ter, Picatinny Arsenal, NJ (contract DAAA21-86-C-0091), and the North Texas State University Faculty Research Committee is gratefully acknowledged.

Registry No. 1, 111933-61-0; 2, 2958-72-7; 3, 54142-92-6; 4, 111933-62-1; 5 (isomer 1), 112018-22-1; 5 (isomer 2), 112018-23-2; 6, 58228-93-6; 7, 111933-63-2; 8, 111933-64-3; 9, 111933-65-4; 10, 111933-66-5; 11, 111933-67-6; 12, 111933-68-7; 13, 111933-69-8.

Group Transfers. 2. Solvolysis of Isopropyl Arenesulfonates in Sulfolane[1]

Barry M. Jacobson and Edward S. Lewis*

Department of Chemistry, Rice University, P.O. Box 1892, Houston, Texas 77251

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An attempt was made to study near identity replacements of one isopropyl arenesulfonate with another arenesulfonate anion. Such results would have paralleled the analogous studies of methyl transfers between arenesulfonates,[2] except with an alkyl group more able to tolerate a positive charge in the transition state. This attempt, however, failed. The isopropyl esters in tetrahydrothiophene 1,1-dioxide (sulfolane) are not stable enough to observe any significant displacement; they lose arenesulfonic acid too rapidly. At 100 °C overnight isopropyl tosylate from the *p*-nitrophenylsulfonate ester and tosylate anion could not be detected even with an initial 56-fold excess of the nitro ester, which was itself over 90% solvolyzed. At 60 °C the same mixture showed barely detectable tosyl ester formation. At 40 °C the level of tosylate ester that was formed reached only 20% of the maximum possible value before declining from its own solvolysis.

Although sulfolane is widely used as a solvent for nucleophilic substitution reactions, yet save for one report on dehydration of some terpenediols,[3] a search of the literature turned up no studies of eliminations in sulfolane. We therefore decided it was worthwhile to study our elimination reaction and have found it to be an ordinary solvolysis. When 1,8-bis(dimethylamino)naphthalene (Proton sponge, Aldrich) is added to suppress readdition of the sulfonic acids to the propene product, the reactions (followed by reverse-phase HPLC analysis of the sulfonic esters) follow a first-order course with the first-order rate constant not affected, within experimental error, by reduction of the Proton Sponge concentration by a factor of 2.

The table gives these first-order rate constants for several different arenesulfonates. The rate constants fit the Hammett equation with $\rho = +1.71$. This is hardly more than the ρ value of +1.46 reported by Jaffe[4] from the data of Robertson[5] for the solvolysis of isopropyl arenesulfonates in ethanol, and not much less than those reported by Kevill[6] for adamantyl arenesulfonates, $\rho = 1.76$ for 1-adamantyl, and 1.86 for 2-adamantyl.

We had anticipated a much higher ρ value, perhaps close to that for the complete conversion of an arenesulfonate ester to the anion, such as the value of 2.9 reported for the equilibrium constant for methylarenesulfonate exchange with 3,4-dichlorobenzenesulfonate ion, or the value 3.2 for phenacylarenesulfonates equilibrating with benzenesulfonate.

Table I. Solvolysis Rates of Isopropyl Arenesulfonates in Sulfolane

parasubstit	concn of ester, M	concn of Proton Sponge, M	10^5K, min^{-1}
H	0.0108	0.0116	4.83[a,b]
H	0.0132	0.0055	4.85[c]
CH_3	0.00945	0.0103	2.57[a,b,d]
Cl	0.00980	0.0118	15.6[a,e]
NO_2	0.0103	0.0109	117[a,e]

[a] Average of 2 runs. [b] Reaction followed for 2 half-lives. [c] Reaction followed for 1 half-life. [d] Decreasing Proton Sponge concentration by 50% produces no decrease in rate measured over the first 25% of reaction. [e] Reaction followed for 3 half-lives.

If the equilibrium ρ for loss of arenesulfonates from the isopropyl esters is about the same as that for loss of arenesulfonates from methyl esters, then we might conclude that the transition state has less sulfonate anion character (1.7/2.9 = 59%) than it does in the methyl transfer between arenesulfonates (about 1.88/2.9 = 65%).[2] However, this unexpected conclusion is probably in error for several reasons.

First, it is possible that the starting isopropyl esters may already have more ionic character than the methyl esters, and the equilibrium ρ would therefore be less than that for the methyl esters.

Second, our treatment of substituent effects in methyl transfers[7] is based upon reactions of the charge type of reaction (1). However, the present reaction has for the

$$X^- + MeY \rightarrow XMe + Y^- \quad (1)$$

rate-determining step presumably an ionization reaction giving an intimate carbonium, arenesulfonate ion pair. Previous assumptions about work-terms for such a charge-creating reaction are certainly incorrect, thus the basis of the interpretation of ρ is less secure. As an example, the descriptions of the transition state for the Menschutkin reaction are very different from reactions of type (1). Thus, Arnett and Reich determined a slope of $\Delta G^{\ddagger}$ vs $\Delta G°$ of 0.26 for the reaction of methyl iodide with substituted pyridines,[8] i.e., less than 30% of the charge is developed, as measured in this way. The solvolysis of methyl iodide in water as described by Kurz and Kurz[9] turned out to be complicated; most of the activation energy is required to reorganize the solvent structure.

In the transition state for a charge-creating reaction, the positive and negative charges are separated by only a short distance. Thus although the value of ρ for departure of arenesulfonates depends on the charge on the sulfonate ion, it is reduced by the positive charge only a little farther away.

The effect of a charge change on ρ is attenuated by about a factor of 2 for each extra bond interposed. So if the full charge were developed on both the sulfonate and the alkyl group in the transition state without any dimensional change, ρ would be reduced below that for complete ion separation by a factor of $1 - {}^1/_2 = {}^1/_2$, where the negative term arises because the effect of the developing positive charge is opposite in sign to that of the negative charge

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on the sulfonate. Similarly, if the distance is twice that in the starting ester, ρ would be reduced by a factor of $1 - (^1/_2)^2$ or $^3/_4$. These two are reasonable limits for an unassisted ionization, but for major solvent participation, where the positive charge is located largely on the solvent, an extra bond distance is again interposed. The reduction factor now might be $1 - (^1/_2)^3 = ^7/_8$. This factor might also be an upper limit for the ρ for the Menschutkin reaction.

These crude estimates cannot now be refined to a level worthy of the name calculation without better ideas about "attenuation" and about transition-state dimensions. Qualitatively the effect must be there and thus a solvolysis ρ cannot be as large as that for the formation of independent isolated ions. Thus the use of ρ compared to that for equilibrium dissociation to estimate the charge development must give too low an answer, and our earlier prediction is in error. We cannot say whether the charge development in the solvolysis is greater than that in the substitutions on methyl arenesulfonates although other evidence strongly suggests that it is.

Experimental Section

Preparation of Esters and Other Materials. The para-substituted benzenesulfonate esters were prepared by using a modification of the method of Schleyer as cited in ref 10 that gave purer products. Freshly purified pyridine (50–75 mL) and dry isopropyl alcohol (3 mL) were cooled to 0 °C and the para-substituted benzenesulfonyl chloride (90 mol % based on alcohol) was added slowly with stirring. When solution was achieved, the well-stoppered flask was placed in a freezer at −10 °C until precipitation of pyridine hydrochloride appeared complete (1 to 2 days). The mixture was poured onto excess concentrated HCl plus 200 g of ice with good stirring. The nitro-, chloro-, and methyl-substituted benzenesulfonates all crystallized after several minutes of stirring and were collected, washed with ice water, and dried in vacuo. The unsubstituted benzenesulfonate remained an oil. It was taken up in ether, the ether layer washed with water, dried over K_2CO_3, and filtered, and the ether was evaporated. Residual solvent was pumped away at $<10^{-2}$ mmHg. The solid esters were all crystallized from petroleum ether. All four esters were >99% pure by HPLC and had melting points of 52–53 °C (*p*-nitro), 36.5–38 °C (*p*-chloro), and 20 °C (*p*-methyl). The *p*-chloro ester does not appear to have been reported in the literature before. NMR ($CDCl_3$) δ 7.75 (m, 2 H), 7.40 (m, 2 H), 4.64 (septet, J = 7 Hz, 1 H), 1.20 (d, J = 7 Hz, 6 H). Anal.[11] Calcd for $C_9H_{11}O_3SCl$: C, 46.06; H, 4.72; S, 13.66; Cl, 15.11. Found: C, 46.52; H, 4.58; S, 14.19; Cl, 15.43. 1,8-Bis(dimethylamino)-naphthalene (Proton Sponge, Aldrich) was sublimed before use. Sulfolane was purified as in earlier work.[12]

Kinetics. The Proton Sponge and 20 to 30 mg of biphenyl (as an internal standard) were weighed into a dry 25-mL volumetric flask and about 20 mL of sulfolane was added. The flask was swirled until solution appeared complete. The ester was then weighed in and the flask filled to the mark with the solfolane and shaken for 10 min. Aliquots of the solution were pipetted into 1-mL ampules and the ampules sealed with a torch. The ampules were placed in a water bath at 65 °C (Neslab Model RTE-8, rated at ±0.02 °C). An ampule was removed periodically, opened, and the extent of reaction measured by direct injection into the HPLC. The latter consisted of a Kontron 414LC pump, Valco C6W valve, 25-cm Custom LC C18 ODS column, and either a Kratos Spectroflow 757 or Hitachi 655A-22 variable wavelength detector. The eluant was 2:1 acetonitrile/water, flowing at 1.5 mL/min. The wavelength monitored depended on the ester (nitro 253 nm, chloro 268 nm, methyl 262 nm, and hydro 267 nm) and was chosen for maximum ester response. All injections were in triplicate. Injection volumes were 4 to 5 μL except for the *p*-nitro ester. Its more intensely absorbing solution was first diluted 20:1 with acetonitrile and then 10-μL injection volumes were used. Peak areas were determined with a HP3390A integrator and first-order rate constants calculated by an unweighted, linear least-squares fit for a plot of the logarithm of the ratio of unreacted ester to biphenyl internal standard vs time.

Registry No. $PhSO_3Pr$-*i*, 6214-18-2; *p*-$MeC_6H_4SO_3Pr$-*i*, 2307-69-9; *p*-$ClC_6H_4SO_3Pr$-*i*, 69564-62-1; *p*-$O_2NC_6H_4SO_3Pr$-*i*, 1830-67-7.

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Robinson–Schopf Condensations with Succinaldehyde

John M. McIntosh

Department of Chemistry, University of Windsor, Windsor, Ontario, Canada N9B 3P4

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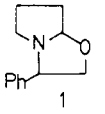
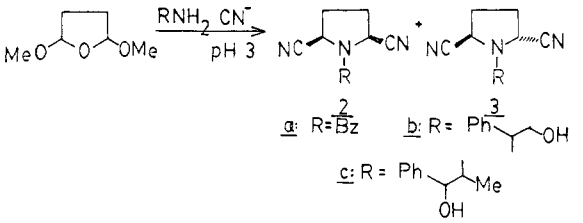
In connection with other work, a general route to chiral (nonracemic) α-substituted pyrrolidines was required. Among other avenues being explored, the Robinson–Schopf[1] condensation using (*R*)-phenylglycinol, succinaldehyde, and cyanide ion was attempted as a route to **1**.



1

This reaction has been very successfully applied, using glutaraldehyde, to the preparation of the corresponding piperidine systems.[2] However, a recent report[3] which suggests that it is unsuccessful using succinaldehyde and other work relating to the condensation of succinaldehyde with primary amines[4] prompts us to report our attempts to effect this and closely related reactions.

Condensation of succinaldehyde, formed in situ from 2,5-dimethoxytetrahydrofuran, benzylamine, and KCN in aqueous citric acid gave two products which were separated by chromatography. These were identified as the cis (**2a**) and trans (**3a**) diastereomers of *N*-benzylpyrrolidine-2,5-



dicarbonitrile. The 300-MHz proton spectrum of **2a** showed the benzylic protons as a clean singlet whereas in **3a** they appeared as an AB quartet.[4] Similar analysis of the cis and trans isomers of *N*-benzyl-2,6-dicyanopiperidine has been published.[5]

Substitution of (*R*)-phenylglycinol for benzylamine led to the formation of two products. Crystallization of the chromatographically more mobile material (**2b**) gave a substance whose carbon NMR spectrum showed only one cyano carbon and two absorptions for the four ring carbons. The proton NMR spectrum showed a narrow

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