Bicyclopropyl-d_4 and -d_5: 90% deuterium at C-2 and C-3, 43% deuterium at C-1.

Pyrolysis Experiments. The pyrolysis of bcp was carried out under both flow and static conditions. The flow pyrolysis apparatus consisted of a thermostated oven and a quartz tube previously washed with alcoholic potassium hydroxide. The pyrolyses were accomplished by attaching two reservoirs to the ends of the quartz pyrolysis tube. One reservoir served as a collection vessel for the products and the other served to contain the compound to be pyrolyzed. In a typical experiment material was transferred to a reservoir on the vacuum line by using standard techniques. The vessel with the substrate was attached to the pyrolysis tube and the system evacuated while the substrate was kept at a temperature of 77 K. When the pressure was reduced to a desirable level (i.e., 5–10 torr), the liquid nitrogen bath was removed from the reservoir with the material to be pyrolyzed and used to cool the collection reservoir.

Static pyrolyses were accomplished by depositing a known quantity of bcp into a glass tube (previously washed in alcoholic potassium hydroxide and thoroughly dried) by standard vacuum line transfer methods. The compound was condensed with liquid nitrogen and the tube sealed with a torch. If a bath gas, such as nitrogen or argon, was to be used, it was added to the tube just prior to sealing it. To perform the actual pyrolysis, we placed the sealed tubes in a "bomb". The temperature was determined either by using a thermocouple or by pyrolyzing a compound with well-defined Arrhenius parameters (i.e., vinycyclopropane).

Conventional infrared spectra of compounds were obtained by using a Beckman infrared spectrometer. Fourier-transform infrared spectroscopy (FTIR) was accomplished by using either a Digilab FTS-10 or FTS-20 spectrometer.

Nuclear magnetic resonance experiments were done with a Varian CFT-80 NMR spectrometer to obtain proton NMR data. For carbon-13 and deuterium NMR experiments a Varian XL-100 was used.

Mass spectral analyses were done by using a Hitachi RMU6 electron-impact mass spectrometer, a Finnigan 4000 chemical ionization/electron-impact mass spectrometer, or an AEI-MS30 spectrometer. High-resolution mass spectral data were obtained by using the AEI-MS30.

Product distribution and yields were ascertained by flame-ionization gas chromatography with a Varian Model 2400 gas chromatograph equipped with a gas-sample injection valve. The GC column used for these analyses consisted of a 10 ft × $^{1}/_{8}$ in. o.d. stainless steel column packed with 10% dinonyl phthalate on Chromosorb W-AWAS (Supelco, Inc.) connected in series with a 20 ft × $^{1}/_{8}$ in. o.d. stainless steel column packed with 20% β,β'-oxydipropionitrile. Typically flow rates of 30 ± 1 mL/min and column temperatures of 55–65 °C were employed.

Acknowledgment. We are grateful for the financial support of the Department of Energy (Grant No. DOE-AC02-80ER-10592) and the Research Corp. M.W.T. thanks Henkel Corp. and Du Pont for fellowship support.

Registry No. Bicyclopropyl, 5685-46-1; 2,2-dibromobicyclopropyl, 22975-42-4; vinylcyclopropane, 693-86-7; bromoform, 75-25-2; cyclohexene, 110-83-8.

Supplementary Material Available: Complete GC data for the pyrolysis mixture, showing typical resolution and unidentified minor components (1 page). Ordering information is given on any current masthead page.

Unusual Secondary to Primary System Rearrangement via Ring Opening of 1-(3-Halopropylene)-4-methoxybenzenium Ions

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The effect of electron-withdrawing groups on the ring opening of benzenium ions has been investigated by kinetics, equilibrium studies, and product analysis. The use of SnX_4 (X = Br or Cl) compounds as highly ionizing solvents and as conveying agents of the X^- nucleophile works quite well. 1,2-Dihalo-3-(4-methoxyphenyl)propanes (**2**; X = Br or Cl) and 1,3-dihalo-2-(4-methoxyphenyl)propanes (**3**; X = Br or Cl) equilibrate at 100 °C in SnX'_4 (X′ = Br or Cl) when X = X′; they undergo halogen exchange with partial rearrangement (**2** → **3** and **3** → **2**) when $X \neq X'$. This **2** → **3** rearrangement is very unusual in benzenium ion chemistry and yields primary halide products. For X = X′, the **3** to **2** equilibrium constant K is 10.1, whatever the halogen; the forward rate constants k_{32} are 1.82×10^{-5} and 1.86×10^{-4} s^{-1} for X = Br and Cl, respectively. For $X \neq X'$ (X = Br, X′ = Cl), as well as for mixed compounds containing both halogens, the relative proportions of rearranged and unrearranged products have been examined in terms of the evolving reactions. Results indicate a mechanism involving 1-(3-halopropylene)-4-methoxybenzenium ions which, when they react with solvated halide ions, yield a mixture of 1,2- and 1,3-dihalides in equal amounts. This absence of ring-opening regioselectivity which contrasts with that of usual unsubstituted propylenebenzenium ions is attributed mainly to the electron-withdrawing effect of the halogen. Benzenium ion involvement in nucleophilic substitution can bring about significant rearrangement in secondary compounds containing electron-withdrawing groups.

The involvement of an aromatic ring leading to a bridged benzenium ion has been demonstrated in the solvolysis of primary and secondary alkyl tosylates with β-aryl substituents.[1-3] Over the last few years, these reactions have been interpreted in terms of competition between the formation (reversible at times) of these intermediate species and bimolecular solvolysis, and many papers deal with the contributions of these two pathways.[4-12] In one

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(1) The role of benzenium-type intermediates in solvolysis reactions has been reveiwed: Olah, G. A.; Schleyer, P. v. R. "Carbonium Ions"; Wiley-Interscience: New York, 1972; Vol. III, pp 1347–1483.

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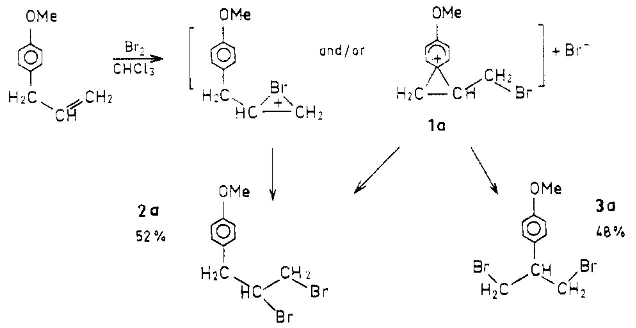
Scheme I



of the most recent papers on secondary tosylates, Lambert et al.[11] demonstrated that an electron-withdrawing substituent in the vicinity of the leaving group diminishes the overall reactivity while increasing the relative importance of the pathway assisted by the aromatic ring. This isolated and original observation has not as yet induced any work on molecular rearrangement. Under such conditions, assistance from the aromatic ring would be a driving parameter for structural reorganization.

We are presenting some of our results along this line which originated from a different starting point than direct solvolysis, i.e., the field of electrophilic addition of bromine on olefins, where reaction product analysis led us to examine the behavior of intermediate bromocarbonium or bromonium ions.

An anomaly in the behavior between benzenium ions and halo-substituted benzenium ions can easily be noted by comparing the difference between their ring-opening regioselectivities. The solvolysis of 1-aryl-2-propyl tosylates occurs without rearrangement, and propylenebenzenium ions react mainly at their most substituted carbon.[13] For benzenium ions bearing an electron-withdrawing substituent, the regioselectivity of the ring opening could be different and demands careful examination.

Indeed, the presence of 1,3-dibromo-2-(4-methoxyphenyl)propane among the end products of bromination of 3-(4-methoxyphenyl)propene can only be explained by some attack at the least-substituted carbon of a (3-bromopropylene)benzenium ion, **1a** (Scheme I).[14] But this ion's ring-opening regioselectivity cannot be assessed since 1,2-dibromo-3-(4-methoxyphenyl)propane (**2a**) could also be formed via a second intermediate species of the bromonium type (Scheme I).

To determine the ring-opening regioselectivity of the (3-halopropylene)benzenium ion, we sought to obtain these intermediate species by ionization of suitable compounds under somewhat original conditions. To avoid bimolecular nucleophilic substitution, we used tin tetrachloride and tetrabromide as the solvents and as conveying agents of the X⁻ nucleophile because of their high ionizing power and low nucleophilicity. For the same reason we chose to ionize a substrate containing a halogen leaving group. This highly ionizing reaction medium, allowing for fairly high temperature studies, compensates for the relative inertness of the substrates which are deactivated by an electron-withdrawing group. In this way the reaction of nucleophilic ions with (3-halopropylene)benzenium ions can be studied. Kinetic and thermodynamic data and reaction products for the halogen exchange and molecular rearrangement of 1,2-dihalo-3-(4-methoxyphenyl)propanes (**2**) and of 1,3-dihalo-2-(4-methoxyphenyl)propanes (**3**) have been obtained. An efficient electron donor, *p*-OMe, was chosen as the aromatic substituent so as to favor the formation of a long-lived benzenium ion.

Table I. Rate Constants for Interconversion of 1,3-Dihalo-2-(4-methoxyphenyl)propanes 3 and 1,2-Dihalo-3-(4-methoxyphenyl)propanes 2 at 100 °C

halogen[a]	solvent	$10^6 k_{32}$, s^{-1}	$10^6 k_{23}$, s^{-1}
Br	$SnBr_4$	18.2	1.80
Cl	$SnCl_4$	186.0	18.3

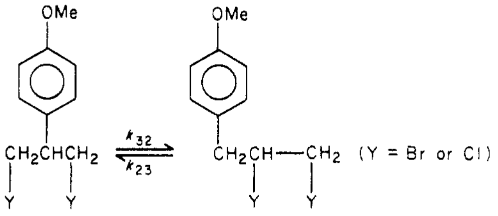
[a] The 3 to 2 equilibrium constant $K = 10.1$ in both cases.

Experimental Results

Equilibration. A single halogen (Cl or Br) was present in the substrate–solvent reaction system.

In $SnBr_4$ at 100 °C, either 1,2-dibromo-3-(4-methoxyphenyl)propane (**2a**) or 1,3-dibromo-2-(4-methoxyphenyl)propane (**3a**) gave an equilibrium mixture of both compounds. Similar behavior was observed for the dichloro(4-methoxyphenyl)propanes **2c** and **3c** in $SnCl_4$. The equilibrium constants, K, for $3 \rightleftharpoons 2$ are given in Table I.

The sum of the apparent rate constants, k_{32} and k_{23}, for



3 2

the reaction below was obtained by kinetic study of the equilibration of 1,3-dihalo-2-(4-methoxyphenyl)propane, which follows the usual equation:

$$\ln ([3] - [3]_{\text{equilibrium}}) = -(k_{32} + k_{23})t + \text{constant}$$

The constants k_{32} and k_{23} were separated by means of K ($K = k_{32}/k_{23}$). Table I summarizes the results.

Replacing Bromine by Chlorine Using Tin Tetrachloride. The replacement of bromine by chlorine, when activated by tin tetrachloride, can be made to occur with or without rearrangement. This reaction can be accompanied by simple isomerization (a rearrangement which is not accompanied by a change in the nature of the halogens).

A series of halogenated compounds shown in Table II [two 1,3-dihalo-2-(4-methoxyphenyl)propanes (dibromide **3a** and chloro bromide **3b**), two 1,2-dihalo-3-(4-methoxyphenyl)propanes (dibromide **2a** and chloro bromide **2b**), 1,3-dibromopropane, and 1,2-dibromodecane] were treated with tin tetrachloride at 100 °C. The first-order rate constants for disappearance of the substrates, k_{exptl}, are given in Table II. 1,3-Dibromopropane was unchanged, whereas 1,2-dibromodecane reacted slowly and yielded mainly bromochlorodecane. For the dihaloarylpropanes studied, the reaction products were exclusively mixtures of other dihaloarylpropanes **2** and **3**. The composition of each mixture, which changed with time, is given in Table II for 25% and 70% reaction. No elimination product was

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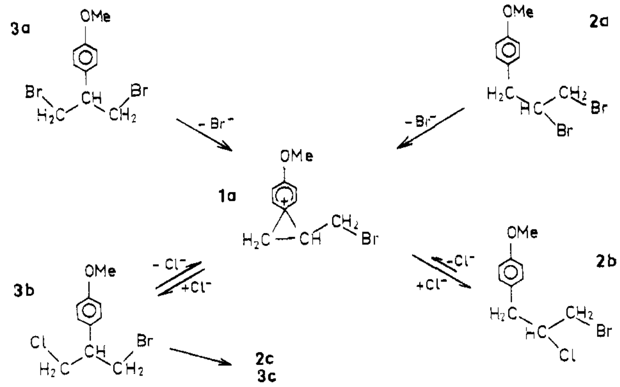
Table II. Halogen Exchange with $SnCl_4$ at 100 °C: Rate Constants and Product Distribution

compd	$10^6 k_{exptl}$, s^{-1}	yields of products, %			
		2b	3b	2c	3c
3a	1800	50[a]	46[a]	2[a]	2[a]
		51[b]	35[b]	7[b]	7[b]
3b	1010	11[a]	(starting material)	46[a]	43[a]
		11[b]		50[b]	39[b]
2a	154	52[a]	20[a]	17[a]	11[a]
		50[b]	5[b]	32[b]	13[b]
2d	145	0[a]	0[a]	58[a]	42[a]
		0[b]	0[b]	74[b]	26[b]
$BrCH_2CH_2CH_2Br$	0[c]				
$BrCH_2CHBr(CH_2)_7CH_3$	2.4				

[a] At 25% reaction. [b] At 70% reaction. [c] For the reference compounds, 98% of the starting material is recovered after 48 h at 140 °C.

Scheme II



detected for substrates with an aromatic ring; product recovery was nearly 100%.

Discussion

Dihalide Equilibrium Constants. The value of 10.1 for the **3** to **2** equilibrium constant (K), whatever the halogen (Cl or Br), indicates that the vicinal dihalide is clearly much more stable than the structure of the compounds would suggest (a greater repulsive interaction between the two C–Cl or C–Br dipoles is expected for the vicinal dihalide) and is also much more stable than expected from comparison with analogous systems. For the thermal equilibration of the 1,3-dibromo-2-propyl esters with 2,3-dibromo-1-propyl esters, it has been reported that vicinal dihalide accounts for 50% of the product at equilibrium for benzoates (at 140 °C)[15] and for 63% of the product at equilibrium for acetates (at 180 °C).[16]

Halogen-Exchange Mechanism in $SnCl_4$. To interpret the behavior of dibromoarylpropanes **2a** and **3a** in $SnCl_4$, we suggest the mechanism described in Scheme II, the first step of which would involve the exclusive formation of a (3-bromopropylene)benzenium ion **1a**. Then, depending on the site of nucleophilic attack, **1a** would lead to 1-bromo-2-chloro-3-arylpropane (**2b**) or to 1-bromo-3-chloro-2-arylpropane (**3b**). Two observations clearly support this mechanism: (i) the rate constants, k_{exptl}, for **2a** and **3a** are at least 10^2–10^3 times higher than those of the reference compounds without an aromatic ring (1,2-dibromodecane and 1,3-dibromopropane), thereby indicating that the transition state for reaction of **2a** and **3a** involves the aromatic ring; (ii) the presence of **3b** in the reaction products of **2a** necessitates the existence of a σ-type bridged ion. Failing this, it would be necessary to invoke the rearrangement of an α-brominated carbenium ion (assistance by the bromine is therefore possible) into a primary carbenium ion.

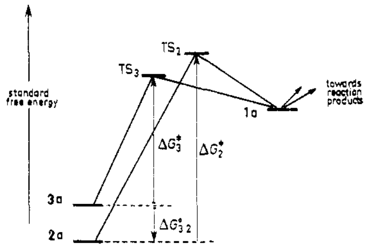


Figure 1. Variation of the standard Gibbs free energy for the reaction of **2a** and **3a** to give **1a**.

Scheme II also depicts the formation of **1a** from either **2a** or **3a** as irreversible; indeed, if there were any significant return, the least reactive dibromoarylpropane, **2a**, would be among the reaction products of the most reactive dibromoarylpropane, **3a**, but this was not observed.

Ring-Opening Regioselectivity from Kinetic and Thermodynamic Results in SnX_4. Our purpose, in this work, was to determine to what extent each of the two electrophilic carbon atoms of the (3-halopropylene)benzenium ion is involved in nucleophilic attack. This is expressed by f_{12} and f_{13}, which represent the fractions of benzenium ions giving 1,2-dihalo-3-arylpropane, **2**, and 1,3-dihalo-2-arylpropane, **3**, respectively. To illustrate the method used in determining f_{12} and f_{13}, we represent the variation of the standard Gibbs free energy in Figure 1 for the reaction of dibromoarylpropanes **2a** and **3a** to **1a**. It is assumed that the intermediate species from **2a** is absolutely identical with that from **3a** and therefore has the same free energy, so that at the moment of nucleophilic attack the structure of the precursor substrate is unimportant. This assumption is based on the fact that p-OMe, a highly efficient electron donor, particularly favors the rapid formation of a benzenium ion with a lifetime sufficiently long for it to acquire its final conformation prior to nucleophilic attack. The lack of return when **3a** is ionized indicates that nucleophilic attack actually occurs after a time long enough for the leaving group to disappear from the immediate environment of the benzenium ion. The difference between the standard free energies of the two transition states, TS_2 and TS_3, for the ionization of **2a** and **3a** is indicative of the regioselectivity of the attack (hypothetical here) of **1a** by a solvated bromide ion. Such an attack, leading to an amount of **2a** and **3a** in a ratio of f_{12}/f_{13}, would indeed occur via the same transition states TS_2 and TS_3 as for the previous ionization of **2a** and **3a**. As no ion pair return was detected for the formation of **1a**, we assume that attack by the solvated bromide ion does

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not occur. In accordance with Eyring's equation, the difference between the standard free energies of TS_2 and TS_3 thus equals $-RT \ln (f_{12}/f_{13})$. It also equals $\Delta G_2^{\ddagger} - \Delta G_3^{\ddagger} + \Delta G^{\circ}_{32}$, where $\Delta G_2^{\ddagger}$ and $\Delta G_3^{\ddagger}$ are the free energies of activation for the ionization of **2a** and of **3a** in $SnCl_4$, and ΔG°_{32} is the difference between the standard free energies of these two compounds. These parameters can be deduced from experimental results as follows: (a) ΔG°_{32} is obtained from K, the constant for the equilibrium between **3a** and **2a** in $SnBr_4$; (b) $\Delta G_2^{\ddagger} - \Delta G_3^{\ddagger}$ is obtained from the rate constants for ionization of **2a** and **3a** to **1a** in $SnCl_4$ by using Eyring's equation. The constants k_{exptl} are significant, since both reactions go through **1a** only and since there is no ion-pair return (significant return would indicate that the ionization step is not rate determining).

It follows from $-RT \ln (f_{12}/f_{13}) = \Delta G_2^{\ddagger} - \Delta G_3^{\ddagger} + \Delta G^{\circ}_{32}$, that

$$f_{12}/f_{13} = K\left[\frac{(k_{\text{exptl}})_{2a}}{(k_{\text{exptl}})_{3a}}\right] = 0.86$$

Hence, $f_{12} = 0.46$ and $f_{13} = 0.54$ [for the hypothetical reaction of solvated Br^- with the (3-bromopropylene)benzenium ion **1a**].

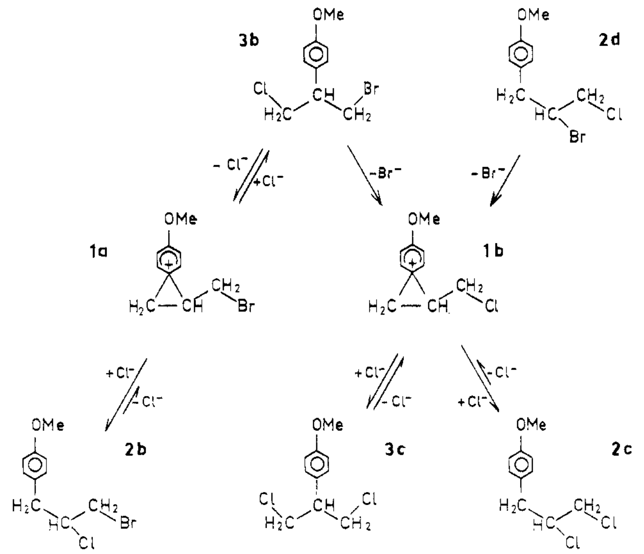
(3-Bromopropylene)benzenium Ion Ring-Opening Regioselectivity from Product Distribution. To confirm our kinetic and thermodynamic results, we sought to determine the f_{12}/f_{13} ratio directly from the reaction product distribution.

In $SnCl_4$, the attachment of a Cl^- to ion **1a** leads to 1-bromo-2-chloro-3-(4-methoxyphenyl)propane (**2b**) for f_{12} and to 1-bromo-3-chloro-2-(4-methoxyphenyl)propane (**3b**) for f_{13} (Scheme II). The first of these two compounds is relatively stable under the conditions under which **1a** is obtained from dibromoarylpropanes **2a** and **3a** ($SnCl_4$, 100 °C). Its rate constant in yielding **3b** via intermediate **1a** (Scheme II) can be identified with the value of k_{23} cited in Table I for **2c**. Its rate constant via another mechanism can only be smaller than that for 1,2-dibromodecane, and therefore very low. The second compound, **3b**, is not stable in $SnCl_4$ at 100 °C, but the end products are known. The f_{12}/f_{13} ratio for the reaction of Cl^- donating species with ion **1a** can be derived from the reaction product distribution originating from **2a** or from **3a** in $SnCl_4$.[17] For the reaction of **3a** in $SnCl_4$, $f_{12} = f_{13} = 0.50$; for that of **2a**, $f_{12} = 0.49$.[18]

(3-Chloropropylene)benzenium Ion Ring-Opening Regioselectivity from Product Distribution. Just as ion **1a** can be obtained from dibromoarylpropanes **2a** and **3a**, it is possible to generate the (3-chloropropylene)benzenium ion **1b** in $SnCl_4$ from 1-bromo-3-chloro-2-(4-methoxyphenyl)propane (**3b**) or from 2-bromo-1-chloro-3-(4-methoxyphenyl)propane (**2d**). As for **2a** and **3a**, the reactivity of these compounds (Table II) can be explained only via a mechanism involving the aromatic ring.

Scheme III represents the formation, in $SnCl_4$, of two benzenium ions from **3b**. Ion **1a** is obtained by the loss of Cl^- and is in turn responsible for the appearance of a bromo chloride which can only be **2b**. Ion **1b**, formed by loss of Br^-, reacts with Cl^-, leading to 1,2-dichloro-3-arylpropane **2c** and to 1,3-dichloro-2-arylpropane **3c**. By analogy with the behavior previously observed for **1a**, it is assumed that there is no ion-pair return in the formation of **1b**. The product distribution from the reaction of **3b** in $SnCl_4$ varies slightly as the reaction progresses (Table II). Thus, direct assessment of the ratio f_{12}/f_{13} by comparing the amounts of **2c** and **3c** is unreliable. It is obvious that these two products equilibrate slowly via ion **1b** as **3b** continues to react. Since the interconversion rate constants k_{23} and k_{32} are available in Table I, a correction term for this equilibration can be introduced; thus, one obtains $f_{13} = 0.49$ for the reaction of Cl^--donating species with ion **1b** originating from **3b** (a substrate with primary leaving groups).[19]

Scheme III



To determine whether an identical value for f_{13} is obtained when ion **1b** results from the ionization of a substrate where the leaving group is secondary, we examined the products from the reaction of **2d** in $SnCl_4$. A complete absence of **3b** confirms that there is no ion-pair return when **1b** is formed. The ratio of the amounts of the two products **2c** and **3c** must be corrected to take into account their equilibration: the latter is important since the reactivity of **2d** is less than that of **3b**. Application of the previously used correction term[19] yields a value of 0.50 for f_{13} during the first half of the reaction.

Ring Opening: Interpretation. The products from the reaction of 1,3-dihalo-2-arylpropanes and of 1,2-dihalo-3-arylpropanes with $SnCl_4$ yield very similar values of f_{12} for the (3-bromopropylene)benzenium ion **1a** (0.50 and 0.49) and the (3-chloropropylene)benzenium ion **1b** (0.51 and 0.50). The fact that the structure of the precursor system (primary or secondary) is unimportant leads us to propose that the benzenium ions have already reached their final conformation when they are attacked by a nucleophile. The difference between the inductive effects of chlorine and bromine being very small, we had expected that the type of halogen present in the ion would be unimportant. This was confirmed.

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[17] Since in $SnCl_4$ **3b** yields 89% of dichloroarylpropanes **2c** and **3c** and 11% of **2b** (Table II), the f_{12}/f_{13} ratio for the reaction of Cl^- with ion **1a** can be calculated through the following equation:

$$f_{12}/f_{13} = \frac{[\mathbf{2b}] - ([\mathbf{2c}] + [\mathbf{3c}])(11/89)}{[\mathbf{3b}] - ([\mathbf{2c}] + [\mathbf{3c}])(100/89)}$$

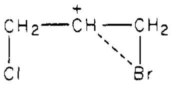
[18] The value calculated for f_{12} is constant during and up to 80% of the reaction of **3a** in $SnCl_4$, whereas for the reaction of **2a** (less reactive than **3a**) in the same medium, it is constant during the early part of the reaction (disappearance of 40% of the substrate) but then decreases slowly during the latter part of the reaction. This decrease is surely due to the fact that the reactivity of **2b** has been neglected.

[19] The following relation is used (k_{exptl} is for the bromochloride substrate):

$$f_{13} = \left(\frac{[\mathbf{3c}]}{[\mathbf{3c}] + [\mathbf{2c}]}\right)\left(\frac{1 - e^{-(k_{\text{exptl}})t}}{e^{-(k_{32} - k_{23})t} - e^{-(k_{\text{exptl}})t}}\right)\left(1 - \frac{k_{32} - k_{23}}{k_{\text{exptl}}}\right)$$

Our initial determination of f_{12} for the (3-bromopropylene)benzenium ion through the use of kinetic and thermodynamic data ($f_{12} = 0.46$) agrees with the results *calculated on the basis of reaction product distribution.* The reaction of solvated halide ions with the (3-halopropylene)benzenium ions gives nearly equal amounts of 1,2-dihalo-3-arylpropane and 1,3-dihalo-2-arylpropane. The nucleophilic attack on the (3-halopropylene)benzenium ion occurs at the two electrophilic sites at the same rate, whereas that on the propylenebenzenium ion has been reported to occur only on the most substituted site,[13,20] in accordance with the well-known fact that a methyl group stabilizes a positive charge. In the (3-halopropylene)benzenium ion, the proximity of the chlorine atom can hinder the development of a positive charge on the carbon atom carrying the halomethyl group and thereby disfavor the transition state leading to 1,2-dihalo-3-arylpropanes. However, the effect of the halomethyl group on the ring-opening regioselectivity appears to be nil. The behavior observed for the (3-halopropylene)benzenium ion is the same as that of the ethylenebenzenium ion, despite the fact that in the latter a hydrogen atom has been replaced by CH_2Br or CH_2Cl, which are clearly more efficient electron-withdrawing groups. It looks as if the electron-withdrawing effect of the chlorine atom was buffered for the electrophilic site carrying the halomethyl group.

Similar behavior was reported by de la Mare et al. for the cyclic (3-chloropropylene)bromonium ion and its CH_2Cl substituent.[21] "In the reaction of hypobromous acid with allyl chloride, intermediate 4 is produced in a conformation which approximates its equilibrium structure, and its further reaction characteristically gives 73% of 2-bromo-3-chloropropan-1-ol and 27% of 1-bromo-3-chloropropan-2-ol."



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Addition of ClOH and IOH to allyl chloride yields similar result: 70% and 71% of primary alcohol among the reaction products.[22,23]

Rearrangements in Nucleophilic Substitution with Aryl Group Participation: Electron-Withdrawing-Group Influence. The rearrangement of a primary system with a β-aryl substituent in solvolysis is a known phenomenon which has often been quantitatively interpreted.[13,24,25] The behavior of 1,3-dihalo-2-(4-methoxyphenyl)propanes in $SnCl_4$ shows that the aptitude of primary systems to rearrange persists when an electron-withdrawing substituent is present; however, the distribution of the nucleophilic attack on the benzenium ion intervenes and limits the extent of the rearrangement.

The solvolysis of secondary systems via an unsymmetrical benzenium intermediate is a totally different matter. In the absence of an electron-withdrawing group, the regiospecificity of nucleophilic addition on the benzenium ion (expected because the two electrophilic carbon atoms carry different substituents) eliminates any possibility of rearrangement. Consequently, solvolysis of 1-aryl-2-propyl tosylates in a water–alcohol mixture leads only to secondary alcohols and esters, even when a propylenebenzenium ion is involved.[20] Our work on 1,2-dihalo-3-(4-methoxyphenyl)propanes shows that this situation is radically modified when the secondary system has an electron-withdrawing group. Indeed, the benzenium ion is no longer attacked exclusively at the most substituted carbon, thus clearing the way to rearrangements.

Lambert et al.,[11] in their work on the acetolysis of 1,4-diaryl-2-butyl tosylates and of *meso*-1,4-diaryl-2,3-butyl ditosylates, have shown that a second tosylate substituent favors the pathway assisted by the aromatic ring and observed that "the products from p-OCH_3 were rearranged (aryl migration, hydride shift)". This observation concerning the final products was not further investigated.[26]

In our work, we were able to demonstrate the general character of this type of rearrangement occurring when a strong aryl participation is associated with the destabilizing influence of an electron-withdrawing group located in the substrate. Thus, it is clear that the aryl-assisted pathway leads to a real aryl transfer. It is satisfying to interpret the formation of the rearranged products in both an electrophilic addition [bromine + 3-(4-methoxyphenyl)propene] and also the halogen nucleophilic exchange of 1,2-dihalo-3-(4-methoxyphenyl)propane by the absence of regioselectivity in ring opening of the destabilized 1-(3-halopropylene)-4-methoxybenzenium ion. It can be assumed that the lessened reactivity of the most substituted carbon results from the halogen atom inductive effect and/or a direct field effect on this site. Steric control of the nucleophilic attack could also be considered. These different factors act coherently.

This destabilization of these benzenium ions, which touches on a little-studied aspect of aryl-assisted solvolysis, that of substrates possessing electron-withdrawing substituents besides the leaving group, has thus far enabled us to approach various rearrangements where halogens are either preserved or exchanged in the SnX_4 medium. Experiments with other aromatic substituents are currently under way in order to test the general character of these conclusions.

Experimental Section

Products. 1,2-Dichloro-3-(4-methoxyphenyl)propane and 1,3-Dichloro-2-(4-methoxyphenyl)propane. A mixture of these two products in equal amounts was obtained by the action of gaseous chlorine on 3-(4-methoxyphenyl)propene in 1,2-dichloroethane. Care was taken to avoid any excess of chlorine. After the mixture was washed with a solution of $NaHCO_3$ and dried over $MgSO_4$ and the solvent evaporated, the two isomers were separated by GLC (0.25 in. × 4 ft column packed with 20% DEGS on Chromosorb).

1,3-Dibromo-2-(4-methoxyphenyl)propane. A solution of bromine (3×10^{-2} mol) in 1,2-dichloroethane (100 mL) was added during 3 h to a solution of 3-(4-methoxyphenyl)propene (3×10^{-2} mol) in the same solvent (500 mL). After the mixture was washed with water and dried and the solvent evaporated, a mixture of 1,2-dibromo-3-arylpropane and 1,3-dibromo-2-arylpropane (50–60%) was obtained. The 1,2-dibromo-3-arylpropane was then destroyed by zinc in methanol as follows: methanol (20 mL) and zinc dust (3 g) were added to the crude dibromide mixture; this was then stirred for 1 h and then refluxed for 30 min. Excess zinc was filtered off. The reaction medium was diluted with hydrochloric acid (2 N) and extracted three times with petroleum ether. The extracts were washed, dried, and concentrated; the crude product was then purified by column chromatography

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(Merck standardized aluminum oxide 90 with pentane as the eluent).

1,2-Dibromo-3-(4-methoxyphenyl)propane. Bromine gas was passed into a stirred solution of 3-(4-methoxyphenyl)propene (1.33×10^{-2} mol) in 10 mL of Me_2SO (used to minimize the formation of 1,3-dibromo-2-arylpropane). After 1 h at room temperature, the reaction mixture was diluted with 100 mL of water and then extracted three times with petroleum ether. The extracts were washed with a solution of $Na_2S_2O_3$, dried over $MgSO_4$, and concentrated; the crude product was then purified by column chromatography as above.

1-Bromo-3-chloro-2-(4-methoxyphenyl)propane. A mixture of equal amounts (1.5×10^{-2} mol) of chlorine and bromine in 1,2-dichloroethane (100 mL) was added to a solution of 3-(4-methoxyphenyl)propene (3×10^{-2} mol) in 1,2-dichloroethane (500 mL). Bromo chloride compounds accounted for 90% of the reaction products, 50% of which was 1-bromo-3-chloro-2-arylpropane. The 1-bromo-2-chloro-3-arylpropane was removed by treatment with zinc in CH_3OH, and the desired product was purified by GLC as above.

2-Bromo-1-chloro-3-(4-methoxyphenyl)propane. 1,2-Dibromo-3-(4-methoxyphenyl)propane (1.5×10^{-3} mol) was added to 10 mL LiCl-saturated DMF. After 40 h at room temperature, the reaction mixture was diluted with water and extracted three times with petroleum ether. After the ether layer was dried and the solvent evaporated, the crude product contained 4% of dibromide, 86% of bromo chloride, and 10% of dichloride. The bromo chloride was purified by GLC. A kinetic calculation indicates that the isolated product consists of 2-bromo-1-chloro-3-(4-methoxyphenyl)propane to the extent of more than 98%.

Other Products. 1,3-Dibromopropane was from Prolabo. 1,2-Dibromodecane was obtained by reaction of bromine with 1-decene. These products were purified by GLC.

Product Identification. Mass spectra were run on a JEOL JMS D100 spectrometer; ^1H NMR spectra were recorded on a JEOL C60 HM spectrometer. The spectra recorded for the 1,3-dihalo-2-arylpropanes were highly characteristic. An additional check on the identification was provided by the conversion of the 1,3-dibromo-2-(4-methoxyphenyl)propane into arylcyclopropane caused by zinc in aqueous alcohol. Unfortunately, there is hardly any difference between the spectra of 2-bromo-1-chloro-3-(4-methoxyphenyl)propane and those of 1-bromo-2-chloro-3-(4-methoxyphenyl)propane [the latter was prepared by reacting BrCl with 3-(4-methoxyphenyl)propene].

Kinetic and Product Studies. A single batch of each tin tetrahalide without further purification was used throughout the entire kinetic study ($SnCl_4$ was a Prolabo RP product; $SnBr_4$ was from Schuchardt).

Each kinetic run was based on ten or more samples subjected to the following treatment. Tin tetrahalide (200 μL) was added to 4 μL of substrate with a reference substance contained in a narrow glass tube. This tube was sealed or quickly capped and then placed in an oil bath at 100 °C for an appropriate length of time; it was then quickly cooled, and its contents were poured into a mixture consisting of 10 mL of HCl (5 N) and 5 mL of pentane. The organic layer was washed with a solution of NaCl and then dried over $MgSO_4$. The pentane was evaporated at room temperature, and the residue was diluted in 200 μL of 1,2-dichloroethane and analyzed by GLC.

When 1,3-dibromopropane is the substrate, a modified procedure, skipping the evaporation of the extraction solvent, was used. The reference substances were *o*-dichlorobenzene, and various 1,2-dichloro-3-arylpropanes [aryl was pentafluorophenyl, (4-trifluoromethyl)phenyl, and 4-chlorophenyl].

GLC was performed on a Varian 1400 chromatograph (0.125 in. × 10 ft column packed with 15% SE-30 on Chromosorb) equipped with a flame-ionization detector. The temperature of the injector was held below 200 °C to avoid any isomerization during injection. For the different samples resulting from each kinetic run, the chromatographic response for the reference substance did not vary (in overall percentage) as the reaction advanced. The sensitivity of the apparatus was checked as being the same for the 1,2-dihalo-3-arylpropanes as for the 1,3-dihalo-2-arylpropanes, whatever the halogens, thereby indicating a product recovery of ca. 100%.

Products were identified on a JEOL JMS D100 mass spectrometer with a JMA-0231 data analysis system coupled with a JGC 20 K gas chromatograph.

Registry No. 2a, 83333-66-8; **2b**, 83333-67-9; **2c**, 67168-94-9; **2d**, 83333-68-0; **3a**, 37983-33-8; **3b**, 83333-69-1; **3c**, 67168-96-1; $SnBr_4$, 7789-67-5; $SnCl_4$, 7646-78-8; 3-(4-methoxyphenyl)propene, 140-67-0.

Kinetics and Mechanism of the Oxidation of *n*-Dodecanethiol and Pyridine-Substituted Ethanethiols by I_2 in Acetonitrile

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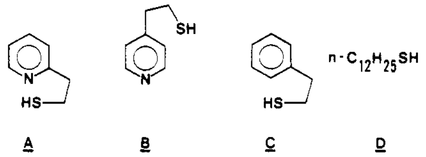
Our investigations of the iodine oxidation of divalent sulfur have been extended to include the thiol group. In acetonitrile the rates of iodine oxidation of thiols can be measured at 25.0 °C by using stopped-flow techniques. The oxidation of the isomeric 2- and 4-(2-pyridyl)ethanethiols (A and B) and two simple sulfides, 2-phenylethanethiol (C) and *n*-dodecanethiol (D), reveals that the rates are extremely sensitive to the basicity of solvent and are maximized for A where the neighboring base is in a position to interact intramolecularly with the thiol. The rates of unsubstituted thiols are also accelerated by added pyridine. Consistent mechanisms of oxidation are proposed.

Chart I



Thiols can be oxidized to disulfides with iodine in good yield under a variety of conditions.[1] One method is to use a 2:1 molar ratio of thiol and iodine in the presence of a tertiary amine in $CHCl_3$. Another method using aqueous iodine and KI is often satisfactory as well; however, Danehy and co-workers[2] found that "overoxidation" occurs in water when the thiol group is situated three atoms away from a carboxylate ion. It was proposed that a cyclic sulfenic carboxylic acid anhydride intermediate forms, which is further oxidized either to sulfinic or sulfonic acids. Most of their work was qualitative in nature and no kinetic

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