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°.

RESEARCH LABORATORY
RALPH L. EVANS ASSOCIATES
250 E. 43RD STREET
NEW YORK 17, N. Y.

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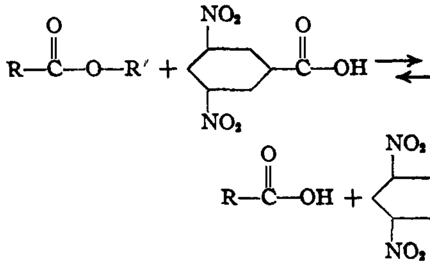
Identification of the Alcohol Components of Simple Esters

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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OBERLIN COLLEGE
OBERLIN, OHIO

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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).

is made in the literature[3] is the bromo-methylation of bromobenzene.

A yield of 66% of a pure product is obtained when the photo-bromination is carried out under similar conditions (but with less bromine) as described for the preparation of *p*-bromobenzal bromide.[4] One hundred and two grams (0.60 mole) *p*-bromotoluene, in a three-necked Pyrex flask, mounted with a mercury-sealed stirrer, a dropping funnel and a reflux condenser with gas-trap, is heated in an oil-bath at 120° (bath temperature) and exposed to the light of a 100-watt lamp. With constant agitation, 102 g. of bromine (0.64 mole) is added during three hours, and the stirring is continued for another thirty minutes. By this time, the evolution of hydrogen bromide has come to a standstill. The product solidifies, upon standing, to a brownish crystalline mass and is filtered by suction from the adhering oil and washed three times with 30 cc. of ethyl alcohol. The yield is 80 g. From the mother liquor, upon cooling with an ice–salt mixture, a second crystallizate (18–20 g.) is obtained. The yield is 66%; m. p. of both crops 61° sharp without further recrystallization. The product was identical with one prepared according to Schramm,[1] and gave the correct analysis. Calcd. for $C_7H_6Br_2$: Br, 64.0. Found: Br, 63.7.

[3] Stephen, Short and Gladding, *J. Chem. Soc.*, **117**, 524 (1920).

[4] "Organic Syntheses," Vol. XVII, p. 20.

DEPARTMENT OF ORGANIC CHEMISTRY
HEBREW UNIVERSITY
JERUSALEM, PALESTINE
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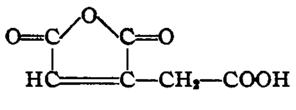
Adduct of Anthracene with *cis*-Aconitic Anhydride

BY JESSE WERNER AND PAUL NAWIASKY

In connection with a research program being carried out in this Laboratory, it was found necessary to prepare the Diels–Alder adduct of anthracene with *cis*-aconitic anhydride. Malachowski, *et al.*,[1] have investigated the chemistry of the so-called *cis* and *trans* forms of aconitic anhydride and found decided differences in chemical behavior. The *cis* anhydride has quinonoidal properties since it adds to dimethylaniline and hydroquinone, whereas the *trans* does not.[2] From this and other evidence, they deduced that the two anhydrides are structural rather than geometrical isomers. The structure which they arrived at for the *cis* form is (I). That for the *trans* form is (II), with a probable equilibrium existing between the keto and enol forms. Schönberg and Ismail[3] have found that the *cis* anhydride gives a red color with triphenyl phosphine, whereas the *trans* form gives no color at all, thus providing further evidence that the *cis* isomer possesses quinonoidal properties, whereas the *trans* does not. The *cis* structure is that of a substituted maleic anhydride. Pfeiffer and Böttler[4] regard maleic anhydride as the quinone of furan, and as such it shows many of the reactions attributed to the quinone structure.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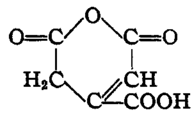
II

On refluxing with anthracene in xylene, the *cis* form was found to react very rapidly and in good yield in the Diels–Alder condensation. However, the *cis* form is rather difficult to obtain in a pure state, in contrast to the *trans* form. Since the *trans* form is slowly converted to the *cis* on melting or keeping in solution above its melting point, it was of interest to determine the relative dienophilic reactivities of the non-quinonoidal *trans* form and the quinonoidal *cis* form by refluxing the *trans* form with anthracene in xylene. The reaction in this case was quite slow, but the product obtained was identical with that from the *cis* isomer. This indicates that the mechanism involved a slow conversion of the *trans* to the *cis* form and a subsequent condensation of the *cis* isomer with anthracene.

It is of interest to note that both forms of aconitic anhydride contain the dienophilic C=C—C=O grouping. However, the dienophilic reactivities of the two are quite different, the quinonoidal nature of the *cis* form evidently enhancing its dienophilic properties.

Procedure.—Six grams of anthracene (Eastman Kodak Company) and 5.2 g. of either *cis* or *trans* aconitic anhydride (prepared according to Malachowski, *et al.*,[1] and melting at 72–73° and 135–136°, respectively) were mixed with 50 cc. of xylene. With the *cis* isomer the mixture was heated rapidly to reflux for one-half hour; with the *trans* isomer the mixture was heated to reflux during one hour and refluxed for four hours. In both cases the mixture was allowed to crystallize at room temperature overnight, after which the crystals were filtered off, washed with 100 cc. of xylene and dried on the steam-bath. The yield of pale yellow plates was 7.0 g. (63%) with the *cis* and 6.7 g. (60%) with the *trans*. Two recrystallizations from ethyl acetate gave pure white crystals, m. p. 262–263° (dec.) in each case.

Anal. Calcd. for $C_{20}H_{14}O_5$: C, 71.85; H, 4.22. Found: (for *cis*), C, 71.72; H, 4.28; for *trans*, C, 71.60; H, 4.37.

Mixtures of the two adducts showed no change in melting point.

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[1] Malachowski, Giedroyć and Jerzmanowska, *Ber.*, **61**, 2525 (1928).

[2] *Cf.* Norton, *Chem. Rev.*, **31**, 468 (1942).

[3] Schönberg and Ismail, *J. Chem. Soc.*, 1374 (1940).

[4] Pfeiffer and Böttler, *Ber.*, **51**, 1819 (1918).

PROCESS DEVELOPMENT DEPARTMENT
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GRASSELLI, NEW JERSEY
RECEIVED SEPTEMBER 11, 1945

2-(4-Homosulfanilamido)-quinoxaline

BY FRANK J. WOLF, RUSSELL M. WILSON, JR., AND MAX TISHLER

Owing to the recent interest in marfanil,[1] the preparation of the corresponding homosulfanila-

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[1] J. Klarer, *Klin. Wochschr.*, **20**, 1250 (1941).