

When the temperature reached 175°, heating was stopped, and the condenser set for refluxing. A single addition of 14.0 g. (0.1 mole) of 3-thienylacetone was made and the temperature was maintained at 160–170° for seven hours. The reaction mixture was cooled, and upon adding 60 ml. of water, the formyl derivative of the amine separated as an oil. The mother liquor was extracted with benzene, the benzene evaporated, and the two portions of the formyl derivative were mixed. This formyl derivative was refluxed with 100 ml. of 3 *N* sodium hydroxide for 20 hours, and the amine extracted with benzene. The benzene solution was extracted with dilute hydrochloric acid, the acid solution was made alkaline with concd. ammonia, and the amine was again extracted with benzene. The solvent was removed under reduced pressure and the product was vacuum distilled, b.p. 64–71° (3 mm.), to yield 1.6 g. (11%).

**B. Reduction of 1-(3-Thienyl)-2-nitropropene.**—1-(3-Thienyl)-2-nitropropene (33.8 g., 0.2 mole) was reduced in ether solution with 22.8 g. (0.6 mole) of lithium aluminum hydride. After isolation of the amine, it was vacuum distilled, b.p. 79° (12 mm.) to 85° (5 mm.), to yield 23.9 g. (85%). Fractionation through a short column gave a product, b.p. 70–74° (7 mm.),  $n_D^{20}$  1.5349,  $d_4^{20}$  1.037.

*Anal.* Calcd. for  $C_7H_7NS$ : S, 22.70. Found: S, 23.03.

The hydrochloride was recrystallized from absolute ethanol, m.p. 135–136°.

*Anal.* Calcd. for  $C_7H_7ClNS$ : N, 7.88. Found: N, 7.91.

The benzamide was recrystallized from ethanol, m.p. 118–118.5°.

*Anal.* Calcd. for  $C_{14}H_{15}NOS$ : C, 68.53; H, 6.16; S, 13.07. Found: C, 68.54; H, 5.88; S, 13.07.

The phenylthiourea derivative was recrystallized from ethanol, m.p. 110.5–111°.

*Anal.* Calcd. for  $C_{14}H_{15}N_2S_2$ : N, 10.14. Found: N, 10.07.

**N-Methyl-1-(3-thienyl)-2-propylamine (Id).**—From 25.5 g. (0.5 mole) of 90% formic acid, 54 ml. (0.5 mole) of 9.34 *M* methylamine solution and 14.0 g. (0.1 mole) of 3-thienylacetone, 7.5 g. (48%) of an amine fraction, b.p. 89–92° (9 mm.), was obtained *via* the Leuckart procedure previously described. Redistillation gave a product, b.p. 67–69° (3 mm.),  $n_D^{20}$  1.5233,  $d_4^{20}$  1.009.

*Anal.* Calcd. for  $C_8H_{13}NS$ : S, 20.65. Found: S, 20.35.

The hydrochloride was recrystallized from a mixture of absolute alcohol and dry ether, m.p. 97–98°.

*Anal.* Calcd. for  $C_8H_{14}ClNS$ : C, 50.11; H, 7.36; S, 16.72. Found: C, 50.65; H, 7.55; S, 16.28.

The phenylthiourea derivative was recrystallized from ethyl alcohol, m.p. 122–122.5°.

*Anal.* Calcd. for  $C_{15}H_{15}N_2S_2$ : N, 9.65; S, 22.08. Found: N, 9.36; S, 22.39.

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### Triphenylmethyl Nitrate<sup>1</sup>

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One of the possible modes of organic nitrate ester decomposition or reduction involves oxygen-nitrogen fission leading to the formation of alkoxy free radicals. We have been interested in the reductive denitration of nitrate esters with alkaline hydrosulfides,<sup>2</sup> and wished to conduct experiments to determine the possibility of free-radical intermediates. Although mixtures of *n*-butyl nitrate and sodium hydrosulfide with the radical detectors acrylonitrile and methyl methacrylate failed to

give any polymer, *n*-butyl nitrate appeared to inhibit the benzoyl peroxide-catalyzed polymerization of acrylonitrile. It was of interest to obtain triphenylmethyl nitrate for use in similar experiments, since the triphenylmethoxy free radical, if formed, should reveal itself by  $\beta$ -cleavage to benzophenone or by the Wieland rearrangement.<sup>3</sup>

Attempts to make triphenylmethyl nitrate from the chloride and silver nitrate in dimethylformamide as a solvent gave only triphenylcarbinol. A similar experiment in acetonitrile gave *N*-triphenylmethylacetamide by way of an intermediate, probably the nitrate of the imidol form of this amide. Even in benzene the reaction gave only the carbinol, by decomposition at higher temperatures or by hydrolysis on exposure of the solution to air at lower temperatures. The nitrate appeared to be inordinately sensitive to hydrolysis. When prepared in carbon tetrachloride, only the carbinol was isolated when the solvent was allowed to evaporate in air. Vacuum-line technique, using carbon tetrachloride as the solvent, gave a solid which melted with decomposition at 73° and re-solidified at a higher temperature.

Exposure of this solid to the laboratory air even for a few minutes converted it almost entirely to the carbinol. We therefore heated freshly prepared solutions of the nitrate in sealed ampoules and isolated the decomposition products without any further attempt to purify the nitrate itself. In carbon tetrachloride and in nitrobenzene the decomposition products were benzophenone, triphenylcarbinol, picric acid and oxides of nitrogen. These products are consistent with  $\beta$ -cleavage of some of the triphenylmethoxy radicals to phenyl radicals and benzophenone, nitration and oxidation of the cleaved phenyl radical by nitrogen dioxide and reduction of some of the triphenylmethoxy radicals by hydrogen atoms supplied in the nitration reaction. In addition some of the alcohol may have resulted from hydrolysis.

#### Experimental

**Formation and Decomposition of Triphenylmethyl Nitrate in Carbon Tetrachloride.**—To 5 g. of silver nitrate and 2.0 g. of triphenylmethyl chloride in an ampoule was added 50 ml. of carbon tetrachloride by distillation from phosphorus pentoxide. The mixture was frozen, degassed, sealed, shaken overnight, then heated to 110° for 15 minutes. The filtrate was concentrated and put onto an alumina column with ordinary chloroform. There was isolated a trace of benzophenone, 1.44 g. of triphenylcarbinol, m.p. and mixed m.p. 162–164°, and 0.4 g. of triphenylmethyl ethyl ether (evidently from alcohol in the chloroform), m.p. and mixed m.p.<sup>4</sup> 83–84°, and 40 mg. of picric acid. From a second experiment in which the heating period was three hours, there was obtained 250 mg. of benzophenone, m.p. and mixed m.p. 47–49° (oxime, m.p.<sup>5</sup> 141–142°), 1.38 g. of carbinol, and 140 mg. of picric acid, m.p. and mixed m.p. 119–121°. Similar results were obtained when the triphenylmethyl nitrate solution was decanted into an ampoule of calcium oxide before sealing. A mixture of carbon tetrachloride and styrene as solvent gave polymer, benzophenone, carbinol and nitrophenols.

**Nitrobenzene.**—A similar experiment in which the product of the reaction in nitrobenzene was decanted, sealed and decomposed at 110–125° gave oxides of nitrogen, benzophenone, carbinol and picric acid.

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