the product mixtures. Dr. Edward Rosenberg supplied helpful comments regarding preparation of the manuscript.

Registry No.—**1**, 61062-52-0; 1, HCl, 61062-53-1; **2**, 61062-54-2; **3**, 30934-66-8; **3** 2,4-DNPH, 30934-67-9; **4**, 1533-04-6; **5**, 30934-68-0; **5** 2,4-DNPH, 30934-69-1; **6**, 61062-55-3; **6** 2,4-DNPH, 61062-58-6; **7**, 349-75-7; **8**, 705-29-3; **9**, 2251-65-2; **10**, 61062-56-4; **11**, 339-58-2; **12**, 455-19-6; *m*-trifluoromethylbenzoic acid, 454-92-2; 3-trifluoromethylacetophenone, 349-76-8; 2-bromo-3′-trifluoromethylacetophenone, 2003-10-3; 2-azido-3′-trifluoromethylacetophenone, 61062-57-5; 4′-trifluoromethylphenylacetic acid, 32857-62-8; 2-amino-4′-trifluoromethylacetophenone HCl, 339-58-2; benzaldehyde, 100-52-7; benzyl bromide, 100-39-0.

References and Notes

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A Comparison of the Addition of Bromine and 4-Chlorobenzenesulfenyl Chloride to β-Substituted Styrenes and Ethylenes[1]

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A comparison has been made of the rates and products of addition of bromine and 4-chlorobenzenesulfenyl chloride to a series of β-substituted styrenes ($C_6H_5CH{=}CHR$) and ethylenes ($CH_2{=}CHR$), where R = $CH(OCOCH_3)_2$, CH_2Cl, CH_2OCOCH_3, CH_2OCH_3, CH_2OH, H, CH_3, C_2H_5. On the basis of structure–reactivity correlations and product compositions, it is concluded that the rate- and product-determining transition states in the mechanism of bromination of styrene derivatives have different structures. The rate-determining transition state is bridged while the product-determining transition state resembles an open α-bromocarbonium ion.

The structure of the rate-determining transition state in the mechanism of electrophilic additions to alkenes is principally a function of the electrophile, the alkene structure, and the solvent.[2] For some electrophiles the effect of alkene structure on the mechanism seems to be negligible. For example, the mechanism of hydration involves an open carbonium-ion-like rate-determining transition state[3] while a bridged one is involved in the mechanism of the reaction of arenesulfenyl chlorides.[4]

The effect of alkene structure on the mechanism of bromination of alkenes is not clear. It is generally agreed that a bridged rate-determining transition state is involved in the addition to simple alkenes.[5,6] However, the involvement of such a structure in the addition to styrene derivatives has been the subject of debate.

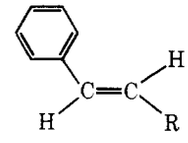
Yates and McDonald have used a thermochemical–kinetic method to probe the structure of the rate-determining transition state.[7] They found that the initial enthalpy difference between pairs of cis–trans isomeric alkenes was increased at the bromination transition state. The results were interpreted as evidence for a bridged rate-determining transition state.

Dubois[6] has compared the bromination of β-substituted styrenes ($C_6H_5C_\alpha H{=}C_\beta HR$) with the corresponding alkenes ($C_\alpha H_2{=}C_\beta HR$) and found that the reactivity of the former series is related to that of the later by a linear equation with slope 0.75. From the value of the slope together with the log k vs. σ^* correlations it was concluded that for the styrene series the rate-determining transition state corresponds to an open carbonium ion with the charge on C_α.

To resolve this problem, we have made a structure–reactivity comparison between bromination and an electrophilic addition whose mechanism is well established. We have chosen the addition of 4-chlorobenzenesulfenyl chloride as our model of a reaction whose mechanism involves a bridged rate-determining transition state independent of olefin structure.[8] Such a comparison should make it possible to arrive at a decision on the structure for the rate-determining transition state of the bromination of styrene derivatives.

Results

We have measured the rates of addition of 4-chlorobenzenesulfenyl chloride to a series of β-substituted trans styrenes, **1a–h**, and to the corresponding alkenes **2a–h** in acetic



1

$CH_2{=}CHR$

2

a, R = $CH(OCOCH_3)_2$
b, R = CH_2Cl
c, R = CH_2OCOCH_3
d, R = CH_2OCH_3
e, R = CH_2OH
f, R = H
g, R = CH_3
h, R = C_2H_5

acid at 25.0 °C. The addition was found to obey a second-order rate law, first order in alkene and first order in sulfenyl chloride to at least 80% completion of the reaction. The rate data are presented in Table I.

The product compositions were determined by NMR spectroscopy. The basis of this method is that protons α or β to chlorine are considerably deshielded relative to those α or β to sulfur.[9,10] The NMR parameters of the adducts obtained in this study are reported in Table II with the exception of data reported previously.[11,12] In every case it was possible to find at least one nonoverlapping signal from which the isomer distribution could be calculated.

The kinetically controlled product composition was determined by immediate NMR analysis of the reaction mixture.

Table I. Second-Order Rate Constants for the Addition of 4-Chlorobenzenesulfenyl Chloride to β-Substituted Ethylenes and Trans Styrenes in Acetic Acid at 25 °C

R	No. of runs	*trans*-$C_6H_5CH{=}CHR$, k_2, l./mol s	No. of runs	$CH_2{=}CHR$, k_2, l./mol s
C_2H_5	8	37.9 ± 0.1	6	18.0 ± 0.1
CH_3	4	30.0 ± 0.1	4	13.7 ± 0.1
H	6	15.9 ± 0.7	4	7.68 ± 0.03
CH_2OH	4	9.90 ± 0.04	7	4.19 ± 0.02
CH_2OCH_3	4	3.51 ± 0.01	3	1.55 ± 0.01
CH_2OCOCH_3	3	0.895 ± 0.006	2	0.340 ± 0.001
CH_2Cl	4	0.602 ± 0.003	4	0.368 ± 0.002
$CH(OCOCH_3)_2$	3	0.0709 ± 0.0004	4	0.0541 ± 0.0013

Table II. NMR Parameters of 4-Chlorobenzenesulfenyl Chloride Adducts

$C_6H_5{-}\underset{Cl}{\overset{\alpha}{C}}H{-}\underset{SC_6H_4Cl}{\overset{\beta}{C}}H{-}R$

Registry no.	R	Chemical shifts, δ, ppm; coupling constants, Hz: δH_α	$J_{\alpha\beta}$	δH_β	$J_{\beta\gamma}$	δH_γ
61062-65-5	$CH_{\gamma_2}OH$	5.03 d	9.5	3.56 dt	4.5	4.01 d
61062-66-6	$CH_{\gamma_2}OCH_3$	5.23 d	7.5	3.36–4.07 m	*	3.36–4.07 m
61062-67-7	$CH_{\gamma_2}OCOCH_3$	5.11 d	8.5	3.70 dt	5.0	4.53 d
61062-68-8	$CH_{\gamma_2}Cl$	5.20 d	8.0	3.47–4.17 m	*	3.47–4.17 m
61062-69-9	$CH_\gamma(OCOCH_3)_2$	4.95 d	10.0	3.77 dd	4.4	6.60 d

$C_\alpha H_2{-}\underset{Cl}{C_\beta}H{-}\underset{SAr}{}R$

Registry no.	R	Chemical shifts, δ, ppm: H_α	H_β	H_γ
61062-70-2	$CH_{\gamma_2}OH$	3.80 d	3.20–3.80 m	3.70 d
61062-71-3	$CH_{\gamma_2}OCH_3$	3.73 d	3.20–3.60 m	3.65 d
61062-72-4	$CH_{\gamma_2}OCOCH_3$	3.70 d	3.30–3.57 m	4.20 d
61062-73-5	$CH_{\gamma_2}Cl$	3.90 d	3.20–4.00 m	3.90 d
61062-74-6	$CH_\gamma(OCOCH_3)_2$	3.70 d	3.43–4.00 m	7.10 d

Table III. Kinetically Controlled Product Composition of the Addition of 4-Chlorobenzenesulfenyl Chloride to β-Substituted Ethylends and Trans Styrenes in Acetic Acid at 25° C

R (X = H)	% M	% aM	% solvent incorporated product
CH_2CH_3	45	55	0
CH_3	43	57	0
H			0
CH_2OH		95	5
CH_2OCH_3		100	0
CH_2OCOCH_3		100	0
CH_2Cl		90	10
$CH(OCOCH_3)_2$		100	0

R (X = C_6H_5)	% erythro M	% solvent incorporated product
CH_2CH_3	≥99	≤1
CH_3	100	0
H	98	2
CH_2OH	82	18
CH_2OCH_3	100	0
CH_2OCOCH_3	100	0
CH_2Cl	≥99	≤1
$CH(OCOCH_3)_2$	100	0

This in situ determination of the adduct isomer ratio is necessary because of the known tendency of many β-chloro sulfides to isomerize.[11-13] The kinetically controlled product compositions are given in Table III.

For all the trans styrene derivatives, the α-chloro β-sulfides are formed as products while for the ethylene series the product composition changes from nonregiospecific to anti-Markownikoff regiospecific as the electronegativity of the substituents increase. Small amounts of solvent incorporated products were also observed.

The NMR data are consistent with products formed by stereospecific anti addition. Unsymmetrical alkenes form two different products whose identity, as established by NMR, is consistent with a pair of Markownikoff and anti-Markownikoff isomers. Furthermore, their isomerization serves to establish their relative configuration. The sole examples of nonstereospecific addition occur in the case of the addition of 2,4-dinitrobenzenesulfenyl chloride to *cis*- and *trans*-1-phenylpropenes containing methoxy, isopropoxy, and phenoxy substituents on the ring.[8] These alkenes are all capable of forming highly stabilized benzylic cations. Our results as well as previous evidence clearly establish that the addition of alkane- and arenesulfenyl chlorides to acyclic alkenes occurs stereospecifically anti.[13]

Discussion

The rates of addition of 4-chlorobenzenesulfenyl chloride to the alkenes studied correlate well with the Taft substituent constants σ_R^*.[14] The following linear relationships were obtained for both series.

For $C_\alpha H_2{=}C_\beta HR$

$$\log k_2 = -1.47\sigma_R^* + 1.18$$

(R = 0.958; standard deviation on the slope = 0.18).

For $C_6H_5C_\alpha H{=}C_\beta HR$

$$\log k_2 = -1.58\,\sigma_R^* + 1.55$$

(R = 0.967; standard deviation on the slope = 0.17).

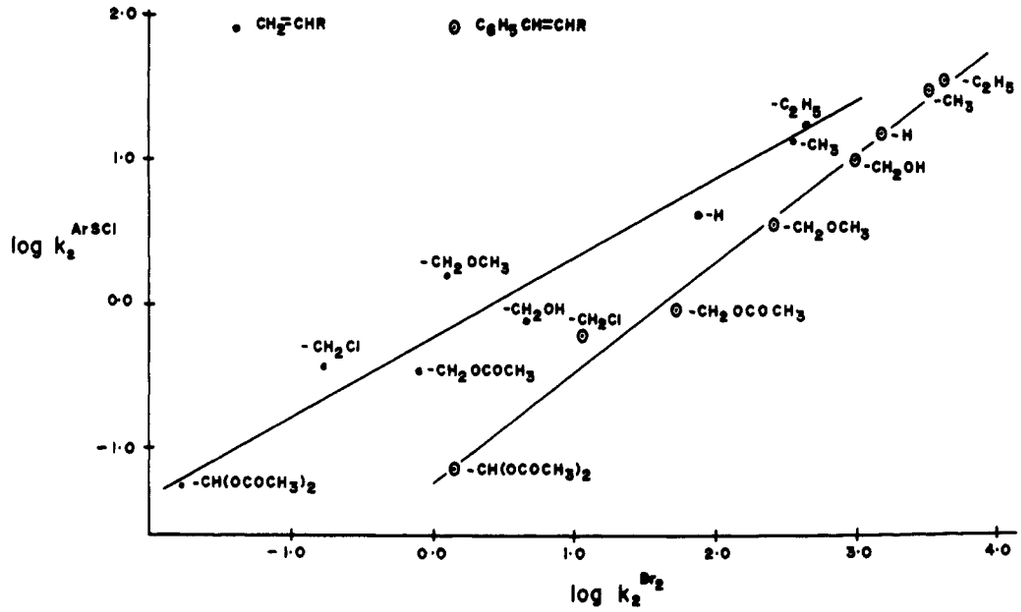


Figure 1. Substituent effects on the rates of addition of bromine and 4-chlorobenzenesulfenyl chloride to ethylene and styrene derivatives.

Since most of the positive charge in the transition state of this reaction is localized on the sulfur atom, the reactivities could be also related to a first approximation to the Taft polar substituents $\sigma_{CH_2R}^*$. Such a correlation again generates two straight lines, described by the following equations.
For $C_\alpha H_2{=}C_\beta HR$

$$\log k_2 = -2.97\,\sigma_{CH_2R}^* + 0.91$$

(R = 0.976; standard deviation on the slope = 0.26).
For $C_6H_5C_\alpha H{=}C_\beta HR$

$$\log k_2 = -3.16\,\sigma_{CH_2R}^* + 1.26$$

(R = 0.978; standard deviation on the slope = 0.27).

For both correlations the corresponding ρ^* values are the same for both unsaturated systems within the standard deviation. This is to be expected due to the similar structure of the rate-determining transition states for both systems.

It is instructive to compare these results with those of Dubois.[6] Dubois found that the reactivity of the ethylene derivatives for bromination correlates well with σ_R^* values ($\log k_{Br_2} = -3.10\sigma_R^* +$ constant), while for the aromatic series the best correlation was obtained when the reactivities were plotted against $\sigma_{CH_2R}^*$ constants ($\log k_{Br_2} = -4.80\sigma_{CH_2R}^* + 3.23$). This was explained as a consequence of the different substituent–positive charge distance in the transition state for both series of compounds. The additional argument presented by Dubois is that the reaction constant sequence ($|\rho^*|_{styrenes} > |\rho^*|_{alkenes}$) remains in agreement with the expected carbonium-ion-like and bridged bromonium-ion-like transition state structures for these two systems.

This last argument does not seem convincing, since the ρ^* values compared were evaluated from different sets of substituent constants (σ_R^* and $\sigma_{CH_2R}^*$). The attenuation factor introduced in the calculation of the $\sigma_{CH_2R}^*$ constants results in an increase in the slope of the log k_2 vs. σ^* plot. This is clearly demonstrated by our results where the slopes of the log k_2 vs. $\sigma_{CH_2R}^*$ for both series are twice as large as the corresponding slopes of the log k_2 vs. σ_R^* plots.

The validity of the use of $|\rho|$ as a quantitative measure of charge on a particular carbon in the rate-determining transition state of a reaction is questionable. The values of $|\rho|$ obtained for the addition of chlorine, bromine, and arenesulfenyl chloride in acetic acid at 25 °C to a series of phenyl-substituted styrenes, −3.22,[15] −4.87,[16] and −2.41,[17] respectively, illustrate the point. On the basis of accumulated data, the relative ability to form a bridged ion should be S > Br > Cl. Therefore if $|\rho|$ were really a good measure of bridging and consequently of the amount of charge on the benzylic carbon, the values should decrease in the order $\rho_{Cl_2} > \rho_{Br_2} > \rho_{ArSCl}$. Since this is not the case, we must question the validity of such an argument.

To avoid the problems of substituent constants, we have plotted log k_{ArSCl} vs. log k_{Br_2} for both series as illustrated in Figure 1. For $C_\alpha H_2{=}C_\beta HR$ the following equation is obtained

$$\log k_2^{Br_2} = 1.7 \log k_2^{ArSCl} + 1.62$$

(R = 0.936, std dev of the slope = 0.3).
For $C_6H_5C_\alpha H{=}C_\beta HR$

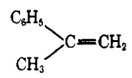
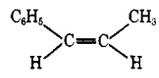
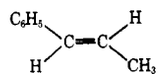
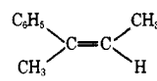
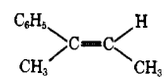
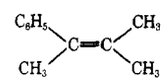
$$\log k_2^{BR_2} = 1.30 \log k_2^{ArSCl} + 2.07$$

(R = 0.994, std dev of the slope = 0.05).

From these correlations, it is clear that a change in alkene structure has a greater effect on the rate of bromination than on the rate of addition of arenesulfenyl chlorides. This is in accord with previous work.[11] From the slopes it is clear that the effect of substituents on the rate of bromination more closely resembles that of addition of 4-chlorobenenesulfenyl chloride to the β-substituted styrenes than it does to the substituted ethylenes. Because of such a similarity in structure reactivity, the conclusion that a similar bridged rate-determining transition state is involved in both the additions of bromine and arenesulfenyl chlorides to these styrene derivatives seems inescapable.

A similar conclusion is evident from a comparison of the effect of methyl substituents on the side chain of styrene on the rates of addition of bromine and 4-chlorobenzenesulfenyl chloride. These data are summarized in Table IV.[12,18] The compounds are separated into two series: those which contain and those which lack a β-methyl cis to phenyl. The effect on the rate of the position of the methyl group is similar for both electrophiles. Thus an α-methyl group has the largest effect while a cis β-methyl group has a general rate-depressing effect. These results are consistent with a bridged rate-determining transition state in which the bridging is less symmetrical for bromine than for sulfur. This similarity between the two electrophiles does not extend to the product-determining transition state. The products of bromination are formed by

Table IV. Rates of Addition of Bromine and 4-Chlorobenzenesulfenyl Chloride to a Series of Side Chain Methyl Substituted Styrenes at 25 °C[12,18]

Compd	Registry no.	Bromine[18] (HOAc)[a] k_2, M^{-1} s^{-1}	k_{rel}	ArSCl[12] (TCE)[a] k_2, M^{-1} s^{-1}	k_{rel}	Compd	Registry no.	Bromine[18] (HOAc)[a] k_2, M^{-1} s^{-1}	k_{rel}	ArSCl[12] (TCE)[a] k_2, M^{-1} s^{-1}	k_{rel}
$C_6H_5CH{=}CH_2$		11.2	1	62.0	1	$C_6H_5CH{=}CH_2$		11.2	1	62.0	1.0
	98-83-9	680	61	265	4.3		766-90-5	8.89	0.8	43.0	0.7
		12.3	1.1	118.3	1.9	$C_6H_5CH{=}C(CH_3)_2$	768-49-0	14.7	1.3	26.0	0.42
							767-99-7	61.7	5.5	42.0	0.7
	768-00-3	300	26.8	442	7.1		769-57-3	56.0	5	9.05	0.15

[a] TCE = tetrachloroethane, HOAc = acetic acid.

Table V. Analytical Data for Sulfenyl Chloride Adducts

Registry No.		% C		% H		% S	
		Calcd	Found	Calcd	Found	Calcd	Found
61062-75-7	$CH_2{=}CHCH_2CH_3$	51.07	51.09	5.14	5.26	13.63	13.74
32326-69-5	$CH_2{=}CHCH_3$	48.88	48.97	4.56	4.77	14.50	14.49
14366-73-5	$CH_2{=}CH_2$	46.39	46.48	3.89	3.93	15.48	15.49
	$CH_2{=}CHCH_2OCH_3$	47.82	47.78	4.82	4.74	12.76	13.25
	$CH_2{=}CHCH_2OCOCH_3$	47.32	47.51	4.33	4.35	11.48	11.69
	$CH_2{=}CHCH(OCOCH_3)_2$	47.25	46.72	4.27	3.64	9.70	9.54
	$C_6H_5CH{=}CHCH_2OCH_3$	58.72	58.55	4.93	5.22	9.79	9.86
	$C_6H_5CH{=}CHCH_2OCOCH_3$	57.47	57.96	4.54	4.53	9.02	8.75
	$C_6H_5CH{=}CH(OCOCH_3)_2$	55.24	54.83	4.39	4.54	7.76	8.26

nonstereospecific addition while those of addition of 4-chlorobenzenesulfenyl chloride are formed stereospecifically anti.

Further evidence for the bromination transition state structure can be obtained by considering the effect of phenyl substituents upon the rate of electrophilic additions to alkenes. Substituting a phenyl ring for a hydrogen on ethylene has little effect upon the rate of addition of 4-chlorobenzenesulfenyl chloride ($k_{CH_2=CH_2}$ = 65 ± 3 M^{-1} s^{-1};[11] $k_{C_6H_5CH=CH_2}$ = 62.0 ± 0.2 M^{-1} s^{-1}).[12] This observation indicates that stabilization by the phenyl ring is nearly the same in both the ground and the transition states. However, a similar substitution causes a tremendous increase in the rate of hydration. The rate of hydration of styrene is about 10^5 times faster than that of ethylene.[18-20] For a reaction involving an open carbonium-ion-like rate-determining transition state, stabilization by a phenyl ring is much more important in the transition state than in the ground state. The substitution of a phenyl ring for the α hydrogen of any of the ethylene derivatives in this study increases the rate of bromination by a factor of 10–100. This effect of changing structure on the rates of bromination more closely resembles that for the addition of arenesulfenyl chloride than hydration consistent with a bridged rate-determining transition state.

On the basis of structure–reactivity correlations and product compositions, it seems clear that the rate- and product-determining transition states in the mechanism of bromination of styrenes have different structures. The data presented here point to a bridged rate-determining transition state while product studies suggest an open ion-like product-determining transition state. A similar situation has been observed for the addition of 2,4-dinitrobenzenesulfenyl chloride to a series of phenyl substituted *cis*- and *trans*-1-phenylpropenes.[8] Such a result suggests that more than one intermediate may exist on the reaction coordinate between these two transition states. Thus the first formed bridged intermediate may rearrange to an open ion prior to the product-determining step. Unfortunately, the present data do not permit a more detailed description of the reaction mechanism.

Experimental Section

All melting and boiling points are uncorrected. Microanalyses were carried out by A. B. Gygli, Microanalysis Laboratory, Toronto, Ontario, Canada.

Materials. Acetic acid was purified by refluxing for several hours with chromium trioxide and acetic anhydride and then distilled through a column.[21]

4-Chlorobenzensulfenyl chloride was prepared as previously described.[13]

***trans*-3,3-Diacetoxy-1-phenylpropene-1** was synthesized from cinnamic aldehyde and acetic anhydride by the method of Hill, mp 86 °C (lit. mp 86 °C[22]).

3,3-Diacetoxypropene-1 was prepared by the method of Wohl,[23] bp 78.5 °C (15 mm) [lit.[23] bp 77 °C (12 mm)].

***trans*-3-Methoxy-1-phenylpropene-1** was obtained from cinnamyl alcohol by treatment with sodium amide followed by methyl iodide according to the preceedure of Beaufour,[24] bp 64 °C (5 mm) [lit.[24] bp 117 °C (16 mm)].

3-Methoxypropene-1 was prepared by methylation of allyl alcohol in the presence of silver oxide.[25] The product contained significant amounts of methyl iodide which could not be removed by fractional distillation. The reaction product was refluxed with methanolic KOH,

filtered, and distilled fractionally through a spinning-band column yielding the pure product, bp 43 °C (lit.[25] bp 43 °C).

***trans*-3-Acetoxy-1-phenylpropene-1** was prepared from cinnamyl alcohol and acetic anhydride,[26] bp 95 °C (5 mm) [lit.[26] bp 135–150 °C (18 mm), 141–142 °C (14 mm)].

3-Acetoxypropene-1 was obtained from allyl alcohol and acetyl chloride in the presence of pyridine,[27] bp 102 °C (lit.[27] bp 103.5 °C).

***trans*-3-Chloro-1-phenylpropene-1** was prepaned from cinnamyl alcohol and hydrogen chloride in CCl_4,[28] bp 104–105 °C (12 mm) [lit.[28] bp 119 °C (17 mm)].

The remaining unsaturated substrates were commercially available and their purity was checked by GLC and NMR.

Kinetics. All kinetic runs were carried out as previously described,[13] following the decrease in 4-chlorobenzenesulfenyl chloride concentration at 385 nm.

Products. 4-Chlorobenzenesulfenyl chloride (20 ml of 0.2 M solution) in acetic acid was added dropwise at 25 °C to 20 ml of 0.2 M solution of an alkene in acetic acid with stirring. The reaction mixture was transferred to a separatory funnel containing 75 ml each of water and benzene. The aqueous layer was removed and the benzene solution was washed with water (100 ml), saturated aqueous $NaHCO_3$ (100 ml), and twice with 100-ml portions of water. After drying ($MgSO_4$), solvent was removed on a rotary evaporator at room temperature. The product composition was then determined in $CDCl_3$.

Elemental Analyses. Attempts to separate the reaction mixtures containing solvent incorporated products by standard methods led to decomposition. Consequently elemental analyses were obtained for only those additions in which no solvent incorporated products were formed. The data are given in Table V.

Registry No.—**1a,** 37973-54-9; **1b,** 21087-29-6; **1c,** 21040-45-9; **1d,** 22688-03-5; **1e,** 4407-36-7; **1f,** 100-42-5; **1g,** 873-66-5; **1h,** 1005-64-7; **2a,** 869-29-4; **2b,** 107-05-1; **2c,** 591-87-7; **2d,** 627-40-7; **2e,** 107-18-6; **2f,** 74-85-1; **2g,** 115-07-1; **2h,** 106-98-9; bromine, 7726-95-6; 4-chlorobenzenesulfenyl chloride, 933-01-7.

References and Notes

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Triphase Catalysis. Applications to Organic Synthesis[1]

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The triphase catalysis principle, as previously developed for *organic phase–aqueous phase* reactions catalyzed by suitable polystyrene-based catalysts (*solid phase*), has been applied to cyanide ion displacement on activated (benzylic) as well as unactivated organic halides and provides a convenient and effective method of preparation of the corresponding nitriles. Other useful transformations to which the triphase catalysis technique has been successfully applied are the synthesis of ethers, dichlorocyclopropanes, organic chlorides, bromides, and iodides as well as the dehalogenation of *vic*-dibromides and oxidation of alcohols.

A significant and recurring problem in organic synthesis stems from the use, or desired use, of a water-soluble reagent in chemically altering a water-insoluble organic substrate. If the reaction is conducted as a heterogeneous process (e.g., organic phase–aqueous phase reaction) observed reaction rates are normally very slow owing to the low concentration of at least one of the reactants in each phase. Techniques currently available to circumvent this problem rely on the use of rapid stirring, cosolvent, and phase-transfer methods. If chemical reaction takes place at a liquid–liquid phase boundary, rapid stirring may have an accelerating effect by increasing interfacial contact.[2] Alternatively, the addition of a cosolvent can bring about a homogeneous state and thereby completely eliminate phase separation. Although this latter approach is often useful, product mixtures are necessarily made more complex and the resulting workup made more difficult. In addition, with aqueous phase–organic phase reactions, use of a cosolvent not only renders the organic substrate accessible to the reagent, but also increases the substrate's contact with water and can promote competing hydrolytic pathways. Recently, a third technique has been developed which appears to have considerable potential; this method has been referred to as phase-transfer catalysis.[3] In brief, an organic-soluble, partially water-soluble catalyst (most commonly a tetraalkylammonium or tetraalkylphosphonium salt) accelerates an aqueous phase–organic phase reaction, presumably, by extracting a given ionic reagent out of water and into the bulk organic phase where reaction can ensue.[4] Based on enhanced reaction rates, high yields of products, and the convenience found with this method, it seems likely that many industrial applications will be forthcoming. One practical limitation to the phase-transfer method, however, is that many of the catalysts used promote the formation of stable emulsions.

It occurred to us that the development of a technique centering around the use of a solid phase catalyst to accelerate