Correlation of the Rates of Solvolysis of Cyclopropylcarbinyl and Cyclobutyl Bromides Using the Extended Grunwald−Winstein Equation[1]

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The reactions of cyclopropylcarbinyl bromide (**1**) and cyclobutyl bromide (**2**) in hydroxylic solvents proceed with both solvolysis and rearrangement. Depending on the solvent, the reactions of **1** are 10−120 times faster than those of **2**, and both are faster than the previously studied allylcarbinyl bromide (**3**). Specific rates are reported for the reactions of **2** proceeding to solvolysis products and **3**. Reactions of **1** proceed to solvolysis products and both **2** and **3**; since **2** slowly undergoes further solvolysis, specific rates are obtained by a modified Guggenheim treatment. The two sets of specific rates are analyzed using the extended Grunwald−Winstein equation to give sensitivities toward changes in solvent nucleophilicity of 0.42 for **1** and 0.53 for **2** and corresponding sensitivities toward changes in solvent ionizing power of 0.75 and 0.94. A mechanism is proposed involving a rate-determining ionization with an appreciable nucleophilic solvation of the incipient carbocation.

The solvolyses and isomerizations of cyclopropylcarbinyl, cyclobutyl, and allylcarbinyl substrates have been extensively studied, and several reviews are available.[2−5] The possible structures for the intermediate carbocation formed in an ionization reaction have also been reviewed.[6,7] The earliest report of the formation of rearranged solvolysis products appears to be by Demjanov,[8] who obtained a mixture of cyclopropylcarbinol and cyclobutanol from the deamination of either cyclopropylcarbinylamine or cyclobutylamine. In 1951, it was further shown[9] that the two mixtures formed had identical compositions.

Solvolyses of allylcarbinyl *p*-toluenesulfonate (tosylate) give rearranged products only in solvents such as formic acid, which are both highly ionizing and weakly nucleophilic; in other solvents the reaction is predominantly S_N2 in character.[10] The bimolecular nature of these solvolyses in the majority of solvents, including 2,2,2-trifluoroethanol (TFE)−water mixtures, was confirmed by showing[11] that the sensitivities of the specific rates of solvolysis of the bromide to changes in both solvent nucleophilicity and solvent ionizing power were essentially identical to those observed for solvolyses of methyl tosylate.

The solvolyses of cyclopropylcarbinyl and cyclobutyl derivatives take place at a rate considerably higher than those of similarly constructed alkyl derivatives. For example, the rates of solvolysis of cyclopropylcarbinyl tosylate are about a million times faster than the identical solvolyses of isobutyl tosylate.[5,12,13] A Hammett treatment of substituent effects upon the kinetics of solvolysis of a series of α-phenyl-substituted cyclopropylcarbinyl *p*-nitrobenzoates leads to a ρ^+ value of −2.76. This value is considerably less than the ρ^+ value of −4.76 for the corresponding isobutyl-based substrates; this was rationalized in terms of a reduced electron demand from the aromatic ring when electrons can be supplied from the cyclopropyl ring.[14] Indeed, it has been found[15] that faster solvolysis rates are observed for $RCHXCH_3$ or $RCHXCF_3$ structures when R is cyclopropyl rather than when R is phenyl, indicating cyclopropyl to be more efficient than phenyl in the stabilization of an adjacent positive charge.

The observation of identical products from solvolyses of the isomeric C_4H_7X structures led to the formulation of a mechanism proceeding through a common intermediate. An early suggestion, consistent with all of the then available observations, was a mechanism proceeding through the bicyclobutonium ion (Scheme 1).[16] The delocalized charge is located at three carbons, and recapture by the leaving group can lead to internal return, with or without rearrangement, and capture by solvent to any of the three indicated solvolysis products. However, a comparison of the kinetic influence of 2,2- or 2,3-dimethyl substitution in the solvolyses of cyclopropylcarbinyl 3,5-dinitrobenzoates showed an acceleration independent of the substitution pattern, inconsistent with a bicyclobutonium ion intermediate. It was suggested[17] that the intermediate can be best represented as a bisected

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[2] Streitwieser, A. *Solvolytic Displacement Reactions*; McGraw-Hill: New York, 1962; pp 138−140.

[3] Richey, H. G. In *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley: New York, 1972; Vol. III, Chapter 25.

[4] Wiberg, K. B.; Hess, B. A.; Ashe, A. J. In *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley: New York, 1972; Vol. III, Chapter 26.

[5] Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Harper and Row: New York, 1987; pp 454−463.

[6] Saunders, M.; Jiménez-Vázquez, H. A. *Chem. Rev.* **1991**, *91*, 375.

[7] Olah, G. A.; Reddy, V. P.; Prakash, G. K. *Chem. Rev.* **1992**, *92*, 69.

[8] Demjanov, N. J. *Chem. Ber.* **1907**, *40*, (a) 4393. (b) 4961.

[9] Roberts, J. D.; Mazur, R. H. *J. Am. Chem. Soc.* **1951**, *73*, 2509.

[10] Servis, K. L.; Roberts, J. D. *J. Am. Chem. Soc.* **1964**, *86*, 3773.

[11] Kevill, D. N.; Abduljaber, M. H. *J. Chem. Soc., Perkin Trans. 2* **1995**, 1985.

[12] Roberts, D. D. *J. Org. Chem.* **1964**, *29*, 294.

[13] Roberts, D. D. *J. Org. Chem.* **1965**, *30*, 23.

[14] Peters, E. N.; Brown. H. C. *J. Am. Chem. Soc.* **1973**, *95*, 2397.

[15] Roberts, D. D. *J. Org. Chem.* **1991**, *56*, 5661.

[16] Mazur, R. H.; White, W. N.; Semenow, D. A.; Lee, C. C.; Silver, M. S.; Roberts, J. D. *J. Am. Chem. Soc.* **1959**, *81*, 4390.

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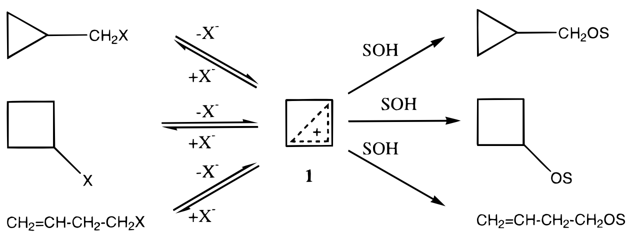
Scheme 1



cyclopropylcarbinyl cation, which would have the charge delocalized over all four carbon atoms.

There has been controversy as to whether solvolysis of cyclobutyl derivatives gives first a cyclobutyl cation that can then rearrange to a cyclopropylcarbinyl cation[18] or the ionization is directly to a cyclopropylcarbinyl cation.[19] A more recent study of the effect of various substituents situated on carbon-3 suggests that for alkyl- and aryl-substituents there is formation of a bridged cyclobutyl cation that then rearranges to the cyclopropylcarbinyl or homoallylic cation.[20]

High level ab initio calculations, including extended basis sets and electron correlation, have indicated that the bicyclobutonium and the bisected cyclopropylcarbinyl cation both occur at energy minima and that these minima lie at approximately the same energy level, with an interconversion barrier of only 0.6 kcal/mol.[6,21] Comparison between calculated and experimental chemical shifts (in superacid at low temperature) suggests the bicyclobutonium ion is favored by about 0.5 kcal/mol.[22] Since the calculations do not take into account interactions with the solvent and with counterions, relative stabilities based on extremely small energy differences may well change dramatically when the ions are generated under solvolytic conditions. In this connection, one would expect perturbations by the solvent to be related to the intensity of nucleophilic solvation of the developing carbocation, which can be estimated using the extended Grunwald−Winstein equation, in terms of the sensitivity of the specific rates of solvolysis toward changes in solvent nucleophilicity. In the presence of appreciable stabilization by interaction with the nucleophilic center of solvent molecules, the small energy differences indicated for isolated ions[21] or for ions in weakly nucleophilic superacid media[22] will make only a minor contribution toward the overall determination of the relative stabilities of the possible intermediate carbocations.

In the present study, we apply the extended (two-term) Grunwald−Winstein equation[23] (eq 1) to the solvolyses

$$\log(k/k_0)_{RX} = l\,N_T + mY_X + c \qquad (1)$$

of cyclopropylcarbinyl bromide (**1**) and cyclobutyl bromide (**2**). These substrates solvolyze at a convenient rate at temperatures a little higher than ambient. In eq 1, k and k_0 are the specific rates of solvolysis of RX in a given solvent and in 80% ethanol, respectively; l is the sensitivity toward changes in solvent nucleophilicity (N_T);[24,25] m is the sensitivity toward changes in solvent ionizing power (Y_{Br} for a bromide ion leaving group[26,27]); and c is a constant (residual) term.

The l and m values will both be of interest. Relatively large l values would suggest that the interactions with the solvent will be dominant in deciding which of the possible candidates serves as the intermediate carbocation. Further, since the solvolyses are extremely well documented as involving rearrangements proceeding through a carbocation, the l values can be assumed to present a measure of the possible values that can be observed during the rate-determining ionization of a moderately hindered substrate. The degree to which the m values fall below unity will reflect both the degree of solvation and the importance of anchimeric assistance within the ionization process.

Results

Specific rates of solvolysis of **1** and **2**, at 50.0 °C, each in 27 solvents, are reported in Table 1. For three of the solvolyses, specific rates of solvolysis at other temperatures are presented, in footnotes to the table, along with the calculated enthalpies and entropies of activation. The relevant N_T[24,25] and Y_{Br}[26,27] values for the solvents are also given in Table 1, as abstracted from the literature. The required values were all available, with the exception of Y_{Br} values for 95% and 90% acetone. These two solvent systems are accordingly not included in the Grunwald−Winstein-type analyses for solvolyses of **1**; nor were they included in the study of the solvolyses of **2**.

The Grunwald−Winstein analyses, using eq 1 with and without the $l\,N_T$ term, of the specific rates of solvolysis of **1** in 25 solvents and of **2** in 27 solvents are presented in Table 2. Since for both solvolyses the four data points for TFE−ethanol mixtures tended to lie below the plot,[28] the analyses were repeated omitting these solvents, and these values are also reported in Table 2. For comparison, previous analyses for **3**,[11] for cyclohexyl tosylate (using N_T and Y_{OTs}),[29] and for *tert*-butyl chloride (using N_T and Y_{Cl})[30] are also included in Table 3.

Since the cyclopropylcarbinyl halides react some 25 times faster in 50% ethanol than the corresponding cyclobutyl halide, which in turn reacts about 200 times faster than the allylcarbinyl halide,[9] rearrangement of **1** to **3** will, under the usual solvolytic conditions, be forming a stable product. However, rearrangements to **2** will be more problematic. In the early stages of reaction, to a close approximation, further reaction of **2** can be neglected. In later stages, however, as the concentration of **1** has significantly diminished and the concentration of **2** has significantly increased, perturbations of the kinetics will occur. In particular, it will not be possible

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[17] Schleyer, P. v. R.; Van Dine, G. W. *J. Am. Chem. Soc.* **1966**, *88*, 2321.

[18] Majerski, Z.; Borčić, S.; Sunko, D. E. *J. Chem. Soc. D* **1970**, 1636.

[19] Schneider, H.-J.; Schmidt, G.; Thomas, F. *J. Am. Chem. Soc.* **1983**, *105*, 3556, including Supporting Information.

[20] Wiberg, K. B.; Shobe, D.; Nelson, G. L. *J. Am. Chem. Soc.* **1993**, *115*, 10645.

[21] Koch, W.; Liu, B.; DeFrees, D. J. *J. Am. Chem. Soc.* **1988**, *110*, 7325.

[22] Saunders, M.; Laidig, K. E.; Wiberg, K. B.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1988**, *110*, 7652.

[23] Winstein, S.; Grunwald, E.; Jones, H. W. *J. Am. Chem. Soc.* **1951**, *73*, 2700.

[24] Kevill, D. N.; Anderson, S. W. *J. Org. Chem.* **1991**, *56*, 1845.

[25] Kevill, D. N. In *Advances in Quantitative Structure−Property Relationships*; Charton, M., Ed.; Jai Press: Greenwich, CT, 1996; Vol. I, pp 81−115.

[26] Bentley, T. W.; Carter, G. E. *J. Am. Chem. Soc.* **1982**, *104*, 5741.

[27] Bentley, T. W.; Llewellyn, G. *Prog. Phys. Org. Chem.* **1990**, *17*, 121.

[28] Takeuchi, K. *Pure Appl. Chem.* **1998**, *70*, 2023.

[29] Kevill, D. N.; Abduljaber, M. H. *Croat. Chem. Acta* **1992**, *65*, 539.

[30] Kevill, D. N.; D'Souza, M. J. *J. Chem. Res., Synop.* **1993**, 174.

Table 1. Specific Rates of Reaction of Cyclopropylcarbinyl Bromide (1) and Cyclobutyl Bromide (2) at 50.0 °C and the Corresponding Solvent Nucleophilicity (N_T) and Solvent Ionizing Power (Y_{Br}) Values

solvent[a]	$10^5\,k$, s^{-1} (**1**)[b]	$10^6\,k$, s^{-1} (**2**)[b]	N_T[c]	Y_{Br}[d]
100% EtOH	0.309 ± 0.009	0.0260 ± 0.0022	+0.37	−2.4
90% EtOH	1.82 ± 0.06	0.601 ± 0.022	+0.16	−0.84
80% EtOH	6.64 ± 0.11[e]	3.53 ± 0.08	0.00	0.00
60% EtOH	71.1 ± 1.9	35.4 ± 2.5	−0.39	1.26
50% EtOH	177. ± 11[f]	114.± 4[g]	−0.58	1.88
40% EtOH		315.± 13	−0.74	2.62
100% MeOH	1.17 ± 0.05	0.135 ± 0.011	+0.17	−1.12
90% MeOH		1.87 ± 0.04	−0.01	−0.14
80% MeOH	13.8 ± 0.1	7.17 ± 0.20	−0.06	0.70
60% MeOH	134.± 3	75.3 ± 2.5	−0.54	2.04
40% MeOH	742.± 20	490.± 6	−0.87	3.14
95% acetone	0.0142 ± 0.0009		−0.49	
90% acetone	0.143 ± 0.009		−0.35	
80% acetone	1.59 ± 0.08	1.20 ± 0.06	−0.37	−0.7
60% acetone	37.9 ± 0.5	24.2 ± 1.0	−0.52	1.03
40% acetone	323.± 9	302.± 9	−0.83	2.44
80% dioxane	1.15 ± 0.04	0.327 ± 0.027	−0.46	−0.60
60% dioxane	23.9 ± 1.4	19.3 ± 0.6	−0.54	0.82
100% TFE	18.4 ± 0.4	6.47 ± 0.27	−3.93	2.53
97% TFE[h]	22.2 ± 0.6	8.57 ± 0.36	−3.30	2.53
90% TFE[h]	41.8 ± 1.2	23.0 ± 1.1	−2.55	2.58[i]
80% TFE[h]	85.6 ± 4.4	86.5 ± 2.3	−2.22	2.67
70% TFE[h]	174.± 3	146.± 5	−1.98	2.79
60% TFE[h]	356.± 7	230.± 10	−1.84[i]	2.91
50% TFE[h]	582.± 19	472.± 18	−1.73	3.04
80% T-20% E[j]	5.34 ± 0.15	1.78 ± 0.08	−1.76	1.62
60% T-40% E[j]	1.74 ± 0.08	0.501 ± 0.028	−0.94	0.31
40% T-60% E[j]	0.678 ± 0.015	0.167 ± 0.012	−0.34	−0.57
20% T-80% E[j]	0.464 ± 0.009	0.0771 ± 0.0042	0.08	−1.42

[a] Unless otherwise indicated, on a vol/vol basis, at 25.0 °C, with the other component water; substrate concentration of ca. 0.0035 mol dm^{-3}. [b] With associated standard deviation. [c] From refs 24 and 25. [d] From refs 26 and 27. [e] With values of 0.414 ± 0.010 at 25.0 °C and 23.6 ± 1.5 at 62.4 °C, leads to values for $\Delta H^{\ddagger}_{298}$ of 21.0 ± 0.3 kcal mol^{-1} and for $\Delta S^{\ddagger}_{298}$ of −12.5 ± 1.0 eu (with associated standard errors). [f] With values of 10.0 ± 0.3 at 25.0 °C (ref 9 gives specific rate of 9.4 × 10^{-5} s^{-1}) and 586 ± 12 at 62.4 °C, leads to values for $\Delta H^{\ddagger}_{298}$ of 20.8 ± 0.2 kcal mol^{-1} and for $\Delta S^{\ddagger}_{298}$ of −7.1 ± 0.6 eu. [g] With values of 4.77 ± 0.12 at 25.0 °C (ref 9 gives specific rate of 4.17 × 10^{-6} s^{-1}), 34.1 ± 0.7 at 39.9 °C, and 427 ± 18 at 62.5 °C, leads to values for $\Delta H^{\ddagger}_{298}$ of 23.3 ± 0.3 kcal mol^{-1} and for $\Delta S^{\ddagger}_{298}$ of −4.8 ± 1.0 eu. [h] On a weight/weight basis. [i] Interpolated value. [j] T-E are TFE−ethanol mixtures.

to get the infinity titer (V_∞) corresponding to the initial reaction by measuring the acid produced at 10 half-lives, because by that time, significant amounts of **2** will already have solvolyzed and the rest will be continuing to solvolyze. This is, of course, a situation that can be analyzed by applying the Guggenheim method[31] to the kinetic data.

Titrations of the acid developed at equal time intervals for up to about 80% reaction are obtained graphically from a plot of the titer at time t (V_t) against t. Analysis is then carried out using eq 2, where Δ is the constant

$$kt + \ln[V_t - V_{(t+\Delta)}] = \ln[(V_0 - V_\infty)(1 - e^{-k\Delta})] \quad (2)$$

time gap chosen between each of the several interpolations of the titer; V_0 and V_∞ are the titers at zero and infinite time, respectively (with V_∞ being unknown); and k is the specific rate of reaction. A plot of $\log[V_t - V_{(t+\Delta)}]$ against t has a slope of $-k/2.303$. However, to get a measure of error comparable to that obtained in conventional runs and also to get a measure of the theoretical V_∞ in the absence of further reaction of initially formed **2**, we do not follow the usual procedure by reporting these k values but, instead, we use them to get the theoretical V_∞ from the intercept, which represents $\log(V_\infty - V_0)(1 - e^{-k\Delta})$. These V_∞ values were then used, in an identical manner to the usual experimental values, to calculate a series of integrated rate coefficients directly from the experimentally determined titration data, leading to the average values with standard deviations reported in Table 1.

The solvolyses of cyclobutyl bromide can be followed in the conventional manner using experimental V_∞ values at approximately 10 half-lives. This is because rearrangement to **1** will be to a much faster-reacting intermediate, which does not accumulate, and rearrangement to **3** is, as for the solvolyses of **1**, to a material that reacts very slowly under the reaction conditions.

The specific rates obtained for **1** in this way are for the sum of all product-forming reactions: the solvolyses to a variety of products, both rearranged and unrearranged, and the rearrangements to both **2** and **3**. The specific rates obtained for **2** are for conversions to solvolysis products (in some instances via **1**) plus rearrangement to **3**.

For the solvolyses of **1**, the ratios between solvolysis products and the sum of the rearrangements to **2** and **3** in the initial stages of reaction, plus the divisions between **2** and **3**, have been determined from studies based on acid production. The *total* acid production from a solution of **1** in 50% ethanol was determined by heating, in a sealed tube at 70 °C, for 10 half-lives for the solvolysis of the slowest reacting isomer **3**.[11]

The modified Guggenheim treatment described above leads to a value for V_∞, the "infinity titer" relevant to the initial stages of reaction. Comparison with the total possible titer gives the initial percentage of reaction proceeding with solvolysis, reported for 10 solvolyses in Table 3. The remaining product will be the sum of initially formed **2** and **3**. An upper limit for the amount of **3** can be obtained by allowing reaction of 5-mL portions for time sufficient for 10 half-lives of reaction of **2** (determined from the specific rates reported in Table 1). These values are also reported in Table 3 and represent upper limit values for the initial reaction because some **3** is produced from subsequent reaction of the initially formed **2**.

If the solvolyses of **1** and **2** are assumed to go through a common intermediate, the ratios between solvolysis and collapse to **3** should be identical, and the amount of **3** formed via **2** can be estimated. Relatively small corrections are applied to the percentage values for **3**, determined at the 10 half-lives for reaction of **2**, and these values are also reported in Table 3. The extent to which the sum of the percentages of initially formed solvolysis products and initially formed **3** is less than 100% represents the initially formed percentage of **2**.

Discussion

Although arguments were presented[32−34] challenging the early reports of isomerization of reactant and/or

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(31) (a) Guggenheim, E. A. *Philos. Mag.* **1926**, *2*, 538. (b) Frost, A. A.; Pearson, R. G. *Kinetics and Mechanism*, 2nd ed.; Wiley: New York, 1961; pp 49−50.

(32) Bergstrom, C. G.; Siegel, S. *J. Am. Chem. Soc.* **1952**, *74*, 145.

(33) Brown, H. C.; Borkowski, M. *J. Am. Chem. Soc.* **1952**, *74*, 1894.

(34) Wu, C. Y.; Robertson, R. E. *J. Am. Chem. Soc.* **1966**, *88*, 2666.

Table 2. Calculated Values from Analyses of Specific Rates[a] Using the Simple (One-Term) and Extended (Two-Term) Forms of the Grunwald−Winstein Equation

substrate	scales	n[b]	l[c]	m[d]	c[d]	R[e]	F[f]
1	Y_{Br}	25		0.57 ± 0.06	−0.20 ± 0.45	0.907	106
	N_T, Y_{Br}[h]	25	0.46 ± 0.07	0.80 ± 0.05	0.03 ± 0.26	0.971	179
	Y_{Br}	21[i]		0.54 ± 0.06	−0.07 ± 0.40	0.915	98
	N_T, Y_{Br}[j]	21[i]	0.42 ± 0.05	0.75 ± 0.03	0.12 ± 0.18	0.984	278
2	Y_{Br}	27		0.71 ± 0.07	−0.40 ± 0.53	0.910	120
	N_T, Y_{Br}[k]	27	0.58 ± 0.08	0.99 ± 0.05	−0.15 ± 0.30	0.975	228
	Y_{Br}	23[i]		0.68 ± 0.06	−0.25 ± 0.49	0.917	111
	N_T, Y_{Br}[l]	23[i]	0.53 ± 0.06	0.94 ± 0.04	−0.07 ± 0.22	0.985	323
3[m]	Y_{Br}	19		−0.07 ± 0.09	−0.27 ± 0.64	0.189	0.6
	N_T, Y_{Br}	19	0.99 ± 0.04	0.46 ± 0.03	0.10 ± 0.11	0.987	297
c-$C_6H_{11}OTs$[n]	Y_{OTs}	18		0.61 ± 0.07	−0.20 ± 0.45	0.913	
	N_T, Y_{OTs}	18	0.35 ± 0.03	0.85 ± 0.03	0.03 ± 0.14	0.992	
t-BuCl[o]	Y_{Cl}	46		0.73 ± 0.03	−0.17 ± 0.41	0.966	
	N_T, Y_{Cl}	46	0.38 ± 0.03	0.86 ± 0.02	0.00 ± 0.19	0.993	

[a] For **1** and **2** from Table 1. [b] Number of solvents. [c] From eq 1. [d] From eq 1, with or without the $l N_T$ term, and with the c value accompanied by the standard error of the estimate. [e] Correlation coefficient. [f] F-test value. [g] At 50.0 °C. [h] Correlation of N_T against Y_{Br} has correlation coefficient of 0.732. [i] Calculated with omission of the four measurements in TFE−ethanol mixtures. [j] Correlation of N_T against Y_{Br} has correlation coefficient of 0.718. [k] Correlation of N_T against Y_{Br} has correlation coefficient of 0.717. [l] Correlation of N_T against Y_{Br} has correlation coefficient of 0.706. [m] Values, at 70.0 °C, from ref 11. [n] Values, at 25.0 °C, from ref 29. [o] Values, at 25.0 °C, from ref 30.

Table 3. Partitioning of Products between Solvolysis and Rearrangement during Early Stages of Reaction in the Solvolyses of 0.0035 M Cyclopropylcarbinyl Bromide (1) at 50.0 °C

solvent[a]	% solvolysis	% **3**[b]	% **2**[c]	% **3**[c]
60% EtOH	79	3	19	2
50% EtOH	79	7	16	5
50% EtOH[d]	78	6	18	4
60% MeOH	79	4	18	3
40% MeOH	80	3	18	2
97% TFE	43	26	39	18
90% TFE	48	18	41	11
80% TFE	64	8	31	5
70% TFE	69	8	25	6
50% TFE	76	2	22	2

[a] See footnote a to Table 1. [b] After complete reaction of both substrate **1** and intermediate **2**. [c] Adjusted for formation of **3** from the initially formed **2** (see text). [d] At 70.0 °C.

formation of rearranged products during solvolyses of cyclopropylcarbinyl and cyclobutyl derivatives, it is now well established that such rearrangements are an important feature of these reactions.

In their early experiments, J. D. Roberts and Mazur[9] claimed that, in acetic acid at 100 °C, cyclopropylcarbinyl chloride gave approximately 44% cyclobutyl chloride, 26% allylcarbinyl chloride, 22% cyclopropylcarbinyl acetate, and 8% cyclobutyl acetate, after a reaction time of approximately 10 half-lives. Similar results, but with less rearranged chloride, were observed in aqueous ethanol. Some 9 years later, after the introduction of vapor-phase chromatography, the products from the solvolysis in 80% ethanol at 97 °C were reinvestigated,[35] and the earlier results were confirmed, with the reduction in substrate concentration being accompanied by increases in the concentrations of cyclobutyl chloride, allylcarbinyl chloride, the three ethyl ethers, and smaller amounts of the three alcohols. Important support for the internal return rearrangement was presented by Servis and J. D. Roberts.[36]

The solvolysis products from cyclobutyl tosylate in acetic acid at 50.0 °C were initially claimed to be 65% cyclopropylcarbinyl acetate, 22% cyclobutyl acetate, and 13% allylcarbinyl acetate.[37] Using vapor-phase chromatography, D. D. Roberts[38] found for this substrate and also for two other cyclobutyl arenesulfonates that the corresponding percentages were 55, 41, and 4, respectively. Although the two reported sets of product percentages are in only moderate agreement, they both indicate extensive formation of rearranged acetates. Further, about 8% internal return isomerization was found[38] in both acetic acid and TFE, but there was no evidence for such return in ethanol. However, we show below that the rates for S_N2 ethanolyses of allylcarbinyl bromides are not very much lower than those for the S_N1 ethanolyses of cyclobutyl bromide, and assuming the tosylates react similarly, a conventional product study would not show the formation of the rearranged substrate. For the 2-naphthalenesulfonate ester,[39] the amount of internal return isomerization in TFE increased to 22%, and it remained undetected in ethanol.

For solvolyses of cyclopropylcarbinyl arenesulfonates, the internal return isomerization to both of the slower-reacting cyclobutyl and allylcarbinyl isomers can be detected. Values based on the difference between theoretical and experimental infinity titers at 10 half-lives will be a little low because of the relatively small amount of solvolysis undergone by the rearranged cyclobutyl arenesulfonate. Values measured in the 20−30 °C range have been reported as 48%−51% in acetic acid and 23%−28% in formic acid.[15] Values were reported[15] of 20% and 28% in 80% and 60% ethanol, which can be compared to our measurement (Table 3) of 21% in 60% ethanol at 50 °C for the bromide. Similarly, our value for **1** in 97% TFE of 57% (Table 3) can be compared with the measurement for arenesulfonates[15] of 30%−32%. Our values are based on the infinity titer estimated from the Guggenheim treatment of the data,[31] and they are independent of the further reaction of **2**.

The solvolysis/isomerization ratio for reaction of **1** is found to be essentially constant at 3.6−4.0 in aqueous

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[35] Caserio, M. C.; Graham, W. H.; Roberts, J. D. *Tetrahedron* **1960**, *11*, 171.

[36] Servis, K. L.; Roberts, J. D. *Tetrahedron Lett.* **1967**, 1369.

[37] Roberts, J. D.; Chambers, V. C. *J. Am. Chem. Soc.* **1951**, *73*, 5034.

[38] Roberts, D. D. *J. Org. Chem.* **1972**, *37*, 1510.

[39] Roberts, D. D. *J. Org. Chem.* **1971**, *36*, 1913.

alcohol mixtures containing 60%−40% ethanol or methanol. A slightly lower value of 3.2 is observed in 50% TFE, and this falls with increasing TFE content, reaching a value of 0.75 for 97% TFE. The low nucleophilicity of TFE-rich solvents[24,25] gives increased opportunity for return of bromide ion, a portion of which leads to rearranged reactant.

From the data of Table 1, it can be seen that at 50.0 °C **1** is more reactive than **2** by a factor of from 10 (in 80% TFE) to 120 (in ethanol). For reactions in binary solvents containing at least 20 vol % of water, the ratio is in a rather narrow range of 10 to 20. For TFE−ethanol mixtures, the ratio of 28 for 100% TFE rises steadily with the ethanol content. The values observed are consistent with a literature value[9] of 23 in 50% ethanol at 25.0 °C. For a chloride-ion leaving group, values of 26 in 50% ethanol at 50.0 °C[9] and of 34 in water at 25.0 °C[34] have been reported.

For the tosylates in 97% TFE at 25.0 °C, a specific rate of 1060×10^{-5} s^{-1} for **1**[40] can be combined with a value for **2**[19] of 33×10^{-5} s^{-1}, for a ratio of 32. However, the value for **2** is in very poor agreement with a value of 5.3×10^{-5} s^{-1} reported[38] for reaction in 100% TFE. Specific rates of solvolysis in 100% and 97% TFE usually differ by only a few percent (2% for cyclopropylcarbinyl tosylate at 25.0 °C[40] and, in the present study, 20% for cyclobutyl bromide at 50.0 °C), and the 6-fold specific rate variation for cyclobutyl tosylate suggests that one of the values is in error. Two observations give support to the value of D. D. Roberts:[38] an accompanying value for reaction in acetic acid is in exact agreement with an earlier value of J. D. Roberts and Chambers,[37] and for studies in TFE and acetic acid, the parent benzenesulfonate and five *para*-substituted derivatives gave excellent Hammett plots with the point for the tosylate being as expected. If we take the 100% TFE specific rate as a good approximation for 97% TFE, the value for the ratio becomes 200. Similar values, of 186 and 130, are obtained for the comparisons in ethanol at 40.0 °C and acetic acid at 30.0 °C.[12,38] These cyclopropylcarbinyl/cyclobutyl ratios are somewhat higher for a tosylate leaving group than for a halide leaving group, and subsequent reaction of the cyclobutyl derivative formed by isomerization during solvolysis of the cyclopropylcarbinyl derivative will be of reduced importance when the tosylate ester is studied.

From our previously reported study[11] of the solvolyses of **3**, two specific rate values at 50.0 °C can be compared with values for **1** and **2** from Table 1. The relative rates (**1**:**2**:**3**) are 250:13:1.0 in 80% ethanol and 2600:170:1.0 in 50% ethanol. The appreciable differences between the two comparisons are due to reaction of **1** and **2** with ionization and **3** by an S_N2 pathway, with different responses to solvent variation for the two types of mechanism. In ethanol, as one would predict, the rate gap between **3** and **2** becomes quite small. The specific rate of ethanolysis of **3** at 70.0 °C[11] can be adjusted, to a reasonable approximation, by using the specific rate ratio for 80% ethanol at 70.0 and 50.0 °C, to a value of 1.2×10^{-8} s^{-1} at 50.0 °C, a value about one-half of that for the ethanolysis of **2**. This is consistent with the observation that at 10 half-lives for ethanolysis of several cyclobutyl arenesulfonates, only solvolysis products were observed.[38,39] Any allylcarbinyl arenesulfonate, formed by isomerization, would have been essentially completely solvolyzed over this time period.

Table 4. Tosylate−Bromide Rate Ratios for Solvolyses of Cyclopropylcarbinyl and Cyclobutyl Derivatives (RX)

R in RX	solvent	temp, °C	$k_{\mathrm{OTs}}/k_{\mathrm{Br}}$	source
c-PrCH$_2$	EtOH	50.0	324	*a*
c-PrCH$_2$	MeOH	50.0	318	*b*
c-PrCH$_2$	80% EtOH	25.0	597	*c*
c-PrCH$_2$	90% Acetone	50.0	332	*d*
c-Bu	EtOH	50.0	235	*e*
c-Bu	TFE	50.0	81	*f*, *g*
c-Bu	97% TFE	50.0	382	*g*, *h*

[a] Value for OTs ester of 100×10^{-5} s^{-1}, by extrapolation of data obtained at 10−30 °C (ref 12). [b] Value for OTs ester of 372×10^{-5}, by extrapolation of data obtained at 20−40 °C (ref 13). [c] Value for OTs ester from ref 12. [d] Value for OTs ester from ref 13. [e] Value for OTs ester from ref 38. [f] Value for OTs ester at 25.0 °C, from ref 38. [g] Value at 25.0 °C adjusted to 50.0 °C by multiplying by 9.9 (the ratio, from ref 39, of the specific rates of solvolysis of the 2-naphthalenesulfonate ester in TFE at 50.0 and 25.0 °C). [h] Value for OTs ester at 25.0 °C from ref 19.

A useful criterion of mechanism is the $k_{\mathrm{OTs}}/k_{\mathrm{Br}}$ ratio introduced by Hoffmann.[41,42] Several of our specific rates for **1** or **2** (k_{Br}) can be compared with values, directly available from the literature or obtained by extrapolation of data from lower temperatures, for the corresponding tosylate ester (k_{OTs}). These values are listed in Table 4, together with the source of the specific rate values for the tosylate ester. The reactions in ethanol, methanol, aqueous ethanol, and aqueous acetone give ratios in the range of 230−600. The discrepancy between specific rate values for cyclobutyl tosylate in 97% TFE[19] and 100% TFE[38] was discussed above, and this is further reflected in the calculated $k_{\mathrm{OTs}}/k_{\mathrm{Br}}$ values in these solvents.

Values of $k_{\mathrm{OTs}}/k_{\mathrm{Br}}$ for S_N2 reactions are usually close to unity for powerful anionic nucleophiles[42,43] and in the 10−20 range for S_N2 solvolyses.[42] An approximate value of 5000 has been suggested for S_N1 reactions.[43] In S_N1 reactions, nonbonded interactions between bulky leaving groups and bulky alkyl groups are of importance. For example, the 1-adamantyl derivatives solvolyze in 80% ethanol with a ratio of almost 10 000 as a result of 1,5-nonbonded interactions involving the sulfonyl oxygens.[44] The values of the present study are consistent with an S_N1 pathway in which the alkyl group involved is of relatively small size compared to the tertiary alkyl groups typically used to establish the reference value.

The analyses using eq 1 of the specific rates of reaction of **1** and **2**, in the solvents listed in Table 1, are reported in Table 2. The analyses are carried out both with and without the $l\,N_T$ term. For both solvolyses, the analysis using the extended Grunwald−Winstein equation (eq 1) give better correlations (standard error of the estimate, correlation coefficient, *F*-test value) than those carried out with omission of the $l\,N_T$ term. Within the correlations using the full equation, the points for the four TFE−ethanol mixtures lie below the correlation line. Although the *l* and *m* values change only slightly after omission of these four solvents from the correlation, there is a

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(40) Fujio, M.; Saeki, Y.; Nakamoto, K.; Kim, S. H.; Rappoport, Z.; Tsuno, Y. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 751.

(41) Hoffman, H. M. R. *J. Chem. Soc.* **1965**, 6753.

(42) Ingold, C. K. *Structure and Mechanism in Organic Chemistry*, 2nd ed.; Cornell University Press: Ithaca, NY, 1969; pp 453−457.

(43) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Harper and Row: New York, 1987; pp 374−375.

(44) Bingham, R. C.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1971**, *93*, 3189.

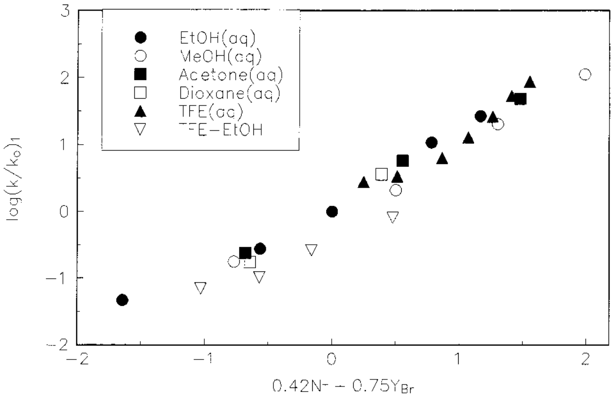

Figure 1. Plot of log(k/k_0) for reactions of cyclopropylcarbinyl bromide (**1**) against (0.42 N_T + 0.75 Y_{Br}).

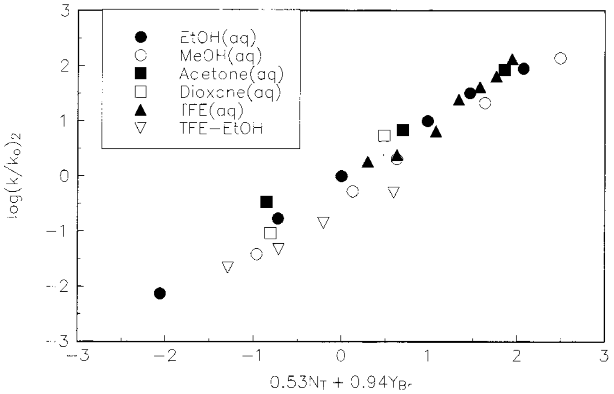

Figure 2. Plot of log(k/k_0) for reactions of cyclobutyl bromide (**2**) against (0.53 N_T + 0.94 Y_{Br}).

considerable improvement in all of the measures of goodness of fit. The plots presented in Figures 1 and 2 are using the *l* and *m* values from the improved plots and the four TFE−ethanol values are then added to the plots to show their deviations.

To allow a comparison, the very different *l* and *m* values from parallel analyses of the S_N2 solvolyses of **3** and the very similar *l* and *m* values for two previously reported solvolyses believed to proceed via a rate-determining ionization with accompanying nucleophilic solvation of the developing carbocation are also included within Table 2. For cyclohexyl tosylate solvolyses,[29] there is independent evidence from isotopic labeling experiments for 1,2-hydride shifts prior to product formation,[45] a good indication of a reaction proceeding through a carbocation. The *tert*-butyl chloride solvolyses were used in setting up the original *Y* value scale.[46]

The *l* value of 0.53 for the solvolyses of **2** can be considered to represent a new highest value for the sensitivity toward changes in solvent nucleophilicity when formation of an intermediate carbocation is involved. The observation of an appreciable *l* value for the solvolyses of **1** has been supported by the observation of an *l* value of 0.31 and an *m* value[47] of 0.93 for the solvolyses of cyclopropylcarbinyl tosylate in 18 solvents at 25.0 °C.[40]

The Y_X scales were derived using adamantyl substrates, which present severe hindrance to rearside nucleophilic solvation.[26,27] As a consequence, for solvolyses of non-cage-type alkyl substrates, except for a few specially constructed so as to be highly hindered at the rear side of the breaking bond,[28,48] there will be varying degrees of nucleophilic solvation of the developing carbocation, reflected in *l* values of varying magnitude such as the four examples given in Table 2 and others available from the literature.[25,49,50]

The *m* values of 0.75 for **1** and 0.94 for **2** are both close to unity, especially the value for **2**, suggesting that there is, at most, a modest anchimeric assistance to the ionization of **1** and that anchimeric assistance is essentially absent during the ionization of **2**.

The *Y* scale based on *tert*-butyl chloride solvolysis[46] is now known to contain a contribution from nucleophilic solvation of the developing carbocation, over and above any small contribution to the solvolyses of the 1-adamantyl chloride presently recommended as the standard for establishing the ionizing power scale for a chloride ion leaving group (Y_{Cl}).[26,27,30] However, in many regards *tert*-butyl chloride solvolysis, with its modest dependence on solvent nucleophilicity, is more typical of solvolyses proceeding with rate-determining ionization, and it will frequently be a better similarity model if a one-term correlation against solvent ionizing power is desired. The criteria for it to function in this way is that the *l*/*m* ratio of 0.44 at 25.0 °C matches reasonably closely the *l*/*m* ratio for the solvolyses under consideration. For the solvolyses of both **1** and **2** at 50.0 °C, the *l*/*m* ratio has a value of 0.56, and for cyclopropylcarbinyl tosylate at 25.0 °C,[40] the *l*/*m* ratio is 0.33. These values suggest that one-term correlations against *Y* values should be reasonably precise, and indeed, D. D. Roberts[51] has demonstrated good one-term correlations for the specific rates of solvolysis of cyclopropylcarbinyl tosylate and pentamethylbenzenesulfonate and of cyclobutyl *p*-bromobenzenesulfonate against the original *Y* values for solvolyses in ethanol−water and acetic acid−formic acid mixtures.

There was also consideration[51] of the $(k_{EW}/k_{ACOH})_Y$ ratios. These are the ratios of the specific rates in acetic acid and in the ethanol−water mixture of identical *Y* value. For S_N1 reactions, one would predict a value of close to unity, and the extent to which they rise above unity can be taken as a measure of the additional nucleophilic assistance to the solvolysis of the substrate over and above that operating for *tert*-butyl chloride. It has been found, however, that values are frequently appreciably below unity even when moderate nucleophilic participation is believed to operate. For arenesulfonate solvolyses, good reference points are the value of 0.13 for 2-adamantyl tosylate solvolysis and 0.16 for 1-adamantyl

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(45) (a) Lambert, J. B.; Putz, G. J.; Mixan, C. E. *J. Am. Chem. Soc.* **1972**, *94*, 5132. (b) Lambert, J. B.; Putz, G. J. *J. Am. Chem. Soc.* **1973**, *95*, 6313.

(46) (a) Grunwald, E.; Winstein, S. *J. Am. Chem. Soc.* **1948**, *70*, 846. (b) Fainberg, A. H.; Winstein, S. *J. Am. Chem. Soc.* **1956**, *78*, 2770.

(47) The *m* value reported was 0.85, but this was based on the use of N_{OTs} values, calculated using a sensitivity of methyl tosylate solvolyses toward Y_{OTs} of 0.3. It has been shown that this methyl tosylate value should have been 0.55. The N'_{OTs} scale so derived is in excellent agreement with the N_T scale (ref 25). Fortunately, sets of *l* and *m* values for solvolyses of other tosylate esters obtained using N_{OTs} in conjunction with Y_{OTs} are easily corrected by adding 0.25 *l* (0.08 in this instance) to the *m* value.

(48) Kevill, D. N.; D'Souza, M. J. *J. Phys. Org. Chem* **1992**, *5*, 287.

(49) Liu, K.-T.; Chen, P.-S.; Hu, C.-R.; Sheu, H.-C. *J. Phys. Org. Chem.* **1993**, *6*, 122 and references therein.

(50) (a) Takeuchi, K.; Ohga, Y.; Ushino, T.; Takasuka, M. *J. Org. Chem.* **1997**, *62*, 4904. (b) Kevill, D. N.; D'Souza, M. J. *Tetrahedron Lett.* **1998**, *39*, 3973.

(51) Roberts, D. D. *J. Org. Chem.* **1984**, *49*, 2521.

tosylate solvolysis.[52] The average value of 0.15 can be used as a lower limit for the almost complete absence of nucleophilic participation. Contrary to the view expressed that values below unity indicate that nucleophilic assistance is not important, the values of 0.44 for cyclopropylcarbinyl pentamethylbenzenesulfonate solvolysis, 0.49 for cyclopropylcarbinyl tosylate solvolysis, and 0.64 for cyclobutyl *p*-bromobenzenesulfonate solvolysis[51] can be considered to represent a moderate nucleophilic participation by the solvent. This view is consistent with the observed l values, and further, the higher $(k_{EW}/k_{ACOH})_Y$ ratio observed for the cyclobutyl derivative is in accord with the higher l value (Table 2) observed for **2** relative to **1**.

Conclusions

When dissolved in a pure or binary hydroxylic solvent, both cyclopropylcarbinyl bromide (**1**) and cyclobutyl bromide (**2**) simultaneously undergo both solvolysis and rearrangement reactions.

Since the reactions of **1** are found to be some 10−120 times faster than those of **2**, reaction of **2** does not lead to the accumulation of **1**, and solvolysis products together with a relatively small amount of rearranged allylcarbinyl bromide (**3**) result. Specific rates for formation of these products are presented in Table 1.

Reactions of **1** proceed with, in addition to solvolysis products, accumulation of both **2** and **3**. The **2** does, however, undergo some further reaction during the 10 half-lives recommended prior to determination of the infinity titer. The kinetics have been treated in terms of a modified Guggenheim approach in which we estimate the V_∞ value on the basis of reaction over a little more than two half-lives and then use this value in the usual way to obtain averages and standard deviations for the specific rates of reaction of **1** to give solvolysis products plus both **2** and **3** (Table 1). Further, we were able to estimate the relative amounts of solvolysis, rearrangement to **2**, and rearrangement to **3**.

The specific rates presented in Table 1 have been analyzed using the extended Grunwald−Winstein equation (eq 1), with incorporation of N_T solvent nucleophilicity values and Y_{Br} solvent ionizing power values. Although the sensitivities l and m do not change appreciably, improved correlations are obtained by omitting the four low-lying TFE−ethanol points (Figures 1 and 2). The m values of 0.75 and 0.94 are consistent with an ionization mechanism with at most only a mild anchimeric assistance. The l values of 0.42 and 0.53 indicate a nucleophilic solvation of the developing carbocation. The two sets of l and m values are very similar to those previously obtained for solvolyses of cyclohexyl tosylate and *tert*-butyl chloride (values presented in Table 2), which were previously proposed to proceed by ionization with accompanying nucleophilic solvation. Indeed, since there is extremely strong evidence for an intermediate carbocation in solvolyses of the type reported in this work, the analyses give strong support to the concept that l values as large as 0.5 can reflect nucleophilic solvation of an incipient carbocation. The appreciable nucleophilic solvation suggests that the small energy differences between the bicyclobutonium and bisected cyclopropylcarbinyl cations, indicated by ab initio calculations and NMR measurements in superacid media, will be swamped out by solvation effects in hydroxylic solvents.

Experimental Section

The cyclopropylcarbinyl bromide (**1**) and cyclobutyl bromide (**2**), 98%, both from Aldrich, were used as received. The purifications of acetone, dioxane, ethanol, and methanol were as previously described,[53] as was also the purification of TFE.[54]

Kinetic Procedures. Concentrations of **1** and **2** of about 3.5×10^{-3} mol dm^{-3} were used. For the solvents not containing fluoro alcohol, 5 mL aliquots were removed from 50 mL of solution and, for the solvents containing fluoro alcohol, 2-mL portions were removed from 25 mL of solution at appropriate time intervals. These aliquots were then added to 25 mL of acetone, at −78 °C, containing Lacmoid (resorcinol blue) indicator. The acid previously developed was titrated against a standardized solution of sodium methoxide in methanol.

Product Studies. The product ratios for the products as initially formed in the solvolysis of **1** were estimated from acid titrations. The Guggenheim treatment of the kinetics allowed an estimate of the initial percentage of the reaction involving solvolysis. The remaining reactant solution was then allowed to stand for the time required for 10 half-lives for the slower solvolysis of **2** under the reaction conditions, and titration of acid was then carried out in the usual manner, representing solvolysis of all organic bromide except for the much slower-reacting[11] allylcarbinyl (but-3-enyl) bromide (**3**). The acid developed after complete solvolysis of all of the reactant and rearranged alkyl bromide was independently determined by carrying out a solvolysis of **1** (0.0035 mol dm^{-3}) in 50% ethanol, using duplicate 5-mL portions of solution in sealed ampules, at 70.0 °C for 18 days.

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(52) Fry, J. L.; Lancelot, C. J.; Lam, L. K. M.; Harris, J. M.; Bingham, R. C.; Raber, D. J.; Hall, R. E.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1970**, *92*, 2538.

(53) Kevill, D. N.; Kolwyck, K. C.; Weitl, F. L. *J. Am. Chem. Soc.* **1970**, *92*, 7300.

(54) Rappoport, Z.; Kaspi, J. *J. Am. Chem. Soc.* **1974**, *96*, 4518.