Phenyl Vinyl Sulfide.—A solution of 40 g. (0.26 mole) of ethyl phenyl sulfoxide in 40 ml. of methylene chloride was added to a heated solution of 34 g. (0.28 mole) of thionyl chloride in 40 ml. of methylene chloride during 2.5 hours. The solvent was distilled off, first at atmospheric pressure and finally with the aid of an aspirator. Distillation of the residue gave 11 g. (31%) yield of phenyl vinyl sulfide, b.p. 72–75° (6 mm.).

In a comparable experiment using 0.15 mole of ethyl phenyl sulfoxide, the residue was heated with 75 ml. of pyridine at the reflux point for 30 minutes, diluted with 300 ml. of water and steam distilled. Extraction of the distillate with ether, drying the ether extract over potassium carbonate and distillation gave 13.3 g. (65%) of phenyl vinyl sulfide, b.p. 77–78° (12 mm.). Oxidation of a sample with hydrogen peroxide in acetic acid gave a 60% yield of phenyl vinyl sulfone, m.p. and mixed m.p. with an authentic sample, 66–67°. Phenyl vinyl sulfide became colored yellow within 24 hours and after one week turned to a black sirup.

The Reaction of Methyl Sulfoxide with Methyl Benzyl Sulfide and Thionyl Chloride.—A solution of 15.6 g. (0.20 mole) of methyl sulfoxide and 27.6 g. (0.20 mole) of benzyl methyl sulfide in 50 ml. of methylene chloride was added to a heated solution of 26.4 g. (0.22 mole) of thionyl chloride in 40 ml. of methylene chloride during 90 minutes. The mixture was distilled, first at atmospheric pressure to yield 8.0 g. (41%) of chloromethyl methyl sulfide, b.p. 104–106°, and then under vacuum giving 12 g. (35%) of α-chlorobenzyl methyl sulfide, b.p. 125–130° (15 mm.).

Methyl benzyl sulfide when treated alone with thionyl chloride in the above manner gave no sharp boiling product.

The Reaction of Phenyl Sulfoxide with Methyl Phenyl Sulfide and Thionyl Chloride.—When the reaction was carried out essentially in the manner used for methyl sulfoxide and methyl benzyl sulfide, 58% of chloromethyl phenyl sulfide, b.p. 78–80° (2 mm.) and 65% of phenyl sulfide, b.p. 115–116° (2 mm.) were obtained. The chloromethyl phenyl sulfide was identified by oxidation to the sulfone, m.p. 52–53°, using 40% peracetic acid.[7] The phenyl sulfide was characterized by way of the sulfilimine, m.p. 109–110°. Tarbell and Weaver[25b] report m.p. 108–110°.

The Reaction of Benzyl Sulfide and Thiacyclopentane 1-Oxide.—No reaction was observable between benzyl sulfide and thiacyclopentane 1-oxide after 16 hours reflux in alcohol solution in the presence or absence of potassium hydroxide. Benzyl sulfide was also recovered after refluxing in benzene solution with methyl sulfoxide (6 hours) or thiacyclopentane 1-oxide (16 hours). However, during 16 hours reflux of 2.14 g. (0.01 mole) of benzyl sulfide and 4.16 g. (0.04 mole) of thiacyclopentane 1-oxide in 25 ml. of acetic acid containing 5 drops of sulfuric acid a black tarry mixture was formed. The mixture was diluted with water and extracted with 200 ml. of ether and the ether layer was washed three times with 100 ml. of water and then diluted with alcohol. After removal of the ether (steam-bath) and treatment with charcoal, concentration of the solution under reduced pressure gave 0.40 g. (17%) of benzyl sulfoxide, m.p. 131–133°. The m.p. after crystallization from benzene–hexane was 133–134° and was not depressed by an authentic sample.

The Reaction of Sulfoxides with Acid Halides.—A solution of 5.6 g. (0.04 mole) of methyl phenyl sulfoxide in 20 ml. of benzene was added to a refluxing solution of 7.5 g. (0.04 mole) of *p*-nitrobenzoyl chloride in 75 ml. of benzene during 15 minutes and the reaction was further heated at reflux for 30 minutes. During the reaction some hydrogen chloride was evolved. Filtration and further concentration yielded in all 6.6 g. (98%) of *p*-nitrobenzoic acid. The concentrate was added to a solution of 11 g. (0.1 mole) of thiophenol in 100 ml. of ethanol containing 7 g. of potassium hydroxide, and this mixture was heated at reflux for one hour. The major portion of the solvent was then distilled off and the residue was poured into water and extracted with ether. The ether layer was washed with 10% potassium hydroxide and dried over anhydrous potassium carbonate. The dried extract was concentrated on a steam-bath to 30 ml. and a 2.5-ml. aliquot was oxidized with 5 ml. of 30% hydrogen peroxide. Dilution with water gave 1.9 g. (64%) of bis-(phenylsulfonyl)-methane, m.p. 117–119°. Recrystallization from alcohol gave material, m.p. 119–120°, which gave no m.p. depression when mixed with an authentic sample. From the remainder of the ether solution bis-(phenylmercapto)-methane was obtained; recrystallization from ether–pentane gave material, m.p. 34–35°, as compared to a literature value of 35–36°.[28]

In similar experiments with methyl benzyl sulfoxide and thiacyclopentane 1-oxide 94% and 48% yields of *p*-nitrobenzoic acid were obtained. Resinous material was formed in the latter case.

A solution of 11.7 g. (0.15 mole) of methyl sulfoxide in 30 ml. of methylene chloride was added during 30 minutes to a refluxing solution of 45 g. (0.32 mole) of benzoyl chloride in 50 ml. of methylene chloride. The mixture was heated an additional hour and then distilled to yield chloromethyl methyl sulfide, b.p. 103–108°; redistillation gave 7 g. (45%) of material, b.p. 104–106°.

[28] R. L. Shriner, W. J. Struck and H. C. Jorison, THIS JOURNAL, **52**, 2060 (1930).

EVANSTON, ILLINOIS

[CONTRIBUTION FROM EATON LABORATORIES, DIVISION OF THE NORWICH PHARMACAL COMPANY]

4-Nitro-2-thenaldehyde. II

BY GABRIEL GEVER

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Previously reported 4-nitro-2-thenaldehyde and its diacetate have been shown to have consisted of mixtures of the 4- and 5-nitro isomers. Pure 4-nitro-2-thenaldehyde and its diacetate have been prepared and characterized.

In a previous publication[1] it was reported that the nitration of 2-thenaldehyde diacetate with acetic anhydride–nitric acid gave a small amount of 4-nitro-2-thenaldehyde diacetate in addition to the main product, 5-nitro-2-thenaldehyde diacetate. The 4-nitro-2-thenaldehyde diacetate was converted to 4-nitro-2-thenaldehyde. Subsequently, Foye[2] nitrated 2-thenaldehyde with a mixture of sulfuric acid and fuming nitric acid to obtain a 64.5% yield of 4-nitro-2-thenaldehyde, no 5-nitro-2-thenaldehyde being obtained.

In view of the known propensity of thiophenes to substitute in the 5-position,[3] reinvestigation of 4-nitro-2-thenaldehyde and its diacetate was instituted. Rinkes[4] had shown that one of the products of the nitration of methyl 2-thienyl ketone, previously reported as pure methyl 5-nitro-2-thienyl ketone was, in reality, a mixture of methyl 4-nitro-2-thienyl ketone and methyl 5-nitro-2-thienyl ketone. It has now been found that the 4-nitro-2-thenaldehyde reported earlier[1,2] is actu-

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[1] G. Gever, THIS JOURNAL, **75**, 4585 (1953).

[2] W. Foye, J. Hefferren and E. Feldmann, *ibid.*, **76**, 1378 (1954).

[3] H. Hartough, "Thiophene and Its Derivatives," Interscience Publishers, Inc., New York, N. Y., pp. 147, 225.

[4] I. Rinkes, *Rec. trav. chim.*, [4] **52**, 538 (1933).

ally a eutectic mixture of 4-nitro-2-thenaldehyde and 5-nitro-2-thenaldehyde.

Repetition of the procedure of Foye[2] resulted in a 77% yield of a product which melted below 27°. Recrystallization from isopropyl alcohol gave two products m.p. 55–56° (I) and m.p. 36–37° (II). II was identical with the previously reported 4-nitro-2-thenaldehyde.[1] I analyzed correctly for a mono-nitrothenaldehyde. When ultraviolet absorption curves for I, II and 5-nitro-2-thenaldehyde were compared, it was found that a composite curve constructed from the curves of 5-nitro-2-thenaldehyde and I was congruent with the curve for II.

When the mixture of nitrothenaldehydes obtained above was heated with acetic anhydride in the presence of sulfuric acid, two nitrothenaldehyde diacetates were obtained, m.p. 79–80° (III) and 55–56° (IV). IV was identical with the previously reported[1] 4-nitro-2-thenaldehyde diacetate. Again a composite ultraviolet absorption curve of 5-nitro-2-thenaldehyde diacetate and III was identical to that of IV.

A melting point curve of varying mixtures of 4- and 5-nitro-2-thenaldehyde diacetates showed that a eutectic mixture melting at 55–56° and containing 50% of each component is formed. A mixed melting point of this 50-50 mixture with IV was not depressed. It may be presumed that similar phenomena occur with the other derivatives.

Separation of the two isomers of II or IV from a variety of solvents proved unsuccessful. Therefore, IV was oxidized with an acid sodium dichromate solution to give a mixture of nitrothiophenecarboxylic acids. Again, separation of the acids was not feasible. The mixture of acids was esterified with methanol and fractional crystallization of the esters from benzene and methanol was attempted.[4] Only pure methyl 4-nitro-2-thiophenecarboxylate, m.p. 99–100°, was isolated. The remainder of the mixture could not be separated, a product melting at 65–67° being obtained. An artificial 50-50 mixture of methyl 4- and 5-nitro-2-thiophenecarboxylates melted in the same range.

Oxidation of III gave only one product, m.p. 154° corresponding to the melting point reported by Rinkes[5] for 4-nitro-2-thiophenecarboxylic acid. Esterification with methanol gave only one ester, m.p. 99–100° (99°[5]).

It is now clear that I is 4-nitro-2-thenaldehyde and III is 4-nitro-2-thenaldehyde diacetate. It also appears that the separation of the 4- and 5-nitrothiophene derivatives is complicated by the formation of eutectic mixtures in almost every case.[4,5]

Experimental[6]

Nitration of 2-Thenaldehyde.—The procedure of Foye[2] gave 9.4 g., 77% of product, b.p. 126–130° at 2.5 mm., m.p. below 27°. Repeated recrystallization from isopropyl alcohol gave 1.5 g. of material, m.p. 55–56° (I), 0.4 g. of m.p. 36–37° (II), and 6.3 g. of low melting material.

Analytical data for I agreed with that calculated for a mono-nitrothenaldehyde.

Anal. Calcd. for $C_5H_3NO_3S$: C, 38.2; H, 1.92; S, 20.4. Found: C, 38.3; H, 2.18; S, 20.0.

Nitrothenaldehyde Diacetates.—The undistilled product of the nitration as above of 29.2 g. of 2-thenaldehyde was heated at 100° with 120 g. of acetic anhydride and three drops of sulfuric acid for 45 minutes. The solution was cooled, poured into 1000 cc. of cold water and the resulting emulsion stirred for 30 minutes. The solid which had formed was filtered and washed with a little cold water to yield 53 g., 78%, m.p. 25–50°. Repeated recrystallizations from methanol gave 16.8 g. of product, m.p. 79–80° (III). Concentration of the filtrates gave 6.3 g. of solid, m.p. 55–58° (IV). Repeated concentration and recrystallizations of the residues gave 21.2 g. more of IV.

TABLE I

ULTRAVIOLET SPECTRAL CHARACTERISTICS[a] OF 4- AND 5-NITRO-2-THENALDEHYDES AND THEIR DIACETATES

Compound	λ_{max} (mμ)	ϵ_{max}
4-Nitro-2-thenaldehyde (I)	251	22,100
5-Nitro-2-thenaldehyde	236	4,300
	315	11,200
Mixture of 4- and 5-nitro-2-thenaldehydes	251	11,800
(1:1) or II	302	7,600
4-Nitro-2-thenaldehyde diacetate (III)	275	7,500
5-Nitro-2-thenaldehyde diacetate	319	8,300
Mixture of 4- and 5-nitro-2-thenaldehyde diacetates (1:1) or IV	292	6,300

[a] Measurements were made in aqueous solutions with a Beckman DR recording quartz spectrophotometer.

Analytical data for III agreed with that calculated for a mono-nitrothenaldehyde diacetate.

Anal. Calcd. for $C_9H_9NO_6S$: C, 41.7; H, 3.50; S, 12.4. Found: C, 41.9; H, 3.60; S, 12.4, 12.6.

Methyl Nitrothiophene-2-carboxylates.—A suspension of 18.2 g. of IV in 105 g. of 33% sulfuric acid was refluxed under nitrogen for 40 minutes. The mixture was cooled to 30° and a solution of 17.5 g. of sodium dichromate in 9 cc. of water was added over a period of 10 minutes, the temperature being kept at 30–40°. The mixture was stirred at 30–35° for one hour and at 0–5° for 45 minutes. The solid was filtered and washed with cold water to yield 10.1 g., 83% of mixed 4- and 5-nitro-2-thiophenecarboxylic acids, m.p. 120–130°. Solution of the mixed acids in sodium bicarbonate solution followed by precipitation with hydrochloric acid did not raise the melting point.

Six grams of the mixed acids was esterified with methanol by Rinkes' procedure[5] to give 3.6 g. of low melting material. Separation of the esters by mechanical separation of the crystals obtained by slow evaporation of a benzene solution[4] was not successful. After laborious recrystallization from benzene and methanol, 0.1 g. of methyl 5-nitro-2-thiophenecarboxylate, m.p. 99–100°, was isolated. From the filtrates were obtained 2.5 g. of mixed esters, m.p. 65–67°.

Using 5 g. of III and the above procedure, there was obtained 2.1 g. of 4-nitro-2-thiophenecarboxylic acid, m.p. 150–154°. The latter gave a 75% yield of methyl 4-nitro-2-thiophenecarboxylate on esterification, m.p. 85–92°. Two recrystallizations from methanol gave an analytically pure sample, m.p. 99–100°.

Anal. Calcd. for $C_6H_5NO_4S$: C, 38.5; H, 2.70; S, 17.1. Found: C, 38.9; H, 2.84; S, 17.1.

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[5] I. Rinkes, *Rec. trav. chim.*, [4] **51**, 1134 (1932).

[6] All melting points were taken on a Fisher–Johns apparatus and are corrected. I am indebted to Mr. Gordon Ginther and Mr. Curtis Eaton of these laboratories for the analytical and ultraviolet absorption data, respectively.