

was washed thoroughly with ether, the ether layer was separated from the filtrate, decolorized, and evaporated *in vacuo*. Crystallization of the residue from Skellysolve B gave 3.2 g. (67%) of 7-phenoxyquinoline, m. p. and mixed m. p. with the above-described authentic sample, 72.5–73.5°. The picrate and methiodide derivatives corresponded in m. p. and mixed m. p. with those described above.

4,7-Diphenoxyquinoline. From 7-Bromo-4-chloroquinoline.—To a solution of anhydrous potassium phenolate prepared from 3.1 g. of potassium hydroxide and 20 g. of phenol was added 5.0 g. of 7-bromo-4-chloroquinoline^{4,13} and 0.5 g. of copper bronze. The resulting mixture was stirred at 185° for one and one-half hours. Upon working up by the general method described above there was obtained 5.6 g. (86%) of product, white prisms from Skellysolve B, m. 81.5–82.0°.

Anal. Calcd. for C₂₁H₁₅NO₂: C, 80.49; H, 4.83; N, 4.47. Found: C, 80.49; H, 4.86; N, 4.49.

The picrate formed long, brilliant yellow needles from alcohol, m. p. 185–186°.

Anal. Calcd. for C₂₇H₁₈N₄O₉: N, 10.33. Found: N, 10.07.

The methiodide formed pale yellow prisms from alcohol, m. p. 262–264° (dec.).

Anal. Calcd. for C₂₂H₁₈INO₂: N, 3.08. Found: N, 3.02.

From 4-Chloro-7-phenoxyquinoline.—Treatment of 4-chloro-7-phenoxyquinoline with potassium phenolate and copper bronze by the above method afforded a 90% yield of 4,7-diphenoxyquinoline, m. p. and mixed m. p. with the above-described authentic sample, 81.5–82.0°. The picrate and methiodide derivatives corresponded in m. p. and mixed m. p. with those previously described.

4-(4-Diethylamino-1-methylbutylamino)-7-phenoxyquinoline.—This compound was prepared in the usual manner.^{2,4,5} The product was obtained in 65.5% yield, b. p. 230–235° at 0.1 mm., m. p. 102–102.5° (lit.² m. p. 102–104°).

The citrate formed rosetts of white prisms from alcohol-ether, m. p. 122.5–124.5° (gas evolution).

Anal. Calcd. for C₂₄H₃₁N₃O·C₆H₅O₇: N, 7.39. Found: N, 7.41.

(13) Although the original description of this compound did not give a rigorous proof of structure, subsequent work in these laboratories has confirmed the assigned structure. Oxidation of 7-bromo-4-hydroxyquinoline with alkaline sodium hypobromite solution by a method analogous to that of Vaughan (THIS JOURNAL, 68, 324 (1946)) gave a 62% yield of 4-bromoanthranilic acid. The m. p. and mixed m. p. with an authentic sample (Claus and Scheulen, *J. prakt. Chem.*, [2] 43, 206 (1891)) was 220–221° (dec.).

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o- and *p*-Nitroacetophenones by Liquid Phase Oxidation

BY WILLIAM S. EMERSON, JOSEF W. HEYD, VICTOR E. LUCAS, JAMES K. STEVENSON AND THOMAS A. WILLS

Ford-Moore and Rydon¹ have recently described two methods for the preparation of *o*- and *p*-nitroacetophenone. One method comprised the nitration and subsequent oxidation of methylphenylcarbinol and the other the treatment of *o*- and *p*-nitroethylbenzene with *t*-butyl nitrite and sodium *t*-butoxide followed by the hydrolysis of the resulting oximes.

(1) Ford-Moore and Rydon, *J. Chem. Soc.*, 679 (1946).

We have found liquid phase oxidation^{2,3} to be suitable for the preparation of these compounds. While the conversions are not as high as is usually the case (14% for the *ortho* and 20% for the *para* isomer), the yields are satisfactory (63 and 66%, respectively) and the procedure is comparatively simple.

Experimental

The *o*-nitroethylbenzene⁴ used boiled at 116° (22 mm.), *n*_D²⁵ 1.5338, and the *p*-nitroethylbenzene at 134–136° (23 mm.), *n*_D²⁵ 1.5431.

***o*-Nitroacetophenone.**—*o*-Nitroacetophenone was prepared by blowing air through an alundum disperser for twenty-eight hours, into 250 g. of *o*-nitroethylbenzene held at 135–145° and containing 4 g. of chromium oxide. This mixture was cooled, filtered, washed free of acid with aqueous sodium carbonate, and fractionated to separate the product. The pure *o*-nitroacetophenone boiled at 112.5–113.5° (2 mm.) [159° (16 mm.)],⁵ *n*_D²⁵ 1.5530, *d*₄²⁵ 1.238, yield 39 g. (63%, 14% conversion).

Anal. Calcd. for C₈H₇O₃N: C, 58.2; H, 4.24. Found: C, 58.6; H, 4.75.

After two crystallizations from alcohol the oxime melted at 113–115° (115°).⁶

***p*-Nitroacetophenone.**—*p*-Nitroacetophenone was prepared in the same manner as the *ortho* isomer. The product, a solid, was collected at 123–130° (2 mm.) and crystallized from acetone and then from hexane, m. p. 78.5–80.0° (80–81°),⁷ yield 29 g. (60%, 10% conversion). In a larger run of 900 g. the conversion rose to 20% with a 66% yield.

(2) Emerson, Heyd, Lucas, Chapin, Owens and Shortridge, THIS JOURNAL, 68, 674 (1946).

(3) Emerson, Heyd, Lucas, Cook, Owens and Shortridge, *ibid.*, 1665 (1946).

(4) Cline and Reid, *ibid.*, 49, 3150 (1927).

(5) Camps, *Ber.*, 32, 3232 (1899).

(6) German Patent 109,663; *Chem. Zentr.*, 71, II, 458 (1900).

(7) Drewsen, *Ann.*, 212, 160 (1882).

CENTRAL RESEARCH DEPARTMENT
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A New Synthesis of Polygalitol Tetraacetate (Tetraacetyl-1,5-anhydro-D-sorbitol)

BY HEWITT G. FLETCHER, JR.

Richtmyer, Carr and Hudson¹ found that the reductive desulfurization of either octaacetyl-β,β-diglucosyl disulfide or tetraacetyl-β-glucotiose with Raney nickel afforded the tetraacetate of 1,5-anhydro-D-sorbitol (polygalitol). Recent work by Wolfrom and Karabinos² as well as by other authors³ has further demonstrated the feasibility of reductive desulfurization as a preparative method. In the course of an investigation of sugar-alcohol anhydrides in this Laboratory it was found that ethyl tetraacetyl-D-glucopyranosyl

(1) N. K. Richtmyer, C. J. Carr and C. S. Hudson, THIS JOURNAL, 65, 1477 (1943); cf. J. Bougault, E. Cattelain and P. Chabrier, *Compt. rend.*, 208, 657 (1939), who introduced the use of Raney nickel for desulfurization.

(2) M. L. Wolfrom and J. V. Karabinos, THIS JOURNAL, 66, 909 (1944); *ibid.*, 68, 1455 (1946).

(3) O. Jeger, J. Norymberski, S. Szpilfogel and V. Prelog, *Helv. Chim. Acta*, 29, 684 (1946); V. Prelog, J. Norymberski and O. Jeger, *ibid.*, 360 (1946); R. Jeanloz, D. A. Prins and T. Reichstein, *ibid.*, 371 (1946).