isopropyl - 5 - (3′ - iodo - 2′ - benzoyloxypropyl)barbituric acid followed by the elimination of the elements of hydrogen and iodine under the influence of silver benzoate. The isolation of halo acyloxy compounds from Prevost oxidations has been previously reported.[3]

Not only did elemental analysis for carbon, hydrogen, and nitrogen support the structure, but also the amount of ammonia evolved on basic digestion corroborated this structure assignment. The fact that only one nitrogen appeared as ammonia indicates that one of the nitrogen atoms in the newly formed compound is now involved in a linkage (*i.e.*, amine linkage) which is not split by heating with 30% alkali. The isolation of 92.5% of the theoretical benzoic acid on hydrolysis of the compound using 4 *N* sodium hydroxide is also in accord with the indicated structure.

EXPERIMENTAL[4,5]

Silver benzoate. This was prepared by the addition of the calculated amount of 10% silver nitrate to a 1 *N* solution of sodium benzoate. The resulting precipitate was washed repeatedly with water, absolute alcohol, and finally ether.

2,4,9-Triketo-7-benzoyloxy-5-isopropyl-1,3-diazabicyclo-[3,3,1]nonane. To 23 g. (0.1 mole) of silver benzoate in 200 ml. of dry benzene was added rapidly with stirring, 12.7 g. (0.05 mole) of iodine in 200 ml. of dry benzene. The reaction mixture became thick and yellow in color. After stirring for an additional few minutes, there was rapidly added with stirring 10.5 g. (0.05 mole) of 5-allyl-5-isopropylbarbituric acid in 100 ml. of hot dry benzene. The reaction mixture was heated to reflux and kept at reflux for 75 minutes and then was allowed to stand overnight at room temperature. Filtration through a layer of Super-Cel gave a clear filtrate which was concentrated to dryness at atmospheric pressure on a steam-bath. The residual oil solidified on cooling. Extraction with 50 ml. of hot absolute alcohol gave after filtration and cooling 6.2 g. (38%) of material melting at 172–173.5°. Additional product could be obtained on concentration of the mother liquor. The material was purified for analysis by recrystallization from absolute ethanol.

Anal. Calc'd for $C_{17}H_{18}N_2O_5$: C, 61.81; H, 5.49; N, 8.48; N as ammonia, 4.24. Found: C, 61.88; H, 5.48; N, 8.52; N as ammonia, 4.25.

In a previous experiment it was found that the residue from the ether evaporation could be taken up in hot benzene and precipitated by cooling. It was attempted to recrystallize the material from benzene but just prior to complete solution, that material which had already dissolved precipitated and could then be recrystallized only from absolute alcohol as above. The material which was obtained by cooling the benzene melted over a range at about 85°.

Hydrolysis of 2,4,9-triketo-7-benzoyloxy-5-isopropyl-1,3-diazabicyclo-[3,3,1]nonane. A solution of 3.5 g. of Prevost oxidation product in 50 ml. of 4 *N* sodium hydroxide was kept at reflux for two and one half hours during which time the solution was concentrated by 50%. The solution was diluted to its original volume and acidified with 4 *N* hydrochloric acid. Filtration gave 1.7 g. of material. On extraction twice with 50-ml. portions of absolute ether and evaporation to dryness, 1.1 g. of benzoic acid melting point 121–122.5° was obtained. On standing the filtered acidified aqueous solution deposited an additional 0.1 g. of benzoic acid, m.p. 122–123°.

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(3) Birckenbach, Goubeau, and Berninger, *Ber.*, **65**, 1339 (1932); Bockemuller and Hoffman, *Ann.*, **519**, 165 (1935); Uschakow and Tchistow, *Ber.*, **68**, 824 (1935); Halperin, Donahoe, Kleinberg, and Vanderwerf, *J. Org. Chem.*, **17**, 623 (1952).

(4) Melting points are uncorrected.

(5) Analyses were carried out by Miss Linda Einstein.

The Decomposition of Picric Acid Complexes with Potassium Chloride*

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The conventional method of composing amine complexes of picric acid by means of aqueous ammonia suffers from the limitation that extensive decomposition sometimes occurs with base-sensitive materials, *e.g.*, 3,3′-dihydroxybenzidine.[1] Having at one time noted that an attempt to salt out an alkaloid picrate from aqueous solution with sodium chloride had resulted in the precipitation of sodium picrate, we investigated the use of potassium chloride (which would give the less soluble potassium picrate) as a dissociative agent for both amine and polynuclear hydrocarbon picrates.

In a typical case, *e.g.*, β-naphthol picrate, a solution of the picrate in alcohol at its boiling point was treated with an excess of a saturated aqueous solution of the chloride, and after cooling, the potassium picrate which deposited was removed by filtration. Evaporation of the filtrate gave a quantitative recovery of the desired material which then was purified by standard procedures. Because one is concerned here with relative solubilities, the situation is not always as straightforward as this, and the proportion of water to alcohol in the system is sometimes of critical importance, as in the case of pyrene picrate. This solvent dependence has the undesirable effect of sometimes requiring trials with different solvent proportions before acceptable yields are obtained. Although the experiments with the picrates of pyrene and 3,3′-dihydroxybenzidine gave recoveries (63 and 52% respectively) which were far from quantitative, in the case of the latter compound the procedure appears to be superior to the use of ammonia water.[1] Except in such special cases, the standard methods of decomposing picrates are preferable.

EXPERIMENTAL

Melting points are uncorrected; micro melting points were taken with a Fisher-Johns apparatus.

β-Naphthol from the picrate. A mixture of 0.50 g. (0.134 mmole) of β-naphthol picrate (m.p. 154–155°), 6 ml. of 95% ethanol, and 1 ml. of a saturated (25°) aqueous solu-

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(1) H. Weinfeld, this laboratory, unpublished results.

tion of potassium chloride was heated to boiling. The residue obtained after chilling and filtering was washed with 1 ml. of ice-cold 95% ethanol, and the combined filtrate and washings were evaporated to dryness. Extraction with ether and evaporation gave a quantitative recovery (0.195 g.) of β-naphthol, micro m.p. 118–123.5°. The slightly yellow product was recrystallized twice from 95% ethanol (once with Darco) to give colorless plates, micro m.p. 123.5°. A mixed micro m.p. with an authentic sample was not depressed.

Pyrene from the picrate. A solution of 0.289 g. (0.67 mmole) of pyrene picrate (m.p. 221–222°) in 15 ml. of 95% ethanol was treated, at the boiling point, with 2 ml. of a saturated ethanolic (95%) solution of potassium chloride and 20 ml. of hot water. The residue obtained after chilling and filtering was washed with 25 ml. of water to give 0.167 g. of mixed colorless and orange solids which were dissolved in 10 ml. of 95% ethanol and treated anew with 2 ml. of saturated ethanolic potassium chloride and 3 ml. of water. The 0.085 g. (62.8%) of pyrene so obtained, micro m.p. 152°, was recrystallized from 95% ethanol to give a nearly colorless product, micro m.p. 151–152°. A mixture micro m.p. with authentic material was not depressed.

3,3'-Dihydroxybenzidine from the picrate. A solution of 0.772 g. (1.20 mmoles) of the picrate (dec. 205°) in 10 ml. of boiling 95% ethanol was treated with 2 ml. of a saturated aqueous solution of potassium chloride. After chilling and filtering, the 0.357 g. of material recovered from the filtrate was recrystallized from aqueous pyridine to give, after washing with water, 0.134 g. (51.6%) of 3,3'-dihydroxybenzidine, m.p. 293° (sealed capillary). A mixture m.p. with authentic material (sealed capillary) was not depressed.

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Transformations of the Stobbe Product from 4,4'-Dimethoxybenzophenone[1]

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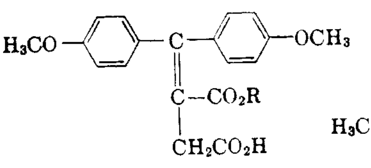
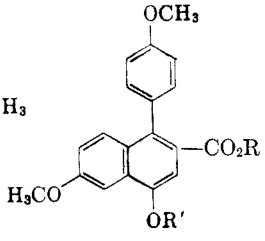
In a previous publication[2] there were reported some transformations of the Stobbe product from 3-methoxybenzophenone as a potential pathway to syntheses of the lignan structure. The present paper concerns similar studies based on the starting material 4,4'-dimethoxybenzophenone. Daub and Johnson[3] conducted Stobbe condensations of the latter ketone with both diethyl succinate and di-*tert*-butyl succinate and indicated that use of the di-*tert*-butyl ester was preferable inasmuch as it resulted in a higher yield and a better quality of product. Accordingly our investigations were confined to the use of I instead of II.

Hydrolysis of I could not be accomplished by refluxing with aqueous alcoholic hydroxide even for 20 hours despite the effectiveness of this method at a reaction time of 2–3 hours for its ethyl counterpart II.[4,5] In view of the facile decarboxylation observed by Johnson and Miller[4] for III under aqueous acidic conditions, it seemed appropriate to attempt non-aqueous solvolysis. However, methanol (with or without added anhydrous hydrogen chloride) proved of no avail, while 100% sulfuric acid appeared to give a reaction though only a trace of product was isolable therefrom. An excellent solution to the problem (resulting in an 87% yield of crystalline III) was found by reversion to the alcoholic hydroxide method but conducted under more strenuous conditions, *viz.* in a sealed bomb at 150° for 7 hours. It is unlikely that these conditions served merely to effect a pyrolysis of the ester[6] rather than a *bona fide* hydrolysis, for little, if any, gas pressure was noted on opening the cooled bomb at the end of the experiment and an attempted reaction conducted in exactly the same fashion as before but *sans* hydroxide produced a non-crystallizable oil. The increased resistance of I, as compared to II, toward alkaline hydrolysis is readily ascribable to the greater bulk and/or electron-donating properties of the *tert*-butyl group over the ethyl group. A rationale for the low reactivity of I toward methanolysis may be that electron-donation by the conjugated *p*-methoxy groups prevents liberation of the *tert*-butyl carbonium ion while the presence of hydrogen chloride in the methanol fails to circumvent this difficulty because it protonates some site in the molecule other than the carbo-*tert*-butoxy moiety.[7]



I, R = *tert*-Bu
II, R = Et
III, R = H



IV, R = *tert*-Bu, R' = Ac
V, R = Et, R' = Ac
VI, R = *tert*-Bu, R' = H
VII, R = R' = H

Cyclization of I to the naphthalene derivative IV was carried out with sodium acetate-acetic anhydride, though in lower yield (24%) than that reported[5] (*ca.* 80% crude) for conversion of II to V.

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[1] From the M.S. thesis of C. Douglas Lind, University of Oregon, June, 1954. Presented at the Northwest Regional Meeting of the American Chemical Society, Eugene, Oregon, June, 1955. Supported in part by a grant-in-aid from the Graduate School, University of Oregon.

[2] Klemm and Largman, *J. Am. Chem. Soc.*, **76**, 1688 (1954).

[3] Daub and Johnson, *J. Am. Chem. Soc.*, **72**, 501 (1950).

[4] Johnson and Miller, *J. Am. Chem. Soc.*, **72**, 511 (1950).

[5] Baddar, El-Assal, and Baghos, *J. Chem. Soc.*, 1714 (1955).

[6] Sheehan and Laubach, *J. Am. Chem. Soc.*, **73**, 4752 (1951); Norris and Rigby, *J. Am. Chem. Soc.*, **54**, 2088 (1932).

[7] Cohen and Schneider, *J. Am. Chem. Soc.*, **63**, 3382 (1941).