

to stand at room temperature until the bulk of the product had crystallized, while two phase mixtures were shaken by machine at room temperature until formation of product was complete. After several days at room temperature, the solid product was filtered off, washed with water until neutral, and air-dried. The solid products were recrystallized to constant melting point. The solvent, melting point and analytical data for each acetal are given in Table I. No solid acetals were obtained from the reaction of tris-(hydroxymethyl)-nitromethane and the following aldehydes under our conditions: propionaldehyde, isobutyraldehyde,  $\alpha$ -ethyl-*n*-hexaldehyde, *n*-heptaldehyde and  $\alpha$ -ethyl- $\beta$ -*n*-propyl-acrolein.

**Benzoates and Tosylates of Cyclic Acetals of Tris-(hydroxymethyl)-nitromethane.**—One-tenth mole of each acetal was dissolved or suspended in 0.2 mole of purified pyridine and 0.1 mole of benzoyl chloride or *p*-toluenesulfonyl chloride was added all at once. If the temperature went above 50° the reaction mixture was cooled until the temperature had gone below this figure. After twenty-four hours at room temperature, the reaction mixtures were poured into water, and the solid products were removed by filtration and washed with additional water. The solvents used in recrystallization together with the melting points and analytical data are listed in Table I.

**2-Phenyl-5-nitro-5-( $\beta$ -cyanoethoxymethyl)-1,3-dioxane.**—One-tenth mole of the benzaldehyde acetal of tris-(hydroxymethyl)-nitromethane was dissolved in 65 cc. of dioxane containing 5.3 g. (0.1 mole) of acrylonitrile, and 0.4 g. of sodium hydroxide dissolved in a little water was added. After standing overnight, the solution was concentrated and the viscous residue was extracted with hot *n*-hexane. After recrystallization from *n*-hexane the substance melted at 77.7°. The analytical data are recorded in Table I.

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## Side Reaction in the Hydrogenation of 4-Nitro-2-chlorobenzoic Acid and Its Esters

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In attempts to prepare diethylaminoethyl 4-amino-2-chlorobenzoate,<sup>1</sup> the catalytic hydrogenation of the corresponding 4-nitro-acid, its ethyl and its  $\beta$ -diethylaminoethyl ester was studied. A number of side reactions were observed which made the method impractical from a preparative point of view.

In some cases, incomplete reduction resulted, leading to hydroxylamino- and azoxybenzene derivatives, in others the chlorine atom was lost—this occurred in hydroxylic solvents, not in ethyl acetate. Sometimes,  $\beta$ -diethylaminoethyl 4-nitro-2-chlorobenzoate suffered hydrogenolysis to give ethyl esters; in one case even a methyl ester was formed, before the nitro group was attacked. These hydrogenolytic reactions are somewhat unusual; they recall similar, very recent observations of Metayer.<sup>2</sup>

### Experimental

**4-Nitro-2-chlorobenzoic acid** is best prepared by the method of Cohen and McCandlish<sup>3</sup> with some modifications: a mixture of 2 g. of 4-nitro-2-chlorotoluene and 6

liters of 33.5% nitric acid (1.32) is heated (autoclave) at 120° for eight hours. While 1010 g. of the starting material remains unattacked, 1090 g. of the desired acid is obtained; m. p. 138–139°; conversion, 49.5%; yield, 93.6%. *Ethyl ester*, b. p. 188° (24 mm.); 145–147° (3 mm.); 122–123° (0.2 mm.).

**Diethylaminoethyl 4-Nitro-2-chlorobenzoate.**—A mixture of 23 g. of ethyl 4-nitro-2-chlorobenzoate and 26.4 g. of diethylaminoethanol was heated for six hours at 140–150° and the reaction product treated with water and ether and fractionated; b. p. 162–163° (0.18 mm.); 140° (0.02 mm.); yield, 16 g. (52%).

*Anal.* Calcd. for  $C_{18}H_{17}O_4N_2Cl$ : C, 52.0; H, 5.7; N, 9.3. Found: C, 51.8; H, 5.5; N, 9.0.

**Hydrochloride** from ethyl acetate, white needles, m. p. 144°.

*Anal.* Calcd. for  $C_{18}H_{18}O_4N_2Cl_2$ : C, 46.3; H, 5.3; N, 8.3; Cl, 21.1. Found: C, 46.6; H, 5.2; N, 8.2; Cl, 21.5.

Approximately the same yield (50%) was obtained when the reaction was carried out under reflux in dioxane as solvent (six hours, bath temperature 120°); *trans*-esterification in presence of toluene and aluminum isopropoxide as catalyst (150°, five hours, with continuous removal of the ethyl alcohol formed) gave a yield of 37.5%.<sup>4</sup>

**Diethylaminoethyl Acetate.**—Azeotropic esterification of 160 g. of ethylene chlorohydrin and 120 g. of acetic acid in 100 cc. of benzene took five hours, when 10 cc. of concentrated sulfuric acid was employed as catalyst. The resulting solution was washed with sodium carbonate and dried and the  $\beta$ -chloroethyl acetate purified by fractionation; b. p. 145–147° (760 mm.); 50° (18 mm.); yield, almost quantitative.<sup>5</sup> The ester obtained (200 g.) was refluxed with an excess of diethylamine (250 g.) for eight hours, and after addition of another 125 g. of diethylamine for the same period again. The filtered solution was fractionated; b. p. 147°; yield, 130 g.

**Hydrogenation of Diethylaminoethyl 4-Nitro-2-chlorobenzoate.**—Three representative experiments are reported: (a) A solution of 9 g. (0.03 mole) of the nitro-ester in 50 cc. of anhydrous ethyl alcohol absorbed, at room temperature and in presence of 1 g. of palladium-barium sulfate catalyst, 2010 cc. of hydrogen (0.09 mole) within five and one-half hours. The oily residue of the filtered solution crystallized partly; trituration with cold chloroform gave a white solid which was recrystallized from butyl acetate and melted at 135°. Analysis and reducing properties pointed to the formation of diethylaminoethyl 4-hydroxylamino-2-chlorobenzoate,  $HONH \cdot C_6H_3(Cl) \cdot COO \cdot CH_2CH_2N(C_2H_5)_2$ .

*Anal.* Calcd. for  $C_{18}H_{19}O_3N_2Cl$ : C, 54.5; H, 6.6; N, 9.8; Cl, 12.2. Found: C, 54.3, 54.7; H, 6.9, 7.1; N, 9.8; Cl, 12.4.

Evaporation of the chloroform solution left a strongly basic oil of anesthetic properties which boiled at 130–135° (0.05 mm.) and gave, with alcoholic hydrogen chloride, crystals of ethyl 4-aminobenzoate hydrochloride, m. p. 210°, which were identified by analysis and mixed m. p.

*Anal.* Calcd. for  $C_9H_{12}O_2NCl$ : C, 53.7; H, 6.0. Found: C, 53.8; H, 5.9.

(b) When a solution of 6 g. (0.02 mole) of the nitro-ester in 30 cc. of diethylaminoethyl acetate was hydrogenated at room temperature in presence of 0.5 g. of the palladium catalyst, a thick precipitate appeared after the absorption of 500 cc. of hydrogen (0.02 mole), and no further absorption took place. Extraction of the solid phase with butyl acetate gave 2 g. of the above hydroxylamino-compound, m. p. 135°, while the liquid phase contained 3 g. of an oil which crystallized partly on standing. Recrystallization from methanol gave ethyl 4-amino-2-chlorobenzoate of m. p. 110°.<sup>1</sup>

(4) For a similar method, see Alix, French Patent 841,343; C. A., 34, 4077 (1940).

(5) For the usual acetylation of ethylene chlorohydrin, see "Beilstein," Vol. II, p. 128; 2nd suppl. Vol. II, p. 136.

(1) Rubin, Marks, Wishinsky and Lanzilotti, THIS JOURNAL, 68, 623 (1946).

(2) Metayer, Bull. soc. chim., 1093 (1948).

(3) Cohen and McCandlish, J. Chem. Soc., 87, 1271 (1905).

In another experiment, the liquid phase gave, upon trituration with petroleum ether, a solid which crystallized from methyl alcohol and melted at 77–78°. Analysis and comparison with an authentic specimen prepared from 4-nitro-2-chlorobenzoic acid (3 g.) and methyl alcohol (20 cc.) in presence of concentrated sulfuric acid (6 drops) indicated that methyl 4-nitro-2-chlorobenzoate had formed.

*Anal.* Calcd. for  $C_8H_6O_4NCl$ : C, 44.7; H, 2.8; N, 6.5; Cl, 16.3. Found: C, 45.0; H, 2.8; N, 6.4; Cl, 16.1.

In addition, a small amount of an unidentified substance was formed which crystallized from butyl alcohol or isobutyl acetate in slightly yellowish leaflets of m. p. 152°.

(c) A solution of 15 g. of diethylaminoethyl 4-nitro-2-chlorobenzoate (0.05 mole) in 105 cc. of ethyl acetate absorbed in presence of palladium-barium sulfate catalyst, 3850 cc. of hydrogen (3.44 moles) at room temperature in three hours. The residue of the filtered solution crystallized upon standing. After trituration with methanol and recrystallization from methanol or petroleum ether, the substance melted at 92°. It is characterized by the formation of dimorphous crystals: yellow needles and orange-red prisms. Analysis proved the formula of diethyl 3,3'-dichloro-azoxybenzene-4,4'-dicarboxylate.

*Anal.* Calcd. for  $C_{18}H_{18}O_6N_2Cl_2$ : C, 52.6; H, 3.9; N, 6.8; Cl, 17.3; mol. wt., 411. Found: C, 52.6; H, 3.9; N, 7.2; Cl, 17.0; 17.1; mol. wt. (in camphor), 396.

3,3'-Dichloroazoxybenzene-4,4'-dicarboxylic acid was isolated in one experiment, in which 5 g. of 4-nitro-2-chlorobenzoic acid was hydrogenated in 30 cc. of isopropyl alcohol at room temperature and the reaction came to a standstill after the absorption of 1.9 moles of hydrogen. Recrystallization from butyl alcohol gave short needles, m. p. 320°.

*Anal.* Calcd. for  $C_{14}H_8O_6N_2Cl_2$ : C, 47.3; H, 2.3. Found: C, 47.5; H, 2.6.

The hydrogenation experiments with 4-nitro-2-chlorobenzoic acid and its ethyl ester were carried out at room temperature and atmospheric pressure, in approximately 10% solutions, using palladium-on-barium sulfate (5%) as catalyst. In ethyl acetate, the acid and the ethyl ester absorbed 3 moles of hydrogen in twenty-four and three hours, respectively, and gave 4-amino-2-chlorobenzoic acid (from toluene, m. p. 213°)<sup>6</sup> and ethyl 4-amino-2-chlorobenzoate (from methanol, m. p. 110°) in quantitative yield. In isopropyl alcohol as solvent, 4 moles of hydrogen were absorbed in sixteen and five hours, respectively, without any break in the rate of absorption. The products isolated were 4-aminobenzoic acid (m. p. 187°; yield, 90%) and the hydrochloride of ethyl 4-aminobenzoate (m. p. 211°, from ethyl acetate; yield, quantitative). Also an aqueous solution of sodium 4-nitro-2-chlorobenzoate absorbed 4 moles of hydrogen (in eight hours) and gave 4-aminobenzoic acid (in 90% yield).

(6) Tiemann, *Ber.*, **24**, 708 (1891).

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## Irreversible Decolorization of Pinacyanol Chloride in the Presence of Paraffin-Chain Salts<sup>1</sup>

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In using pinacyanol chloride as a means of determining the critical concentration of paraffin-chain salts,<sup>2</sup> we have observed that the color fades upon standing. Since we do not plan to pur-

(1) Taken from a thesis submitted by A. M. Timbers in partial fulfillment of the requirements for the M.S. degree, June, 1947.

(2) Corrin, Klevens and Harkins, *J. Chem. Phys.*, **14**, 487 (1946).

sue this investigation, we wish at this time to report some preliminary observations on the factors which affect the rate of disappearance of the color.

1. The disappearance of color is not due to the familiar effect of hydrogen ion, since it is not reversed by the addition of hydroxide ion.

2. The disappearance of color is due to an oxidation, since the rate is decreased by removing oxygen (either by passing nitrogen through the solution or by adding hydroquinone) and is increased by the addition of hydrogen peroxide. The oxidation of pinacyanol chloride to colorless products by nitric acid and by alkaline potassium ferricyanide has been reported previously.<sup>3</sup>

3. The reaction is photosensitive, the rate being markedly increased by exposure to intense illumination. For example, a solution containing  $10^{-5}$  M pinacyanol chloride, 0.27 M hydrogen peroxide, and 0.01 M sodium decanesulfonate showed no loss of color after several days in the dark, but was completely decolorized after ninety-five minutes in daylight or after eight minutes of exposure to a Cenco mercury arc.

4. The rate of decolorization is independent of the concentration of added sodium chloride but is markedly affected by the presence of paraffin-chain salts. The results of three sets of experiments using sodium decanesulfonate (critical concentration, 0.04 M) are shown in Fig. 1. Similar results were obtained with other concentrations of hydrogen peroxide and also with sodium octane-

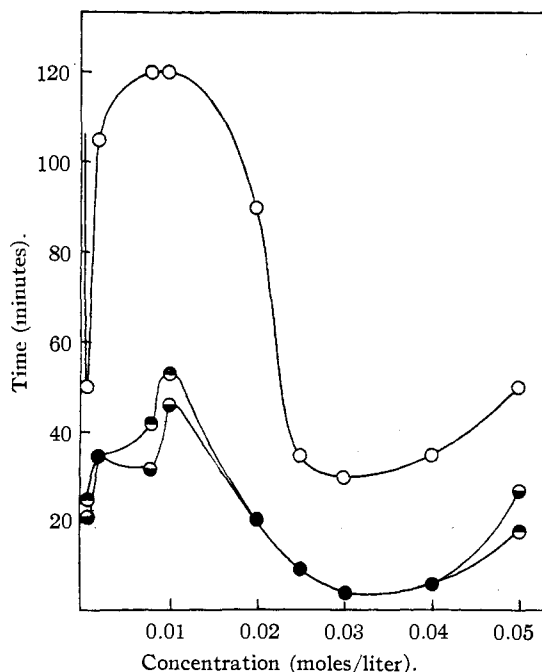


Fig. 1.—Time for complete decolorization of  $10^{-5}$  M pinacyanol chloride as a function of concentration of sodium 1-decanesulfonate: ○, 0.03 M  $H_2O_2$ ; ●, 0.35 M  $H_2O_2$ ; ◐, 0.53 M  $H_2O_2$ .

(3) Mills and Hamer, *J. Chem. Soc.*, **117**, 1550 (1920).