In addition to bovine gamma globulin, we have reacted dinitrobenzene sulfonate with egg albumin, beef serum, sheep serum, gelatin and tuberculin with results similar to those given above.

The support of this work by grants from the Standard Oil Company (N. J.), New York City, and the United States Public Health Service is gratefully acknowledged.

INSTITUTE OF INDUSTRIAL MEDICINE
NEW YORK UNIVERSITY POST-
GRADUATE MEDICAL SCHOOL
NEW YORK, N. Y.

4-Nitro-2-thenaldehyde

BY GABRIEL GEVER

RECEIVED MARCH 31, 1953

The nitration of 2-thenaldehyde diacetate has been reported to give 5-nitro-2-thenaldehyde diacetate.[1,2] Since Rinkes[3] found that nitration of methyl 2-thienyl ketone gave a mixture of methyl 5-nitro-2-thienyl ketone and methyl 4-nitro-2-thienyl ketone, it was thought that the nitration of 2-thenaldehyde diacetate should produce 4-nitro-2-thenaldehyde diacetate as well as the 5-nitro derivative. It was found that this was indeed the case. Concentration of the alcoholic filtrates from the recrystallization of the 5-nitro-2-thenaldehyde diacetate, m.p. 72–73°, yielded another nitrothenaldehyde diacetate, m.p. 54–55°. Acid hydrolysis of the latter gave the nitroaldehyde, m.p. 36–37°. Oxidation of the nitroaldehyde to the nitroacid, followed by esterification with methanol, gave a methyl ester, m.p. 99°, corresponding to the melting point of methyl 4-nitro-2-thiophenecarboxylate reported by Rinkes.[4]

Experimental

Since the conditions for the nitration of 2-thenaldehyde diacetate differ in some respects from the procedure used by Patrick and Emerson,[1] these differences are reported here.

To 143 g. of acetic anhydride at −5° was added, over a period of 17 minutes, 43.7 g. of fuming nitric acid (sp. gr. 1.5), the temperature being kept at −5 to 0°. A solution of 55 g. of 2-thenaldehyde diacetate in 102 g. of acetic anhydride was then added slowly, keeping the temperature a −5 to −10°. After addition was complete, the solution was stirred at 0° for three hours and then poured onto 1.0 kg. of ice. The mixture was allowed to stand for one hour and was then filtered. The precipitate was washed with a little cold water followed by cold alcohol and then dried, yielding 58.5 g., 88%, of the isomeric 5-nitro-2-thenaldehyde diacetates, m.p. 55–65°.[5] Three recrystallizations from alcohol gave a 64% yield of 5-nitro-2-thenaldehyde diacetate,[6] m.p. 68–69°.

4-Nitro-2-thenaldehyde Diacetate.—The combined alcoholic filtrates from the first two recrystallizations of the 5-nitro-2-thenaldehyde diacetate were evaporated to dryness. The residue was recrystallized from 18 cc. of alcohol, giving 5.2 g. of solid, m.p. about 50°. The 5.2 g. were recrystallized again from 7 cc. of alcohol, giving 4.0 g. of solid, m.p. 50–55°. A third recrystallization from 10 cc. of alcohol, gave 3.7 g., m.p. 54–55°. Crystallization of a sample from petroleum ether did not further raise the melting point. The ultraviolet absorption maximum in water occurred at 2925 Å., E_M 6,300.

Anal.[7] Calcd. for $C_9H_9NO_6S$: C, 41.70; H, 3.50; N, 5.40; S, 12.37. Found: C, 41.81; H, 3.37; N, 4.97; S, 12.31.

4-Nitro-2-thenaldehyde.—To a solution of 12.5 g. of sulfuric acid in 25 cc. of water was added 6.7 g. of 4-nitro-2-thenaldehyde diacetate. The mixture was refluxed in an atmosphere of nitrogen for 20 minutes, cooled and the resulting precipitate removed by filtration and then washed with cold water. It was recrystallized from a mixture of ether–petroleum ether to give 2.0 g., 50% of 4-nitro-2-thenaldehyde, m.p. 34–37°. Further recrystallization from petroleum ether raised the melting point to 36–37°. The ultraviolet absorption maximum in water occurred at 3025 Å., E_M 7,600.

Anal. Calcd. for $C_5H_3NO_3S$: C, 38.21; H, 1.92; N, 8.92; S, 20.40. Found: C, 37.74; H, 1.94; N, 8.95; S, 20.50.

The semicarbazone melted at 234–235°. A mixed melting point with the 5-nitro-2-thenaldehyde semicarbazone was depressed to 225–230°.

Anal. Calcd. for $C_6H_6N_4O_3S$: C, 33.64; H, 2.82; S, 14.97. Found: C, 33.87; H, 3.07; S, 14.69.

A similar hydrolytic procedure when applied to 5-nitro-2-thenaldehyde diacetate gave a 95% yield of 5-nitro-2-thenaldehyde,[8] m.p. 70–72°.

Methyl 4-Nitro-2-thiophenecarboxylate.—To a suspension of 0.5 g. of 4-nitro-2-thenaldehyde in 3 cc. of 35% sulfuric acid was added dropwise a solution of 0.8 g. of sodium dichromate in 0.5 cc. of water, keeping the temperature below 40°. The mixture was stirred for 3 hours at room temperature and then kept at 0° for 15 hours. The precipitate was removed by filtration, washed with a little cold water, and then dried. It was dissolved in 5 cc. of methanol, 0.1 g. of sulfuric acid added and the solution refluxed for 3 hours. At the end of this time the solution was poured into 15 cc. of ice-water and sufficient sodium bicarbonate solution added to neutralize any excess acid. The solid which formed was removed by filtration and recrystallized twice from petroleum ether. The melting point was 98–99° (99°[4]).

Anal. Calcd. for $C_6H_5NO_4S$: S, 17.13. Found: S, 17.44.

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[1] T. Patrick and W. Emerson, THIS JOURNAL, **74**, 1356 (1952).

[2] V. M. Zubarovskii, *Doklady Akad. Nauk S.S.S.R.*, **83**, 85 (1952); *C. A.*, **47**, 2166^{a} (1953).

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

[4] I. Rinkes, *ibid.*, [4] **51**, 1134 (1932).

[5] All melting points were taken on a Fisher-Johns apparatus and are corrected.

[6] The ultraviolet absorption maximum, in water, of an analytically pure sample occurred at 3190 Å., E_M 8,300.

[7] All the analyses were carried out by Mr. Joseph Corrado of these laboratories.

[8] The ultraviolet absorption maximum, in water, of an analytically pure sample occurred at 3150 Å., E_M 11,200.

CHEMISTRY DIVISION
EATON LABORATORIES, INC.
NORWICH, NEW YORK

The Resolution of *p*-Ethylphenylmethylcarbinol. Infrared Spectra of Enantiomorphs and Racemates

BY ERNEST L. ELIEL AND JAMES T. KOFRON

RECEIVED APRIL 17, 1953

In connection with another problem we had occasion to resolve *p*-ethylphenylmethylcarbinol. The resolution was carried out by crystallization of the brucine and cinchonidine salts of the acid phthalate of the alcohol[1] and is described in detail in the experimental part. Melting point data of the active and racemic phthalates indicate that the racemic phthalate is a *dl*-compound.

Routine examination of the infrared spectra of the enantiomorphs and racemic phthalates revealed that while the (+)-, (−)- and racemic phthalates had identical spectra in chloroform solution—as was to be expected[2a] the mull spectrum of the racemate (see Fig. 1) showed significant differences

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[1] A. W. Ingersoll in R. Adams, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 376.