

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 $C_{18}H_{16}O_6N_2Cl_2$: 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°)⁶ 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 Salts¹

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In using pinacyanol chloride as a means of determining the critical concentration of paraffin-chain salts,² 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, Kleven 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.³

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-

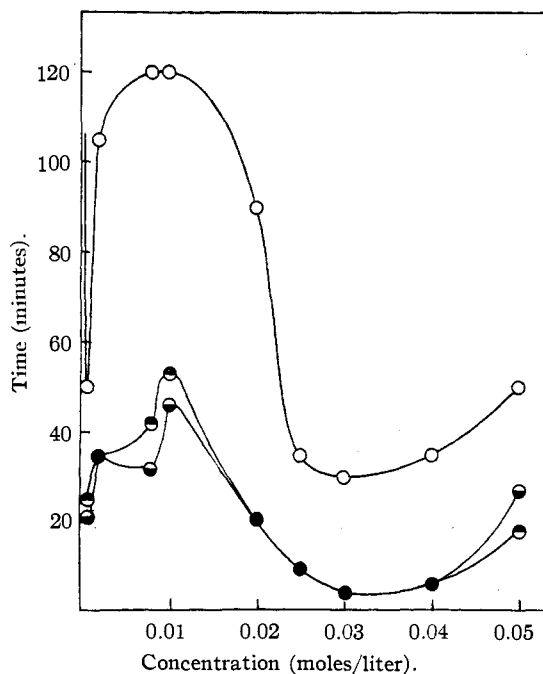


Fig. 1.—Time for complete decolorization of 10^{-5} M pinacyanol chloride as a function of concentration of sodium 1-decanesulfonate: ○, 0.03 M H_2O_2 ; ◐, 0.35 M H_2O_2 ; ●, 0.53 M H_2O_2 .

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

sulfonate and sodium dodecyl sulfate as the paraffin-chain salts.

We have no explanation to offer at the present time for the effect of concentration of paraffin-chain salt, although the phenomenon is not surprising in view of the profound effect of paraffin-chain salts upon the absorption spectrum of the dye.

CONTRIBUTION FROM THE
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NEW COMPOUNDS

p,p'-Dichlorobenzhydryl- β -cyanoethyl Ether

Ten grams (0.04 mole) of *p,p'*-dichlorobenzhydryl (m. p. 88–89°) and 1.0 ml. of phenyltrimethylammonium hydroxide (Monsanto, 20% aqueous solution) were dissolved in 40 ml. of purified dioxane. A solution of 2.3 g. (0.04 mole) of redistilled acrylonitrile in 10 ml. of dioxane was added dropwise with stirring. After pouring into 200 ml. of water, the oil layer was separated. On standing overnight 11 g. (91%) of solid melting 52–66° formed. Crystallization from 50 ml. of 95% ethanol gave 7.6 g. (87%) melting 74–76°. For analysis a sample was recrystallized; m. p. 75–76.5°.

Anal. Calcd. for $C_{16}H_{15}OC_2N$: Cl, 23.2; N, 4.58. Found: Cl, 22.45; N, 4.43.

Attempts to hydrolyze this cyanide in alkaline solution to β -(*p,p'*-dichlorobenzhydroxy)-propionic acid unexpectedly cleaved the ether linkage with the formation of *p,p'*-dichlorobenzhydryl. Five grams (0.016 mole) of the ether and 50 ml. of 15% aqueous sodium hydroxide were refluxed for twenty-four hours. At the end of this time the evolution of ammonia had practically ceased. After cooling and filtering 2.5 g. of solid, m. p. 83–85°, was collected. A mixed melting point with authentic *p,p'*-dichlorobenzhydryl was 84–88°. Acidification of the filtrate gave no precipitate. With 50 ml. of 25% sodium hydroxide solution and four hours of refluxing, the yield of alcohol was 97% of the theoretical.

(1) Montagne, *Rec. trav. chim.*, **24**, 120 (1905).

(2) This is essentially the procedure used by Bruson, *THIS JOURNAL*, **64**, 2457 (1942), and subsequent papers, to prepare many cyanoethyl ethers.

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Derivatives of Di-(*p*-chlorophenyl)-acetic Acid

Di-(*p*-chlorophenyl)-acetic acid, m. p. 164–166°, was made by the alkaline hydrolysis of DDT.¹

Methyl Di-(*p*-chlorophenyl)-acetate.—From 16.9 g. (0.06 mole) of di-(*p*-chlorophenyl)-acetic acid, 20 ml. (14.2 g., 0.44 mole) of methanol and 1 ml. of concentrated sulfuric acid reacted at reflux for four hours there was obtained 9 g. (54%) of ester boiling at 208–212° (5–6 mm.). On standing overnight the product crystallized; m. p. 37–39° (see Table I for analysis).

Phenacyl Di-(*p*-chlorophenyl)-acetate.—From 8 g. (0.03 mole) of acid as the salt and 6.23 g. (0.032 mole) of

phenacyl bromide reacted in the usual way at reflux for two hours 8.0 g. (71%), m. p. 129–130°, of ester formed.² A sample purified by crystallization from benzene melted 132–133°.

Di-(*p*-chlorophenyl)-acetic Anhydride.—A mixture of 20 g. (0.07 mole) of acid and 15.7 g. (0.15 mole) of reagent grade acetic anhydride was refluxed gently for two hours. Distillation at 0.5 mm. gave 2.1 g. at 135–165°, 14.7 g. at 165–195°, 0.2 g. at 195–260° and 2 g. of black residue. Redistillation of the 165–195° fraction gave 11.6 g. at 180–190° (0.5 mm.). Addition of ether precipitated 8.9 g. of yellow solid melting 82–123°. Crystallization from 12 ml. of dry chloroform gave 2.6 g., m. p. 158–163°; a mixed melting point with di-(*p*-chlorophenyl)-acetic acid gave 159–164°. Repeated crystallizations of the chloroform-soluble portion from benzene-petroleum ether (b. p. 60–70°) (1/2 by volume) finally gave 2.6 g. of faintly yellow needles melting 104–105.5°.

Hydrolysis of 0.5 g. of the anhydride by refluxing with 10 ml. of 10% sodium hydroxide solution gave 0.4 g. of di-(*p*-chlorophenyl)-acetic acid, m. p. 163–165°; mixed m. p. 163–165°.

2-(*p,p'*-Dichlorobenzhydryl)-benzimidazole.—From 8 g. (0.028 mole) of acid and 3.2 g. (0.03 mole) of freshly crystallized *o*-phenylenediamine reacted in the usual way there was obtained 5.0 g., 50%, melting 246–248°, after crystallization from 1/1 alcohol-benzene.³

Di-(*p*-chlorophenyl)-acetyl Chloride.—A mixture of 8 g. (0.029 mole) of acid and 11 g. (0.09 mole) of purified thionyl chloride was refluxed for four hours. Removal of the excess chloride gave 8.5 g. (95%) of a brown oil which decomposed on vacuum distillation at 3–4 mm. Attempted crystallization from petroleum ether (b. p. 60–70°) gave an oil which did not crystallize at 0°. Hydrolysis of 2.0 g. of the acid chloride with ice yielded 1.7 g. of di-(*p*-chlorophenyl)-acetic acid, m. p. 158–162°, mixed melting point, 159–163°.

Di-(*p*-chlorophenyl)-acetamide.—Seven grams (0.023 mole) of the acid chloride and 12 ml. (0.092 mole) of ice cold concentrated ammonium hydroxide gave 5.5 g., (85%) of crude amide melting 136–138° dec. Several crystallizations from 95% ethanol gave a product melting 152–154°.

Di-(*p*-chlorophenyl)-acetanilide.—A mixture of 8 g. (0.03 mole) of the acid chloride, 5.5 g. (0.06 mole) of redistilled aniline and 100 ml. of benzene was refluxed for one-half hour. The benzene layer was decanted from the aniline hydrochloride, washed with water, 5% sodium carbonate solution, 10% hydrochloric acid, and water, and evaporated to give 1.2 g. melting 205–206°. Extraction of the aniline hydrochloride with benzene in a Soxhlet extractor gave 5.8 g., m. p. 203–206°, for a total yield of 7.0 g., 75%. Crystallization from 1/1 benzene-pyridine gave a product melting 205–206°.

Di-(*p*-chlorophenyl)-aceto-4-chloranilide.—Prepared as the acetanilide from 9.5 g. (0.034 mole) of acid chloride, 8.9 g. (0.07 mole) of *p*-chloroaniline and 50 ml. of benzene with two and one-half hours' reflux. The crude product, 9.5 g., 72% melting 220–240° dec. was crystallized from benzene: m. p. 258–260°.

***p,p'*-Dichlorobenzhydryl Phenyl Ketone.**—A Friedel-Crafts reaction of 9.4 g. (0.088 mole) of aluminum chloride in 50 ml. of reagent grade benzene with 18.2 g. (0.06 mole) of di-(*p*-chlorophenyl)-acetyl chloride in 100 ml. of benzene at 0–10° for one hour gave 19.5 g. (94%) of crude ketone melting 81–86°. Crystallization from 80 ml. of 95% ethanol gave 14.0 g. (67%), m. p. 90–91°.

Di-(*p*-chlorophenyl)-acetomitrile.—A mixture of 5.0 g. (0.018 mole) of di-(*p*-chlorophenyl)-acetamide and 9.5 g. (0.08 mole) of freshly purified thionyl chloride was refluxed for four hours, cooled, and poured onto 200 g. of ice. After extraction with ether the crude nitrile was vacuum distilled at 2 mm. but decomposition was apparent. Another portion of the ether extract on standing

(2) Shriner and Fuson, "Identification of Organic Compounds," 3rd edition, John Wiley & Sons, New York, N. Y., 1948, p. 157.

(3) Pool, Harwood and Ralston, *THIS JOURNAL*, **59**, 178 (1937).

(1) Grummitt, Buck and Egan, *Org. Syn.*, **26**, 21 (1946).