out in five portions with very slow, cautious heating and continual stirring. Lazier and Vaughen[5] have found that the final heat treatment very materially affects the activity of the catalyst. The material was then leached with 600 ml. of 10% acetic acid and washed with six 100-ml. portions of water. The catalyst was sifted before use on a twenty-mesh sieve to remove the fine material. The portion that did not pass through the sieve was used for the dehydrogenation of normal butanol. The yields of suitable catalyst average 220 g.

To test the effectiveness of this catalyst we have studied the dehydrogenation of *n*-butanol on a fresh sample of catalyst and on one which had been in use continuously for fifteen hours. Butanol is well suited for such a test because of the consistent yields of aldehyde it affords and the minimum yields of unsaturated hydrocarbon and ester.

The representative results obtained are shown in the following table where 100 g. of *n*-butanol was employed, using equipment similar to that described by Conant[6] and with a catalyst maintained at a temperature of 330–350°.

TABLE I

	Fresh catalyst	Used catalyst
Butyraldehyde, g.	60.2	49.4
Unchanged butanol, g.	2.0	6.5
n-Butyl butyrate, g.	10.0	11.0
Condensation products, g.	1.5	2.0
Gases collected, liters	27.8	24.3
Water, g.	2.5	2.8

The yields given are those actually separated from the reaction mixture, mechanical losses and the weight of the gaseous products accounting for the deficit between the starting material and the products finally recovered. It can be seen that this catalyst gives yields of about 50% even after fifteen to twenty hours of continuous use.

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(5) Lazier and Vaughen, THIS JOURNAL, **54**, 3080 (1932).

(6) Conant, "The Chemistry of Organic Compounds," The Macmillan Company, New York, 1933, p. 106.

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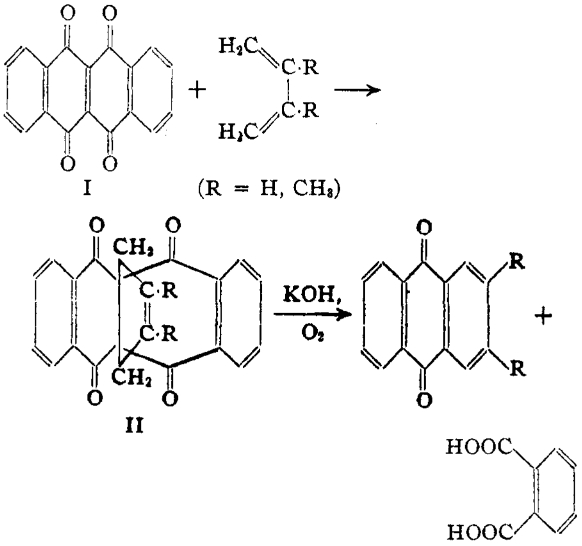
RECEIVED MAY 4, 1936

The Addition of Dienes to Naphthacenediquinone

BY L. F. FIESER AND J. T. DUNN

In view of the renewed interest in the chemistry of naphthacene as a result of the discovery[1] that rubrene is a derivative of this hydrocarbon, an account may be given of an observation pertinent to the subject which was made in the course of a further study of the addition of dienes to substituted quinones.[2] Having found that the two alkyl groups of 2,3-dimethyl-1,4-naphthoquinone do not interfere seriously with the course of the Diels–Alder reaction,[2a] it seemed possible that naphthacenediquinone, I,[3] might be capable of adding dienes, for there is evidence that this substance contains a highly active double bond.[4] In the case of butadiene and dimethylbutadiene addition was found to occur rapidly in glacial acetic acid solution at 100°, giving beautifully crystalline, colorless products. That the substances have the expected endocyclic structure II was established by the isolation of characteristic cleavage products. Like other 1,3-diketones which are incapable of enolization,[5] the compounds are quite susceptible to alkaline hydrolysis, giving anthraquinone, or 2,3-dimethylanthraquinone, and phthalic acid. The primary rupture of the molecule evidently gives a tetrahydroanthraquinone which becomes isomerized and oxidized to an anthraquinone under the influence of alkali and air.



Experimental Part

Naphthacenediquinone-2,3-dimethylbutadiene (II, R = CH_3).—A suspension of 1 g. of naphthacenediquinone in 45 cc. of glacial acetic acid containing 2 cc. of 2,3-dimethylbutadiene was heated at 100° for four to five hours, when the initially brown solution had become pale yellow. The solution was boiled to expel unchanged diene, clarified with active carbon, and concentrated to one-fifth its volume. The product separated in a good condition and the yield of once recrystallized material was 1.1 g. (87%). The substance is readily soluble in benzene, glacial acetic acid, chloroform or acetone, and moderately soluble in alcohol or ether. By crystallization from a hot, concentrated solution in acetic acid it was obtained as small colorless, transparent orthorhombic prisms, m. p. 255–256°, while from a cool, dilute solution the substance was

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(1) Dufraisse and Velluz, *Compt. rend.*, **201**, 1394 (1935).

(2) Previous papers: Fieser and Seligman, (a) THIS JOURNAL, **56**, 2690 (1934); (b) *Ber.*, **68**, 1747 (1935).

(3) Gabriel and Leupold, *ibid.*, **31**, 1272 (1898).

(4) Voswinckel, *ibid.*, **38**, 4015 (1905); **42**, 458 (1909).

(5) Beckham and Adkins, THIS JOURNAL, **56**, 1119, 2676 (1934).

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-dimethylanthraquinone, 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

BY L. F. FIESER, H. L. HOLMES AND M. S. NEWMAN

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 method[1] 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 picrate[2] a sample of the ketone was prepared from methyl α-naphthoate and ethyl acetate, following the procedure of Mosettig and van de Kamp[4] 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^{27}D 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).