does not present large variations. The *trans* coupling constant $^3J_{BB'}$ of IVc is approximately 2 Hz less than the *cis* coupling constant $^3J_{BB'}$ in I. On the basis of these considerations the nmr spectral analysis of the N-methyl derivatives of substituted carbostyril photodimers IVb and IVd (Figure 3) was performed and their nmr spectra at 60 MHz and 100 MHz were calculated. The results are shown in Table I. The coupling constants show that the dimers have formed by h–h fusion (V) rather than by h–t fusion (VI), since in the latter case $J_{AB'}$ would be considerably greater than $J_{AA'}$, whereas the reverse was found. The values of the $J_{AA'}$ coupling constants in IVc and IVd and the negative sign of the $^4J_{AB'}$ coupling together with the close similarity of the coupling constants to those of IVb show that the geometry of the cyclobutane ring of all three compounds is the same.

As very little information on the effect of substituents on the course of dimerization reactions is available, it is interesting to note that in these few examples the course of dimerization does not appear to be affected by the substituents. It is also important to emphasize that the choice of a suitable solvent and the analysis of the nmr spectra of these photodimers can give very useful information about their stereochemistry which is otherwise very difficult to obtain.

Experimental Section

The nmr spectra were determined in liquid SO_2 on Varian A-60 and Varian HA-100 spectrometers, using tetramethylsilane as an internal standard.

Dimers of Coumarin.—These were prepared according to the previously published procedure.[2]

Dimers of Carbostyril.—These were prepared according to the recently described procedure.[3]

N-Methyl Derivatives.—The N-methyl derivatives of the photodimers were prepared using the procedure of Lederer, *et al.*[5]

The N-methyl-6-chlorocarbostyril photodimer had mp 240° from methanol.

Anal. Calcd for $C_{20}H_{16}N_2O_2Cl_2$: C, 62.03; H, 4.16. Found: C, 61.94; H, 4.2.

The N-methyl-6-methylcarbostyril photodimer had mp 252–253° from ethyl acetate.

Registry No.—I, 21044-76-8; IVb, 22040-14-8; IVc, 22040-15-9; IVd, 22040-16-0.

Small-Ring Compounds. XXII. Solvolysis of 2-Arylcyclopropylcarbinyl 3,5-Dinitrobenzoates

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A series of *trans*-2-arylcyclopropylcarbinyl 3,5-dinitrobenzoates was synthesized and solvolyzed in 75 wt % aqueous dioxane at 130°. The Hammett plot of the relative rates gave a straight line with slope −1.5, suggesting a substantial extent of delocalization of the positive charge to the 2 position of the cyclopropylcarbinyl cation. A bisected-type cation was suggested for the conformation of 2-arylcyclopropylcarbinyl cation.

The character of cyclopropylcarbinyl cation has been studied extensively by several workers.[1] Bicyclobutonium ion, bisected cation, or homoallylic cation have been proposed as a conformation of the cyclopropylcarbinyl cation in order to explain the somewhat peculiar property of the cation. On the other hand, it has been reported in some of the early literature that the cyclopropylcarbinyl cations bearing substituents showed substantially different behavior from that of the nonsubstituted cation. For example, the main product obtained in the deamination of cyclopropylcarbinylamine-α-^{14}C was an equimolar mixture of cyclobutanol and cyclopropylcarbinol, in which the carbon isotope was substantially scrambled,[2] while the deamination of 1-methylcyclopropylcarbinylamine-α-^{14}C gave 1-methylcyclobutanol as the exclusive product, showing a minor extent of the isotope scrambling.[3]

In another investigation, the attachment of a phenyl or methyl group to the 1 position of the cyclopropylcarbinyl cation caused a considerable change in the activation entropy of the formation of the cation.[4]

An electron-donating group substituted in the α position of the cyclopropylcarbinyl cation remarkably stabilizes the cation and prevents the skeletal rearrangement of the ring under the solvolytic conditions.[5] On the other hand, the same group attached to the 1 position of the cation makes only a minor contribution to the stabilization of the cation and brings on the formation of the corresponding cyclobutyl product.[6] Thus, it is conceivable that the character of the substituted cyclopropylcarbinyl cation is substantially influenced by the property and location of the substituent. Thus far, little attention has been focused on the role of the substituent in the 2 position of the cation. The effect of a methyl group substituted in the 2 position has been studied by Schleyer and coworker, and a bisected-type conformation has been suggested for the cation.[1] Sneen has reported that a phenyl substituent in the 2 position of cyclopropylcarbinyl cation showed no remarkable influence on the stability of the cation.[7]

In the present study, the role of a phenyl group attached to the 2 position of the cyclopropylcarbinyl cation and the conformation of some 2,2- or 2,3-disubstituted cations were studied.

(1) P. von R. Schleyer and G. W. VanDine, *J. Amer. Chem. Soc.*, **88**, 2321 (1966), and references cited therein.

(2) R. H. Mazur, W. N. White, D. A. Semenow, C. C. Lee, M. S. Silver, and J. D. Roberts, *ibid.*, **81**, 4390 (1959).

(3) E. F. Cox, M. C. Caserio, M. S. Silver, and J. D. Roberts, *ibid.*, **83**, 2719 (1961).

(4) D. D. Roberts, *J. Org. Chem.*, **29**, 294 (1964).

(5) T. Shono, A. Oku, and R. Oda, *Tetrahedron*, **24**, 421 (1968).

(6) D. D. Roberts, *J. Org. Chem.*, **30**, 23 (1965).

(7) R. A. Sneen, K. M. Lewandowski, I. A. I. Taha, and B. R. Smith, *J. Amer. Chem. Soc.*, **83**, 4843 (1961).

Results

***trans*-2-Arylcyclopropylcarbinyl 3,5-Dinitrobenzoates.** —A series of 2-arylcyclopropanecarboxylic acids were synthesized and the stereoisomers were separated according to the method reported by Trachtenberg.[8] The 3,5-dinitrobenzoates (**2a–2d**) were obtained by the

X—⟨benzene⟩—▽—CH₂ODNB
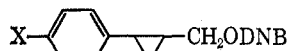
2a, X = OCH₃
**b**, X = CH₃
c, X = H
d, X = Cl

usual method from the corresponding alcohols (**1a–1d**) prepared by the reduction of *trans*-2-arylcyclopropane-carboxylic esters. Each of the benzoates gave satisfactory results in elemental and spectroscopic analyses.

2,2- or 2,3-Disubstituted Cyclopropylcarbinyl 3,5-Dinitrobenzoates. —Diphenyl (2,2- or 2,3-) or methylphenyl (2,2- or 2,3-) cyclopropylcarbinols (**4**,[9] **5**,[10] **6**,[11] and **7**[12]) were synthesized by the reaction of the corre-

C₆H₅ / C₆H₅ ... CH₂OH
4

C₆H₅ ... C₆H₅ CH₂OH
5

C₆H₅ / CH₃ ... CH₂OH
6

C₆H₅ ... CH₃ CH₂OH
7
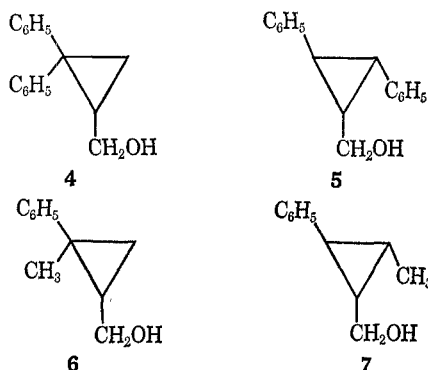
sponding olefins with ethyl diazoacetate followed by reduction. The separation of stereoisomers was achieved by the recrystallization of the corresponding acids. The 3,5-dinitrobenzoates of these alcohols were obtained by the usual way and the structures of the benzoates were determined by elemental and spectroscopic analyses.

Hydrolysis of 2c in 75 Wt % Aqueous Dioxane. Products Studies. —The 3,5-dinitrobenzoate **2c** was hydrolyzed in 75 wt % aqueous dioxane at 130° to study the configuration and distribution of the products. The product consisted of 85–88% **3** and 12–15%

⟨benzene⟩—CH—CH₂—CH=CH₂
       |
       OH
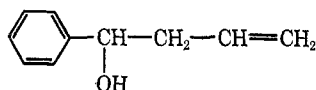
3

1c. The distribution of the products was slightly varied with reaction time (see Experimental Section, Table V). Compound **3** was stable under the hydrolysis condition. An equimolar solution of **1c** and 3,5-dinitrobenzoic acid in 75 wt % aqueous dioxane was heated at 130° to study the extent of the rearrangement of **1c** to **3** under the hydrolysis condition. The

(8) E. N. Trachtenberg and G. Odian, *J. Amer. Chem. Soc.*, **80**, 4015 (1958).
(9) F. J. Impastato and H. M. Walborsky, *ibid.*, **84**, 4838 (1962).
(10) J. K. Blatchford and M. Orchin, *J. Org. Chem.*, **29**, 839 (1964).
(11) J. Smejkal and J. Farkas, *Collect. Czech. Chem. Commun.*, **28**, 1557 (1963).
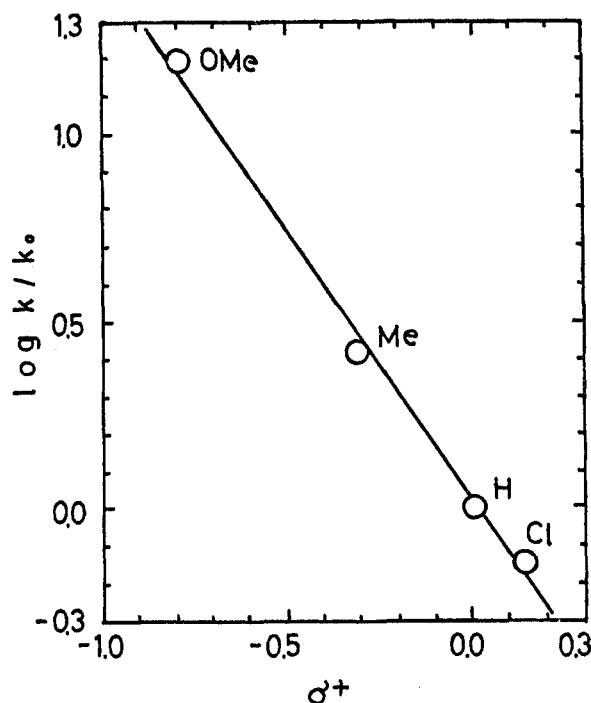(12) J. Farkas, P. Kourim, and F. Sorm, *ibid.*, **24**, 2460 (1959).

Figure 1.—Hammett-type plot for the solvolysis of **2a–2d** in 75 wt % aqueous dixane at 130°.

results (Experimental Section, Table VI) indicated that **1c** is fairly stable under the reaction condition.

Although the formation of some more highly rearranged products has been observed in the deamination reaction of *trans*-2-phenylcyclopropylcarbinyl-amine,[18] the hydrolysis of **2c** did not give such rearranged products. Hydrolysis of the 3,5-dinitrobenzoate of **3** under the same reaction conditions resulted in the exclusive formation of the parent alcohol, **3**, and no cyclopropyl compound could be detected in the products.

Methanolysis of 2c. —Methanolysis of **2c** catalyzed by *p*-toluenesulfonic acid was carried out to establish the intervention of alkyl–oxygen cleavage in the solvolysis of **2c** (AAL1 mechanism[14]). The methanolysis reaction gave methyl ethers of **3** and **1c** (trace) and 3,5-dinitrobenzoic acid in a 76% yield, indicating alkyl–oxygen cleavage.

Acyl–oxygen cleavage (AAC2 mechanism[14]) in this methanolysis reaction would result in the formation of **1c**, **3**, and methyl 3,5-dinitrobenzoate. Thus, an unimolecular reaction mechanism is indicated for the solvolysis of **2c**.

Kinetic Study. —The rates of solvolysis of **2a–2d** in 75 wt % aqueous dioxane at 130° were first order. The absolute and relative first-order rate constants are shown in Table I.

The Hammett plot of the relative rates shown in Table I against σ_p^+ showed a straight line with slope -1.48 (correlation coefficient 0.998, standard deviation 0.040, Figure 1). The plot of the relative rates against σ_p gave a rather poor correlation. The ρ value was -1.75 with a correlation coefficient of 0.827 and a standard deviation of 0.409. The activation parameters obtained for the solvolyses of **2c** and the 3,5-di-

(13) C. Dupin and R. F. Jullien, *Bull. Soc. Chim. Fr.*, 1993 (1964).
(14) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt & Co., Inc., 1959, p 339.

TABLE I

RATE CONSTANTS OF SOLVOLYSIS OF 2a–2d IN 75 WT % AQUEOUS
DIOXANE AT 130° AND RELATIVE RATES

Ester	Rate constant, $k \times 10^6$, sec^{-1}	Relative rate
2a	49.2	15.3
2b	7.11	2.22
2c	3.20	1.00
2d	2.32	0.742

nitrobenzoate of cyclopropylcarbinol, **8**, are shown in Table II. The solvolysis of 3,5-dinitrobenzoates of

TABLE II

RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE
SOLVOLYSES OF 2c AND CYCLOPROPYLCARBINYL
3,5-DINITROBENZOATE IN 75 WT % AQUEOUS DIOXANE

Ester	$k \times 10^6$, sec^{-1} 130°	139°	$\Delta H^{\pm}$, kcal/mol	$\Delta S^{\pm}$, eu at 130°
2c[a]	3.20	6.80	26.8	−17.6
DNB[b] of 8	1.02[c]	2.34	26.5[d]	−20.6[d]
DNB[b] of 3	1.86			

[a] $k = 1.33 \times 10^{-6}$ sec^{-1} at 120°. [b] 3,5-Dinitrobenzoate. [c] Measured at 129°. [d] The activation parameters might involve small error, as the temperature ranges may be insufficient to establish the parameters.

4, 5, 6, and **7** were carried out in 75 wt % aqueous dioxane to get some information on the conformation of the cyclopropylcarbinyl cations. Owing to the low solubility of the 3,5-dinitrobenzoate of **7** in 75 wt % aqueous dioxane, its solvolysis was performed in 85 wt % aqueous dioxane, and the solvolysis rates in 75 wt % aqueous dioxane were estimated from those measured in 85 wt % aqueous dioxane.[15] The rate constants and some activation parameters are shown in Table III.

TABLE III

RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE
SOLVOLYSIS OF THE 3,5-DINITROBENZOATES OF **4, 5, 6,** AND
7 IN 75 AND 85 WT % AQUEOUS DIOXANE

Ester	$k \times 10^6$, sec^{-1} 130°	140°	$\Delta H^{\pm}$, kcal/mol	$\Delta S^{\pm}$ at 130°, eu
DNB[a] of 4		1.35		
DNB[a] of 5		1.03		
DNB[a] of 6	12.5	29.1	27.0[b]	−14.3[b]
		(7.14)[c]		
DNB[a] of 7	7.20[d]	16.1[d]	25.9[b]	−18.3[b]
	(1.76)[c]	(3.95)[c]		

[a] 3,5-Dinitrobenzoate. [b] The activation parameters might involve small error, as the temperature ranges may be insufficient to establish the parameters. [c] Measured in 85 wt % aqueous dioxane. [d] Estimated from the values obtained in 85 wt % aqueous dioxane.

Discussion

A minor extent of delocalization of positive charge to the methylene carbon atom of the cyclopropane ring in the cyclopropylcarbinyl cation systems has been suggested by Sneen and coworkers on the basis of the small kinetic effect of a phenyl substituent in the 2 position of the cation.[7] As shown in the Table II, the same kinetic effect was observed in the present study. The results given in Table I, however, clearly indicate a substantial extent of delocalization of posi-

tive charge to the 2 position of the cyclopropylcarbinyl cation. Although the value of ρ (−1.48) is absolutely smaller than that expected for a benzylic cation,[16] the value is similar to that obtained in the solvolysis of *trans*-2-arylcyclopropyl tosylate (ρ −1.8). The solvolysis of this tosylate has been elucidated by a concerted ring-opening reaction mechanism.[17] Moreover, the products obtained in the solvolysis of **2c** mainly consisted of the ring-opened product, **3**.

It thus appears that, in the transition state of the solvolyses of **2a–2d**, the positive charge delocalized to a large extent to the 2 position of the cyclopropylcarbinyl cations, and that the stabilization of the positive charge by a phenyl group at this position is less effective than at a benzylic position.

As is known, a phenyl group stabilized a cation through resonance and destabilizes it inductively. The accomplishment of a sufficient π interaction between the π electrons of a phenyl ring and the vacant p orbital of a carbonium ion attached to the phenyl group requires a particular conformation in which the axes of all p orbitals must be parallel. When this conformational requirement is not satisfied, the resonance effect of a phenyl group is cancelled out by the inductive effect, resulting in a decrease in the extent of the stabilization of a carbonium ion by a phenyl group. For example, the fact that the rate of solvolysis of **9** is twice as fast as that of **10** has been rationalized by the cancellation effect.[18]

$$\text{RCH=CHCH}_2\text{CH}_2\text{OTs}$$
9, R = CH$_3$
10, R = C$_6$H$_5$
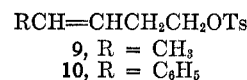
Thus, the relatively small absolute value of ρ obtained in the solvolyses of **2a–2d** could be explained reasonably by assuming that the conformation of the cyclopropylcarbinyl cation formed in the transition state of the solvolysis of **2a–2d** does not allow a sufficient π interaction between the π orbitals of the phenyl group and the p orbital of the carbonium ion.

As was mentioned earlier, the symmetrical bisected cation, the unsymmetrical bicyclobutonium ion, and the homoallylic cation have been suggested as possible conformations for the cyclopropylcarbinyl cation, and a preference for the bisected cation has been indicated in the solvolysis of 2,2- or 2,3-dimethylcyclopropylcarbinyl 3,5-dinitrobenzoate.[1] The solvolysis of 3,5-dinitrobenzoates of **4, 5, 6,** and **7** was studied to learn the effect of the introduction of a phenyl or a methyl group into the 2 or 3 position of 2-phenylcyclopropylcarbinyl cation.

Unexpectedly, the rates of solvolysis of 3,5-dinitrobenzoates of **4** and **5** were considerably slower than that of the parent compound **2c**. As was observed in an earlier investigation,[7] the rate of solvolysis of the *cis*-2-phenyl compound was slower than that of the parent nonsubstituted compound. In the solvolysis of the 3,5-dinitrobenzoate of **4** or **5**, the steric interaction between 1-methylene and *cis*-2-phenyl groups of the intermediate cation would transform the conformation of the cation into one which is unfavorable for the

(15) The ratio of solvolysis rates obtained for the 3,5-dinitrobenzoate of **6** in 75 and 85 wt % aqueous dioxane was used for the estimation.

(16) A ρ value of −3.6 was observed in the solvolysis of α-arylcyclo-propylcarbinyl *p*-nitrobenzoate.[5]

(17) C. H. Depuy, L. G. Schnack, J. W. Hausser, and W. Wiedemann, *J. Amer. Chem. Soc.*, **87**, 4006 (1965).

(18) K. L. Servis and J. D. Roberts, *ibid.*, **87**, 1331 (1965).

Table IV

Properties and Elemental Analyses of 3,5-Dinitrobenzoates of ROH

ROH	Mp, °C	Found C	Found H	Found N	Calcd C	Calcd H	Calcd N	Nmr[a–c] (multiplicity, number of protons)
1a	137	58.51	4.46	7.25	58.60	4.33	7.52	7.80–9.20 (m, 4.1), 6.43 (s, 3), 5.73 (d, 2.1)
1b	135	60.59	4.67	7.73	60.67	4.53	7.86	7.80–9.20 (m, 4.1), 7.83 (s, 3.1), 5.70 (d, 2.1)
1c	128	56.95	3.97	7.89	56.98	3.94	7.82	7.80–9.20 (m, 4.1), 5.72 (d, 2)
1d[d]	129	54.44	3.54	7.23	54.21	3.46	7.44	7.70–9.15 (m, 4.1), 5.70 (d, 1.9)
3	92	59.47	4.25	8.20	59.65	4.12	8.18	7.28 (t, 2), 4.80–5.20 (m, 1.9), 3.95–4.70 (m, 1.9)
4	144	65.93	4.34	6.56	66.02	4.34	6.70	8.25–9.00 (m, 3.1), 5.99 (m, 2.1)
5	155	65.94	4.51	6.61	66.02	4.34	6.70	6.95–8.10 (m, 3.2), 5.67 (m, 2)
6	110	60.67	4.58	7.85	60.67	4.53	7.86	8.25–9.25 (m, 3.2), 8.57 (s, 3.2), 5.53 (m, 2.1)
7	192	60.30	4.54	7.86	60.67	4.53	7.86	7.80–8.82 (m, 3), 8.7 (d, 3), 5.40 (m, 2)
8	102	49.62	3.82	10.61	49.63	3.79	10.52	8.35–9.67 (m, 5), 5.83 (d, 2)

[a] Measured in DMSO-d_6. [b] Absorptions originated in phenyl protons are omitted. [c] m = multiplet; t = triplet; d = doublet. [d] Calcd: Cl, 9.41. Found: Cl, 9.29.

delocalization of the positive charge. This transformation might be one of the factors decreasing the rate of solvolysis.

The attachment of a *cis*-methyl group to the 2 or 3 position of 2c resulted in a three- or four-fold rate increase, suggesting the delocalization of positive charge to the 2 or 3 position of the 2-phenylcyclopropylcarbinyl cation.[19] The small difference between the solvolysis rate of the 3,5-dinitrobenzoates of 4 and 5 or that between the 3,5-dinitrobenzoates of 6 and 7 implies that the conformation of cations formed from these esters is similar to the symmetrical bisected cation. Moreover, the resemblance of the activation parameters indicated in Tables II and III might suggest that the conformations of the intermediate cations generated from these 3,5-dinitrobenzoates are similar to each other.

Thus, it may be concluded that the conformation of 2-phenylcyclopropylcarbinyl cation is similar to the symmetrical bisected cation in which the positive charge is substantially delocalized to the 2 and 3 positions, and that the stabilization of the carbonium ion by the resonance effect of the 2-phenyl group is cancelled out by the inductive electron-withdrawing effect of the phenyl group.

Experimental Section

Substituted Cyclopropylcarbinyl 3,5-Dinitrobenzoates.—According to the published procedure, substituted cyclopropanecarboxylic acids were prepared by the reaction of corresponding styrene derivatives with ethyl diazoacetate followed by alkaline hydrolysis. The following acids were obtained and recrystallized from water or petroleum ether to separate the geometric isomers: *trans*-2-(*p*-methoxyphenyl)cyclopropanecarboxylic acid, mp 114° (lit.[8] mp 112–113°); *trans*-2-(*p*-methylphenyl)cyclopropanecarboxylic acid, mp 119.5° (lit.[8] mp 119.5–120.5°); *trans*-2-phenylcyclopropanecarboxylic acid, mp 93° (lit.[8] mp 92–93°); *trans*-2-(*p*-chlorophenyl)cyclopropanecarboxylic acid, mp 116° (lit.[8] mp 115.5–116.5°); 2,2-diphenylcyclopropanecarboxylic acid, mp 171.5° (lit.[9] mp 170–171°); *cis,trans*-2,3-diphenylcyclo-

propanecarboxylic acid, mp 158° (lit.[10] mp 157–158°); *trans*-2-phenyl-*cis*-2-methylcyclopropanecarboxylic acid, mp 105° (lit.[11] mp 104°); and *trans*-2-phenyl-*cis*-3-methylcyclopropanecarboxylic acid, mp 78° (lit.[12] mp 77.5°). The esters prepared from the acids were reduced to the corresponding alcohols by lithium aluminum hydride (70–80% yield). The 3,5-dinitrobenzoates were obtained by the usual method (50–60% yield) and recrystallized from a mixed solvent of petroleum ether and benzene. The properties and results of elemental analysis of the esters are shown in Table IV. The multiplet observed in high field of the nmr spectra of the 3,5-dinitrobenzoates (except that of 3) indicates that the cyclopropane ring in the esters is not opened.

Hydrolysis of 2c.—A solution of 1.710 g (0.005 mol) of 2c in 20 ml of 75 wt % aqueous dioxane was heated at 130° in an ampoule for 72–120 hr. The reaction mixture was cooled, poured into 300 ml of water, and neutralized with sodium bicarbonate. The mixture was extracted with 300 ml of ether, and the ethereal layer was dried over anhydrous magnesium sulfate. The ether was evaporated under reduced pressure. The residue was analyzed by the usual gas chromatographic technique to determine the yield and distribution of the products (column, silicon DC-550, 2 m; PEG 2M, 2.5 m). Diphenyl ether was used as an internal standard. The analysis indicated that 3[13] and 1c were the products (except for 3,5-dinitrobenzoic acid). They were isolated by preparative gas chromatography and identified by comparison of their gas chromatographic and spectroscopic data with those of authentic specimens. The following compounds expected to be formed in the hydrolysis of 2c were synthesized, but the existence of these compounds was not observed in the hydrolysis products: *cis*-2-phenylcyclopropylcarbinol, bp 134–135° (16 mm) [lit.[13] bp 137–138° (18 mm)]; α-phenylcyclopropylcarbinol, bp 76–78° (4 mm) [lit.[5] bp 75–78° (4 mm)]; and 4-phenylbut-3-en-1-ol, mp 49–51° (lit.[13] mp 36°). The distribution of the products was slightly varied with reaction time (Table V).

Table V

Variation of the Product Distribution with Reaction Time

Reaction time, hr	Conversion, %	1c, %	3, %
72	56.4	15.0	85.0
96	66.9	14.4	85.6
120	74.9	12.0	88.0

A solution of 0.403 g (0.0027 mol) of 1c and 0.576 g (0.0027 mol) of 3,5-dinitrobenzoic acid in 20 ml of 75 wt % aqueous dioxane was heated in an ampoule for 72–120 hr to study the extent of rearrangement of 1c to 3 under the hydrolysis condition. The reaction mixture was treated and analyzed in the same manner as described above. The results are shown in Table VI.

(19) The kinetic effect of 2- or 3-methyl group observed in the present study is smaller than that reported by Schleyer and Van Dine.[1] The character of the intermediate cations generated from the 2-phenyl compounds (3,5-dinitrobenzoates of 6 and 7) may be different to some extent from those formed from nonphenyl compounds. This difference may be one of the factors bringing about the smaller kinetic effect of methyl substituent.
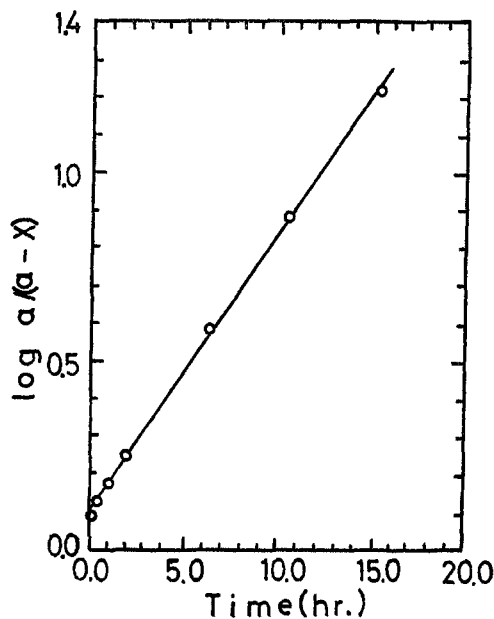
Figure 2.—Typical first-order plot for the solvolysis of **2a** in 75 wt % aqueous dioxane at 130°.

TABLE VI

THE EXTENT OF REARRANGEMENT OF **1c** TO **3** UNDER THE HYDROLYSIS CONDITION

Reaction time, hr	1c, %	3, %
72	95.8	4.2
96	93.6	6.4
120	92.8	7.2

Methanolysis of 2c.—A solution of 3.42 g (0.01 mol) of **2c** and 17.2 g (0.1 mol) of *p*-toluenesulfonic acid in 100 ml of anhydrous methanol was refluxed for 50 hr. The reaction mixture was cooled and filtered to remove the unchanged **2c**. Methanol was evaporated under reduced pressure and the residue was poured into 300 ml of water. The mixture was neutralized with sodium bicarbonate and extracted with 300 ml of ether. The ethereal layer was dried and the ether was evaporated *in vacuo*. The analysis of the products was performed in the same manner as that used in the hydrolysis of **2c**.

The gas chromatographic data indicated that the products were methyl ethers of **3** and **1c** (trace) and 3,5-dinitrobenzoic acid (76% yield). The authentic samples of the methyl ethers were synthesized independently and were used for the identification of the products.

Methyl Ether of 3.—A mixture of 14.8 g (0.1 mol) of **3** and 2.4 g (0.1 mol) of sodium hydride in 150 ml of anhydrous ether was refluxed for 3 hr. To the reaction mixture was added dropwise 28.4 g (0.2 mol) of methyl iodide. After it was refluxed for additional 3 hr, the mixture was poured into ice–water and extracted with ether. The ethereal layer was dried with magnesium sulfate and distilled to give 12.2 g (75%) of the methyl ether of **3**; bp 96–97° (20 mm); ir 1640, 990, 903 (CH=CH₂), and 1100 cm⁻¹ (OCH₃); nmr (CCl₄) τ 7.52–8.10 (m, 2, CH₂), 6.80 (s, 3, OCH₃), 5.61 (t, 1, CHOCH₃), 4.85–5.30 (m, 2, =CH₂), 3.90–4.60 (m, 1, CH=), and 2.83 (s, 5, C₆H₅).

Anal. Calcd for C₁₁H₁₄O: C, 81.44; H, 8.70. Found: C, 81.73; H, 8.89.

Methyl Ether of 1c.—The title compound was prepared by a similar method to that described above: yield 70%; bp 101–103° (18 mm); ir 1100 cm⁻¹ (OCH₃); nmr (CCl₄) τ 7.75–9.35 (m, 4, *c*-C₃H₄), 6.78 (s, 3, OCH₃), 6.66 (d, 2, CH₂O), and 2.98 (m, 5, C₆H₅).

Anal. Calcd for C₁₁H₁₄O: C, 81.44; H, 8.70. Found: C, 81.68; H, 8.73.

Kinetic Study.—The solvolysis of the 3,5-dinitrobenzoates in 75 wt % aqueous dioxane was carried out by means of the ampoule technique. The rates of solvolysis of the esters were determined using solutions 0.05 *M* in the ester and titrating the liberated 3,5-dinitrobenzoic acid with 0.05 *N* sodium hydroxide in 70 wt % aqueous dioxane to a bromthymol blue end point. The base was frequently restandardized against benzoic acid during the course of the work. The rate constants reported in Tables I, II, and III were the mean value of three runs and six or seven experimental points were taken in each run. A typical kinetic run is illustrated in Figure 2.