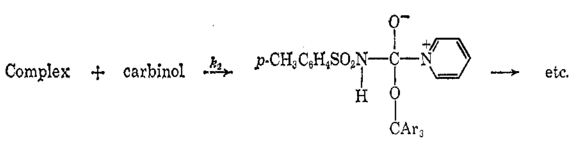
is, therefore, proposed for the catalyzed reaction. What we show as isocyanate–alcohol intermediate could, of course, be unstable urethan (see paper VII).[12]

The formation of a complex and subsequent attack by carbinol is somewhat analogous with a mechanism proposed by Baker and Gaunt for the reaction of phenyl isocyanate and alcohols.[13] Those workers proposed that isocyanate forms a complex with the first molecule of alcohol and the complex is then attacked by another molecule of alcohol. It was also found that the apparent second-order rate constant was dependent upon initial alcohol concentration.

**Registry No.**—I, 4083-64-1; II, 76-84-6.

**Acknowledgment.**—Support for this work was received through Grant 2571 from the Petroleum Research Fund, administered by the American Chemical Society. For such support we are deeply grateful.

[12] A reviewer suggested that the isocyanate-pyridine complex reacts with carbinol to form an intermediate with a good leaving group. The intermediate loses pyridine to give urethan, which further decomposes.



[13] J. W. Baker and J. Gaunt, *J. Chem. Soc.*, **151**, 19 (1949).

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# The Chemistry of Sulfonyl Isocyanates. VII. Kinetics of the Reactions with Substituted Triphenylmethanols

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4-Toluenesulfonyl isocyanate (I) reacted with triphenylmethanol (II) and substituted triphenylmethanols at 100°. The products were N-(triarylmethyl)-4-toluenesulfonamides and $CO_2$, except that tris(4-nitrophenyl)methanol gave the urethan. A kinetic study revealed that the reactions obeyed second-order kinetics, first order in isocyanate and first order in carbinol. The relative rates of reaction were $(4\text{-}CH_3OC_6H_4)_3COH$ > $(4\text{-}C_6H_5C_6H_4)_3COH$ > $(C_6H_5)_3COH$ > $(4\text{-}ClC_6H_4)(C_6H_5)_2COH$ > $(4\text{-}NO_2C_6H_4)(C_6H_5)_2COH$ > $(4\text{-}NO_2C_6H_4)_2(C_6H_5)COH$ > $(4\text{-}NO_2C_6H_4)_3COH$. The results were correlated according to a modified Hammett function.

It has been shown in this laboratory that sulfonyl isocyanates react with triarylmethanols to give in most cases the corresponding N-(triarylmethyl)sulfonamides.[2-4] The kinetics of the reaction between benzenesulfonyl isocyanate or 4-toluenesulfonyl isocyanate (I) and triphenylmethanol (II) were studied.[3,4] The reactions were first order in each of the reagents in cases of the uncatalyzed and pyridine-catalyzed reactions.

A mechanism was proposed for the above reaction which consisted of the intermediate formation of a complex between isocyanate and carbinol. The complex was then hypothesized to decompose to an ion pair, one of the ions being triphenylmethyl carbonium ion.

This paper records the results which were obtained by using substituted triphenylmethanols in their reactions with I. It was of interest to determine what effect substituents would have on the rates of reactions. The reaction rates were followed by measuring the disappearance of isocyanate.

## Experimental Section

**Reagents.**—4-Toluenesulfonyl isocyanate (I) was obtained from the Upjohn Co., Carwin Organic Chemicals, and used without further purification. Triphenylmethanol (II) was a commercial product. Tris(4-methoxyphenyl)methanol (III), tris(4-biphenylyl)methanol (IV), (4-chlorophenyl)diphenylmethanol (V), and tris(4-nitrophenyl)methanol (VI) were prepared as indicated before.[2] The other triarylmethanols were prepared as shown below. Toluene was reagent grade and dried over sodium before use. The di-*n*-butylamine was Eastman White Label grade reagent.

**Kinetics.**—The method used for measuring isocyanate concentration was similar to that already reported.[3] The only two modifications follow. Instead of removing 2-ml samples, *ca.* 2 ml of sample was removed and weighed. This was accomplished by weighing the 10 ml of di-*n*-butylamine solution to the nearest 0.5 mg before and after adding the aliquot. For the conversion of weight into volume, it was assumed that the density of solution was the same as the density of pure toluene solvent at 100°. *Ca.* 1.0 g of tetramethylammonium chloride was added to the alcohol solution before it was titrated with HCl. The salt helped to eliminate noise encountered in the high-resistance alcohol solution and improved the separation of end points.

For the reactions using a 1:1 ratio of isocyanate/carbinol, plots of $1/(c - c_\infty)$ *vs.* time gave straight lines over a span of at least 2 half-lives. Second-order kinetics were followed from at least 4:1 to 1:4 isocyanate/carbinol ratios. For the reactions in which initial concentrations of isocyanate and carbinol were not similar, plots of $\log [b(a - x)/a(b - x)]$ *vs.* time were linear. Duplicate runs were made for each reaction and the average rate constant is reported. The reactions were all carried out at 100 ± 0.1° in toluene solvent.

**Synthesis of Carbinols. (4-Nitrophenyl)diphenylmethanol (VII).**—A slurry of 30 g (0.093 mol) of (4-nitrophenyl)diphenylchloromethane in 600 ml of water, 600 ml of dioxane, and 60 ml of 70% $HClO_4$ was heated under reflux for 1 hr. The cooled mixture was poured into 5 l. of $H_2O$ and stored at 0° overnight. The crude product weighed 29 g. Recrystallization from benzene–petroleum ether (bp 60–70°) gave 21.0 g (74.0%) of VII, mp 97.5–99° (lit.[5] mp 97–98°).

**Bis(4-nitrophenyl)phenylmethanol (VIII).**—Bis(4-nitrophenyl)chloromethane (13.8 g, 0.037 mol) was suspended in a mixture of 200 ml of $H_2O$, 200 ml of dioxane, and 20 ml of 70% $HClO_4$ and stirred and heated under reflux for 2.5 hr. The mixture was cooled, added to 4 l. of $H_2O$, and cooled at 0° overnight. The $H_2O$ was decanted and the oil was washed with $H_2O$ and then dissolved in 150 ml of warm toluene. Dilution with 150 ml of petroleum ether precipitated an oil which crystallized upon scratching, yield 10.4 g (80.0%), mp 137–138°. Recrystallization did not change the melting point.

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[1] Taken in part from the M. S. Thesis of D. J. T., DePauw University, 1967.

[2] J. W. McFarland, D. E. Lenz, and D. J. Grosse, *J. Org. Chem.*, **31**, 3798 (1966).

[3] J. W. McFarland D. E. Lenz, and D. J. Grosse, *ibid.*, **33**, 3514 (1968).

[4] J. W. McFarland, D. Green, and W. Hubble, *ibid.*, **35**, 702 (1970).

[5] P. D. Bartlett and J. D. Cotman, *J. Amer. Chem. Soc.*, **72**, 3095 (1950).

*Anal.* Calcd for $C_{19}H_{14}N_2O_5$: C, 65.14; H, 4.03; N, 8.00. Found: C, 65.31; H, 4.23; N, 7.81.

**Isolation of Products.**—Products were isolated from the reaction of I and triarylmethanols as reported before.[3] The products from triphenylmethanol (II), tris(4-biphenylyl)methanol (IV), and tris(4-nitrophenyl)methanol (VI) have been described.[2] (4-Chlorophenyl)diphenylmethanol (V) gave N[(4-chlorophenyl)-diphenylmethyl]-4-toluenesulfonamide (IX), yield 80%, mp 176.5–178.5°. The product from I and (4-nitrophenyl)diphenylmethanol (VII) was N-[(4-nitrophenyl)diphenylmethyl]-4-toluenesulfonamide (X), yield 94%, mp 153–154.5°. Bis-(4-nitrophenyl)phenylmethanol (VIII) gave 4-[bis(4-nitrophenyl)phenylmethyl]-4-toluenesulfonamide (XI), yield 56%, mp 183–184°. Tris(4-methoxyphenyl)methanol (III) reacted with I to give N-[tris(4-methoxyphenyl)methyl]-4-toluenesulfonamide (XII), yield 82.3%, mp 180–181°.

## Results

4-Toluenesulfonyl isocyanate (I) reacted with all of the triarylmethanols studied in toluene solution at 100°. The products were the N-(triarylmethyl)-4-toluenesulfonamides except in one case. When the rings of the carbinol were all substituted in the *para* position with $-NO_2$, the product was the urethan (Table I).[2]

TABLE I

REACTIONS OF 4-TOLUENESULFONYL ISOCYANATE (I) WITH TRIARYLMETHANOLS AT 100°

| Carbinol | Product | $k_r$ | Log $(k_r/k_0)$ | $n\sigma$ |
|---|---|---|---|---|
| $(CH_3OC_6H_4)_3COH$ | Amide + $CO_2$ | 0.70 | +0.525 | −1.071 |
| $(4\text{-}C_6H_5C_6H_4)_3COH$ | Amide + $CO_2$ | 0.274 | +0.118 | +0.03 |
| $(C_6H_5)_3COH$ | Amide + $CO_2$ | 0.209 | 0.00 | 0.00 |
| $(4\text{-}ClC_6H_4)(C_6H_5)_2COH$ | Amide + $CO_2$ | 0.149 | −0.148 | 0.227 |
| $(4\text{-}NO_2C_6H_4)(C_6H_5)_2COH$ | Amide + $CO_2$ | 0.070 | −0.473 | 0.778 |
| $(4\text{-}NO_2C_6H_4)_2C_6H_5COH$ | Amide + $CO_2$ | 0.012 | −1.242 | 1.556 |
| $(4\text{-}NO_2C_6H_4)_3COH$ | Urethan | 0.005 | −1.614 | 2.334 |

All reactions showed the same kinetic order, including the reaction which gave urethan. The reactions were first order in isocyanate and first order in carbinol through at least 2 half-lives.

The second-order rate constants, $k_r$, were sensitive to the type of substituent on the aromatic rings of the carbinol. Electron-donating groups, such as methoxyl, speeded the reaction, while electron-withdrawing groups caused a slower reaction.

The second-order rate constants for the disappearance of isocyanate were compared according to eq 1[6,7]

$$\log (k_r/k_0) = n\sigma\rho \qquad (1)$$

[where $(k_r/k_0)$ is the ratio of the rate constant for a particular carbinol to the rate constant for triphenylmethanol (II), $n$ is the number of identical groups substituted on the rings of the carbinol, and the $\sigma$ values are those given in ref 10].

A plot of log $(k_r/k_0)$ *vs.* $n\sigma$ was made as shown in Figure 1. The carbinols all fell on or near a straight line, the slope $\rho$ of which was −0.66. The fact that tris(4-biphenylyl)methanol showed a deviation is not too surprising, inasmuch as the $\sigma$ value for *para* phenyl is not too well established.

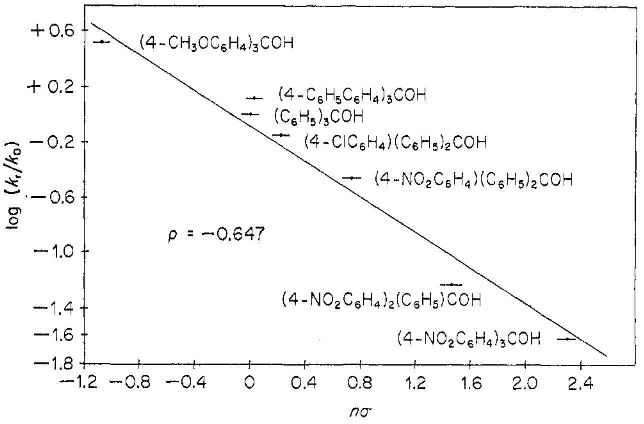
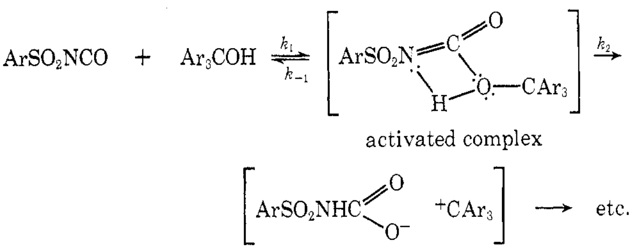


Figure 1.—Reactions of 4-toluenesulfonyl isocyanate with triarylmethanols at 100°.

The yields of amides from those reactions which gave them were 80% or better except when bis(4-nitrophenyl)phenylmethanol (VIII) was used. In that case only a 56% yield was realized. Those reaction mixtures which yielded amide developed a color during the reaction.[2,3] On the other hand, the trinitrocarbinol gave a practically colorless reaction solution.

## Discussion

The mechanism which was proposed for the reaction of sulfonyl isocyanate with triarylcarbinol to give N-(triarylmethyl)sulfonamide would have predicted the relative rates of reaction obtained in this study. The first two steps in the proposed mechanism involved complex formation between isocyanate and carbinol, followed by decomposition of the complex to an ion pair, or just ions.



If, as was proposed, $k_2$ measures the rate of isocyanate disappearance, the stability of the carbonium ion would affect the rate of reaction. The relative rates of the carbinols (see abstract) are precisely the relative stabilities of the corresponding carbonium ions.[6,8]

At the outset of this work it was thought that, if those carbinols which give N-(triarylmethyl)arylsulfonamides and $CO_2$ fell on the same line as those giving urethan, the implication might be that all of the reactions proceeded through a urethan intermediate. Unfortunately, only one carbinol produced urethan.

While it may only be fortuitous that the trinitro compound falls on the line of the Hammett plot, a second and simpler mechanism is consistent with most of the data presented here and in previous papers. The "activated complex" referred to in the above mecha-

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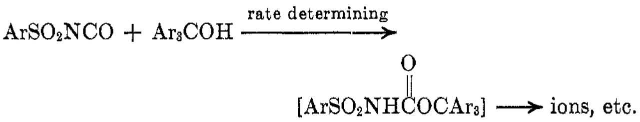
(6) N. C. Deno and A. Schriesheim, *J. Amer. Chem. Soc.*, **77**, 3051 (1955).

(7) H. Jaffe, *Chem. Rev.*, **53**, 191 (1953).

(8) N. C. Deno, J. J. Jaruzelski, and A. Schriesheim, *J. Amer. Chem. Soc.*, **77**, 3044 (1955).

nism may be urethan despite our failure to isolate it from I and II even at 0°.[3] Furthermore, the first step, and not the second, may be the rate-determining step for isocyanate disappearance. Our data do not clearly differentiate the two possibilities. The relative rates for the different carbinols should be the same whether urethan or carbonium ion formation is rate controlling.[9]



$$ArSO_2NCO + Ar_3COH \xrightarrow{\text{rate determining}} [ArSO_2NH\overset{O}{\overset{\|}{C}}OCAr_3] \longrightarrow \text{ions, etc.}$$

Electron-withdrawing groups probably cause slow urethan formation because of the reduced nucleophilicity of the carbinol oxygen. Also, the carbinol oxygen would have a partial positive charge on it in the transition state.

In summary, we do not believe that the results obtained prove or disprove a common intermediate for the different reactions. While a common step involving urethan formation is the simplest explanation, it is still disturbing that urethan cannot be isolated at low temperatures in most cases. If, on the other hand, the mechanisms are different for consumption of isocyanate, it might be concluded that three nitro groups have approximately the same effect in the urethan reaction as they would have in the amide-producing reaction.

It is interesting to note that 4-toluenesulfonyl isocyanate (I) is slightly less reactive than is benzenesulfonyl isocyanate[3] toward triphenylmethanol (II). (The rate constants are 0.209 and 0.296, respectively, at 100°.) Apparently, the methyl group destabilizes the transition state (which may have partial negative charges on the carbon or nitrogen of the isocyanate) or the subsequent ions. As expected from the above result, we have found that 4-chlorobenzenesulfonyl isocyanate is considerably more reactive than is I toward hindered phenols.[10]

**Registry No.**—I, 4083-64-1; VIII, 21112-03-8; IX, 22566-46-7; X, 22566-47-8; XI, 22566-48-9; XII, 22566-49-0.

[9] A reviewer suggested that the Hammett value is too small in absolute magnitude if carbonium ion formation is rate determining, but is consistent with urethan formation.

[10] Unpublished results obtained in this laboratory by Mr. Samuel Gaskins.

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# The Synthesis and Stereochemistry of Triarylsulfonium Salts[1]

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*Received July 8, 1969*

Several triarylsulfonium salts were prepared from the reaction of arylmagnesium halides with diarylethoxysulfonium salts. Optically active diarylethoxysulfonium salts gave only racemic triarylsulfonium salts. Possible reasons for the cause of racemic products are discussed. A series of 9,9-dihydro- and 9,9-dimethyl-10-aryl- and alkylthioxanthylium perchlorates were synthesized. A variable-temperature nmr study was done on 9,9-dimethyl-10-phenylthioxanthylium perchlorate. Coalescence of the 9,9-dimethyl doublet occurred at 200 ± 5° in benzophenone. A value for $\Delta G^{\ddagger}$ of 25.4 kcal/mol was calculated for the barrier to pyramidal sulfur inversion for this molecule.

The synthesis of triarylsulfonium salts from the reaction of arylmagnesium halides with diarylethoxysulfonium salts was reported in a preliminary communication (eq 1).[3] When optically active diaryl-

$$ArAr'SOC_2H_5^+ + Ar''MgX \longrightarrow ArAr'Ar''S^+ \qquad (1)$$

ethoxysulfonium salts were used, inactive triarylsulfonium salts were obtained, which was surprising, since other examples of nucleophilic substitution at sulfur involving optically active tricoordinate sulfur compounds proceeded with inversion to give optically active products (eq 2,[4] 3,[5] 4,[6] and 5[7]). This article

$$ArS(O)OR + RMgX \longrightarrow ArRSO \qquad (2)$$

$$ArS(O)OR + R'OH \longrightarrow ArS(O)OR' + ROH \qquad (3)$$

$$ArRSO + Ar'SONH_2 \xrightarrow[(C_2H_5)_3N]{P_4O_{10}} ArRSNSO_2Ar' \qquad (4)$$

$$ArAr'SOC_2H_5^+ + OH^- \longrightarrow ArAr'SO \qquad (5)$$

presents the details of additional research into the causes of racemization as well as the details of our earlier work.

The sulfonium salts synthesized as in eq 1 are listed in Table I together with their physical properties. The sulfonium salts synthesized starting with optically active sulfoxides as the source of the ethoxysulfonium salt showed no optical activity between 600 and 300 mμ.

Racemization could conceivably occur in various ways. The ethoxysulfonium salt might racemize before it reacts with the Grignard reagent to form products. The reaction (eq 1) could proceed through a symmetrical intermediate or transition state. For example, if a tetracoordinate intermediate analogous in structure to sulfur tetrafluoride is formed, it might undergo pseudorotation before going on to products, with the consequent formation of racemic sulfonium salts.[8] Finally, an optically active sulfonium salt might be formed but suffer rapid loss of optical

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[1] The authors gratefully acknowledge support from the U. S. Public Health Service, Grant GM-10800. Presented at the 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 13–18, 1969.

[2] Part of this research is from the Ph.D. thesis of N. E. P., University of New Hampshire, 1966.

[3] K. K. Andersen and N. E. Papanikolaou, *Tetrahedron Lett.*, 5445 (1966).

[4] M. Axelrod, P. Bickart, J. Jacobus, M. M. Green, and K. Mislow, *J. Amer. Chem. Soc.*, **90**, 4835 (1968), and references cited therein.

[5] H. Phillips, *J. Chem. Soc.*, **127**, 2552 (1925).

[6] J. Day and D. J. Cram, *J. Amer. Chem. Soc.*, **87**, 4398 (1965).

[7] C. R. Johnson and D. McCants, Jr., *ibid.*, **87**, 5404 (1965), and references cited therein.

[8] P. C. Lauterbur and F. Ramirez, *ibid.*, **90**, 6722 (1968).