624. *Hydrogen Transfer. Part XII.*[1] *Dehydrogenation of "Blocked" Hydroaromatic Compounds by Quinones.*

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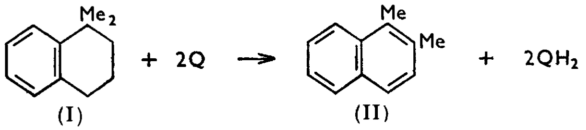
Aromatisation of *gem*-substituted hydroaromatic compounds by high-potential quinones has been shown to be accompanied by a Wagner–Meerwein rearrangement. The reaction has been tested for a number of mono- and bi-cyclic systems and for several related compounds in the aliphatic series. Syntheses of some new hydroaromatic compounds and naphthalenes are described.

THE evidence, accumulated in earlier papers (Parts II,[2] III,[3] X,[4] and XI [1]), concerning the mechanism of dehydrogenation of hydroaromatic compounds by quinones has strongly favoured a two-step ionic process involving a carbonium ion as intermediate. Viewed in this light the reaction is seen to possess the characteristics of a unimolecular elimination (E_1).[5] In the dehydrogenation the leaving group is the hydride ion (H^-), and the quinone assumes the rôle of solvent or electrophilic catalyst in effecting the ionisation. Unimolecular elimination is, of course, but one of a number of reactions which a carbonium ion intermediate may undergo.[5] Thus substitution, both intra- and inter-molecular, as well as a variety of rearrangements may compete with the simple elimination process. It is therefore to be expected that hydrogen-transfer to quinones of high potential should be capable of considerable elaboration in that, for certain donor structures, reactions more subtle than the conventional dehydrogenation might occur. This has been found to be so, and in this and the following three papers some alternative transfer reactions are examined.



(I) (II)

The present paper describes hydrogen-transfers which are accompanied by a Wagner–Meerwein rearrangement. In particular, consideration is given to the dehydrogenation of hydroaromatic systems in which aromatisation is formally "blocked" by *gem*-substituents (dialkyl, diaryl, or arylalkyl). Two examples have been the subject of a preliminary report,[6] and the conversion of 1,1-dimethyltetralin (I) into 1,2-dimethylnaphthalene (II) by high-potential quinones illustrates the process. The course of this reaction is in direct contrast to that followed by the conventional methods of dehydrogenation. Catalytic dehydrogenation, as well as dehydrogenation by elemental sulphur and selenium, usually results in the elimination of a blocking substituent.[7] Some exceptions to this general rule have been noted by Adkins *et al.*[8] but even in these cases, which involve the use of a specially prepared nickel–kieselguhr catalyst, the rearrangement is by no means the exclusive reaction. We have now examined the dehydrogenation of a wide range of *gem*-substituted hydroaromatic compounds by quinones and found that in all cases the sole aromatised product is that formed by rearrangement.

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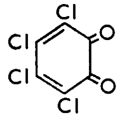
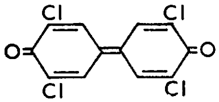
[1] Part XI, Braude, Jackman, Linstead, and Shannon, preceding paper.
[2] Braude, Jackman, and Linstead, *J.*, 1954, 3548.
[3] Braude, Jackman, and Linstead, *J.*, 1954, 3564.
[4] Barnard and Jackman, *J.*, 3110.
[5] Ingold, "Structure and Mechanism in Organic Chemistry," Bell, London, 1953.
[6] Linstead, Braude, Jackman, and Beames, *Chem. and Ind.*, 1954, 1174.
[7] Linstead, *Ann. Reports*, 1936, **33**, 294; Linstead *et al.*, *J.*, 1936, 470; 1937, 1140, 1146; 1940, 720, 1127; Plattner in "Newer Methods of Preparative Organic Chemistry," Interscience Publ. Inc., New York, 1948, p. 21; Cocker *et al.*, *J.*, 1952, 72; 1953, 2355.
[8] Adkins and Davies, *J. Amer. Chem. Soc.*, 1949, **71**, 2955; Adkins and England, *ibid.*, p. 2958.

Three of the high-potential quinones examined in Part IV [9] have been employed in the present investigation. They are tetrachloro-1,2-benzoquinone (III), 3,3',5,5'-tetrachloro-4,4'-diphenoquinone (IV), and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (V). Of these, the last is the most powerful but the first is the most readily available.


(III)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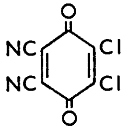
(V)

The attempted dehydrogenation of β-ionone with tetrachloro-1,2-benzoquinone yielded only polymeric material. To overcome this the corresponding propylene ketal was examined. In refluxing benzene much polymerisation occurred. However, the ultraviolet-light absorption of the recovered monomeric material indicated some dehydrogenation (<10%) to 4-(3-pseudocumyl)buten-2-one:[10] the protecting group had been lost, presumably under the influence of traces of hydrogen chloride which are usually formed during reactions with the quinone.[11] When the dichlorodicyanoquinone (V) was used the proportion of dehydrogenated material in the monomeric fraction increased to 19%. Again the product was the ketone rather than the ketal. In contrast, dehydro-β-ionone was rapidly dehydrogenated by tetrachloro-1,2-benzoquinone to the aryl ketone, which was isolated as its 2,4-dinitrophenylhydrazone. This ease of reaction is, of course, a consequence of the cyclohexa-1,3-diene structure of dehydro-β-ionone. β-Ionone itself resembles cyclohexene in its reactivity, the unsaturated side chain adding little to the stabilisation of the intermediate carbonium ion because of the steric inhibition of resonance in this system.[12] The detailed results of these experiments are presented in Table 1.

TABLE 1. *Dehydrogenation of β-ionone and related compounds in benzene at* 80°.

Compound and concn.	Quinone and concn.	Time	Recovered (%)	Dehydrogn (%)
β-Ionone 0·50M	(III) 1·10M	20 hr.	80	0
β-Ionone propylene ketal 0·36M	(V) 0·72M	2 hr.	49	19
,, ,, ,, 0·57M	(III) 1·16M	20 hr.	58	<10
,, ,, ,, 0·64M	(III) 1·32M	20 hr.	95	<10
Dehydro-β-ionone 0·25M	(III) 0·26M	2 min.	35	87
,, 0·14M	(III) 0·15M	10 min.	52	84

The dehydrogenation of 1,5,5-trimethyl-3-methylenecyclohexene was described in a preliminary note [6] although at that time the compound was believed to be the homo-annular isomer. The conversion of the diene into isodurene is rather involved as it requires a prototropic shift as well as a Wagner–Meerwein rearrangement. Dichlorodicyanoquinone reacted rapidly at room temperature with the diene, but isodurene (1,2,3,5-tetramethylbenzene) was only a minor product. The major product was a pale yellow solid decomposing at 165°, which analysis indicated was a 1 : 1 adduct derived from the two reactants. Its infrared spectrum possessed no hydroxyl absorption but had bands at 2254 ($C{\equiv}N$) and 1695 cm.$^{-1}$ ($C{=}O$). These, together with the ultraviolet-light absorption [$\lambda_{max.}$ 2500 Å (ε 7500)], suggest that the compound is a normal Diels–Alder adduct in which the side of addition to the quinone is uncertain. This result is in accord with the fact that the diene readily forms an adduct with maleic anhydride (see below) and with the very high reactivity with dienes shown by cyano-quinones. The use of tetrachloro-1,2-benzoquinone increased the yield of isodurene, but again there was, as by-product, a

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[9] Braude, Brook, and Linstead, *J.*, 1954, 3569.

[10] Lowe, Torto, and Weedon, *J.*, 1958, 1855.

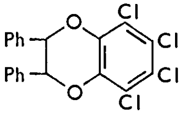
[11] Braude, Linstead, and Wooldridge, *J.*, 1956, 3070.

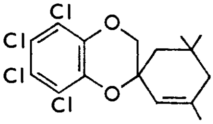
[12] Braude, Jones, Koch, Richardson, Sondheimer, and Toogood, *J.*, 1949, 1890.

crystalline 1 : 1 adduct, whose ultraviolet spectrum is very similar to that of the adduct (VI) prepared by Horner and Merz from the quinone and *trans*-stilbene.[13] Neither adduct shows a carbonyl stretching band in the infrared spectrum but both have an intense band near 1425 cm.$^{-1}$, apparently a C–O stretching frequency. As the compound yields no formaldehyde on ozonolysis, its structure is most probably (VII) although alternative structures arising from the isomeric homoannular diene cannot be excluded. Tetrachlorodiphenoquinone (IV), which, although less reactive than the other two quinones, is not as prone to side reactions, gave the highest yield of isodurene. Chloranil was the least reactive. These results are summarised in Table 2.

Experiments on the dehydrogenation of seven 1,1-disubstituted tetralins by tetrachloro-1,2-benzoquinone are recorded in Table 3. From that with 1,1,6-trimethyltetralin a small quantity (2%) of a by-product was recovered with the expected trimethylnaphthalene. The same compound was obtained when 1,2,6-trimethylnaphthalene was heated with the quinone in benzene, and analytical and spectroscopic data indicated that it was a hexamethylbinaphthyl. Naphthalene itself under similar conditions gives 1% of 2,2′-binaphthyl. The dehydrogenation of 1,1-diethyl- and 1,1-di-isopropyl-tetralin led to the hitherto unknown 1,2-diethyl- and 1,2-di-isopropyl-naphthalene. 1,2-Di-isopropylnaphthalene is noteworthy in that it does not yield solid complexes with picric acid, styphnic acid, or 2,4,7-trinitrofluorenone. 1-Methyl-1-phenyltetralin underwent phenyl migration exclusively, the sole product being 1-methyl-2-phenylnaphthalene.

(VI)





(VII)

TABLE 2. *Dehydrogenation of* 1,5,5-*trimethyl*-3-*methylenecyclohexene in benzene.*

Concn. (M) of diene	Quinone and concn. (M)	Temp.	Time (hr.)	Recovered (%)	Isodurene (%)	By-product (%)
0·68	(V) 0·81	20°	0·17	62	9	91
1·84	(III) 2·03	20	0·17	92	35	22
0·17	(IV) 0·21	80	4	90	55	—
0·40	Chloranil 0·43	80	20	91	0	—

TABLE 3. *Dehydrogenation of* 1,1-*disubstituted tetralins in benzene at* 80° (*reaction time,* 20 *hr.*).

Tetralin and concn. (M)		Quinone and concn. (M)	Recovered hydrocarbon (%)	Dehydrogn. (%)
1,1-Me$_2$	0·40	(III) 0·88	90	34
,,	0·40	,, 1·76	82	60
,,	0·40	,, 3·52	50	12
,,	0·80	,, 3·52	54	48
,,	0·48	(V) 1·06	78	84[a]
1,1-Et$_2$	1·20	(III) 2·65	85	40
1,1-Pr$^i_2$	1·08	,, 2·72	93	57
1-Me-1-Ph	1·07	,, 2·54	90	56
1,1-Ph$_2$	0·36	,, 0·73	96	47
-1-spirocyclopentane	0·31	,, 1·30	99	50
-1-spirocyclohexane	0·26	,, 1·32	95	63

[a] 5 hours.

The reaction of tetralin-1,1-spirocyclopentane with four molecular equivalents of tetrachloro-1,2-benzoquinone resulted in rearrangement and complete dehydrogenation to phenanthrene. The spirocyclohexane, on the other hand, rearranged to 1,2-cyclohepteno-naphthalene but no further unsaturation was introduced into the seven-membered ring. This is a consequence of a steric factor which is elaborated in the following paper.

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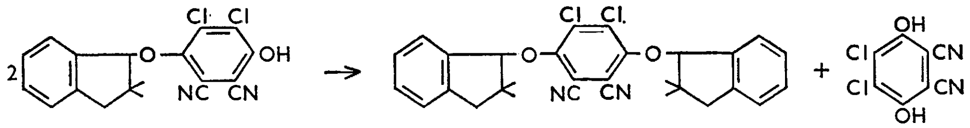
[13] Horner and Merz, *Annalen*, 1950, **570**, 89.

Indane reacted smoothly with dichlorodicyanoquinone (V), to yield indene which was isolated as its bromohydrin. Extension of this reaction to 2,2-dimethylindane did not yield the expected 1,2-dimethylindene, but instead gave a colourless crystalline compound, which from its analysis appeared to be a bis(dimethylindanyl) ether formed from the corresponding quinol. The infrared spectrum showed bands at 2239 (C≡N) and 1401 cm.$^{-1}$ (ether) and a doublet at 1383 and 1357 cm.$^{-1}$ (CMe_2). There were no bands corresponding to OH, C=O or CMe. The compound therefore has structure (IX) and presumably arises from the monoether (VIII). That in this system the intermediate ion-pair collapses to the ether rather than rearranging and undergoing elimination is probably a consequence of the planar nature of the cyclopentene ring which precludes the ideal orientation of leaving and migrating groups.

The octahydro-octamethylanthracene (X) was inert under conditions where all the tetralins reacted with tetrachloro-1,2-benzoquinone. This establishes the point that the reaction commences by attack at benzylic or allylic hydrogen atoms.

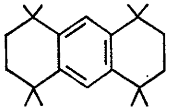
Attempts to extend the rearrangement to acyclic systems failed, owing to a conformational effect discussed in the following paper. Both 1,1,1-triphenylethane and 1,1,1,2-tetraphenylethane were recovered unchanged after being heated with dichlorodicyanoquinone in benzene at 80° for 160 hours.



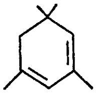
(VIII) (IX)

In summary, a number of simple "blocked" hydroaromatic systems are readily dehydrogenated by quinones to rearranged aromatic structures but the reaction is limited by steric effects and electronic activation.

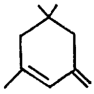
Preparations.—Attempts to form the ethylene ketal of β-ionone gave a product, whose ultraviolet absorption was that of an impure trienol ether rather than of the expected ketal. However, propylene glycol reacted smoothly with β-ionone to give the desired propylene ketal.



(X)



(XI)



(XII)

In the preliminary communication[6] the dehydrogenation to isodurene of a diene believed at the time to be 1,3,5,5-tetramethylcyclohexa-1,3-diene (XI) was described. The diene was prepared by the action of methylmagnesium iodide on isophorone followed by dehydration as described by Kharasch and Tawney,[14] who assigned structure (XI) to it because of the ease with which it formed as adduct with maleic anhydride. Wheeler's recent observations[15] indicate that it is in fact 1,5,5-trimethyl-3-methylenecyclohexene (XII). We agree with Wheeler's structure which is based on the infrared and ultraviolet absorption and the formation of formaldehyde on ozonolysis. We do not, however, concur with his statement that the diene forms a maleic anhydride adduct only under the influence of acid, for we obtained it by using purified maleic anhydride in refluxing benzene. The adduct itself appears to be normal. It gives no formaldehyde on ozonolysis and its infrared spectrum is very similar to that of the corresponding adduct of cyclohexa-1,3-diene.

1,1-Disubstituted tetralins (XIV) were prepared by the method of Perlman *et al.*[16]

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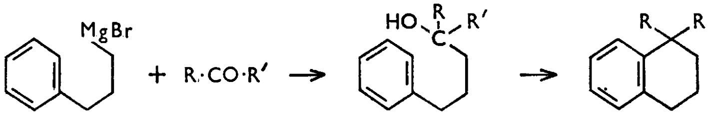
[14] Kharasch and Tawney, *J. Amer. Chem. Soc.*, 1941, **63**, 2308.

[15] Wheeler, *J. Org. Chem.*, 1955, **20**, 1672.

[16] Perlman, Davidson, and Bogert, *J. Org. Chem.*, 1937, **1**, 300.

This proved effective for a number of compounds including the corresponding spirocyclopentane and -hexane derivatives. Preservation of the quaternary carbon atom during cyclisation was confirmed for each example by oxidation to the corresponding α-substituted homophthalic acid. Two alcohols failed to undergo cyclodehydration. The di-t-butyl alcohol (XIII; $R = R' = Bu^t$) gave an uncyclised hydrocarbon which yielded benzoic acid on oxidation and, from its infrared spectrum, appeared not to possess a terminal methylene group. The carbonium-ion intermediate derived from this alcohol will possess considerable strain energy[17] which will be increased on cyclisation. Presumably the steric strain in the ion can be partially relieved by elimination, to afford the open-chain olefin (XV). 1,1-Di-*p*-methoxyphenyl-4-phenylbutan-1-ol could not be induced to undergo cyclodehydration but instead yielded, under a variety of conditions, an olefin which from its analysis and light absorption was the triarylbut-1-ene (XVI). The course of this reaction is probably due to the greatly reduced electrophilic character of the intermediate di-*p*-methoxyphenylmethyl ion. An E_1 elimination is preferred to electrophilic attack on the phenyl group. Alternatively, one may regard the failure to cyclise as a consequence of a complete lack of phenyl participation (Ar_1-5 or Ar_2-6)[18] in the forward step of the equilibrium $ROH_2^+ \rightleftharpoons R^+ + H_2O$.



(XIII) (XIV)

(XV) $Ph\cdot[CH_2]_2\cdot CH{=}CBu^t_2$ $Ph\cdot[CH_2]_2\cdot CH{=}C(C_6H_4\cdot OMe)_2$ (XVI)

The octahydro-octamethylanthracene (X) was prepared by the method of Bruson and Kroeger,[19] and 2,2-dimethylindane by Wolff–Kishner reduction of 2,2-dimethylindan-1-one.

EXPERIMENTAL

Microanalyses were carried out in the Microanalytical Laboratory (Miss J. Cuckney) and ultraviolet and infrared spectra were measured in the Spectrographic Laboratory (Mrs. A. I. Boston and Mr. R. L. Erskine) of this Department. Unless otherwise stated, ultraviolet spectra refer to ethanol solutions.

Preparation of Quinones.—Tetrachloro-1,2-benzoquinone was obtained from Messrs. Hopkin and Williams Ltd. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone was prepared by Brook's method,[20] and 3,3′,5,5′-tetrachloro-4,4′-diphenoquinone by that described in Part XI.[1]

Reaction of β-*Ionone with Ethylene Glycol.*—β-Ionone (20 g.), ethylene glycol (20 ml.), toluene-*p*-sulphonic acid (0·3 g.), and dry toluene (200 ml.) were refluxed and the water formed was removed in a Dean and Stark apparatus. After 6 hr. the mixture was washed with saturated sodium hydrogen carbonate solution, followed by water. The solvent was removed from the dried (Na_2SO_4) solution, and the residue distilled. The product (10 g., 43%), b. p. 80°/0·5 mm., n_D^{20} 1·4985 (Found: C, 76·5; H, 10·3. $C_{15}H_{24}O_2$ requires C, 76·3; H, 10·2%) had $\lambda_{max.}$ 2260 (ε 9440) and 2790 Å (ε 2830). The infrared spectrum had no OH stretching band.

β-*Ionone Propylene Ketal.*—This was prepared in 85% yield by the method of Bachli and Schinz.[21] The redistilled material had b. p. 71°/0·06 mm., n_D^{20} 1·4889, $\lambda_{max.}$ 2370 Å (ε 8400).

1,5,5-*Trimethyl*-3-*methylenecyclohexene.*—The diene was prepared in 84% yield from isophorone by Wheeler's method.[15] The redistilled product had b. p. 59—61°/18 mm., n_D^{21}

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[17] Brown *et al.*, *J. Amer. Chem. Soc.*, 1953, **75**, 1.

[18] Heck and Winstein, *J. Amer. Chem. Soc.*, 1957, **79**, 3105, 3114.

[19] Bruson and Kroeger, *J. Amer. Chem. Soc.*, 1940, **62**, 36.

[20] Brook, *J.*, 1952, 5040.

[21] Bachli and Schinz, *Helv. Chim. Acta*, 1951, **34**, 1160.

1·4706, $\lambda_{max.}$ 2350 Å (ε 11,000). The spectrum was unchanged at 80° and in the presence of acetic acid (2% v/v) at 24° and 80°.

1,5,5-*Trimethyl*-3-*methylenecyclohexene*.—*Maleic anhydride adduct.* Pure maleic anhydride (1·38 g.; m. p. 54°) and the diene (1·90 g.) in dry benzene (3·5 ml.) were refluxed for 30 min. by which time the yellow colour had faded. Next morning, cooling at −40° induced crystallisation of the adduct as colourless prisms (1·44 g., 44%), m. p. 98—99° (Found: C, 71·7; H, 7·8. Calc. for $C_{14}H_{18}O_3$: C, 71·8; H, 7·7%). The infrared spectrum of the adduct in chloroform had strong bands at 1852, 1770, 1078, 949, and 920 cm.$^{-1}$, which may be compared with the spectrum of the maleic anhydride adduct of cyclohexa-1,3-diene (strong bands at 1838, 1773, 1083, 950, and 911 cm.$^{-1}$).

Ionene.—This hydrocarbon was prepared in 53% yield from β-ionone by the method of Bogert and Fourman.[22] The redistilled product had b. p. 246—248°, n_D^{21} 1·5239, $\lambda_{max.}$ 2160 (ε 9050), 2690 (ε 660), and 2780 Å (ε 660).

1,1-*Disubstituted Tetralins*.—These compounds were prepared by the general method used by Bogert and his co-workers [16, 23] which is here described for 1,1-diethyltetralin.

3-Phenylpropyl bromide (94 g.) was added slowly to a stirred mixture of magnesium turnings (12·0 g.) and ether (100 ml.). When the reaction was complete, dry diethyl ketone (42 g.) was added dropwise to the cooled and stirred solution. The mixture was refluxed for 5 hr., kept at room temperature overnight, and then decomposed with ice and dilute hydrochloric acid. The product was extracted with ether, dried (Na_2SO_4), and distilled to give the crude alcohol (71 g., 73%), b. p. 118—124°/0·8 mm.

The alcohol (71 g.) was slowly added with stirring to 85% sulphuric acid (150 ml.), cooled by ice. Then stirring was continued for a further 20 min. and the mixture extracted with light petroleum (b. p. 60—80°). The extract was washed with 85% sulphuric acid, water, and sodium carbonate solution. Removal of the solvent from the dried (Na_2SO_4) extract and distillation of the residue from sodium afforded 1,1-diethyltetralin (38 g.).

Yields, physical constants, and analytical data of compounds prepared by this method are given in Table 4.

TABLE 4. 1,1-*Disubstituted tetralins.*

	Alcohols (XIII)			Tetralins (XIV)						
Subst.	B. p./mm.	n_D^{20}	Yield (%)	B. p./mm.	n_D^{20}	Yield (%)	Found (%) C	Found (%) H	Reqd. (%) C	Reqd. (%) H
R = R′ = Me * ...	100—103°/0·3	1·5046	75	40°/0·04	1·5278	50	90·2	10·3	90·0	10·0
R = R′ = Et	118—124°/0·8	—	73	68°/0·3	1·5286	58	89·6	10·4	89·4	10·6
R = R′ = Pr^i	124—128°/0·1	1·5100	58	80°/0·03	1·5251	76	88·9	11·2	88·9	11·1
R = Me; R′ = Ph	210—212°/0·05	1·5646	35	100°/1	1·5872	66	91·8	8·4	91·9	8·1
R = R′ = Ph	199—204°/0·7	1·6056	25	M. p. 125°	—	45	93·0	7·3	93·0	7·1
-spirocyclopentane *	120°/0·5	1·5248	42	86°/0·7	1·5545	80	—	—	—	—
-spirocyclohexane *	133°/0·2	1·5288	29	103°/0·1	1·5547	83	89·8	10·1	90·0	10·0

* Known compounds.

Attempted Preparation of 1,1-*Di-t-butyltetralin*.—To a stirred solution of the Grignard reagent from 3-phenylpropyl bromide (80 g.) in ether (200 ml.) was added di-t-butyl ketone [24] (60 g.) in anhydrous toluene (250 ml.). The ether was removed and the toluene solution refluxed for 15 hr. Working-up yielded an oil which gave fractions (*a*) b. p. 60—62°/12 mm., n_D^{23} 1·4578 (50 g.), (*b*) b. p. 40°/1·5 mm., solid (5 g.), (*c*) b. p. 90—95°/1·5 mm., n_D^{23} 1·5167 (12 g.), and (*d*) b. p. 120—130°, n_D^{23} 1·5210 (8 g.).

Fraction (*d*) (8 g.) was treated with 85% sulphuric acid and worked up as above, to yield an oil (4·0 g.), b. p. 120—126°/1·0 mm., n_D^{23} 1·5231 (Found: C, 88·8; H, 10·9. $C_{18}H_{28}$ requires C, 88·6; H, 11·4%). This *hydrocarbon* showed only very weak absorption at 901 cm.$^{-1}$ and therefore did not contain a terminal methylene group.

A solution of the hydrocarbon (1 g.) in glacial acetic acid (20 ml.) was slowly added to a refluxing solution of chromium trioxide (10 g.) in acetic acid (10 ml.) and water (10 ml.). Refluxing was continued for 1 hr. and the solution was then cooled and diluted with water

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[22] Bogert and Fourman, *J. Amer. Chem. Soc.*, 1933, **55**, 4670.
[23] Bogert, Davidson, and Apfelbaum, *J. Amer. Chem. Soc.*, 1934, **56**, 959.
[24] Whitmore and Stahly, *J. Amer. Chem. Soc.*, 1933, **55**, 4153.

(100 ml.). The aqueous solution was extracted with chloroform, and benzoic acid (0·46 g., 92%), m. p. and mixed m. p. 119—121°, was obtained on removal of the chloroform.

Attempted Preparation of 1,1-*Di*-p-*methoxyphenyltetralin.*—A suspension of 4,4′-dimethoxybenzophenone (90 g.) in ether (400 ml.) was added to a solution of 3-phenylpropylmagnesium bromide (from 90 g. of the bromide) in ether (200 ml.), and the mixture was stirred and refluxed for 10 hr., cooled, decomposed with ice and dilute hydrochloric acid, and filtered to remove unchanged ketone (70 g.). The ethereal layer was separated, dried (Na_2SO_4), and evaporated. The semi-solid residue had b. p. >220°/0·3 mm., and was used in the next stage without further purification.

The crude alcohol was treated with 85% sulphuric acid (150 ml.) at 0° and worked up as in the previous experiments to yield a solid (15 g.), m. p. 60—63°, which on recrystallisation from hexane afforded pure 1,1-*di*-p-*methoxyphenyl*-4-*phenylbut*-1-*ene* as colourless needles, m. p. 64°, $\lambda_{max.}$ 2100 (ε 41,400), 2480 (ε 21,000), $\lambda_{infl.}$ 2630 Å (ε 19,000) (Found: C, 83·8; H, 7·1. $C_{24}H_{24}O_2$ requires C, 83·7; H, 7·0%).

Attempts to effect cyclisation under various acidic conditions included the use of 85% sulphuric acid for 44 hr. at 25°, sulphuric in acetic acid (0·1 g./ml.) for 44 hr., and perchloric acid in acetic acid (0·1 ml./ml.) for 12 days, but the only recovered hydrocarbon was the above olefin.

Oxidation of 1,1-*Di-isopropyltetralin.*—Chromium trioxide (20 g.) in acetic acid (10 ml.) and water (10 ml.) was slowly added to a refluxing solution of 1,1-di-isopropyltetralin (4·0 g.) in acetic acid (80 ml.). A vigorous reaction ensued and the mixture was refluxed for 1 hr. After removal of much of the solvent (80 ml.) under reduced pressure the residue was treated with water (250 ml.) and extracted with chloroform. The chloroform solution was washed with water and dried (Na_2SO_4) and the solvent removed. The residual oil was treated with sodium hydroxide (4 g.) and hydrogen peroxide (100-vol.; 40 ml.). The cooled solution was acidified to Congo Red with 50% sulphuric acid, and the precipitated acid filtered off. The crude acid, m. p. 135—145°, rapidly became gummy and an analytically pure specimen could not be obtained.

A solution of the crude acid (0·10 g.) in 2N-sodium hydroxide was made just acid to litmus and treated with 4-phenylphenacyl bromide (0·30 g.) in ethanol, to yield *di*-4-*phenylphenacyl* αα-*di-isopropylhomophthalate*, m. p. 111—112° (from ethanol) (Found: C, 78·5; H, 6·2. $C_{43}H_{40}O_6$ requires C, 79·1; H, 6·1%).

Oxidation of 1,1-*Diphenyltetralin.*—1,1-Diphenyltetralin (0·6 g.) was refluxed with a solution of chromium trioxide (3 g.) in glacial acetic acid (18 ml.) and water (6 ml.) for 1 hr. Part of the solvent (12 ml.) was removed and the residue diluted with water (60 ml.). The solution was extracted with ether. The extract was dried (Na_2SO_4) and evaporated. The residue was taken up in ethanol and reprecipitated with water. The crude material was digested with a little hot ethanol, filtered off, and crystallised from glacial acetic acid containing a trace of sulphuric acid. In this way αα-diphenylhomophthalic anhydride (0·3 g.) was obtained as colourless crystals, m. p. 228—229° (lit.,[25] m. p. 227—228°) (Found: C, 79·9; H, 4·6. Calc. for $C_{21}H_{14}O_3$: C, 80·2; H, 4·5%).

Synthesis of 2,2-*Dimethylindane.*—(i) 2-*Methylindan*-1-*one.* The preparation of this ketone and of the dimethyl-ketone have been recorded by Haller and Bauer [26] without experimental details.

A solution of indan-1-one [27] (55 g.) in dry toluene (100 ml.) was added cautiously to a stirred and refluxing suspension of sodamide (18 g.) in toluene (200 ml.) under nitrogen. The mixture was then refluxed for 1 hr., cooled, treated slowly with dimethyl sulphate (80 g.), refluxed for 30 min., and kept at room temperature overnight. A solution of ammonia (*d* 0·88; 50 ml.) in water (100 ml.) was added to the mixture. After 2 hours' stirring, the organic layer was removed and the aqueous layer extracted with benzene. The combined extracts were washed with dilute hydrochloric acid and evaporated. Distillation of the residue afforded 2-methylindan-1-one (8·5 g., 15%), b. p. 86—92°/2 mm.

(ii) 2,2-*Dimethylindan*-1-*one.* 2-Methylindanone (8·5 g.) was methylated as in the preceding experiment. The crude product was chromatographed on alumina and eluted with hexane–benzene (1 : 1). Distillation of the eluate gave 2,2-dimethylindan-1-one (2·8 g., 30%), b. p. 56°/0·02 mm., n_D^{22} 1·5394 (Found: C, 82·5; H, 7·6. Calc. for $C_{11}H_{12}O$: C, 82·5; H, 7·5%).

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[25] Koelsch and Le Claire, *J. Org. Chem.*, 1941, **6**, 516.

[26] Haller and Bauer, *Compt. rend.*, 1910, **150**, 1472.

[27] Fieser and Hershberg, *J. Amer. Chem. Soc.*, 1939, **61**, 1272.

(iii) 2,2-*Dimethylindane.* 2,2-Dimethylindanone (2·5 g.), potassium hydroxide (4·0 g.), 100% hydrazine hydrate (3 ml.), and diethylene glycol (30 ml.) were refluxed for 2 hr., then distilled until the temperature of the residue was 200°. The distillate was diluted with water and extracted with ether. The solvent was removed from the dried (Na_2SO_4) extract and the residue distilled, to afford 2,2-*dimethylindane* (1·0 g., 44%), b. p. 80°/16 mm., n_D^{22} 1·5144 (Found: C, 90·3; H, 9·7. $C_{11}H_{14}$ requires C, 90·4; H, 9·6%).

1,2,3,4,5,6,7,8-*Octahydro*-1,1,4,4,5,5,8,8-*octamethylanthracene*.—This hydrocarbon, m. p. 218°, was synthesised in an overall 11% yield from 2,5-dimethylhex-3-yne-2,5-diol by the method of Bruson and Kroeger.[19]

Dehydrogenation.—General method. The substrate and quinone were heated in a solvent, usually benzene, then diluted with light petroleum (b. p. 40—60°) and filtered to remove the precipitated quinol. Chromatography of the filtrate over alumina and elution with benzene removed excess of quinone and any unprecipitated quinol and afforded the product of the dehydrogenation. Reactions with dichlorodicyanobenzoquinone (V) were generally carried out in sealed tubes to prevent hydrolysis of the quinone; with this quinone precipitation of the quinol from benzene is quantitative and provides a useful guide to the extent of reaction.

Reaction of the Quinone (III).—(*a*) β-*Ionone.* A solution of β-ionone (1·92 g.) and tetrachloro-1,2-benzoquinone (5·25 g.) in benzene (20 ml.) was refluxed for 20 hr. Chromatography yielded fractions (*a*), a yellow viscous oil (0·60 g.), $\lambda_{\text{infl.}}$ 2280 (ε 12,000), $\lambda_{\text{max.}}$ 2940 Å (ε 1600), and (*b*) a red viscous oil (0·93 g.), $\lambda_{\text{infl.}}$ 2300 (ε 7900) and 2940 Å (ε 2260). Neither fraction corresponded to 4-(3-pseudocumyl)but-3-en-2-one, $\lambda_{\text{max.}}$ 2850 Å (ε 9400).[10]

(*b*) β-*Ionone propylene ketal.* A solution of the ketal (9·05 g.) and the quinone (20·0 g.) in benzene (70 ml.) was refluxed for 20 hr., yielding an oil (4·0 g., 58%) which had $\lambda_{\text{max.}}$ 2850 Å (ε 1410) and therefore contained >10% of 4-(3-pseudocumyl)but-3-en-2-one.

(*c*) *Dehydro*-β-*ionone.* A solution of the quinone (IX) (1·25 g.) in benzene (3 ml.) was mixed with dehydro-β-ionone (0·95 g.) (for which we thank Dr. O. Isler) in benzene (0·5 ml.). The mixture became warm and dark. After 2 min. the colour faded to pale red. The reaction afforded an oil, $\lambda_{\text{max.}}$ 2850 Å (ε 8300), which contained 84% of 4-(3-pseudocumyl)but-3-en-2-one (2,4-dinitrophenylhydrazone,[10] m. p. and mixed m. p. 154°).

(*d*) 1,5,5-*Trimethyl*-3-*methylenecyclohexene.* The diene (2·49 g.) was added to tetrachloro-1,2-benzoquinone (5·0 g.) in benzene (10 ml.) at room temperature. The solution became hot and the benzene boiled. After 2 min. the reaction subsided and, on cooling, the dark green solution deposited crystalline tetrachlorocatechol (1·0 g., 22%) which was filtered off. Chromatography of the filtrate gave a semisolid mixture. Some liquid was separated by decantation and the residue was triturated with light petroleum. The solid thus obtained crystallised from ethanol, to give a colourless *adduct* (1·42 g.), m. p. 149—150° (Found: C, 50·0; H, 4·4; Cl, 37·3. $C_{16}H_{16}O_2Cl_4$ requires C, 50·3; H, 4·2; Cl, 37·2%), $\lambda_{\text{max.}}$ 2190 (ε 77,000) and 3040 Å (ε 3300), $\lambda_{\text{infl.}}$ 2340 (ε 14,400). The infrared spectrum had no band corresponding to OH stretching but had a very strong band at 1428 cm.$^{-1}$; a similar band (1422 cm.$^{-1}$) characterised the spectrum of 5,6,7,8-tetrachloro-2,5-diphenyl-1,4-benzodioxin prepared from the quinone and *trans*-stilbene.[13] Ozonolysis of the adduct at −40° produced no formaldehyde.

The liquid decanted from the adduct was distilled, to give material (0·81 g.), b. p. 88°/18 mm., n_D^{23} 1·5103, $\lambda_{\text{max.}}$ 2170 (ε 9000) and 2700 Å (ε 335) (Found: C, 89·2; H, 10·6. Calc. for $C_{10}H_{14}$: C, 89·5; H, 10·5%). The distillate (100 mg.) was shaken with concentrated sulphuric acid (0·4 g.) for 10 min., and then poured on ice (0·5 g.). The crystals (0·120 g.) obtained were dissolved in water (2 ml.), and hydrogen chloride was bubbled through the solution. White crystals separated and were filtered off. After drying in air, the crystals had m. p. 79—80° undepressed on admixture with isodurenesulphonic acid hydrate.

The recovered material (92%) therefore contained isodurene (35%) and an adduct (22%).

(*e*) 1,1-*Disubstituted tetralins.* These experiments were carried out by the general method, the concentrations shown in Table 3 being used. The yields given in Table 3 were determined spectrotroscopically. The characterisation of the products is given below.

(i) 1,1-Dimethyltetralin afforded 1,2-dimethylnaphthalene (picrate, m. p. 129°).

(ii) 1,1-Diethyltetralin gave 1,2-*diethylnaphthalene*, b. p. 95—97°/0·5 mm., n_D^{21} 1·5794, $\lambda_{\text{max.}}$ 2290 (ε 92,000), 2740 (ε 13,000), and 2820 Å (ε 18,000) (Found: C, 90·9; H, 9·0. $C_{14}H_{16}$ requires C, 91·3; H, 8·7%), isolated as its orange-red *picrate* (from ethanol), m. p. 107—108° (Found: C, 57·9; H, 4·7; N, 9·8. $C_{14}H_{16},C_6H_3O_7N_3$ requires C, 58·1; H, 4·6; N, 10·2%). Arnold and

Barnes [28] report a diethylnaphthalene picrate, m. p. 105·5—107°, but give no analytical data.

(iii) 1,1-Di-isopropyltetralin gave a product whence repeated distillation afforded 1,2-*di-isopropylnaphthalene*, b. p. 90°/0·8 mm., n_D^{21} 1·5640, $\lambda_{\max.}$ 2250 (ε 61,400) and 2600 Å (ε 5500) (Found: C, 90·5; H, 9·7. $C_{16}H_{20}$ requires C, 90·6; H, 9·4%).

(iv) 1-Methyl-1-phenyltetralin afforded an oil from which crude 1-methyl-2-phenylnaphthalene, m. p. 79—84°, separated. Two recrystallisation from ethanol gave the pure hydrocarbon,[28] m. p. 85°, $\lambda_{\max.}$ 2170 (ε 41,500), 2310 (ε 46,000), 2400 (ε 46,000), 2770 (ε 7600), and 2850 Å (ε 7600) (Found: C, 93·2; H, 6·6. Calc. for $C_{17}H_{14}$: C, 93·5; H, 6·5%). Fractionation of the residual oil yielded a further quantity of the naphthalene and 1-methyl-1-phenyltetralin, b. p. 105°/2 mm., n_D^{25} 1·5854.

1-Methyl-2-phenylnaphthalene (0·1 g.) and picric acid (0·15 g.), dissolved in hot ethanol and left overnight, afforded the *picrate* as orange-red needles, m. p. 89·5—90·5° (from ethanol) (Found: C, 61·5; H, 3·9; N, 9·4. $C_{17}H_{14},C_6H_3O_7N_3$ requires C, 61·7; H, 3·8; N, 9·4%).

1-Methyl-2-phenylnaphthalene (0·182 g.) and picric acid (0·01 g.) similarly gave a hemipicrate,[29] m. p. 84—85° (Found: C, 71·8; H, 4·9; N, 6·2. Calc. for $2C_{17}H_{14},C_6H_3O_7N_3$: C, 72·2; H, 4·7; N, 6·3%).

(v) 1,1-Diphenyltetralin yielded 1,2-diphenylnaphthalene, m. p. 95—119°, from which the pure hydrocarbon,[30] m. p. 114°, $\lambda_{\max.}$ 2300 (ε 28,000), 2420 (ε 39,000) and 2870 Å (ε 8400), was obtained by way of its picrate, m. p. 146°.

(vi) Tetralin-1,1-spirocyclopentane yielded a semisolid product from which phenanthrene was isolated as its picrate, m. p. 140°.

(vii) Tetralin-1,1-spirocyclohexane gave 1,2-*cycloheptenonaphthalene*, a liquid, $\lambda_{\max.}$ 2300 (ε 86,000) and 2860 Å (ε 5880) (Found: C, 91·3; H, 8·3. $C_{15}H_{16}$ requires C, 91·8; H, 8·2%), isolated as its *picrate*, m. p. 108° (Found: C, 59·1; H, 4·5; N, 10·2. $C_{21}H_{19}O_7N_3$ requires C, 59·3; H, 4·5; N, 9·9%).

(*f*) *Ionene*. Ionene (1·92 g.) and tetrachloro-1,2-benzoquinone (5·77 g.) in benzene (20 ml.) were refluxed for 20 hr. They gave an oil (1·80 g.) which was dissolved in the minimum quantity of hot acetic acid. After 3 days at 0° the crystalline deposit was filtered off. It (0·035 g., 2·4%) was a 1,1′,2,2′,6,6′-*hexamethylbinaphthyl*, m. p. 199°, $\lambda_{\max.}$ 2300 (ε 146,000) and 2880 (ε 12,600) [Found: C, 91·2; H, 7·8%; *M* (Rast), 299. $C_{26}H_{26}$ requires C, 92·3; H, 7·7%; *M*, 338]. The acetic acid mother-liquors were diluted with water and extracted with ether. Removal of the solvent from the dried (K_2CO_3) extract afforded crude 1,2,6-trimethylnaphthalene (1·50 g.), $\lambda_{\max.}$ 2300 (ε 47,000) and 2800 Å (ε 3100), containing 61% of the naphthalene. The pure hydrocarbon was isolated by way of its picrate, m. p. 121°, and had $\lambda_{\max.}$ 2300 (ε 76,500) and 2800 Å (ε 5100).

Naphthalene. A solution of naphthalene (2·02 g.) and tetrachloro-1,2-benzoquinone (2·02 g.) in dry benzene (20 ml.) was refluxed for 20 hr. Chromatography over alumina then yielded 2,2′-binaphthyl (1 mg.), m. p. 187° (lit.,[31] m. p. 187—188°).

(*g*) 1,2,3,4,5,6,7,8-*Octahydro*-1,1,4,4,5,5,8,8-*octamethylanthracene*. The hydrocarbon (0·50 g.) tetrachloro-1,2-benzoquinone (1·9 g.), and benzene (4 ml.), refluxed for 20 hr., afforded the original hydrocarbon (0·49 g.), m. p. and mixed m. p. 218°.

Reaction of the Quinone (IV) *with* 1,5,5-*Trimethyl*-3-*methylenecyclohexene*.—The diene (1·66 g.), quinone (4·7 g.), and benzene (70 ml.) were refluxed for 4 hr., yielding the quinol (2·0 g., 42%) and an oil (1·48 g.) from which isodurene (0·81 g., 50%), $\lambda_{\max.}$ 2150 (ε 7700) and 2640 Å (ε 580), was isolated by fractional distillation.

Reaction of 1,5,5-*Trimethyl*-3-*methylenecyclohexene with Chloranil*.—The diene (6·42 g.), chloranil (12·8 g.), and benzene (120 ml.) were heated at 80° for 20 hr. Chloranil (10·5 g., 82%), m. p. 288—290°, and the diene (5·88 g., 91%), n_D^{22} 1·4690, $\lambda_{\max.}$ 2350 Å (ε 11,600), were recovered.

Reactions of the Quinone (V).—(a) β-*Ionone propylene ketal*. The ketal (0·81 g.) and dichlorodicyanobenzoquinone (1·6 g.) in anhydrous benzene (10 ml.), heated for 2 hr. at 80°, yielded the quinol (1·1 g., 69%), and an oil (0·30 g., 49%), $\lambda_{\max.}$ 2850 Å (ε 2630). On the assumption that the other constituent is the original ketal the oil contained 19% of 4-(3-pseudocumyl)-but-3-en-2-one.

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[28] Arnold and Barnes, *J. Amer. Chem. Soc.*, 1944, **66**, 960.

[29] Spring, *J.*, 1934, 1332.

[30] Crawford, *J. Amer. Chem. Soc.*, 1939, **61**, 608.

[31] Chattaway and Lewis, *J.*, 1895, **67**, 879.

(b) *Indane.* Indane (0·80 g.) and dichlorodicyanobenzoquinone (1·68 g.) in dry benzene (7 ml.) were heated in a sealed tube for 4 hr. at 80°. The quinol (1·70 g., 100%) was removed by filtration and light petroleum (b. p. 40—60°; 50 ml.) added. The solution was chromatographed over alumina and most of the solvent removed from the eluate by fractionation through a 25 cm. helix-packed column. The residue was shaken with *N*-bromosuccinimide (1·23 g.), water (15 ml.), and acetic acid (0·1 ml.) for 24 hr. The organic layer was extracted with ether, and the ethereal solution washed with sodium hydrogen sulphite solution and water. Removal of the solvent from the dried (Na_2SO_4) extract afforded a solid (1·1 g.), m. p. 120—127°. Recrystallisation from aqueous methanol raised the m. p. to 128—130°, undepressed on admixture with indene bromohydrin.

(c) 2,2-*Dimethylindane.* 2,2-Dimethylindane (0·76 g.) and the quinone (1·30 g.) in benzene (3 ml.) were heated at 80° for 2 hr. The reaction gave the quinol (1·05 g.) and 2,3-*dichloro*-5,6-*dicyanoquinol bis*-(2,2-*dimethylindan*-1-*yl*) *ether*, colourless needles, m. p. 188°, $\lambda_{max.}$ 2280 (ε 9800) and 3300 Å (ε 1400) (Found: C, 69·5; H, 5·2; N, 5·3; Cl, 13·7. $C_{30}H_{26}O_2N_2Cl_2$ requires C, 69·6; H, 5·0; N, 5·4; Cl, 13·7%). The infrared spectrum (in CCl_4) contained bands at 2239 (C≡N), 1401vs (quinol ether), 1383 and 1357 cm.$^{-1}$ (CMe_2), but none corresponding to OH, C=O, or CMe deformation.

(d) 1,5,5-*Trimethyl*-3-*methylenecyclohexene.* The diene (1·85 g.) was added to a solution of the quinone (3·67 g.) in benzene (20 ml.). The solution became hot and dark brown. The quinol (0·3 g., 10%) was recovered from the benzene solution on cooling. On dilution with light petroleum (b. p. 40—60°; 100 ml.), concentration to a small volume (*ca.* 20 ml.), and further cooling, a solid (2·8 g.) separated which was filtered off. Chromatography of the filtrate in the usual way gave an oil which was distilled. The distillate (0·10 g.) had n_D^{23} 1·5112, $\lambda_{max.}$ 2160 (ε 8700) and 2680 Å (ε 340).

The solid *adduct* recrystallised from ethanol as pale yellow prisms, decomp. 165°, $\lambda_{max.}$ 2190 (ε 7000), 2230 (ε 6400), and 2500 Å (ε 7500) (Found: C, 59·1; H, 4·7; N, 7·9; Cl, 19·4. $C_{18}H_{16}O_2N_2Cl_2$ requires C, 59·5; H, 4·4; N, 7·7; Cl, 19·6%). The infrared spectrum had no absorption corresponding to OH stretching, but had bands at 2254 (C≡N) and 1695 cm.$^{-1}$ (conjugated ketone). The recovered material (62%) therefore contained isodurene (9%) and an adduct (91%).

(e) 1,1-*Dimethyltetralin.* The hydrocarbon (1·07 g.), quinone (3·36 g.), and benzene (14 ml.) were heated for 5 hr. at 80°, yielding the quinol (3·0 g., 102%) and oil (0·83 g., 78%) containing 84% of 1,2-dimethylnaphthalene.

(f) 1,1,2-*Tri*-[32] *and* 1,1,2,2-*tetra-phenylethane.*[33] These compounds were recovered unchanged (mixed m. p.s) after being heated with the quinone in benzene for 20 and 160 hr. respectively.

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[32] Späth, *Monatsh.*, 1913, **34**, 2013.
[33] Gomberg and Cone, *Ber.*, 1906, **39**, 1461.