934. *Reactions of Organic Peroxides. Part VIII.** 1 : 3 : 3-*Trimethylindan*-1-*yl Hydroperoxide and its Conversion into* 2 : 4 : 4-*Trimethylchroman Derivatives.*

By William Webster and Donald P. Young.

1 : 1 : 3-Trimethylindane is readily oxidised to a hydroperoxide, the structure of which follows from its reduction to the known 1 : 3 : 3-trimethylindan-1-ol. In presence of acids, the hydroperoxide rearranges to give 2 : 4 : 4-trimethylchroman-2-ol and 2 : 4 : 4-trimethylchrom-2-en; the former compound has been synthesised. The hydroperoxide with ferrous sulphate in dilute aqueous ethanol gives 1-ethoxy-1 : 3 : 3-trimethylindane.

Commercial samples of di*iso*propylbenzene usually contain up to 10% of 1 : 1 : 3-trimethylindane,[1] which can be isolated from the mixture by distillation. Presumably it arises from cyclisation of *o*-di*iso*propylbenzene with loss of hydrogen.

1 : 1 : 3-Trimethylindane (I) was readily converted by oxygen at 90°, in the presence of alkali, into a hydroperoxide. This hydroperoxide was not soluble in dilute sodium hydroxide but, on treatment of the oxidate with 40% sodium hydroxide solution, its sodium salt crystallised. The free hydroperoxide was regenerated from the salt by means of carbon dioxide, and was obtained as a solid, m. p. 38·5—40°; its structure as 1 : 3 : 3-trimethylindan-1-yl hydroperoxide (II) followed from its reduction to be known 1 : 3 : 3-trimethylindan-1-ol.[1]

When treated with a little fuller's earth or sulphuric acid in boiling acetone, trimethylindanyl hydroperoxide gave 2 : 4 : 4-trimethylchroman-2-ol (III) (40—50%) and its dehydration product, 2 : 4 : 4-trimethylchrom-2-en (IV) (25—40%). This is the first

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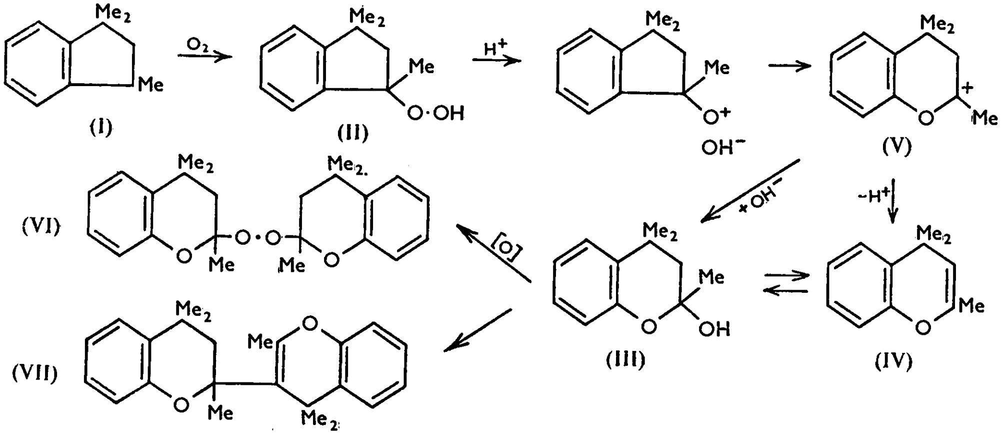
* Part VII, *J.*, 1955, 3463.

[1] Colonge and Garnier, *Bull. Soc. chim. France*, 1948, 438.

recorded case where a hemiketal has been obtained directly from a hydroperoxide, although hemiketal esters have previously been obtained from hydroperoxide esters.[2] A ring-homologue of our hydroperoxide, 1 : 2 : 3 : 4-tetrahydro-1-methyl-1-naphthyl hydroperoxide, gives the expected keto-phenol.[3] The emergence of the cyclic hemiketal in the present case is attributed to its high stability. The amount of trimethylchromen (IV) formed could not be accounted for by dehydration of the chromanol (III) under the reaction conditions, and the two products probably arose simultaneously from a common cationic intermediate (V).[4]



2 : 4 : 4-Trimethylchroman-2-ol (III) has previously been obtained[5] by decarbonylation of 2 : 4 : 4-trimethylchroman-1-carboxylic acid, the structure of which was established by synthesis. The m. p. of our product was in agreement with that previously recorded. To confirm its structure, it was synthesised by the method already used for its homologue.[5] 2 : 4 : 4-Trimethylchroman-2-carboxylic acid was converted into its amide, which was submitted to Hofmann rearrangement. Surprisingly, the product was not the expected trimethylchromanylamine but the chromanol (III) itself. Evidently the amine (which would be tautomeric with a phenolic ketimine) has an amino-group so labile that it was hydrolysed under the reaction conditions. Our proposed structure for the chromen (IV) rests on its relationship to the chromanol (III); the isomer with an exocyclic double bond is not excluded, but seems less likely.

2 : 4 : 4-Trimethylchroman-2-ol has also been reported[6] as arising from condensation of phenol and mesityl oxide in presence of sulphuric acid, but other workers[5, 7] besides ourselves have been unable to repeat this preparation. The compound from the same reactants and hydrogen chloride, formerly regarded as (IV),[8] has recently been shown to be the isomeric 2 : 2 : 4-trimethylchrom-3-en;[9] we had independently come to the same conclusion, since the compound was not identical with our chroman (IV) and had an ultraviolet absorption spectrum indicating that the double bond was conjugated with the aromatic ring.

Rearrangement of the hydroperoxide (II) in presence of " Indoil " alkanesulphonic acid (a mixture, approximately $C_4H_9{\cdot}SO_3H$) was accompanied by the formation of a

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[2] Criegee and Zogel, *Chem. Ber.*, 1951, **84**, 215; Criegee, *Annalen*, 1948, **560**, 127; Wieland and Maier, *Ber.*, 1931, **64**, 1205.

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

[4] Cf. Kharasch, Fono, and Nudenberg, *J. Org. Chem.*, 1950, **15**, 748; Seubold and Vaughan, *J. Amer. Chem. Soc.*, 1953, **75**, 3790.

[5] Baker, Curtis, and McOmie, *J.*, 1952, 1774.

[6] Niederl, *J. Amer. Chem. Soc.*, 1929, **51**, 2426.

[7] Smith and Pritchard, *ibid.*, 1940, **62**, 771.

[8] Dianin, *J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1310.

[9] Baker and McOmie, *Chem. and Ind.*, 1955, 256; Baker, Floyd, McOmie, Pope, Weaving, and Wild, *J.*, 1956, 2010.

by-product shown to be bis-2 : 4 : 4-trimethylchroman-2-yl peroxide (VI) by analysis. It appeared to have arisen by oxidation of the chromanol (III), and it was also obtained in small yield therefrom by use of hydrogen peroxide and a little sulphuric acid.

The trimethyl-chromanol (III) and -chromen (IV) had most of the usual properties of such compounds.[5, 10] The chromen (IV) readily added water and alcohols in presence of acid to give the chromanol (III) and ethers thereof respectively, and these were easily split to regenerate the chromen. Dehydration of the chromanol in presence of sulphuric acid, however, gave considerable amounts of a dimer (VII). The chromen was only hydrogenated to trimethylchroman under comparatively drastic conditions, and it reacted with bromine by substitution rather than addition. Trimethylchromanol (III) did not show any of the normal properties of the tautomeric keto-phenol. Only by drastic treatment with an excess of concentrated sodium hydroxide solution and dimethyl sulphate was the methyl ether of the corresponding keto-phenol obtained.[11] Such stability is unusually high for an α-pyranol derivative, and may be connected with the heavy substitution on the heterocyclic ring. Chroman-2-ol, for example, readily yields a dinitrophenylhydrazone.[10] The action of dilute nitric acid on the chromanol (III) resulted in oxidative breakage of the pyran ring with simultaneous nitration of the benzene ring, the product being a (probably mixed) α-*o*-hydroxydinitrophenyl-α-methylpropionic acid.

The trimethylindanyl hydroperoxide reacted rather slowly with warm aqueous ferrous sulphate, and the product was almost entirely trimethylindene, evidently from dehydration of initially formed trimethylindanol. In dilute aqueous ethanol the reaction was much faster, and the major product was 1-ethoxy-1 : 3 : 3-trimethylindane. This ether was obtained for comparison by Williamson synthesis from trimethylindanol. The ether is presumably formed from the hydroperoxide (R·O·OH) by the attack of R·O· radicals on the ethanol. An etherification of ethanol in dilute aqueous solution must be unprecedented. Trimethylindanol was obtained here as a minor product, but only traces of ketonic material, apparently 3 : 3-dimethylindan-1-one and not *o-tert.*-butylacetophenone.

EXPERIMENTAL

No explosions or violent decompositions occurred during the preparation or handling of trimethylindanyl hydroperoxide, but the usual precautions were always observed. The hydroperoxide and its sodium salt are skin irritants.

" Light petroleum," unless otherwise stated, refers to the grade, b. p. 40—60°.

1 : 1 : 3-*Trimethylindane* (I).—Commercial di*iso*propylbenzene (Dow Chemical Co.) was fractionated through a 100-plate column. The intermediate cuts, b. p. 204—210°, between the *m*- and the *p*-di*iso*propylbenzene fractions from several distillations were combined and refractionated through a similar column, yielding fairly pure 1 : 1 : 3-trimethylindane, b. p. 204·8—204·9°/760 mm. (corr.), 81—84°/15 mm., n_D^{20} 1·5077 (Colonge and Garnier[1] give b. p. 90°/21 mm., n_D^{20} 1·5059). This contained 2—3% of other impurities detectable spectroscopically. The infrared spectrum showed a doubled band at 750 cm.$^{-1}$, and typical bands for an *ortho*-disubstituted benzene in the 1660—2000 cm.$^{-1}$ region; in the ultraviolet spectrum, the strongest band was at 2720 Å. These bands were not in agreement with any known dialkylbenzene or alkyltetralin, but were consistent with recorded data for indane and its homologues. Oxidation with chromium trioxide in acetic acid gave αα-dimethylhomophthalic acid, m. p. 121—122°, forming an anhydride, m. p. 80—81° (lit.,[1] 123° and 82·5—83° respectively).

1 : 1 : 3-*Trimethyl*-x-*nitroindane*.—Trimethylindane (20 ml.) was nitrated with fuming nitric acid (5 ml.) in acetic acid (20 ml.) and anhydride (14 ml.) at 30°, with cooling, affording a mixed mononitro-derivative (6 g.), b. p. 160—166°/18 mm. (Found : C, 70·6; H, 7·3; N, 6·4. Calc. for $C_{12}H_{15}O_2N$: C, 70·3; H, 7·4; N, 6·8%). This on dilution with methanol precipitated a solid of indefinite m. p., which after repeated recrystallisation from ethanol, methanol, and light petroleum gave a small amount of a sharp-melting *nitro-derivative*, m. p. 76—77° (Found : C, 70·1; H, 7·5; N, 6·8%). The infrared spectrum suggested that it was the 5- or 6-nitro-compound.

1 : 3 : 3-*Trimethylindan*-1-*yl Hydroperoxide* (II).—A mixture of 400 g. of trimethylindane

[10] Maitte, *Ann. Chim.* (*France*), 1954, **9**, 462.

[11] Cf. Baker, Curtis, and McOmie, ref. 5.

(93% pure) and 100 ml. of 2·5% aqueous sodium carbonate was stirred vigorously at 90° in a stream of oxygen. The rate of oxygen absorption at first accelerated to 10—11 mol.-% per hr., and then decreased slowly. Oxygenation was stopped after 8 hr., when 29 l. (N.T.P.) had been absorbed (52% calc. on hydrocarbon). The organic phase was diluted with 200 ml. of light petroleum; iodometric titration showed that it contained 1·15 equiv. (86% on oxygen absorbed) of hydroperoxide. The aqueous layer was rejected. A saturated solution of 70 g. of sodium hydroxide was added to the product with cooling and stirring. The sodium salt of the hydroperoxide crystallised, and after a few hours was collected, well washed with light petroleum, and decomposed by suspension in water and light petroleum and neutralisation with carbon dioxide. On concentration and strong cooling of the petroleum layer, the *hydroperoxide* crystallised in long fine needles, m. p. 38·5—40°, b. p. 70—71°/0·2 μ (Found: C, 74·7; H, 8·1%; iodometric equiv., 193. $C_{12}H_{16}O_2$ requires C, 75·0; H, 8·4%; equiv., 192).

The oxidation was also carried out with 400 g. of hydrocarbon and 5 g. of calcium hydroxide at 90°, with similar results.

Rearrangement of 1 : 3 : 3-*Trimethylindan*-1-*yl Hydroperoxide*.—(*a*) A solution of 100 g. of the hydroperoxide (II) (99% pure) in 200 ml. of acetone was added during 10 min. to a boiling solution of sulphuric acid (0·5 g.) in acetone (800 ml.). After boiling for a further 20 min., the solution contained very little hydroperoxide. It was neutralised by stirring with magnesium oxide (20 g.) for a few minutes, then separated, and the acetone driven off. The residue was dissolved in twice its weight of light petroleum. When this solution was cooled to −40°, 2 : 4 : 4-trimethylchroman-2-ol (III) crystallised; after recrystallisation it had m. p. 93·5—94° (Baker *et al.*[5] give 91°) (Found: C, 74·9; H, 8·2%; *M* in C_6H_6, 198. Calc. for $C_{12}H_{16}O_2$: C, 75·0; H, 8·4%; *M*, 192). The mother-liquors were freed from solvent and distilled through a short column into fractions as follows, analyses being by infrared spectroscopy:

B. p./mm.	Wt. (g.)	(IV) (%)	(III) (%)	Trimethyl-indene (%)	Trimethyl-indanol (%)
102—105°/16	7·27	60	1	10	—
105—122°/16	25·68	75	7	3	5
122—140°/16	9·36	15	40	—	—

The last fraction deposited some more solid trimethylchromanol (III). On the basis of the above analyses, the yields were (III) 48%, (IV) 28%. The indene and indanol could be accounted for by thermal decomposition of unrearranged hydroperoxide during distillation.

Refractionation of combined liquid products from several runs gave 2 : 4 : 4-*trimethylchrom*-2-*en* (IV), b. p. 104—106°/16 mm., n_D^{20} 1·5320, d_D^{20} 1·0049, $\lambda_{max.}$ 2850, 2775, and 2420 Å (ε 1500, 1670, and 4820 respectively) in *cyclo*hexane (Found: C, 83·0; H, 8·3. $C_{12}H_{14}O$ requires C, 82·8; H, 8·1%).

(*b*) A similar result obtained from the hydroperoxide (12 g.) with fuller's earth (No. 237, Fullers' Earth Union Ltd.; 2·0 g.) in boiling benzene (100 ml.) for 1·5 hr.

(*c*) The hydroperoxide (50 g.) with "mixed alkanesulfonic acid" (Indoil Chemical Co.; 4 ml.) in boiling acetone (400 ml.) yielded trimethylchromen (41%) and trimethylindene (7%). The solid product was a mixture of trimethylchromanol (28%), which was separated by leaching with hot ethanol, and *bis*-2 : 4 : 4-*trimethylchroman*-2-*yl peroxide*, m. p. 156° from ethyl acetate (Found: C, 75·4; H, 7·7%; *M* by peroxide estimation,[12] 378. $C_{24}H_{30}O_4$ requires C, 75·5; H, 7·9%; *M*, 382). This compound was also obtained (0·4 g. yield) from trimethylchromanol (III) (3·84 g.), 30% hydrogen peroxide (1·0 ml.), and sulphuric acid (1 drop) in ethanol (50 ml.), refluxed for 1 hr. and then set aside for 3 days.

Synthesis of 2 : 4 : 4-*Trimethylchroman*-2-*ol*.—2 : 4 : 4-Trimethylchroman-2-carboxylic acid[5] was converted into its *amide*, m. p. 140—142° (Found: C, 71·2; H, 8·0; N, 6·3. $C_{13}H_{17}O_2N$ requires C, 71·2; H, 7·8; N, 6·4%), which (7·1 g.) was subjected to the action of potassium hypobromite by the method used by Baker *et al.*[5] for its homologue. The product contained no acid-soluble material. The neutral organic product was leached with warm light petroleum, which left 0·85 g. of unchanged amide. The extract yielded 1·5 g. of trimethylchromanol, which after recrystallisation had m. p. 86—88°.

By omitting the dioxan solvent and any treatment with acid, a similar experiment yielded a solid product, m. p. 176—178°. This might have been bistrimethylchromanylurea (Found: N, 6·7. Calc. for $C_{25}H_{32}O_3N_2$: N, 6·9%), but no recognisable product was obtained from it hydrolysis.

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[12] Dickey, Raley, Rust, Treseder, and Vaughan, *Ind. Eng. Chem.*, 1949, **41**, 1673.

Interconversion of 2 : 2 : 4-*Trimethylchroman*-2-*ol* (III) *and* 2 : 2 : 4-*Trimethylchrom*-2-*en* (IV).—The chromanol (50 g.), benzene (150 ml.), and anhydrous oxalic acid (1 g.) were boiled in a Dean and Stark apparatus. The theoretical amount of water separated within 30 min. The undissolved oxalic acid was removed, and the solution was fractionated to give 43·2 g. (96%) of 2 : 2 : 4-trimethylchrom-2-en, b. p. 103—104°/15 mm., n_D^{20} 1·5320, spectroscopically identical with the compound obtained from rearrangement of the hydroperoxide.

Catalysis with small amounts of sulphuric or phosphoric acid likewise gave quantitative yields of chromen, but dehydration in a similar manner of the chromanol (30 g.) over toluene-*p*-sulphonic acid (0·5 g.) gave 43% of chromen and 36% of 2 : 4 : 4-*trimethyl*-3-(2 : 4 : 4-*trimethylchroman*-2-*yl*)*chrom*-2-*en* (VII), b. p. 156—164°/0·1 mm.; this crystallised from ethanol in small flat needles, m. p. 70° (Found : C, 82·5; H, 8·2%; *M* in C_6H_6, 346. $C_{24}H_{28}O_2$ requires C, 82·8; H, 8·1%; *M* 352). The infrared spectrum showed no functional groups but contained the chromen bands at 1230 and 1696 cm.$^{-1}$, the latter (double bond) being reduced in intensity to half that in the chromen itself. This dimer (2·6 g.) with bromine in carbon tetrachloride at room temperature evolved hydrogen bromide and yielded a *monobromo-derivative*, short needles (from light petroleum), m. p. 122° (Found : C, 68·0; H, 6·3. $C_{24}H_{27}O_2Br$ requires C, 67·5; H, 6·3%). The dimer (5 g.) by oxidation with potassium permanganate in boiling acetone gave a little 2 : 4 : 4-trimethylchroman-2-carboxylic acid (0·05 g.), m. p. 167—170°, not depressed by an authentic sample.

The dimer was also obtained as a major product by dehydration of trimethylchromanol in presence of " Indoil " alkanesulphonic acid.

Trimethylchromanol was mainly unchanged when boiled in acetone containing 0·1% sulphuric acid for 1 hr.

Trimethylchromen (IV) (10 g.) and N-sulphuric acid (100 ml.) were refluxed for 3 hr. The product was extracted with light petroleum, which on evaporation and cooling deposited 2·3 g. (21%) of trimethylchromanol (III). The mother-liquor yielded 6·6 g. of unchanged chromen. Doubling the reaction time gave the same amount of (III). When exposed to the atmosphere in the presence of a trace of sulphuric acid, the chromen changed within a few days into a crystalline mass of the chromanol (III).

2-*Alkoxy*-2 : 4 : 4-*trimethylchromans*.—2 : 4 : 4-Trimethylchroman-2-ol (III; 10 g.) and N-hydrogen chloride in methanol (100 ml.) were boiled under reflux for 2·5 hr. The methanol was distilled off, and the residue was taken up in light petroleum and washed free from acid, giving 2-*methoxy*-2 : 4 : 4-*trimethylchroman* (7·0 g.), b. p. 121—124°/17 mm., n_D^{20} 1·5135, d_4^{20} 1·0306 (Found : C, 75·7; H, 8·5; OMe, 14·2. $C_{13}H_{18}O_2$ requires C, 75·6; H, 8·8; OMe, 15·0%).

2 : 4 : 4-Trimethylchrom-2-en (IV; 10 g.) similarly treated gave the same product (8·8 g.). The analogously prepared *ethoxy-compound* had b. p. 126°/15 mm., n_D^{20} 1·5039, n_4^{20} 1·0028 (Found : C, 76·7; H, 9·2. $C_{14}H_{20}O_2$ requires C, 76·3; H, 9·1%). Although apparently pure it gave persistently low Zeisel ethoxyl values.

Distilling the methoxy- or ethoxy-trimethylchroman over a trace of sulphuric acid immediately regenerated trimethylchromen.

2 : 4 : 4-*Trimethylchroman*.—2 : 4 : 4-Trimethylchrom-2-en (IV) absorbed 1 mol. of hydrogen at 100—110°/700 lb./sq. in. over Raney nickel. The product was the *chroman*, b. p. 113·5°/16 mm., n_D^{20} 1·5219, d_4^{20} 0·9921 (Found : C, 82·0; H, 9·1. $C_{12}H_{16}O$ requires C, 81·9; H, 9·2%). The chromen could not be hydrogenated over Adams catalyst at or below 50°.

Bromination of 2 : 4 : 4-*Trimethylchrom*-2-*en*.—Bromine (9·2 g., 1 mol.) in carbon tetrachloride (100 ml.) was added to the chromen (10 g.). The bromine was immediately decolorised and hydrogen bromide was evolved. The solvent was removed under reduced pressure and the residue was distilled. The fraction, b. p. 100—105°/0·5 mm., n_D^{20} 1·5710 (5·56 g.), solidified. Recrystallised from aqueous ethanol, the 3-*bromo*-2 : 4 : 4-*trimethylchrom*-2-*en* had m. p. 76—77° (Found : C, 56·8; H, 5·1; Br, 32·0. $C_{12}H_{13}OBr$ requires C, 57·0; H, 5·2; Br, 31·6%). No bromide ion was formed by boiling methanolic sodium methoxide in 1·5 hr.

The higher fractions, b. p. >105°/0·1 mm., from this reaction contained more bromine than the monobromo-compound. This material (15 g.) was treated with bromine (20 ml.) without solvent for an hour, finally being warmed to 50° to drive off hydrogen bromide and most of the excess of bromine. The residue was taken up in carbon tetrachloride, washed with 25% sodium carbonate solution, and distilled. The product, 3 : x : y : *z-tetrabromo*-2 : 4 : 4-*trimethylchrom*-2-*en*, came over at 178—180°/0·2 mm., and, after recrystallisation from light petroleum (b. p. 60—80°), had m. p. 120·5—122·5° (Found : Br, 65·4. $C_{12}H_{10}OBr_4$ requires Br, 65·1%). This was likewise resistant to sodium methoxide.

Action of Nitric Acid on 2 : 4 : 4-*Trimethylchroman*-2-*ol*.—A mixture of the chromanol

(20 g.), 70% nitric acid (100 ml.), and water (200 ml.) was warmed to 60°, whereupon a vigorous reaction took place which was moderated by cooling. After 30 min. the mixture was heated to the b. p. for 1 hr. Next morning the semisolid organic product was separated and leached with boiling benzene. The benzene solution was extracted with 2N-sodium hydroxide; acidification of this precipitated a solid which was recrystallised from toluene and then had m. p. 204—205° (decomp.). This was probably an *α-(2-hydroxy-*x : y*-dinitrophenyl)-α-methylpropionic acid* (Found: C, 44·8; H, 3·8; N, 10·0%; equiv., 137. $C_{10}H_{16}O_7N_2$ requires C, 44·5; H, 3·7; N, 10·4%; equiv., 135); the infrared spectrum was in accordance with this, but did not locate the nitro-groups.

Methylating Ring-fission of 2 : 4 : 4-*Trimethylchroman*-2-*ol*.—The chromanol (III) (0·4 g.) was boiled with sodium hydroxide (8 g.) in water (10 ml.) for 5 min., then cooled, and methanol (5 ml.) added, followed by methyl sulphate (5 ml.) slowly after 5 min.[11] The mixture was boiled for 15 min., cooled, diluted with water, and extracted with ether. The extract yielded an oil which was converted into the 2 : 4-*dinitrophenylhydrazone*, m. p. 106—107° (from ethanol), of 4-*o*-methoxyphenyl-4-methylpentan-2-one (Found: C, 59·4; H, 5·2; N, 14·8. $C_{19}H_{22}O_5N_4$ requires C, 59·1; H, 5·7; N, 14·5%).

No reaction occurred when the chromanol (2 g.) was boiled with 2N-sodium hydroxide (20 ml.) and methyl iodide (1 ml.) for 2 hr.

Action of Sodium Sulphite on 1 : 3 : 3-*Trimethylindan*-1-*yl Hydroperoxide*.—(*a*) The hydroperoxide (98% pure; 19 g.) was stirred at 60° for 7 hr. with anhydrous sodium sulphite (100 g.) in water (300 ml.). The mixture was boiled for 3 hr. to complete the reaction. Extraction with benzene afforded 11·0 g. of 1 : 3 : 3-trimethylindan-1-ol, b. p. 66°/0·2 mm., m. p. 46—47°, which crystallised from light petroleum in fine needles (Colonge and Garnier [1] found m. p. 45°, b. p. 128°/25 mm.). The infrared spectrum was in accordance with their structure.

(*b*) The product from 71 g. of hydroperoxide (80% pure) was distilled at 14 mm., and proved to be mainly 1 : 1 : 3-trimethylindene, b. p. 98—105°/14 mm., leaving 10 g. of solid *bis*-1 : 3 : 3-*trimethylindan*-1-*yl peroxide*. This was slightly decomposed by recrystallisation from hot solvents, and was purified by dissolution in ether and reprecipitation with cold ethanol. It then had m. p. 77—79° (incomplete) (Found: C, 82·0; H, 8·3%; *M*, cryoscopic in C_6H_6, 334; by peroxide estimation,[12] 370. $C_{24}H_{30}O_2$ requires C, 82·4; H, 8·6%; *M*, 350). There was no detectable peroxide in the starting material.

Hydrogenation of 1 : 3 : 3-*Trimethylindan*-1-*yl Hydroperoxide*.—The hydroperoxide (82% pure; 30 g.) in methanol (30 ml.) was hydrogenated at room temperature and pressure over *ca.* 0·3 g. of 0·7% palladium-on-alumina. About 90% of the calculated quantity of hydrogen was absorbed in 3·5 hr. Evaporation of the filtered solution under reduced pressure left 26·7 g. of trimethylindanol.

Action of Ferrous Sulphate on 1 : 3 : 3-*Trimethylindan*-1-*yl Hydroperoxide*.—(*a*) The hydroperoxide (98% pure; 50 g.) in ethanol (200 ml.) was added in the course of 1·5 hr. to a solution of ferrous sulphate heptahydrate (168 g.) in water (400 ml.). The reaction was exothermic and was moderated by cooling; ferric hydroxide was precipitated. After a further 1·5 hours' stirring the organic product was extracted with benzene, washed, and distilled through an efficient column. The first fraction, b. p. 105—113°/16 mm. (5·3 g.), contained small amounts of a ketone, probably 3 : 3-dimethylindan-1-one (cf. next paragraph). It formed a scarlet 2 : 4-*dinitrophenylhydrazone*, m. p. 256—257° (decomp.) (from benzene) (Found: N, 16·1. $C_{17}H_{16}O_4N_4$ requires N, 16·4%), and a semicarbazone, m. p. 209·5—210·5° (from water) (von Auwers [13] gives m. p. 205—207° for 3 : 3-dimethylindan-1-one semicarbazone). The main product was 1-*ethoxy*-1 : 3 : 3-*trimethylindane*, b. p. 116—118°/16 mm. (17 g.) (Found: C, 82·9; H, 9·6. $C_{14}H_{20}O$ requires C, 82·5; H, 9·9%), n_D^{20} 1·5094, identified by comparison of its infrared spectrum with a synthetic sample (see below). The higher fractions, b. p. 120—121°/15 mm., were 1 : 3 : 3-trimethylindan-1-ol (12 g.).

(*b*) The hydroperoxide (33 g.) was stirred with ferrous sulphate heptahydrate (11 g.) in water (300 ml.) at 40° for 1 hr., and the mixture was then raised slowly to the b. p. Dilute sulphuric acid was added to the cooled mixture, and the organic product was collected in light petroleum, washed, and distilled. The main fraction, b. p. 88°/12 mm., n_D^{20} 1·5382, was 1 : 1 : 3-trimethylindene (19 g.). The higher fractions, b. p. 100—128°/12 mm. (3·2 g.), consisted by spectroscopic analysis of 25% of trimethylindene and 15—20% of trimethylindanol, besides some ketone. The last named was probably 3 : 3-dimethylindan-1-one again; it gave a dinitrophenylhydrazone, m. p. 275° (decomp.) (Found: C, 59·8; H, 4·7. $C_{17}H_{16}O_4N_4$ requires C, 59·9; H, 4·7%), and

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[13] von Auwers, *Ber.*, 1921, **54**, 994.

semicarbazone, m. p. 212—214° (decomp.) (Found: C, 65·3; H, 7·0; N, 19·3. Calc. for $C_{12}H_{15}ON_3$: C, 66·4; H, 6·9; N, 19·4%).

1 : 3 : 3-*Trimethylindene*.—1 : 3 : 3-Trimethylindan-1-ol (10 g.) in boiling benzene with toluene-*p*-sulphonic acid (1 g.) rapidly eliminated water, which was separated in a Dean and Stark trap. The washed solution yielded trimethylindene, b. p. 87·5°/15 mm., n_D^{20} 1·5370, d_4^{20} 0·9359 (Colonge and Garnier[1] record b. p. 94°/15 mm., n_D^{25} 1·5346, d_4^{25} 0·925).

1 : 3 : 3-*Trimethylindene Dimer*.—In an attempt to hydrate it, trimethylindene (30 g.) was boiled under reflux with sulphuric acid (54 g.) and water (30 ml.) for 4 hr. The product, isolated by dilution and extraction with light petroleum, was mainly unchanged olefin, but afforded 10·4 g. of the dimer, presumably 1 : 1 : 3-*trimethyl*-2-(1 : 3 : 3-*trimethylindan*-1-*yl*)*indene*, b. p. 181°/2 mm., n_D^{20} 1·5641 (Found: C, 91·0; H, 9·0. $C_{24}H_{28}$ requires C, 91·1; H, 8·9%). The ultraviolet absorption spectrum had $\lambda_{max.}$ 2920, 2620, and 2580 Å (ε 752, 6210, and 6210 respectively) in ethanol, indicating a conjugated double bond.

1-*Ethoxy*-1 : 3 : 3-*trimethylindane*.—Potassium (3·9 g.) was dissolved in a solution of 1 : 3 : 3-trimethylindan-1-ol (17·6 g.) in toluene (100 ml.), the mixture being boiled to complete the reaction. Ethyl iodide (30 g.) was then added, and the solution was boiled under reflux for 9 hr., a further 20 g. of ethyl iodide being added after 5 hr. The precipitated potassium iodide was washed out, after which the product was dried and fractionated. It contained much unchanged trimethylindanol, but the first fraction, b. p. 103—113°/18 mm., n_D^{20} 1·5108 (1·44 g.), consisted (by spectrographic analysis) of 80% of the ethyl ether, identical with the material described above.

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