300. *The Condensation of 2 : 3-Dimethyl-1 : 3-butadiene and* p-*Benzoquinone.*

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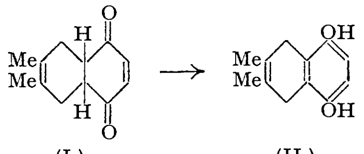
The paper describes a preliminary examination, using 2 : 3-dimethylbutadiene, of conditions for the quantitative estimation of conjugated butadienoid systems by combination with *p*-benzoquinone. At ordinary temperatures these compounds combine in 1 : 1 ratio. The product, m. p. 116°, on heating passes into an isomeride, m. p. 235°. Only the original product gives an oxime, but both isomerides yield the same acetyl derivative. The original product is therefore regarded as the normal adduct, and the higher-melting compound as the isomeric quinol derivative. Morgan and Coulson have already reported the addition of 2 : 3-dimethylbutadiene to *p*-benzoquinone in 2 : 1 ratio at higher temperatures. It is now shown that not only addition in 1 : 1 ratio under the conditions now described, but also addition in 2 : 1 ratio under Morgan and Coulson's conditions, can be made the basis of a method of estimating 2 : 3-dimethylbutadiene by measurement of uptake of *p*-benzoquinone.

THE Diels condensation between conjugated dienes and maleic anhydride is used for the estimation of the former by volumetric determination of the residual maleic anhydride (*Fette und Seife*, 1936, **43**, 93). Developed by Kaufmann under the name of " dienometry ", it has been introduced especially in the analysis of fats and of essential oils, a new constant having been established for them, the " diene index " (*Ber.*, 1937, **70**, 903, 905).

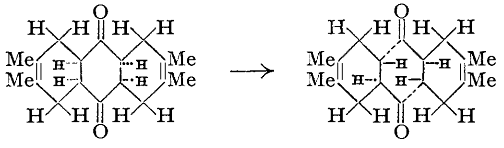
But these analytical applications are unfavourably influenced by phenomena of isomerisation, and, above all, by the possibility of the maleic anhydride's reacting with other unconjugated and even simple ethylene compounds by a process of addition involving the splitting of a C–H bond (Alder, *Ber.*, 1943, **76**, 27; Lora, *Rev. Acad. Farm. Madrid*, 1944, **10**, 1).

Consequently, while we were engaged on other work on condensations with *p*-benzoquinone (Lora and Fernandez, *Anal. Fis. Quím.*, 1944, **40**, 1178; 1946, **42**, 1183), we undertook the investigation of the quantitative determination of conjugated systems using this philodiene. This presupposed in every case a knowledge of the conditions for obtaining the addition product, in order to fix those most suitable for the quantitative application of the reaction. The estimation of *cyclo*pentadiene by its reaction with benzoquinone has been described by Wasserman (*J.*, 1936, 1032).

Among the compounds investigated, 2 : 3-dimethylbutadiene gave special results in its condensation with *p*-benzoquinone. Morgan and Coulson (*J.*, 1931, 2323) investigated it in alcoholic solution in a sealed tube at 97° for 5 hours, and obtained a product whose melting point was 202—203°, and whose formula corresponded to the addition of two molecules of diene to one of *p*-benzoquinone. Working at ordinary temperatures, we found that the alcoholic solution, treated with water, precipitated some crystalline needles of a pale yellow colour and m. p. 116°, whose analysis corresponded to a *compound* of one molecule of 2 : 3-dimethylbutadiene and one of *p*-benzoquinone.



(I.) (II.)



(III.) (IV.)

Morgan and Coulson's product (m. p. 202—203°), after melting, solidified and melted again at 304°. Ours (m. p. 116°) after melting solidifies at 185° and finally melts at 234°.

In both cases the new products are isomeric with their precursors : a similar phenomenon has been reported for adducts of butadiene and isoprene (Diels and Alder, *Ber.*, 1929, **62**, 2337). Morgan and Coulson, in view of the fact that their isomer is not capable of acetylation, did not consider it as a derivative of quinol, but rather as a stereoisomer (III and IV) analogous to that of bisisoprene–quinone (Diels and Alder, *loc. cit.*, p. 2366), probably originating through an intermediate form of quinol.

In our case both products acetylate and give the same *diacetyl* derivative (m. p. 134°), but only that of lower melting point gives an *oxime*. This shows that the isomerism leads to the quinol *form* (II), as is found in the transformation of monobutadiene–quinone (Diels and Alder, *loc. cit.*, p. 2362). D.R.-PP. 324,661 and 521,621 (*Chem. Zentr.*, 1930, II, 809; 1931, II, 1758) refer to these products of 1 : 1 addition of dimethylbutadiene and *p*-benzoquinone.

Neither of the two products (I and II) adds 2 : 3-dimethylbutadiene under Morgan and Coulson's conditions. With regard to (II), this was due to lack of the appropriate conjugation, and with regard to (I) it was because (I) isomerises to (II). The isomerisation can also be produced by the action of hydrochloric acid.

With regard to the analytical applications of the condensation, these were tried, in the first place in the cold, the basic reaction in this case being the formation of the 1 : 1-addition product. A procedure was also studied which involved heating the reactants in sealed tubes at 100° for 5 hours, calculations being then made on the assumption that addition had taken place in the 2 : 1 ratio. In each case the operation was carried out with excess of *p*-benzoquinone in alcoholic solution. The residual *p*-benzoquinone was estimated according to Willstätter and Majina's method (*Ber.*, 1910, **43**, 1171), the iodine liberated from an acid solution of potassium iodide being determined. The combined quinone was deduced as a difference between the initial amount, given by a blank determination, and the measured excess. As an example we give some results in the experimental section.

EXPERIMENTAL.

Condensation of 2 : 3-*Dimethylbutadiene and* p-*Benzoquinone*. 6 : 7-*Dimethyltetrahydro-α-naphthaquinone*.—The dimethylbutadiene used was prepared from pinacol by reduction with hydrobromic acid (Kyriakides, *J. Amer. Chem. Soc.*, 1914, **36**, 991). An alcoholic solution of *p*-benzoquinone (10 g.) and dimethylbutadiene (4 g.) was kept at room temperature for 4 hours. Water was then added. The pale yellow needles were filtered off and washed well with water to eliminate the excess of quinone. After being dissolved in alcohol and precipitated with water, the product (8·5 g.) was very pale yellow and had m. p. 116° (I). When heated above its melting point, it solidified between 186° and 190° to a white *product* which melted at 235° (II). When the preparation was repeated with different concentrations of benzoquinone and dimethylbutadiene, the result obtained was always the same (Found : C, 75·7; H, 7·7. $C_{12}H_{14}O_2$ requires C, 75·8; H, 7·4%).

Isomerisation with Hydrochloric Acid.—The product, m. p. 116° (2 g.), was dissolved in alcohol, a few drops of concentrated hydrochloric acid were added, and the mixture was boiled under reflux for 5—10 minutes. To the cooled solution, which had lost its yellow colour, water was added, and a white product was thus precipitated. This was collected, washed with water, and purified as described above. Crystallised from chlorobenzene, it had m. p. 235° (Found : C, 75·8; H, 7·7%).

1 : 4-*Diacetyl*-6 : 7-*dimethyl*-5 : 8-*dihydro*-1 : 4-*naphthaquinol*.—In separate flasks 1·5 g. of (I) and (II) were heated under a reflux for 2 hours with 10 g. of acetic anhydride. On cooling, beautiful crystals of the *diacetyl* compound separated, which on recrystallisation from alcohol gave white needles, m. p. 134° in both cases [Found : (I) C, 69·9; H, 6·5. (II) C, 69·8; H, 6·4. $C_{16}H_{18}O_4$ requires C, 70·1; H, 6·5%].

6 : 7-*Dimethyl*-5 : 8 : 9 : 10-*tetrahydro*-1 : 4-*naphthaquinone Dioxime*.—The test was carried out simultaneously with (I) and (II) in alcoholic solution using 1 g. of either, 1 g. of hydroxylamine hydrochloride, and the appropriate quantity of sodium hydroxide. In the case of (I), after ½ hour's heating, the *oxime* was formed, and was then recrystallised from alcohol. It had m. p. 234° (Found : N, 12·5. $C_{12}H_{16}O_2N_2$ requires N, 12·7%). In the case of (II), the starting product was always recovered unchanged even though heating was prolonged to 3 hours.

Reactions of (I) *and* (II) *with Dimethylbutadiene.*—An attempt was made to condense (I) and (II) with another molecule of dimethylbutadiene. Morgan and Coulson's method (*loc. cit.*) was followed, an alcoholic solution (50 c.c.) of (I) or (II) (0·6 g.) being heated with dimethylbutadiene (0·4 g.) in a sealed tube at 90—100° for 6 hours. In both cases the product was precipitated with water, collected, and washed. Purified as usual, and finally recrystallised from monochlorobenzene, the product was (II), m. p. 235°.

Analytical Application.—We used dimethylbutadiene, purified by distillation, and *p*-benzoquinone, purified by recrystallisation from alcohol. The operations were always carried out in alcoholic solution, and for each determination a blank was done using *p*-benzoquinone alone in the same quantity and at the same dilution. Two different types of method were used. In the one the reaction was allowed to go in the cold for 24 hours, as for the preparation of 6 : 7-dimethyltetrahydro-1 : 4-naphthaquinone, in which the ratio of diene to philodiene was 1 : 1. The results are in Table I. The second group of tests were carried out in sealed tubes at 90—100° in order to obtain the diene–philodiene ratio of 2 : 1, as was done by Coulson and Morgan (*loc. cit.*). The results are given in Table II.

TABLE I.

Diene taken.	Quinone added.	Quinone condensed.	Diene found.	Error, %.
0·2691	0·5016	0·3473	0·2657	1·3
0·2691	0·5016	0·3475	0·2639	1·9
0·1345	0·2142	0·1739	0·1325	1·4
0·1345	0·2142	0·1743	0·1326	1·4

TABLE II.

Diene taken.	Quinone added.	Quinone condensed.	Diene found.	Error, %.
0·2691	0·1908	0·1737	0·2638	1·9
0·2691	0·1908	0·1740	0·2642	1·5
0·1345	0·1825	0·0869	0·1329	1·2
0·1345	0·1825	0·0872	0·1328	1·2

In both cases the technique employed was the same in every detail. At the end of the period of reaction the product formed was precipitated with water, collected, and washed abundantly, the filtrate being collected quantitatively in a graduated flask. The volume was made up with water and portions were taken for the iodometric determination of benzoquinone. For this the volume taken was diluted to 150 ml. Excess of potassium iodide was added, and the solution acidified with hydrogen chloride and left in the dark for 10 to 15 minutes so that the liberation of iodine by the quinone should proceed to completion. Then the free iodine was evaluated with thiosulphate using starch indicator. At the same time a blank was carried out with *p*-benzoquinone. From the figures for quinone found in the blank, the excess found in the tests with dimethylbutadiene was subtracted, the value for the condensed quinone being thus obtained.

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