Anal. Calcd. for $C_{12}H_{16}O_2Pb$: Pb, 51.8. Found: Pb, 50.8, 53.2.

When 3.4 g. of VI in 5 ml. of acetic acid was treated with 9 g. of bromine in 10 ml. of acetic acid, it was converted into **3,6-dibromo-4,5-dipropyl-*o*-quinone**, deep red prisms (4.2 g.) from acetic acid, m. p. 144–146°.

Anal. Calcd. for $C_{12}H_{14}Br_2O_2$: C, 41.1; H, 4.0. Found: C, 41.0; H, 4.2.

The quinone gave no pure product when it was treated with aqueous sodium hydroxide or with alkaline hydrogen peroxide. When it was warmed with zinc dust in acetic acid, it was rapidly and quantitatively reduced to **3,6-dibromo-4,5-dipropylpyrocatechol**, fine white needles from acetic acid, m. p. 83–84°.

Anal. Calcd. for $C_{12}H_{16}Br_2O_2$: C, 40.9; H, 4.6. Found: C, 41.0; H, 4.9.

4,5-Dipropylcyclohexanediol-1,2 (VII).—Experiments on the hydrogenation of VI with Raney nickel and hydrogen at 200 atm. and 175° were carried out before the promoting effect of alkali on similar reactions had been discovered,[4] and the results were erratic. Even in the best experiment, involving 43 g. of VI with freshly prepared catalyst, hydrogen absorption stopped after five hours, and there was obtained a mixture (43 g.) of VI and VII, b. p. 170–183° at 14 mm. Nothing was extracted from this mixture by aqueous alkali, and it was completely extracted from ligroin by Claisen alkali. Separation of 25 g. of the mixture was effected by treatment with alcoholic lead acetate, which precipitated the VI as its lead salt, removed by centrifuging. There was obtained 13 g. of VII, a colorless viscous oil, b. p. 170–173° at 13 mm.

Anal. Calcd. for $C_{12}H_{24}O_2$: C, 72.0; H, 12.0. Found: C, 71.9; H, 11.7.

β,β'-Dipropyladipic Acid (VIII).—A solution of 6.2 g. of VII in 20 ml. of acetic acid was kept at 25–30° by cooling while 6.4 g. of chromic anhydride in 5 ml. of water and 15 ml. of acetic acid was added in small portions. The mixture was allowed to stand at room temperature for eight hours, and then distilled to a sirup under reduced pressure. This was taken up in ether, washed with dilute sulfuric acid and then with sodium carbonate, giving 1.35 g. of neutral material and 3.45 g. of crude acidic product. Crystallization of the latter from ligroin gave 3.3 g., m. p. 86–91°, and distillation of this at 15 mm. followed by crystallization from dilute acetic acid gave 2.65 g. of VIII, colorless needles, m. p. 94–95°.

Anal. Calcd. for $C_{12}H_{22}O_4$: C, 62.6; H, 9.5. Found: C, 62.3; H, 9.7.

No attempt to resolve VIII was made, but it may be noted that the formation of a *cis*-form of VII (and therefore a *meso*-form of VIII) is not certain because of the drastic conditions used for hydrogenating VI.

The author thanks Dr. S. T. Rolfson for most of the analyses reported in this paper.

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[4] Ungnade and McLaren, THIS JOURNAL, **66**, 118 (1944); Ungnade and Nightingale, *ibid.*, **66**, 1218 (1944).

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A New Synthesis of 7,8-Diaminoquinoline

BY FRED LINSKER AND RALPH L. EVANS

Although 7,8-diaminoquinoline has been prepared previously[1] by coupling diazotized aniline with 7-aminoquinoline and reduction of the resulting azo-dye, we found it advisable to look for another procedure when large amounts of the diamine were needed. The following process was developed and it has been found to give satisfactory results.

When 7-nitroquinoline, obtained in a Skraup reaction from *m*-nitroaniline, was reduced by iron and 50% acetic acid, it gave an almost quantitative yield of 7-aminoquinoline. The latter was treated with toluenesulfonyl chloride in pyridine solution and the tosyl compound was nitrated below 70°. A nearly theoretical yield of the crude 7-tosylamino-8-nitroquinoline was obtained, and this was hydrolyzed by means of warm sulfuric acid. The resulting nitroamine was then reduced in the usual way with stannous chloride and hydrochloric acid. The yield of diaminoquinoline was 64% of the theoretical.

Experimental

7-Nitroquinoline.—Knueppel's procedure[2] was used. The compound melted without recrystallization at 128–130° (lit.[3] 130°); yield 14% (lit.[3] 6%).

7-Aminoquinoline.—One hundred and twenty-nine grams of 7-nitroquinoline was dissolved in 645 cc. of glacial acetic acid and 645 cc. of water was added while the solution was warmed to 60°. Maintaining the temperature at 60–70°, 103 g. of powdered iron was added in small portions to the well-stirred reaction mixture. When the reduction was complete, the mixture was cooled to room temperature and made alkaline by adding solid sodium carbonate in small portions with external cooling and stirring. After some standing, the precipitate was filtered, washed with water, and dried over calcium chloride in a desiccator. The dried powdered precipitate was extracted by refluxing with two liters of ether for two hours and repeating this process three times with fresh portions of solvent. The combined ether extracts were then dried with sodium sulfate and evaporated to dryness. Eighty-eight grams of fairly pure 7-aminoquinoline was obtained; m. p. 91–93° (lit.[4] 93.5–94°).

7-Tosylaminoquinoline.—Thirty-five grams of 7-aminoquinoline was dissolved in 250 cc. of dry pyridine and to the cold solution 45 g. of *p*-toluene-sulfonyl chloride was slowly added. The reaction mixture was heated for thirty minutes in a boiling water-bath under a reflux condenser, then cooled and poured into two liters of water. The precipitate was allowed to settle at 0°, filtered, washed with water and dried over calcium chloride; yield 47.5 g. The compound crystallized from ethyl alcohol in colorless prisms; m. p. 184–185°.

Anal. Calcd. for $C_{16}H_{14}N_2O_2S$: C, 64.43; H, 4.70. Found: C, 64.57; H, 4.72.

7-Tosylamino-8-nitroquinoline.—Seventeen grams of 7-tosylaminoquinoline was stirred slowly into 51 g. of concentrated nitric acid and the solution was maintained at 60–70° for two hours. After cooling, the solution was poured over 340 g. of ice. The mixture was kept in the refrigerator overnight, and the precipitated nitro compound was then filtered, washed with water, and dried in a desiccator; yield 24 g. The product was recrystallized, first from ethanol and then from 65% methyl alcohol. It formed colorless needles, m. p. 180°.

Anal. Calcd. for $C_{16}H_{13}N_3O_4S$: C, 55.98; H, 3.79. Found: C, 55.93; H, 3.95.

7-Amino-8-nitroquinoline.—Twenty-four grams of crude 7-tosylamino-8-nitroquinoline was stirred in small portions into 120 cc. of concentrated sulfuric acid. The solution was heated for one hour in a boiling water-bath, cooled to room temperature, and poured onto 700 g. of ice. An excess of ammonium hydroxide was added with stirring and

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[1] Renshaw, Friedman and Gajewski, THIS JOURNAL, **61**, 3322 (1939).

[2] Knueppel, *Ber.*, **29**, 706 (1896).

[3] Kochanska and Bobranski, *ibid.*, **69**, 1807 (1936).

[4] Hamer, *J. Chem. Soc.*, 1436 (1921).

external cooling and, after standing at 0° overnight, the precipitated base was filtered and washed with a little dilute ammonia, yield 8.3 g. Recrystallized from absolute ethyl alcohol, the compound melted at 194°.[5]

7,8-Diaminoquinoline.—A solution of 45 g. of stannous chloride dihydrate in 65 cc. of concentrated hydrochloric acid was added slowly to a suspension of 7 g. of 7-amino-8-nitroquinoline in 150 cc. of 4 *N* hydrochloric acid. The mixture was heated on a steam-bath until all dissolved and for one hour thereafter. The solution was cooled in the refrigerator overnight, the tin double salt was then removed by filtration and washed with a little concentrated hydrochloric acid. It was dissolved in 350 cc. of *N* hydrochloric acid with gentle warming, and hydrogen sulfide was passed through the solution until the precipitation of the tin sulfides was complete. The precipitate was filtered and the tin-free solution was evaporated on a water bath to dryness. Five and five-tenths grams of fairly pure dihydrochloride was thus obtained. Addition of alkali to the aqueous solution of the salt precipitated the free base, which was then recrystallized from boiling water, yielding the monohydrate as light yellow needles, m. p. 94–97° (lit.[1] 95–97°).

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[5] Fourneau, *et al.*, *Ann. Inst. Pasteur*, **44**, 719 (1930). These authors prepared the same compound by heating 7-chloro-8-nitroquinoline with ammonia in a sealed tube to 160° and found the base to melt at 194°.

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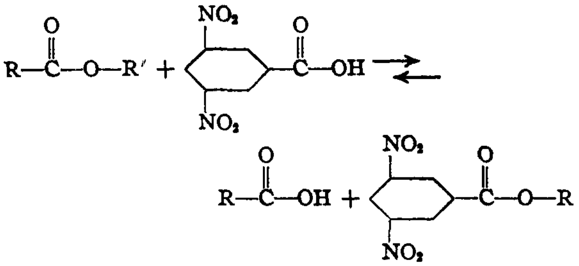
Identification of the Alcohol Components of Simple Esters

BY W. B. RENFROW AND ALAN CHANEY

In an attempt to devise a more satisfactory method for preparation of solid derivatives of the alcohol components of simple esters,[1] we have investigated the interchange reaction between 3,5-dinitrobenzoic acid and a number of esters.



Preliminary experiments with *n*-butyl acetate[2] demonstrated that a catalyst was necessary. Sulfuric acid was a good catalyst for the interchange and *p*-toluenesulfonic acid monohydrate was fairly good. The following compounds were found to have little or no catalytic action: sulfamic acid, aluminum chloride, anhydrous hydrogen chloride, acetic anhydride, 85% phosphoric acid, phosphorus pentoxide and pyridine.

With sulfuric acid as a catalyst, the 3,5-dinitrobenzoates of the alcohol components of the following esters were prepared: ethyl formate, methyl acetate, ethyl acetate, *n*-propyl acetate, isopropyl acetate, *n*-butyl acetate, isobutyl acetate, *s*-butyl acetate, isoamyl acetate, ethylene glycol diacetate, β-phenylethyl acetate, ethyl monochloroacetate, ethyl trichloroacetate, methyl propionate, *n*-propyl propionate, *n*-octyl propionate, *n*-dodecyl propionate, ethyl butyrate, ethyl trimethylacetate, *n*-butyl valerate, *n*-amyl valerate, ethyl α,α-dibutylacetate, ethyl laurate, ethyl lactate, ethyl acetoacetate, diethyl carbonate, dimethyl oxalate, diethyl oxalate, diethyl malonate, diethyl adipate, dibutyl tartrate, methyl benzoate, ethyl benzoate, methyl salicylate, ethyl salicylate, ethyl benzoylacetate, diethyl phthalate and dibutyl phthalate.

Derivatives could not be obtained from the following esters: vinyl acetate, *t*-butyl acetate, cholesteryl acetate, *n*-octadecyl propionate, diglycol laurate, ethyl stearate, *n*-butyl stearate, phenyl acetate, benzyl acetate, guaiacol acetate, methyl cinnamate, ethyl cinnamate, ethyl anisate, diethyl sulfate and ethyl *p*-aminobenzoate.

The method is apparently not applicable to esters that will react readily with concentrated sulfuric acid or that have molecular weights in excess of about two-hundred-fifty.

Experimental

Sulfuric acid (2 drops) was completely dissolved in the ester (2 ml.) and 3,5-dinitrobenzoic acid (1.5 g.) added. If the boiling point of the ester was below 150°, the mixture was refluxed gently, but if the ester boiled above 150° the mixture was heated in an oil-bath (frequent stirring at first) at approximately 150°. The reaction time was usually thirty minutes, but if the 3,5-dinitrobenzoic acid failed to dissolve within fifteen minutes the mixture was heated for one hour.

The reaction product was cooled, dissolved in ether (25 ml.) and thoroughly extracted with 5% sodium carbonate solution (25 ml.). The ether solution was washed with water and the ether removed by evaporation or distillation. The product remaining (usually an oil) was dissolved in about 5 ml. of hot ethanol. Crystallization of the 3,5-dinitrobenzoates was induced by cautious addition of water, cooling and stirring. Yields of purified 3,5-dinitrobenzoates ranged from 0.2 g. in the favorable cases to 0.1 g. in the less favorable cases.

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[1] The usual method of identification involves saponification and isolation of the alcohol. For example, see: Shriner and Fuson, "Identification of Organic Compounds," John Wiley and Sons, New York, N. Y., 1940, p. 152.

[2] The course of the reaction was followed in preliminary experiments by isolation of unreacted 3,5-dinitrobenzoic acid.

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p-Bromobenzyl Bromide

BY M. WEIZMANN AND S. PATAI

For experiments in the stilbene series, we needed considerable quantities of *p*-bromobenzyl bromide. Schramm's[1] claim that bromination of *p*-bromotoluene in sunlight at ordinary temperature gives the desired product in almost quantitative yield, could not be substantiated. The yield we obtained under these conditions was 14–15%, in accordance with Hantzsch and Schultze.[2] The other method to which reference

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[1] Schramm, *Ber.*, **17**, 2922 (1884).

[2] Hantzsch and Schultze, *ibid.*, **29**, 2252 (1896).