and thus the partial rate factors may be controlled by the rate of mixing and diffusion of the reagents. If this were indeed the case we would expect no correlations for Olah's data or at the very least entirely different behavior for these sets. This is apparently not the case. There seems to be no difference in behavior between Olah's data and the other sets studied.

Variation of *ortho* Substitution with Reagent.—Equation 29 predicts that for a constant substrate, *e.g.*, toluene

$$\log \left(\frac{p_o}{2p_p}\right)^X = m'\beta_p + h' \qquad (30)$$

where

$$m' = -0.23\sigma_{R,X} \qquad (31)$$

Thus the variation of the *ortho–para* ratio with reagent should be a linear function of β_p for any given substrate. Equation 30 does not seem to be obeyed. We may perhaps account for this at least in part in terms of a steric effect of the reagent which is constant throughout a set of substituted benzenes but varies from one reagent to another. The small value of m' expected for most substituents suggests that the predominant effect of the reagent may well be steric.

Cyclopropylcarbinyl 3,5-Dinitrobenzoate Solvolysis. 1-Ring Substituent Effect Study

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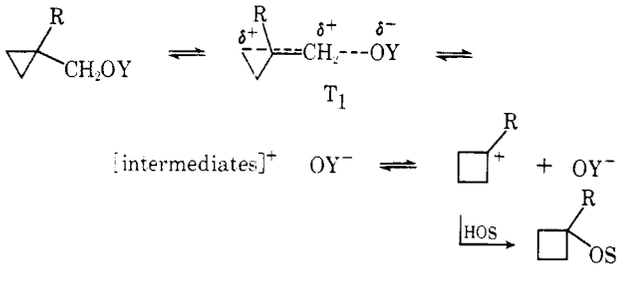
The solvolysis rates of the 3,5-dinitrobenzoate derivatives of cyclopropylcarbinol (**3**-H), 1-methylcyclopropylcarbinol (**3**-Me), 1-phenylcyclopropylcarbinol (**3**-Ph), 1-*p*-anisylcyclopropylcarbinol (**3**-An), cyclobutanol (**4**-H), 1-methylcyclobutanol (**4**-Me), and 1-phenylcyclobutanol (**4**-Ph) have been determined in 50 vol % aqueous dioxane. The relative first-order rates were found to parallel closely those for the acetolysis of the corresponding tosylate derivatives. The implications of this solvolytic behavior are discussed in terms of transition-state geometry and charge distribution.

In a recent paper,[1] a rationale was advanced explaining the insensitivity of the rate of solvolysis of cyclopropylcarbinyl tosylate to 1-ring substituents, in terms of a molecular reorganization mechanism (Scheme I) paralleling the solvolysis mechanism of similarly substituted allylcarbinyl tosylates. The lack of substituent effect upon solvolysis rate was attributed to a homoallyllike transition state, T_1, while the exclusive formation of ring expanded products was accommodated by a subsequent but greater structure reorganization, leading to a tertiarylike carbonium ion eventually captured by solvent.

SCHEME I



That a poorer leaving group in a solvolysis reaction will generate a transition state with less charge development but with greater orbital reorganization is a generally accepted postulate.[2] Furthermore, it is well established by the extensive work in the linear free-energy field[3] that substituent effects respond to variable charge development in classical SN1-type reactions. On the other hand, there is increasing evidence[4] against a simple extension of substituent effects in classical ion formation to nonclassical ion formation. Accordingly, based upon the slight influence of γ substituents upon the reactivity of allylcarbinyl substrates,[4d] one would predict little substituent effect dependency upon leaving group in the solvolysis of 1-ring-substituted cyclopropylcarbinyl derivatives.

As a test of this thinking, the solvolytic behavior of seven cyclopropylcarbinyl 3,5-dinitrobenzoate derivatives was studied. The selection of leaving group was dictated by several considerations: (a) relative to tosylates, much more slowly ionizing 3,5-dinitrobenzoates would afford a more rigorous test of the proposed insensitivity of the transition state to 1-ring substituents; (b) high-purity substrates could be prepared with good room-temperature stability; and (c) *t*-cyclobutyl derivatives could be synthesized which would permit an assessment of the substituent effect upon the proposed intermediate capture by solvent.

Results and Discussion

The kinetic data are summarized in Table I. Each of the esters was allowed to solvolyze in 50 vol % aque-

(1) D. D. Roberts, *J. Org. Chem.*, **33**, 2712 (1968).

(2) (a) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 67, 72; (b) H. M. R. Hoffman, *J. Chem. Soc.*, 6762 (1965); (c) E. R. Thornton, *J. Amer. Chem. Soc.*, **89**, 2915 (1967); and (d) C. J. Frisone and E. R. Thornton, *ibid.*, **90**, 1211 (1968).

(3) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley & Sons, Inc., New York, N. Y., 1963, Chapter 7.

(4) (a) R. A. Sneen, *J. Amer. Chem. Soc.*, **80**, 3982 (1958); (b) E. J. Corey and H. Vda, *ibid.*, **85**, 1788 (1963); (c) H. C. Brown, F. J. Chloupek, and M. H. Rei, *ibid.*, **86**, 1246 (1964); (d) K. L. Servis and J. D. Roberts, *ibid.*, **87**, 1331 (1965); and (e) M. Nikoletic, S. Borcic, and D. E. Sunko, *Tetrahedron*, **23**, 649 (1967).

TABLE I

SUMMARY OF SOLVOLYSIS RATES FOR ORGANIC 3,5-DINITROBENZOATES IN 50 VOL % DIOXANE

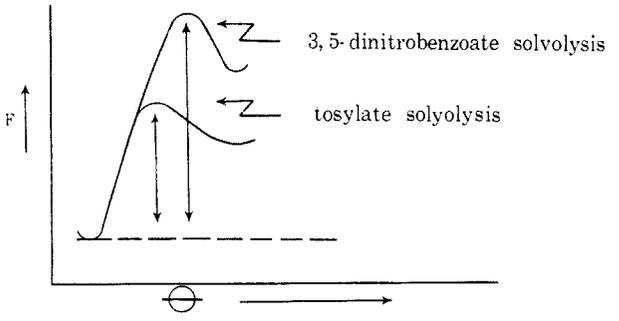
Compound	Temp, °C	k_1,[a] 10^7 sec^{-1}	$\Delta H^{\pm}$, kcal/mol	$\Delta S^{\pm}$, eu
H—(3-H)—CH_2ODNB	70.0	0.44	26.9	−14
	80.0	1.50		
	90.0	4.45		
	100.0	11.1		
Ph—(3-Ph)—CH_2ODNB	70.0	2.58	25.4	−15
	80.0	7.50		
	90.0	21.4		
	100.0	55.5		
Me—(3-Me)—CH_2ODNB	70.0	0.61	23.2	−24
	80.0	1.50		
	90.0	4.44		
	100.0	9.73		
p-An—(3-An)—CH_2ODNB	70.0	0.86	24.2	−20
	80.0	2.42		
	90.0	6.66		
	100.0	15.82		
H—(4-H)—ODNB	90.0	1.39		
Me—(4-Me)—ODNB	70.0	1.97	24.3	−17
	80.0	5.28		
	90.0	14.15		
	100.0	37.50		
Ph—(4-Ph)—ODNB	60.0	700	22.4	−11
	70.0	1,860		
	80.0	5,400		
	90.0	12,100		
$(CH_3)_2CCH_2ODNB$ **5**	90.0	0.36		
$(CH_3)_3CODNB$ **6**	70.0	75	28.7	2
	80.0	270		
	90.0	810		

[a] The uncertainties varied from 0.5 to 1.8 standard deviation units from the mean.

ous dioxane and the course of reaction was followed by titrating the liberated 3,5-dinitrobenzoic acid. The reactions followed strictly first-order kinetic law up to at least 75% conversion and most furnished, within experimental error,[5] 100% of the theoretical amount of acid present. That cyclopropylcarbinyl 3,5-dinitrobenzoate derivatives hydrolyze by an uncatalyzed, alkyl-oxygen fission reaction has been established by Schleyer's work.[6] Additional support for this conclusion is evidenced in this work by the strict adherence of the rates to first-order kinetics, and the enhanced reactivity of the tertiary substrates.[7]

In Table II, the relative rates of selected 3,5-dinitrobenzoate and tosylate derivatives are listed. It is readily apparent that the 1-ring substituent effect is nearly insensitive to leaving group. This finding is even more marked when one notes that the ~500,000-fold difference in reactivity between the 3,5-dinitrobenzoate series and the tosylate series is equivalent to an approximately 9 kcal/mol difference in $\Delta\Delta F^{\pm}$. As shown diagrammatically in Scheme II, a $\Delta\Delta F^{\pm}$ value of this magnitude would reflect greater orbital

SCHEME II



change for the 3,5-dinitrobenzoate series and, therefore, to the extent that the substituent effect is dependent upon orbital type and/or geometry, a significant change in the relative rate values listed in Table II would be expected. The fact that this is not the case is consistent with mechanism proposed in Scheme I.

TABLE II

RELATIVE SOLVOLYSIS RATES OF CYCLOPROPYLCARBINYL AND CYCLOBUTYL DERIVATIVES

Compound	k_{rel}[a] (X = ODNB)	k_{rel}[b,c] (X = OTS)
H—(3-H)—CH_2X	1.0	1.0
Me—(3-Me)—CH_2X	4.9	4.9
Ph—(3-Ph)—CH_2X	1.0	2.0
p-An—(3-An)—CH_2X	1.5	3.1
H—(4-H)—X	0.31	0.008[d]
Me—(4-Me)—X	3.2	
Ph—(4-Ph)—X	27,000	
$(CH_3)_2CHCH_2X$ **5**	0.06	
$(CH_3)_3C$ **6**	180	

[a] Relative rates in 50 vol % aqueous dioxane at 90°. [b] Relative rates in acetic acid at 30°. [c] Taken from data of ref 1. [d] Relative rate in acetic acid at 90°, taken from data of H. C. Brown and G. Ham, *J. Amer. Chem. Soc.*, **78**, 2735 (1956).

Examination of the relative rate data for the substituted cyclobutyl compounds is also instructive. Although a methyl group produces only a small rate acceleration, the response to the 1-phenyl substituent reveals the greater stability of the benzyllike cation compared to the nonclassical carbonium ion proposed[8] for the four-membered ring. This result clearly demonstrates that the transition state for the solvolysis of **3**-Ph has little resemblance to the 1-phenylcyclobutyl cation.

Interpretation of activation parameters in a mixed solvent system is difficult;[9] however, the limited struc-

(5) The more slowly reacting cyclobutyl and isobutyl 3,5-dinitrobenzoates were followed only up to 20 and 10% reaction, respectively.

(6) P. von R. Schleyer and G. W. Van Dine, *J. Amer. Chem. Soc.*, **88**, 2321 (1966).

(7) The relative rates are **4**-Ph, 450,000; **6**, 3000; **4**-H, 5.2; **5**, 1.0.

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

(9) See ref 3, p 397 ff.

tural difference between isomeric substrates minimizes solvation differences. The kinetic data reveal that the ionization of **4**-Me is moderately influenced by methyl group assistance. Roberts has speculated[10] that the ionization of 1-methylcyclobutyl chloride is accompanied by significant but not complete reduction of bicyclobutonium ion character. In view of this reduced molecular reorganization, it is not unexpected that the partitioning of the free energy of activation for **4**-Me is similar to that for **3**-Me (see Table I).

On the other hand, the kinetic data reveal that the ionization of **4**-Ph is greatly influenced by phenyl group assistance, suggesting a transition state with appreciable benzyl ion character, while the ionization of **3**-Ph is unassisted by the phenyl group, supporting a transition state with considerable homoallylic ion character. It is, therefore, to be expected that **3**-Ph would ionize with a greater decrease in $\Delta S^{\ddagger}$ than **4**-Ph. The entropy values reported in Table I for the hydrolysis of **3**-Ph and **4**-Ph are in accord with these suggested differences in transition-state structure.

Experimental Section

Melting points were not corrected for stem exposure and were taken on a Mel-Temp apparatus. Spectra were determined on a Varian A-60A spectrophotometer. All microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Cyclopropylcarbinyl 3,5-Dinitrobenzoate (3-H).—Recrystallized 3,5-dinitrobenzoyl chloride (4.62 g, 20 mmol) was added in 10 min to a solution of cyclopropylcarbinol (1.48 g, 20 mmol) in 15 ml of pyridine (Baker Analyzed Reagent) maintained at 0°. After standing 2 hr at room temperature, the yellow mixture was poured, with vigorous stirring, into 70 ml of ice water. The resulting ester was collected by filtration, stirred 20 min with 100 ml of 10% sodium carbonate solution, recollected by filtration, and air dried to yield 2.8 g (53%) of crude ester (mp 99–102°). Three recrystallizations from 4:1 petroleum ether (bp 30–60°)–benzene gave the ester **3**-H: mp 100–101° (lit.[11] mp 101.2–101.4°); nmr (CCl_4) δ 0.6 (complex multiplet, 5 cyclopropyl H), 4.3 (d, J = 8 Hz, 2 methylene H), and 9.1 ppm (m, 3 aryl H).

1-Methylcyclopropylcarbinyl 3,5-dinitrobenzoate (3-Me) was prepared from 1-methylcyclopropylcarbinol[12] as described above in 57% yield: mp [after three recrystallizations from 4:1 petroleum ether (bp 30–60°)–benzene] 85–86° (lit.[13] mp 85.5–85.7°); nmr (CCl_4) δ 0.58 (m, 4 cyclopropyl H), 1.38 (s, 3 methyl H), 4.27 (s, 2 methylene H), and 9.1 ppm (m, 3 aryl H).

1-Phenylcyclopropylcarbinyl 3,5-dinitrobenzoate (3-Ph) was prepared from 1-phenylcyclopropylcarbinol[14] as described above in 68% yield: mp [after three recrystallizations from 2.3:1 petroleum ether (bp 30–60°)–benzene] 106–107°; nmr (C_6H_6) δ 0.97 (s, 4 cyclopropyl H) and 4.38 ppm (s, 2 methylene H).

Anal. Calcd for $C_{17}H_{14}N_2O_6$: C, 59.65; H, 4.12; N, 8.18. Found: C, 59.83; H, 4.02; N, 8.19.

1-*p*-Anisylcyclopropylcarbinyl 3,5-dinitrobenzoate (3-An) was prepared from 1-*p*-anisylcyclopropylcarbinol[1] as described above in 73% yield: mp [after three recrystallizations from 2.3:1 petroleum ether (bp 30–60°)–benzene] 89–90°; nmr (C_6H_6) δ 0.88 (s, 4 cyclopropyl H), 3.57 (s, 3 methoxyl H), and 4.28 ppm (s, 2 methylene H).

Anal. Calcd for $C_{18}H_{16}N_2O_7$: C, 58.00; H, 4.32; N, 7.56. Found: C, 58.21; H, 4.29; N, 7.40.

Cyclobutyl 3,5-Dinitrobenzoate (4-H).—Cyclobutanol (1.45 g, 20 mmol) was added rapidly to a solution of 3,5-dinitrobenzoic acid (4.24 g, 20 mmol) and *p*-toluenesulfonyl chloride (7.63 g, 40 mmol) in 130 ml of pyridine (Baker Analytical Reagent grade) cooled in an ice–water bath. After 1 hr at ice–water bath temperature, the mixture was hydrolyzed by addition to 400 ml of ice–water with vigorous stirring. The resulting ester was separated by filtration, stirred 20 min with 100 ml of 10% sodium carbonate solution, reseparated by filtration, air dried, and recrystallized from 2.5:1 petroleum ether (bp 30–60°)–benzene to yield 3.0 g (56%) of the ester (mp 105–107°). Three additional recrystallizations yielded the analytical sample of **4**-H (mp 108–109°).

Anal. Calcd for $C_{11}H_{10}N_2O_6$: C, 49.63; H, 3.78; N, 10.52. Found: C, 49.81; H, 3.81; N, 10.50.

1-Methylcyclobutyl 3,5-dinitrobenzoate (4-Me) was prepared from 1-methylcyclobutanol[12] as described above for **4**-H in 82% yield: mp [after three recrystallizations from 2.5:1 petroleum ether (bp 30–60°)–benzene] 133.0–133.5°; nmr ($CHCl_3$) δ 1.72 (s, 3 methyl H), and 2.0 and 2.4 (m, 6 cyclobutyl H), and 9.1 ppm (m, 3 aryl H).

Anal. Calcd for $C_{12}H_{12}N_2O_6$: C, 51.43; H, 4.31; N, 9.99. Found: C, 51.42; H, 4.50; N, 9.79.

1-Phenylcyclobutyl 3,5-dinitrobenzoate (4-Ph) was prepared from 1-phenylcyclobutanol[12] as described previously for **3**-H in 50% yield: mp [after three recrystallizations from 3:1 petroleum ether (bp 30–60°)–benzene] 107–108°; nmr (C_6H_6) δ 1.6 (complex multiplet) and 2.6 ppm (complex multiplet).

Anal. Calcd for $C_{17}H_{14}N_2O_6$: C, 59.65; H, 4.12; N, 8.18. Found: C, 59.85; H, 4.09; N, 8.18.

Isobutyl 3,5-dinitrobenzoate (5) was prepared from isobutyl alcohol as described previously for **3**-H in 86% yield: mp [after recrystallization from 6:1 petroleum ether (bp 30–60°)–benzene] 85.5–86° (lit.[15] mp 86°).

***t*-Butyl 3,5-dinitrobenzoate (6)** was prepared from *t*-butyl alcohol as described previously for **4**-H in 55% yield: mp [after recrystallization 6:1 petroleum ether (bp 30–60°)–benzene] 142–143° (lit.[16] mp 142°).

Rate measurements were accomplished by the ampoule technique. The titrating solution was 0.020 N sodium hydroxide and the indicator was bromothymol blue.

Solvent.—Dioxane was purified according to method of Fieser.[17]

Treatment of Kinetic Data.—The activation parameters were obtained by IBM 1620 computer regresson analysis of $\ln k/T$ *vs.* $1/T$.

Registry No.—**3**-H, 10364-97-3; **3**-Me, 10364-98-4; **3**-Ph, 18592-76-2; **3**-An, 18592-77-3; **4**-H, 18592-78-4; **4**-Me, 18592-79-5; **4**-Ph, 18592-80-8; **5**, 10478-01-0; **6**, 5342-97-2.

Acknowledgment.—This work was supported in part by the Petroleum Research Fund of the American Chemical Society. This support is gratefully acknowledged.

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