid internal rearrangement on being dissolved in a part aqueous medium, and that the ester whose solvolysis rate was measured solvolyzes more slowly than authentic Vb (see ref. 13), or that indeed what is claimed to be Vb is actually a rearranged ester, rearrangement possibly having occurred during the preparation or workup. That neither of these is correct was demonstrated by two additional experiments. Partial solvolysis (50%) of Vb in 80% aqueous dioxane, followed by recovery of unsolvolyzed ester gave Vb, identical (m.p., mixed m.p., infrared spectrum) with the original ester, demonstrating no rearrangement during solvolysis. Reduction of this recovered ester with lithium aluminum hydride (the reaction is slow, and lithium borohydride was without effect on the ester) gave triisopropylcarbinol (Va), infrared spectrum identical in every detail with that of authentic Va. We feel, therefore, that the reference standard is valid. [b] This is the only example involving solvolysis *and* rearrangement, in this solvent. The figure given is for the total rate of ester disappearance, by both processes. A value of 195 is obtained from data in 70% dioxane at 60°, where rearrangement of IIIb is negligible. [c] Calculated for 60° from measurements at 7, 16 and 25°. [d] Obtained from the ratio of $k_{\text{IIb}}/k_{\text{Ib}}$ at 7°, which was 5.26.

But the steric requirements of cyclopropyl are very likely less than isopropyl, because the methyls are pinned back. Inductive electron release (which would stabilize a carbonium ion) is also considerably less for cyclopropyl than for isopropyl. Quantitative data to this effect were obtained from the integrated O–H absorption intensities for the cyclopropylcarbinols reported in this paper, together with several reference compounds. The σ^*-value[18] for the cyclopropyl group is +0.11 ± 0.03,[19] intermediate between H (+0.49) and CH_3 (0.00), and strongly electron-withdrawing when compared with isopropyl ($\sigma^* = -0.19$). If, then, the relative rates in Table III were corrected for steric and inductive changes, both of which should decrease the solvolysis rates, the rate increase per cyclopropyl group would be even greater than observed.

It seems reasonable to attribute the rate enhancement to stabilization of the carbonium ion by some mechanism of electron-release from each cyclopropyl group attached to the carbonium carbon. This may be expressed in terms of the hyperconjugative resonance structures



or some alternative, less clearly defined release mechanism.[20]

It is significant that the ester solvolysis products corresponded structurally in every case to the original alcohol from which the ester had been prepared, indicating that the positive charge in the in-

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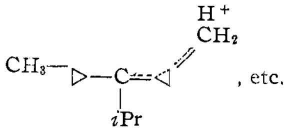
[18] See R. W. Taft, Jr., in M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, pp. 605 ff.

[19] T. L. Brown, *Spectrochim. Acta*, in press.

[20] H. C. Brown, O. H. Wheeler and K. Ichikawa, *Tetrahedron*, **1**, 214 (1957), and H. C. Brown and K. Ichikawa, *ibid.*, **1**, 221 (1957), have recently used the carbonyl group as a model for a carbonium ion and found an excellent correlation of sodium borohydride reduction rates with what might have been predicted on this model. Professor Brown also found (private communication) a large and successive decrement in reduction rates as methyl groups were replaced by cyclopropyl groups in the series acetone, methyl cyclopropyl ketone, dicyclopropyl ketone. A common factor appears to be operative in the solvolyses and reductions.

termediate was concentrated on the tertiary (or with IV, the secondary) carbon atom.

Two methyl substituents on the cyclopropyl groups increased the solvolysis rates fivefold; this would be rather large for an inductive effect transmitted through saturated bonds to the tertiary carbon in IIb, and suggests the possibility of hyperconjugative release transmitted through the three-membered ring.



Alternatively, the methyls may increase the rate due to relief of steric crowding.

There is no direct correlation between over-all solvolysis rates of the esters, and their tendency to rearrange; Ib, for example, which solvolyzes at a rate intermediate between IIIb and IIb (see Tables III and IV) shows the least rearrangement of the three esters in comparable solvents.

TABLE IV

PERCENTAGE REARRANGEMENT AS A FUNCTION OF STRUCTURE AND SOLVENT

Ester	Dioxane, %		
	95	90	80
Ib	8	0	0
IIb		9	0
IIIb		72	35

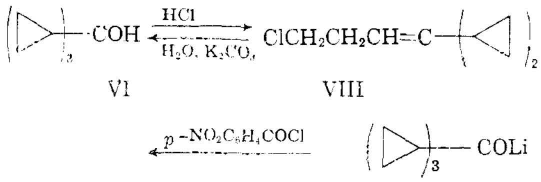
Rearrangement appears to be favored by bulky groups which might hinder the approach of solvent molecules to the ion-pair.

In a given solvent, the rate seems controlled more by entropy than by energy changes (compare Ib, IIIb and IVb in 80% dioxane, Table I). The effects are consistent with the ion-pair mechanism. The important structural change in going from the dicyclopropylcarbinyl (IVb) to the dicyclopropylisopropylcarbinyl (Ib) ester is from a secondary to a tertiary carbinyl group. In the latter, because of steric requirements, the number of degrees of freedom is less than in the secondary ester. But in the ion-pairs derived from each ester, charge would be about equally dispersed (each ester has two cyclopropyl groups), requiring similar orientations of solvent molecules. Therefore, in going from reactant to transition state, the tertiary ester would experience less of a change in degrees of freedom than the secondary ester, and would have the more positive $\Delta S^{\ddagger}$.

On the other hand, dicyclopropylisopropylcarbinyl (Ib) and diisopropylcyclopropylcarbinyl (IIIb) *p*-nitrobenzoates have roughly equivalent steric requirements restricting atomic motions in the ester. But in the former, the two cyclopropyl groups permit greater charge dispersion in the transition state than in the latter (only one cyclopropyl group). This will result not only in a lower $\Delta H^{\ddagger}$ (about 1.5 kcal.) but will also require less restriction in orientation of solvent molecules; hence $\Delta S^{\ddagger}$ would be expected to be, and is, more positive for the ester with two cyclopropyl groups.

The energetics of Vb are worthy of further investigation. There is a large solvent effect on both the enthalpy and entropy of activation; both decreased ($\Delta H^{\ddagger}$ from 30.4 to 27.2 kcal., $\Delta S^{\ddagger}$ from +6.2 to −0.6 e.u.) when the water content was raised from 20 to 30%. This is apparently a trend, for Bartlett and Stiles[13] reported $\Delta H^{\ddagger} = 23.5$ kcal., $\Delta S^{\ddagger} = -9.0$ e.u., for this ester in 60% aqueous dioxane.

It would have been instructive to include a case with three cyclopropyl groups in this series, to determine whether the cumulative rate effect obtains. Several attempts to prepare VIb from tricyclopropylcarbinol failed, possibly due to the anticipated sensitivity of the product to moisture, and to side reactions. The lithium alcoholate, with *p*-nitrobenzoyl chloride, gave a homoallylic chloride VIII, which also was produced from the alcohol and hydrochloric acid.



VI VIII

Its structure was proved by oxidation to dicyclopropyl ketone and β-chloropropionic acid, and by reconversion to VI.

Acknowledgment.—We wish to express appreciation to the American Viscose Corporation (J.M.S.) and the John Simon Guggenheim Memorial Foundation (H.H.) for fellowships which facilitated this work.

Experimental[20a]

Di-(2-methylcyclopropyl) Ketone.—The procedure was essentially the same as that used by Hart and Curtis[1a] to prepare dicyclopropyl ketone, γ-valerolactone being used in place of γ-butyrolactone. From 600 g. (6 moles) of γ-valerolactone there was obtained 207 g. (50%) of di-(2-methylcyclopropyl) ketone, b.p. 66° at 7 mm., $n^{25}\text{D}$ 1.4602.

Anal. Calcd. for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.11; H, 10.39.

The 2,4-dinitrophenylhydrazone, after recrystallization from 95% ethanol, melted at 101–102°.

Anal. Calcd. for $C_{15}H_{18}N_4O_4$: C, 56.59; H, 5.70; N, 17.60 Found: C, 56.88; H, 5.56; N, 17.53.

Cyclopropyllithium.—The procedure for the preparation and use of this organometallic has already been described.[1b] Initiation of the reaction with ethyl bromide is often helpful.

Preparation of the Alcohols.—The tertiary alcohols were all prepared from appropriate organometallics and ketones in the usual fashion. The reagents, yields, physical constants and analyses are given in Table V.

Preparation of the *p*-Nitrobenzoates.—The *p*-nitrobenzoates of the tertiary alcohols were prepared according to a single procedure, of which the following for dicyclopropylisopropylcarbinyl *p*-nitrobenzoate (Ib) is typical. The lithium salt of Ia was prepared in pentane solvent from 28 g. (4 g. atoms) of lithium, 157 g. (2 moles) of isopropyl chloride and 220 g. (2 moles) of dicyclopropyl ketone. The flask was cooled in an ice–salt-bath and a solution of 223 g. (1.2 moles) of *p*-nitrobenzoyl chloride in 1800 ml. of dry ether was added slowly, the temperature being kept between −5 and 0°. The mixture was stirred at 0° for 8 hours, then filtered and the solid extracted with hot ligroin (b.p. 66–75°). The extracts were combined with the filtrate and the solvent evaporated *in vacuo*. The residue (which contained unchanged ketone and tertiary carbinol as well as the desired ester) was taken up in a little ligroin and crystallization induced

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[20a] Analyses were performed by Clark Microanalytical Laboratory, Urbana, Illinois; Micro-Tech Laboratories, Skokie, Illinois, and Spang Microanalytical Laboratory, Ann Arbor, Michigan.

TABLE V

PREPARATION AND PROPERTIES OF CERTAIN TERTIARY ALCOHOLS

Alcohol	Organo-metallic[a]	Yield, %	Boiling point °C.	Boiling point Mm.	$n^{25}D$	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
VI	C-Li	94	88.5	10	1.4802	78.89	78.60	10.59	10.65
Ia	I-Li	69	81	10	1.4648	77.87	77.72	11.76	11.56
	I-MgCl	67							
IIa	I-Li	83	67	3	1.4570	79.06	79.12	12.17	12.22
Dicyclopropylmethylcarbinol	M-MgI	70	45	4	1.4618	76.14	75.93	11.18	10.89
IIIa	C-Li	75	75	10	1.4518	76.86	77.08	12.90	13.12

[a] C = cyclopropyl; I = isopropyl; M = methyl. The other reagent in each instance was the appropriate ketone.

TABLE VI

MELTING POINTS, YIELDS AND ANALYSES OF SEVERAL *p*-NITROBENZOATES

p-Nitrobenzoate	Yield, %	M.p., °C.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
Ib	22	114–115 d.	67.30	67.27	6.98	6.81	4.62	4.49
IIb	20	73–74 d.	68.86	68.81	7.60	7.57	4.23	4.22
IIIb	22	91–92	66.86	66.84	7.59	7.63	4.59	4.65
IVb	15	74–75	64.35	64.59	5.79	5.79	5.36	5.48
Vb[a]	20	74–75	66.42	66.58	8.20	8.11	4.56	4.56

[a] This ester was described recently by P. D. Bartlett and M. Stiles,[18] and is included here for comparison purposes and for completeness.

(Dry Ice). The crude ester (80 g., 22%) was freed of *p*-nitrobenzoic acid by stirring a warm ligroin solution of the ester with activated alumina. After several recrystallizations from ligroin, there was obtained 66 g. of pure Ib. Yields and physical constants are given in Table VI.

Dicyclopropylcarbinyl *p*-nitrobenzoate (IVb) was prepared by the general method recently described by Brewster and Ciotti.[21] *p*-Nitrobenzoic acid (16.7 g., 0.1 mole) was dissolved in 800 ml. of warm pyridine. To the cooled (room temperature) solution 17.7 g. (0.1 mole) of benzenesulfonyl chloride was added, the whole cooled in an ice-bath and 11.2 g. (0.1 mole) of dicyclopropylcarbinol (IVa)[1a] was added in one portion. After two hours with occasional shaking at 0° the mixture was poured into 1500 ml. of ice-water and filtered immediately, yielding 4 g. (15%) of IVb which was recrystallized several times from low-boiling petroleum ether. Physical constants are listed in Table VI.

Kinetic Measurements. (a) **Solvents.**—The dioxane was purified by the method of Fieser.[22] CO_2-free distilled water was used for making up solvent mixtures and reagents. Methanol was distilled over magnesium methoxide. All solutions are in weight per cent.

(b) **Standardization of Reagents.**—Sodium hydroxide was made up approximately 0.01 *N* in aqueous dioxane of the same composition as the solvent for the particular kinetic experiment. It was standardized immediately before each run against Bureau of Standards benzoic acid using phenolphthalein. If a run required more than one day, the base was standardized each day.

(c) **Procedure.**—Approximately 0.01 *M* solutions of ester were employed and the reaction was followed by titrating the liberated *p*-nitrobenzoic acid with standard sodium hydroxide. Reactions were conducted in a constant temperature bath maintained at ±0.1° of the desired temperature.

The aqueous dioxane solvent was equilibrated in the constant temperature bath before each run was started. Approximately 0.001 mole of the ester was weighed accurately into a dry 100-ml. volumetric flask. At zero time, 100 ml. of the equilibrated solvent was pipetted into the flask containing the ester and the solution was thoroughly mixed. At various time intervals, 5-ml. aliquots were withdrawn, quenched by cooling (ice–salt-bath) and titrated immediately with standard base using phenolphthalein. Usually 10 to 15 points were taken for each run, at least two runs were made for each set of conditions, and solvolyses were followed nearly to completion.

An alternative procedure involved addition of excess base in small increments and recording the time at which the phenolphthalein lost its color. This method was only used in a few runs and was abandoned in favor of the aliquot procedure, because the end-points were easier to observe. The two methods agreed well, when applied to the same ester under the same conditions. The rate data are summarized in Table I.[23]

Product Analysis. (a) **Dicyclopropylisopropylcarbinyl *p*-Nitrobenzoate** (Ib).—The products of solvolysis in 80% aqueous and 80% methanolic dioxane were determined. A solution of Ib (12.4 g., 0.041 mole) in 300 ml. of 80% aqueous dioxane was maintained at 25° for 48 hours. then poured into 700 ml. of water, made slightly alkaline with sodium hydroxide and extracted with eight 100-ml. portions of petroleum ether. The combined extracts were washed with several portions of water to remove the dioxane, dried over Drierite, and the solvent removed. Distillation of the residue gave 6.0 g. (95%) of Ia, b.p. 64° at 4 mm., $n^{25}D$ 1.4645, infrared spectrum identical with that of an authentic sample. Similar results were obtained in a duplicate experiment altered only by scaling down the amounts used, and shortening the time to six hours.

In a preliminary experiment, methanolysis of the ester in 80% methanolic dioxane at 25° gave the theoretical amount of *p*-nitrobenzoic acid (titration) in 17 hours. A solution of 10 g. (0.033 mole) of Ib in 100 ml. of 80% methanolic dioxane was maintained at 25° for 18 hours, then worked up as for the hydrolysis just described. There was obtained 4.5 g. (81%) of Ic, b.p. 61° at 4 mm., $n^{25}D$ 1.4566.

Anal. Calcd. for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.55; H, 11.98.

The infrared spectrum, which showed an intense ether band at 9.2 μ and no absorption in the 2.7–3.0 or 5.9–6.3 μ regions, was identical with that of an authentic sample prepared as follows. A mixture of 11.1 g. (0.072 mole) of Ia, 150 ml. of anhydrous benzene and 2.81 g. (0.072 g. atom) of potassium was refluxed (protected from moisture of the air) for 72 hours. A solution of 23.4 g. (0.172 mole) of methyl iodide in 50 ml. of benzene was added, and the mixture refluxed for 20 hours, then filtered and the residue (potassium iodide) rinsed with several portions of benzene. Removal of the solvent and distillation gave 10.5 g. (87%) of the desired methyl ether.

(b) **Diisopropylcyclopropylcarbinyl *p*-Nitrobenzoate** (IIIb).—The nature and relative amounts of products depended on the solvent used. (1) **70% aqueous dioxane:** Refluxing a solution of 0.2971 g. of IIIb in 100 ml. of solvent for 26 hours gave only 93.6% of the theoretical acid titer. In an isolation experiment, a solution of 6.42 g. of IIIb in 200 ml. of solvent was heated at 60° for 12 hours, and worked up as above. The residue (3.0 g.) showed both hydroxyl (2.85 μ) and carbonyl (5.8 μ) in the infrared. Petroleum ether (5

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(21) J. H. Brewster and C. J. Ciotti, Jr., THIS JOURNAL, **77**, 6214 (1955).

(22) L. F. Fieser, "Experiments in Organic Chemistry," second edition, D. C. Heath and Co., Boston, Mass., 1941, p. 368.

(23) For more complete details, consult the doctoral thesis of J. M. S. (ref. 3), especially the appendix which gives the concentrations of ester, titrant, etc.

ml.) was added and the solution was placed on crushed Dry Ice, whereupon some crystals were formed (75 mg.), m.p. 46–48°. This was subsequently shown to be 4-isopropyl-5-methyl-3-hexenyl *p*-nitrobenzoate (VII) (*vide infra*). The filtrate from these crystals yielded 2.3 g. (70%) of IIIa, b.p. 60–61° at 4 mm., $n^{25}D$ 1.4516, infrared identical with an authentic sample. (2) **90% aqueous dioxane:** The ester (10.43 g., 0.0341 mole) in 250 ml. of solvent was maintained at 60° for 48 hours, then worked up as above. There was obtained 6.4 g. (63%) of VII, m.p. 46–48°.

Anal. Calcd. for $C_{17}H_{23}NO_4$: C, 66.86; H, 7.59; N, 4.58. Found: C, 66.91; H, 7.30; N, 4.49.

From the filtrate, 0.7 g. (13%) of IIIa was isolated. (3) **Absolute methanol:** A preliminary experiment showed that the theoretical PNBA titer was obtained from a solution which had been refluxed 12 hours. In an isolation experiment, 6.57 g. (0.0215 mole) of ester in 300 ml. of absolute methanol was refluxed for 12 hours, then worked up as usual. There was obtained 3.2 g. (81%) of ether, presumably 3-cyclopropyl-3-methoxy-2,4-dimethylpentane (IIIc), b.p. 56° at 4 mm., $n^{25}D$ 1.4338, intense band at 8.93 μ (ether), none at 2.7–3.0 or 5.9–6.3 μ.

Anal. Calcd. for $C_{11}H_{22}O$: C, 77.58; H, 13.02. Found: C, 78.29; H, 13.03.

(4) **70% methanolic dioxane:** A preliminary experiment showed that after 16.25 hours at 60°, only 34% of the theoretical PNBA titer was obtained, and no additional acid was liberated after 37.5 hours. In an isolation experiment, 5.71 g. (0.0187 mole) of ester in 100 ml. of solvent was maintained at 60° for 36 hours, then worked up as usual. The petroleum ether extracts were concentrated to 50 ml. and cooled in Dry Ice. There was obtained 3.5 g. (61%) of VII, m.p. 46–48° and, from the filtrate, 0.7 g. (22%) of IIIc, infrared spectrum identical with that obtained from solvolysis in absolute methanol.

Structure Proof of 4-Isopropyl-5-methyl-3-hexenyl *p*-Nitrobenzoate (VII). (a) Reduction with Lithium Borohydride.—A solution of 8.0 g. (0.026 mole) of the ester in 50 ml. of tetrahydrofuran was added slowly (no noticeable heat evolved) to 2.2 g. (0.1 mole) of lithium borohydride in 100 ml. of tetrahydrofuran, and the mixture stirred at room temperature for 12 hours, cooled in an ice-bath, 300 ml. of water slowly added and the resulting mixture extracted with several portions of ether. The ether extracts, after drying (Drierite) and removal of the solvent *in vacuo*, left a residue which was taken up in a little petroleum ether and filtered, yielding 3.2 g. (81%) of *p*-nitrobenzyl alcohol, m.p. 91–93° (lit.[24] value 93°). The filtrate was distilled, from which was obtained 3.0 g. (74%) of presumably 4-isopropyl-5-methyl-3-hexenol, b.p. 83° at 5 mm., $n^{25}D$ 1.4505 with infrared bands at 3.0 μ (broad, -OH) and 6.0 μ (weak).

Anal. Calcd. for $C_{10}H_{20}O$: C, 76.86; H, 12.90. Found: C, 76.91; H, 12.87.

(b) Oxidation of 4-Isopropyl-5-methyl-3-hexenol.—Oxidation of the lithium borohydride reduction product (1 g.) with neutral permanganate (4 g. in 100 ml. of water) at room temperature for four hours gave diisopropyl ketone (0.65 g.) identified by its infrared spectrum and vapor chromatogram.

Attempted Preparation of Tricyclopropylcarbinyl *p*-Nitrobenzoate (VIb).—Several attempts to prepare this ester from the lithium alcoholate and *p*-nitrobenzoyl chloride according to the general procedure which was successful for the other esters (*vide supra*) failed over a temperature range from −70° to refluxing pentane. Identifiable products were *p*-nitrobenzoic acid and its anhydride, unchanged alcohol, and a chlorine-containing liquid, b.p. 82° at 3 mm., $n^{25}D$ 1.4998, shown to be 1,1-dicyclopropyl-4-chloro-1-butene (VIII). The infrared showed a carbon-carbon double bond (6.06 μ). The structure follows from the oxidation products.

Anal. Calcd. for $C_{10}H_{16}Cl$: C, 70.37; H, 8.86; Cl, 20.77. Found: C, 70.31; H, 8.90; Cl, 20.79.

Other attempts to prepare the desired ester from the potassium alcoholate and *p*-nitrobenzoyl chloride, from the lithium alcoholate and *p*-nitrobenzoic anhydride, and *via* the method of Brewster and Ciotti[21] all failed.[23]

Oxidation of VIII.—A mixture of 17 g. (0.1 mole) of VIII, 31.6 g. (0.2 mole) of potassium permanganate and 400 ml. of water was stirred for two hours at 0° and 28 hours at room temperature, then filtered and the filtrate extracted with five 70-ml. portions of ether. After drying (magnesium sulfate) and removal of the solvent, there remained 4 g. (40%) of dicyclopropyl ketone, b.p. 65° at 18 mm., infrared spectrum identical with an authentic sample.[18]

The aqueous solution (after ether extraction) was acidified (hydrochloric acid) and again extracted as above. From the residue there was isolated 3 g. (30%) of β-chloropropionic acid, m.p. 38–39° (lit.[25] value 39°). Its infrared spectrum was identical with that of an authentic sample.

Reaction of Tricyclopropylcarbinol (VIa) with Hydrochloric Acid.—To a test-tube containing 10 ml. of ice-cold concentrated hydrochloric acid there was added 5 g. (0.033 mole) of VIa and the mixture was shaken frequently for 30 minutes at 0°. The organic layer and ether extracts of the aqueous layer were combined, dried (potassium carbonate) and distilled, yielding 4.5 g. (80%) of VIII, identical with that obtained from the lithium alcoholate and *p*-nitrobenzoyl chloride.

Hydrolysis of 1,1-Dicyclopropyl-4-chloro-1-butene (VIII).—A mixture of 34 g. (0.2 mole) of VIII and 200 ml. of 10% aqueous potassium carbonate was refluxed with stirring for 24 hours. The organic layer and ether extracts of the aqueous layer were combined, dried (magnesium sulfate) and, after removal of the solvent, gave 27 g. (89%) of VIa, b.p. 71° at 4 mm., infrared spectrum identical with that of an authentic sample.

EAST LANSING, MICH.

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[24] I. Heilbron, "Dictionary of Organic Compounds," Oxford University Press, London, 1953, Vol. 3, p. 645.

[25] Reference 24, Vol. 1, p. 556.

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CHICAGO]

Solvent Effects in the Solvolyses of Alkyl Bromides in Aqueous Ethanol[1]

BY ROBERT A. CLEMENT AND MARIAN R. RICE

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The rates of solvolysis of ethyl, isopropyl and *t*-butyl bromides have been determined at 25.10° in aqueous ethanol containing 24.1 and 1.00% by weight water. Distribution coefficients have been determined for the vapor-liquid equilibria of these same alkyl bromides in the same media at the same temperature. The results are discussed in terms of the Brönsted rate law. A significant fraction of the kinetic solvent effect observed for each alkyl bromide is due to the different activity of the alkyl bromide in the two media.

Introduction

The Brönsted rate law,[2] although fundamental to all chemical rate processes, has been applied only infrequently to organic reactions in spite of its relevance to investigations of kinetic medium effects. This paper is concerned with the application of the Brönsted rate law to the kinetic solvent effects observed in the solvolyses of ethyl, isopropyl and *t*-butyl bromides in aqueous ethanol.

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[1] Presented at the 133rd Meeting of the American Chemical Society, San Francisco, Calif., April, 1958.

[2] J. N. Brönsted, *Z. physik. Chem.*, **102**, 169 (1922).