462. *Reactions of Organic Peroxides. Part IX.** *Hydroperoxides of Some Alkyltetralins.*

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1 : 4-Dimethyl- and 1 : 4-diethyl-tetralin are each easily oxidised successively to the 1-monohydroperoxide and two stereoisomeric 1 : 4-dihydroperoxides. 1-Ethyltetralin similarly yields the 1-hydroperoxide and small amounts of an unstable 1 : 4-dihydroperoxide. Acid-cleavage of the dihydroperoxides gives catechol and diketones; the monohydroperoxides give the expected keto-phenols.

1-METHYLTETRALIN was oxidised to its 1-hydroperoxide by Hock, Depke, and Knauel[1] who experienced some difficulty in carrying out the oxidation at 45°. We find that 1-ethyl-, 1 : 4-dimethyl-, and 1 : 4-diethyl-tetralin are all oxidised easily and rapidly with oxygen at 90°, suitably in presence of dilute alkali solution. These cyclic hydrocarbons absorb oxygen much more readily than the corresponding alkylbenzenes. Comparative maximum rates of absorption (for the hydrocarbons emulsified with one-quarter of their volumes of 2·5% aqueous sodium carbonate at 90°) are: 1-ethyltetralin 10, 1 : 4-diethyltetralin 12, 1 : 4-dimethyltetralin 18, 1 : 1 : 3-trimethylindane[2] 10, *m*-di*iso*propylbenzene 4 mol. % per hr., and *o*-di*iso*propylbenzene[3] 0. The difference between 1 : 4-dimethyltetralin and the substantially unoxidisable *o*-di*iso*propylbenzene is especially

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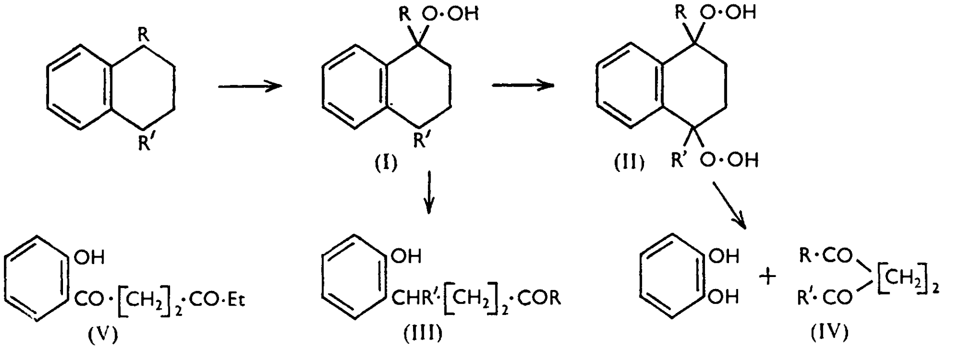
* Part VIII, *J.*, 1956, 4785.

[1] Hock, Depke, and Knauel, *Chem. Ber.*, 1950, **83**, 238.

[2] Webster and Young, *J.*, 1956, 4785.

[3] Distillers Co. Ltd., Hawkins, Quin, and Salt, B.P. 641,250/1950.

striking, and demonstrates the large effect of immobilising the oxidisable carbon atom in a ring. The increased sensitivity of hydrogen atoms to radical attack when they are attached to a cyclic carbon atom appears to be a general phenomenon, probably arising from a combination of entropy factors, facilitation of resonance in the resulting free radical, and prevention of steric hindrance between bulky rotatable groups. The effect has been discussed by Russel,[4] who considers that the bond dissociation energy of a C–H bond (where the carbon atom is in the α-position to an ethylenic or aromatic carbon) is lowered when the carbon atom is incorporated in a 6-membered ring. He calculated that the C–H bond in the α-position in tetralin is 5·6 kcal./mole weaker than in *iso*propylbenzene. Since a tertiary C–H bond is 3—4 kcal./mole weaker than a secondary one, the difference between the α-C–H bond strengths in a 1-alkyltetralin and an *iso*alkylbenzene would be roughly 9 kcal./mole.



The dialkyltetralins could be oxidised to 80—100% conversion at about 80% efficiency in respect of oxygen to hydroperoxide. They initially formed monohydroperoxides (I; R = R′ = Me or Et), the constitution of which was confirmed by their acid-cleavage to ketophenols (III). Continued oxidation led to dihydroperoxides (II). The latter were soluble in dilute aqueous sodium hydroxide and were separated from the oxidation mixture by this means; the monohydroperoxides were not appreciably soluble in aqueous sodium hydroxide of any concentration, but they passed from the dihydroperoxide-free product in light petroleum into aqueous-methanolic sodium hydroxide. In each case, two isomeric dihydroperoxides were obtained, although only the higher-melting and less soluble ones were obtained pure. Diethyltetralin gave one solid isomer, which crystallised from chloroform or toluene with solvent of crystallisation, probably held in a clathrate structure (compounds with bulky 1 : 1-disubstitution on a bicyclic skeleton appear to be prone to form clathrate compounds). The other isomer did not solidify. Both dihydroperoxides from dimethyltetralin were crystalline, but not solvated. Each pair of isomers gave the same acid-cleavage products, and they were evidently *cis*- and *trans*-isomers. Similar stereoisomerism might be expected with the monohydroperoxides, but was not definitely observed. The starting hydrocarbons appeared to be homogeneous.

The planar formula (II; R = R′ = Et), with both hydroperoxide groups attached to tertiary carbon atoms, was proved by reduction of the dihydroperoxide to what was clearly 1 : 4-diethyl-1 : 4-dihydroxytetralin, since it readily eliminated water to give 1 : 4-diethylnaphthalene. Further, acid-cleavage of the dihydroperoxides (II; R = R′ = Me or Et) gave catechol and a diketone (IV). From 1 : 4-diethyl-1 : 4-dihydroperoxytetralin the yields of these were poor, and a third product, $C_{12}H_{14}O_3$, was also formed. This was phenolic and possessed two keto-groups of differing reactivities, and thus was *o*-4-oxohexanoylphenol (V) formed by irregular cleavage at one of the hydroperoxide centres.

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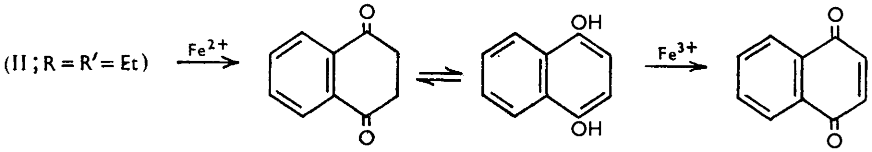
[4] Russel, *J. Amer. Chem. Soc.*, 1955, **77**, 4583.

Ferrous sulphate converted the dihydroperoxides (II; R = R′ = Et) into 1 : 4-naphthaquinone in small yield, presumably by the route shown.



1-Ethyltetralin was oxidised similarly, giving mainly a tertiary monohydroperoxide (I; R = Et, R′ = H), which was extracted from the oxidate by means of aqueous-methanolic sodium hydroxide; we did not observe any special instability towards alkali such as was encountered by Hock *et al.*[1] in the case of 1-methyltetralyl hydroperoxide. Acid-cleavage of this hydroperoxide proceeded normally, giving the product (III; R = Et, R′ = H). Continued oxygenation of the hydrocarbon led to small amounts of a dihydroperoxide, although oxidation could not be carried beyond 50% conversion. The dihydroperoxide, in which one of the hydroperoxy-groups must be secondary, was soluble in, but rapidly decomposed by, dilute sodium hydroxide solution. It was precipitated from the crude product by light petroleum, but it could not be purified. Insufficient crystalline material was obtained to investigate its cleavage, but an impure dihydroperoxide isolated by alkali extraction gave catechol and the phenolic diketone (V); the latter may have arisen from 1-ethyl-1-hydroperoxy-4-oxotetralin formed by decomposition of the dihydroperoxide by alkali. The oxidation residues contained small amounts of a ketone which, from the m. p. and analysis of derivatives, appeared to be 4-ethyl-1-oxotetralin. If this is so it would have arisen from decomposition of an unstable 4-monohydroperoxide.

EXPERIMENTAL

The remarks on handling peroxides in Part VIII [2] apply equally here. " Light petroleum " refers to the grade of b. p. 40—60°.

Materials.—1-Ethyltetralin,[5] b. p. 240·0°/760 mm., n_D^{20} 1·5520, d_4^{20} 0·9547, and 1 : 4-diethyltetralin, b. p. 266·5°/760 mm., n_D^{20} 1·5262, d_4^{20} 0·9433, were kindly supplied by Ethyl Corp., New York. 1 : 4-Dimethyltetralin was prepared according to Colonge and Pichat's directions; [6] 5-phenylhexan-2-one was conveniently hydrogenated to the alcohol over copper–chromium oxide at 160°/50 atm., rapidly and quantitatively: the hydrocarbon boiled at 231·5°/749 mm., and had n_D^{20} 1·5297, and no change of b. p., n_D, or infrared spectrum during fractionation through a 50-plate column. Our constants differ appreciably for those recorded [7] for the *cis*-hydrocarbon of unstated provenance.

Oxidation of 1 : 4-*Diethyltetralin.*—The hydrocarbon (400 g., 2·13 moles) and 2·5% aqueous sodium carbonate (100 ml.) were vigorously stirred in oxygen at 90° for 14 hr., by which time 1·47 moles of oxygen had been taken up and 1·10 equiv. of hydroperoxide formed. Benzene (400 ml.) was added, whereupon some solid dihydroperoxide crystallised and was filtered off. The aqueous layer was rejected, and the liquid organic phase was extracted with 2N-sodium hydroxide (4 × 150 ml.).

The alkaline extract was neutralised with carbon dioxide, then shaken with benzene, and the whole filtered. The rest of the " solid " 1 : 4-*diethyl*-1 : 4-*dihydroperoxytetralin* (II; R = R′ = Et) was thereby removed [the combined solid products amounted to 21 g. (0·20 equiv. of hydroperoxide)]. This recrystallised from chloroform as a solvate, m. p. 104—107° (sealed tube; rapid heating) (Found: dihydroperoxide, by titration, 75·3; loss in wt. at 78°/0·1 mm., 19·0%), or from toluene as a solvate, m. p. 105—108° (sealed tube; rapid heating) (Found: dihydroperoxide, 80·6; loss in wt., 13·2, 13·5%). When heated slowly in an open tube, these solvates melted indefinitely at about 115°. They lost solvent in 1 hr. at 78°/0·1 mm., or in a few days

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[5] Ethyl Corp., B.P. 766,215/1957.
[6] Colonge and Pichat, *Bull. Soc. chim. France*, 1949, 853, 855.
[7] Dreisbach, " Physical Properties of Chemical Compounds," Amer. Chem. Soc., 1955, p. 251.

in the atmosphere, leaving the solvent-free dihydroperoxide, m. p. 120° (Found: C, 66·9; H, 7·8%; iodometric equiv., 127, 131. $C_{14}H_{20}O_4$ requires C, 66·7; H, 8·0%; equiv., 126). The benzene layer of the filtrate, when washed, dried and evaporated *in vacuo*, left the crude "liquid" dihydroperoxide as a viscous oil, assaying 77% of diethyldihydroperoxytetralin by titration. It could not be purified further.

The alkali-extracted products from several oxidations were combined and the benzene was removed under reduced pressure below 50°. The residue was diluted with thrice its volume of light petroleum, and extracted repeatedly with a mixture containing 200 g. of sodium hydroxide and 500 ml. of methanol per l., the rest being water. The alkaline extract was diluted and neutralised with carbon dioxide, and the liberated hydroperoxide collected in light petroleum. By repeated recrystallisation from light petroleum, 1 : 4-*diethyl*-1-*hydroperoxytetralin* was obtained as needles, m. p. 63—64° (Found: C, 75·8; H, 8·8%; equiv., 214. $C_{14}H_{20}O_2$ requires C, 76·3; H, 9·1%; equiv., 220. The analysis suggested that it still contained a little dihydroperoxide).

A purer sample of hydrocarbon was oxidised to 100% absorption at 79% efficiency. The oxidation by-products were mainly a mixture of ketones.

Acid-cleavage of 1 : 4-*Diethyl*-1 : 4-*dihydroperoxytetralin*.—The "liquid" dihydroperoxide (II; R = R′ = Et) (16·3 g., 72% pure) in acetone (80 ml.) was added during 5 min. to sulphuric acid (0·1 g.) in boiling acetone (80 ml.). After the mixture had been boiled for 40 min., all the peroxide had disappeared. The product was neutralised and concentrated as previously, and partitioned between carbon tetrachloride (or benzene) and water. The aqueous layer yielded 1·52 g. (30%) of catechol, m. p. 104—106°, accompanied by some tar. The carbon tetrachloride layer was extracted twice with 2N-sodium hydroxide (75 ml.), whence acidification precipitated an oil which was isolated by means of ether and then lixiviated with hot light petroleum. The extract, on cooling, deposited waxy plates of o-4-*oxohexanoylphenol* (V), m. p. 39·5—40°, b. p. 115—125°/0·1 mm. (1·67 g.) (Found: C, 70·0; H, 7·0. $C_{12}H_{14}O_3$ requires C, 69·9; H, 6·8%) (for derivatives see below). The alkali-extracted carbon tetrachloride layer, on being washed and distilled, afforded octane-3 : 6-dione (1·41 g., 22%), m. p. 34—36°, b. p. 106—112°/25 mm., and material, b. p. up to 170°/25 mm. (2·82 g.). The diketone (for which Blaise [8] recorded b. p. 98°/14 mm., m. p. 34—35°) was characterised as 1-anilino-2 : 5-diethylpyrrole,[9] m. p. 67° (lit., 65·5°), and 2 : 5-diethyl-1-*p*-nitrophenylpyrrole,[10] m. p. 96° (lit., 95—96°).

The "solid" isomer of the dihydroperoxide gave the same products in similar yields. Various other acid catalysts were tried, without improvement in yields.

Characterisation of o-4-*Oxohexanoylphenol* (V).—The infrared spectrum showed the general characteristics of an *o*-disubstituted aromatic compound, a saturated open-chain ketone (1718 cm.$^{-1}$), and an *o*-hydroxyphenyl ketone (1640 cm.$^{-1}$). As with other compounds containing the ·C(OH)⁚C·CO· structure,[11] the hydroxyl absorption was only just detectable as a broad weak band superimposed on the CH band. The substance was strongly fluorescent in ultraviolet light. Warming the compound with one equiv. of hydroxylamine hydrochloride and sodium acetate in aqueous ethanol for 1 hr. afforded the *monoxime*, m. p. 103—108°; the m. p. was unsharp after repeated recrystallisation from light petroleum or 50% ethanol, and the oxime may have been a mixture of isomers (Found: C, 65·0; H, 6·8; N, 6·1. $C_{12}H_{15}O_3N$ requires C, 65·1; H, 6·8; N, 6·1%). The *dioxime* was obtained by heating the keto-phenol under reflux with a large excess of hydroxylamine hydrochloride in pyridine and ethanol. Recrystallised from benzene, it had m. p. 125—127·5° (Found: C, 60·5; H, 6·8; N, 11·5. $C_{12}H_{16}O_3N_2$ requires C, 61·0; H, 6·8; N, 11·8%).

Other ketonic derivatives prepared in the usual way were the *monosemicarbazone*, m. p. 157—158° (from ethanol) (Found: C, 59·6; H, 6·6; N, 16·5. $C_{13}H_{17}O_3N_3$ requires C, 59·3; H, 6·5; N, 16·0%), and the orange *mono*-2 : 4-*dinitrophenylhydrazone*, m. p. 167—169° (from chloroform) (Found: N, 14·9. $C_{18}H_{18}O_6N_4$ requires N, 14·5%).

The 3 : 5-*dinitrobenzoate* had m. p. 130—132° (from ethanol or acetone) (Found: C, 57·1; H, 4·0. $C_{19}H_{16}O_8N_2$ requires C, 57·0; H, 4·0%). The *methyl ether*, prepared by means of methyl iodide and aqueous-methanolic sodium hydroxide, had b. p. 143°/0·5 mm. (Found: C, 70·7; H, 7·4. $C_{13}H_{16}O_3$ requires C, 70·9; H, 7·3%).

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[8] Blaise, *Compt. rend.*, 1914, **158**, 506.

[9] *Idem, ibid.*, 1920, **171**, 34.

[10] Fetizon and Baranger, *ibid.*, 1953, **236**, 1428.

[11] Bellamy, "Infra-red Spectra of Complex Molecules," Methuen, London, 1954, p. 91.

Acid-cleavage of 1 : 4-*Diethyl*-1-*hydroperoxytetralin* (I; R = R′ = Et).—The monohydroperoxide (I; R = R′ = Et) by treatment with sulphuric acid in acetone, as described above, gave 6-o-*hydroxyphenyloctan*-3-*one* (64%), m. p. 34—35·5°, b. p. 195°/15 mm. (Found: C, 76·4; H, 8·7. $C_{14}H_{20}O_2$ requires C, 76·3; H, 9·2%). This depressed the m. p. of the diketo-phenol (V). A number of derivatives were prepared, but none crystallised; the oily 1-naphthylurethane yielded a pale orange *naphthylurethane* 2 : 4-*dinitrophenylhydrazone*, m. p. 167—169° (from benzene–ethanol) (Found: C, 65·2; H, 5·5; N, 12·8. $C_{31}H_{32}O_6N_5$ requires C, 65·4; H, 5·5; N, 12·3%).

Action of Ferrous Sulphate on 1 : 4-*Diethyl*-1 : 4-*dihydroperoxytetralin.*—To the solid dihydroperoxide (II; R = R′ = Et) (20 g.) in ethanol (150 ml.) was added ferrous sulphate heptahydrate (60 g.) in water (600 ml.), the temperature being kept below 30°. After an hour the mixture was warmed to 50° for an hour and then to the b. p. for a further hour. Concentrated hydrochloric acid (50 ml.) was added to dissolve the ferric hydroxide. The organic product, isolated by extraction with ether, was naphtha-1 : 4-quinone (2 g.), m. p. 124·5—125·5° (lit., 125°). The orange mono-2 : 4-dinitrophenylhydrazone had m. p. 264—268° (decomp.) [lit.,[12] 278° (decomp.)] (Found: C, 57·2; H, 3·3. Calc. for $C_{16}H_{10}O_5N_4$: C, 56·7; H, 3·0%).

Hydrogenation of 1 : 4-*Diethyl*-1 : 4-*dihydroperoxytetralin.*—The solid isomer of the dihydroperoxide (II; R = R′ = Et) in methanol was hydrogenated at room temperature and pressure over 0·7% palladium–alumina. The theoretical amount of hydrogen was absorbed. Removal of catalyst and solvent left 1 : 4-*diethyl*-1 : 4-*dihydroxytetralin*, which was recrystallised from benzene–light petroleum and then carbon tetrachloride to m. p. 93—94° (Found: C, 76·2; H, 9·0. $C_{14}H_{20}O_2$ requires C, 76·3; H, 9·2%).

This diol (1·0 g.) in boiling benzene in the presence of a trace of toluene-*p*-sulphonic acid eliminated water which was removed azeotropically. The washed evaporated solution yielded 1 : 4-diethylnaphthalene, identified by its ultraviolet spectrum and its *picrate*, yellow needles (from ethanol), m. p. 93—95° (Found: C, 57·9; H, 4·6. $C_{14}H_{16},C_6H_3O_7N_3$ requires C, 58·1; H, 4·6%) (Arnold and Barnes [13] found m. p. 91—93°, but did not analyse their picrate).

Oxidation of 1 : 4-*Dimethyltetralin.*—The hydrocarbon (247 g., 1·56 mole) was oxidised in the manner described above. After 7 hr., 1·40 moles of oxygen had been absorbed, and 1·15 equivalents of hydroperoxide had been formed. Absorption was still proceeding rapidly at this point. The products were worked up as described before, except that as the dihydroperoxide was completely soluble in benzene the filtrations were omitted. The hydroperoxide fraction was obtained as a solid (25 g.) which melted over a wide range. Recrystallisation from chloroform afforded a sharp-melting 1 : 4-*dihydroperoxy*-1 : 4-*dimethyltetralin* (II; R = R′ = Me), m. p. 149—150° (decomp.) (Found: C, 64·1; H, 7·1%; iodometric equiv., 111. $C_{12}H_{16}O_4$ requires C, 64·2; H, 7·2%; equiv., 112). The mother-liquors were diluted with light petroleum, and the precipitate recrystallised repeatedly from toluene and then benzene, yielding a dihydroperoxide melting indefinitely at about 90°. The hydroperoxide titre of this eventually fell to 79% of the theoretical, showing that decomposition was occurring. 1 : 4-*Diethyl*-1-*hydroperoxytetralin* was obtained as a viscous oil which could not be distilled without decomposition (Found: C, 75·0; H, 8·5%; equiv., 209. $C_{12}H_{16}O_2$ requires C, 75·0; H, 8·4%; equiv., 192).

Acid-cleavage of 1 : 4-*Dimethyltetralin Hydroperoxides.*—The method already described was used. A mixture of the dihydroperoxide (II; R = R′ = Me) isomers (92% pure) gave catechol (100%) and hexane-2 : 5-dione (31%), identified as its phenylhydrazone, m. p. and mixed m. p. 116—118°. The pure dihydroperoxide isomer, m. p. 150°, gave 71% of catechol (estimated in the aqueous extract as lead iodate [14]).

Cleavage of the monohydroperoxide (I; R = R′ = Me) yielded 5-o-*hydroxyphenylhexan*-2-*one* (III; R = R′ = Me) (28·7 g.), b. p. 130—135°/0·3 mm., n_D^{20} 1·5330 (supercooled), m. p. 42—44° (from light petroleum) (Found: C, 74·8; H, 8·3. $C_{12}H_{16}O_2$ requires C, 75·0; H, 8·4%). The *semicarbazone*, crystallised from ethanol, had m. p. 175—176° (Found: C. 62·9: H, 7·7; N, 16·5. $C_{13}H_{19}O_2N_3$ requires C, 62·7; H, 7·7; N, 16·9%). The dinitrophenylhydrazone and benzoate were not crystalline.

Oxidation of 1-*Ethyltetralin.*—(*a*) The hydrocarbon (400 g., 2·50 moles) and 2·5% aqueous sodium carbonate (100 ml.) were oxygenated at 90° for 9·75 hr. After 6·5 hr., 40 mol. % of

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[12] Roduta and Quibilan, *Rev. filip. Med. Farm.*, 1936, **27**, 123.

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

[14] Baernstein, *J. Biol. Chem.*, 1945, **161**, 684.

oxygen had been absorbed, 95% of which had been converted into hydroperoxide, but beyond this time the hydroperoxide content did not increase despite further absorption of oxygen. The product was diluted with an equal volume of light petroleum, and the aqueous phase rejected. Extraction with 2N-sodium hydroxide removed 0·14 equiv. of hydroperoxide; the extract was very dark. Neutralising it with carbon dioxide liberated an oil (*A*) which was collected with light petroleum and did not crystallise (15·0 g.); titration showed an iodometric equivalent of 202, corresponding to 54% purity as dihydroperoxide, and to a total of only 0·07 equiv.; therefore half the hydroperoxide had been lost during neutralisation. The alkali-washed organic phase was next extracted with a mixture (divided into 3 parts) of 80 g. of sodium hydroxide and 400 ml. of methanol made up to 800 ml. with water. The hydroperoxide (*B*), regenerated from this extract in the usual way, formed a viscous oil assaying 85·2% as monohydroperoxide (I; R = Et, R′ = H).

(*b*) The organic phase from a similar oxidation was dried, diluted with a large volume of light petroleum, and cooled to −80°. The gummy precipitate was repeatedly dissolved in benzene and precipitated with light petroleum, finally being brought to m. p. 118—119° [depressed by (II; R = R′ = Et)], then assaying as 83% dihydroperoxide (II; R = Et, R′ = H). Attempts to purify it further were unsuccessful; it amounted to less than 1 g.

Distillation of oxidation residues after removal of all hydroperoxide afforded a small amount of ketonic material, b. p. 128°/13 mm. to 95°/0·3 mm., which appeared to be mainly 4-ethyl-1-oxotetralin; it yielded an *oxime*, m. p. 80—81° (Found: C, 75·9; H, 8·0; N, 6·9. $C_{12}H_{15}ON$ requires C, 76·1; H, 8·0; N, 7·4%), semicarbazone, m. p. 182·5—183° (Found: N, 18·1. Calc. for $C_{13}H_{17}ON_3$: N, 18·2%), and scarlet 2 : 4-*dinitrophenylhydrazone*, m. p. 198—200° (Found: C, 61·1; H, 4·9; N, 16·3. $C_{18}H_{18}O_4N_4$ requires C, 61·1; H, 5·1; N, 15·8%). Levy[15] records a m. p. of 183° for the semicarbazone.

Acid-cleavage of 1-*Ethyltetralin Hydroperoxides.*—The dihydroperoxide concentrate (*A*) mentioned above (14·4 g.) gave, by the usual procedure, catechol (0·28 g.) and *o*-4-oxohexanoylphenol (V) (1·37 g), m. p. and mixed m. p. 35—38°. Distillation of the neutral part of the product gave no definite fraction.

Cleavage of the monohydroperoxide concentrate (*B*) required 80 min. at reflux temperature, and yielded 6-o-*hydroxyphenylhexan*-3-*one*, b. p. 196—198°/22 mm., n_D^{20} (supercooled) 1·5322, m. p. 32—33° (Found: C, 74·5; H, 8·0. $C_{12}H_{16}O_2$ requires C, 75·0; H, 8·4%). Its pale orange 2 : 4-*dinitrophenylhydrazone* had m. p. 136—137° (from aqueous alcohol and then benzene) (Found: C, 57·8; H, 5·2; N, 15·4. $C_{18}H_{20}O_5N_4$ requires C, 58·1; H, 5·4; N, 15·0%).

Thanks are offered to Ethyl Corp. for the gift of 1-ethyl- and 1 : 4-diethyl-tetralin, to Messrs. A. R. Philpotts and W. F. Maddams for the spectroscopic work, and to Mr. B. Gnyra for fractionating hydrocarbons.

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GREAT BURGH, EPSOM, SURREY.
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[15] Levy, *Compt. rend.*, 1933, **197**, 772.