74. *Adducts from Quinones and Diazoalkanes. Part IV.*[1] *Tropones from Acetylquinones.*

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Adducts from 5-acetyl-2-methoxy-1,4-benzoquinone and diazoalkanes R·CHN_2 afford tropones and alkylquinones on pyrolysis, unless R = H when only a methylquinone results. The adducts are unusually sensitive to hydroxylic solvents and with methanol rapidly give derivatives of bicyclo-[4,1,0]heptene.

The insertion of an alkyl substituent into the 6-position of the hydroxyquinol nucleus presents difficulties discussed elsewhere,[2] and we now offer a solution based upon " blocked " quinone–diazoalkane adducts of the kind described earlier.[1a,b] Moreover, these adducts

[1] Parts I—III, *J.*, (*a*) 1962, 5186; 1963, (*b*) 5336, (*c*) 5342.
[2] Dean, Randell, and Winfield, *J.*, 1959, 1071.

provide the simple preparation of tropones originally envisaged by other workers [3] though never conducted successfully.[4] The adducts also supply derivatives of bicyclo[4,1,0]-heptene with exceptional ease.

It is known [1a] that, in the methoxyquinone nucleus, the methoxyl group deactivates one carbonyl group, allowing the other to direct the anionoid carbon of diazomethane into position 5. In the 5-acetyl derivative (I; R = H), however, the acetyl group can be expected to provide the decisive influence and direct anionoid carbon to position 6 instead. That the adducts from diazoalkanes R·CHN$_2$ (R = H, Me, or Et) are correctly formulated as the tetrahydroindazoles (II; R = H, Me, or Et) was established by the ^{1}H resonance spectrum of one of them (Table 1): all these indazoles had the appropriate infrared absorption bands near 1705 (acetyl C=O), 1670 (ring C=O), 1605 (C=C), and 1550 cm.$^{-1}$ (N=N).

TABLE 1.

Assignments for the ^{1}H resonance spectrum * of 7a-acetyl-3a,4,7,7a-tetrahydro-5-methoxy-3-methyl-4,7-dioxo-3*H*-indazole (II; R = Me).†

Band	τ	Relative intensity	Assignment	Band	τ	Relative intensity	Assignment
1	4·12	1	Vinyl H (posn. 6)	3	6·18	3	Methoxy-Me
2	5·09, 5·19, 5·22			4	6·93, 7·07	1	CH (posn. 3a)
	5·32, 5·35, 5·45,	1	CH (posn. 3)	5	7·26	3	Acetyl-Me
	5·47, 5·59			6	8·30, 8·44	3	Me (posn. 3)

* At 60·0 Mc/sec., and in $CDCl_3$. † In contrast to another diazoethane adduct,[1b] this appeared to consist of a single stereoisomer. The difference may merely reflect the fact that the present compound was amenable to recrystallisation.

Unlike adducts from alkylquinones,[1a,b] those from the acetylquinone (I; R = H) were rapidly decomposed by methanol to give nitrogen and bicyclo[4,1,0]hept-3-ene derivatives (III; R = H, Me, or Et), all of which had the appropriate ultraviolet spectra and infrared bands close to 3060 (cyclopropane CH), 1696 (acetyl C=O), 1664 (conj. C=O), and 1616 cm.$^{-1}$ (C=C). The conversion of one of these cyclopropanes (III; R = H) into the chloromethylquinol (IV; R = Cl) by means of hydrogen chloride was difficult and not reproducible, but the ^{1}H resonance spectrum (Table 2) confirmed the structure given.

TABLE 2.

Assignments for the ^{1}H resonance spectrum * of 1-acetyl-4-methoxybicyclo[4,1,0]-hept-3-ene-2,5-dione (III; R = H_{β}').

Band	Shift (c./sec.)	Relative intensity	Assignment	Band	Shift (c./sec.)	Relative intensity	Assignment
0–1	63	1	Vinyl H (posn. 3)	0–7	201		
0–2	142	3	Methoxyl-Me	0–8	203		
0–3	177			0–9	210		
0–4	182	1	Cyclopropane-H_{α}	0–10	212	2	Cyclopropane-H_{β} and -H_{β}'
0–5	185			0–11	216		
0–6	194	3	Acetyl-Me	0–12	219		
				0–13	221		
				0–14	225		

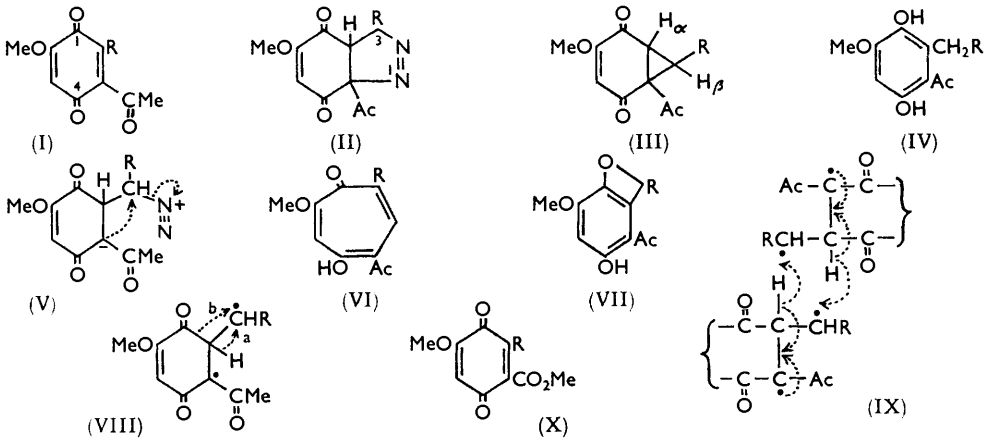
* At 40·00 Mc./sec., chloroform as solvent and reference compound.

We believe that the adducts are sensitive to methanol because of ring-opening to zwitterions of type (V). While the addition is itself considered to involve such ions,[1a] ether has little ability to solvate and stabilise them [5] so that cyclisation would be rapid and irreversible. On the other hand, solvation by methanol would promote ring-fission and hence provide opportunity for extrusion of nitrogen as indicated by arrows in (V). Formation of this zwitterion would also be favoured by distribution of the negative charge

[3] Bartels-Keith, Johnson, and Taylor, *J.*, 1951, 2352.
[4] Pauson, *Chem. Rev.*, 1955, **55**, 9; Eistert, *Chem. Ber.*, 1959, **92**, 1247.
[5] Parker, *Quart. Rev.*, 1962, **16**, 163.

over two carbonyl groups, thus accounting for the reactivity of adducts containing acetyl as opposed to alkyl groups.

When heated in benzene, the diazomethane adduct (II; R = H) was converted by loss of nitrogen into 5-acetyl-2-methoxy-6-methylquinone (I; R = Me) along with a little of the corresponding quinol. These products were easily separated as they are too highly substituted to form quinhydrones,[6] and they were identified by an alternative synthesis



from orcacetophenone. The homologous adducts behaved in a substantially different fashion, for they supplied, not only the expected quinones (I; R = Et or Pr), but also the tropones (VI; R = Me or Et) that are isomeric with the latter. The tropones possessed the requisite spectroscopic properties and behaved as strongly bonded phenols. However, these facts seemed insufficient to exclude a benzoxeten structure (VII) which, like the tropones, could have been arrived at by way of a biradical (VIII); and so tropone (VI; R = Me) was hydrogenated. The product was a complex mixture, as is usual in the tropone series, and no quinol (IV; R = Me) was detected although it should have resulted from hydrogenolysis of the benzyl ether link in benzoxeten (VII). Finally, the general nature of tropone (VI; R = Me) was established by its ^1H resonance spectrum (Table 3) although the position accorded the methyl substituent had to be deduced from arguments presented below.

TABLE 3.

Assignments for the ^1H resonance spectrum * of 5-acetyl-4-hydroxy-2-methoxy-6-methyltropone (VI; R = Me).

Band	Shift (c./sec.)	Relative intensity	Assignment	Band	Shift (c./sec.)	Relative intensity	Assignment
0–1	−340	1	Chelated OH	0–4	124	3	Methoxyl-Methyl
0–2	−29	1	Ring CH (posn. 3 or 6)	0–5	178	3	Acetyl-Me
0–3	20	1	Ring CH (posn. 3 or 6)	0–6	194	3	Me (posn. 7)

* Conditions as for Table 2.

That pyrolysis proceeds through intermediate biradicals (VIII) is supported to a limited extent by the formation in all cases of some of the quinols (IV)—presumably because of abstraction of hydrogen from the medium. Formation of cyclopropanes would also be expected, but it is a special feature of the present series that this does not happen. Cyclopropanes do not come into being and then suffer further conversions, because they are stable in the conditions used. Consequently, we attribute this behaviour to the presence of the acetyl group which, by helping to disperse one radical centre, will

[6] Dean, Osman, and Robertson, *J.*, 1955, 11.

slow down cyclisation and give time for other reactions including quinone and tropone generation.

Since in biradical (VIII) one centre is highly dispersed while the other is not, the fate of the system must be decided at the latter. A quinone might result by migration of hydrogen (following arrow *a*), a tropone by migration of carbon (following arrow *b*): no other simple migration will furnish a tropone which is why the alkyl substituents are held to occupy the position shown. In such circumstances the ratio of hydrogen migration to carbon migration would determine the ratio of quinone to tropone and, since diazomethane adducts yield no tropone, an alkyl group R in (VIII) must favour the latter migration rather than the former. But within a single molecule there seems to us to be no steric or electronic factor able to account for this, so we suggest that, while tropone formation follows the course already suggested, quinones result mainly from a bimolecular hydrogen abstraction as indicated in (IX). Here a change of R from hydrogen to alkyl will introduce steric effects, making it more difficult to attain the necessary arrangement and thus indirectly favouring tropone formation.

The quinone ester (X; R = H) was studied but only in diazomethane addition. Clearly of type (II), the adduct slowly decomposed in contact with ether and was quickly destroyed by water. No pure product was isolated from these reactions, but pyrolysis afforded an alkylated quinone (X; R = Me) that was identified by an alternative synthesis.

Experimental

Light petroleum refers to the fraction of b. p. 60—80°. Ultraviolet spectra were determined for *ca.* 10^{-3}M-ethanol solutions, and infrared spectra for mulls in paraffin.

5-Acetyl-2-methoxy-1,4-benzoquinone (I; R = H).—(i) Gradual addition of sodium dichromate (4·5 g.) in water (200 ml.) containing sulphuric acid (5 ml.) to a stirred solution of 5-acetyl-2-methoxyquinol [2] (6 g.) in dioxan (50 ml.) at 10° led to separation of a red solid which slowly became bright yellow and was then collected, washed with water, and dried in air. Purified from benzene–light petroleum, the product gave the *acetyl-quinone* in yellow plates (3·5 g.), m. p. 121—122°, $\nu_{max.}$ 1721 (acetyl C=O), 1675 and 1650 (quinone C=O), and 1610 cm.$^{-1}$ (C=C) (Found: C, 60·1; H, 4·7; OMe, 16·7. $C_8H_5O_3$·OMe requires C, 60·0; H, 4·4; OMe, 17·2%). The compound rapidly decomposed in warm water, giving amorphous material, and when exposed to light slowly afforded a red substance. The solution in alkali was dark brown, in sulphuric acid red-brown. Reduction with ethanolic sulphur dioxide regenerated the quinol, m. p. and mixed m. p. 164°; an equimolecular mixture of the quinone and quinol crystallised from benzene–light petroleum (b. p. 60—80°) as the *quinhydrone*, forming red prisms, m. p. 125°.

(ii) Potassium carbonate (4·3 g.) and freshly prepared silver oxide (8 g.) were shaken at *ca.* 45° with 5-acetyl-2-methoxyquinol (2·0 g.) in benzene (50 ml.; redistilled before use). After 10 min., evaporation of the filtered solution gave the crude acetylquinone which was purified as before, giving plates (1·2 g.), m. p. and mixed m. p. 121—122°.

3,6-Dihydroxy-4-methoxy-2-methylacetophenone (IV; R = H).—2-Hydroxy-4-methoxy-6-methylacetophenone [7] (3·0 g.) in 10% aqueous sodium hydroxide (50 ml.) at 10° was oxidised by potassium persulphate (5 g.), in water (90 ml.), added with stirring during 2 hr. After a further 12 hr. at *ca.* 20°, the mixture was neutralised with dilute sulphuric acid, and unattacked phenol was removed by two extractions with ether. Concentrated hydrochloric acid (25 ml.) and sodium sulphite (3 g.) were added and the temperature raised to 90° for 35 min. The product was isolated by means of ether and formed a brown mass which, when crystallised from benzene, yielded the *dihydroxyacetophenone* as pale yellow prisms (2·0 g.), m. p. 169—170°, $\lambda_{max.}$ 240, 281, and 344 mμ (log ε 3·91, 3·91, and 3·58), giving a deep green ferric reaction (Found: C, 61·2; H, 6·0; OMe, 16·0. $C_9H_9O_3$·OMe requires C, 61·2; H, 6·1; OMe, 15·8%).

Oxidation of this quinol (0·7 g.) by the silver oxide method and crystallisation of the product from light petroleum furnished *2-acetyl-5-methoxy-3-methyl-1,4-benzoquinone* (I; R = Me) as yellow tablets (0·55 g.), m. p. 93·4°, $\lambda_{max.}$ 264 and 362 mμ (log ε 4·11 and 2·87), $\nu_{max.}$ 1696 (acetyl

[7] Hoesch, *Ber.*, 1915, **48**, 1127.

C=O), 1675 and 1643 (quinone C=O), and 1605 cm.$^{-1}$ (C=C). Crystallisation of mixtures of this quinol and the related quinone gave no quinhydrone but only crystals of the individual compounds which were separated by hand and identified.

Methyl 6-methoxy-1,4-benzoquinone-3-carboxylate (X; R = H).—2,5-Dihydroxy-4-methoxybenzoic acid (2·5 g.) was esterified during 12 hr. by boiling methanol (25 ml.) containing sulphuric acid (1 ml.). Concentration of the solution and addition of water gave *methyl 2,5-dihydroxy-4-methoxybenzoate*, separating from aqueous ethanol in plates (1·8 g.), m. p. 145°, giving a blue and then a green ferric reaction [Found; C, 54·5; H, 5·3; OMe, 31·2. $C_7H_4O_3(OMe)_2$ requires C, 54·5; H, 5·05; OMe, 31·8%]. The same ester was obtained by the diazomethane technique.

Attempts to oxidise this quinol to the quinone with dichromate failed. The quinol (1·0 g.) in benzene (30 ml.) at 50° was shaken for 10 min. with potassium carbonate (1·6 g.) and silver oxide (3 g.). The *quinonecarboxylate* was isolated by filtration and evaporation and crystallised from benzene–light petroleum as orange flakes (0·6 g.), m. p. 114°, $\nu_{max.}$ 1734 (ester), 1669 (quinone C=O), 1627, and 1600 cm.$^{-1}$ [Found: C, 55·0; H, 4·1; OMe, 30·5. $C_7H_2O_3(OMe)_2$ requires C, 55·1; H, 4·1; OMe, 31·6%]. It was more stable than the acetyl analogue, but gave brown solutions in alkali, sulphuric acid, and alcoholic ferric chloride. Reduction with sulphur dioxide regenerated the quinol, m. p. and mixed m. p. 145°. The *quinhydrone* separated from benzene in red tablets, m. p. 126°.

Methyl 5-Methoxy-3-methyl-1,4-benzoquinone-2-carboxylate (X; R = Me).—(i) Methyl 3,6-dihydroxy-4-methoxy-2-methylbenzoate (1·0 g.) was oxidised by the silver oxide method and the product was recrystallised from light petroleum, giving the *methylquinonecarboxylate* as yellow prisms (0·6 g.), m. p. 81°, $\lambda_{max.}$ 269 and ~365 mμ (log ε 4·13 and ~2·9), $\nu_{max.}$ 1727 (ester), 1675 and 1641 (quinone C=O), and 1605 cm.$^{-1}$ (C=C) [Found: C, 57·2; H, 4·7; OMe, 29·4. $C_8H_4O_3(OMe)_2$ requires C, 57·15; H, 4·8; OMe, 29·5%]. Reduction by sulphur dioxide regenerated the quinol, m. p. and mixed m. p. 154°.

(ii) Diazomethane (from 1·8 g. of methylnitrosourea) in ether was slowly added to methyl 6-methoxy-1,4-benzoquinone-3-carboxylate (1·0 g.) in ice-cooled ether (200 ml.). The mixture soon lost its colour but the crystalline adduct which separated seemed unstable and was not further purified. This material was heated in boiling benzene for 35 min., whereafter removal of the solvent left a crystalline residue which, purified from light petroleum, gave the methylquinonecarboxylate in yellow prisms (0·63 g.), m. p. and mixed m. p. 81°, further identified spectroscopically.

7a-*Acetyl*-3a,4,7,7a-*tetrahydro*-5-*methoxy*-4,7-*dioxo*-3*H*-*indazole* (II; R = H).—The solution obtained by adding diazomethane (from 1·4 g. of methylnitrosourea) in ether (50 ml.) to 5-acetyl-2-methoxy-1,4-benzoquinone (1·0 g.) in ether (300 ml.) at 5° was kept until all the colour was discharged (usually about 5 min.). It was then evaporated to 100 ml. under nitrogen and under reduced pressure and kept at 0° overnight. The *tetrahydroindazole* separated in needles (0·9 g.), m. p. 87° (decomp.), $\nu_{max.}$ 1704, 1659, 1605, and 1558 cm.$^{-1}$ (Found: C, 54·0; H, 4·9; N, 12·5. $C_{10}H_{10}N_2O_4$ requires C, 54·1; H, 4·5; N, 12·6%). This compound is unstable to heat, moisture, and light and recrystallisation did not improve material made by the technique described.

7a-*Acetyl*-3a,4,7,7a-*tetrahydro*-5-*methoxy*-3-*methyl*-4,7-*dioxo*-3*H*-*indazole* (II; R = Me).—This adduct was prepared as was the lower homologue, but with diazoethane from ethylnitrosourea (2·0 g.); the resulting solution was concentrated to 50 ml. before being set aside. The resulting *tetrahydro*-3-*methylindazole* formed needles (0·96 g.), m. p. 90° (decomp.), $\nu_{max.}$ 1701, 1656, 1603, and 1550 cm.$^{-1}$ (Found: C, 55·65; H, 5·3; N, 12·2. $C_{11}H_{12}N_2O_4$ requires C, 55·9; H, 5·1; N, 11·9%).

7a-*Acetyl*-3-*ethyl*-3a,4,7,7a-*tetrahydro*-5-*methoxy*-4,7-*dioxo*-3*H*-*indazole* (II; R = Et).—Made as was the 3-methyl analogue but with diazopropane from nitroso-n-propylurea (3·2 g.), this 3-*ethyltetrahydroindazole* crystallised in prisms (0·81 g.), m. p. 73° (decomp.), $\nu_{max.}$ 1706, 1656, 1605, and 1541 cm.$^{-1}$ (Found: C, 57·5; H, 5·8; N, 11·3. $C_{12}H_{14}N_2O_4$ requires C, 57·6; H, 5·6; N, 11·2%.

1-*Acetyl*-4-*methoxybicyclo*[4,1,0]*hept*-3-*ene*-2,5-*dione* (III; R = H).—The tetrahydroindazole (II; R = H) (1·0 g.) was powdered and sifted into methanol (20 ml.) at 5°. Evolution of nitrogen was immediate, and a yellow solution resulted. An hour later, the solvent was removed *in vacuo* and the residue purified by elution with benzene–chloroform (3 : 1) from a silica column. Evaporation of the solvents and crystallisation of the product from benzene afforded the *bicycloheptenedione* as prisms (0·65 g.), m. p. 159—160°, $\lambda_{max.}$ 279 mμ (log ε 3·88)

(Found: C, 61·75; H, 5·25; OMe, 15·95. $C_9H_7O_3$·OMe requires C, 61·85; H, 5·15; OMe, 16·0%). The same product resulted when ethanol or water replaced methanol: but the yields were much lower.

When the bicycloheptenedione (0·5 g.) in chloroform (7 ml.) was subjected to a stream of hydrogen chloride for 2 hr. and the solvent evaporated, there was left a solid which was recrystallised from benzene, giving *2-chloromethyl-3,6-dihydroxy-4-methoxyacetophenone* (IV; R = Cl) in yellow prisms (0·2 g.), m. p. 116—117°, $\nu_{max.}$ 3370, 1605 (broad), and 1493 cm.$^{-1}$, having a dark brown ferric reaction which slowly faded (Found: C, 52·0; H, 5·1; Cl, 14·8; OMe, 13·5. $C_9H_8ClO_3$·OMe requires C, 52·1; H, 4·8; Cl, 15·4; OMe, 13·5%).

The bicycloheptenedione was unaffected by acetic anhydride and sodium acetate at the b. p. for 2 hr.

1-Acetyl-4-methoxy-7-methylbicyclo[4,1,0]*hept-3-ene-2,5-dione* (III; R = Me).—Treated with methanol in the same way as the lower homologue, the 3-methyltetrahydroindazole (II; R = Me) (1·0 g.) supplied a viscous yellow oil on evaporation of the solvent. The oil was taken up in benzene and passed down a silica column. The first eluates contained *2-ethyl-3,6-dihydroxy-4-methoxyacetophenone* (IV; R = Me), crystallising from light petroleum (b. p. 60—80°) in pale yellow rosettes (0·12 g.), m. p. 105°, $\lambda_{max.}$ 238, 275, and 316 mμ (log 3·95, 3·62, and 3·55), $\nu_{max.}$ 3333, 1603, and 1486 cm.$^{-1}$ (Found: C, 62·75; H, 6·6. $C_{11}H_{14}O_4$ requires C, 62·8; H, 6·7%). Continued elution with benzene furnished a yellow oil which, on trituration with ether, gave the *7-methylbicycloheptenedione*, crystallising from light petroleum as colourless needles (0·28 g.; a yield of 0·49 g. was attained once), m. p. 79°, $\lambda_{max.}$ 274 mμ (log 3·89), $\nu_{max.}$ 3067, 1701, 1658, and 1618 cm.$^{-1}$ (Found: C, 63·0; H, 5·9; O, 31·6. $C_{11}H_{12}O_4$ requires C, 63·5; H, 5·8; O, 30·8%). Kuhn–Roth estimations gave values corresponding to about 0·8 *C*-methyl group.

1-Acetyl-7-ethyl-4-methoxybicyclo[4,1,0]*hept-3-ene-2,5-dione* (III; R = Et).—Prepared from the 3-ethyltetrahydroindazole (II; R = Et) (0·1 g.), this *7-ethylbicycloheptenedione* crystallised from light petroleum in needles (0·25 g.), m. p. 70°, $\lambda_{max.}$ 271 mμ (log ε 3·90), $\nu_{max.}$ 3049, 1695, 1661, and 1618 cm.$^{-1}$ (Found: C, 64·5; H, 6·1. $C_{12}H_{14}O_4$ requires C, 64·9; H, 6·4%).

Pyrolyses of Tetrahydroindazoles (II).—The tetrahydroindazole (1·0 g.) was pyrolysed in boiling benzene (freshly dried by distillation; 30 ml.) for 35 min., and the solvent was removed *in vacuo*, leaving an oil that was purified by chromatography on silica.

(i) Tetrahydroindazole (II; R = H) gave a product eluted with benzene–light petroleum (1 : 1) and crystallised from light petroleum. Thus purified, 3,6-dihydroxy-4-methoxy-2-methylacetophenone (IV; R = H) formed pale yellow prisms (0·02 g.), m. p. and mixed m. p. 169°. Further elution with benzene gave 2-acetyl-5-methoxy-3-methyl-1,4-benzoquinone which separated from light petroleum in yellow plates (0·73 g.), m. p. and mixed m. p. 93—94°.

(ii) Elution of the products from tetrahydro-3-methylindazole (II; R = Me) with benzene–light petroleum (1 : 1) afforded 2-ethyl-3,6-dihydroxy-4-methoxyacetophenone (IV; R = Me), crystallising from benzene in pale yellow needles (0·04 g.), m. p. and mixed m. p. 105—106°. Elution with benzene alone then gave *2-acetyl-3-ethyl-5-methoxy-1,4-benzoquinone* which, purified from light petroleum, formed bright yellow needles (0·36 g.), m. p. 88°, $\lambda_{max.}$ 264 and 360 mμ (log ε 4·18 and 2·90), $\nu_{max.}$ 1704, 1675, 1642, and 1603 cm.$^{-1}$ (Found: C, 63·3; H, 5·9. $C_{11}H_{12}O_4$ requires C, 63·45; H, 5·8%). Finally, elution with chloroform afforded *4-acetyl-5-hydroxy-7-methoxy-2-methyltropone* (VI; R = Me) which crystallised from light petroleum in yellow rosettes (0·33 g.), m. p. 148°, $\lambda_{max.}$ 247, 344, and 382 mμ (log ε 4·38, 3·98, and 4·02), $\nu_{max.}$ 1623, 1600, 1520, and 1264 cm.$^{-1}$ (acetyl C=O and tropone nucleus) [Found: C, 63·8; H, 5·8; O, 30·35%; *M*, (Rast) 217, (Signer) 210. $C_{11}H_{12}O_4$ requires C, 63·5; H, 5·8; O, 30·8%; *M*, 208].

(iii) The products from pyrolysis of the 3-ethyltetrahydroindazole (II; R = Et) were eluted first with benzene–light petroleum (1 : 1). This gave 3,6-dihydroxy-4-methoxy-2-propylacetophenone (IV; R = Et), crystallising from ethanol in lime-green plates (0·05 g.), m. p. 117—118°, not depressed on admixture with an authentic specimen.[2] Further elution with benzene furnished *2-acetyl-5-methoxy-3-propyl-1,4-benzoquinone*, separating from light petroleum in orange-yellow elongated plates (0·32 g.), m. p. 54°, $\lambda_{max.}$ 268 and 367 mμ (log ε 4·16 and 2·89), $\nu_{max.}$ 1695, 1687, 1645, and 1605 cm.$^{-1}$ (Found: C, 64·6; H, 6·2. $C_{12}H_{14}O_4$ requires C, 64·85; H, 6·35%), which supplied the corresponding quinol, m. p. and mixed m. p. 117°, when reduced with sulphur dioxide. Finally, elution with chloroform afforded *4-acetyl-2-ethyl-5-hydroxy-7-methoxytropone* (VI; R = Et), crystallising from benzene–light petroleum in yellow needles (0·33 g.), m. p. 109°, and giving a deep red-brown ferric reaction and a deeply

yellow solution in dilute aqueous sodium hydroxide (Found: C, 64·55; H, 6·5. $C_{12}H_{14}O_4$ requires C, 64·85; H, 6·35%). This tropone had $\lambda_{max.}$ 246, 344, and 375 mμ (log ε 4·40, 4·00, and 4·03) and $\nu_{max.}$ 1621, 1592, 1515, and 1266 cm.$^{-1}$.

We thank Drs. L. H. Sutcliffe and J. Feeney for determining the nuclear magnetic resonance spectra (Tables 2 and 3). Messrs. C. Tomlinson and D. G. Newman and their colleagues we thank for the microanalyses.

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[*Received, May 29th,* 1963.]