line sulfoxide was recovered. Freeze-drying the turbid suspension re-formed the complex largely, as indicated by infrared spectra. A suspension of 0.5 g. of complex in 50 ml. of distilled water had a *p*H of 1.6.

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Derivatives of Sulfenic Acids. XL. Phenyl Migration during Sulfenylation of *trans*-Stilbene

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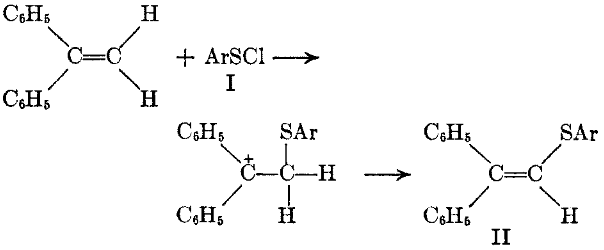
In connection with a study of the kinetics of addition of 2,4-dinitrobenzenesulfenyl chloride, I, to *cis* and *trans*-stilbene, we encountered a migration of the phenyl group in the reaction of I with *trans*-stilbene at elevated temperatures. To our knowledge, this is the first example of a phenyl group rearrangement during the course of addition of a sulfenyl halide to an olefin.

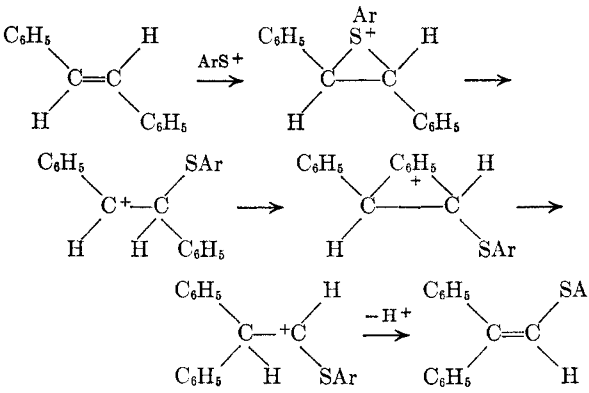
Previous studies[1] have shown deviations from 1:1 adduct formation with 2,4-dinitrobenzenesulfenyl chloride, I, and olefins. The product of the reaction of 4-methoxystyrene and I were governed by the reaction temperature, the vinyl sulfide being formed at the higher temperatures,[2] and olefins like 1,1-diphenylethylene were found also to lead to the vinyl sulfide.[1]

It has now been found that the product from the reaction of I with *trans*-stilbene in refluxing acetic acid was not the 1:1 adduct, but a vinyl sulfide. Oxidation of the vinyl sulfide to benzophenone and desulfuration of the vinyl sulfide with Raney nickel to 1,1-diphenylethane showed the vinyl sulfide to be 1,1-diphenyl-(2′,4′-dinitrophenylthio)-ethane, which is the expected product from 1,1-diphenylethylene assuming addition of ArS$^+$ and subsequent loss of a proton; Ar = 2,4-dinitrophenyl. The product from 1,1-diphenylethylene and the rearrangement product from *trans*-stilbene were shown to be identical.

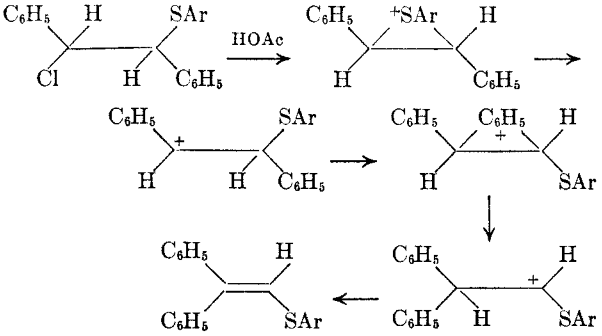


II

The following sequence is suggested to explain the rearrangement with *trans*-stilbene, involving a cyclic episulfonium ion, subsequent participation by phenyl, followed by loss of a proton.



Since acetolysis of the 1:1 adducts of I and olefins have been postulated to proceed through a sulfonium ion with sulfur participation,[3] acetolysis of the 1:1 adduct in acetic acid would be expected to yield the vinyl sulfide. Acetolysis of the 1:1 adduct yielded the vinyl sulfide and some β-acetoxy compound while acetolysis with sodium acetate added yielded only the β-acetoxy compound. SN$_2$ acetolysis conditions with sodium acetate in anhydrous acetone, failed to give detectable reaction. The sequence leading to the same product, as shown above from *trans*-stilbene, is given below.



Systems such as those used in this study can thus permit interesting comparisons of the relative participations by neighboring sulfur and aryl groups.

EXPERIMENTAL

Reaction of 2,4-dinitrobenzenesulfenyl chloride, I, with trans-stilbene. To a refluxing solution of dry acetic acid was

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(1) N. Kharasch, *J. Chem. Ed.*, **33**, 585 (1956); *Cf.* also, R. B. Langford and D. D. Lawson, *J. Chem. Ed.*, **34**, 510 (1957) and N. Kharasch, *Organic Sulfur Compounds, Vol. I*, Pergamon Press, New York–London. (In press).

(2) W. L. Orr and N. Kharasch, *J. Am. Chem. Soc.*, **78**, 1201 (1956).

(3) A. J. Havlik and N. Kharasch, *J. Am. Chem. Soc.*, **78**, 1207 (1956).

added *trans*-stilbene (2.31 g., 0.0128 mol.) and 3.74 g. of I. The reaction mixture was refluxed 2 hr., during which time the solution turned dark. The reaction mixture was aspirated to dryness, dissolved in benzene, and chromatographed on a column of alumina (2.5 × 20 cm.) using a 50% by volume mixture of benzene and mixed alkanes (b. range 50–60°) to elute the first fraction. Methanol was gradually added to elute the second fraction.

Fraction (1) gave 2.8 g., m.p. 133–134°.

Fraction (2) gave 0.7 g., m.p. 122–125°. The separations indicate that two distinct products are formed. Both products gave negative Beilstein tests, and had similar infrared spectra but 2 showed an absorption maximum in the 5.9μ region while 1 did not.

Elemental analysis of 1 indicated that it was the vinyl sulfide (compound II, in text).

Anal. Calcd. for $C_{20}H_{14}N_2O_4S$: C, 63.47; H, 3.73. Found C, 63.70; H, 3.55.

Elemental analysis of 2 indicated that it was the β-acetoxy compound.

Anal. Calcd. for $C_{22}H_{18}N_2O_6S$: C, 60.26; H, 4.14. Found: C, 60.33; H, 4.01.

Reaction of 2,4-dinitrobenzenesulfenyl chloride with 1,1-diphenylethylene. Reaction of 5.0 g. of I and 3.3 g. of 1,1-diphenylethylene, in 40 ml. of dry acetic acid for 24 hr. at room temperature yielded crude II, which after recrystallization from 95% ethanol yielded 5.5 g. of product, m.p. 134–135° (80%).

Anal. Calcd. for $C_{20}H_{14}N_2O_4S$: C, 63.47; H, 3.73. Found: C, 63.70; H, 3.55.

This product was identical with the one from *trans*-stilbene, as shown by infrared spectra and mixture melting point.

Acetolysis of the 1:1 adduct in refluxing acetic acid. To a refluxing solution of dry acetic acid was added 2.1 g. of 1:1 adduct. The reaction mixture was refluxed 4 hr. Employing a similar chromatographic procedure as above, it was found that the 1:1 adduct was converted into 70% vinyl sulfide, II, and 10% of the acetoxy compound of fraction 2. A 10% loss in work-up was sustained.

Acetolysis of the 1:1 adduct with sodium acetate and acetic acid. To a refluxing solution of dry acetic acid was added 5.0 g. of anhydrous sodium acetate and 1.6 g. of 1:1 adduct. The reaction mixture was refluxed 4 hr. The yellow reaction mixture was aspirated nearly to dryness and poured onto ice. The yellow material was collected and recrystallized from methanol. The product melted at 125–126°; yield, 1.4 g.; 89%.

Desulfuration and reduction of the vinyl sulfide with Raney nickel. A solution of 4.0 g. (0.011 mol.) of the vinyl sulfide was dissolved in 50 ml. of absolute ethanol containing 15 g. of Raney nickel. The solution was refluxed 2 hr. on the steam bath. About 5 g. more of catalyst was added, and refluxing continued an additional hour. The mixture was filtered through diatomaceous earth, and the catalyst washed with two 15-ml. portions of absolute ethanol. The washings were added to the filtrate, which was then concentrated in an air stream to dryness. The dark oil was distilled under reduced pressure yielding a colorless oil, b.p. 110°/2 mm., m.p. −8° (1.0 g., 57%).

Oxidation of the vinyl sulfide. The vinyl sulfide (4.0 g., 0.011 mol.) was added to an aqueous solution of potassium dichromate. Concentrated sulfuric acid was added to the solution. An hour later, the solution was poured onto ice. The white crystals were collected and reprecipitated from 95% ethanol with ice to give 1.6 g. of product, m.p. 47–48° (84%). This product was shown to be benzophenone by infrared spectra and mixture melting point.

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Organic Disulfides and Related Substances. II. 2,4,6-Triisopropylphenyl Disulfide, the 2,4,5-Isomer, and Related Compounds[1]

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The first disulfide named in the title is new, the second has been mistaken for the first, and in our opinion, the disulfides and related compounds deserve further study and comment.

Triisopropylbenzene made from propylene and benzene with sulfuric acid as a catalyst has been shown to consist mainly of the 1,2,4-isomer.[2] Evidently, Costanza and co-workers[3] believed that the commercial mixture was mainly the symmetrical 1,3,5-isomer for the properties of their sulfonyl chloride and disulfide made from the hydrocarbon, reported as the 2,4,6-isomers, agreed well with the physical properties of our 2,4,5-isomers. Our confidence in the correctness of the structures given here is based on three facts: (1) The equilibration of a trialkylbenzene with large amounts of aluminum chloride (which provided our 1,3,5-triisopropylbenzene) gives predominantly the symmetrical 1,3,5-isomer, as this isomer is the strongest Lewis base and forms the most stable Lewis salt.[2,4,5] (2) The hydrocarbon obtained from the equilibration in this work differed considerably in physical properties from the original hydrocarbon. And both hydrocarbons gave derivatives which had sharp melting ranges and were distinctly different from each other. (3) 2,4,5-Triisopropylbenzenesulfonyl chloride (I) and its 2,4,6-isomer (II) were made by the method of Newton and agreed well in physical properties and derivative formation with his descriptions.[6]

The study of models of 2,4,6-triisopropylbenzenesulfonyl chloride (II) suggested that the chlorosulfonyl group would be tilted out of the ring plane so that the rear of the group would be more exposed to the attack of a nucleophilic reagent than that of the 2,4,5-isomer which is in the plane of the ring and is hindered by a ring substituent. The solvolysis of such sulfonyl chlorides has been shown

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[1] Supported in part by funds provided by the Office of Ordnance Research, U. S. Army. Abstracted from the M.S. thesis of D.C., Vanderbilt University, January, 1956. Paper I. L. Field and J. E. Lawson, *J. Am. Chem. Soc.*, **80**, 838 (1958).

[2] A. Newton, *J. Am. Chem. Soc.*, **65**, 320 (1943).

[3] A. J. Costanza, R. J. Coleman, R. M. Pierson, C. S. Marvel, and Charles King, *J. Pol. Sci.*, **17**, 319 (1955).

[4] J. P. Wibaut and B. Paulis, *Rec. trav. chim.*, **77**, 769 (1958).

[5] For references bearing on the general problem. D. A. McCaulay and A. P. Lien, *J. Am. Chem. Soc.*, **74**, 6246 (1952); **77**, 1803 (1955); **79**, 5953 (1957); H. C. Brown, B. A. Bolto, and F. R. Jensen, *J. Org. Chem.*, **23**, 417 (1958).

[6] A Newton, *J. Am. Chem. Soc.*, **65**, 2439 (1943).