(2) the apparent rate at high pressures, practically unchanged at 529°, was decreased at lower temperatures, being only about half the normal value at 465°; (3) the induction period was no longer apparent at any temperature.

These effects are practically sufficient to prove the reaction a chain. On the chain hypothesis, the short induction period appears naturally as the time necessary for the chain-carrying radicals to attain their steady-state concentrations; packing shortens the chains, rendering the induction period inappreciable and reducing the rate most at the lower temperatures, where chains of this type are longest.[3] The change of shape of the rate-pressure curve by packing also shows the great complexity of the reaction.

Though packing may lower the apparent rate by promoting condensation reactions, it seems very unlikely that a 50% reduction could be caused in this way. An induction period might conceivably occur if the reaction proceeded through some active form of acetone, in equilibrium with the ordinary form, the active form decomposing unimolecularly; but in this case, if increased surface shortened the induction period it must increase, rather than decrease, the observed rate.[4] Hence the reaction must be a chain.

The most likely mechanism for the reaction is the Rice–Herzfeld one

$$\mathrm{CH_3COCH_3 = 2CH_3 + CO} \tag{1}$$
$$\mathrm{CH_3 + CH_3COCH_3 = CH_4 + CH_2COCH_3} \tag{2}$$
$$\mathrm{CH_2COCH_3 = CH_3 + CH_2CO} \tag{3}$$
$$\mathrm{2CH_3 = C_2H_6} \tag{4}$$
$$\mathrm{CH_3 + CH_3COCH_3 = C_2H_5COCH_3} \tag{5}$$

The combination of two acetonyl radicals is not included, as the diacetonyl formed would decompose rapidly at the temperatures used;[3] a steady-state concentration of diacetonyl must exist, however, and it is probably the building-up of this compound that causes the induction period. Rice and Herzfeld have attempted to obtain, from this type of mechanism, expressions for the pressure and temperature dependence of the reaction rate. This procedure assumes that the reactions involved have a simple order of one or two; this cannot be the case, unfortunately, for in the range of pressures used, reactions (1), (3), (5) and possibly (4) will have "fallen off" from their high-pressure rates by the well-known theory of unimolecular reactions, and will thus possess no definite order. This effect introduces so many unknown variables into the picture that it seems impossible to make any real progress by further study of the thermal reaction alone.

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[4] The argument is as follows: Let the reaction scheme be

$$X = Y \text{ (active)} \tag{1}$$
$$Y = X \tag{2}$$
$$Y = \text{products} \tag{3}$$

Then $dY/dt = k_1X - k_2Y - k_3Y$. At the steady state, this equals zero, whence $Y = k_1X/(k_2 + k_3)$; observed rate $= k_3Y = k_3k_1X/(k_2 + k_3)$. Then increasing k_3, the only way in which increased surface could decrease Y and hence lower the induction period, will increase the observed rate.

Pumice as a Support for Copper–Chromium Oxide Catalysts in Dehydrogenations[1]

BY RALPH E. DUNBAR, DONALD COOPER AND ROBERT COOPER

Investigations involving the dehydrogenation of various alcohols to the corresponding aldehydes have been reported from time to time.[2] Oxide catalysts, pressed into pellets of approximately 0.15 g. each, have frequently been used.[3] Since the formation of the catalyst into pellets is extremely laborious and time consuming, it seemed advisable to find a suitable support so that the catalyst could be prepared directly for immediate use.

Experimental Part

The best results in the preparation of this catalyst were achieved by precipitating and decomposing with heat the catalyst in the presence of finely divided pumice. Two solutions were prepared as follows: (A) 300 ml. of a solution containing 87 g. of cupric nitrate hexahydrate and 10.4 g. of barium nitrate. The barium nitrate was first dissolved in the least amount of water possible at a temperature near the boiling point of water. The cupric nitrate hexahydrate was then added and the solution diluted to the 300 ml. required. Solution (B) was prepared from 300 ml. of a solution containing 50.4 g. of ammonium dichromate and 75 ml. of a 28% solution of ammonium hydroxide. Solution (B) was added to 177 g. of Italian, acid washed, pumice of size 20. This was allowed to digest for one hour on a steam-bath with frequent stirring. Solution (A) was then heated to 80° and added to solution (B) with thorough stirring. The treatment from this point was identical with that of Connor, Folkers and Adkins[4] except that the final decomposition was carried

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[1] Original manuscript received April 22, 1935.

[2] Bouveault, *Bull. soc. chim.*, [4] **3**, 119 (1908); Conant, Webb and Mendum, THIS JOURNAL, **51**, 1250 (1929); Adkins, Folkers and Kinsey, *ibid.*, **53**, 2714 (1931); Weston and Adkins, *ibid.*, **50**, 1930 (1928).

[3] Adkins, Kommes, Struss and Dazler, *ibid.*, **55**, 2992 (1933).

[4] Connor, Folkers and Adkins, *ibid.*, **54**, 1138 (1932).

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.

CONTRIBUTION FROM THE
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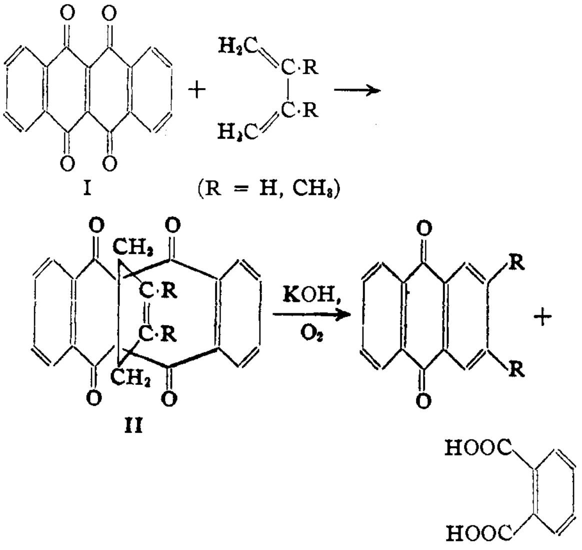
The Addition of Dienes to Naphthacenediquinone

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).