repeated scanning between 220 and 370 nm or at constant wavelength. The detailed procedure follows that previously described for the hydrazinolysis of methyl *p*-nitrophenyl sulfate.[36]

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Registry No. Methoxyamine, 67-62-9; 4-picoline, 108-89-4; hydroxylamine, 7803-49-8; glycine ethyl ester, 459-73-4; butylamine, 109-73-9; hydrazine, 302-01-2; *p*-nitrophenyl methyl sulfate, 38319-17-4; *m*-nitrophenyl methyl sulfate, 66735-53-3; *p*-bromophenyl methyl sulfate, 66735-54-4; phenyl methyl sulfate, 66735-55-5; *p*-methylphenyl methyl sulfate, 46231-81-6.

Sulfonyl Radicals. 7.[1] Kinetics and Mechanism of the Thermal Decomposition of α-Phenylalkanesulfonyl Chlorides Proceeding via Ionic Intermediates

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Kinetics and mechanism of the decomposition of α-phenylalkanesulfonyl chlorides [α-toluenesulfonyl chloride, TSC, and α-phenyl-β-(methanesulfonyl)ethanesulfonyl chloride, PMC] were studied. It was found that the rate of decomposition increased with increasing polarity of solvent or addition of LiCl, but the rate was not affected by addition of radical inhibitors. An ionic chain mechanism involving a heterolytic scission of a C–SO_2 bond was proposed for the thermal decomposition of the sulfonyl chlorides. The activation energies for the heterolytic scissions were found to be 33.7 and 27.3 kcal/mol for TSC and PMC, respectively.

The decomposition of alkanesulfonyl chlorides by a homolytic scission of a S–Cl bond has been used as a method for generation of sulfonyl radicals.[2-6] The homolytic scission requires certain reaction conditions such as high temperature,[7] induced by ultraviolet light[3] or γ-radiation,[5] or the addition of radical initiators, like peroxides[3] or copper chlorides.[6,8] The mechanistic study of the decomposition of alkanesulfonyl chloride was first made by Herbrandson et al.[9] By following the optical activity of 2-chlorooctane which was formed from optically active 2-octanesulfonyl chloride, they concluded that the thermal decomposition of the sulfonyl chloride in the absence of solvent, in diphenyl ether, in the presence of ultraviolet light, or in the presence of peroxide proceeds by a free-radical reaction. Furthermore, they suggested the formation of an adduct between the sulfonyl chloride and *N,N*-dimethylformamide solvent, which decomposed ionically. In a more detailed study on the kinetics and mechanism of the thermal decompositions of alkanesulfonyl chlorides in the gas phase, Geiseler and Kuschmiers[7] found that the overall activation energies for the decompositions were in the range of 42–46 kcal/mol. In view of their finding that the values of the activation energies were much less than the bond dissociation energies for the C–S bond (69–74 kcal/mol)[10] or the S–Cl bond (71 kcal/mol),[11] they proposed the radical chain mechanism shown in eq 1–5.

Scheme I

$$RSO_2Cl \rightarrow RSO_2\cdot + Cl\cdot \quad (1)$$

$$RSO_2\cdot \rightarrow R\cdot + SO_2 \quad (2)$$

$$RSO_2Cl + R\cdot \rightarrow RCl + RSO_2\cdot \quad (3)$$

$$RSO_2Cl + Cl\cdot \rightarrow \cdot R'SO_2Cl + HCl \quad (4)$$

$$\cdot R'SO_2Cl + \text{wall} \rightarrow \text{olefin} + SO_2 + Cl\cdot \quad (5)$$

$$R = CH_3,\ C_2H_5,\ n\text{-}C_3H_7,\ i\text{-}C_3H_7$$

The key step in this chain mechanism is step 3 in which the R· radical abstracts a Cl atom from sulfonyl chloride to regenerate a sulfonyl radical. This mechanism (eq 1–3) has been accepted for the decomposition of methanesulfonyl chloride in the liquid phase.[5] The decomposition induced by ultraviolet light or radical initiators can be also explained by this mechanism with the modification that the $RSO_2\cdot$ radical in eq 1 is generated by photodecomposition of sulfonyl chloride or by Cl atom abstraction of radical initiators from sulfonyl chloride.

On the other hand, it is interesting to note that an α-phenyl substituent apparently favors the thermal decomposition of alkanesulfonyl chloride. Indeed, TSC decomposes at 95 °C[12] while methanesulfonyl chloride (MSC) is stable up to 150 °C.[13] Furthermore, the stabilities of the sulfonyl chlorides having an α-phenyl substituent strongly depend on their structures: while TSC is quite stable at room temperature, α-phenylethanesulfonyl chloride (PEC)

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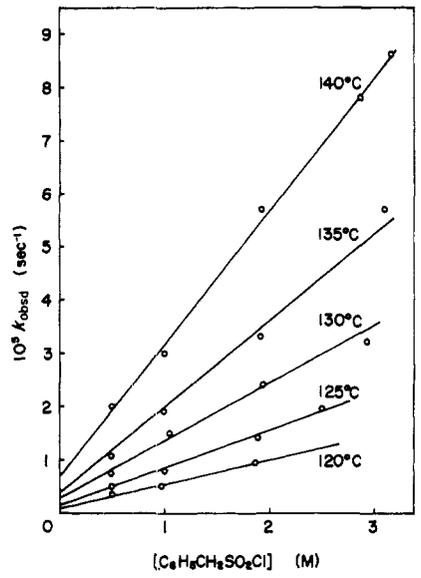

Figure 1. Plots of the observed first-order rate constants (k_{obsd}) for the disappearance of TSC vs. the initial concentration of TSC at various temperatures.

Table I. Effects on Solvent Polarity on the Rate of Decomposition of α-Toluenesulfonyl Chloride

solvent	dielectric const (at 20 °C)[b]	$10^6 k_7$,[c] s^{-1} (at 130 °C)
chloroform[a]	4.8	2.6
tetrahydrofuran	7.6	15
acetone[a]	20.7	120

[a] Deuterated solvents were used. [b] Dielectric constant of undeuterated solvents (Riddick, J. A.; Bunger, W. B. "Technique of Organic Chemistry"; Wiley-Interscience: New York, 1970; Vol. 2). [c] Value obtained by extrapolating the plots of k_{obsd} vs. the initial concentration of TSC.

is so labile that it could not be prepared.[14] However, we have succeeded in preparing α-phenylethanesulfonyl chloride with an electron-withdrawing substituent such as SO_2 at C_β (PMC, $CH_3SO_2CH_2CH(Ph)SO_2Cl$). These observations suggest that the thermal decomposition of these α-phenyl-substituted sulfonyl chlorides may possibly involve ionic intermediates. This encouraged us to investigate the mechanism of the decomposition of these sulfonyl chlorides. We have first investigated the effects of the polarity of solvents and the addition of radical inhibitors on the rate of decomposition of TSC. Next the activation energies for the decomposition of TSC and PMC were determined. Finally, an ionic chain mechanism for the decomposition has been proposed.

Results

Thermal Decomposition of α-Toluenesulfonyl Chloride. The decomposition of TSC resulted in the formation of benzyl chloride in 96% yield (measured by NMR), together with sulfur dioxide (98%, by iodometry[15]). Under the conditions of this study, neither toluene nor bibenzyl was detected. The rate of disappearance of sulfonyl chloride was followed by NMR. The sulfonyl chloride disappears according to pseudo-first-order kinetics; i.e., the observed rate of disappearance is first order

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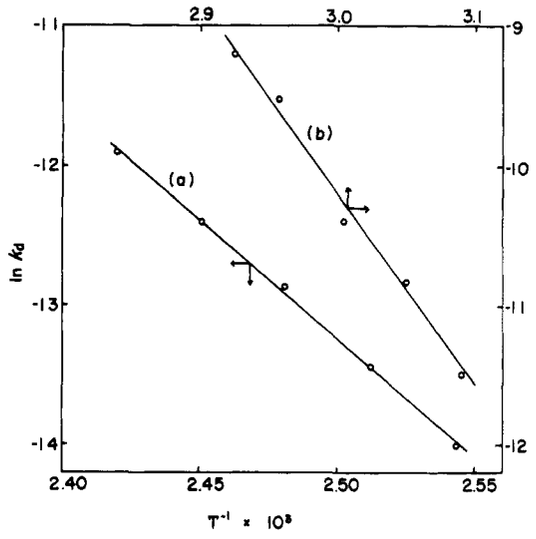

Figure 2. Arrhenius plots for the thermal decompositions of TSC (plot a) and PMC (plot b).

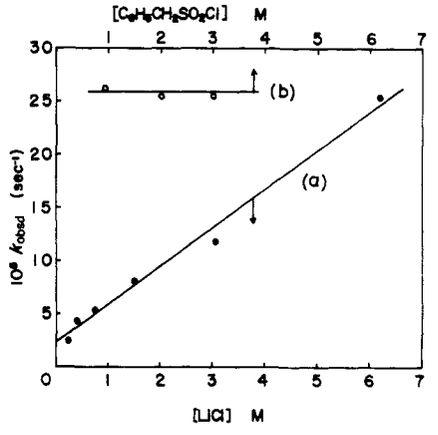

Figure 3. Dependence of the observed first-order rate constants (k_{obsd}) on the concentration of reactants at 90 °C in deuterated acetone: (a) variation of [LiCl], [TSC] = 2.1 M; (b) variation of [TSC], [LiCl] = 6.2 M.

Table II. Effects of Radical Inhibitors on the Rates of Decomposition of α-Toluenesulfonyl Chloride

inhibitor	$10^5 k_{obsd}$,[a] s^{-1}	inhibitor	$10^5 k_{obsd}$,[a] s^{-1}
none	3.1	hydroquinone[b]	5.3
O_2	3.4	benzoquinone[b]	3.1

[a] In $CDCl_3$ at 130 °C; [TSC] = 2.6 M. [b] 10 wt %.

at each initial concentration of sulfonyl chloride, and its rate constant, k_{obsd}, depends on the initial concentration of sulfonyl chloride (Figure 1). An Arrhenius plot for the thermal decomposition of TSC in $CDCl_3$ is shown in Figure 2 (plot a) in which the first-order rate constants, k_7's, were obtained from the intercepts of the plots in Figure 1.

The effects of solvent polarity on the rate of decomposition are shown in Table I. The rate increases considerably with increasing solvent dielectric constants. The rate of decomposition is not affected by addition of radical inhibitors such as oxygen, hydroquinone, and benzoquinone (Table II). However, on addition of LiCl, the rate of disappearance increases markedly, and the k_{obsd} becomes independent of the initial concentration of TSC (Figure 3). Furthermore, both benzyl chloride and benzyl bromide were detected in the decomposition of TSC in the presence of LiBr. An Arrhenius plot for the decomposition of TSC in the presence of LiCl in deuterated acetone gives an

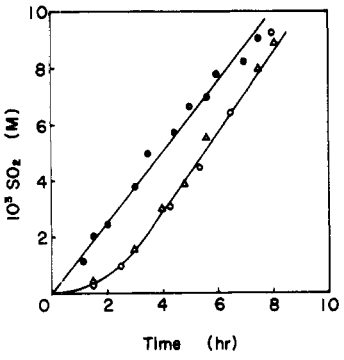

Figure 4. Rates of evolution of SO_2 in the decomposition of methanesulfonyl chloride in tetralin at 175 °C, [MSC] = 5.07 M: (◐) without additive, (●) in LiCl saturated tetralin, (△) 7 wt % of benzoquinone added, (○) 10 wt % of benzoquinone added.

activation energy of 23.0 kcal/mol.

Thermal Decomposition of α-Phenyl-β-(methanesulfonyl)ethanesulfonyl Chloride. The products of the thermal decomposition of PMC are chloride I, vinyl sulfone II, SO_2, and HCl (eq 6). Chloride I and vinyl sulfone II

$$\underset{\text{I}}{CH_3SO_2CH_2CH(Ph)Cl} + \underset{\text{II}}{CH_3SO_2CH{=}CHPh} + SO_2 + HCl \quad (6)$$

were identified by comparison of their NMR spectra with those of their authentic compounds. The ratio of I to II is in range of 1.5–2.5. The rate of disappearance of PMC was determined by monitoring the NMR peaks due to the protons of the CH_3 group of PMC, I, and II. It should be noted that the CH_3 protons of PMC, I, and II give absorption peaks at δ 2.50, 2.75, and 3.00 in CH_2Cl_2, respectively. As in the case of TSC, PMC disappeared according to pseudo-first-order kinetics. An Arrhenius plot for the decomposition of PMC in CH_2Cl_2 is shown in Figure 2 (plot b), in which the values of the k_7's are the extrapolated values at $[PMC]_0 = 0$ of the plots of the observed rate constant for the disappearance of PMC vs. the initial concentration of PMC (the plot is omitted).

In order to ascertain whether the decomposition occurred by a radical mechanism or not, we carried out the decomposition of PMC in the presence of Koelsch's radical. We found that the concentration of Koelsch's radical (followed by UV) was unchanged in the course of the decomposition of PMC.

Thermal Decomposition of Methanesulfonyl Chloride. The thermal decomposition of MSC has been considered to proceed by a radical mechanism. For comparison purposes, we have investigated the effects of the addition of LiCl and radical inhibitor on the decomposition of MSC. The results are shown in Figure 4. The addition of LiCl gives no effect on the rate of decomposition. The decomposition of MSC is retarded by adding benzoquinone, although the retardation effect is not strong.

Discussion

Two possible mechanisms for the thermal decomposition of α-phenylalkanesulfonyl chlorides are discussed here: a free-radical chain mechanism and an ionic chain mechanism. According to the radical chain mechanism (see eq 1–3), the decomposition is initiated by a homolytic scission of a S–Cl bond. In the ionic mechanism (see Scheme II), the reaction starts with a heterolytic scission of the C–S bond. However, the data in Tables I and II and in Figure 3 exclude the possibility of the radical mechanism. Indeed, the results in Table I show that the rate of the decomposition strongly depends on the polarity of solvent, and it increases markedly with increasing solvent dielectric constants. More straightforward evidence for excluding the radical mechanism is shown in Table II, in which radical inhibitors such as hydroquinone, benzoquinone, and oxygen give no effect on the rate of decomposition. Furthermore, the fact that Koelsch's radical did not decay in the decomposition of PMC is also evidence against the radical mechanism. It should be noted that sulfonyl radicals react with Koelsch's radical[16] and hydroquinone.[17] The rate of decomposition increases considerably when LiCl or LiBr was added. As shown in Figure 3, the rate of disappearance of TSC is proportional to the concentration of LiCl. The results favor the ionic mechanism. It is instructive to note that the behavior of the thermal decomposition of TSC toward the addition of LiCl and radical inhibitors is different from that of MSC, which is known to undergo decomposition by the radical mechanism. Contrary to the case of TSC, the rate of decomposition of MSC is unchanged by addition of LiCl, and it is retarded by benzoquinone.

We propose the ionic chain mechanism shown in Scheme II for the decompositions of α-phenylalkanesulfonyl chlorides. Reactions 7 and 8 are initiation steps, i.e., the Cl^--forming steps. Reaction 9 is a propagation step, and reactions 10 and 11 are termination steps.

Scheme II

$$RSO_2Cl \xrightarrow{k_7} R^+ + SO_2Cl^- \quad (7)$$

$$SO_2Cl^- \underset{k_{-8}}{\overset{k_8}{\rightleftharpoons}} SO_2 + Cl^- \quad (8)$$

$$RSO_2Cl + Cl^- \xrightarrow{k_9} RCl + SO_2 + Cl^- \quad (9)$$

$$R^+ + SO_2Cl^- \xrightarrow{k_{10}} RCl + SO_2 \quad (10)$$

$$R^+ + SO_2Cl^- \xrightarrow{k_{11}} R'CH{=}CH(Ph) + HCl + SO_2 \text{ (for the case of PMC)} \quad (11)$$

$$R = PhCH_2,\ CH_3SO_2CH_2CH(Ph)$$

On the assumption that $[SO_2Cl^-] \gg [Cl^-]$, Scheme II leads to the expression $k_{obsd} = k_7 + \text{constant}([RSO_2Cl]^{1/2}/[SO_2])$. This assumption is reasonable since it has been reported[18] that $K(35\ °C) = [SO_2Cl^-]/[SO_2][Cl^-] = 321$. Unfortunately, the order of the dependence of k_{obsd} on $[RSO_2Cl]$ derived from Scheme II deviates from the order observed in Figure 1 ($k_{obsd} = k_7 + \text{constant}[RSO_2Cl]$). We have considered other schemes, but none of them lead to the type of kinetic dependence observed. At present, one possible explanation for the discrepancy is that we have neglected the effect of the ion pair $R^+SO_2Cl^-$ which would be the real attacking species in reactions 9, 10, and 11. An alternative explanation is described in ref 19.

Although we could not give a definite feature for the propagation and termination steps, the first-order rate constant, obtained by extrapolation to $[RSO_2Cl] = 0$, is

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(19) One referee suspects that the result that the first-order decay constant k_{obsd} is a linear function of $[RSO_2Cl]$ is due to the presence of traces of chloride ion in $PhCH_2SO_2Cl$ used. We could not exclude definitely this possibility, but good reproducibility in the repetitive experiments for TSC and PMC suggests that this possibility is unlikely.

attributed to reaction 7. Consequently, we attribute the activation energies obtained from Figure 2 to the activation energies for process 7. These values of the activation energies are 33.7 and 27.3 kcal/mol for the decomposition of TSC and PMC, respectively. These values favor the heterolytic scission rather than the homolytic process, since one would expect higher activation energies for the decompositions of the sulfonyl chlorides if the latter process occurred. It should be noted that the bond dissociation energies are 69–74 and 71 kcal/mol for the C–S[10] and S–Cl bonds,[11] respectively. In this connection, Kice et al.[15,20] have reported the value of 31 kcal/mol for the heterolytic scission of the C–S bond in the thermal decomposition of benzyl diphenylmethanethiolsulfonate (Ph_2CH-SO_2SCH_2Ph).

The stability of the sulfonyl chlorides is very sensitive to their structure, suggesting that the scission is at the C–S bond but not at the C–Cl bond. If the S–Cl bond was cleavaged, the stability of the sulfonyl chloride would not so sensitively depend on the R moiety (see relationship I).

$$\underset{\substack{\text{TSC}\\(E = 33.7\ \text{kcal/mol})}}{PhCH_2SO_2Cl} > \underset{\substack{\text{PMC}\\(E = 27.3\ \text{kcal/mol})}}{CH_3SO_2CH_2CH(Ph)SO_2Cl} > \underset{\substack{\text{PEC}\\\text{(decomposes rapidly even at 0 °C;}\\\text{see Experimental Section)}}}{CH_3CH(Ph)SO_2Cl} \quad \text{(I)}$$

TSC is much more stable than PEC. This may be attributed to the methyl substituent which stabilizes the benzyl cation by hyperconjugation ($PhC^+HCH_3 \leftrightarrow PhCH{=}CH_2H^+$) and by electron-donating inductive effects. On the other hand, PMC is more stable than PEC. We explain this result as follows. In the case of PMC, one hydrogen of the methyl group which stabilizes the benzyl cation by hyperconjugation is substituted by a CH_3SO_2 group. In addition to this, the electron-withdrawing inductive effects of SO_2 also destabilize the benzyl cation.

The evidence showing that process 9 was operated was obtained when we detected benzyl bromide together with benzyl chloride in the decomposition of TSC in the presence of LiBr. King and Smith[21] also have found that a reaction of type 9 actually occurs for the reaction of $PhCH_2SO_2Br$ with Br^-. They have suggested that, from kinetic and stereochemical results, the reaction is a bimolecular nucleophilic displacement on the carbon atom with a concerted fragmentation of the S–Br bond ($Br^{\delta-}\cdots CH_2(Ph)\cdots SO_2\cdots Br^{\delta-}$). A similar process also has been suggested in the decomposition of alkyl chlorosulfites[22] ($Cl^- + ROSOCl \rightarrow RCl + SO_2 + Cl^-$).

The kinetic behavior in the presence of LiCl, as shown in Figure 3, can be clearly explained by reactions 9 and 8. The rate of disappearance of sulfonyl chloride is expressed by eq 12. Consequently, the result that the

$$-d[TSC]/dt = k_9[Cl^-][TSC] = k_{obsd}[TSC] \quad (12)$$

$$k_{obsd} = k_9[Cl^-]$$

first-order rate constant for the disappearance of TSC (k_{obsd}) is independent of the initial concentration of TSC but is proportional to the concentration of LiCl (Figure 3) can be explained by eq 12. Finally, the activation energy for reaction 9 is found to be 23.0 kcal/mol. This value is reasonable for an S_N2 substitution reaction.[23]

In view of ionic intermediates involving in the decomposition, alternative processes such as an S_Ni mechanism (eq 13) should be considered. However, this process is not in agreement with the result that k_{obsd} depends on the initial concentration of sulfonyl chloride.

$$RSO_2Cl \rightarrow [R^{\delta+}\cdots SO_2\ Cl^{\delta-}] \rightarrow RCl + SO_2 \quad (13)$$

Finally, it is instructive to mention that our conclusion that the thermal decomposition of α-phenylalkanesulfonyl chlorides proceeds by an ionic mechanism will not be against the radical chain mechanism proposed by Kandrov et al.[24] for the decomposition of TSC initiated by dicyclohexyl peroxydicarbonate (Scheme III, where In· denotes radicals generated from the initiator).

Scheme III

$$PhCH_2SO_2Cl + In\cdot \rightarrow PhCH_2SO_2\cdot + InCl \quad (14)$$

$$PhCH_2SO_2\cdot \rightarrow PhCH_2\cdot + SO_2 \quad (15)$$

$$2PhCH_2\cdot \rightarrow PhCH_2CH_2Ph \quad (16)$$

$$PhCH_2\cdot \xrightarrow{TSC} PhCH_2Cl + PhCH_2SO_2\cdot \quad (17)$$

In the presence of a radical initiator, the decomposition would be initiated by chlorine abstraction by the initiator from sulfonyl chloride (eq 14) rather than by the heterolytic scission of the C–S bond (eq 7). In this connection, Iino et al.[25] have reported that TSC and PMC have large chain-transfer constants, suggesting that alkyl radicals easily abstract a chlorine atom (eq 7) from these sulfonyl chlorides.

Conclusion

The decompositions of sulfonyl chlorides (alkane or α-phenylalkanesulfonyl chlorides) initiated by radical initiators or ultraviolet light proceed by a radical chain mechanism. On the other hand, in the thermal decomposition of sulfonyl chlorides, while alkanesulfonyl chlorides would decompose by a radical chain reaction, the α-phenylalkanesulfonyl chlorides seem to decompose according to the ionic chain mechanism.

Experimental Section

Materials. Spectrograde deuterated chloroform ($CDCl_3$) and acetone (CD_3COCD_3) were used without further purification. Dichloromethane was dried over $CaCl_2$ for 2 days and then distilled over fresh $CaCl_2$. Tetrahydrofuran was dehydrated over sodium wire and then purified by distillation. Spectrograde tetralin was used. Commercially available methanesulfonyl chloride was purified by distillation under reduced pressure.

α-Toluenesulfonyl chloride was prepared from benzyl chloride and thiourea by the method of Johnson and Sprague.[26] The crude sulfonyl chloride obtained was purified by recrystallization twice from chloroform.

α-Phenyl-β-(methanesulfonyl)ethanesulfonyl chloride was prepared[26] from $CH_3SO_2CH_2CHCl(Ph)$ which was obtained by the reaction of methanesulfonyl chloride and styrene.[8] The crude sulfonyl chloride was purified by recrystallization three times from CH_2Cl_2 at low temperature and was then stored in a freezer: NMR ($CDCl_3$) δ 7.50 (5 H, s, Ph), 5.10–5.40 (1 H, q, CH, decoupling s), 3.90–4.0 (2 H, t, CH_2, decoupling s), 2.5 (3 H, s, CH_3); UV (CH_2Cl_2) λ_{max} 236 nm (ϵ 8.73 × 10^3). Anal. Calcd for $C_9H_{11}ClO_4S_2$: C, 38.22; H, 3.92; Cl, 12.53; S, 22.68. Found: C, 38.02; H, 4.09; Cl, 12.40; S, 22.20.

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β-Methanesulfonyl styrene (CH_3SO_2CH=$CH(Ph)$) used as an authentic compound was obtained by dehydrochlorogenation of $CH_3SO_2CH_2CHCl(Ph)$ with triethylamine at room temperature: NMR ($CDCl_3$) δ 7.45 (5 H, s, Ph), 7.80–6.80 (2 H, q, CH=CH), 3.00 (3 H, s, CH_3).

Attempt To Prepare α-Phenylethanesulfonyl Chloride. Kharasch et al.[14] have reported the failure of the preparation of this sulfonyl chloride from salts of its sulfonic acid and PCl_5. We have tried to prepare this sulfonyl chloride by oxidizing its thiourea salt ($CH_3CH(Ph)SCN_2H_4Cl$) by Cl_2 at 0 °C (Johnson and Sprague's method)[26] in the hope that the forming sulfonyl chloride is not so unstable at 0 °C. However, when chlorine gas was conducted into the aqueous solution of the thiourea salt, a white solid which is believed to be sulfonyl chloride precipitated, and then it decomposed rapidly. So, we believe that the sulfonyl chloride is unstable even at 0 °C.

Kinetic Measurements. The rates of disappearances of α-toluenesulfonyl chloride and α-phenyl-β-(methanesulfonyl)-ethanesulfonyl chloride were determined by NMR. The sample was prepared directly in an NMR sample tube which can be connected to a vacuum line for degassing of the sample. The thermal decomposition was carried out by placing the degassed sample tube in a temperature-controlled silicon oil bath. ^1H NMR measurements were performed at room temperature at 60 MHz. The rate of decomposition of α-toluenesulfonyl chloride was determined by measuring the ratio of the areas of the peaks due to the CH_2 protons of α-toluenesulfonyl chloride and benzyl chloride. It should be noted that aromatic solvents cannot be used here since the peaks due to the CH_2 protons of α-toluenesulfonyl chloride and benzyl chloride are overlapped in these solvents. The rate of decomposition of α-phenyl-β-(methanesulfonyl)ethanesulfonyl chloride was measured by taking advantage of the fact that that the peaks due to CH_3 protons of reactant and products absorb at different positions.

The decomposition of methanesulfonyl chloride in tetralin was followed by measuring the amount of SO_2 formed by iodometry.[20]

Registry No. I, 6038-47-7; II, 5342-84-7; α-phenyl-β-(methanesulfonyl)ethanesulfonyl chloride, 70551-57-4; α-toluenesulfonyl chloride, 1939-99-7.

Crown Cation Complex Effects. 10. Potassium *tert*-Butoxide Mediated Penultimate Oxidative Hydrolysis of Nitriles

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The failure of phase-transfer catalysis to improve either the yield or rapidity of basic nitrile hydrolysis is due, in part, to the poor solubility of quaternary ammonium hydroxides in nonpolar solutions. An alternative hydrolysis method which involves potassium *tert*-butoxide mediated oxidative cleavage of the nitrile with loss of the cyano carbon is presented. The isolated yields reported here range from 21–93% and are found to be highest for long-chain aliphatic nitriles such as cyanohexadecane.

Introduction

The basic hydrolysis of nitriles directly to the corresponding acids is a simple and high-yield transformation in only the most favorable of cases.[1b] Nitriles often resist basic hydrolysis to amides or acids, sometimes with considerable tenacity. Although the conversion of nitriles to amides (especially in the presence of peroxide[2]) has been known for some time, even this transformation continues to inspire new methodology.[3] We encountered the hydrolysis problem in connection with other work[4] and sought a simple, general method for hydrolysis of common nitriles, especially lipophilic ones.

Results and Discussion

The expedient of phase-transfer catalysis[5] proved of only marginal value in improving the basic hydrolysis of several nitriles which we examined. These experiments were conducted under two-phase conditions using benzene as solvent for the nitrile and aqueous sodium hydroxide as the source of base. Although the notion of using phase-transferred hydroxide seems logical at first, the poor solubility of quaternary ammonium hydroxides in nonpolar media[6] dooms this approach to failure.

In the absence of a phase-transfer catalyst, increasing the concentration of sodium hydroxide in the aqueous phase from 10–50% in increments of 10% did not improve the yield of benzoic acid obtained by hydrolysis of benzonitrile. In fact, with 10%, 20%, 30%, 40%, and 50% aqueous sodium hydroxide solutions and an equal volume of benzene as cosolvent, phenylacetonitrile was converted into phenylacetic acid in 82%, 77%, 54%, 30%, and 4% isolated yields, respectively, after 24 h at reflux (see Experimental Section). The trend can be clearly discerned from Figure 1. The slope of the line is −2.03 and the correlation coefficient is surprisingly good (−0.98). Note that the predicted y intercept is 110% yield, a value which is misleading as well as impossible. The hydrolysis of a nitrile is likely to be very slow under completely neutral conditions. The predicted value (y for x = 5%) of 100% yield at 5% aqueous concentration seems quite reasonable for this simple nitrile.

***tert*-Butoxide-Catalyzed Oxidative Hydrolysis.** Strongly basic conditions such as those available by using phase-transfer catalysis have proved useful for a number

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