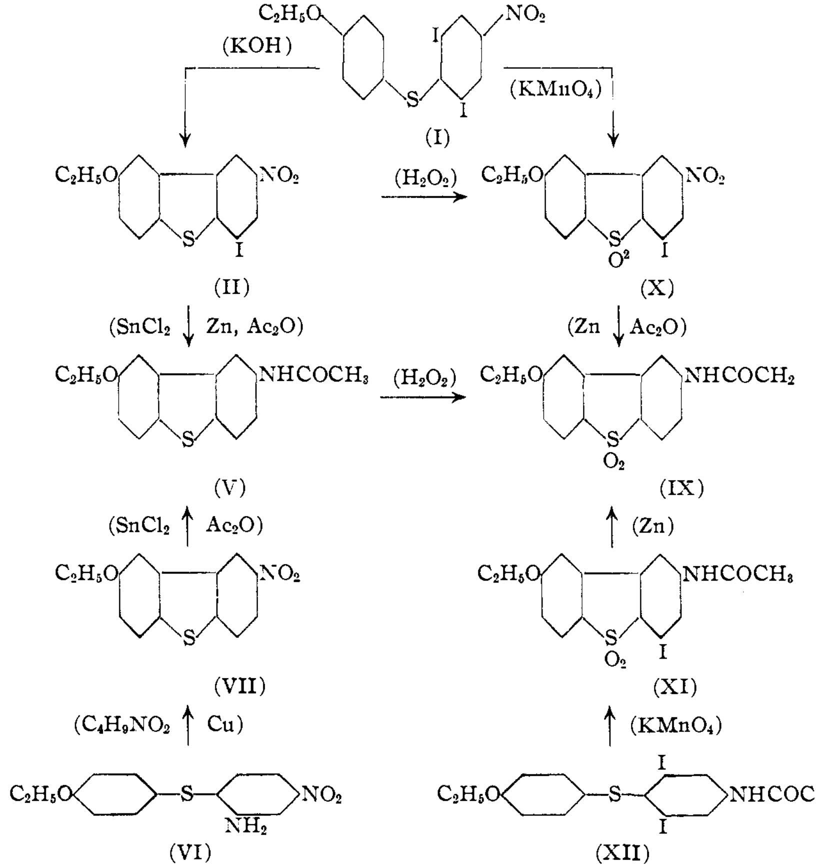
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TOLEDO]

Cyclization of a Diiodinated Diphenyl Sulfide

BY PAUL BLOCK, JR.

In a previous paper[1] it was shown that 4'-ethoxy-2,6-diiodo-4-nitrodiphenyl sulfide (I) can be prepared in excellent yield by allowing 3,4,5-triiodonitrobenzene to react with *p*-ethoxythiophenol at room temperature. The present study deals with another compound isolated from the same reaction mixture if instead of taking place at room temperature, the reaction was heated under reflux for several hours. In this case, a mixture resulted from which a single pure constituent could be obtained by repeated recrystallization from benzene or, preferably, toluene. The compound contained considerably less iodine than calculated for a diiodinated diphenyl sulfide.

In spite of its low iodine content, this compound was less soluble and had a higher melting point than the pure diiodinated diphenyl sulfide; the reverse would have been the normal expectation. Thus it appeared that, in addition to a loss of iodine, the molecule had suffered some fundamental skeletal change. The compound was therefore examined further with the result that it has been found to be a monoiodinated dibenzothiophene (II) formed by the elimination of the respective elements of hydrogen iodide from the two substituted benzene rings of the diphenyl sulfide (I), one ring contributing hydrogen, the other, iodine.



A compound of similar properties has been described by Bass[2] who studied the reaction of 3,4,5-triiodonitrobenzene with *p*-thiocresol. He was able to eliminate the formation of a monoiodinated product by diluting with water the ethanol used as a reaction solvent to 90%. Although his work has been amply confirmed in this laboratory, dilution of the ethanol did not suppress deiodination sufficiently in the present case where ethoxy was the substituent instead of methyl. Here the problem of eliminating the formation of the unwanted dibenzothiophene derivative in favor of the diiodinated diphenyl sulfide was solved by performing the reaction at room temperature.

This new formation of a dibenzothiophene structure does not appear to be associated with the condensation of the thiophenol and the halogen compound since it was entirely feasible to cause the cyclization after condensation to a diphenyl sulfide. This was effected either under the conditions of the condensation, in slightly alkaline ethanol, or in dioxane containing potassium hydroxide. A cyclized product did not appear to be formed in pyridine or quinoline. Nor did it prove possible to isolate any pure product from the heating in alkaline ethanol of either the amino analog, 4'-ethoxy-2,6-diiodo-4-aminodiphenyl sulfide,[1] or the monoiodo compound, 4'-ethoxy-2-iodo-4-nitrodiphenyl sulfide.[1] Thus the presence of the nitro group as well as of both iodine atoms, appears to

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(1) P. Block, Jr., and J. L. Balmat, THIS JOURNAL, 72, 5638 (1950).

(2) S. L. Bass, Thesis, Yale University, 1929. The compound isolated, but not studied, by Bass appears to be the methyl analog of the ethoxy compound (II) reported here, 4-iodo-8-methyl-2-nitrodibenzothiophene. The compound was described as crystallizing from benzene in light yellow needles melting at 270°. and having I, 35.0; S, 8.7. $C_{13}H_8O_2NSI$ requires I, 34.4; S, 8.7.

be necessary for the condensation under the conditions used.

Cyclization with simultaneous oxidation, however, could be effected both in the case of the nitro compound (I) and the acetylated amino compound (XII). When either of these or the corresponding sulfoxides was oxidized in acetic acid with potassium permanganate, the sulfone of the cyclized compound could be isolated. In the case of (XII) some of the dibenzothiophene-5-dioxide was invariably produced. With the nitro compound (I), oxidation in very dilute solution yielded the diphenyl sulfone, but with dilutions necessary for a practical synthesis, and particularly if a small amount of water was present in the acetic acid, the yield of the diphenyl sulfone was lowered and more or less cyclization occurred.

The structure of the dibenzothiophene derivatives was proved by the synthesis (by a standard method) of an analogous compound to which the compound under study could be converted.

Cullinane and associates[3] first applied Pschorr's ring closure[4] to diphenyl sulfides in order to prepare dibenzothiophene derivatives; they used 50% sulfuric acid instead of copper powder to cause cyclization through elimination of a diazotized amino group located ortho to the sulfide linkage. The presence of the ethoxy group in the present instance dictated a return to the copper powder of Pschorr, with gratifying results.

Since it was not feasible to synthesize a suitable compound containing iodine, a related uniodinated compound was prepared and the compound in question deiodinated. Deiodination, however, was accompanied by reduction of the nitro group, so actual comparison was made on the amine and its acetyl derivative. The acetamido compound (V) could readily be oxidized to the sulfone (IX), and this was used to show the structure of the iodinated sulfone (XI), from which the iodine atom had been removed.

That the oxidized molecules were in fact sulfones and not sulfoxides was shown by the failure of acetic acid plus zinc dust to reduce them. It is thus apparent that with the uniodinated and monoiodinated cyclized sulfides reported in this paper, oxidation with excess hydrogen peroxide yielded sulfones as in the case of uniodinated and monoiodinated diphenyl sulfides, and in contrast to the behavior of diiododiphenyl sulfides whose oxidation by excess hydrogen peroxide stopped at the sulfoxide stage.[1]

Experimental[5]

8-Ethoxy-4-iodo-2-nitrobenzothiophene (II).—(a) 3,4,5-Triiodonitrobenzene[6] (10 g.) was suspended in 400 ml. of ethanol, 3.1 g. of *p*-ethoxythiophenol[7] was added, followed by 1.1 g. of potassium hydroxide dissolved in 5 ml. of water. After heating under reflux for 3 hours, the yellow precipitate was filtered and recrystallized twice from toluene; m. p. 222°.

Anal. Calcd. for $C_{14}H_{10}O_3NSI$: I, 31.8; mol. wt., 399. Found: I, 31.4; mol. wt. (Rast), 396.

(b) Alternatively, the compound could be prepared from 4′-ethoxy-2,6-diiodo-4-nitrodiphenyl sulfide[1] (I) by heating 4.5 g. of this compound in 450 ml. of 95% ethanol containing 0.6 g. of potassium hydroxide under reflux 3 hours. The reaction mixture was diluted with water, and the precipitate filtered off and dried. Several recrystallizations from toluene gave a product, m. p. 222°.

Dioxane (100 ml.) could be substituted for ethanol, in which case the potassium hydroxide was dissolved in 3 ml. of water. Two phases were present, and the reaction mixture was heated under reflux for 10 hours, followed by precipitation with water and recrystallization from toluene.

In neither method (a) nor (b) were conditions found which caused more than 35% of the theoretical cyclization to occur.

8-Ethoxy-4-iodo-2-aminodibenzothiophene (III).—The nitro compound (II) was reduced with stannous chloride in acetic acid to give an amine which, after one crystallization from ethanol, had m. p. 148.5–149.5°.

Anal. Calcd. for $C_{14}H_{12}ONSI$: I, 34.4. Found: I, 34.2.

The acetamide (IV) was prepared from acetic anhydride and pyridine; m. p. 214.5–215.5° after recrystallization from ethanol.

Anal. Calcd. for $C_{16}H_{14}O_2NSI$: C, 46.71; H, 3.41; I, 30.9. Found: C, 46.77; H, 3.28; I, 31.0.

8-Ethoxy-2-acetamidodibenzothiophene (V).—The iodine-containing acetamido compound (IV) was deiodinated with zinc in acetic acid and the product was recrystallized twice from ethanol; m. p. 195.5–196.5°.

Anal. Calcd. for $C_{16}H_{15}O_2NS$: C, 67.37; H, 5.26. Found: C, 67.33; H, 5.15.

4′-Ethoxy-2-amino-4-nitrodiphenyl Sulfide (VI).—2-Chloro-5-nitroaniline[8] (2.1 g.) was treated with 1.9 g. of *p*-ethoxythiophenol and 0.75 g. of potassium hydroxide in 25 ml. of 95% ethanol. The reaction was heated under reflux for 1 hour, cooled, and the crystalline material separated. After 2 recrystallizations from methanol, there resulted 2.3 g. (65%) of a product, m. p. 92.5–93.5°.

Anal. Calcd. for $C_{14}H_{14}O_3N_2S$: C, 57.92; H, 4.83. Found: C, 57.94; H, 4.73.

A derivative resulted smoothly when the amine was dissolved in acetic anhydride and a drop of sulfuric acid added, m. p. 170°.

8-Ethoxy-2-nitrodibenzothiophene (VII).—The amine (VI) (1.6 g.) was converted into its hydrochloride by dissolving in dry benzene and saturating with dry hydrogen chloride. After filtering off and drying, 1.75 g. of the salt was suspended in 15 ml. of acetic acid and treated at 15–18° with 0.63 ml. of butyl nitrite. The dark orange solution which resulted was cooled to 10–15° and diluted with 60 ml. of 50% aqueous acetic acid cooled to below 15°. Precipitated copper powder (2 g.) was added slowly enough to prevent excessive frothing resulting from the evolution of gas. After standing for 15 minutes the reaction mixture was heated to 40° and allowed to stand a further 15 minutes. The yellow precipitate that had formed, together with the copper was filtered off, washed successively with dilute sodium hydroxide solution and with water, and dried. The mixture was extracted with hot benzene (100–125 ml.), filtered to remove copper, treated with decolorizing carbon, refiltered, and boiled down to incipient crystallization. On cooling there resulted 1 g. (69%) of yellow needles melting at 209.5–210.5°, unchanged by a second crystallization from benzene.

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(3) Cullinane, Davies and Davies, *J. Chem. Soc.*, 1435 (1936).

(4) R. Pschorr, *et al.*, *Ber.*, **33**, 162 (1900); **39**, 3113 (1906); **40**, 2001 (1907).

(5) All melting points are corrected.

(6) R. B. Sandin and T. L. Cairns, "Organic Syntheses," Coll. Vol. II, John Wiley & Sons, Inc., New York, N. Y., 1943, p. 604.

(7) C. M. Suter and H. L. Hansen, THIS JOURNAL, **54**, 4100 (1932).

(8) Lobry de Bruyn, *Rec. trav. chim.*, **36**, 136 (1917).

Anal. Calcd. for $C_{14}H_{11}O_3NS$: C, 61.54; H, 4.03; N, 5.13. Found: C, 61.42; H, 4.18; N, 5.07.

8-Ethoxy-2-aminodibenzothiophene (VIII).—The nitro compound (VII) was reduced with stannous chloride and acetic acid; m. p. 109–110°.

Anal. Calcd. for $C_{14}H_{13}ONS$: C, 69.13; H, 5.35. Found: C, 69.27; H, 5.31.

The acetyl derivative (V), prepared with pyridine and acetic anhydride, melted at 196–196.5°, after recrystallization from ethanol. A sample mixed with the 195.5–196°-melting compound prepared from (IV) melted at 195.5–196.5°.

8-Ethoxy-2-acetamidodibenzothiophene-5-dioxide (IX).—The sulfide (V) was oxidized to the sulfone with 30% hydrogen peroxide in acetic acid, m. p. 313°, recrystallized from acetic acid.

Anal. Calcd. for $C_{16}H_{15}O_4NS$: C, 60.57; H, 4.73. Found: C, 60.43; H, 4.87.

8-Ethoxy-4-iodo-2-nitrodibenzothiophene-5-dioxide (X).—4'-Ethoxy-2,6-diiodo-4-nitrodiphenyl sulfide (5 g.) was oxidized in 100 ml. of acetic acid with 8 ml. of 30% peroxide as previoulsy described.[1] At the conclusion of the oxidation, but before diluting the reaction solution, 9 g. of potassium permanganate was added, very slowly with cooling at first, until the evolution of oxygen had practically ceased. The reaction mixture was stirred for 30 minutes, diluted with water, decolorized with sodium bisulfite, and the precipitate separated and dried. Recrystallization from dioxane yielded 1.5 g. of white microcrystals melting at 300°. From the dioxane solution, 2 g. of the yellow diphenyl sulfone was recovered. It was purified by recrystallization from amyl acetate.

Anal. Calcd. for $C_{14}H_{10}O_5NSI$: I, 29.5. Found: I, 29.1.

This compound was also prepared from the dibenzothiophene derivative (II) by oxidation with hydrogen peroxide and acetic acid; m. p. 300°, not lowered by admixture with the compound prepared directly from the diphenyl sulfide.

The product (X) could be converted into the acetamido sulfone (IX) by simultaneous reduction and deiodination with zinc and acetic acid, followed by acetylation with acetic anhydride and pyridine. Recrystallized from acetic acid, it had m. p. 313.5°.

8-Ethoxy-4-iodo-2-acetamidodibenzothiophene-5-dioxide (XI).—4'-Ethoxy-2,6-diiodo-4-acetamidodiphenyl sulfide[1] (XII) (1 g.) was heated under reflux for 20 minutes in 50 ml. of acetic acid to which had been added an excess of potassium permanganate. Water (50 ml.) was added, and sufficient sodium bisulfite to reduce the manganese dioxide. After standing in the refrigerator for several hours, the precipitate was filtered off, dried, and leached out thoroughly with hot ethanol. After recrystallization of the ethanol-insoluble residue from acetic acid, the material melted at 289°.

Anal. Calcd. for $C_{16}H_{14}O_4NSI$: C, 43.34; H, 3.16; N, 3.16. Found: C, 43.08; H, 3.27; N, 3.39.

Oxidation of the dibenzothiophene derivative (IV) with 30% hydrogen peroxide and acetic acid provided another route to the sulfone; m. p. 292–293°. A mixture of this with the product above melted at 291–292°.

Deiodination of (XI) with zinc dust and acetic acid gave (IX), m. p. 313°, recrystallized from acetic acid.

Acknowledgment.—The author wishes to record his appreciation to Dr. S. L. Bass, Dow Corning Corp., Midland, Mich., for making available a copy of his thesis as well as the unpublished notes of his work on diphenyl sulfides, and to Dr. R. Stuart Tipson, Mellon Institute, Pittsburgh, Pa., for his continuing interest and advice.

Summary

1. A substituted diphenyl sulfide, containing two ortho iodine atoms and one para nitro group in the same ring can be caused to cyclize to a substituted dibenzothiophene derivative with loss of the elements of hydrogen iodide.

2. Such a substituted diphenyl sulfide as well as one containing an acetamido in place of a nitro group was cyclized and oxidized simultaneously to a substituted dibenzothiophene-5-dioxide derivative.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS]

Allylic Chlorides. XII. Preparation and Properties of *cis*- and *trans*-Cinnamyl Chloride

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Many investigators have reported the preparation and utilization of cinnamyl chloride but none has noted the geometrical configuration of the chloride involved. The present paper describes the preparation of both *cis*- and *trans*- cinnamyl chloride from the corresponding cinnamyl alcohols. Both alcohols have been prepared and characterized previously.[2]

The preparation of *trans*-cinnamyl alcohol presented no problem because the commercially available cinnamyl alcohol has the *trans* configuration. The synthesis of the *cis* isomer followed the method of Tchao Yin Lai[3] and Gredy[2b] which starts with phenylacetylene and has as the characterizing step the *cis* hydrogenation of 3-phenyl-2-propyn-1-ol. In an attempt to prepare 3-phenyl-2-propyn-1-ol by a more convenient method, cinnamyl alcohol was brominated to give 2,3-dibromo-3-phenylpropan-1-ol. This bromo alcohol was subsequently treated with alcoholic potassium hydroxide but no 3-phenyl-2-propyn-1-ol could be isolated from the reaction mixture.

trans-Cinnamyl alcohol was converted to *trans*-cinnamyl chloride using thionyl chloride,[4] while phosphorus trichloride in pyridine[5] was used in

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(1) Research Corporation Fellow 1947–1948; du Pont Fellow 1948–1949. E. I. du Pont de Nemours and Company, Arlington, New Jersey.

(2) (a) Bourguel and Ynon, *Compt. rend.*, **182**, 224 (1926); (b) Gredy, *Bull. soc. chim.*, [5] **3**, 1093 (1936).

(3) Tchao Yin Lai, *ibid.*, **53**, 682 (1933).

(4) Gilman and Harris, *Rec. trav. chim.*, **50**, 1052 (1931).

(5) Clark and Streight, *Trans. Roy. Soc. (Canada)*, [3] **23**, III, 77 (1929).