

deposited in the form of needles having the same melting point.

Anal. Calcd. for $C_{24}H_{18}O_4$: C, 77.82; H, 4.90. Found: C, 78.03; H, 5.27.

Naphthacenediquinone-butadiene (II, R = H) was obtained in a slightly less smooth reaction in 74.5% yield. Crystallized from glacial acetic acid it formed colorless, transparent plates melting at 243–244°.

Anal. Calcd. for $C_{22}H_{14}O_4$: C, 77.17; H, 4.13. Found: C, 77.12; H, 4.36.

Alkaline Cleavage.—Half-gram samples of the addition products were heated on the steam-bath with 15-cc. portions of 25% methyl alcoholic potassium hydroxide for ten to fifteen minutes and the mixture was shaken with air until there were no further color changes. In the absence of air the solid dissolves to a deep red solution and on exposure this becomes green and then yellow and deposits pale yellow needles, sometimes with a greenish tinge. The products were collected and recrystallized from glacial acetic acid containing a little chromic anhydride. From the dimethyl compound there was obtained 0.31 g. (97%) of 2,3-dimethylantraquinone, m. p. 208–210°, which gave no depression when mixed with a known sample. The parent substance yielded 0.26 g. (93%) of anthraquinone, m. p. 284–285°, similarly identified.

In each case the alkaline mother liquor was acidified and evaporated to dryness. The residue was extracted thoroughly with ether and the ethereal solution extracted with 2% alkali and the product precipitated with hydrochloric acid. The phthalic acid which separated was sublimed and identified in the form of the anhydride (0.09–0.1 g.), m. p. and mixed m. p., 129.5–130.5°.

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The Oxidation of Methyl α - and β -Naphthyl Ketones

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In view of the usefulness of α - and β -naphthoic acid in synthetic operations and the high current price of these materials the preparation of the compounds by the hypochlorite oxidation of the corresponding methyl ketones was investigated. It was found that β -naphthoic acid can be prepared very conveniently by this method. A solution of potassium hypochlorite was prepared by dissolving 250 g. of commercial calcium hypochlorite ("HTH"), containing 65% of the active ingredient, in 1 liter of water, adding a warm solution of 175 g. of potassium carbonate and 50 g. of potassium hydroxide in 500 cc. of water, shaking well, filtering and washing the precipitate. The solution was heated to 55°, stirred mechanically, and 85 g. of methyl β -naphthyl ketone was added,

the temperature subsequently being controlled to 60–70° by frequent cooling in an ice-bath. After about one hour the excess hypochlorite was destroyed by adding 50 g. of sodium bisulfite in 200 cc. of water and the solution was cooled and acidified. The colorless acid which precipitated (85 g., m. p. 181–183°) was crystallized while moist from 600 cc. of alcohol, giving 75 g. (87%) of β -naphthoic acid, m. p. 184–185° (corr.).

The methyl naphthyl ketone prepared by Caille's method¹ at temperatures as low as –15°, using either acetyl chloride or acetic anhydride, was found by oxidation to contain at least 30% of the β -isomer. This is in conformity with the observations of St. Pfau and Ofner,² who found that methyl α -naphthyl ketone can be isolated easily from the mixture in the form of the picrate. On submitting to hypochlorite oxidation the ketone separated from the mixture by a single crystallization as the picrate, we obtained pure α -naphthoic acid, the yield of once recrystallized material, m. p. 161.5–162.5° (corr.) being 90%. Although this constitutes a practical method of preparing the acid, it is less convenient than to treat α -naphthylmagnesium bromide with carbon dioxide or ethyl carbonate,³ in the latter case with subsequent hydrolysis. We obtained α -naphthoic acid in 85% yield from the bromide, the Grignard reagent being poured onto solid carbon dioxide.

For comparison with the methyl α -naphthyl ketone isolated through the picrate² a sample of the ketone was prepared from methyl α -naphthoate and ethyl acetate, following the procedure of Mosettig and van de Kamp⁴ for a comparable case. The constants (corr.) were as follows: b. p. 151.5–152° at 9 = 0.5 mm., 302° at 760 mm.; n_D^{20} 1.6233; picrate, m. p. 119–120°; oxime, m. p. 139.5–140.5°; semicarbazone, m. p. 228.5–229.5°. The picrate isolated according to St. Pfau and Ofner and once recrystallized likewise melted at 119–120° (corr.) and it is concluded that the pure ketone can be obtained in an entirely satisfactory condition by the Friedel and Crafts reaction and separation of the isomers through the picrates.

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- (1) Caille, *Compt. rend.*, **153**, 393 (1911).
- (2) St. Pfau and Ofner, *Helv. Chim. Acta*, **9**, 669 (1926).
- (3) Loder and Whitmore, *This Journal*, **57**, 2727 (1935).
- (4) Mosettig and van de Kamp, *ibid.*, **55**, 3442 (1933).