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 $C_{21}H_{15}NO_2$: 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 $C_{27}H_{18}N_4O_9$: N, 10.33. Found: N, 10.07.

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

Anal. Calcd. for $C_{22}H_{18}INO_2$: 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 rosets of white prisms from alcohol-ether, m. p. 122.5–124.5° (gas evolution).

Anal. Calcd. for $C_{24}H_{31}N_3O\cdot C_6H_8O_7$: N, 7.39. Found: N, 7.41.

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[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 Rydon[1] 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.

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*-nitroethylbenzene[4] used boiled at 116° (22 mm.), n^{25}_{D} 1.5338, and the *p*-nitroethylbenzene at 134–136° (23 mm.), n^{25}_{D} 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^{25}_{D} 1.5530, d^{25}_{25} 1.238, yield 39 g. (63%, 14% conversion).

Anal. Calcd. for $C_8H_7O_3N$: 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.

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

[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).

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

BY HEWITT G. FLETCHER, JR.

Richtmyer, Carr and Hudson[1] found that the reductive desulfurization of either octaacetyl-β,β-diglucosyl disulfide or tetraacetyl-β-glucothiose with Raney nickel afforded the tetraacetate of 1,5-anhydro-D-sorbitol (polygalitol). Recent work by Wolfrom and Karabinos[2] as well as by other authors[3] 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

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[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).