TABLE I

Isopropyl ester of...	CH_3-COOH	$ClCH_2$-COOH	Cl_2CH-COOH	Cl_3C-COOH	C_6H_5-COOH
Yield of ester from alcohol and acid, %	16.8	38.8	48.6	57.8	60.0
Yield of ester from propylene and acid, %	7.0	34.2	39.5	48.8	88.0
B. p., °C. (747 mm.)	87–89	149.5	164.0	173.5	215.5
n_D^{25}	1.3745	1.4175	1.4306	1.4409	1.4890
MR_D (obs.)	27.240	31.791	36.884	42.010	46.741
MR_D (calcd.)	26.823	31.770	36.717	41.664	46.551
d_4^{25}	0.8570	1.0812	1.1989	1.2911	1.0102

The results in Table I may be varied greatly by changing somewhat the conditions of the experiment. If carbon tetrachloride, for example, is used in conjunction with chloroacetic acid as a solvent or suspension medium and the mixture agitated, one mole of the acid can be practically converted to the ester in one hour.

Solubility of Propylene in Acids and Esters.—Propylene was passed into the flask containing the liquid compound with shaking at a pressure of 25 cm. of mercury above atmospheric. The flask was then brought to 64° and a weight taken. This process was repeated until there was no further gain in weight. The flask, containing a weighed amount of the compound, was fitted with a stopcock for weighing at this pressure. The results are recorded in Table II.

The propylene used in this study was obtained from the Carbon and Carbide Chemicals Corporation. Similar reactions are being investigated with other olefins and acids.

TABLE II

SOLUBILITY OF PROPYLENE IN GRAMS PER MOLE OF COMPOUND

No. of Cl sub.	0	1	2	3
Acetic acids	0.96	1.71	2.41	2.69
Isopropyl acetates	1.40	1.90	2.99	3.76

Summary

A method has been described by which propylene can be condensed with acids to form the corresponding esters.

The methods of esterification by condensation and by double decomposition have been compared, the order of ester formation being found the same when boron fluoride is the catalyst used.

The solubility of propylene in the acids and esters of the acetic acid series has been determined. The effect of this factor in determining the yields when condensing propylene with the various acetic acids has been noted.

A difference in the catalytic activity of boron fluoride and hydrochloric acid has been observed.

The effect of the hydroxyl and the carboxyl on the benzene nucleus has been noted.

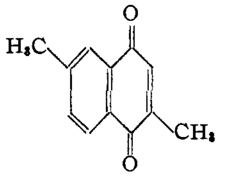
NOTRE DAME, INDIANA RECEIVED SEPTEMBER 4, 1934

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

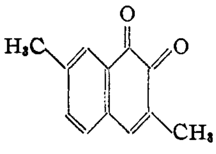
A Study of the Addition Reactions of Certain Alkylated Naphthoquinones[1]

BY LOUIS F. FIESER AND ARNOLD M. SELIGMAN

Although the unsubstituted quinones derived from benzene and naphthalene are known to combine with a great variety of different reagents by way of an addition to the double bond, the carbonyl group or the system of conjugated linkages, there has been little systematic investigation of the possible hindrance to such additions exerted by substituent groups since the classical work of Kehrmann on oxime formation, although two papers bearing on the problem have appeared during the course of the present study.[2] It occurred to us that particularly promising compounds for investigation would be found in the quinones I and II, which were prepared several years ago by Weissgerber and Kruber[3] from 2,6-dimethylnaphthalene.



I



II

As an example of a carbonyl addition it was of interest to establish the course of the oximation of 2,6-dimethyl-3,4-naphthoquinone, II. Like β-naphthoquinone itself, this was found to form a β- rather than an α-oxime, for there was obtained on reduction not the known 2,6-dimethyl-4,3-aminonaphthol[3] but an unstable substance which probably is the 3,4-isomer. The methyl group retards somewhat the oximation of the carbonyl group to which it is adjacent, but it does not alter the direction of the reaction.

Toward reagents which attack ordinary quinones by way of a 1,4-addition, the isomers I and II showed a marked difference in behavior. The

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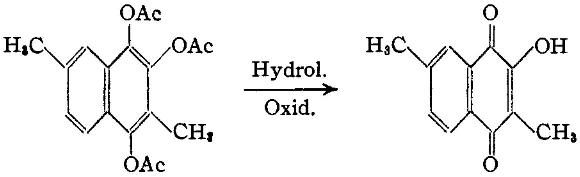
[1] The greater part of the work here reported was described in a thesis presented by the junior author in candidacy for the A.B. degree with honors.

[2] (a) Erdtmann, *Proc. Roy. Soc.* (London), **A143**, 177 (1933); (b) Madinaveita, *Anales soc. españ. fís. quím.*, **31**, 750 (1933).

[3] Weissgerber and Kruber, *Ber.*, **52**, 346 (1919).

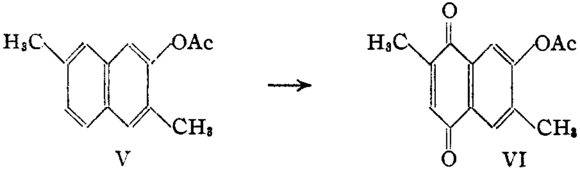
β-quinone reacts easily with the Thiele reagent (acetic anhydride–sulfuric acid), with sodium bisulfite, with aryl sulfinic acids and with aniline, and as far as can be judged from purely preparative work there is little difference in the velocity of 1,4-addition to the system $—CH{=}C(CH_3)\overset{|}{C}{=}O$ present in this compound and to the system $—CH{=}CH\overset{|}{C}{=}O$ of β-naphthoquinone. In the case of the isomer, I, there was little or no reaction under comparable conditions with any of the above reagents. The methyl group thus definitely inhibits this mode of addition to the 1,4-naphthoquinone. The same conclusion was reached by Madinaveita,[2b] who found that 2-methyl-1,4-naphthoquinone could be caused to add hydrogen bromide but not the Thiele reagent.

The α-quinone, I, is no more easily hydroxylated by the ordinary methods than is 2-methyl-1,4-naphthoquinone.[4] The hydroxyl derivative, IV, however, was obtained easily from the isomeric β-quinone (II) through the triacetate, III.



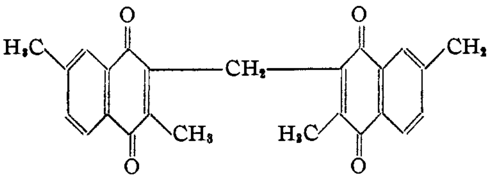
III IV

Since compound IV is of some interest in that it is a homolog of the phthiocol isolated from tubercle bacilli,[5] and since a quantity of the material was required for an oxidation study to be reported in a later paper, an attempt was made to prepare the compound by a shorter method. Thinking that it might be obtainable through the direct oxidation of the acetate of 2,6-dimethyl-3-naphthol (V), this oxidation was investigated. A quinone was indeed obtained, and in 30% yield, but it proved to be isomeric with the acetate of IV and not identical with it. Since the substance is yellow and hence undoubtedly a paraquinone it may be assigned the structure of VI. Oxidation thus attacks the ring not carrying the acetoxy group.



V VI

From what has been said of the 1,4-addition reactions it might be expected that of the isomers I and II the first one would manifest the greater reactivity toward other types of reagents and it was surprising to find that this is not the case. Diazomethane adds smoothly to the ethylenic linkage of α-naphthoquinone[6] and, although the mode of addition to β-naphthoquinone has not yet been established, it may be said that the ortho quinone reacts at least as fast as the isomer. With the dimethyl-β-naphthoquinone II, however, there was no sign of reaction and the quinone was recovered unchanged even after using somewhat drastic conditions. The α-isomer on the other hand reacted rather easily and gave in 40% yield the dinaphthylmethane derivative VII.



VII

The two hydrogen atoms lost in the insertion of the methylene radical probably serve to reduce some of the starting material. So far as we are aware this represents one further mode of reaction to be added to the long list of those of which diazomethane is capable.

Our most interesting observations have to do with the Diels diene reaction. Although the addition of dienes to para quinones has been studied extensively, no work with ortho quinones appears to have been published. This probably is not due to any lack of interest but rather to the fact that β-naphthoquinone, the most readily available starting material for such a study, is an extremely sensitive compound and gives with dienes reaction mixtures of a most unpromising character. Noting that the dimethyl derivative II is a decidedly more stable and easily handled compound, and having found it quite reactive to certain reagents, it seemed worth while to test its reaction with 2,3-dimethylbutadiene. Although there was no appreciable combination in alcoholic solution after twelve hours at the boiling point, it was found that a reaction can be brought about by heating an alcoholic solution of the quinone and the diene in a sealed tube at 100–105° and that after a period of a few days a

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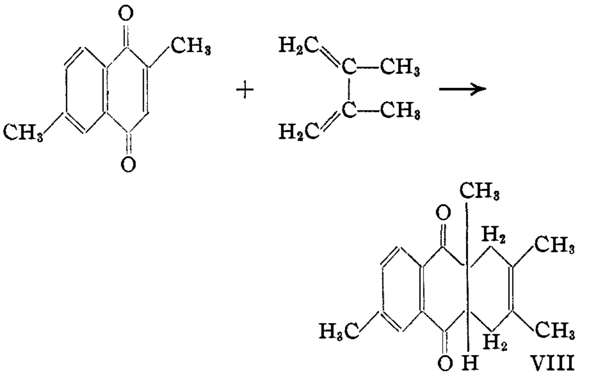
(4) Anderson and Newman, *J. Biol. Chem.*, **103**, 405 (1933).

(5) Anderson and Newman, *ibid.*, **101**, 773 (1933); **103**, 197 (1933).

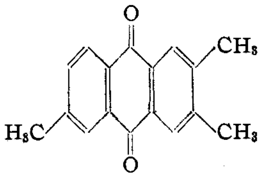
(6) Fieser and Peters, THIS JOURNAL, **53**, 4080 (1931).

crystalline reaction product can be isolated in fairly good yield. It was later found that 2,6-dimethyl-1,4-naphthoquinone (I) reacts even more rapidly and smoothly, giving in nearly quantitative yield a substance having the composition of an addition product. The properties of the compound are such as to indicate that it has the structure of VIII, and that it is thus the product of a normal diene addition.

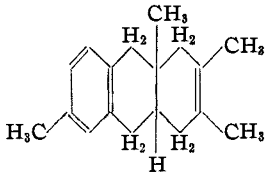


VIII

The substance is colorless, it melts at 75–77°, it adds bromine and it forms a mono-semicarbazone. The presence of the three carbon rings was established by dehydrogenation with sulfur, which gave in good yield a trimethylanthraquinone having the properties described for the 2,3,6-derivative, IX, by Morgan and Coulson.[7] The bridge methyl group presumably is eliminated as mercaptan. Reduction of the diketone by the Clemmensen method gave a liquid hydrocarbon of composition corresponding to formula X. All of these observations correspond well with the structure of a hydroaromatic diketone with a bridge methyl group, as indicated in formula VIII. The diene addition thus follows the normal course, in spite of the presence of the blocking methyl group attached to the quinone nucleus. That the reaction is somewhat slow is of no great consequence in preparative work for the quinone is not decomposed under the conditions required to effect combination.

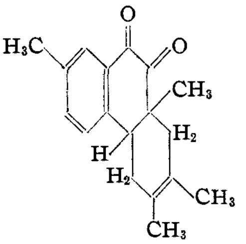


IX

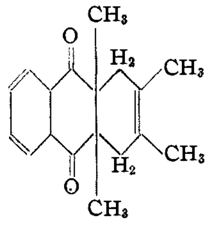


X

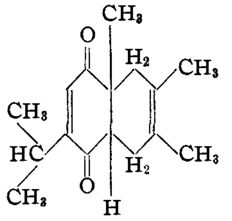
Our experiments with other substituted quinones are not yet very extensive, but the present indications are that the reaction is quite general. 2,6-Dimethyl-3,4-naphthoquinone yields with 2,3-dimethylbutadiene a yellow addition product melting at 106°.



XI



XII



XIII

Degradation with sulfur was in this case unsuccessful, the compound undergoing deep-seated decomposition. Further investigation will be required before the provisional structure XI can be accepted. Using the same diene (because of its availability and its symmetry) there was obtained from 2-methyl-1,4-naphthoquinone a liquid adduct having the expected composition and yielding 2,3-dimethylanthraquinone on treatment with sulfur. With 2,3-dimethyl-1,4-naphthoquinone[8] the reaction was very slow (100 hrs.), the addition product could not be obtained as a solid and, unlike the other adducts, it could not be distilled *in vacuo* without decomposition. The substance corresponding to formula XII thus was not obtained in an entirely pure condition. Thymoquinone gave a yellow, distillable oil; it is not yet known whether this is a mixture of isomers or a pure substance having the more probable of the two possible structures, XIII.

It is of interest that although alkyl groups retard some quinone additions beyond the point of practical usefulness, they do not appear to impose a serious limitation on the Diels reaction. Lee Smith has found this to be true also of the Grignard reaction.[9] The present extension of the diene synthesis offers a promising method of approach to substances of an interesting type and bearing some relationship to certain of the important sterols and sex hormones and we plan to

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(7) Morgan and Coulson, *J. Chem. Soc.*, 2551 (1929).

(8) Kruber, *Ber.*, **62**, 3044 (1929).

(9) Smith, THIS JOURNAL, **50**, 869 (1928).

investigate the matter further. It may be possible, also, by a suitable modification of the above reaction of thymoquinone, to synthesize compounds of the α-selinene series. A study of the diene additions of unsubstituted ortho quinones is also planned.

Experimental Part

1. Reactions of 2,6-Dimethyl-3,4-naphthoquinone (II)

In preparing the quantity of this quinone required it was possible to introduce some improvements in the process as described by Weissgerber and Kruber.[8] For the preparation of 2,6-dimethylnaphthalene-3-sulfonate 275 g. of the molten hydrocarbon was stirred mechanically in a bath kept at 135–140° and treated slowly with 190 cc. of concd. sulfuric acid preheated to 100°. After four hours 50 cc. more of the acid was added and the stirring and heating continued for one-half hour longer. The mixture was poured into 800 cc. of water and the 3-sulfonic acid which separated on cooling was collected (the 4-acid passes into the mother liquor). The solid was taken up in hot water, the solution was filtered from a little unchanged hydrocarbon and slowly neutralized while hot with potassium hydroxide. The potassium salt separated in large, colorless plates and was sufficiently pure for the next reaction; yield, 50%; *p*-toluidine salt, m. p. 286°.[10]

For the fusion of 200 g. of the potassium salt in a melt from 700 g. of potassium hydroxide and 40 cc. of water about one hour (mechanical stirring) was required and the average yield of the naphthol was 55%.

2,6-Dimethyl-4-amino-3-naphthol was obtained in 55–60% yield by the standard procedure[11] of coupling with diazotized sulfanilic acid, reducing the dye with sodium hydrosulfite, and crystallizing the amine hydrochloride in the presence of stannous chloride (anti-oxidant). Since the hydrochloride is only sparingly soluble in water it was best obtained by making the amine (0.5 mole) into a thin paste with 1 liter of water, pouring this into a solution of 25 cc. of concd. hydrochloric acid and 1 g. of stannous chloride in 3 liters of hot water, and stirring for one hour at 95°. The salt separated as colorless or pale pink needles on adding more acid to the filtered solution. The oxidation to the quinone was best carried out in several small portions. Seven grams of the hydrochloride was dissolved together with 10 cc. of concd. hydrochloric acid in 4 liters of water at room temperature and treated with a solution of the calculated amount of ferric chloride added all at once. The quinone separated as fine orange crystals in practically quantitative yield and in a very pure condition.

This quinone reacts easily with aniline; on adding the base to a cold, alcoholic solution of the material the red anilino quinone began to separate within one or two minutes. On heating on the steam-bath a solution of the quinone and *p*-toluene sulfinic acid the red color was soon discharged and the pale yellow sulfone was soon deposited. The crude material melted at 170° and was very sparingly soluble in the usual solvents.

2,6-Dimethyl-3,4-naphthoquinone-3-oxime.—To a solution of 2 g. of the quinone in 50 cc. of methyl alcohol was added a filtered solution prepared from 2 g. of hydroxylamine hydrochloride, 4 g. of fused sodium acetate, 5 cc. of water and 60 cc. of methyl alcohol. The mixture was refluxed for five hours and treated with 400 cc. of water to precipitate the orange oxime. This was dissolved in alkali and carefully precipitated with hydrochloric acid at the neutral point, thus leaving in solution dark red by-products. The oxime crystallized from benzene–ligroin as fine, bright orange needles melting with decomposition at 222°.

Anal. Calcd. for $C_{12}H_{11}O_2N$: C, 71.61; H, 5.51. Found: C, 71.63; H, 5.41.

The oxime was easily reduced in alkaline solution with sodium hydrosulfite, but the amine so formed proved to be so very sensitive to oxidation that we were unable to isolate it even in the form of the hydrochloride. Attempts were then made to isolate an acetate by acetylation in aqueous solution, but they were not entirely successful. Apparently the N-mono-acetyl derivative is itself highly reactive and when the reaction was pushed until an air-stable product resulted, the substance obtained did not crystallize well and it was not isolated in a pure condition (m. p. 245°, unsharp). The composition was closer to that of a tri- than a di-acetyl derivative.

This behavior of the amine is entirely different from that of 2,6-dimethyl-4-amino-3-naphthol, which is easily isolated even in the free state. For comparison the latter compound was acetylated as follows: 2 g. of the hydrochloride was suspended in 75 cc. of water at 5°, 1.5 cc. of acetic anhydride was added followed by 1 g. of sodium acetate. The acetyl derivative was formed at once and after shaking for a few minutes the solid was collected and crystallized repeatedly from glacial acetic acid. 2,6-Dimethyl-4-acetylamino-3-naphthol forms long, colorless needles melting at 107.5°. It dissolves easily in alcohol or benzene and it is soluble in warm, dilute alkali.

Anal. Calcd. for $C_{14}H_{15}O_2N$: C, 73.32; H, 6.60. Found: C, 73.41; H, 6.39.

Potassium 2,6-Dimethyl-3,4-naphthoquinone-1-sulfonate.—The finely-powdered dimethyl-β-naphthoquinone (1.5 g.) was dissolved by stirring in a solution of sodium bisulfite (0.6 g.) in water (15 cc.). After one-half hour the dark solution was diluted to a volume of 50 cc., acidified with sulfuric acid, and the sulfur dioxide expelled by boiling. After cooling (the hydroquinone can be obtained at this point as colorless crystals) dichromate solution was added, followed by saturated potassium chloride solution. The sulfonated quinone separated on cooling as bright red crystals. The material was crystallized from 75 cc. of water at 50°, adding 15 cc. of bromine water to destroy traces of impurities, filtering and adding potassium chloride solution. The product separated in the form of brilliant carmine-red needles which were dried at room temperature.

Anal. Calcd. for $C_{12}H_9O_5SK \cdot H_2O$: S, 9.95. Found: S, 9.81.

The quinone dissolves easily in cold water and on adding aniline to the solution a precipitate of the red anilino quinone soon forms. An interesting color change was observed on adding alkali to a cold aqueous solution of the quinone: the orange-red solution bleached at once and became faintly yellow.

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[10] Compare Fieser, THIS JOURNAL, **55**, 4977 (1933).

[11] See, for example, Fieser, *ibid.*, **51**, 940 (1929).

2,6-Dimethyl-1,3,4-triacetoxynaphthalene (III).—To a suspension prepared by dissolving 5 g. of 2,6-dimethyl-3,4-naphthoquinone in 30 cc. of acetic anhydride and cooling to 10° there was added slowly 0.5 cc. of concd. sulfuric acid while cooling. The quinone dissolved rapidly and toward the end of the reaction the temperature was allowed to rise to 60°. After the quinone had all dissolved the solution was poured into water and the tan precipitate was dried and crystallized from benzene–ligroin until pure. The triacetate forms stout, colorless needles melting at 161°.

Anal. Calcd. for $C_{18}H_{18}O_6$: C, 65.42; H, 5.50. Found: C, 65.45; H, 5.44.

2,6-Dimethyl-3-hydroxy-1,4-naphthoquinone (IV).—To a solution of 10 g. of the above triacetate in 200 cc. of alcohol there was added 10 g. of sodium hydroxide dissolved in 75 cc. of water. The resulting red solution was diluted with water, filtered and acidified, when the yellow hydroxy quinone separated in a very pure and crystalline condition (80% yield from the hydroxyl-free quinone). The quinone is very sparingly soluble in water and readily soluble in alcohol or benzene. Crystallization from benzene–ligroin gave stout, bright-yellow needles melting at 194°. The sodium salt is red in color.

Anal. Calcd. for $C_{12}H_{10}O_3$: C, 71.26; H, 4.99. Found: C, 71.09; H, 4.84.

The methyl ether was obtained by the use of diazomethane. (As was to be expected, the hydroxyquinone was not etherified on prolonged boiling with alcohol and sulfuric acid.) The compound formed fine, pale yellow needles melting at 108° from dilute methyl alcohol.

Anal. Calcd. for $C_{13}H_{12}O_3$: C, 72.19; H, 5.60. Found: C, 71.93; H, 5.38.

The acetate formed small yellow crystals, m. p. 75–76° from alcohol.

Anal. Calcd. for $C_{14}H_{12}O_4$: C, 68.83; H, 4.96. Found: C, 68.56; H, 5.05.

2. 2,6-Dimethyl-1,4-naphthoquinone and Related Compounds

The quinone was prepared by the method given in the literature[3] but it was purified by the following very convenient method. The crude oxidation product was dissolved in ether, the solution was shaken with decolorizing carbon for a few minutes, filtered and evaporated until crystals began to separate. After collecting the crop of crystals deposited on cooling, the mother liquor was treated with charcoal and evaporated as before. The process was continued until there was an almost negligible, dark residue, being careful each time to wash the yellow crystals free from dark mother liquor with fresh solvent. The material was all bright yellow in color and melted at 136–137°; yield, 60%.

In addition to the observations already made it may be noted that this quinone failed to react with sodium hypochlorite after standing for several days at room temperature. The quinone reacts with dilute alkali on being heated and in very small tests it is sometimes possible to obtain a clear, deep red solution of the hydroxyquinone. The solution more often becomes very dark and deposits a sparingly soluble substance which is probably the diquinone. This is the chief product of the air-oxidation of the hydroquinone in alkaline solution.

Addition of Diazomethane.—To an ethereal solution of diazomethane from 1.3 cc. of nitrosomethyl urethan there was added 1 g. of 2,6-dimethyl-1,4-naphthoquinone and sufficient benzene to bring the quinone into solution. The partially-filled flask was stoppered with a wired-on cork, heated on the steam-bath for fifteen minutes, and allowed to stand overnight. Clusters of fine, yellow needles had separated by this time in amount corresponding to 40% of the quinone used and the remainder of the starting material was recovered on working up the mother liquor. The result seemed independent of the excess of diazomethane used or the time allowed for the reaction and it is probable that the recovered quinone was present in the mother liquor in the form of the hydroquinone.

The reaction product, formula VII, is very sparingly soluble in the ordinary solvents. A sample for analysis was crystallized from nitrobenzene, when it formed very small, yellow needles melting at 300°. The substance is not acidic, it has the properties of a quinone (reducible), and it contains no nitrogen.

Anal. Calcd. for $C_{25}H_{20}O_4$: C, 78.10; H, 5.25. Found: C, 78.06; H, 5.62.

2,6-Dimethyl-7-acetoxy-1,4-naphthoquinone (VI).—2,6-Dimethyl-3-acetoxynaphthalene[3] (20 g.) was oxidized in glacial acetic acid solution (300 cc.) with a solution of 22 g. of chromic anhydride in 20 cc. of water diluted with 30 cc. of acetic acid. The reaction was controlled at the start by cooling and the mixture was later heated just below the boiling point for ten minutes and then poured into water. The quinone was then extracted with benzene and ether and the solution, dried and clarified, deposited the reaction product in a very pure condition; yield 30%. The compound crystallizes from glacial acetic acid as long, citron-yellow needles melting at 171°. The solution in concd. sulfuric acid is deep red, while in alkali it is purple red. The alkaline hydrolysis did not proceed well and the hydroxyquinone was not isolated.

Anal. Calcd. for $C_{14}H_{12}O_4$: C, 68.83; H, 4.96. Found: C, 69.08; H, 4.97.

2,6-Dimethyl-1,4,7-triacetoxynaphthalene.—On reductive acetylation of the above quinone it was found necessary to heat the material with acetic anhydride and zinc dust until the quinone was completely reduced and to add sodium acetate to complete the acetylation only after this point had been reached. When sodium acetate was present from the beginning the reaction followed an anomalous course and a product of unknown structure (m. p. 149–150°) was obtained.

The triacetate formed long, fine, colorless needles, m. p. 139°, from benzene–ligroin.

Anal. Calcd. for $C_{18}H_{18}O_6$: C, 65.42; H, 5.50. Found: C, 65.71; H, 5.63.

3. Diene Additions

For the preparation of 2,3-dimethylbutadiene by the dehydration of pinacol the catalytic method of Kyriakides[12] proved unreliable, and we found it much more

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[12] Kyriakides, This Journal, 36, 987 (1914).

efficient and simple to distil anhydrous pinacol or pinacolone through a tube of activated alumina heated to a temperature of 450–470° in an electric furnace. The pinacol was sent through the tube as rapidly as it could be distilled for otherwise the diene appeared to polymerize. The yield after fractionation was 70% of the theoretical amount.

The general procedure for carrying out the Diels reaction was as follows: a mixture of 1 g. of the quinone, 2 cc. of 2,3-dimethylbutadiene and 10–25 cc. of absolute alcohol (depending upon the solubility of the quinone) was sealed in a tube and heated in a steam-bomb at 100–105° until the reaction appeared to be complete. This usually required several days and as the steam supply was not continuous accurate times cannot be specified. In some cases the fading of the original color of the solution gave an indication of the progress of the reaction; in other cases it was more reliable to remove the tube from time to time, cool it thoroughly in ice and see if any starting material would crystallize. The addition products always remained in solution. With the para quinones there was no decomposition over the long period of heating, but 2,6-dimethyl-3,4-naphthoquinone is a more sensitive substance and in one instance the chief product isolated was the 2,6-dimethyl-3-hydroxy-1,4-naphthoquinone (probably formed by the addition of water or alcohol to the quinone, followed by oxidation). It was found inadvisable to use a too concentrated solution or a suspension, for the quinone decomposed badly when the solid was in contact with the hot glass. In some experiments with this quinone and with the para quinones a few drops of acetic acid added to the solution appeared to arrest the decomposition and to shorten the time of reaction but this point needs to be tested further. The yields were good; the crystalline product from 2,6-dimethyl-1,4-naphthoquinone could be obtained in nearly theoretical yield once seed was available.

In working up the reaction mixtures the general procedure was to dilute the alcoholic solution with water and extract with ether. The ethereal solution was washed well with water, dried over sodium sulfate, clarified with charcoal and the solvent evaporated. The residual material, if it was found to stand such treatment, was then distilled at 2 mm. pressure. The solids were crystallized from dilute methyl alcohol; they tend to separate as oils unless seed has been secured.

4. Reactions of the Addition Product from 2,6-Dimethyl-1,4-naphthoquinone and 2,3-Dimethylbutadiene (Compound No. 1)

The semicarbazone was prepared by refluxing for one hour a solution of the above compound and of semicarbazide in methyl alcohol. The reaction product separated from the hot solvent and it was recrystallized from glacial acetic acid as fine colorless needles, m. p. 263°. The compound failed to react further on using a large excess of semicarbazide and on prolonged boiling.

Anal. Calcd. for $C_{19}H_{23}O_2N_3$: C, 70.11; H, 7.13. Found: C, 70.45; H, 7.30.

The hydrocarbon, X, was prepared by refluxing for fifteen hours a mixture of 1.5 g. of the addition product, 15 cc. of concd. hydrochloric acid, 2 cc. of water, 10 cc. of glacial acetic acid and 4.5 g. of amalgamated zinc. Fresh acid was added frequently and 2 g. of zinc was added after ten hours. The cooled mixture was extracted with ether and the oil obtained was vacuum distilled repeatedly to separate it from a trace of higher boiling material. The hydrocarbon forms no picrate and it gives a red coloration to concd. sulfuric acid.

Anal. Calcd. for $C_{18}H_{24}$: C, 89.93; H, 10.07. Found: C, 89.72; H, 10.08.

Conversion to 2,3,6-Trimethylanthraquinone.—In a small two-bulb distilling flask a mixture of 1.5 g. of the addition product and 0.38 g. of sulfur was heated under gentle suction until no further gas was evolved and the liquid was then vacuum distilled. The yellow distillate solidified at once and it was crystallized from glacial acetic acid, and thus obtained as pale yellow needles melting at 232° (uncorr.).

Anal. Calcd. for $C_{17}H_{14}O_2$: C, 81.57; H, 5.64. Found: C, 81.82; H, 5.99.

The substance forms a characteristic red vat with alkaline sodium hydrosulfite solution and corresponds in other respects with the description of Morgan and Coulson,[7] who report a melting point of 240° (corr.). Since the yield in the sulfur treatment is good and the product easily purified, this is perhaps an easier synthesis of the anthraquinone than that employed by the English investigators.

The addition product No. 3 was converted in exactly the same way into 2,3-dimethylanthraquinone, m. p. 205–206°. Fairbourne[13] reports a melting point of 208°, Heller[14] gives a value of 205–206°.

ADDITION PRODUCTS OF QUINONES WITH 2,3-DIMETHYLBUTADIENE

Addn. prod.					Analyses, %			
					Carbon		Hydrogen	
No.	Formula	Quinone	Description	M. p., °C.	Calcd.	Found	Calcd.	Found
1[a]	VIII	2,6-Dimethyl-1,4-naphthoquinone	Colorless needles	75–77	80.55	80.45	7.52	7.46
2[b]	XI (?)	2,6-Dimethyl-3,4-naphthoquinone	Yellow needles	106	80.55	80.77	7.52	7.63
3	...	2-Methyl-1,4-naphthoquinone	Oil	..	80.25	80.57	7.14	7.42
4[c]	XII	2,3-Dimethyl-1,4-naphthoquinone	Oil	..	80.55	(79.63)	7.52	(6.84)
5	XIII (?)	Thymoquinone	Oil	..	77.99	77.85	9.01	9.18

[a] The cold solution in concd. sulfuric acid is purple and becomes deep red on warming. The compound decolorizes anhydrous bromine solution at once. [b] Gives a yellow solution in concd. sulfuric acid; insoluble in alkali but dissolves in alcoholic alkali with a yellow color and the yellow material precipitates on dilution with water; rather easily reducible with sodium hydrosulfite in dilute alcohol. [c] Decomposed on attempted vacuum distillation, not obtained pure. The substance failed to react with semicarbazide in boiling alcohol solution.

The properties and analyses of the new compounds are recorded in the above table.

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(13) Fairbourne, *J. Chem. Soc.*, **119**, 1573 (1921).

(14) Heller, *Ber.*, **43**, 2891 (1910).

Summary

2,6-Dimethyl-1,4-naphthoquinone does not react with certain reagents which easily add to the conjugated system of 2,6-dimethyl-3,4-naphthoquinone. Of the two isomeric quinones, on the other hand, only the α-quinone reacts with diazomethane, and this in an unusual manner. Both quinones, as well as other alkyl-substituted benzo- and naphthoquinones are capable of adding dienes, if somewhat slowly, making available an interesting type of compound containing bridge methyl groups between two cyclohexane rings.

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE UNIVERSAL OIL PRODUCTS COMPANY]

Isomerization of Normal Butenes

BY V. N. IPATIEFF, HERMAN PINES AND R. E. SCHAAD

The rearrangement of normal butenes in the presence of catalysts has not been studied quantitatively previously. Gillet[1] found that 1-butene changes into 2-butene when passed over heated aluminum sulfate. According to Hurd[2] such rearrangement also occurred during pyrolysis, with the ratio of the lower boiling 2-butene (0.5°) to the higher boiling 2-butene (2.5°) being 3/2.

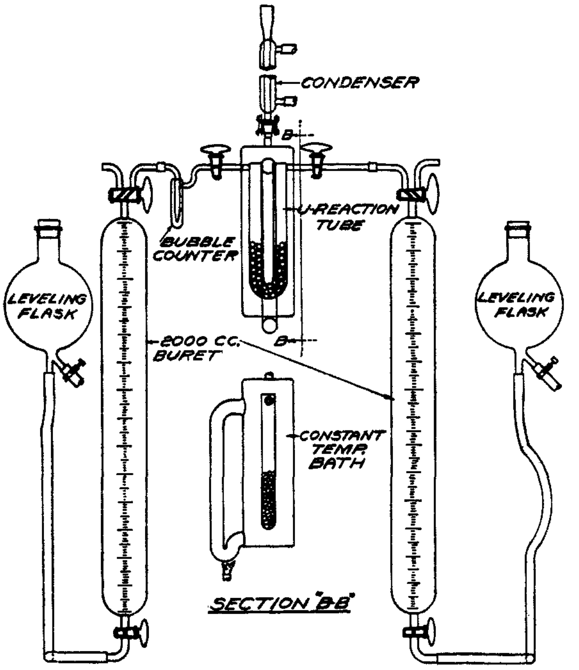
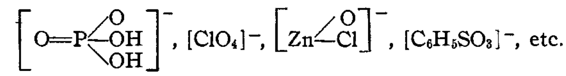


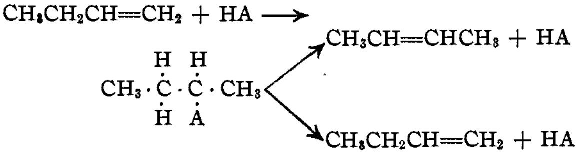
Fig. 1.

Runge and Mueller-Cunradi[3] patented a method of converting 1- into 2-butene by heating to 400–600° in an empty quartz tube or at 420° in contact with lime, aluminum phosphate, pumice or bauxite.

The present paper deals with rearrangements of normal butenes in the presence of catalysts. It is here assumed that the isomerization reaction consists of two steps: (1) formation of an addition product of the olefin with the catalyst and (2) the decomposition of such addition product whereby the same olefin or one with a different structure is split off and the catalyst is regenerated. In the following equations illustrating the isomerization, "A" represents groups such as



$$\left[\mathrm{O{=}P}\begin{matrix}\mathrm{O}\\ \mathrm{OH}\\ \mathrm{OH}\end{matrix}\right]^-,\ [\mathrm{ClO_4}]^-,\ \left[\mathrm{Zn}\begin{matrix}\mathrm{O}\\ \mathrm{Cl}\end{matrix}\right]^-,\ [\mathrm{C_6H_5SO_3}]^-,\ \text{etc.}$$



$$\mathrm{CH_3CH_2CH{=}CH_2 + HA \longrightarrow \begin{matrix} & & H & H & \\ CH_3 & \cdot & C & \cdot\ C & \cdot\ CH_3 \\ & & H & A & \end{matrix} \begin{matrix} \nearrow\ CH_3CH{=}CHCH_3 + HA \\ \\ \searrow\ CH_3CH_2CH{=}CH_2 + HA \end{matrix}}$$

Experimental Part

Apparatus and Procedure.—The apparatus used (Fig. 1) for studying isomerization of butenes at ordinary pressure consisted of two 2-liter gas burets, two leveling flasks, and a U-shaped reaction tube one-third full of glass spheres (3 to 5 mm. diameter) and surrounded by a jacket in which water and organic liquids were refluxed to maintain chosen, constant temperatures. The butene under investigation contained in the left buret was passed at a rate of 400–450 ml. per hour through a weighed quantity of the liquid isomerizing catalyst in the U-reaction tube and collected in the other buret which was always kept at approximately atmospheric pressure by manipulation of the leveling flasks.

For the experiments at superatmospheric pressure, the liquid butene under the desired nitrogen pressure in a steel charger provided with a gage glass, was passed through small copper tubing to the steel tube (13 mm. inside diameter) containing the solid catalyst. The speed of the butene flow was controlled by a needle valve at the exit end of the catalyst tube and a calibrated flowmeter

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[1] Gillet, *Bull. soc. chim. Belg.*, **29**, 192 (1920).

[2] Hurd, *Ind. Eng. Chem.*, **26**, 51 (1934); Hurd and Goldsby, THIS JOURNAL, **56**, 1812 (1934).

[3] Runge and Mueller-Cunradi, U. S. Patent 1,914,674, June 20, 1933; *C. A.*, **27**, 4253 (1933).