as $(CF_3)_2NF$. It would seem from the boiling points, the infrared peak at 5.55 μ, the mol. wt. and the formation of ammonia on hydrolysis that the second component of these two fractions was $CF_3N{=}CF_2$, b.p. −33°, mol. wt. 133.

Distillation of the pot residue, 8 g., gave a major fraction boiling at 73.5–74.0° which had a mol. wt. of 135–137, melted at −40° to −38°, and reacted with water to give insoluble cyanuric acid. Reported[21] values for $(CNF)_3$ are m.p. −38°, b.p. 74°. The liquid air condensate, 12 g., had a mol. wt. of 88–115. Neither the mol. wt. range or the infrared spectrum was substantially modified by passage of the material through aqueous base. The spectrum showed weak evidence for NF_3 and strong indications of both CF_3-NF_2 and CF_4.

Acknowledgments.—The authors wish to thank Dr. Max Rogers of Michigan State University, East Lansing, Mich., and Dr. Keith McCallum of Rohm & Haas, Redstone Arsenal, Huntsville, Ala., for running n.m.r. spectra used in this paper, and Dr. C. B. Colburn of Rohm and Haas for the mass spectrographic analysis of one of the compounds cited.

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[21] A. F. Maxwell, J. S. Fry and L. A. Bigelow, This Journal, **80**, 548 (1958).

[Contribution from the Departments of Chemistry of Purdue University, Lafayette, Ind., and of Saint Louis University, St. Louis, Mo.]

Solvents of Low Nucleophilicity. I. Reactions of Hexyl Tosylates and Hexenes in Trifluoroacetic Acid and Other Acids[1]

By Paul E. Peterson[2]

Received March 24, 1960

The solvolysis of 2-hexyl tosylate in trifluoroacetic acid containing sodium trifluoroacetate occurred at approximately four times the rate of the solvolysis in formic acid, which has been regarded as the best ionizing solvent suitable for solvolysis studies. The substitution product from solvolysis in trifluoroacetic acid contained about 20% of 3-hexyl trifluoroacetate, the product which may arise *via* hydride shift, in addition to 2-hexyl trifluoroacetate. The substitution product from formic acid solvolysis, sometimes regarded as the best rearranging solvent, contained about 6% of 3-hexyl formate. Trifluoroacetic acid added readily to hexenes at 25°, yielding trifluoroacetates. Pyridine was found to be a suitable solvent for acylation of alcohols with trifluoroacetic anhydride.

Solvolysis reactions of the type thought to proceed *via* intermediate carbonium ions or their equivalent have been carried out in a variety of solvents, of which aqueous alcohol or aqueous dioxane, acetic acid and formic acid are perhaps the most important. Recently trifluoroacetic acid has been employed for some solvolyses of cyclooctane derivatives, and in each case the solvolysis products were quite unlike the products from solvolysis of the same starting materials in acetic acid. Thus solvolysis of cycloöctene oxide in trifluoroacetic acid gave exclusively products arising *via* a transannular hydrogen shift, while solvolysis with acetic acid containing sodium acetate gave 76% of normal products and only 24% of products arising *via* hydride shift.[3] In another study[4] the products obtained from solvolysis of 4-cycloöcten-1-yl brosylate in trifluoroacetic acid contained 31% of a product arising *via* a carbon shift and 12% of a product arising *via* an apparent hydrogen shift. Solvolysis of the same compound in acetic acid yielded no detectable products arising *via* carbon or hydrogen shift.[5] The reactions just mentioned are illustrations of the fact that although simple carbonium ion theory frequently can account adequately for products of reactions, the theory frequently does not allow prediction of the products.

Since the interpretation of the solvolysis reactions mentioned above is complicated by the proximity effects which may influence the reactions of cycloöctane derivatives, it was of interest to determine whether there are any unusual effects associated with carbonium ion reactions of simpler molecules in trifluoroacetic acid. The present work reports such a study involving reactions of the hexenes and derivatives of 2-hexanol and 3-hexanol. The choice of this system was determined in part by the fact that both the hexanols and the hexenes are well suited for gas chromatographic analysis.[6] In addition the system is well suited for the study of hydride shifts which may occur during carbonium ion reactions. The large percentage of hydrogen and carbon shift is the most striking common feature of the previously mentioned solvolysis reactions in trifluoroacetic acid. The equation (in Fig. 1) for solvolysis of 2-hexyl toluenesulfonate (2-hexyl tosylate), whose solvolysis is reported here, illustrates the pos-

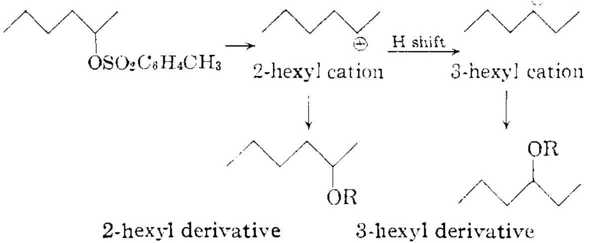

Fig. 1.

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[1] (a) Supported in part by a grant from Research Corporation. (b) Presented at the 137th National Meeting of the American Chemical Society, Cleveland, Ohio, April, 1960.

[2] Department of Chemistry, Saint Louis University, St. Louis 4, Mo.

[3] A. C. Cope, J. Martin Grisar and P. E. Peterson, This Journal, **81**, 1640 (1959).

[4] A. C. Cope, J. Martin Grisar and P. E. Peterson, *ibid.*, **82**, 1299 (1960).

[5] A. C. Cope and P. E. Peterson, *ibid.*, **81**, 1643 (1959).

[6] Procedures were kindly supplied by Prof. H. C. Brown and his research group.

TABLE I

COMPOSITION OF PRODUCTS FROM SOLVOLYSIS AND ADDITION REACTIONS

Starting material	Conditions	Composition of substitution and/or addition product, % 2-Hexyl	3-Hexyl
2-Hexyl tosylate	CF_3COOH, CF_3COONa, 24 hr., 25°	51	49
	CF_3COOH, CF_3COONa, 2 hr., 25°, bromine added	78	22
	HCOOH (98%), HCOONa, 72 hr., 25°	94	6[a]
	CH_3COOH, CH_3COONa, 14 hr., 80–90°	98	2[b]
3-Hexyl tosylate	CF_3COOH, CF_3COONa, 24 hr., 25°	32	68
	CF_3COOH, CF_3COONa, 2 hr., 25°, bromine added	19	81
1-Hexene	CF_3COOH, CF_3COONa, 2 hr., 25°	81	19
1-Hexene, 3-hexyl trifluoroacetate[c]	CF_3COOH, CF_3COONa, bromine, sodium toluenesulfonate, 25°, 2 hr.	0	100

[a] From a formolysis in the presence of bromine, 8.8% 3-hexyl formate was found. [b] In several experiments the amount of 3-hexyl acetate formed varied from 1 to 3.5%. Differences in reaction temperature or water content of the solvent may account for the variation. [c] This experiment showed the effectiveness of the bromine trapping method as well as the stability of 3-hexyl trifluoroacetate.

sibility of observing hydride shift in both the substitution and elimination products. Thus for solvolysis in trifluoroacetic acid the amount of 3-hexyl trifluoroacetate formed is a direct measure of the amount of substitution which occurs *via* the 3-hexyl cation.

In the present study the solvolysis of 2-hexyl tosylate and 3-hexyl tosylate was carried out in trifluoroacetic acid in the presence of a 25% excess of sodium trifluoroacetate, and some comparison studies were made in a similar manner using formic acid and acetic acid. Although the addition of sodium acetate frequently is effective in preventing acid-catalyzed isomerizations of tosylate solvolysis products in acetic acid, it could not be assumed that the hexyl trifluoroacetates and hexenes would be stable in the moderately strong[7] trifluoroacetic acid.

The hexyl trifluoroacetates were readily shown by gas chromatography to be stable under the solvolysis conditions, but both 1-hexene and a mixture of *cis*- and *trans*-2-hexene were shown to add trifluoroacetic acid, forming trifluoroacetates. This interesting addition reaction was investigated separately; in the solvolysis of the hexyl tosylates the formation of trifluoroacetates *via* the additional pathway of addition of trifluoroacetic acid to the elimination products was prevented effectively by the addition of bromine to the reaction mixture. The bromine trapped the hexenes as they formed, presumably by forming dibromohexanes or bromohexyl trifluoroacetates. Since most of the added bromine remained as an insoluble separate phase, there was probably little effect of the added bromine on the solvent properties of the trifluoroacetic acid. Control experiments described in the Experimental section indicated that formic acid did not add appreciably to hexenes under the conditions used in this study.[8] The analysis of products of the various solvolyses, reported in Table I, were performed by a variety of gas chromatographic procedures described in the Experimental section.

In the preparation of the hexyl trifluoroacetates required as reference compounds it was desired to use a method which would later prove suitable in the case of alcohols more sensitive to acids than the hexanols. The reaction of trifluoroacetic anhydride in pyridine was the logical choice, but it is reported[9] that pyridine is decomposed rapidly to a brown product by trifluoroacetic anhydride. It was found, however, that the pyridine employed did not darken very much in the presence of trifluoroacetic anhydride, and that the trifluoroacetates could be prepared in good yield using a reaction time of only a few seconds.

The rates of solvolysis of the hexyl tosylates in trifluoroacetic acid were of interest but could not be measured by the indicator procedure used in formic acid[8] because the indicator was protonated by the stronger trifluoroacetic acid. Accordingly, approximate rates were measured by a gas chromatographic method involving an internal standard. The total amount of ester formed in the various solvolyses was measured by a similar method. Table II reports the resulting rates and percentages of substitution products.

TABLE II

RATES AND PERCENTAGE SUBSTITUTION FOR TOSYLATE SOLVOLYSES; RATE OF ADDITION OF TRIFLUOROACETIC ACID TO 1-HEXENE

Reactant	Solvent[a]	$k \times 10^4$, sec.$^{-1}$, 25°	Substitution, %
2-Hexyl tosylate	CF_3CO_2H	2.2 ± 0.2[b]	13.5 ± 2
2-Hexyl tosylate	CH_3CO_2H		86.5 ± 2[c]
2-Hexyl tosylate	HCO_2H	0.55[d]	80 ± 2
3-Hexyl tosylate	CF_3CO_2H	7.5 ± 0.8[b]	16 ± 2
1-Hexene	CF_3CO_2H	0.51 ± 0.05[b]	

[a] In all cases the sodium salt of the acid was present. [b] The rate constant was evaluated from a first-order plot, although the gas-chromatographically determined points were not accurate enough to establish the order of the reaction. [c] Reaction rates of secondary tosylates in acetic acid are too slow for convenient measurement at 25°. The percentage substitution was measured for reaction at 80–90°. [d] The rate was determined titrimetrically.

Finally a convenient preparative procedure was developed for hydration of alkenes *via* addition of trifluoroacetic acid to alkenes, using molar ratios of trifluoroacetic acid to alkene of not more than 2 to 1.

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(7) (a) Dissociation constant in water: 0.59 or 1.8. See footnotes 8, 9 and 10 of ref. 3 for references to the physical constants of acids used in the present study. (b) The Hammett acidity function of pure trifluoroacetic acid is −4.4. References are given by F. A. Bovey and G. V. D. Tiers, THIS JOURNAL, **81**, 2870 (1959). Presumably the presence of sodium trifluoroacetate made the solvent less acidic in the present study.

(8) See, however, S. Winstein and N. J. Holness, THIS JOURNAL, **77**, 5562 (1955).

(9) E. J. Bourne, C. E. M. Tatlow and J. C. Tatlow, *J. Chem. Soc.*, 1367 (1950).

Discussion.—As in the cases already cited,[3-5] the reactions in trifluoroacetic acid reported here exhibited several novel features. Of interest are the rapid rate of the tosylate solvolyses, the high per cent. of rearrangement of the substitution products from the tosylate solvolyses, the high percentage of elimination products from the tosylate solvolyses and the rapidity of addition of trifluoroacetic acid to 1-hexene.

Of the above features the rapidity of the tosylate solvolyses is perhaps the most surprising. The solvolysis of 2-hexyl tosylate was about four times as fast in trifluoroacetic acid as in formic acid, which is frequently regarded as the best ionizing solvent suitable for solvolysis studies. The high rate of solvolyses in formic acid has been attributed to its high dielectric constant (57.9 at 20°).[7] The dielectric constant of trifluoroacetic acid, however, is only 8.42 at 20°,[7] comparable to that of acetic acid (6.15 at 20°)[7] in which solvolyses are relatively slow. A possible explanation is that the solvolyses in trifluoroacetic acid were acid catalyzed. If such is the case, unusual rate relationships may be found in comparing tosylate solvolysis rates with rates of other compounds such as halides or sulfonium salts. It may be noted that in an early study[4] solvolyses of 4-cycloöcten-1-yl brosylate and of bicyclo[3.3.0]-oct-2-yl brosylate in trifluoroacetic acid were carried out below room temperature, indicating that these reactions of secondary brosylates were even faster than the solvolysis of 2-hexyl tosylate (half-life about 0.9 hr. at 25°). For several reasons the compounds studied in ref. 4 would be expected to react more rapidly than 2-hexyl tosylate, but it nevertheless seems likely that arylsulfonate solvolyses will in general be found to be relatively fast in trifluoroacetic acid.[10]

For the reactions of 2-hexyl tosylate the amount of hydride shift leading to substitution product varied with solvent as follows: trifluoroacetic acid > formic acid > acetic acid. The same sequence was found in the study of the amount of transannular hydride shift which occurred during the solvolysis of cycloöctene oxide.[3] In the case of the cyclooctene oxide solvolysis[3] the large amount of hydrogen shift observed in trifluoroacetic acid was correlated with the presumed low nucleophilicity of trifluoroacetic acid. A similar explanation may be applied in the present case: that in the solvent of lowest nucleophilicity any intermediate cationic species may undergo substitution with unusual slowness but may undergo hydride shift at a rate less affected by solvent. A number of mechanisms incorporating this interpretation are possible, depending on whether hydrogen shift occurs during the rate-determining step[11] or at a later stage, and on the possible effects due to acid catalysis.[12] It should be noted that in some more complex carbonium ion reactions formic acid sometimes shows and sometimes apparently fails to show a markedly greater tendency than acetic acid to promote hydrogen shift[8,11,13,14] or carbon shift.[15]

Study of the addition of trifluoroacetic acid to alkenes, first encountered during tosylate solvolyses in trifluoroacetic acid, indicated that trifluoroacetic acid is unusually well suited for the study of such reactions. Thus 0.1 molar 1-hexene in trifluoroacetic acid 0.125 molar in sodium trifluoroacetate was found to undergo addition with a half-life of about 4 hours, but was found not to react appreciably with 98% formic acid 0.125 molar in sodium formate. Furthermore 1-hexene was too insoluble in the latter solvent to form a 0.1 molar solution. In several other cases trifluoroacetic acid was superior to formic acid as a solvent for alkenes, although two phases were formed in some experiments. Qualitative observations indicated that the addition of trifluoroacetic acid to alkenes was greatly slowed by high concentrations of alkene or trifluoroacetate. In the addition on a preparative scale (Experimental section) a reaction temperature of 65–70° was employed to compensate for the relatively slow rate encountered in the absence of a large excess of trifluoroacetic acid. The preparative procedure may be compared with that involving the heterogeneous perchloric acid-catalyzed addition of formic acid to alkenes.[16] Both procedures may give considerable product which has undergone a hydride shift. If, as is likely, the rate of addition of trifluoroacetic acid to other hexenes is found to be comparable to the rate of addition to 1-hexene, it will be possible to determine the composition of the elimination products of 2-hexyl tosylate in trifluoroacetic acid by analysis of the hexenes formed after only a small fraction of the tosylate has solvolyzed. A mixture of *cis*- and *trans*-2-hexene was observed qualitatively to undergo addition at a rate comparable to the rate of addition to 1-hexene.

Experimental

Hexyl tosylates.—2-Hexanol and 3-hexanol (from K & K Laboratories, Long Island City, N. Y.) were converted to tosylates by the procedure of Brown and Ham[17] after each alcohol was shown by gas chromatography to be free of the other isomer. 2-Hexyl tosylate was a liquid and 3-hexyl tosylate crystallized after several weeks to a solid melting at room temperature.

Solvolysis Procedures.—The following is representative of procedures used both for product studies and rate studies. The weight of sodium trifluoroacetate required to make 10 ml. or 25 ml. of 0.125 molar solution was dissolved in an almost sufficient quantity of trifluoroacetic acid (Matheson, Coleman and Bell) and brought to 25 ± 0.3° in a constant temperature bath. The solution was added to sufficient 2-hexyl tosylate to make a 0.1 molar solution and made up to 10 or 25 ml. with a small additional quantity of trifluoroacetic acid.

Formolyses were conducted in a similar manner in 98% formic acid 0.125 molar in sodium formate. In a control experiment formates were shown by gas chromatography not to be formed by addition of formic acid 0.125 molar in sodium formate to 1-hexene at 25°. Furthermore a formolysis of

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[10] Because the rapid rates may be due to acid catalysis it seems preferable to avoid making the generalization that trifluoroacetic acid has been found to be the best ionizing solvent yet studied. Other workers may not agree with this viewpoint; the difficulty arises from the lack of a clear definition of "ionizing power" in the case where solvolysis reactions are demonstrably acid catalyzed. The view taken here depends on using only rates of reaction not directly connected with acid catalysis as a measure of ionizing power.

[11] *Cf.* D. Cram and J. Tadanier, THIS JOURNAL, **81**, 2737 (1959).

[12] Mechanistic details of some reactions involving hydride shift have been discussed by A. Streitwieser, Jr., *Chem. Revs.*, **56**, 571 (1956); see also A. Streitwieser, Jr., *J. Org. Chem.*, **22**, 861 (1957).

[13] J. D. Roberts, C. C. Lee and W. H. Saunders, Jr., THIS JOURNAL, **76**, 4502 (1954).

[14] S. Winstein, *Experentia*, Suppl. No. 2, 1954.

[15] I. Dostrovsky and D. Samuel, *J. Chem. Soc.*, 658 (1954).

[16] M. B. Knight, R. E. Koos and D. Swern, THIS JOURNAL, **75**, 6212 (1953).

[17] H. C. Brown and G. Ham, *ibid.*, **78**, 2735 (1956).

2-hexyl tosylate in the presence of bromine gave no decrease in the amount of 3-hexyl formate found (*cf.* Table I, footnote *a*), indicating that the 3-hexyl formate does not result from addition of formic acid to 2-hexene or 3-hexene.

Acetolyses were carried out in a stoppered flask in an oven at 80–90°, using Mallinckrodt reagent grade acetic acid in which anhydrous sodium acetate was dissolved to make a 0.125 molar solution.

Gas Chromatographic Analyses.—An apparatus similar to the one described previously was employed.[18] For analysis of substitution products of solvolysis a 1-, 2- or 3- ml. portion of solvolysis mixture was added to a separatory funnel containing a cold solution of 10 g. of potassium carbonate in 35 ml. of water and 4 ml. of ether. If an internal standard was to be employed, 1 ml. of a standard *p*-bromotoluene solution in acetic acid was added. The ether extract was washed with 2 additional ml. of potassium carbonate solution and 2 ml. of water and was partially dried in the funnel with magnesium sulfate.

The *p*-bromotoluene had a retention time between that of the trifluoroacetates or formates and that of the acetates and alcohols in the hexyl series, and could accordingly be used in the determination of all of these compounds. 3-Hexyl trifluoroacetate, 3-hexyl acetate and 3-hexanol were eluted faster than the corresponding 2-hexyl compounds on a tris-(2-cyanoethoxy)-propane column[5] at 85°, allowing direct measurement of the composition of mixtures of these compounds from peak areas. (The areas were approximated by multiplying the peak height by the width at half the height.) The formates did not separate and were converted to the alcohols with lithium aluminum hydride. In a number of cases the analysis of acetates and of trifluoroacetates was checked by conversion to alcohols by lithium aluminum hydride. A series of known mixtures of 2-hexanol and 3-hexanol and of 2-hexyl trifluoroacetate, 3-hexyl trifluoroacetate and *p*-bromotoluene were employed to check the analytical method. The hexanol peaks were badly skewed but it was found that the areas as measured required no correction provided the larger 2-hexanol peak was of a certain height.

The ether solutions of 2-hexyl trifluoroacetates were conveniently analyzed without concentrating, but the acetate and alcohol solutions were sometimes concentrated. The percentage of the more volatile 3-hexanol in alcohol mixtures dropped somewhat if all of the ether was accidentally boiled off.

The alcohol obtained by hydrolysis of the trifluoroacetates from a 2-hexyl tosylate solvolysis had an infrared spectrum characteristic of a mixture of 2-hexanol and 3-hexanol, as expected (*cf.* Table II).

3-Hexyl Trifluoroacetate.—Trifluoroacetic anhydride (3 ml.) was added to 1.02 g. of 3-hexanol in 10 ml. of cold pyridine. Following the vigorous reaction the mixture was poured after 15 seconds into 50 ml. of an ice–water mixture and 10 ml. of ether. Additional ether was added to form a second layer and the ether extract was washed with two 30-ml. portions of cold dilute hydrochloric acid, water, and two 20-ml. portions of 5% sodium carbonate solution. The dried ether layer was distilled, giving 1.02 g. (52%), b.p. 36° (15 mm.), $n^{20}\text{D}$ 1.3570.

Anal. Calcd. for $C_8H_{13}F_3O_2$: C, 48.48; H, 6.61. Found: C, 48.51; H, 6.67.

Addition of Trifluoroacetic Acid to 1-Hexene.—1-Hexene (7.32 g., 0.087 mole) was allowed to react with trifluoroacetic acid (25 g., 0.22 mole) containing sodium acetate (0.2 g., present as a buffer to ensure reproducibility of results in presence of adventitious traces of trifluoroacetate salts or strong acids) for 72 hr. at 65–70°. (The reaction was conveniently carried out in an ordinary screw cap bottle with aluminum foil in the cap.) The product was poured into a separatory funnel containing 250 ml. of 5% sodium carbonate (0.118 mole), 25 ml. of ether and some ice. The organic layer was dried in the funnel with magnesium sulfate and distilled through a modified Holzmann column, giving 14.18 g. (82%), b.p. 65–68° (64 mm.). Gas chromatography showed the product to be 76% 2-hexyl trifluoroacetate and 24% 3-hexyl trifluoroacetate. No 1-hexyl trifluoroacetate (less than 1%) was present.

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[18] A. C. Cope, A. H. Keough, P. E. Peterson, H. E. Simmons, Jr., and G. W. Wood, THIS JOURNAL, **79**, 3900 (1957).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA, LOS ANGELES 7, CALIF.]

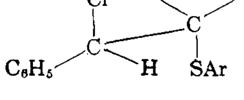
Derivatives of Sulfenic Acids. XXXIX. The Reaction of 2,4-Dinitrobenzenesulfenyl Chloride with *cis*- and *trans*- Stilbene[1]

BY NORMAN R. SLOBODKIN AND NORMAN KHARASCH

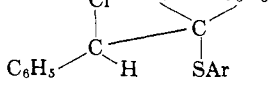
RECEIVED MAY 14, 1960

2.4-Dinitrobenzenesulfenyl chloride (I) adds to *cis*-stilbene to give *threo*-2-chloro-1-(2′,4′-dinitrophenylthio)-1,2-diphenylethane (II). In acetic acid, the reaction follows the rate expression $-\mathrm{dArSCl}/\mathrm{d}t = k_2(\mathrm{ArSCl})(\mathrm{stilbene})$, with values for k_2, in (moles/l.)$^{-1}$ sec.$^{-1}$, of 1.09×10^{-3}, 2.11×10^{-3} and 3.95×10^{-3}, at 45°, 55° and 65°, respectively. With *trans*-stilbene the *erythro* adduct III is obtained and the corresponding values of k_2 are 1.85×10^{-3}, 3.00×10^{-3} and 4.08×10^{-3}, at 45°, 55° and 63°, respectively. For the addition of I to *cis*-stilbene, $E_a = 13.8 \pm 1$ kcal./mole and $-\Delta S^{\ddagger} = 28.8$ cal./deg. For *trans*-stilbene, the corresponding values are $E_a = 9.4 \pm 1$ kcal./mole and $-\Delta S^{\ddagger} = 41.5$ cal./deg. A positive salt effect was demonstrated in the addition to *trans*-stilbene. The results are compared with previous rates of addition of I to olefins and with peroxidations of *cis*- and *trans*-stilbene and *cis*- and *trans*-azobenzenes.

From previous work,[2] it is known that 2,4-dinitrobenzenesulfenyl chloride (I) adds to *cis*- and *trans*-2-phenyl-2-butene and to other olefins in a stereospecific manner. In acetic acid, these reactions are suitably interpreted as *trans*, ionic additions, leading to the corresponding diastereomeric adducts. The additions to *cis*- and *trans*-stilbenes would thus lead, respectively, to the *threo* adduct II and the *erythro* adduct III. It is on this basis that the products obtained in this study have been assigned the structures (Ar = 2,4-dinitrophenyl)



II, *threo* adduct, m.p. 153–154°



III, *erythro* adduct, m.p. 173–174°

At the temperatures used for the kinetic comparisons in this study, no phenyl migration was found in formation of the adducts. However, as previously reported for the case of *trans*-stilbene,

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[1] This study was supported, in part, by a grant from the National Science Foundation.

[2] N. Kharasch and A. J. Havlik, THIS JOURNAL, **75**, 3734 (1953), and **78**, 1207 (1956); *cf.* also, D. J. Cram, *ibid.*, **74**, 2155 (1952); and N. Kharasch, "Organic Sulfur Compounds," Vol. I, Pergamon Press, New York, N. Y., Chapt. 32, in press.