those for authentic samples of *p*-toluenesulfonyl chloride and III. There were two small peaks, one (1/6 the area of III) before and one (1/25 the area of III) after the appearance of III. These peaks were not identified.

The oil obtained from the methylene chloride evaporation was placed on an aluminum oxide filled chromatograph column and eluted with 80% petroleum ether (b.p. 35–37°) and 20% benzene. The column became heated[4] as the materials moved down. Compound III came through quickly and continued to pass through the column as the eluent was varied to pure benzene. A total of 18.2 g. of III (32% conversion) was obtained and purified by recrystallization from ethanol, m.p. 72–74°, mixed with an authentic sample, m.p. 72–74°. The infrared spectra of the authentic compound and the reaction product were superimposable.

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(4) When *p*-toluenesulfonyl chloride in chloroform was placed on an aluminum oxide filled column, the column became heated and the sulfonyl chloride did not pass through the column upon further elution.

Oxygen-to-Nitrogen Rearrangement of Diethyl *N*-(*p*-Tolylsulfonyl)imidocarbonate

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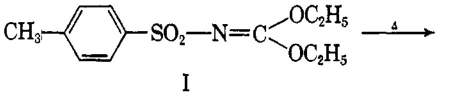
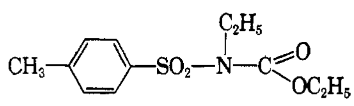
In our work on sulfonylurea derivatives, diethyl N-(*p*-tolylsulfonyl)imidocarbonate (I) was prepared by reaction of *p*-toluenesulfonamide with tetraethyl orthocarbonate in analogy to the known reaction of sulfonamides with triethyl orthoformate to give ethoxymethylenesulfonamides.[1] In a second preparation in which the temperature reached 200° a different product, ethyl ethyl(*p*-tolylsulfonyl)carbamate (II), was obtained in high yield by O → N shift of one ethyl group. The same rearrangement was observed by heating I alone to 200° for about one hour.

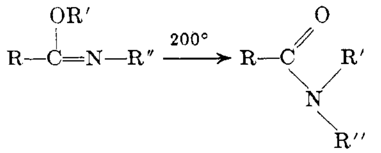


I



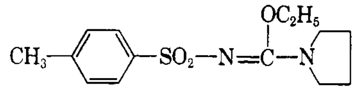
II

This, to my knowledge, novel rearrangement is reminiscent of the Chapman rearrangement[2] which consists in the conversion of alkylimido or arylimido esters into amides by heat.



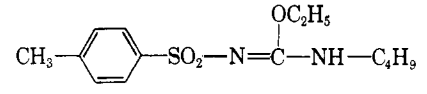
The mechanism of the conversion of I into II is probably similar to that of the Chapman rearrangement.[3] The structure of II, a colorless oil, was established by hydrolysis to N-ethyl-*p*-toluenesulfonamide and infrared data. II showed strong carbonyl absorption at 5.77 μ. On the other hand, I, a solid, m.p. 70–71°, showed very strong absorption at 6.33 μ typical of C=N— stretching.

Aminolysis of I with pyrrolidine gave ethyl N-(*p*-tolylsulfonyl)-1-pyrrolidinecarboximidate (III) which again showed C=N stretching absorption at 6.3 μ.



III

Reaction of I with *n*-butylamine gave the ethyl ether of tolbutamide, namely, 3-butyl-2-ethyl-1-*p*-tolylsulfonylpseudourea.



IV

Its C=N— stretching absorption in the infrared was shifted to 6.18 μ, but n.m.r. clearly established the structure of IV (having the C=N— double bond to the *p*-tolylsulfonyl nitrogen rather than to the butyl nitrogen) by absence of the peak at 4.91 p.p.m. which was present in the n.m.r. spectrum of N-ethyl-*p*-toluenesulfonamide due to the proton on the sulfonamide nitrogen.[4]

Experimental[5]

Diethyl N-(*p*-Tolylsulfonyl)imidocarbonate (I).—A mixture of 85.5 g. (0.5 mole) of *p*-toluenesulfonamide (Eastman) and 144 g. (0.75 mole) of tetraethyl orthocarbonate (Kay Fries) was heated with stirring. At 120–130° ethanol distilled. Within about 2 hr. the temperature of the reaction mixture had reached 160° as distillation of ethanol ceased. It was allowed to cool. Next day the compact crystalline solid was collected and washed with several portions of petroleum ether (b.p. 35–60°). The crude product, 91.2 g. (67%) melted at 69–70°. An analytical sample was prepared by recrystallization from absolute ether, m.p. 70–71°.

Anal. Calcd. for $C_{12}H_{17}NO_4S$: C, 53.12; H, 6.32; N, 5.16. Found: C, 53.06; H, 6.40; N, 5.06.

Ethyl Ethyl(*p*-tolylsulfonyl)carbamate (II).—A mixture of 85.5 g. (0.5 mole) of *p*-toluenesulfonamide and 115 g. (0.6 mole) of tetraethyl orthocarbonate was heated as for I except that the temperature was allowed to reach 200–205° at the end of the reaction. No solid was obtained on cooling. On distillation at 150–152° (0.5 mm.) 124.1 g. (92%) of colorless oil was collected.

Anal. Calcd. for $C_{12}H_{17}NO_4S$: C, 53.12; H, 6.32; N, 5.16. Found: C, 53.37; H, 6.49; N, 5.43.

In a separate experiment a 20-g. sample of I was heated to 200–205° for 1 hr. On distillation 19.1 g. of II was obtained, identified by infrared data.

Either by heating a sample with excess pyrrolidine at reflux for 3 hr. or by warming with an excess of *N* sodium hydroxide on the steam bath after acidification a good yield of N-ethyltoluenesulfonamide, m.p. 64–65°, was obtained, which was identical in every respect to a reference sample.

Ethyl N-(*p*-Tolylsulfonyl)-1-pyrrolidine Carboximidate (III).—A solution of 5.4 g. (0.02 mole) of I in 100 ml. of absolute ether was treated dropwise with 3.5 ml. of pyrrolidine. The solution was evaporated on the steam bath and finally *in vacuo*. The colorless oil crystallized on treatment with 20 ml. of ice–water, yielding 5.8 g. (98%) of a white crystalline solid, m.p. 84–86°. One recrystallization raised the m.p. to 86–87°.

Anal. Calcd. for $C_{14}H_{20}N_2O_3S$: C, 56.73; H, 6.80; N, 9.45. Found: C, 56.97; H, 6.96; N, 9.40.

3-Butyl-2-ethyl-1-*p*-tolylsulfonylpseudourea (IV).—To 20 ml. of *n*-butylamine was added 13.5 g. (0.05 mole) of I. The solution was warmed on the steam bath for 10 min. Excess butylamine

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(1) G. Tosolini, *Ber.*, **94**, 2731 (1961).

(2) A. W. Chapman, *J. Chem. Soc.*, **127**, 1992 (1925); 1743 (1927); W. G. Dauben and R. L. Hodgson, *J. Am. Chem. Soc.*, **72**, 3479 (1950).

(3) *Cf.* E. R. Alexander, "Principles of Ionic Organic Reactions," John Wiley and Sons, Inc., 1950, pp. 74–75.

(4) N.m.r. values were run in deuteriochloroform. The NH-peak of N-ethyl-*p*-toluenesulfonamide at 4.91 p.p.m. integrated for one proton.

(5) The melting points were taken on a Fisher-Johns block and are corrected.

was evaporated *in vacuo*. A colorless oil was obtained which crystallized on cooling in ice but melted at room temperature. It was treated with 20 ml. of water and the white crystalline solid was filtered, washed with ice–water, and air dried yielding 9.5 g. (64%), m.p. 34–36°. Two recrystallizations from ether raised the m.p. to 38–39°.

Anal. Calcd. for $C_{14}H_{22}N_2O_3S$: C, 56.35; H, 7.43; N, 9.39. Found: C, 56.52; H, 7.34; N, 9.20.

Acknowledgment.—We wish to express our gratefulness to Mr. C. Childs and co-workers for the microanalytical data and to Dr. J. M. Vandenbelt, Mr. E. J. Schoeb, and Mr. R. B. Scott for spectral data.

Solvent Effects on the Reaction of Sodium Azide with Substituted Benzyldimethylsulfonium *p*-Toluenesulfonates[1]

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In a reaction involving the destruction of ions, the effect of solvent changes on the reaction rate may be used as a criterion of the extent of charge destruction at the transition state. Since a recently proposed rule[2] suggests a relation between the electronic nature of substituents and the structure of the transition state, it is of interest to examine the influence of substituents on such a solvent effect.

Rate constants for the reactions of sodium azide with substituted benzyldimethylsulfonium *p*-toluenesulfonates (tosylates) at 60° in both water and 80% dioxane–20% water are listed in Table I.

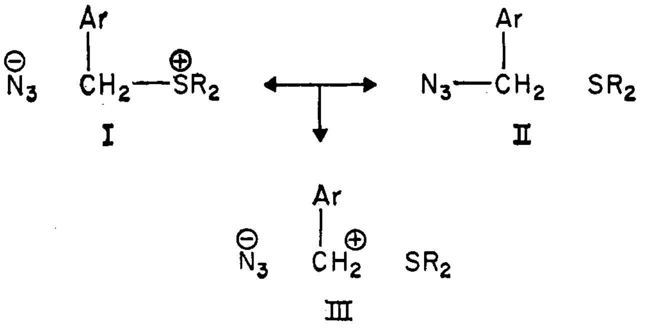
TABLE I

REACTIONS OF SODIUM AZIDE WITH SUBSTITUTED BENZYLDIMETHYLSULFONIUM TOSYLATES AT 60.1°

Substituent	k_2 in water, M^{-1} sec.$^{-1}$	k_2' in 80% dioxane, M^{-1} sec.$^{-1}$	k_2'/k_2
p-CH_3	10.45×10^{-5}	11.99×10^{-3}	115
H	4.78×10^{-5}	9.65×10^{-3}	202
m-Cl	3.50×10^{-5}	8.43×10^{-3}	241

The data indicate that the effect of electron-supplying substituents is to make the transition state more polar. It is convenient to discuss this result by considering the transition state as a resonance hybrid of structures I, II, and III.

Structure III is probably not quite so polar as I, but much more polar than II. The observed increase of the transition-state polarity with increasing electron supply indicates that the contribution of I or of III is increased at the expense of II. Since II is the only structure having a C–N bond, we may conclude that electron supply leads to a weaker C–N bond at the transition state. This is in agreement with the rule.[2]



It is more difficult to determine the substituent effect on the length of the C–S bond, since the bond will become stronger if the contribution of I is increased but weaker if the contribution of III is increased. However, an electron-supplying substituent would be better able to stabilize the positive charge in III than in I; therefore it is probable that the principal effect is to increase the contribution of III and lengthen the C–S bond at the transition state, as the rule predicts. This accords with the conclusion from the increasing sulfur isotope effect in the closely related reaction of hydroxide ion with the same benzylidimethylsulfonium tosylates in water at 60°.[3]

Experimental

Materials.—Water used in kinetic studies was distilled from sodium hydroxide–potassium permanganate and boiled prior to use to remove carbon dioxide. Dioxane was Fisher reagent grade. Eastman grade sodium tosylate was recrystallized from water–ethanol. Technical sodium azide was purified by recrystallization from an aqueous ethanolic solution which had been acidified with hydrazoic acid.[4] The sulfonium salts were prepared previously.[3]

Kinetics in Aqueous Solution.—A volumetric flask containing 100 ml. of a solution 0.05 *M* sulfonium salt, 0.10 *M* in sodium azide, and 0.35 *M* in sodium tosylate was placed in a constant temperature bath operating at 60.08 ± 0.04°. At intervals 5-ml. aliquots were removed from the flask and added to a measured excess of 0.20 *M* silver nitrate. The silver azide was filtered at 0° and washed with water. The excess silver ion was determined by adding a measured excess of 0.20 *M* potassium iodide and back-titrating with the 0.20 *M* silver nitrate with eosin Y as indicator.

During this investigation a somewhat simpler analytical method[5] was found to give rate constants agreeing with the first method. A 4-ml. aliquot of the reaction mixture was placed in a glass-stoppered erlenmeyer flask. Ten milliliters of a 10% ferric chloride indicator solution 1 *M* in sulfuric acid was added. The resulting hydrazoic acid was titrated with 0.25 *M* sodium nitrite. The flask was stoppered and shaken vigorously just before the end point was reached. The end point was determined by comparison with a standard solution prepared by mixing appropriate amounts of the indicator and sodium nitrite solutions.

Kinetics in Aqueous Dioxane.—A reaction mixture 0.0125 *M* in the sulfonium salt, 0.025 *M* in sodium azide, and 0.0875 *M* in sodium tosylate was prepared by weighing appropriate quantities of the three salts into a 250-ml. volumetric flask, dissolving in 50 ml. of water, and adding 200 ml. dioxane. Both water and dioxane had been preheated to 60° and volumes were measured at that temperature. The volumetric flask was placed in a bath at 60.08 ± 0.04°. At intervals 5-ml. aliquots were removed from the flask and added to a measured excess of 0.05 *M* silver nitrate. Filtration of the silver azide was followed by addition of an excess of 0.05 *M* potassium iodide and back-titration with 0.05 *M* silver nitrate with eosin Y as indicator.

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[1] Supported in part by the National Institutes of Health, the National Science Foundation, and the Atomic Energy Commission and by National Science Foundation and National Institute of Health predoctoral fellowships to L. J. T.

[2] C. G. Swain and E. R. Thornton, *J. Am. Chem. Soc.*, **84**, 817 (1962).

[3] C. G. Swain and E. R. Thornton, *J. Org. Chem.*, **26**, 4808 (1961).

[4] A. W. Browne, *Inorg. Syn.*, **1**, 79 (1939).

[5] J. F. Reith and J. H. A. Bouwman, *Pharm. Weekblad.*, **67**, 475 (1930); *Chem. Abstr.*, **24**, 3968 (1930).