996. *Adducts from Quinones and Diazoalkanes. Part I. 3-Hydroxythymoquinone and Diazomethane.*

By F. M. DEAN, PETER G. JONES, and PADET SIDISUNTHORN.

Diazomethane methylates and adds to 3-hydroxythymo-1,4-quinone, giving an adduct that is unable to increase its stability by enolisation or oxidation and therefore retains considerable reactivity. Pyrolysis affords 3-methoxy-6-methylthymo-1,4-quinone and a cyclopropane derivative with a bicyclo[4,1,0]heptane skeleton. Acid treatment also gives the latter product, but alkali produces a bimolecular coupling product containing two quinone rings. The mechanism suggested for the last reaction is extended to the conversion of 1,4-naphthaquinone into its 2-amino-derivative by hydrazoic acid. The structure of the initial diazomethane adduct is also discussed.

ALTHOUGH the addition of diazomethane and its derivatives to quinones presumably first gives adducts of type (I; R = H), the compounds described[1-5] have almost always been the relatively stable tautomers (II) or their oxidation products (III). Adducts (I; R = Br) from bromoquinones lose hydrogen bromide spontaneously, thus attaining the more stable structure (III) in a different way.[4] Fieser and Hartwell[5a] prepared the only exceptional adduct, formulated as (IV), by treating 2-diphenylmethyl-1,4-naphthaquinone with diazomethane. Here the diphenylmethyl substituent blocks all the above modes of stabilisation and the product should therefore retain some of the reactivity associated with the azo-link: however, these authors have examined only the behaviour upon pyrolysis. Other " blocked " adducts have now been studied, this paper describing results in the thymoquinone series where the main reactions are thermal decomposition to quinone and to cyclopropane derivatives, and alkaline decomposition to a diquinone formed by some kind of oxidative coupling.

3-Hydroxythymo-1,4-quinone[6] (V), which we obtained by an improved method, gave with diazomethane an adduct (VI), the structure of which is considered below. Above 130°, this adduct loses nitrogen, giving an inseparable mixture of the dimethylquinone (VII; R = Me) and the cyclopropane (bicyclo[4,1,0]heptane) derivative (VIII;

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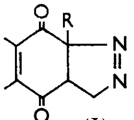
[1] Bartels-Keith, Johnson, and Taylor, *J.*, 1951, 2352.
[2] Fieser and Peters, *J. Amer. Chem. Soc.*, 1931, **53**, 4080.
[3] Wallenfels, *Ber.*, 1942, **75**, 787.
[4] Bergmann and Bergmann, *J. Org. Chem.*, 1938, **3**, 125.
[5] Fieser and Hartwell, *J. Amer. Chem. Soc.*, 1935, **57**, (*a*) 1479, (*b*) 1482.
[6] Mazzara, *Ber.*, 1890, **23**, 1390.

R = Me). Fortunately, mild alkaline hydrolysis attacked the cyclopropane preferentially, and the dimethylquinone (VII; R = Me) was then isolated easily. The related hydroxyquinone (VII; R = H) resulted from much more vigorous hydrolyses, and had ultraviolet (Fig. 1) and infrared characteristics very like those of the parent quinone (V) as well as giving a purple solution in alkali (Fig. 2). Kuhn–Roth determinations[7a] showed a new *C*-methyl group to be present. These and other properties establish structure (VII; R = Me) in spite of the fact that Zeisel determinations[7b] (Table 1) were always high. We attribute the anomaly to the reduction, in Zeisel conditions, of the quinone to the quinol (IX) which is a fully substituted benzene and therefore liable to the extrusion of substituents. In strongly acidic media, quinol (IX) could suffer a reversed Friedel–Crafts reaction, eliminating the isopropyl group (rather than a methyl group) as isopropyl iodide able to augment the methyl iodide from the usual reaction. The corresponding quinol from 3-hydroxythymo-1,4-quinone (V) would not be a fully substituted benzene: accordingly, this quinone does not respond in Zeisel conditions (Table 1).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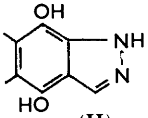
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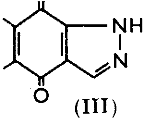
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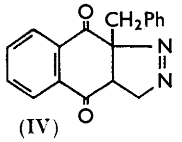
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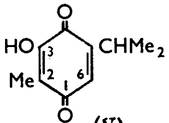
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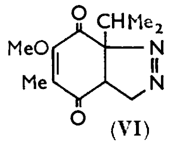
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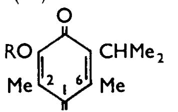
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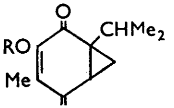
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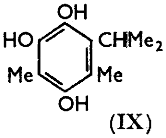
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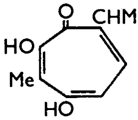
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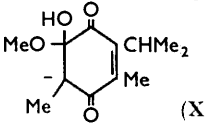
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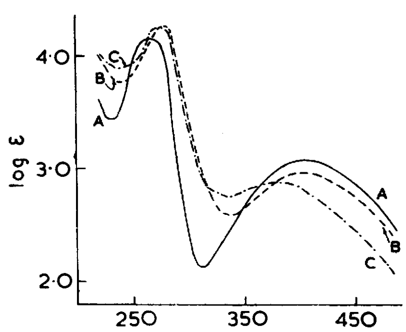

FIG. 1.

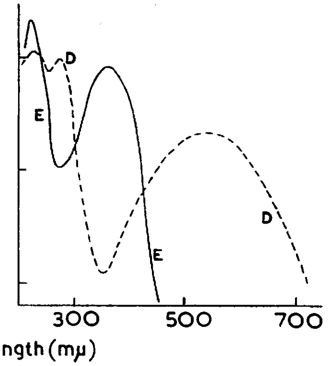

FIG. 2.

FIG. 1. Ultraviolet spectra of: (in ethanol). (A) 3-hydroxythymoquinone (V), (B) 3-hydroxy-6-methylthymoquinone (VII; R = H), and (C) 3,3′-dimethoxy-6,6′-ethylenedithymoquinone (XII).

FIG. 2. Bathochromic shifts: (D) solution as for (A) (Fig. 1), and (E) solution as for (G) (Fig. 3), but each containing 1 drop of 10N-aqueous sodium hydroxide.

The methoxycyclopropane (VIII; R = Me) is assumed to be a pyrolysis product although it has not been isolated, the alkaline hydrolysis demethylating it. The weakly

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[7] Roth, in "Methoden der Organischen Chemie," ed. Müller, Georg Thieme Verlag, Stuttgart, 1953, Vol. II, pp. (*a*) 273, (*b*) 401.

acidic product is pale yellow and has infrared absorption characteristics similar to those of hydroxy-quinones, but it is not a quinone for it does not have the appropriate ultraviolet spectrum (Fig. 3) and only a small bathochromic shift occurs in alkali (Fig. 2). Though isomeric with the hydroxy-quinone (VII; R = H), the compound does not possess a second *C*-methyl group and must therefore be either the bicyclo[4,1,0]heptane derivative (VIII; R = H) or the tropolone (X). It is not a tropolone, however, for the infrared spectrum differs widely from those of authentic tropolones [1,8] and it does not give a diacetate but only a neutral monoacetate transparent at 3 μ. On the other hand, this acetate has the ultraviolet absorption (Fig. 3) of an enedione, while the nuclear magnetic resonance spectrum (Table 2) confirms the presence of cyclopropane protons as well as the presence of an isopropyl group and of a propenyl-methyl group. A slight complication arises from the fact that, as scale models show, the isopropyl substituent in (VIII) is prevented from rotating freely by the cyclopropyl-methylene group and hence the two methyl groups of the substituent are not equivalent, each supplying its own doublet.

TABLE 1.

Methoxyl determinations.

Thymo-1,4-quinone deriv.		Found (%)	Formula	Required (%)
3-Hydroxy-	(V)	0·0	$C_{10}H_{12}O_3$	0·0
3-Hydroxy-6-methyl-	(VII; R = H)	5·2	$C_{11}H_{14}O_3$	0·0
3-Methoxy-6-methyl-	(VII; R = Me)	20·1	$C_{11}H_{13}O_2{\cdot}OMe$	14·9
3,3′-Dihydroxydithymo-1,4-quinone	(XII; OH for OMe)	6·56	$C_{22}H_{26}O_6$	0·0
3,3′-Dimethoxydithymo-1,4-quinone	(XII)	21·2	$C_{22}H_{24}O_4(OMe)_2$	14·7

Alkaline hydrolysis of the methoxy-quinone (VII; R = Me) presumably consists of addition of hydroxide ion, giving carbanion (XI), followed by elimination of methoxide ion; the hydrolysis of bicycloheptene (VIII; R = Me) would be similar. The charges in the carbanions are stabilised by the adjacent carbonyl groups, but as the carbonyl group in the quinone derivative (XI) is also conjugated with a double bond it will be less effective than its counterpart in the bicycloheptane derivative, thus accounting for the difference in the rates of hydrolysis.

TABLE 2.

Assignments for the ^1H resonance spectrum * of 3-acetoxy-1-isopropyl-4-methyl-bicyclo[4,1,0]hept-3-ene-2,5-dione (VIII; R = Ac).

Band	Shift (c.p.s.)	Relative intensity	Assignment	Band	Shift (c.p.s.)	Relative intensity	Assignment
0—1	188	1	Multiplet † from methine hydrogen in isopropyl	0—7	229	1	Cyclopropane
0—2	195			0—8	234		
0—3	199			0—9	248	3	Methyl group in isopropyl ($J = 7$) ‡
0—4	202	3	Acetyl-methyl	0—11	255		
0—5	214	1	Cyclopropane	0—10	253	3	Methyl group in isopropyl ($J = 7$) ‡
0—6	220	3	Ring methyl	0—12	260		

* At 40·00 Mc./sec. in chloroform as solvent and with chloroform as reference compound.
† Partly obscured by other signals. ‡ Unchanged at 16 Mc./sec.

Acid decomposes adduct (VI), giving nitrogen and the bicycloheptane (VIII; R = Me), which again resisted purification and had to be hydrolysed and identified as the hydroxy-compound. In marked contrast, alkali induces a rapid elimination of nitrogen leading to diquinone (XII), so formulated because of its great similarity to the dimethyl-quinone (VII; R = Me) in infrared and in ultraviolet absorption (Fig. 1) and its hydrolysis to a dihydroxy-diquinone again with the appropriate properties. Because of the behaviour of the simpler quinone (VII; R = Me), the high results (Table 1) from Zeisel determinations were expected. Much more discordant was our failure to oxidise the diquinone to

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[8] Doering *et al.*, *J. Amer. Chem. Soc.*, 1952, **74**, 5683, 5688; 1953, **75**, 297.

succinic acid: at best, nitric acid or permanganate oxidations gave small amounts of a substance devoid of methoxyl groups but very like dimethylmaleic anhydride in spectroscopic properties and having a similar stability to water.[9] This product is regarded as the dianhydride (XIII), while the absence of succinic acid is attributed to the fact that in both the diquinone (XII) and the dianhydride (XIII) the methylene groups would themselves be susceptible to attack as they are conjugated with carbonyl groups. According to Bergmann and Bergmann,[4] for example, air dehydrogenates the naphthaquinone (XIV) in alkaline media, giving the related ethylene derivative. Structure (XII) was eventually established by means of nuclear magnetic resonance which characterised protons belonging to the isopropyl, methoxyl, propenyl-methyl, and, most important, the allylic methylene groups (Table 3).

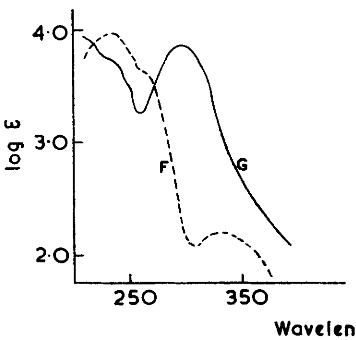


FIG. 3.

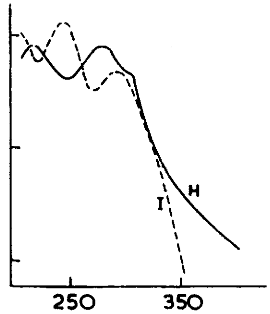
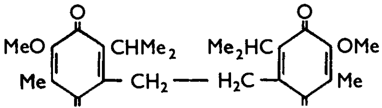


FIG. 4.

FIG. 3. Ultraviolet spectra of enediones: (F) 3-acetoxybicyclo[4,1,0]hept-3-ene-2,5-dione (VIII; R = Ac); and (G) 3-hydroxybicyclo[4,1,0]hept-3-ene-2,5-dione (VIII; R = H).

FIG. 4. Ultraviolet spectra of isomeric pyrazolines: (H) tetrahydro-4,7-dioxo-3*H*-indazole (VI); and (I) dihydro-4-hydroxy-7-oxo-1*H*-indazole (XX).

Abstraction of a proton by base would convert adduct (VI) into carbanion (XV) therefore into nitrogen and carbanion (XVI), where the charge can still be shared by a carbonyl group. Oxidation to the corresponding radical and coupling could now give diquinone (XII). Support for the last stage in this sequence comes from the formation of the naphthaquinone (XIV) when 2,3-dimethylnaphthaquinone is treated with a strong base:[4] here again a carbanion (XVII) would probably be produced and suffer oxidation to a radical able to dimerise. The oxidation of ion (XVI) to a radical is not necessarily effected by oxygen, since exclusion of this does not diminish the yield. If one of the components of the reaction mixture is solely responsible, however, one quinonoid system



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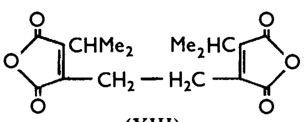

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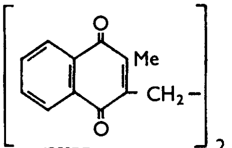

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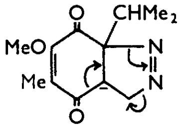

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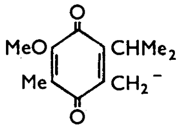

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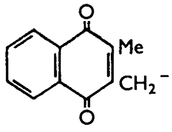

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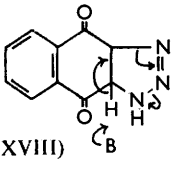

(XVIII)

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[9] Anschütz, *Annalen*, 1928, **461**, 155.

would be destroyed in linking together two others, and the yield could not exceed 66·7%. Whether air was admitted or not, yields were about 62% and we searched the residual tar without finding any discrete reduction product.

TABLE 3.

Assignments for the ^{1}H resonance spectrum * of 3,3′-dimethoxy-6,6′-ethylenedithymoquinone (XII).

Band	Shift (c.p.s.)	Relative intensity	Assignment	Band	Shift (c.p.s.)	Relative intensity	Assignment
0—1	139	6	Methoxyl	0—6	194	4	Two allylic methylene
0—2	164	2	Methine hydrogens in isopropyl groups (ill-defined septet)	0—7	222	6	Ring methyl
0—3	171			0—8	243	12	Four equivalent methyl groups in isopropyl
0—4	177			0—9	250		
0—5	184						

* Conditions as for Table 2.

The argument also applies to the conversion of 1,4-naphthaquinone into the 2-amino-derivative by sodium azide in acetic acid.[5b] Strong analogy [5a] exists for an initial step in which hydrazoic acid adds to the quinone giving triazole (XVIII). A base (azide or acetate) could now abstract a proton as indicated and the resulting charge could circulate so as to eliminate nitrogen and leave the nitrogen analogue (XIX) of carbanion (XVI). The amide anion now merely takes up a proton, giving 2-aminonaphthaquinone, possibly because coupling through nitrogen atoms is generally much less favoured than that through carbon atoms, or perhaps because the basicity of nitrogen would favour the approach of the proton at an early stage and, in consequence, the synchronisation of proton removal and proton addition, thus leaving little scope for the formation of radicals.

The tar left after isolation of diquinone (XII) contains a small quantity of a compound isomeric with the initial adduct (VI), the yield increasing as the alkalinity of the reaction mixture is increased. In contrast to its parent, the isomer is stable to heat. It is amphoteric, and the solutions in acids or bases are also stable. Attempted methylation gave only gums, and after acetylation, which apparently induced some reaction, only the original material was recovered. The infrared spectrum showed the absence of the common kinds of ketonic or quinonoid carbonyl groups, but the presence of hydroxyl or imino-groups (or both). On the basis of this limited information we tentatively regard the isomer as a vinylogous amide (XX) whose hydroxyl group is acidic because of conjugation with an aldimine group. The numerous possibilities for tautomerism and quaternisation would account for the gums resulting from methylation; and the derived acetate would have the character of an acid anhydride and be very easily hydrolysed by water. That bases catalyse the isomerisation of azo-compounds [10,11] such as (XXI) to the hydrazones (XXII) encourages the idea that the essential step in the isomerisation of adduct (VI) gives carbanion (XXIII) and thence hydrazone (XXIV), which bears the same relation to the final product (XX) as a β-diketone to its enol. The reaction produces more of the diquinone (XII) than of the " amide " (XX) because carbanion (XV) is more stable than carbanion (XXIII); but at higher concentrations of base relative stabilities are less important, so the proportion of " amide " increases. These arguments rationalise the chief features of the reaction.

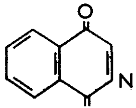
In conclusion, the ascription of structure (VI) to the initial adduct needs comment. Although Bartels-Keith, Johnson, and Taylor [1] prepared an adduct from methoxybenzoquinone and ethyl diazoacetate, they did not discuss the orientation. However, conjugation of the hydroxyl (methoxyl) group in quinone (V) will inactivate one carbonyl group, leaving the other group to direct [12] the incoming, anionoid carbon atom of the

[10] Overberger, Lombardino, Tashlick, and Hiskey, *J. Amer. Chem. Soc.*, 1957, **79**, 2662.

[11] Wang, Hsiano, Saklad, and Cohen, *J. Amer. Chem. Soc.*, 1957, **79**, 2661.

[12] Smith and Howard, *J. Amer. Chem. Soc.*, 1943, **65**, 165, and references quoted therein.

diazomethane molecule to position 6. But we cannot follow precedent and argue that the 6-methyl group in quinone (VII) proves the methylene group to be placed as in (VI), because the quinone might have been formed through the cyclopropane (VIII; R = Me). Fortunately, the diquinone (XII) supplies the required proof, for it cannot be obtained by treating the cyclopropane (VIII; R = Me) with base and must have originated from an adduct (VI).



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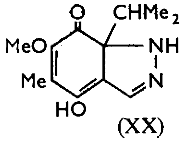

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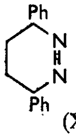

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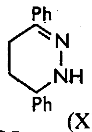

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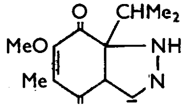

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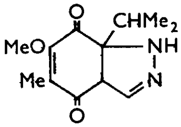

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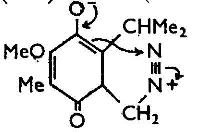

(XXV)

Cipher (XXV) represents a possible intermediate stage in the production of the adduct. The reaction does not stop here, for the adduct has no strong infrared absorption band near 5 μ such as are found in aliphatic diazo-compounds [12] and in diazonium salts,[13] it does not behave as a salt, and it does not couple with phenoxide ions. On the other hand, structure (VI) (which would have to be *cis*-fused to avoid excessive strain) can be reached as indicated and is supported by the absorption band at 1563 cm.$^{-1}$ in a region appropriate to an aliphatic azo-compound [13] and also by strong carbonyl absorption near 6 μ. The lack of absorption near 3 μ shows that hydroxyl and imino-groups are absent.

The ultraviolet spectrum (Fig. 4) of the adduct has the expected resemblance to that of the cyclopropane (VIII; R = Me) but, unexpectedly, contains no component obviously attributable to the azo-link. Compounds [10,11] of type (XXII) have $\lambda_{\text{max.}}$ ~390 mμ (log ε ~2·5), while acylic (*trans*) analogues [14] have $\lambda_{\text{max.}}$ ~350 mμ (log ε ~2). Despite this discrepancy, we believe structure (VI) to be correct.

EXPERIMENTAL

Light petroleum refers to the fraction of b. p. 60—80° unless some other is specified. Ultraviolet spectra were generally determined for ~10^{-3}M-ethanol solutions and infrared spectra for mulls in paraffin.

3-*Hydroxythymo*-1,4-*quinone* (V).—Hydrazine hydrate (commercial 100%) (10 ml.) was added at 40° to 2,4-dinitrothymol (10 g.) in methanol (100 ml.) containing Raney nickel (1 g.). After 5 min. the vigorous reaction had subsided and the red mixture was heated under reflux until the colour faded and ammonia was no longer evolved. As quickly as possible, the mixture was filtered and the filtrate added to ferric sulphate hydrate (100 g.) in water (300 ml.) and distilled in steam. The red deposit from the distillate (1 l.) furnished 3-hydroxythymo-1,4-quinone in orange-red plates (2·9 g.), m. p. 168—169°, identical with an authentic specimen.[6] This compound had $\nu_{\text{max.}}$ 3233 (weakly bonded OH), 1669 and 1643 (quinone-carbonyl), and 1610 cm.$^{-1}$ (C⁚C) at the higher frequencies, and gave a red-brown ferric reaction in alcohol. The solution in aqueous sodium hydrogen carbonate and sodium hydroxide was violet. *C*-Methyl determinations (Kuhn–Roth) gave values between 11·2 and 11·7%, of which ~8% can be attributed to the propenyl-methyl group and ~3% to the isopropyl group.[7a] Reductive acetylation yielded 2,3,6-triacetoxy-4-isopropyltoluene in needles, m. p. 88° (from ethanol) (Bargellini [15] gives m. p. 83—85°) (Found: C, 62·2; H, 6·9. Calc. for $C_{16}H_{20}O_6$: 62·3; H, 6·5%). This compound had $\lambda_{\text{max.}}$ 264 mμ (log ε 2·60) and $\nu_{\text{max.}}$ 1773 and 1754 (aryl acetate C=O) and 1220 and 1190 cm.$^{-1}$ (acetate C–O stretch).

3a,4,7,7a-*Tetrahydro*-7a-*isopropyl*-6-*methoxy*-5-*methyl*-4,7-*dioxo*-3H-*indazole* (VI).—A solution

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[13] Bellamy, " The Infra-Red Spectra of Complex Molecules," Methuen and Co., London, 2nd edn., 1585, Chapter 15.

[14] Cohen, Groszos, and Sparrow, *J. Amer. Chem. Soc.*, 1950, **72**, 3947.

[15] Bargellini, *Gazzetta*, 1923, **53**, 240.

of diazomethane from nitrosomethylurea (3·5 g.) in ether was dried for 3 hr. over solid potassium hydroxide (renewed every hour) and then mixed with 3-hydroxythymo-1,4-quinone (1 g.) in ether (100 ml.; freshly distilled from phosphorus pentoxide). During 15 min. evolution of nitrogen came to an end and the colour of the solution changed from red to orange. Eight hr. later, the colour was yellow and removal of the solvent *in vacuo* left an orange solid which, crystallised from light petroleum, afforded the *tetrahydroindazole* in colourless prisms (0·9 g.), m. p. 74°, $\lambda_{max.}$ 217 and 277 mμ (log ε 3·92, 3·91) (Found: C, 60·8; H, 6·9; N, 11·8; OMe, 13·0. $C_{11}H_{13}N_2O_2$·OMe requires C, 61·0; H, 6·8; N, 11·9; OMe, 13·1%). This indazole is sensitive to acids and bases but is freely soluble in most organic solvents and sublimes without decomposition at 90°/1 mm. It gives no ferric reaction.

Pyrolysis of Tetrahydroindazole (VI).—3-*Methoxy*-6-*methylthymo*-1,4-*quinone* (VII; R = Me).—The tetrahydroindazole (1·0 g.) was heated under nitrogen. Decomposition began at about 130°, and was complete in 20 min. at 140°. The oily product failed to crystallise and attempts to purify it by chromatography, sublimation, and distillation were unsuccessful. The oil was then warmed with N-aqueous sodium hydroxide (40 ml.) on the steam-bath (30 min.) and some of it dissolved. The residual oil was separated from the alkaline solution by steam-distillation and, when isolated from the distillate by means of ether, gave 3-*methoxy*-6-*methylthymo*-1,4-*quinone* as a pungent yellow oil (0·20 g.), b. p. 94—98/1 mm., n_D^{20} 1·5190 (Found: C, 69·1; H, 8·0; OMe, 20·1. $C_{11}H_{13}O_2$·OMe requires C, 69·2; H, 7·7; OMe, 14·9%). As a film, this methoxyquinone has $\nu_{max.}$ 1667, 1645 (C=O) and 1608 cm.$^{-1}$ (C:C), and $\lambda_{max.}$ 278 and 380 mμ (log ε 4·26, 2·87), and is hardly soluble in water but is readily soluble in organic solvents: it gives no ferric reaction. A Kuhn–Roth determination gave *C*-methyl, 18·9%: $\sim$3% would be contributed by the isopropyl group and $\sim$16% by the two propenyl-methyl groups.

The methoxy-quinone (0·10 g.) in ethanol (10 ml.) containing 10N-aqueous sodium hydroxide (2 ml.) was heated under reflux under nitrogen for 2 hr. Acidification with 2N-sulphuric acid turned the dark red solution orange, and an orange gum separated when ethanol was removed in a current of air. The gum was washed with water, dried *in vacuo* over phosphorus pentoxide, and extracted with light petroleum (b. p. 40—60°). Evaporation of the extracts left material which, when repeatedly crystallised from light petroleum (b. p. 40—60°), afforded 3-*hydroxy*-6-*methylthymo*-1,4-*quinone* as bright orange needles (0·03 g.), m. p. 88°, $\nu_{max.}$ 3225 (weakly bonded OH), 1672 and 1640 (quinone C=O) and 1605 cm.$^{-1}$ (C:C), giving a red-brown ferric reaction in ethanol and a purple solution in aqueous sodium hydrogen carbonate or sodium hydroxide (Found: C, 67·8; H, 7·3. $C_{11}H_{14}O_3$ requires C, 68·0; H, 7·3%).

3-*Hydroxy*-1-*isopropyl*-4-*methylbicyclo*[4,1,0]*hept*-3-*ene*-2,5-*dione* (VIII; R = H).—(i) The steam-distillation described in the preceding experiment gave a residual alkaline solution which was extracted with ether. An intractable tar remained on evaporation of the extract, but acidification of the alkaline solution with dilute sulphuric acid gave an orange gum. Washed with water and dried *in vacuo* over phosphorus pentoxide, the gum was found to be partly soluble in cold light petroleum (b. p. 40—60°), nearly all the orange colour passing into solution. From the solution was obtained 3-hydroxy-6-methylthymoquinone (0·018 g.), m. p. and mixed m. p. 88°. That part of the gum not soluble in petroleum sublimed at 100°/1 mm. and then crystallised from light petroleum, giving the 3-*hydroxybicyclo*[4,1,0]*heptenedione* as dull yellow needles (0·18 g.), m. p. 165°, $\nu_{max.}$ 3230 (weakly bonded OH), 1675 and 1642 cm.$^{-1}$ (enedione C=O) [Found: C, 68·4; H, 7·4%; *M* (Rast), 202. $C_{11}H_{14}O_3$ requires C, 68·0; H, 7·3%; *M*, 194]. *C*-Methyl estimations (Kuhn–Roth) gave values near to 10·6%, the isopropyl group accounting for $\sim$3% and the propenyl methyl group for $\sim$8%. The compound gives a red-brown ferric reaction in ethanol and yellow solutions in dilute alkalis: heated for some time in light petroleum, it becomes dark orange. The *acetate* (prepared by use of acetic anhydride–pyridine) separated from light petroleum in prisms, m. p. 46°, $\nu_{max.}$ 1773 (vinyl-attached OAc), 1681 (enedione C=O), and 1190 cm.$^{-1}$ (OAc) (Found: C, 65·8; H, 6·8. $C_{13}H_{16}O_4$ requires C, 66·1; H, 6·8%).

(ii) The tetrahydroindazole (VI) (0·50 g.) in ethanol (4 ml.) evolved nitrogen and became yellow when treated with sulphuric acid (3 ml.) in water (3 ml.). After about 10—15 min. the reaction ceased and the mixture was diluted with water, giving an oil that was isolated with ether. This oil did not impart a colour to ferric chloride in ethanol but, as it evaded further purification, it was hydrolysed by 2% aqueous sodium hydroxide at 100° for 25 min. Acidification and isolation of the product in the usual way furnished the 2-hydroxybicyclo[4,1,0]-heptenedione as needles (0·08 g.), m. p. and mixed m. p. 165° (from light petroleum).

3,3′-*Dimethoxy*-6,6′-*ethylenedithymo*-1,4-*quinone* (XII).—When treated with 2% aqueous sodium hydroxide (1·0 ml.) at 0°, the tetrahydroindazole (VI) (1·0 g.) in ethanol (15 ml.) quickly became red and gave off nitrogen. Shortly afterwards, a yellow solid appeared: when purified from ethanol this supplied the *ethylenedithymoquinone* as bright yellow plates (0·55 g.), m. p. 170°, $\nu_{max.}$ 1660 and 1639 (quinone C=O) and 1610 cm.$^{-1}$ (quinone C:C), $\lambda_{max.}$ 274 and 371 mμ (log ε 4·47, 2·83) [Found: C, 69·6; H, 7·3%; *M* (Rast), 403. $C_{24}H_{30}O_6$ requires C, 69·5; H, 7·3%; *M*, 414]. Reductive acetylation gave 1,2-*bis*-(2,5-*diacetoxy*-6-*isopropyl*-4-*methoxy*-3-*methylphenyl*)*ethane*, which crystallised from ethanol in plates, m. p. 190°, $\lambda_{max.}$ 272 mμ (log ε 2·94), $\nu_{max.}$ 1764 (aryl OAc) and 1196 cm.$^{-1}$ (C–O stretch) (Found: C, 65·8; H, 7·6. $C_{32}H_{42}O_{10}$ requires C, 65·5; H, 7·2%).

The alkaline filtrate from the yellow solid was neutralised with acetic acid and extracted with ether. The tar remaining after volatilisation of the ether was triturated with benzene: most of it dissolved, leaving a white solid which, crystallised from benzene, afforded 7,7a-*dihydro*-4-*hydroxy*-7a-*isopropyl*-6-*methoxy*-5-*methyl*-7-*oxo*-1H-*indazole* (XX) as needles (0·053 g.), m. p. 176° [Found, on sample dried at 120°/1 mm. for 3 hr.: C, 60·8; H, 7·0; N, 11·4; OMe, 13·6%; *M* (Rast), 244. $C_{11}H_{13}N_2O_3 \cdot OMe$ requires C, 61·0; H, 6·8; N, 11·9; OMe, 13·1%; *M*, 236], $\nu_{max.}$ 3367 and 3145 (OH and NH) and 1631 cm.$^{-1}$ (C:O conjugated with NH), $\lambda_{max.}$ 244 and 294 mμ (log ε 4·13, 3·70), dissolving easily in most organic solvents but not in light petroleum or cold benzene. Solutions in 2N-sodium hydroxide or 2N-hydrochloric are stable, and no ferric reaction is given in ethanol.

The reaction between alkali and the tetrahydroindazole (VI) was repeated under nitrogen and with air-free solvents, etc. The result was identical with that already described. Another repetition, conducted with 10% instead of 2% sodium hydroxide, gave the diquinone (0·53% g.) as before, but a markedly improved yield (0·21 g.) of the indazole (XX).

3,3′-*Dihydroxy*-6,6′-*ethylenedithymo*-1,4-*quinone* (XII; OH for OMe).—The dimethoxy-diquinone (XII) (0·10 g.) was warmed on the steam-bath for 1 hr. with acetic acid (10 ml.) containing 20% aqueous hydrogen chloride (3 ml.). The initial yellow of the mixture became deep red, and orange crystals separated. Recrystallised from benzene, this solid supplied the *dihydroxy-dithymoquinone* as orange plates (0·08 g.), m. p. 251° (Found: C, 68·5; H, 6·8. $C_{22}H_{26}O_6$ requires C, 68·4; H, 6·8%). The compound gave a red-brown ferric reaction in ethanol, and purple solutions in aqueous alkalis. It had $\nu_{max.}$ 3225 (weakly bonded OH), 1656, 1642 (quinone C=O) and 1603 cm.$^{-1}$ (C:C), and $\lambda_{max.}$ 278 and 404 mμ (log ε 4·42, 3·00). Reductive acetylation gave 1,2-*bis*-(2,4,5-*triacetoxy*-6-*isopropyl*-3-*methylphenyl*)*ethane* forming needles, m. p. 223°, from benzene [Found: C, 63·1; H, 6·6%; *M* (Rast), 625. $C_{34}H_{42}O_{12}$ requires C, 63·5; H, 6·6%; *M*, 643], $\nu_{max.}$ 1776 and 1764 (aryl acetate C=O) 1217 and 1202 cm.$^{-1}$ (C–O stretching), $\lambda_{max.}$ 266 mμ (log ε 2·80).

2,9-*Dimethyldeca*-cis-3-cis-7-*diene*-3,4,7,8-*tetracarboxylic* 3,4:7,8-*Dianhydride* (XIII).—(i) When the dimethoxy-diquinone (XIII) (0·25 g.) was boiled under reflux with nitric acid (*d* 1·4; 3 ml.) and water (2 ml.) the colour was bleached in 5 min. Water (10 ml.) was added and the resulting turbid solution slowly distilled to dryness. There remained a mixture of a water-soluble acid (rejected since it was not succinic acid) and an insoluble neutral compound which was sublimed at 140°/1 mm. Crystallisation from benzene then gave the *dianhydride* in plates (0·023 g.), m. p. 178° [Found: C, 62·6; H, 6·0%; *M* (Rast), 306. $C_{16}H_{18}O_6$ requires C, 62·7; H, 5·9%; *M*, 306]. The compound had $\nu_{max.}$ 1835 and 1779 (anhydride C=O), 1656 (C:C) and 1280 cm.$^{-1}$ (C–O stretching) and, in hexane, $\lambda_{max.}$ 207 mμ (log ε 5·38). In the same conditions dimethylmaleic anhydride had $\nu_{max.}$ 1821, 1770, and 1271 cm.$^{-1}$ and $\lambda_{max.}$ 207 mμ (log ε 4·72).

(ii) During 1 hr., potassium permanganate (1 g.) was added in small portions to a boiling solution of the dimethoxy-diquinone (XII) (0·25 g.) in acetone (25 ml.). Evaporation of the acetone and addition of water (25 ml.) gave a brown mixture which was clarified with sulphur dioxide and saturated with ammonium sulphate. Continuous extraction with ethyl acetate, evaporation of the extract, and repeated recrystallisation of the residue from ethyl acetate–light petroleum gave the dianhydride in prisms (0·01 g.), m. p. and mixed m. p. 178°.

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