

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°.⁴

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°).

(5) Fournau, *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°.

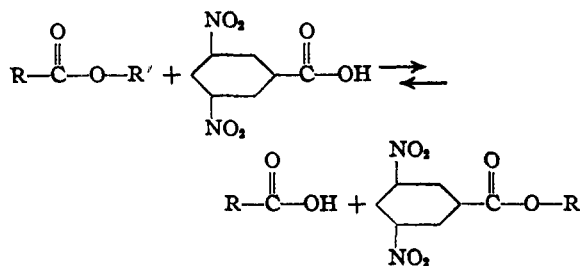
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Identification of the Alcohol Components of Simple Esters

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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 acetate² 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

(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.

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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p-Bromobenzyl Bromide

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For experiments in the stilbene series, we needed considerable quantities of *p*-bromobenzyl bromide. Schramm's¹ 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

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

(2) Hantzsch and Schultze, *ibid.*, **20**, 2252 (1896).