1018. *Adducts from Quinones and Diazoalkanes. Part II.*[1] *Diquinones and Tricyclic Diketones from 2-Alkyl-*1,4-*naphthaquinones.*

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

With diazomethane, 2-methyl-1,4-naphthaquinone forms an adduct, giving 2,3-dimethylnaphthaquinone on pyrolysis and, on treatment with acids, a derivative of cyclopropanaphthalenedione. Treatment of the adduct with alkali affords an ethylenediquinone, but if 2-methylnaphthaquinone is present a methylenediquinone results instead. An adduct with similar properties is obtained from 2-diphenylmethyl-1,4-naphthaquinone and diazomethane.

Diazoethane adds to 2-methylnaphthaquinone giving a mixture of geometrical isomers. Diphenyldiazomethane does not give an adduct in the usual conditions but affords a cyclopropanaphthalenedione at 100°.

MACBETH and WINZOR[2] have stated that 2-methyl-1,4-naphthaquinone (I; R = H) does not react with diazomethane in ordinary conditions, but Fieser and Seligman[3] heated 2,6-dimethyl-1,4-naphthaquinone (I; R = Me) with this reagent in a sealed tube and formulated the product as the methylenediquinone (II; R = Me). Bergmann and

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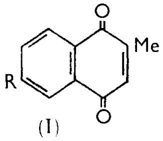
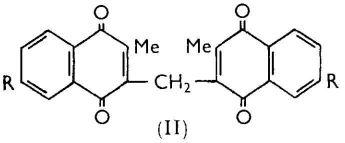
[1] Part I, Dean, Jones, and Sidisunthorn, *J.*, 1962, 5186.
[2] Macbeth and Winzor, *J.*, 1935, 334.
[3] Fieser and Seligman, *J. Amer. Chem. Soc.*, 1934, **56**, 2690.

Bergmann[4] showed subsequently that heat is not required, but they regarded the product as a quinhydrone supplying the diquinone (II; R = Me) only after oxidation. The Bergmanns[4] also re-examined 2-methylnaphthaquinone (I; R = H) and obtained an adduct without difficulty, although it was accompanied by a second product identified as the methylenediquinone (II; R = H). Removal of these products and distillation of the residue gave 2,3-dimethylnaphthaquinone.



(I)



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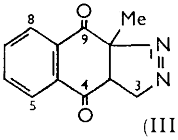

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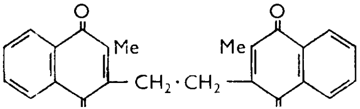

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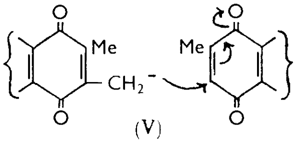

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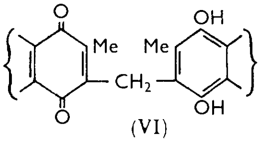

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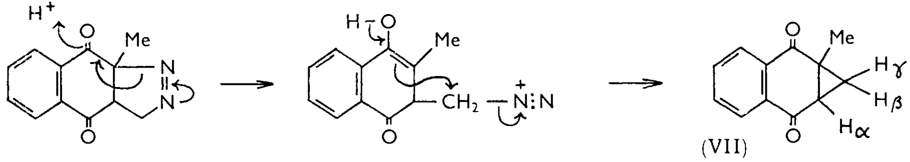
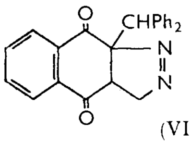
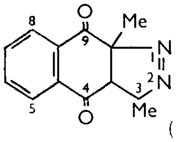


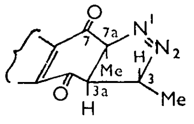
(VII)



(VIII)



(IX)



(X)

These results being at variance with our experience in the thymoquinone series,[1] we have examined 2-methylnaphthaquinone afresh. In ice-cold ether, diazomethane added rapidly, giving adduct (III) with the properties described by the Bergmanns, but no quinhydrone or diquinone was detected at this stage. The adduct had the appropriate infrared spectrum which, in particular, showed by the absence of bands near 3 μ that prototropic shifts to oxygen or nitrogen had not occurred, while the ^{1}H resonance spectrum (Table 1) confirmed the orientation by exhibiting peaks corresponding to the grouping $CH{\cdot}CH_2$. With methanolic sodium hydroxide the adduct (III) at once gave nitrogen and a high yield of the ethylenediquinone (IV), the ^{1}H resonance spectrum (Table 1) proving the quinone nuclei to be separated by two methylene groups.

Thus the behaviour of the "blocked" adduct (III) is exactly parallel to that of the thymoquinone analogue,[1] and some explanation has to be found for the earlier divergent reports. One source of discrepancies could have been the presence of alkali in the diazomethane used, for the ethylenediquinone (IV) would then be formed immediately after addition occurred. Moreover, following the earlier argument[1] where a carbanion of type (V) was held to be the intermediate in the production of an ethylenediquinone, we treated a mixture of adduct (III) and a slight excess of 2-methylnaphthaquinone with base so as to permit the Michael addition shown. This would result in a quinhydrone (VI) unless rapid oxidation afforded the derived methylenediquinone (II; R = H). In practice, it was the methylenediquinone which resulted and not a quinhydrone, while the presence of but one methylene group between the quinone nuclei was established by the ^{1}H resonance spectrum (Table 1). The methylenediquinone described by the Bergmanns did not tally with this product, nor did it tally with the ethylenediquinone: again, true quinhydrones were made by standard methods from both diquinones and were found to resemble ordinary

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[4] Bergmann and Bergmann, *J. Org. Chem.*, 1938, **3**, 125.

TABLE 1.

Assignments for ^1H resonance spectra at 60 Mc./sec.

(i) 3a,4,9,9a-Tetrahydro-9a-methyl-3*H*-benz[*f*]-indazole-4,9-dione (III) (in $CDCl_3$).

Band	τ	Relative intensity	Assignment
1	1·8—2·3	4	Aryl H
2	4·93 5·06	2	CH_2 (posn. 3)
3	6·78 6·90 7·02	1	CH (posn. 3a)
4	8·32	3	Me

(iii) 3,3′-Dimethyl-2,2′-methylenedi-1,4-naphthaquinone (II; R = H) (in $CF_3{\cdot}CO_2H$).

Band	τ	Relative intensity	Assignment
1	1·60—2·14	8	Aryl H
2	5·75	2	CH_2
3	7·55	6	Me

(ii) 3,3′-Dimethyl-2,2′-ethylenedi-1,4-naphthaquinone (IV) (in $CF_3{\cdot}CO_2H$).

Band	τ	Relative intensity	Assignment
1	1·60—2·14	8	Aryl H
2	6·91	4	$CH_2{\cdot}CH_2$
3	7·54	6	Me

(iv) 1a,7a-Dihydro-1a-methyl-1*H*-cyclopropa-[*b*]naphthalene-2,7-dione (VII) (in benzene).

Band	τ	Relative intensity	Assignment
1	7·64 7·72 7·78 7·87	1	Hα
2	8·80	3	Me
3 *	8·85 8·96 9·01 9·13 9·22	2	Hβ and Hγ

* Slightly obscured by methyl absorption. In $CDCl_3$ the confusion was much worse.

quinhydrone and not the " quinhydrone " reported by the same workers.* Reduction in the proportion of 2-methylnaphthaquinone available for Michael addition resulted in mixtures of ethylene- and methylene-diquinones which could not be resolved by crystallisation. One such mixture did resemble closely the materials obtained by the earlier workers, and we now presume that all the former descriptions refer to similar mixtures.

Pyrolysis of adduct (III) gave 2,3-dimethylnaphthaquinone along with a small amount of the tricyclic dione (VII), the structure of which was inferred from the lack of phenolic properties and from the infrared spectrum and supported by the ^1H resonance spectrum (Table 1). This dione was much more easily accessible by action on the adduct (III) of mineral acids, the reaction perhaps having the mechanism indicated. A similar reaction in the thymoquinone series [1] had given much less satisfactory results, probably because of the presence of further groups sensitive to acids.

Adduct (VIII) from 2-diphenylmethylnaphthaquinone was first made by Fieser and Hartwell [5] who converted it into 2-methyl-3-diphenylmethylnaphthaquinone by pyrolysis: we have confirmed this transformation and have also demonstrated the acid-catalysed conversion into a dione analogous to (VII), as well as the alkali-catalysed conversion into an ethylenediquinone analogous to (IV).

From the addition of diazoethane to 2-methyl-1,4-naphthaquinone two isomers resulted. Their properties precluded separation, but the ^1H resonance spectrum (Table 2) showed that both corresponded to the structure (IX), the minor component constituting about 8% of the mixture. Because no parallel isomerism occurs with any diazomethane adduct and because a *trans*-fused ring system would be highly strained, we consider both isomers to be *cis*-fused. While the major isomer might be that having the *exo*-3-methyl configuration (X), which is relatively favourable because the methyl group abuts no other large atom or group, we have no direct evidence. The ^1H resonance spectrum is difficult to interpret, for models seem to show that geometrical would be bound up with configurational isomerism arising partly from the existence of the central ring in two boat

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* It is not clear whether the quinhydrones we describe are 1 : 1 molecular complexes of diquinone and diquinol, or whether they are complexes where each molecule contains one quinone and one quinol nucleus.

TABLE 2.

Assignments for ^{1}H resonance spectrum of 3a,4,9,9a-tetrahydro-3,9a-dimethyl-3*H*-benz[*f*]indazole-4,9-dione (IX) (in $CDCl_3$).

Band	τ (IXa)	τ (IXb)	Assignment
1	1·80—2·26		Aryl H
2		~4·7 (weak and indistinct	CH (posn. 3)
3	5·15 5·27 5·30 5·38 5·42 5·51 5·54 5·66		CH (posn. 3)
4		6·77 6·93	CH (posn. 3a)
5	7·31 7·46		CH (posn. 3a)
6	8·06		9a-Me
7		8·19	9a-Me
8	8·21 8·32		3-Me
9		8·78 8·91	3-Me

* Bands 3, 5, 6, and 8 had relative intensities 1, 1, 3, 3. Bands 7 and 9 had relative intensities 1,1; other bands were too weak for such measurements.

forms and partly from a twisting, unknown in extent, of the nitrogen ring. Although the adduct is very sensitive to acids, bases, and heat, it affords only complex gums.

Diphenyldiazomethane failed to form an adduct with 2-methylnaphthaquinone in the usual conditions. When heated, the mixture produced a cyclopropanaphthalenedione, but such a reaction could result from biradicals formed by preliminary loss of nitrogen from the diazo-compound and is not evidence for the formation of adducts.

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.

3a,4,9,9a-*Tetrahydro*-9a-*methyl*-4,9-*dioxo*-3H-*benz*[*f*]*indazole* (III).—Prepared by distillation from methylnitrosourea (16 g.), ethereal diazomethane was dried by decantation on to fresh potassium hydroxide pellets every half-hour for 2 hr., followed by slow re-distillation. 2-Methyl-1,4-naphthaquinone (4·0 g.) in ether (dried over phenylmagnesium bromide; 200 ml.) was added to the diazomethane solution at 0°, and after 2 hr. the flocculent precipitate was collected and washed with light petroleum (b. p. 40—60°). A further crop was obtained by concentrating the mother-liquor at 0° and adding light petroleum gradually. The combined products (3·8 g.) were repeatedly recrystallised by dissolving them in chloroform, adding light petroleum (b. p. 40—60°) until precipitation was incipient, and cooling to 0°, a process which removed all traces of yellow contaminants and gave the *dioxoindazole* in needles, m. p. 111° (decomp.), $\nu_{max.}$ 1673 (C=O), 1589 (aromatic), 1550 cm.$^{-1}$ (N=N),* $\lambda_{max.}$ 229, 252, and 302 mμ (log ε 4·50, 4·03, and 3·25) (Found: C, 67·3, 67·4; H, 4·4, 4·6; O, 15·6, 15·0. $C_{12}H_{10}N_2O_2$ requires C, 67·3; H, 4·7; O, 14·9%). Further concentration of the mother-liquors furnished a mixed product which was not easily separated.

3,3′-*Dimethyl*-2,2′-*ethylenedi*-1,4-*naphthaquinone* (IV).—A solution of the foregoing indazole (0·18 g.) in chloroform (2 ml.) was diluted with methanol (10 ml.), cooled to 0°, and treated with three drops of 2% aqueous sodium hydroxide. Nitrogen was evolved and the solution became red at once: a precipitate appeared a few seconds later and, when purified from dioxan–methanol or dioxan, gave the *ethylenedinaphthaquinone* in yellow prisms (0·13 g.), m. p. 278°, $\nu_{max.}$ 1654 (quinone C=O), 1612 (C=C), 1593 (aromatic), 792, 716, and 690 cm.$^{-1}$, $\lambda_{max.}$ (in dioxan) 248, 268, and 330 mμ (log ε 4·58, 4·45, and 3·80) (Found: C, 77·8; H, 4·9; O, 17·3. $C_{24}H_{18}O_4$ requires: C, 77·8; H, 4·95; O, 17·6%). Reduction of a suspension of the diquinone in dioxan with sodium borohydride in water eventually bleached the colour and gave a solution of the diquinol. This compound was liberated by acidification but was rapidly oxidised to a

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* In such compounds, the extinction coefficient of the azo-group is roughly one-quarter that of the quinone carbonyl band.

purple quinhydrone and was therefore immediately acetylated (pyridine–acetic anhydride), giving 1,2-*bis*-(1,4-*diacetoxy*-3-*methyl*-2-*naphthyl*)*ethane*, which separated from acetic acid in needles, m. p. 291—292° (Found: C, 70·4; H, 5·6. $C_{32}H_{30}O_8$ requires C, 70·8; H, 5·6%). Partial reduction of the diquinone and acidification of the brown solution gave the *quinhydrone* as a purple powder, decomp. >220°, which failed to dissolve in most solvents and, in hot dioxan, was re-oxidised to the diquinone (Found: C, 77·1; H, 5·2. $C_{24}H_{20}O_4$ requires C, 77·4; H, 5·4%).

3,3′-*Dimethyl*-2,2′-*methylenedi*-1,4-*naphthaquinone* (II; R = H).—The foregoing indazole (0·115 g.) and 2-methyl-1,4-naphthaquinone (0·117 g.) were dissolved in chloroform (1 ml.), and methanol (20 ml.) was added, followed by N-aqueous sodium hydroxide (0·1 ml.). Nitrogen was evolved and the solution became red. As the colour faded, a solid separated and after 10 min. this was collected and crystallised from dioxan, giving the *methylenedinaphthaquinone* in yellow needles (0·123 g.), m. p. 270° (decomp.), $\nu_{max.}$ 1658 (quinone C=O), 1615, 1605 (C=C), 1592 (aromatic), 732, 702, and 691 cm.$^{-1}$, $\lambda_{max.}$ (in dioxan) 247, 262 sh, and 330 mμ (log ε 4·60, 4·43, and 3·81) (Found: C, 77·5; H, 4·4; O, 18·3. $C_{23}H_{16}O_4$ requires; C, 77·5; H, 4·5; O, 18·0%).

When ethereal diazomethane from methylnitrosourea (4·5 g.) was added to 2-methylnaphthaquinone (1·0 g.) in ether (100 ml.), and the mixture was immediately treated with 1% methanolic sodium hydroxide (0·05 ml.); the yellow precipitate formed within 5 min. consisted entirely of the methylenediquinone, m. p. 270°, identified spectroscopically. Mixtures of adduct (III) with varying proportions of 2-methylnaphthaquinone were treated with alkali to give what appeared, on spectroscopic evidence, to be mixtures of methylene- and ethylenedinaphthaquinones. These mixtures all melted below 270° and could not be resolved by crystallisation from dioxan.

Reductive acetylation of the methylenediquinone with acetic anhydride, acetic acid, pyridine, and zinc furnished *bis*-(1,4-*diacetoxy*-3-*methyl*-2-*naphthyl*)*methane*, crystallising from acetic acid in needles, m. p. 243° (Found: C, 70·3; H, 5·4. $C_{31}H_{28}O_8$ requires C, 70·4; H, 5·3%). Partial reduction of the diquinone in dioxan with potassium borohydride led to rapid separation of the purple *quinhydrone*, decomp. >220°, insoluble in organic solvents (Found: C, 76·3; H, 5·2. $C_{23}H_{18}O_4$ requires C, 77·1; H, 5·1%). The alkaline solution was brown and rapidly gave the diquinone. Complete reduction was best effected by shaking a suspension of the diquinone in ethyl acetate with zinc and 2N-hydrochloric acid: thus obtained, *bis*-(1,4-*dihydroxy*-3-*methyl*-2-*naphthyl*)*methane* separated from ethyl acetate–light petroleum in needles, m. p. 250—252°, rapidly re-oxidised by air to the *quinhydrone* (Found: C, 76·2; H, 5·6. $C_{23}H_{20}O_4$ requires C, 76·7; H, 5·6%).

Pyrolysis of the Tetrahydroindazole (III).—The tetrahydroindazole (1·30 g.) was refluxed in toluene for 10 min. Evaporation under reduced pressure of the deep yellow solution left a semi-crystalline mass which was taken up in benzene–light petroleum (1 : 1) and passed down a column of silica. The eluates contained 2,3-dimethyl-1,4-naphthaquinone which crystallised in yellow prisms (0·68 g.), m. p. 123°. Further elution with benzene alone gave the dione (VII) (see below), crystallising from light petroleum in prisms (0·22 g.), m. p. and mixed m. p. 68°.

1a,7a-*Dihydro*-1a-*methyl*-1*H*-*cyclopropa*[*b*]*naphthalene*-2,7-*dione* (VII).—The indazole (0·60 g.) was dissolved in dry methyl cyanide (20 ml.) and treated with one drop of 72% perchloric acid. Nitrogen was evolved rapidly and after 5 min. the yellow-brown solution was poured into ether 100 ml. and the methyl cyanide washed out with water. The yellow ethereal solution was dried ($MgSO_4$), and the ether removed, leaving a red oil (0·50 g.) which, after it had solidified, was passed in benzene down a silica column. The first eluates contained 2,3-dimethylnaphthaquinone (0·06 g.), m. p. 123°. Further elution by benzene–chloroform (9 : 1) gave the 2,7-*dione*, crystallising from ice-cold light petroleum in prisms (0·4 g.), m. p. 68°, $\nu_{max.}$ 3060 (cyclopropane CH), 1672 (C=O), and 1590 cm.$^{-1}$ (aromatic), $\lambda_{max.}$ 222 and 229 mμ (log ε 4·56 and 3·26) (Found: C, 77·3; H, 5·35. $C_{12}H_{10}O_2$ requires C, 77·4; H, 5·4%).

Reactions of 9a-*Diphenylmethyl*-3a,4,9,9a-*tetrahydro*-4,9-*dioxo*-3H-*benz*[*f*]*indazole* (VIII).—Prepared as described by Fieser and Hartwell,[5] the indazole named crystallised from ethanol–benzene in needles, m. p. 168° (decomp.), $\nu_{max.}$ 1715, 1682 (C:O), 1602 (aromatic), and 1572 cm.$^{-1}$ (N:N). When this compound (1·0 g.) was kept at 175° under nitrogen gas evolution ceased after 15 min. and the product was purified from benzene–light petroleum on a column of silica, the

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[5] Fieser and Hartwell, *J. Amer. Chem. Soc.*, 1935, **57**, 1479.

eluates contained 2-diphenylmethyl-3-methyl-1,4-naphthaquinone which formed yellow prisms (0·49 g.), m. p. 162° (lit.,[5] 162°), $\lambda_{max.}$ (in dioxan) 247 and 325 mμ (log ε 4·55 and 3·82), $\nu_{max.}$ 1656 (C:O), 1595 (C:C), and 1488 cm.$^{-1}$ (aromatic). Conducted with benzene alone, further elution gave 1a-*diphenylmethyl*-1a,7a-*dihydro*-1*H*-*cyclopropa*[*b*]*naphthalene*-2,7-*dione*, which separated from light petroleum in needles (0·15 g.), m. p. 150°, $\nu_{max.}$ 3060 (cyclopropane CH), 1681 (C:O), and 1498 cm.$^{-1}$ (aromatic), $\lambda_{max.}$ (in dioxan) 223 and 300 mμ (log ε 4·66 and 3·35) (Found: C, 85·2; H, 5·3; $C_{24}H_{18}O_2$ requires C, 85·2; H, 5·4%).

When sulphuric acid (3 ml.) in acetic acid (7 ml.) was added to the indazole (0·50 g.), also in acetic acid (15 ml.), there was immediate evolution of nitrogen and the solution became yellow. After 15 min. the product was precipitated by addition of water (50 ml.), collected, dried in air, and crystallised from light petroleum, giving the tricyclic dione in needles (0·30 g.), m. p. and mixed m. p. 150°.

2% Aqueous sodium hydroxide (3 ml.) was added to the indazole (1·0 g.) in dioxan (15 ml.). The reaction was complete in about 15 min. and the precipitate was then collected and recrystallised from a large volume of dioxan, giving 3,3′-*diphenylmethyl*-2,2′-*ethylenedinaphthaquinone* in yellow plates (0·57 g.), m. p. 320° (decomp. from ~280°), $\nu_{max.}$ 1661 (C:O), 1597 (C:C), and 1493 cm.$^{-1}$ (aromatic), $\lambda_{max.}$ (saturated solution in dioxan) 247 mμ (log ε 4·66) (Found: C, 84·3; H, 5·2. $C_{48}H_{34}O_4$ requires C, 85·4; H, 5·1%). Pyridine and dioxan are the only common organic solvents in which this diquinone is soluble in more than traces.

3a,4,9,9a-*Tetrahydro*-3,9a-*dimethyl*-4,9-*dioxo*-3H-*benz*[*f*]*indazole* (IX).—Ethereal diazoethane, prepared by distillation from ethylnitrosourea (12 g.) and dried as was the homologue, was added to a solution of 2-methyl-1,4-naphthaquinone (2·0 g.) in dry ether (200 ml.), and the mixture was kept at 0°. After 2 hr. the solution was concentrated under reduced pressure to about 50 ml., and the crystalline adduct separated. Recrystallisation from ether–light petroleum (1:1) gave the *indazoledione* as colourless needles (1·5 g.), m. p. 110°, $\nu_{max.}$ 1675 (C:O), 1589 (aromatic), and 1553 cm.$^{-1}$ (N:N), $\lambda_{max.}$ 229, 252, and 302 mμ (log ε 4·53, 4·10, and 3·26) (Found: C, 68·4; H, 5·2; O, 14·2. $C_{13}H_{12}N_2O_2$ requires C, 68·4; H, 5·3; O, 14·0%).

1a,7a-*Dihydro*-1a-*methyl*-1,1-*diphenyl*-1*H*-*cyclopropa*[*b*]*naphthalene*-2,7-*dione*.—2-Methyl-1,4-naphthaquinone (1 g.) and diphenyldiazomethane (1 g.) were heated in boiling light petroleum for 24 hr. after which time there was no evidence of any adduct formation. The solvent was distilled off and the liquid residue heated to 100°, vigorous evolution of nitrogen taking place. The resulting red-brown oil was taken up in chloroform (10 ml.), and light petroleum (10 ml.) was added. Purified by crystallisation from chloroform–light petroleum, the solid so produced gave the 2,7-*dione* in prisms (0·5 g.), m. p. 213°, $\nu_{max.}$ 3055 (cyclopropane CH), 1668 (C:O), and 1593 cm.$^{-1}$ (aromatic), $\lambda_{max.}$ 224 and 303 mμ (log ε 4·58 and 3·44). (Found: C, 85·1; H, 5·2; O, 9·4. $C_{24}H_{18}O_2$ requires C, 85·2; H, 5·4; O, 9·5%).

We thank Dr. R. J. Abraham for his help in interpreting some of the ^1H resonance spectra.

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[*Received, April 8th,* 1963.]