

A solution of 12.0 g. of *o*-xylyl-*n*-propylamine in 10.5 g. of 88% formic acid and 8.5 g. of 35% formalin was heated on the steam-bath 2 hours, and then refluxed 2 hours. After adding 25 ml. of 5 *N* sulfuric acid, the volatile material was removed at the water-pump. The resulting sirup was dissolved in water, made alkaline with 50% sodium hydroxide, and the oil taken up in ether to give 11.3 g. (86%) of *o*-xylyl-*n*-propylmethylamine (VI), b.p. 98–99° at 10 mm.; picrate, m.p. 125.5–126°.

The melting point of the picrate of tertiary amine VI from the rearrangement of V was not depressed by admixture with a sample of the picrate of the amine from this independent synthesis.

Tertiary amine VIII was prepared from *o*-ethylalaniline (obtained from Monsanto Chemical Company).⁶ This amine (1 mole), b.p. 114° at 30 mm., was diazotized and treated with potassium iodide to form *o*-ethyliodobenzene (89%), the Grignard reagent of which was carbonated to give *o*-ethylbenzoic acid (68%), m.p. 62–63.5° and 65–65.5° after two recrystallizations from water (reported m.p. 68°).¹⁰ This acid (0.33 mole, m.p. 62–63.5°) was converted

(10) G. Giebe, *Ber.*, **29**, 2534 (1896).

by thionyl chloride to the acid chloride which was stirred with a cold solution of 60 g. of sodium hydroxide in 500 ml. of water while excess dimethylamine was passed in to give *o*-ethyl-*N,N*-dimethylbenzamide (74%), b.p. 112–114° at 3 mm.

Anal. Calcd. for C₁₁H₁₅NO: C, 74.54; H, 8.53; N, 7.90. Found: C, 74.41; H, 8.45; N, 7.82.

A solution of 0.236 mole of *o*-ethyl-*N,N*-dimethylbenzamide in 200 ml. of ether was added during 1 hour to a stirred suspension of 0.236 mole of lithium aluminum hydride in 300 ml. of ether, and the mixture refluxed 1 hour. After cautiously adding water, followed by a solution of 250 g. of sodium potassium tartrate in 600 ml. of water; there was isolated 36 g. (93%) of *o*-ethylbenzylidimethylamine (VIII), b.p. 94° at 16 mm., *n*_D²⁰ 1.5027 (see note *e*, Table II); picrate, m.p. 140.5–141°.

The melting point of the picrate of tertiary VIII from the rearrangement of VII was not depressed by admixture with a sample of the picrate of the amine from this independent synthesis.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Allyl Ethers in the Thiophene Series

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The allyl ethers of three nitrothiophenes have been prepared by a modified Williamson procedure. The ethers darkened extensively on heating but did not give rise to allylthienols as products of rearrangement. Nitration of 5-chloro-2-thiophenesulfonyl chloride yielded not only the expected 4-nitro-5-chloro-2-thiophenesulfonyl chloride, but also 2-chloro-3,5-dinitrothiophene, pointing to substitution of chlorosulfonyl by nitro. 5-Nitro-2-thienyl sulfide is formed as a result of interaction of 2-chloro-5-nitrothiophene and sodium ethoxide or sodium allyl oxide.

Certain nitrothienyl alkyl ethers were prepared by Hurd and Kreuz,¹ the alkyl group being methyl and ethyl. They were prepared from nitrohalothiophenes and alcohols by use of alcoholic potassium hydroxide.

It was desired to extend this synthesis to include the allyl ethers so that the latter might be examined for their behavior on heating. If the conventional Claisen rearrangement occurred, as in the change of aryl allyl ethers into allylphenols, this would become a synthesis of allylthienols. Also, it would be a means of testing whether or not neighboring positions on the thiophene ring exhibit an "ortho" effect comparable to that shown in the phenyl ethers.

The procedure used for the preparation of methyl and ethyl ethers¹ using alcoholic potassium hydroxide needed to be modified when applied to allyl ether preparations. It was found that these ethers could be prepared by the addition of the theoretical amount of sodium in an excess of allyl alcohol to a solution of the nitrohalothiophene in benzene. The reaction took place at room temperature over one or two days; any attempt to speed the reaction by heating resulted in a rapid decomposition to a foul smelling black tar.

The three ethers prepared by this method were 5-allyloxy-4-nitro-2-acetothienone, 3-nitro-2-allyloxythiophene and 2-nitro-3-allyloxythiophene. They were all unstable compounds, becoming yellowish to bright yellow within 24 hours. The first of these compounds was the most stable and the second the

most unstable. In less than a week the latter had become an oily brown solid with a sharp odor. It was necessary to carry out the elementary analyses of these compounds within 24 hours.

It was found that these allyl ethers did not undergo a smooth thermal rearrangement into allylthienols. Actually no pure products were obtainable from the tarry residues of the pyrolytic procedure.

During the preparation of 3-nitro-2-chlorothiophene by the method of Hurd and Kreuz² it was necessary to nitrate 5-chloro-2-thiophenesulfonyl chloride. After treatment of the reaction mixture with boiling 1:1 sulfuric acid to hydrolyze off the chlorosulfonyl group it was found that some 2-chloro-3,5-dinitrothiophene had been formed. This would indicate that the nitro group had replaced the chlorosulfonyl group to a small extent during the nitration. Although replacement of one group by another is fairly common in thiophene reactions, replacement of chlorosulfonyl by nitro under these conditions never has been reported.

All attempts to convert 2-nitro-5-chlorothiophene to the corresponding allyl ether by the above method were unsuccessful. In most trials the starting material was recovered. Heating caused a vigorous reaction to set in with evolution of hydrogen sulfide. From the black tar a yellow solid was extracted which proved to be 5-nitro-2-thienyl sulfide. The same compound was obtained from the reaction with sodium ethoxide, so its formation is independent of the base used.

(1) C. D. Hurd and K. L. Kreuz, *THIS JOURNAL*, **74**, 2965 (1952).

(2) C. D. Hurd and K. L. Kreuz, *ibid.*, **72**, 5543 (1950).

Experimental

Reagents.—2-Chlorothiophene was supplied by The Texas Company. 5-Chloro-4-nitro-2-acetothienone was prepared by the method of Hurd and Kreuz¹ from a sample of 5-chloro-2-acetothienone. The conversion was 86% of theory, m.p. 85–87° after two recrystallizations from ethanol. 3-Nitro-2-chlorothiophene was prepared by the method of Hurd and Kreuz.¹

5-Chloro-2-thiophenesulfonyl chloride was obtained in 72% yield from 2-chlorothiophene by the method of Steinkopf and Köhler.³ This compound (0.15 mole) was then nitrated with fuming nitric acid at 30–50° for 2 hours to give 78% of 4-nitro-5-chloro-2-thiophenesulfonyl chloride, m.p. 50–51° after two recrystallizations from hexane. The crude compound (m.p. 42–47°) was converted by hydrolysis with boiling 1:1 sulfuric acid and steam distillation to 3-nitro-2-chlorothiophene in 71% yield. The colorless needles melted at 48–50° after crystallization from pentane. In the forerun of the steam distillation 1.1 g. (3.5% yield) of 2-chloro-3,5-dinitrothiophene was found, m.p. 122.5–123° after recrystallization from ethanol. The sample showed no depression of melting point when mixed with an authentic sample of the compound.

2-Nitro-3-bromothiophene was prepared by the nitration of 3-bromothiophene obtained from the high temperature bromination of thiophene.⁴ After two recrystallizations from hexane the m.p. was 79–81°.

5-Allyloxy-4-nitro-2-acetothienone.—In each of three 50-ml. conical flasks 1.0 g. of 5-chloro-4-nitro-2-acetothienone was dissolved in 20 ml. of benzene. To each solution was added 0.15 g. of sodium in 10 ml. of allyl alcohol. Sample (a) was stored at –10° for 30 hr., (b) at room temperature for 24 hr. and (c) was refluxed for 30 minutes. The processing was the same for each. The sample was made slightly acid with dilute ethanolic hydrogen chloride, the sodium chloride removed by filtration and washed with pentane, then all the solvent was removed in a stream of dry air. The brown oily solid was extracted repeatedly with hot hexane and the solid was given a preliminary treatment with Norit in hot alcohol to decolorize it, then was crystallized from cyclohexane; m.p. 89–91°. The yield was 0.4 g. from (a), 0.6 g. from (b) but only 0.02–0.03 g. from (c). After several more recrystallizations from cyclohexane the m.p. was 92–93°. The compound slowly turned from a light cream color to a pale yellow when allowed to stand in a closed vial for several days. Recrystallization from alcohols caused partial decomposition.

Anal. Calcd. for $C_8H_9NO_4S$: C, 47.57; H, 3.99; N, 6.17. Found: C, 47.37; H, 3.98; N, 6.09.

3-Nitro-2-allyloxythiophene.—One-half gram of 3-nitro-2-chlorothiophene was dissolved in 15 ml. of benzene, and 0.1 g. of sodium in 5 ml. of allyl alcohol was added. The reaction mixture was left for 40 hours at room temperature, then was processed in the manner of the preceding compound. After several recrystallizations from cyclohexane the pale yellow rhombs (0.2 g.) melted at 55–56°. The

product turned a bright orange color within a day. It had to be analyzed immediately.

Anal. Calcd. for $C_7H_7NO_3S$: C, 45.40; H, 3.82; N, 7.56. Found: C, 44.82; H, 3.64; N, 7.46.

2-Nitro-3-allyloxythiophene.—One gram of 2-nitro-3-bromothiophene was converted to the ether in the same manner as the previous preparations. The product, 0.7 g. of black shiny solid, was recrystallized with decolorization from cyclohexane several times. The bright yellow rhombs melted at 66.5–67°. The compound turned a bright orange in a few days.

Anal. Calcd. for $C_7H_7NO_3S$: C, 45.40; H, 3.82; N, 7.56. Found: C, 46.05; H, 3.99; N, 7.34.

Heating of the Ethers.—Half-gram samples of 2-nitro-3-allyloxythiophene (A) and 3-nitro-2-allyloxythiophene (B) were heated in a nitrogen atmosphere in solution with 2 ml. of dimethylaniline and 2 ml. of acetic anhydride, a method devised by Fieser and Lothrop⁵ for rearrangement of ethers which produced sensitive allylphenols. Intense darkening occurred on heating, but the only substances isolable were the starting ethers in some experiments. One-third of A was recoverable after heating for an hour at 120°, and one-sixth after an hour at 160°. One-third of B was recoverable after 2 hours at 100°, but none after one hour at 180° or 1.5 hours at 150–160°.

Behavior of 2-Chloro-5-nitrothiophene toward Sodium Allyl Oxide and Sodium Ethoxide.—Addition of 10 g. of 2-chloro-5-nitrothiophene to a solution of 1.5 g. of sodium in 25 ml. of allyl alcohol caused a vigorous reaction and immediate darkening. After three hours of heating on the steam-bath the mixture was acidified. The black oil that separated was taken up in chloroform, and evaporation left a tar from which 0.7 g. of yellow rhombs was obtained by extraction with hot hexane and crystallization from aqueous alcohol; m.p. 107–107.5°.

The same solid was obtained if cooling was maintained at the outset to prevent the initial vigorous reaction, or if ethanol was used instead of allyl alcohol. It dissolved in concd. sulfuric acid forming a bright red solution, and was recovered unchanged by dilution with water. It gave no indophenin test, and did not react with 2,4-dinitrophenylhydrazine or with bromine in carbon tetrachloride (*Anal.* C, 33.6; H, 1.36; N, 10.0; S, 33.9), was satisfactory for $C_8H_8N_2O_4S_2$, and the compound was identical to the 5-nitro-2-thienyl sulfide, m.p. 104–106°, of Dann and Möller.⁶ Professor Otto Dann of Erlangen, Germany, kindly sent a sample of his material for comparison, and the m.p. of a mixture of the two was not depressed. Also, our material, on oxidation, yielded the sulfone of m.p. 157–159° which agrees with his value of 158–159°.

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(3) W. Steinkopf and W. Köhler, *Ann.*, **532**, 250 (1937).

(4) C. D. Hurd and H. J. Anderson, *THIS JOURNAL*, **75**, 3517 (1953).

(5) L. Fieser and W. C. Lothrop, *ibid.*, **58**, 749 (1936).

(6) O. Dann and E. F. Möller, *Chem. Ber.*, **80**, 23 (1947).