molecules are produced in close proximity (*i.e.*, the same solvent cage in solution) in the 1,2-dioxetane decompositions.

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Cyclopropyl Participation in the Solvolysis of 2-Cyclopropylethyl Brosylates[1]

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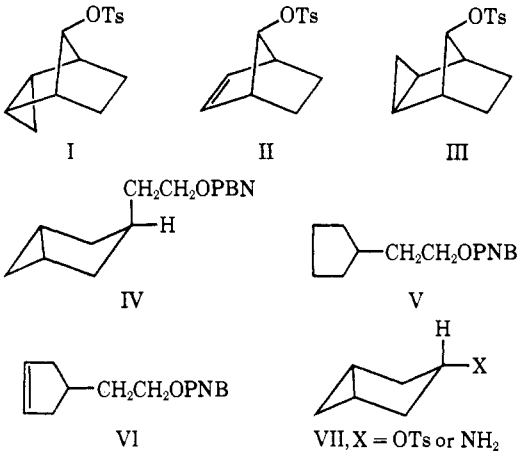
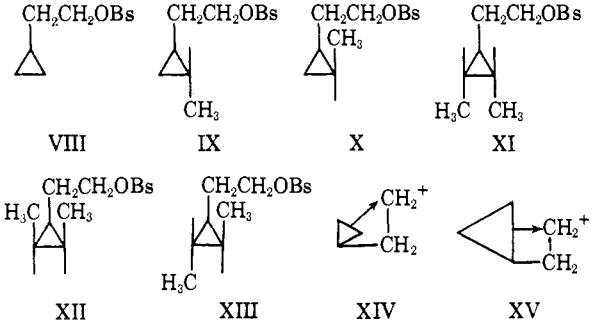
Abstract: Rates of solvolysis are reported for 2-cyclopropylethyl brosylate, and its *cis*- and *trans*-2′-methyl and 2′,3′-dimethyl derivatives, in formic acid containing sodium formate. The results indicate that cyclopropyl can participate, but less efficiently than vinyl.

It has recently been reported[2,3] that the cyclopropane analog (I) of *trans*-7-norbornenyl tosylate (II) solvolyses 10^{14} times faster than the isomer III, and 10^{3} times faster than II itself. This was taken as evidence that cyclopropane acts as a more effective neighboring group than a double bond, a claim which has led to widespread interest in the reactions of analogous cyclopropyl derivatives.[4-6] Thus Sargent, *et al.*,[4] found that the rate of solvolysis of IV (PNB = *p*-nitrobenzoyl) is almost the same as that of the cyclopentane analog V, and 87-fold less than that of the cyclopentene analog VI; this observation certainly seems to suggest that cyclopropane is inherently a less effective neighboring group than ethylene and that the exceptional activating effect of cyclopropane in the case of I is due to other factors, *e.g.*, the fact that the geometry of I is ideally suited to participation, and to possible relief of ring strain. There is also the long-standing controversy concerning participation in the solvolytic and deamination reactions of VII.[7]



Here we wish to report some studies of cyclopropyl participation, based on rates of solvolysis of 2-cyclopropylethyl brosylate (VIII) and its *cis*- and *trans*-2′-methyl and 2′,3′-dimethyl derivatives (IX–XIII). If the cyclopropyl group does not participate, all these compounds would be expected to react at similar rates, because the methyl groups are too far away from the reaction center to have any significant field or inductive effects. If, however, the reaction takes place *via* nonclassical π-complex analogs such as XIV, methyl substitution in the 2′ and 3′ positions should enhance the rate. A similar argument has been used very effectively by Schleyer[8] in a study of analogous participation in the solvolysis of cyclopropylcarbinyl derivatives.



(1) This work was supported by the Air Force Office of Scientific Research through Grant No. AF-AFOSR-1050-67. A preliminary account of some of this work has appeared: M. J. S. Dewar and J. M. Harris, *J. Amer. Chem. Soc.*, 90, 4468 (1968). Full details will be found in a thesis by J. M. Harris, Ph.D. Dissertation, The University of Texas at Austin, 1969.

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(3) M. A. Battiste, C. L. Deyrup, R. E. Pincock, and J. Haywood-Farmer, *ibid.*, **89**, 1954 (1967).

(4) G. D. Sargent, R. L. Taylor, and W. F. Demisch, *Tetrahedron Lett.*, **18**, 2275 (1968).

(5) M. A. Eakin, J. Martin, and W. Parker, *Chem. Commun.*, 956 (1967).

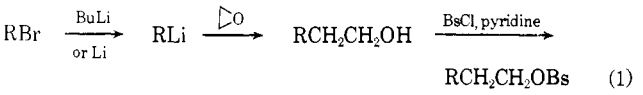
(6) Y. E. Rhodes and T. Takino, *J. Amer. Chem. Soc.*, 90, 4470 (1968).

(7) See H. Tanida, *Accounts Chem. Res.*, **1**, 239 (1968).

(8) P. von R. Schleyer and G. W. Van Dine, *J. Amer. Chem. Soc.*, **88**, 2322 (1966).

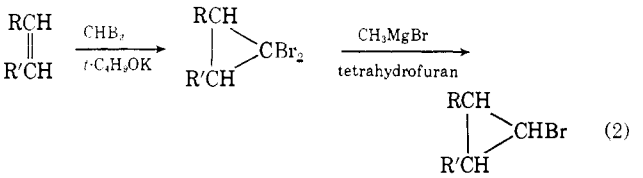
Procedure

The required esters VIII–XIII were prepared from the bromocyclopropanes as follows (R = cyclopropyl; Bs = *p*-bromobenzenesulfonyl)



(1)

Bromocyclopropane was obtained from Aldrich Chemical Co., while the methyl derivatives were prepared from propene or butene as follows (R = R′ = CH_3 or H)



(2)

Propene and *cis*-2-butene gave mixtures of isomers corresponding to (IX + X) and (XI + XII), respectively; these were separated at the penultimate stage (cyclopropylethanol) by preparative glc.

It was established that the conversion of the bromides to the ethanols *via* the lithio derivatives took place with complete retention of configuration; when the lithio derivative was prepared from the bromo derivative with metallic lithium, the product was formed with only partial retention of configuration. This result suggests that the lithium reaction involves intermediate pyramidal cyclopropyl radicals that invert only relatively slowly; details have been published elsewhere.[9]

Rates of solvolysis were measured spectrophotometrically in formic acid containing a slight excess of sodium formate; in the absence of sodium formate, secondary acid-catalyzed reactions lead to opening of the cyclopropane ring. Products were identified by their glc retention times and nmr spectra.

The reactions followed first-order kinetics accurately throughout two or more half-lives. The rate constants reported are averages of duplicate runs and are thought to be accurate to ±3%.

Results and Discussion

The rate constants and relative rates of solvolysis (*i.e.*, appearance of NaOBs) for VIII–XIII, and for ethyl brosylate, are listed in Table I. It is known[10] that the solvolysis of VIII gives a complex mixture of rearrangement products in addition to unrearranged ester; since we are interested only in the first step of the reaction, the proportions of the various rearrangement products are not very relevant. However the amount of unrearranged ester is of relevance since this should be formed if solvolysis takes place without participation by cyclopropyl, through S_N2 attack by solvent on the primary CH_2OBs group. Table II shows the results of product analyses for the solvolyses of VIII and IX: since cyclopropanes are known to react slowly with formic acid to give derivatives of 1-propanol,[6] the analyses were carried out after three half-lives (90% conversion) to minimize this side reaction.

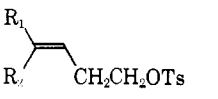
Table I. First-Order Rate Constants (k_1) for the Solvolysis of Brosylates in Anhydrous Formic Acid at 75°

Compd	$k_1 \times 10^5$, sec^{-1}	Relative rate
Ethyl brosylate	4.26	1.00
VIII	3.94	0.93
IX	13.80	3.24
X	5.65	1.33
XI	15.50	3.64
XII	10.90	2.56
XIII	13.30	3.12

Table II. Products from the Formolysis of VIII and IX

Compd	Unrearranged formate, %	Rearranged formate, %
VIII	64	36
IX	49	51

As can be seen from Table I, methyl substitution does lead to a very significant increase in the rate of solvolysis, especially in the case of methyl groups *trans* to the side chain. This must mean that cyclopropyl does participate in the reaction, at least in the case of the methyl derivatives (see the first part of this article). The effect is, however, much smaller than that observed in the corresponding derivatives of 4-hydroxy-1-butene.[11] Here even the parent compound XVIa solvolyzed 3.7 times faster than *n*-butyl tosylate (XVII), while the *cis* (XVIb) and *trans* (XVIc) methyl derivatives showed rate enhancements of 165 and 770, respectively, over XVII. These results show very clearly that cyclopropyl is much less effective than vinyl as a neighboring group, in agreement with the earlier work referred to above.[4–6,9]



XVIa, $R_1 = R_2 = H$
b, $R_1 = H$; $R_2 = CH_3$
c, $R_1 = H$; $R_2 = CH_3$

$CH_3CH_2CH_2CH_2OTs$

XVII

Normally one cannot draw any convincing conclusions from differences in rate as small as those between the esters listed in Table I; there are, however, reasons for believing that this may be one of the rare exceptions. An enormous amount of work has been carried out on the solvolysis of alkyl derivatives.[12] One of the most striking features of this is the extraordinary constancy in the rates of solvolysis of compounds where the structure in the immediate vicinity of the reaction center is the same. Thus the rates of solvolysis of the 2-bromo-*n*-alkanes from 2-propyl through 2-octyl, in 60% aqueous ethanol at 80°, vary by less than 10% from the mean, and many other similar examples could be cited. There is no reason to suppose that the same would not be true for VIII–XIII if cyclopropyl were not participating; the data in Table I therefore provide very strong evidence for such

(9) M. J. S. Dewar and J. M. Harris, *J. Amer. Chem. Soc.*, **91**, 3652 (1969).

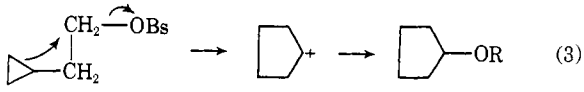
(10) R. R. Sauers and R. W. Ubersax, *J. Org. Chem.*, 31, 495 (1966).

(11) K. L. Servis and J. D. Roberts, *J. Amer. Chem. Soc.*, **87**, 1331 (1965).

(12) See, *e.g.*, A. Streitwieser Jr., *Chem. Rev.*, **56**, 571 (1956); C. K. Ingold, "Structure and Mechanism in Organic Chemistry," G. Bell & Sons Ltd., London, England, 1953, Chapter VII.

participation. This conclusion is further supported by the extensive formation of rearranged products (Table II); since primary carbonium ions are unstable, any unassisted solvolysis should take place through SN2 attack by the solvent and so should lead exclusively to unrearranged products. The following arguments are therefore based on the assumption that the differences in rate in Table I are mechanistically significant.

Participation might involve a synchronous ring opening with formation of a cyclopentyl cation, the relief of strain in the cyclopropane ring acting as a driving force; *i.e.*



(3)

If, however, this were so, we would have to assume that the unrearranged ester is formed entirely through SN2 reaction with the solvent, and as indicated above, such a process should take place at similar rates for VIII and IX. The proportions of unrearranged ester in these two cases (Table II) would then correspond to a ratio of overall rates of solvolysis for IX and VIII of 1.3:1; the observed ratio is much greater. One must conclude that the initial reaction of IX leads in part to an intermediate which in turn reacts with solvent to give both rearranged and unrearranged products; a π complex analog such as XIV seems a likely candidate.

Even if we accept this, however, there are still two alternative possibilities, depending on which bond in the ring participates; the intermediate could be either XIV or XV. In either case there will of course be steric difficulties if methyl is *cis* to the side chain; one can therefore account equally well on either basis for the fact that X solvolyses more slowly than IX.

The results for the dimethylcyclopropyl derivatives XI–XIII do, however, seem to allow a distinction to be drawn between XIV and XV. If the intermediate were XV, the effects of successive methyl groups on the rate should be additive, *i.e.*, the difference in rate between VIII and IX should be the same as that between IX and XI, and the difference between VIII and X should be the same as that between X and XII. The values of Table I do not follow this pattern at all.

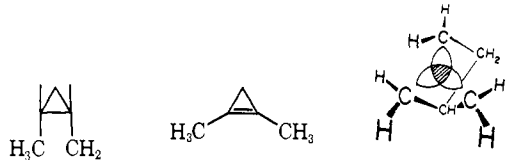
If, on the other hand, the intermediate is XIV, the effect of methyl groups on its stability should be additive, and their effect on the rate consequently multiplicative; thus in the case of *cis* methyl, the ratios of rate constants k(X):k(VIII) and k(XII):k(X) should be equal, assuming that the reaction takes place entirely by cyclopropyl participation *via* XIV. The ratios (Table I) are 1.43 and 1.93, respectively; clearly they follow the expected pattern, and the fact that they are not equal could be attributed to a concomitant SN2 process whose rate should be the same for VIII, X, and XII. Indeed, if the SN2 rates are the same, with pseudounimolecular rate constant k, the values in Table I would fit the multiplicative relation exactly if

$$k = 3.1 \times 10^{-5}\ \text{sec}^{-1} \qquad (4)$$

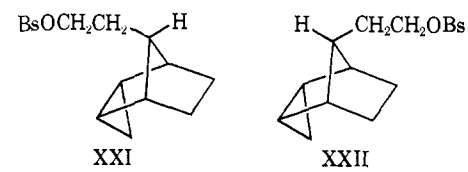
Admittedly k cannot be quite as large as this since the results in Table II show that one-third of VIII solvolyses with rearrangement, *i.e.*, by some process other than SN2 attack by solvent; this would imply that $k \leqslant 2.6 \times 10^{-5}\ \text{sec}^{-1}$. However, the fact that VIII solvolyses more slowly than ethyl brosylate certainly suggests that a large fraction undergoes unassisted solvolysis; the unassisted reaction of VIII should be retarded by the inductive field effect of cyclopropyl, the bond between it and the adjacent methylene being approximately of sp^3–sp^2 type.[13]

We are left with the problem of explaining the rates for the *trans* derivatives IX and XI, which at first sight seem to fit neither the additive nor the multiplicative relation. However, a reasonable explanation can be given in terms of steric repulsion between the methyl groups in XI, provided that the intermediate is XIV rather than XV.

Recent SCF—MO calculations[14] have indicated that the strain energy of *cis*-1,2-dimethylcyclopropane (XVIII) is considerably greater than that of cyclopropane, due to mutual replusion between the two methyl groups. In 1,2-dimethylcyclopropene (XIX) the methyl groups are further apart than in XVIII; the calculations indicate that the difference in strain energy between XIX and cyclopropene should be correspondingly less than that between XVIII and cyclopropane. Conversion of XIX to XVIII should then be more difficult than the conversion of cyclopropene to cyclopropane, since in the former case the reaction leads to an increase in methyl repulsion. This indeed is the case. The heat of hydrogenation of XIX is much less than that of cyclopropene, the difference being much greater than one would expect from analogy with open chain olefins.[15] Now in forming XIV from VIII, the methylene groups in the ring will have to rotate somewhat in order to allow the intervening σ MO to overlap with the AO of the terminal methylene group (see XX). In the case of XI, such a rotation will force the methyl groups closer together and so increase the repulsive strain. This could easily counterbalance any electronic effects of the second methyl group and so account for the fact that XI solvolyses only a little faster than IX. Note that this effect can selectively hinder the solvolysis of XI *only* if the intermediate is XIV; if it were XV, a corresponding rotation would increase the distance between the methyl groups.



XVIII XIX XX



XXI XXII

(13) Such an inductive effect presumably accounts for the fact that 2-phenylethyl tosylate solvolyses 2.68 times more slowly than ethyl tosylate, in acetic acid at 75°: S. Winstein and R. Heck, *J. Amer. Chem. Soc.*, 78, 4801 (1956).

(14) N. C. Baird and M. J. S. Dewar, *ibid.*, 89, 3966 (1967).

(15) R. B. Turner, P. Goebel, B. J. Mallon, W. von E. Doering, J. F. Coburn, Jr., and M. Pomerantz, *ibid.*, 90, 4315 (1968); personal communication from Professor W. von E. Doering.

A similar effect could of course also operate in the case of XII, this time leading to a decrease in methyl repulsion with a consequent increase in rate. It was pointed out above that the ratio k(XII):k(X) is greater than k(X):k(VIII), and that the difference seemed rather too large to be entirely due to a concomitant SN2 reaction.

These conclusions are supported by some very recent observations by Muneyuki, Yano, and Tanida,[16] who have found that the rate of solvolysis of the *syn* ester XXI in 2,2,2-trifluoroethanol at 75° is three times that of the *anti* isomer XXII, implying some participation by the cyclopropane ring. No such rate enhancements have been observed in related open chain systems. The behavior of XXI therefore seems to support the suggestion that the high reactivity of I is due largely to relief of ring strain in forming the intermediate nonclassical ion (analogous to XV), since the same factor could operate in the case of XXI.

Experimental Section

2-(*cis,trans*-2′,3′-Dimethylcyclopropyl)ethyl *p*-Bromobenzenesulfonate. Reduction of *cis,trans*-2,3-dimethyl-1,1-dibromocyclopropane[17] (0.055 mol) by treatment with methylmagnesium bromide (0.055 mol) in tetrahydrofuran[18] followed by hydrolysis gave *cis,trans*-2,3-dimethyl-1-bromocyclopropane as a colorless liquid, bp 111°, in 64% yield: proton nmr spectrum (CCl_4) multiplets at τ 7.36 (1 H), 8.86 (6 H), and 9.28 (2 H). This bromide (20.2 g, 0.135 mol) was added to a suspension of powdered lithium (2.44 g, 0.25 g-atom) in dry ether (50 ml) and ethylene oxide (15.3 g, 0.35 mol) passed into the filtered (under argon) solution at 0°. After hydrolysis, 2-(*cis,trans*-2′,3′-dimethylcyclopropyl)ethanol was isolated as a viscous liquid and purified by preparative glc (Carbowax) (9.1 g, 59%): bp 88–89° (15 mm); proton nmr spectrum (CCl_4) triplet at τ 6.41 (J = 6.5 Hz, 2 H), quartet at 8.49 (J = 6.5 Hz, 2 H), doublet at 8.96 (J = 6.0 Hz, 6 H), multiplet 9.2–10.0 (3 H). *p*-Bromobenzenesulfonyl chloride (13.8 g, 0.054 mol) was added to a solution of the alcohol (5.6 g, 0.049 mol) in dry pyridine (20 ml) at −5°. After hydrolysis, the *p*-bromobenzenesulfonate was isolated with chloroform and recrystallized from pentane at low temperatures until the ir band at 1730 cm^{-1} disappeared (three to four recrystallizations). The resulting very viscous liquid (8.4 g, 51%) showed bands in the infrared at 1190 and 1380 cm^{-1} (brosylate); proton nmr spectrum (CCl_4) singlet at τ 2.27 (4 H); triplet at 5.92 (J = 6.5 Hz, 2 H), quartet at 8.36 (J = 6.5 Hz, 2 H), multiplet 8.9–10.0, including doublet (methyl) at 9.2 (9 H).

Anal. Calcd for $C_{13}H_{17}O_3SBr$: C, 46.85; H, 5.14. Found: C, 46.83; H, 4.53.

2-(*cis*-2′-Methylcyclopropyl)ethyl *p*-Bromobenzenesulfonate. Reduction of 1,1-dibromo-2-methylcyclopropane as before gave a mixture of *cis*- and *trans*-1-bromo-2-methylcyclopropanes which could be separated by glc (*cis*/*trans* ratio, 1.9) and distinguished by the chemical shift of the proton adjacent to bromine (*cis*, τ 7.0; *trans*, 7.5). The mixture of bromides was converted as above to a mixture of *cis*- and *trans*-2-(2′-methylcyclopropyl)ethanols and the mixture was separated by preparative glc (Carbowax). The isomers were identified by comparison with authentic specimens prepared from the separated bromides by treatment with methyllithium followed by ethylene oxide, a reaction which takes place with complete retention of configuration:[9] proton nmr spectra (CCl_4), *cis* isomer, singlet at τ 5.14 (1 H), triplet (J = 6.5 Hz) at 6.40 (2 H), quartet (J = 6.5 Hz) at 8.50 (2 H), doublet (J = 3 Hz) at 9.00 (3 H), multiplet at 9.1–9.65 (4 H); *trans* isomer, singlet at 5.27 (1 H), triplet (J = 6.5 Hz) at 6.42 (2 H), quartet (J = 6.5 Hz) at 8.58 (2 H), doublet (J = 5 Hz) at 8.95 (3 H), multiplet 9.2–10.0 (4 H). The *cis* alcohol was converted as before to the *p*-bromobenzenesulfonate which formed a colorless viscous liquid: proton nmr spectrum (CCl_4), singlet at 2.32 (4 H), triplet (J = 6.5 Hz) at 5.94 (2 H), quartet (J = 6.5 Hz) at 8.45 (2 H), doublet (J = 4.5 Hz) at 9.02 (3 H), multiplet at 9.3–10.0 (4 H).

Anal. Calcd for $C_{12}H_{15}O_3SBr$: C, 45.14; H, 4.74. Found: C, 45.30; H, 4.84.

2-(*trans*-2′-Methylcyclopropyl)ethyl *p*-bromobenzenesulfonate was prepared as above from the corresponding alcohol: proton nmr spectrum (CCl_4), singlet at τ 2.31 (4 H), triplet (J = 6.5 Hz) at 5.92 (2 H), quartet (J = 6.5 Hz) at 8.38 (2 H), doublet (J = 3 Hz at 9.06 (3 H), multiplets at 9.1–9.5 (3 H) and 10.20–10.35 (1 H).

Anal. Calcd for $C_{12}H_{15}O_3SBr$: C, 45.14; H, 4.74. Found: C, 45.11; H, 4.82.

2-(*cis,cis*-2′,3′-Dimethylcyclopropyl)ethyl *p*-Bromobenzenesulfonate. Reduction as before of 1,1-dibromo-*cis*-2,3-dimethylcyclopropane gave a mixture of *cis,cis*- and *trans,trans*-2,3-dimethyl-1-bromocyclopropanes which could be separated by glc (*cis*/*trans*, 3:1): proton nmr spectrum (CCl_4) of *cis,cis* isomer, multiplets at τ 6.83 (1 H) and 8.98 (8 H); of *trans,trans* isomer, multiplets at 7.82 (1 H) and 8.90 (8 H). Treatment of the *cis,cis* isomer with lithium and ethylene oxide as before gave a mixture of 2-(*cis,cis*-2′,3′-dimethylcyclopropyl)ethanol (54%) and 2-(*trans,trans*-2′,3′-dimethylcyclopropyl)ethanol (46%), separated by preparative glc (Carbowax), while analogous treatment of the *trans,trans*-dimethylbromocyclopropane gave the *cis,cis*-alcohol (31%) and the *trans,trans* alcohol (69%). When the lithio derivatives were prepared using methyllithium instead of lithium, the alcohols were formed with complete retention of configuration:[9] proton nmr spectrum (CCl_4) of *cis* alcohol, singlet at τ 5.16 (1 H), triplet (J = 6.5 Hz) at 6.42 (2 H), quartet (J = 6.5 Hz) at 8.53 (2 H), multiplet at 8.9–9.5 (9 H); of *trans* alcohol, singlet at 5.26 (1 H), triplet (J = 6.5 Hz) at 6.42 (2 H), quartet (J = 6.5 Hz) at 8.55 (2 H), doublet (J = 5 Hz) at 8.97 (6 H); multiplet at 9.2–10.2 (3 H). The *cis* alcohol was converted as before to the *p*-bromobenzenesulfonate, also a viscous liquid.

Anal. Calcd for $C_{13}H_{17}O_3SBr$: C, 46.85; H, 5.14. Found: C, 47.31; H, 5.23.

2-(*trans,trans*-2′,3′-Dimethylcyclopropyl)ethyl *p*-Bromobenzenesulfonate. Prepared as before from the *trans* alcohol, the *p*-bromobenzenesulfonate formed a colorless viscous liquid.

Anal. Calcd for $C_{13}H_{17}O_3SBr$: C, 46.85; H, 5.14. Found: C, 47.49; H, 5.37.

2-Cyclopropylethyl *p*-Bromobenzenesulfonate. Prepared as before from the alcohol[19] the *p*-bromobenzenesulfonate was obtained[19] as a colorless viscous liquid: proton nmr spectrum (CCl_4) singlet at τ 2.25 (4 H), triplet (J = 6.5 Hz) at 5.89 (2 H), quartet (J = 6.5 Hz) at 8.42 (2 H), multiplet at 9.0–10.1 (5 H).

Anal. Calcd for $C_{11}H_{13}O_3SBr$: C, 43.29; H, 4.29. Found: C, 43.36; H, 4.49.

Purification of Formic Acid.[20] Formic acid (Eastman, 97%) was stirred with excess boric anhydride for 1 week and distilled through a 3-ft Vigreux column, bp 33–34° (45 mm). Karl Fischer titration indicated <0.1% water.

Rate Measurements. Formic acid (10 ml) was placed in a two-necked 25-ml flask with septum and condenser sealed with a mercury bubbler in a thermostat at 75 ± 0.05°. Sodium carbonate (0.0222 g) was added to give a 0.042 M solution of sodium formate, followed by sufficient brosylate to give a 0.04 M solution. Aliquots (0.6 ml) were withdrawn at intervals and quenched in ice water. The aliquot (0.5 ml) was placed in a 10-ml volumetric flask, neutralized with standardized sodium hydroxide solution (5 ml), and filled to the mark with saturated sodium bicarbonate solution. The contents of the flask were extracted with three 5-ml portions of carbon tetrachloride, centrifuged, and analyzed spectrophotometrically (265 mμ) for sodium *p*-bromobenzenesulfonate. A Beer's law plot was linear over the concentration range. The reactions were followed to at least 75% conversion and infinity points agreed with theory to ±2%. The neutralization–extraction procedure was necessary since the solutions became colored toward the end of the reaction. Rate constants were calculated by a least squares procedure, using the CDC 6600 computer at the University of Texas Computation Center and a program written by Dr. J. Hashmall.

Product Determinations. The amounts of unrearranged formates from the solvolysis of 2-cyclopropylethyl and 2-(*trans*-2′-methylcyclopropyl)ethyl *p*-bromobenzenesulfonates were determined by extracting the product with pentane followed by glc on SE-30–Chromosorb P at 95°, and by carrying out the reactions in nmr tubes and observing the signal for the cyclopropyl protons. The initial concentrations of alkyl brosylate and sodium brosylate were 0.04 and 0.042 M, respectively.

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(18) D. Seyferth and B. Prokai, *J. Org. Chem.*, **31**, 1701 (1963).
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