were observed in the spectrum of bibenzyl when solutions in cyclohexane, acetonitrile, 95% ethyl alcohol or carbon tetrachloride were illuminated. Increases in absorbance in the region 230–270 mμ were observed as has been reported.[2]

Solutions of both *cis*- and *trans*-stilbene, about 0.02 *M* in 95% ethyl alcohol, after illumination for about 20 days yielded enough phenanthrene so that it could be isolated and purified. The spectrum of the purified sample of product from 205 to 350 mμ in 95% ethyl alcohol was virtually identical with that found for pure phenanthrene. The thirteen peaks observed for phenanthrene in this region checked those reported[3] as far as wave length was concerned and checked semi-quantitatively as to extent of absorption.

None of the dimer, 1,2,3,4-tetraphenylcyclobutane, which has been reported[4] as a product of the illumination of *trans*-stilbene in benzene, was isolated from the illumination of either *cis*- or *trans*-stilbene. Presumably higher concentrations would be necessary for the effective formation of this type of product.

The absorption spectra reported for bibenzyl[5] and for *cis*- and *trans*-stilbene[1a,6] agree fairly well with those found for the compounds used in the present work. For the two stilbenes spectra with molar absorbancy indices roughly twice those found also have been reported, however.[1b,7]

Experimental Part

Purification of Solvents and Hydrocarbons.—Cyclohexane and acetonitrile were purified as described for an earlier investigation[8]; carbon tetrachloride was purified with alkaline potassium permanganate as outlined by Bauer and Daniels[9]; and commercial 95% ethyl alcohol was used without further purification.

Freshly distilled *cis*-stilbene,[10] b.p. 115–116° (5.8 mm.), was used. Bibenzyl, m.p. 52.5–53.0°, and *trans*-stilbene, m.p. 123–124°, were obtained by crystallization from 95% ethyl alcohol.

The purest phenanthrene, m.p. 98.5–99.0°, was obtained by the method[11] involving the debromination of 9,10-dibromo-9,10-dihydrophenanthrene, m.p. 96–97° dec. Eastman Kodak Co. phenanthrene, 97.5–98.5° also was used. Purification[12] of technical phenanthrene by crystallization and distillation gave a product of m.p. 102–103°. This latter product was shown to be unsatisfactory spectrophotometrically. It showed two extra peaks at 355 and 373 mμ of molar absorbancy between 300 and 400, and other peaks in the spectrum were higher than they were for other samples.

Phenanthrene from *cis*- and *trans*-Stilbene.—A solution of 2.0 g. of either *cis*- or *trans*-stilbene in 500 ml. of 95% ethyl alcohol in a fused silica flask was illuminated for 20 days at room temperature with a Hanovia mercury arc (Alpine Burner type 19418). The photochemical change (appearance of phenanthrene peak at 250 mμ) was followed spectrophotometrically—small samples being diluted approximately 4000:1. Evaporation of the solvent gave a mixture of relatively white crystals and a sticky, brown amorphous substance. The crystals (m.p. 94–96°) were removed mechanically and sublimed at reduced pressure. The sublimate was crystallized from 95% ethyl alcohol to give phenanthrene, m.p. 98–99°, which was nearly identical spectrophotometrically with a pure sample. Attempts to crystallize or to sublime the residue from the illumination directly gave only very impure phenanthrene (m.p. 75–80°).

Absorption Spectra Measurements.—Stock solutions of the hydrocarbons were made up by weight and diluted to suitable concentrations for measurements. All solutions were kept in the dark because of their sensitivity to light. This sensitivity was especially noticeable with very dilute solutions of the stilbenes. Such solutions were completely stable for 12 months when kept in the dark, however.

Illumination of the solutions was carried out at room temperature in the silica cells used for the measurement of the spectra. The cells were placed about 5 cm. from the Hanovia mercury arc. Measurements of the spectra were made from time to time in order to follow the changes which were taking place. In these experiments the unfiltered radiation would have been absorbed by both the solvents and the solutes.

All of the absorption spectra measurements were carried out at 25° with a Cary model 11 recording spectrophotometer. Calibrated silica cells of path length 1.00 ± 0.01 cm. were used. The uniform nomenclature and symbology suggested by the National Bureau of Standards[13] has been used throughout this note.

---

[2] H. Ley and H. Specker, *Z. wiss. Phot.*, **38**, 13 (1939).

[3] W. S. Johnson and F. J. Mathews, This Journal, **66**, 211 (1944); M. S. Newman and A. S. Hussey, *ibid.*, **69**, 3023 (1947); W. V. Mayneord and E. M. F. Roe, *Proc. Roy. Soc.* (*London*), **A152**, 299 (1935).

[4] M. Pailer and U. Miller, *Monatsh.*, **79**, 615 (1948).

[5] H. Ley and H. Dirking, *Ber.*, **67**, 133 (1934).

[6] R. N. Beale and E. M. F. Roe, *J. Chem. Soc.*, 2755 (1953); M. Calvin and H. W. Alter, *J. Chem. Phys.*, **19**, 765 (1951).

[7] A. Smakula and A. Wassermann, *Z. physik. Chem.*, **A155**, 353 (1931).

[8] R. E. Buckles and J. F. Mills, This Journal, **76**, 4845 (1954).

[9] W. H. Bauer and F. Daniels, *ibid.*, **56**, 378 (1934).

[10] R. E. Buckles and N. G. Wheeler, *Org. Syntheses*, **33**, 88 (1953).

[11] C. C. Price, C. E. Arntzen and C. Weaver, This Journal, **60**, 2837 (1938).

[12] C. A. Dornfeld, J. E. Callen and G. H. Coleman, *Org. Syntheses*, **28**, 19 (1948).

[13] National Bureau of Standards Letter-Circular LC-857 (1947).

Department of Chemistry
State University of Iowa
Iowa City, Iowa

Derivatives of Sulfenic Acids. XVIII. Synthesis of 2,4-Dinitrophenyl Sulfur Trifluoride and of Antimony(III) Halide Adducts with *p*-Toluenesulfenyl Chloride[1]

By David L. Chamberlain, Jr.,[2] and Norman Kharasch

Received October 4, 1954

While sulfenyl chlorides and bromides, RSX, are now well known, there is as yet no unequivocal example of a sulfenyl fluoride.[3a,b,c] The purpose of this study was to find whether 2,4-dinitrobenzenesulfenyl fluoride or *p*-toluenesulfenyl fluoride could be prepared by certain reactions which were considered as possible routes to these substances.

Direct fluorination of bis-(2,4-dinitrophenyl) disulfide, in liquid hydrogen fluoride, at 0–5°, did not give the corresponding sulfenyl fluoride. The product was 2,4-dinitrophenyl sulfur trifluoride (51% yield), which was characterized by analysis and by conversion to 2,4-dinitroaniline and to N-phenyl-2,4-dinitroaniline, by reactions with ammonia and aniline. The isolation of this stable compound, which is the first example of an organo-substituted sulfur tetrafluoride, is of interest in comparison

---

[1] Presented before the American Chemical Society, Symposium on Fluorine Chemistry, Chicago, Ill., September, 1953.

[2] Research Corporation Predoctoral Fellow, University of Southern California, 1951–1953.

[3] (a) A product cited as $CF_3(CF_2)_7SF$ is recorded in U. S. Patent 2,519,983, but details and structure proof are not given. (b) A unique product, presumed to be 2-nitrobenzenesulfenyl fluoride, has been synthesized in this Laboratory, by reaction of the sulfenyl chloride and hydrogen fluoride; *cf.* the abstracts of the Symposium cited in footnote 1. (c) For an unsuccessful attempt to prepare Cl_3CSF, *via* the corresponding sulfenyl chloride, *cf.* O. B. Helfrich and E. E. Reid, This Journal, **43**, 591 (1921).

with the known instabilities of the alkyl and aryl sulfur trichlorides ($RSCl_3$)[4,5] and with the postulate of Emeleus and Heal[6] that compounds as $ArSF_3$ occur only as unstable intermediates during fluorination of certain aryl disulfides and thiophenols. The relatively good yield of product is also notable, since from the few recorded studies of the direct fluorinations of sulfur compounds, predominant formation of products in which sulfur attains the VI-valent state, as well as considerable carbon–sulfur bond cleavage might have been anticipated.[7]

In contrast to the smooth reaction with the above disulfide, and to the ease with which chlorination of 2,4-dinitrothiophenol yields the corresponding sulfenyl chloride,[8] the fluorination of the thiophenol gave only tarry products. Other attempts to prepare 2,4-dinitrobenzenesulfenyl fluoride included: (a) reactions of the corresponding sulfenyl chloride and sulfenamide with anhydrous hydrogen fluoride, in an inert solvent; and (b) fluorinations of the sulfenyl chloride with mercury(II) fluoride and antimony fluorides. Observations on these attempts are recorded briefly in the Experimental part, but the desired 2,4-dinitrobenzenesulfenyl fluoride was not obtained.

The reaction of *p*-toluenesulfenyl chloride with antimony (III) fluoride did not give the sulfenyl fluoride. The product obtained, instead, was a deep blue 1:1 adduct. A similar product resulted from the reaction of *p*-toluenesulfenyl chloride and antimony(III) chloride. These substances appear to be the first examples of such sulfenyl chloride–metal halide addition compounds. The interactions of 2,4-dinitrobenzenesulfenyl chloride with metal halides have, however, been noted in earlier papers of this series.[9]

Acknowledgment.—We are indebted to Research Corporation for a grant in support of this study, and to Professor Anton B. Burg for help in constructing a fluorine cell which was used in the early phases of the work.

Experimental[10]

Apparatus and Materials.—Reactions with elementary fluorine in liquid hydrogen fluoride were carried out in a 500-ml. copper flask with a wide, flanged opening. The flask was sealed with a Teflon gasket, and a flat, copper cover, held in place by a split-ring clamp. Inlet and outlet ports in the cover were made of one-half of a $^1/_4$-inch brass compression coupling, which was silver-soldered to the cover. Connections were made to $^1/_4$-inch copper tubing with brass compression fittings.

Direct Fluorination of Bis-(2,4-dinitrophenyl) Disulfide.—Hydrogen fluoride (200 ml) was added to a 500-ml. copper flask (see above) which contained 3.5 g. of the disulfide. The mixture was kept at 0–5° (ice-bath), and a very slow stream of fluorine gas was passed in for 2.5 hours. The mixture was let stand 24 hr. at room temperature, and the remaining hydrogen fluoride evaporated (steam-bath, hood). Hot carbon tetrachloride (100 ml.) was added, and the mixture was treated with sufficient, powdered sodium fluoride to remove the last traces of hydrogen fluoride, then filtered. The residue was extracted twice more with hot carbon tetrachloride, and the extract filtered, concentrated and cooled. Total yield of pale yellow leaflets, 2.1 g. (51%), m.p. 94–96°, and raised to 96.5–97° by recrystallization from carbon tetrachloride.

Anal.[11] Calcd. for $C_6H_3F_3N_2O_4S$: C, 28.12; H, 1.17; N, 10.94; S, 12.50; F, 22.22; mol. wt., 256. Found: C, 28.21; H, 1.23; N, 10.70; S, 12.55; F, 21.55; mol. wt. (cryoscopically in benzene), 236.

The product gave distinct tests for fluorine by treatment with aqueous ammonia and precipitation of fluoride from the hydrolysate. Identity of this precipitate was confirmed by liberating hydrogen fluoride from it by reaction with 25% sulfuric acid, receiving the gas in dilute alkali, and reprecipitation of the cerium(III) fluoride.

2,4-Dinitrophenylsulfur trifluoride dissolves without reaction in halogenated hydrocarbons, acetone, ethyl acetate and ethers. It is soluble in alcohols without noticeable reaction, is not affected by atmospheric moisture, and is entirely stable to keeping under ordinary conditions. The infrared spectrum (sample mulled in Nujol) had maxima at 837 and 855 cm.$^{-1}$, at 1350 cm.$^{-1}$ and at 1550 cm.$^{-1}$ (compared to 849, 1349 and 1518 cm.$^{-1}$), which are given as the three maxima characteristic for nitro groups by Randle and Whiffen.[12]

To convert the trifluoride to 2,4-dinitroaniline, 0.25 g. of the former was shaken with 25 ml. of concd. ammonia, and the mixture extracted with ether. The conversion to crude 2,4-dinitroaniline (m.p. 172–173°) was nearly quantitative, and two recrystallizations from carbon tetrachloride gave product (m.p. 179–180°), which did not depress the melting point of authentic amine (m.p. 179–180°). Similarly, reaction of the fluorine compound (0.35 g.) with aniline (0.26 g.) in 25 ml. of ether, gave a deep red solution, which—on evaporation to half-volume—gave a water-soluble fluoride precipitate. This was collected, and the filtrate diluted with 25 ml. of carbon tetrachloride, charcoaled, filtered and cooled, giving 0.2 g. of brick-red needles, m.p. 148–150°, raised to 155.5–156° by three recrystallizations from carbon tetrachloride. The product was identical (m.p. and m.m.p.) with authentic N-phenyl-2,4-dinitroaniline.[13]

Other Attempts to Prepare 2,4-Dinitrobenzenesulfenyl Fluoride.—(a) The reaction of 2,4-dinitrothiophenol[13] with elementary fluorine, carried out similarly as the reaction with the disulfide, gave only tarry products. (b) Similar difficulties (formation of intractable, tarry materials) were encountered in the attempted reactions of 2,4-dinitrobenzenesulfenyl chloride with liquid hydrogen fluoride (*cf.* footnote 3b). (c) The interaction of 2,4-dinitrobenzenesulfenamide with gaseous hydrogen fluoride (excess HF bubbled into 0.9 g. of the sulfenamide dissolved in 50 ml. of chloroform) gave only a white precipitate, from which the original sulfenamide (m.p. and m.m.p.) was recovered by treatment with anhydrous sodium fluoride. The white precipitate is quite likely the hydrofluoride of the sulfenamide, but it was not further investigated. (d) Reaction of 2,4-dinitrobenzenesulfenyl chloride (1.2 g., 0.005 mole), in 25 ml. of purified tetrahydrofuran, with 1.2 g. (0.005 mole) of mercury(II) fluoride was carried out by heating briefly to boiling, cooling and allowing to stand 24 hr. The supernatant liquid was discarded, and the residue extracted with chloroform (in which it was but slightly soluble) and then with hot acetone. Concentrating the acetone extracts gave a pale green solid, melting indefinitely above 230°, and having the percentage composition: C, 36.31; H, 1.78; N, 15.68, 15.97. This product may possibly contain polymeric material [$(C_6H_2N_2O_4S)_n$, calcd.: C, 36.4; H, 1.0; N, 14.2], but it is distinct in its decomposition behavior from the familiar bis-(2,4-dinitrophenyl) disulfide, $(C_6H_2N_2O_4S)_2$, which has the same empirical formula. (e) 2,4-

---

[4] K. R. Brower and I. B. Douglass, THIS JOURNAL, **73**, 5787 (1951).

[5] I. B. Douglass, K. R. Brower and F. T. Martin, *ibid.*, **74**, 5770 (1952).

[6] H. J. Emeleus and H. G. Heal, *J. Chem. Soc.*, 1126 (1946).

[7] Carbon–sulfur bond cleavages, with formation of SF_6 and CF_4, and compounds as CF_3SF_5, $CF_3SF_4CF_3$ and $F_5S–CF_2–SF_5$ have been noted in the direct fluorination of CH_3SH, CS_2 and CH_3SCH_3. *Cf.* G. A. Silvey and G. H. Cady, THIS JOURNAL, **72**, 3624 (1950); and A. F. Clifford, H. K. El-Shamy, H. J. Emeleus and R. N. Haszeldine, *J. Chem. Soc.*, 2372 (1952).

[8] G. W. Perold and H. L. F. Snyman, THIS JOURNAL, **73**, 2379 (1951).

[9] *Cf.*, *e.g.*, *ibid.*, **72**, 3529 (1950); **75**, 1081 (1953); **75**, 3065 (1953).

[10] Melting points were taken on a Fisher–Johns block.

[11] These elementary analyses were made, respectively, by Dr. Adalbert Elek and Mr. W. J. Schenck.

[12] R. R. Randle and D. H. Whiffen, *J. Chem. Soc.*, 4153 (1952). *Cf.* also footnote 5, THIS JOURNAL, **75**, 3734 (1953). The infrared determination was kindly performed by the Samuel P. Sadtler Laboratory of Philadelphia, Pa.

[13] C. Willgerodt, *Ber.*, **9**, 977 (1876).

Dinitrobenzenesulfenyl chloride (0.24 g. in 20 ml. dry benzene) failed to react with antimony(III) fluoride (0.18 g.) on refluxing 100 min. Only unchanged sulfenyl chloride was found. Repetition of the experiment with the addition of bromine in amount equivalent to SbF_3 (to activate the fluorinating agent[14]) caused vigorous interaction, with decomposition of the organic materials, and isolation only of dark tarry residues.

Reaction of *p*-Toluenesulfenyl Chloride with Antimony(III) Fluoride and Antimony(III) Chloride. (a).—To a solution of 10.0 g. of the sulfenyl chloride in 25 ml. of dry carbon tetrachloride, 11.4 g. of antimony(III) fluoride was added. The reaction proceeded rapidly, and when the mixture turned deep green, it was filtered through a sintered-glass funnel. The filtrate was let stand for 0.5 hr. and the intensely blue crystals which deposited were collected, washed with dry chloroform and dried at 80° and 15 mm. pressure; m.p. 144–146°. The yield of product was quite low (*ca.* 5%), for it was necessary to filter the reaction solution before reaction was complete, to avoid precipitation of the product in the presence of the insoluble antimony(III) fluoride.

Anal. Calcd. for $C_7H_7ClF_3SSb$: S, 9.50. Found: S, 9.26.

The blue adduct dissolved readily in organic solvents—such as ketones, nitroalkanes, amines, dioxane, benzene, nitrobenzene, and chloro- or bromobenzene—to give deep blue solutions. In all but the last four solvents, the color faded completely in one to three minutes, but a distinct product could not be obtained from the resulting colorless solutions. A dilute nitrobenzene solution of the adduct required several minutes to become colorless. The blue color was, however, regained when the solution was heated, and this process of color change seemed indefinitely reversible, suggesting a preferential complexing of the antimony fluoride by nitrobenzene at the lower temperature. The adduct was practically insoluble in carbon tetrachloride or chloroform. On long storage, it decomposed—as evidenced by change in color, low analysis for fluorine and etching of the glass vial. In bromo- and in chlorobenzene, at room temperature, the blue color of the solutions required several hours to fade. The aged solutions had a dark brown or reddish color. Removal of solvent left a brown-red oil which could not be identified.

(b).—The reaction of antimony(III) chloride with *p*-toluenesulfenyl chloride gave a 1:1 adduct whose color and solubility characteristics were entirely similar to those of the one with antimony trifluoride, but which was obtained in better yield (50–60%), since the problem of contamination (*cf.* above) with the chloroform-soluble antimony(III) chloride did not arise.

Anal. Calcd. for $C_7H_7Cl_4SSb$: Cl, 37.07. Found: Cl, 37.07.

---

[14] R. N. Haszeldine and A. G. Sharpe, "Fluorine and Its Compounds," Methuen and Co., Ltd., London, 1951, p. 67.

LOS ANGELES 7, CALIFORNIA

Cyclic Dienes. XII. Substituted Cyclohexadienes[1]

BY WILLIAM J. BAILEY[2] AND MILTON MADOFF[3]

RECEIVED JULY 21, 1954

Since the cyclic diene, 1,2-dimethylenecyclohexane, was used successfully to produce a high molecular weight all-*cis* diene polymer,[4] it seemed possible that some derivative of 1,3-cyclohexadiene also would produce an all-*cis* polymer. Cyclohexadiene itself would not be expected to produce a high molecular weight product with free radical initiators since the active hydrogens on the end of the diene system allow the monomer to react as its own chain transfer agent. For this reason, derivatives of cyclohexadiene I, II and III which do not contain any allylic hydrogens were prepared. The cyclic diene, 1,2-dimethyl-3,5-cyclohexadiene-1,2-dicarboxylic acid (I), which was prepared according to the method of Ziegler,[5] Woodward and Loftfield[6] was reduced with lithium aluminum hydride to produce a 71% yield of 1,2-dimethyl-1,2-dimethylol-3,5-cyclohexadiene (II). II was converted to the dibenzoate III by treatment with benzoyl chloride and pyridine.

Peroxide-catalyzed polymerization of the cyclic diene I produced only a low molecular weight polymer IV. Under similar conditions neither II nor III gave high polymers. Since it is unlikely that an impurity that could act as a polymerization inhibitor would persist through the two reactions and subsequent recrystallizations, it must be concluded that steric hindrance prevents the formation of a high polymer.

Experimental[7]

Polymerization of 1,2-Dimethyl-3,5-cyclohexadiene-1,2-dicarboxylic Acid (I)—The 1,2-dimethyl-3,5-cyclohexadiene-1,2-dicarboxylic acid (I), m.p. 147–148° dec., was prepared by a modification of the method of Ziegler[5] and Woodward and Loftfield.[6] In a 100-ml., round-bottom flask was placed a solution of 0.40 g. of 1,2-dimethyl-3,5-cyclohexadiene-1,2-dicarboxylic acid (I) and 0.002 g. of benzoyl peroxide in 45-ml. of dry benzene. After this solution was heated under reflux for 24 hours, the benzene was evaporated and the residue was reprecipitated several times from benzene with petroleum ether to obtain 0.34 g .of poly-1,2-dimethyl-3,5-cyclohexadiene-1,2-dicarboxylic acid (IV), softening point 76–78°, intrinsic viscosity (benzene) 0.08. Because of the very low molecular weight of IV no attempt was made to determine its structure.

1,2-Dimethyl-1,2-dimethylol-3,5-cyclohexadiene (II).—In a 1-liter, three-necked flask, equipped with a stirrer, a dropping funnel and an exhaustive ether extractor, was placed 5.67 g. (0.16 mole) of lithium aluminum hydride in 400 ml. of ether. The ether in the reaction flask was refluxed as rapidly as possible to extract from the reservoir of the extractor 12.4 g. (0.063 mole) of 1,2-dimethyl-3,5-cyclohexadiene-1,2-dicarboxylic acid (I) in 3.5 hours. After the addition of the diacid I was complete, the reaction mixture was heated for an additional 2 hours. The excess hydride was decomposed with water and just enough 10% hydrochloric acid was added to dissolve the aluminum precipitate. The aqueous layer was extracted for 3 days in an exhaustive ether extractor and the ether extracts were added to the original ether layer. The resultant solution was dried over potassium carbonate, the ether was removed by distillation and the solid residue was recrystallized from a mixture of petroleum ether and chloroform to yield 3.4 g. (71%) of very light tan 1,2-dimethyl-1,2-dimethylol-3,5-cyclohexadiene (II), m.p. 172–173°.

Anal. Calcd. for $C_{10}H_{16}O_2$: C, 71.43; H, 9.52; mol. wt., 168. Found: C, 71.41; H, 9.70; mol. wt. (Rast), 164.

Attempts to polymerize II by the procedure described above led only to recovery of starting material.

1,2-Dimethyl-1,2-di-(benzoxymethyl)-3,5-cyclohexadiene (III).—In accordance with the procedure of Hickinbottom,[8] a mixture of 0.2 g. (0.0012 mole) of 1,2-dimethyl-1,2-dimethylol-3,5-cyclohexadiene (II), 0.8 g. (0.0057 mole) of benzoyl chloride and 2 ml. of pyridine in 30 ml. of benzene was heated under reflux for 36 hours in a 50-ml. flask. The reaction mixture was diluted with 100 ml. of ether and extracted in succession with 30 ml. of 2 *N* hydrochloric acid,

---

[1] Previous paper in this series, THIS JOURNAL, **77**, 992 (1955).

[2] Department of Chemistry, University of Maryland, College Park, Md.

[3] Office of Naval Research Fellow, 1949–1950.

[4] W. J. Bailey and H. R. Golden, THIS JOURNAL, **76**, 5418 (1954).

[5] K. Ziegler, G. Schenck, E. W. Krockow, A. Siebert, A. Wenz and H. Weber, *Ann.*, **551**, 1 (1952).

[6] R. B. Woodward and R. G. Loftfield, THIS JOURNAL, **63**, 3167 (1941).

[7] All melting points are corrected. The authors are grateful to Arthur Tomasewski for the analyses.

[8] W. J. Hickinbottom, "Reactions of Organic Compounds," Longmans, Green and Co., London, 1938, p. 99.