dried *in vacuo* at 125°; $\lambda^{\text{Chl}}_{\max}$ 264 mμ, ϵ 13,600; 303 mμ, ϵ 8,600; 395 mμ, ϵ 24,800.

Anal. Calcd. for $C_{14}H_{11}N_5O_5$: C, 51.1; H, 3.4; N, 21.3. Found: C, 50.8; H, 3.4; N, 21.3.

6-Carbethoxy-6-(4'-carbethoxy)-butyl-2-chloro-5-oxo-6,7-dihydro-1,5H-pyrindine (XVI).—To a solution of sodium ethoxide (prepared by dissolving 0.58 g. of sodium in 100 ml. of anhydrous ethanol) was added 6.10 g. of XIV. The mixture was heated to reflux, and a solution of 7.00 g. of ethyl 5-iodovalerate[12] in 10 ml. of absolute ethanol was added dropwise over a 0.5-hour period. The mixture was refluxed for 3.5 hours longer and the solvent was removed *in vacuo*, water was added, and the oil which separated was extracted with ether. The combined ether extracts were washed with 10% aqueous sodium hydroxide and water, and were dried over anhydrous sodium sulfate.

The combined alkaline and water washings were acidified with concentrated hydrochloric acid and extracted with ether. Removal of the solvent gave 2.58 g. of XIV, m.p. 93–96°.

The combined ether extracts from above were distilled to remove solvent and unreacted 5-iodovalerate (2.44 g., b.p. 60–65° at 0.5 mm.). The residue was submitted to a molecular distillation giving 3.42 g. of XVI at 190° (0.05 mm.). A two-stage molecular distillation (145° at 0.001 mm.) gave the analytical sample of XIV as a clear, pale yellow, mobile oil: $\lambda^{\text{EtOH}}_{\max}$ 238 mμ, ϵ 10,300; 289 mμ, ϵ 11,900; 297 mμ, ϵ 11,400; bands at 5.80, 5.85, 6.30 and 6.35 μ (chloroform).

Anal. Calcd. for $C_{18}H_{22}ClNO_5$: C, 58.8; H, 6.0; N, 3.8; Cl, 9.6. Found: C, 58.7; H, 5.8; N, 4.1; Cl, 9.9.

6-(4'-Carboxy)-butyl-2-hydroxy-5-oxo-6,7-dihydro-1,5H-pyrindine (II) from 6-Carbethoxy-6-(4'-carbethoxy)-butyl-2-chloro-5-oxo-6,7-dihydro-1,5H-pyrindine (XVI).—A mixture of 0.30 g. of XVI and 3 ml. of 85% phosphoric acid was heated at 185° for 30 minutes. The cooled reaction mixture was poured onto 18 g. of crushed ice and filtered to give 0.18 g. (90%) of pale yellow crystals, m.p. 260–261° (dec., darkens at 255°), which did not depress the melting point of II, and whose infrared spectrum was identical to that of II.

The **2,4-dinitrophenylhydrazone** of the product obtained in this experiment melted at 256–257° dec. and did not depress the melting point of the 2,4-dinitrophenylhydrazone of II.

1,6-Dimethyl-5-carbethoxy-2-pyridone (XVII) and Ethyl 2-Methyl-6-methoxynicotinate (XVIII). (a).—A mixture containing 7.24 g. of ethyl 2-methyl-6-oxynicotinate,[2] 11.36 g. of methyl iodide, 8.40 g. of potassium carbonate (anhydrous, ignited) and 50 ml. of acetone was refluxed with stirring for 16 hours. The solvent was evaporated on the steam-bath, and the residue was treated with *ca.* 50 ml. of water. The resulting mixture was extracted with chloroform, and the combined chloroform extracts were dried over anhydrous sodium sulfate. Removal of the solvent gave a residue which was recrystallized from cyclohexane to give 6.20 g. (80%) of colorless crystals, m.p. 79–80°. The analytical sample of XVII was obtained as fine, colorless needles, m.p. 80–81°, from cyclohexane; $\lambda^{\text{EtOH}}_{\max}$ 265 mμ, ϵ 15,400; 303 mμ, ϵ 5,600; bands at 5.88, 6.06 (strong), 6.26 (weak), and 6.50 μ, and narrow band in the 3.0–4.0 μ region (chloroform).

Anal. Calcd. for $C_{10}H_{13}NO_3$: N, 7.2. Found: N, 6.9.

The cyclohexane filtrate from above was evaporated to dryness on the steam-bath to give 1.02 g. (13%) of yellowish oil, whose infrared spectrum showed it to be the O-alkylated product XVIII. On distillation this material afforded a colorless oil, b.p. 65–67° (0.2 mm.), n^{25}D 1.5107. The analytical sample of XVII was obtained as a colorless oil, n^{25}D 1.5098, by a two-stage molecular distillation (bath temperature 80°, 0.4 mm.); $\lambda^{\text{EtOH}}_{\max}$ 247 mμ, ϵ 10,600; 274 mμ, ϵ 7,300; 282 mμ, ϵ 5,500; bands at 5.86, 6.25 (strong), and 6.34 (weak) μ (chloroform).

Anal. Calcd. for $C_{10}H_{13}NO_3$: N, 7.2. Found: N, 7.0.

(b).—To a stirred mixture of the sodio salt of ethyl 2-methyl-6-oxynicotinate (prepared by refluxing for 20 hours under anhydrous conditions a stirred mixture of 3.00 g. of the pyridone) and 0.44 g. of sodium hydride in 35 ml. of anhydrous benzene was added 4.0 ml. of methyl iodide over a 0.5-hour period. The reaction mixture was refluxed for 18 hours, an additional 5 ml. of methyl iodide was added and refluxing continued for 6 hours longer. The solvent and excess methyl iodide were removed by distillation *in vacuo* and the colorless residue was treated with water and extracted with chloroform. The combined chloroform extracts were washed with 10% aqueous sodium hydroxide, then water, and finally dried over anhydrous sodium sulfate. On removal of the chloroform, the residue was steam distilled, and the pot residue was extracted with ether. After drying over anhydrous magnesium sulfate, the ether was distilled to give 0.80 g. (26%) of XVII, m.p. 68–75°.

NEW YORK 27, N. Y.

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[12] N. J. Leonard and W. E. Goode, THIS JOURNAL, **72**, 5404 (1950).

NOTES

Illumination of *cis*- and *trans*-Stilbenes in Dilute Solutions

BY ROBERT E. BUCKLES

RECEIVED JULY 19, 1954

In connection with studies of the photochemical isomerization of *trans*-stilbene to *cis*-stilbene it was observed[1] that *cis*-stilbene itself underwent photochemical decomposition to give a product reported[1b] to have an absorption spectrum peak at 247 mμ in hexane. In the present investigation the illumination of *cis*- and *trans*-stilbene in dilute solutions with a mercury arc has been carried out and the main product has been identified as phenanthrene.

Most of the experiments were carried out on solutions of the stilbenes of concentration suitable (about 5×10^{-5} *M*) for the measurement of the high absorption peak characteristic of phenanthrene in the neighborhood of 250 mμ. From this peak (molar absorbancy index or molar extinction coefficient about 6.6×10^4) the extent of phenanthrene formation was estimated. In cyclohexane, illumination for ten minutes converted 95% of the *cis*-stilbene to phenanthrene. In 60 minutes about 70% of the *cis*-stilbene in either 95% ethyl alcohol or acetonitrile was converted to phenanthrene. No higher conversion was observed in any case on continued illumination because phenanthrene, itself, underwent a slow decomposition on illumination. In carbon tetrachloride it was evident that the phenanthrene decomposed so fast that it did not accumulate in solution. The spectrum of phenanthrene was also observed for illuminated, dilute solutions (*ca.* 5×10^{-5} *M*) of *trans*-stilbene in cyclohexane, acetonitrile and 95% ethyl alcohol. No absorption peaks characteristic of phenanthrene

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[1] (a) G. N. Lewis, T. T. Magel and D. Lipkin, THIS JOURNAL, **62**, 2973 (1940); (b) A. Smakula, *Z. physik. Chem.*, **B25**, 90 (1934).

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.

Department of Chemistry
State University of Iowa
Iowa City, Iowa

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[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).

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

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[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).