

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'-Dimethoxybenzophenone¹

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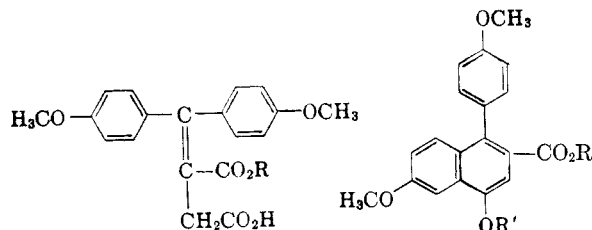
In a previous publication² there were reported some transformations of the Stobbe product from 3-methoxybenzophenone as a potential pathway to syntheses of the lignan structure. The present paper concerns similar studies based on the starting material 4,4'-dimethoxybenzophenone. Daub and Johnson³ conducted 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.

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

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

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 Miller⁴ for III under aqueous acidic conditions, it seemed appropriate to attempt non-aqueous solvolysis. However, methanol



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

(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 ester⁶ 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

Cyclization of I to the naphthalene derivative IV was carried out with sodium acetate-acetic anhydride, though in lower yield (24%) than that reported⁵ (*ca.* 80% crude) for conversion of II to V.

(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).

Deacetylation of IV to the naphthol VI occurred readily (89% yield) with refluxing aqueous alcoholic hydroxide, while subsequent removal of the *tert*-butyl group to produce VII was again accomplished by the bomb procedure (94% yield) but failed to occur with methanolic hydrogen chloride.

Quantitative reduction of III to 3-carboxy-4,4-di(4-methoxyphenyl)butanoic acid was effected catalytically using 30% palladium-on-charcoal in glacial acetic acid. Attempts to reduce III using sodium and ethanol, sodium amalgam, or an electrolytic procedure (with sodium amalgam produced *in situ*) were unsuccessful. These latter results contrast sharply with those of Stobbe and Kohlmann⁸ and Klemm and Largman² who found sodium amalgam an excellent reagent for reducing the diacids obtained from Stobbe condensations of benzophenone and 3-methoxybenzophenone, respectively. They are, however, in accordance with the mechanistic point of view that sodium reductions involve initial attack on the carbon-carbon double bond by an electron;⁹ while catalytic hydrogenation effectively involves attack, by a hydrogen ion¹⁰ or atom.¹¹ Hence, the former method of reduction should be hindered by the presence of groups such as the *p*-methoxy ones in III which serve to increase electron density at the site of attack while the latter method ought to be electronically aided, if anything, by the presence of these groups.

EXPERIMENTAL¹²

Hydrolysis of 3-(carbo-tert-butoxy)-4,4-di(4-methoxyphenyl)-3-butenic acid (I). A mixture of 25 g. of I,³ 70 g. of barium hydroxide octahydrate, 100 ml. of water, and 150 ml. of ethanol was heated at 150°, with shaking, for 6–7 hours in the sealed 500-ml. bomb of a Parr high pressure hydrogenation apparatus. The cooled contents were diluted with water, acidified, and extracted with ether. The ethereal layer was extracted with excess 10% aqueous sodium carbonate. Acidification of the alkaline extract produced a brown oil which solidified on standing and was collected as the crude product, 3-carboxy-4,4-di(4-methoxyphenyl)-3-butenic acid (III); av. yield 18.7 g. (87%), m.p. 154–156°. Recrystallization of a sample for analysis from methanol gave white needles, m.p. 158–158.5° [reported m.p. 161–162°⁶; blades from dilute alcohol, m.p. 161–161.5°⁴], $\lambda_{\text{max}}^{\text{EtOH}}$: 236 m μ (log ϵ 4.17), 278 (4.16).

Anal. Calc'd for C₁₉H₁₈O₆: C, 66.66; H, 5.30; Neut. equiv., 171.2. Found: C, 67.09; H, 5.58; Neut. equiv., 171.2.

Refluxing I with aqueous ethanolic barium hydroxide for 20 hours or with anhydrous methanol⁷ for 6 days yielded

(8) Stobbe and Kohlmann, *Ann.*, **308**, 100 (1899).

(9) Ingold, *Structure and Mechanism in Organic Chemistry*, Cornell University Press, Ithaca, 1953, pp. 700–701.

(10) Baker and Newby, *Abstracts of the 118th Meeting of the American Chemical Society*, Chicago, September 1950, p. 61N.

(11) Emmett, *Catalysis*, Reinhold Publishing Corp., New York, 1954, Vol. I, p. 219.

(12) Melting points are uncorrected. Elemental analyses were performed by Micro-Tech Laboratories, Skokie, Illinois. Ultraviolet absorption spectra were determined by means of a Beckman spectrophotometer, model DU.

only starting material. Allowing a solution of I in cold, saturated anhydrous methanolic hydrogen chloride⁷ to warm to room temperature and stand for 2 hours gave the same result. Allowing a solution of I in 100% sulfuric acid¹³ to stand for 5 minutes and then pouring it onto ice and extracting with ether gave only a trace of red powder.

3-Carboxy-4,4-di(4-methoxyphenyl)butanoic acid. Into a Parr low pressure hydrogenation apparatus fitted with a heating mantle surrounding the reaction chamber were placed 5 g. of III, 0.17 g. of 30% palladium-on-charcoal catalyst, and 75 ml. of glacial acetic acid. The mixture was shaken for 2½ hours at 80° and a hydrogen pressure of 3.7 atm. Filtration and concentration of the reaction mixture gave 5 g. (quantitative) of needles, m.p. 148–150°, raised to 154–155° on recrystallization from fresh acetic acid, $\lambda_{\text{max}}^{\text{EtOH}}$: 234 m μ (log ϵ 4.24), 275 (3.44).

Anal. Calc'd for C₁₉H₂₀O₆: C, 66.27; H, 5.85. Found: C, 66.14; H, 6.30.

Treatment of III with sodium and ethanol or sodium amalgam² gave no reaction. Electrolysis¹⁴ of 2 g. of III with a current of 2 amps. for 45 minutes and fractional crystallization of the product from benzene yielded mostly starting material and a trace of tan powder, m.p. 195–197°. When this powder was added to the molten product from catalytic hydrogenation at a temperature just above 155° the whole mass solidified and re-melted at 195–197°. Variations of current, reaction time, or reaction temperature (up to 100°) did not improve the yield of product from electrolysis.

tert-Butyl 4-acetoxy-6-methoxy-1-(4-methoxyphenyl)-2-naphthoate (IV). A mixture of 10 g. of I, 1 g. of anhydrous sodium acetate, and 30 ml. of acetic anhydride was refluxed for 6 hours. The solvent was removed under reduced pressure and an ethereal solution of the brown residue was washed with water and dried with magnesium sulfate. The residue from evaporation of the ether crystallized from benzene as light yellow needles, yield 3 g. (24%), m.p. 148–149°. Recrystallization of a sample from methanol gave white needles, m.p. 151.5–152°, $\lambda_{\text{max}}^{\text{EtOH}}$: 246 m μ (log ϵ 4.64), 301 (3.93).

Anal. Calc'd for C₂₅H₂₆O₆: C, 71.07; H, 6.20. Found: C, 71.24, 70.59; H, 6.46, 6.21.

tert-Butyl 4-hydroxy-6-methoxy-1-(4-methoxyphenyl)-2-naphthoate (VI). A mixture of 2 g. of IV, 20 ml. of 10% aqueous sodium hydroxide, and 20 ml. of ethanol was refluxed for 15 min. and then was concentrated to 10 ml. It was diluted with 20 ml. of water, acidified, and extracted with ether. The residue from evaporation of the dried (with magnesium sulfate) ethereal solution crystallized from methanol as prisms, yield 1.6 g. (89%), m.p. 188–190°, raised to 192–193° on recrystallization from the same solvent, $\lambda_{\text{max}}^{\text{EtOH}}$: 222 m μ (log ϵ 4.41), 242 (4.47), 258 (4.28), 283 (3.95).

Anal. Calc'd for C₂₃H₂₄O₅: C, 72.61; H, 6.36. Found: C, 73.02, 72.44; H, 6.62, 6.55.

4-Hydroxy-6-methoxy-1-(4-methoxyphenyl)-2-naphthoic acid (VII). Using the bomb procedure as for hydrolysis of I, a mixture of 1 g. of VI, 10 g. of barium hydroxide octahydrate, 75 ml. of water, and 75 ml. of ethanol yielded 0.8 g. (94%) of crude product, m.p. 215–217°. A sample recrystallized from 50% methanol formed needles, m.p. 219–220° [reported⁵ m.p. 219–220°], $\lambda_{\text{max}}^{\text{EtOH}}$: 247 m μ (log ϵ 4.46), 306 (3.76).

Anal. Calc'd for C₁₉H₁₆O₅: C, 70.36; H, 4.97. Found: C, 70.17; H, 5.12.

(13) Newman and McCleary, *J. Am. Chem. Soc.*, **63**, 1537 (1941).

(14) Blatt, *Org. Syntheses*, Coll. Vol. I, 2nd Ed., 311 (1941).