[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF HARVARD UNIVERSITY AND TRINITY COLLEGE]

Further Evidence on the Mills–Nixon Effect

BY WARREN C. LOTHROP

In view of much recent evidence[1] indicating that in the case of hydrindene no quantitative stabilization of one Kekulé form exists as had been proposed,[2] it seemed well to describe some further confirmatory observations of our own. The successful diazo coupling of 5-hydroxy-6-methylhydrindene[3] gave evidence in agreement with the above, and Table I contains the results of these coupling tests on 0.1-g. samples with excess diazotized *p*-nitroaniline.

TABLE I

Case	Soln., cc.	*N* NaOH	Crude product, g.	% yield
1	10.5	0.119	0.072	35.9
2	11.0	.226	.046	23.0
3	12.0	.415	.029	14.5
4	14.0	.679	.017	8.5
5	16.0	.932	.009	4.5
6	20.0	1.24	.002	1.0
7	15.0	2.49	.001	0.5

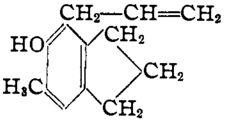
The apparent importance of the alkaline concentration to the coupling was investigated in further tests using buffered solutions and the theoretical quantities of a freshly prepared solution of *p*-nitrobenzenediazonium sulfate with the results given in Table II as the percentage yield of alkaline insoluble material. This seemed justifiable since the coupling products are the chief substances present which are insoluble in alkali and have all been reported and prepared by the same method. These figures indicate that the derivatives of hydrindene and tetralin are all inferior to β-naphthol in coupling ability and are more comparable with 2,4-dimethylphenol.

TABLE II

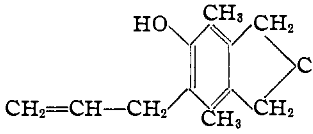
PER CENT. YIELD OF CRUDE COUPLING PRODUCT

Compound	*p*H 7.5	*p*H 11.3	10% NaOH
β-Naphthol	95.0	96.0	4.0
2,4-Dimethylphenol	71.5	52.5	5.8
5-Hydroxy-6-methylhydrindene (I)	69.0	68.7	0.5
5-Hydroxy-4,7-dimethylhydrindene (II)		69.5	5.7
6-Hydroxy-5,8-dimethyltetralin		55.5	7.0
1-Benzyl-2-hydroxynaphthalene	Alkali-soluble tars		
1,5-Diallyl-2,6-dihydroxynaphthalene	Alkali-soluble tars		

While this evidence seemed sufficient to classify hydrindene among the benzenoid compounds, samples of both I and II were converted into their allyl ethers and subjected to pyrolysis in sealed tubes, when both the ethers underwent the Claisen rearrangement to yield the corresponding substituted phenols (III) and (IV)



III



IV

These results are in complete agreement with all the evidence cited and with the similar case of fluorene.[4]

In conclusion the author wishes to express his appreciation to Professor L. F. Fieser for many helpful suggestions.

Experimental Part

The **preliminary coupling tests** (Table I) require no special description, but for the **buffered coupling tests** (Table II) the procedure was varied from the usual in that dioxane (5 to 10 cc.) was added to each 10-cc. portion of the buffer (containing 0.000675 mole of the substance to be tested) in order to achieve complete solution. The buffers were standard sodium and potassium phosphate mixtures, and the standardized diazonium solution was prepared[5] and standardized[6] as described in the literature.

5-Alloxy-6-methylhydrindene (allyl ether of I).—A mixture of 2.0 g. of 5-hydroxy-6-methylhydrindene (I), 2.2 g. of powdered anhydrous potassium carbonate and 1.8 g. of allyl bromide in 50 cc. of methyl ethyl ketone was refluxed for sixty-four hours and poured into water. The light brown oil which separated was warmed with 5% potassium hydroxide for one hour, recovered by ether extraction and distilled *in vacuo*, being thus obtained as a colorless oil (b. p. 95–97° at 3 mm.). The yield was 2.5 g. or 98%.

Anal. Calcd. for $C_{13}H_{16}O$: C, 82.92; H, 8.55. Found: C, 82.90; H, 8.88.

4-Allyl-5-hydroxy-6-methylhydrindene (III).—A mixture of 0.97 g. of the above allyl ether and 2.75 g. of dimethylaniline was heated in a sealed tube at 245° for

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[1] Arnold, THIS JOURNAL, **61**, 1405 (1939); Clapp, *ibid.*, **61**, 2733 (1939); Sandin and Evans, *ibid.*, **61**, 2916 (1939); Lindner, *et al.*, *Monatsh.*, **72**, 330, 335, 354, 361 (1939).

[2] Mills and Nixon, *J. Chem. Soc.*, 2510 (1930); Fieser and Lothrop, THIS JOURNAL, **58**, 2050 (1936).

[3] Fieser and Lothrop, *ibid.*, **59**, 945 (1937).

[4] Lothrop, *ibid.*, **61**, 2115 (1939).

[5] Hantzsch and Jochem, *Ber.*, **34**, 3337 (1901); Schoutissen, *Rec. trav. chim.*, **40**, 763 (1921).

[6] Hantzsch, *Ber.*, **33**, 2517 (1900).

one hour. The pale brown solution was then poured into cold dilute hydrochloric acid. On standing the product solidified in faintly purple needles. It weighed 0.83 g. (86%) and was soluble in alkali. The material had a phenolic odor and showed a characteristic tendency to sublime, filling the tube in which it was stored with a dense mass of fine needles (m. p. 43–45°).

Anal. Calcd. for $C_{13}H_{16}O$: C, 82.92; H, 8.55. Found: C, 82.86; H, 8.74.

5-Alloxy-4,7-dimethylhydrindene (allyl ether of II).—A mixture of 2.2 g. of 5-hydroxy-4,7-dimethylhydrindene (II) 2.2 g. of finely powdered anhydrous potassium carbonate and 1.8 g. of allyl bromide in 35 cc. of methyl ethyl ketone was refluxed for twenty-four hours. The product was a colorless oil distilling at 107–108° at 2 mm. The yield was nearly quantitative.

Anal. Calcd. for $C_{14}H_{18}O$: C, 83.14; H, 8.95. Found: 3, 83.20; H, 8.70.

5-Hydroxy-6-allyl-4,7-dimethylhydrindene (IV).—When a mixture of 1.34 g. of the above allyl ether and 3.00 g. of dimethylaniline was heated to 280° in a sealed tube and the amine was removed by dilute hydrochloric acid, the product was obtained in 75% yield as a pink solid. The color was removed by two crystallizations from petroleum ether but always returned on standing in contact with air. A sample stored in the ordinary way turned a bright violet in the course of two months while one kept in a sealed tube showed no color change. The melting point remained unaffected, however, at 66–67°.

Anal. Calcd. for $C_{14}H_{18}O$: C, 83.14; H, 8.95. Found: C, 83.38; H, 8.94.

Summary

The diazo coupling of and the rearrangement of the allyl ethers of 5-hydroxy-6-methylhydrindene and 5-hydroxy-4,7-dimethylhydrindene have been investigated with results which concur with much other evidence that the Mills–Nixon effect is at the most qualitative in the case of hydrindene.

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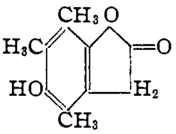
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

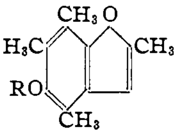
The Reaction between Quinones and Metallic Enolates. X. Trimethylquinone and the Enolates of β-Diketones[1]

BY LEE IRVIN SMITH AND E. W. KAISER[2]

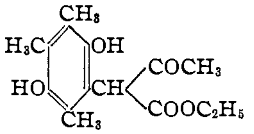
A few years ago, Smith and MacMullen[3] added the enolates of malonic ester and acetoacetic ester to trimethylquinone. From the malonic ester addition, one product, the isocoumaranone I, was obtained, while the addition of acetoacetic ester led to two substances, the isocoumaranone I, and the coumaron II. The formation of these products was interpreted as a primary 1,4-addition of the enolate to the quinone conjugated system which carried no substituent in the β-position, to give III (from acetoacetic ester), followed by the usual cleavages and ring closure.



I

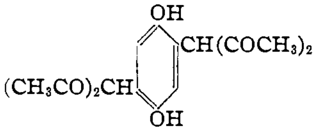


II, R = H
IX, R = Ac



III

Ionescu[4] studied the reaction between acetylacetone and *p*-benzoquinone. The reaction was interpreted as an initial 1,4-addition of the β-diketone (two molecules), leading first to IV (not isolated) which was then oxidized by excess quinone or by air to V (also not isolated). The latter



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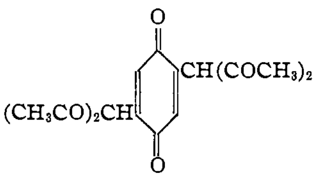
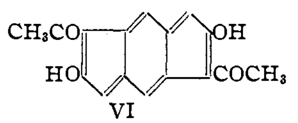


V



VI

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(1) Paper IX, *J. Org. Chem.*, **4**, 342 (1939).

(2) Abstracted from a thesis by E. W. Kaiser, presented to the Graduate Faculty of the University of Minnesota, in partial fulfilment of the requirements for the Ph.D. degree, August, 1939.

(3) THIS JOURNAL, **58**, 629 (1936).

(4) Ionescu, *Bull. soc. chim.*, **37**, 913 (1925); **41**, 1094 (1927); **51**, 171 (1932).