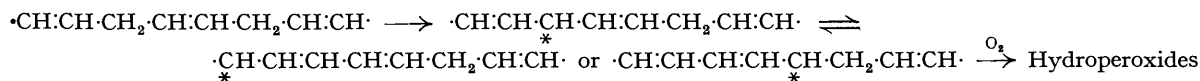


### 3. The Course of Autoxidation Reactions in Polyisoprenes and Allied Compounds. Part XI. Double Bond Movement during the Autoxidation of a Mono-olefin.

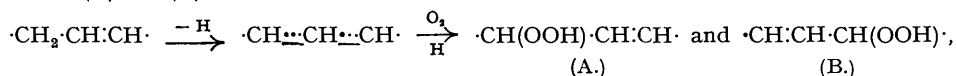
By E. HAROLD FARMER and DONALD A. SUTTON.

The peroxidation product obtained by photo-oxidation of 1 : 2-dimethyl- $\Delta^1$ -cyclohexene appears to contain both 1 : 2-dimethyl- $\Delta^1$ -cyclohexene-3-hydroperoxide and 1 : 2-dimethyl- $\Delta^2$ -cyclohexene-1-hydroperoxide in accordance with the radical hydroperoxidation hypothesis previously advanced (Part VII), since its hydrogenation product contains about equal amounts of the corresponding saturated secondary and tertiary alcohols. The crystalline acidic by-product obtained by the action of alkali on the hydroperoxidation product of either 1-methyl- $\Delta^1$ -cyclohexene or 1 : 2-dimethyl- $\Delta^1$ -cyclohexene is the dihydroresorcinol, 2-methylcyclohexan-1 : 3-dione.

IN Part VII (Farmer, Koch, and Sutton, *J.*, 1943, 541) it was shown that the autoxidation of  $\Delta^{1:4}$ -dienes and  $\Delta^{1:4:7}$ -, etc., polyene compounds produces peroxido-derivatives containing conjugated units, and to explain the formation of the latter a reaction-mechanism was proposed which postulated the detachment of hydrogen atoms from the reactive methylene groups under the action of molecular oxygen, and subsequent re-arrangement of the resonating radical residues before oxygen and, finally, hydrogen combine therewith to give hydroperoxides :



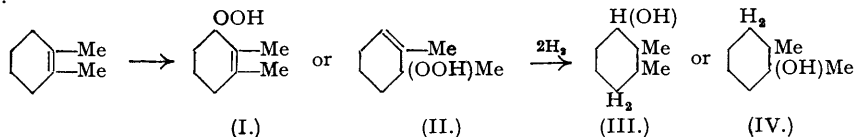
It was recognised that, if this mechanism is valid for methylene-interrupted diene- or polyene-systems, it might reasonably be expected to apply also to the formation of hydroperoxides by the action of oxygen either on simple olefins or on polyolefins containing two or more methylene groups between the double bonds. In order to demonstrate successfully that even the simplest olefin system capable of hydroperoxidation can give both of the oxygenated forms (A) and (B),



it is necessary for practical reasons to fulfil three conditions, viz., (a) the hydroperoxide(s) formed by autoxidation must be sufficiently stable to survive in good yield until the required amount of oxygen has been absorbed, (b) the olefin selected must be of such convenient constitution that the task of distinguishing structurally between the expected isomeric hydroperoxides is not unduly difficult, and (c) the hydroperoxides formed must be capable of transformation into identifiable derivatives without undergoing too high a proportion of secondary change (*i.e.*, change involving isomerisation by oxygen-redistribution or oxidative degradation). Various of the simple olefinic substances so far used in our autoxidation experiments, and especially the cyclohexenes as a group, satisfy the first condition, some few are able to satisfy the second, but few are found in practice to satisfy the third. For a first attempt, to demonstrate the occurrence of double bond shift during hydroperoxidation, 1 : 2-dimethyl- $\Delta^1$ -cyclohexene seemed most suitable, for, although the degree of its satisfaction of the third condition left a good deal to be desired—at any rate in respect of identification by hydrogenation—it successfully complied with the second in that its two alkyl groups could serve as reference points for recognising double bond shift if it occurred, and also by their presence could prevent unwanted isomerism arising from hydroperoxidation at alternative methylene groups in the system  $\cdot\text{CH}_2\cdot\text{CH}:\text{CH}\cdot\text{CH}_2\cdot$ .

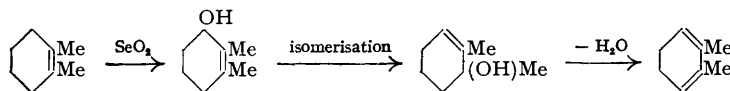
The formation and rectification of the hydroperoxide of 1 : 2-dimethyl- $\Delta^1$ -cyclohexene has already been described by Farmer and Sundralingam (*J.*, 1942, 121). An unexpected feature of the freshly distilled peroxide was that the peroxide-content ( $\cdot\text{O}\cdot\text{O}\cdot$ ) as measured by the colorimetric method of Bolland *et al.* (*Trans. Inst. Rubber Ind.*, 1941, 16, 29), which has usually been found to be very dependable for this type of peroxide, was considerably higher than the theoretical, but as measured by the potassium iodide method of Dastur and Lea (*Analyst*, 1941, 66, 90) was considerably lower than the theoretical. When the peroxide had been kept for 5 days at 0° the colorimetric value fell to near the theoretical, while the content as measured by the potassium iodide method fell somewhat also. The causes controlling the appearance of this phenomenon are not understood at present, but as the phenomenon has now been observed in connection with several other olefinic

peroxides it apparently means that some of the molecules of certain freshly distilled peroxides are able to use both of their oxygen atoms for the oxidation of ferrous sulphate and not only one as is normally the case.\* By use of a mixed platinum-palladium catalyst which is usually more successful than platinum alone for peroxide reductions (cf. Bodendorf, *Arch. Pharm.*, 1933, 271, 1) the hydrogenation of the peroxide in the normal fashion could only be effected to the extent of ca. 75%, and the product of this reaction was a mixture of alcohols having the required composition  $C_8H_{15}(OH)$ . This mixture proved to consist of approximately equal amounts of the secondary alcohol (III) (isolated and identified), and of the tertiary isomer (IV), the presence of which was indicated by the production of 1 : 2-dimethyl- $\Delta^1$ -cyclohexene on dehydration by heat in the presence of traces of iodine.



Thus, it may be inferred that the two hydroperoxides (I) and (II), *i.e.*, the structures which are to be expected in terms of the radical hydroperoxidation hypothesis, were both present in the oxidation product, and hence that the autoxidation of simple olefins can actually be accompanied by a considerable degree of double bond shift.

This demonstration of course depends for its validity on the absence of anionotropic interchange between the alcohols (III) and (IV), or between the formed hydroperoxide molecules (I) and (II), but since (i) the existing evidence relating to the mechanism of peroxidation (especially photo-oxidation as here used) is overwhelmingly in favour of a radical chain-process, and (ii) the experimental conditions of peroxidation and hydrogenation were not such as would promote the separation of anions, the occurrence of any significant degree of anionotropy seems unlikely. In the comparable case of the oxidation of 1 : 2-dimethyl- $\Delta^1$ -cyclohexene by selenium dioxide, the product from which was shown by Guillemonat (*Ann. Chim.*, 1939, 11, 141) to contain the conjugated diene 1 : 2-dimethyl- $\Delta^2$ -cyclohexadiene, formed in his view by the following steps :



the absence of anionotropy is perhaps less certain, since the selenium oxide was used in conjunction with acetic acid-acetic anhydride. If, however, oxidation by selenium dioxide, like peroxidation, involves a radical mechanism, the secondary alcohol represented above as the precursor of the diene might well be a primary product of reaction.

It should be mentioned that dimethylcyclohexene prepared by distillation of the tertiary alcohol (V) in presence of a little iodine, which has been assumed by successive workers to be the pure 1 : 2-dimethyl- $\Delta^1$ -



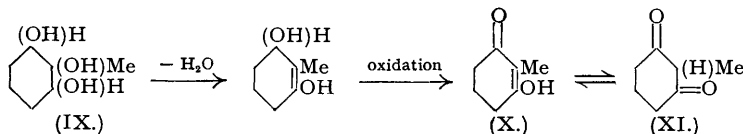
cyclohexene, could conceivably contain substantial amounts of the isomeric  $\Delta^2$  compound (VI) as also a little of the isomeric methylene compound (VII) and, indeed, Lebedev *et al.* (*J.*, 1925, 417; 1930, 321) have claimed that rate-of-hydrogenation tests show that the dimethylcyclohexene formed by a variant process, *viz.*, the dehydration of (V) with 30% sulphuric acid, is actually a mixture of all three isomeric olefins. The foregoing demonstration was carried out in the first place with carefully rectified dimethylcyclohexene prepared by the iodine-dehydration method, which at no stage gave indication of containing any significant amount of (VI) or (VII), the former of which by its presence must have invalidated the work. To remove all uncertainty, the demonstration was repeated with a sample of homogeneous dimethylcyclohexene regenerated from the crystalline dibromide (VIII) (which incidentally agreed exactly in physical constants with the iodine-dehydration product) without any important difference accruing in the result.

The opportunity presented by the present investigation has been taken to identify the only secondary derivative of cyclohexene autoxidation products so far isolated which remained uncorrelated with the general hydroperoxidation scheme developed in previous papers of the series. The compound in question was the crystalline acidic by-product,  $C_7H_{10}O_2$ , formed by the action of aqueous alkali on (apparently)† either 1-methylcyclohexene-3-hydroperoxide or 1 : 2-dimethylcyclohexene-3-hydroperoxide. The compound, from the mono-methyl-hydroperoxide, was re-prepared and found to exhibit a characteristic absorption spectrum, that of 2-methylcyclohexan-1 : 3-dione. This, together with its mono-acidity, its crystalline nature, and easy oxidisability by permanganate (cf., Farmer and Sundralingam, *loc. cit.*, pp. 136, 137) to give an acid, identified as

\* The peroxide content is by definition twice the active oxygen content as measured experimentally, so that if more than one atomic proportion of oxygen from each  $\cdot OO \cdot$  grouping becomes available as active oxygen, the peroxide value found experimentally may considerably exceed the total oxygen content in the compound as determined by elementary analysis. This apparent absurdity is encountered in the present case.

† The formation from either has now been shown with certainty.

glutaric acid, leaves no doubt as to its being the methyl-dihydroresorcinol (X, XI). The formation of the latter cannot easily be accounted for except on the basis of dehydration of the triol (IX) (a major product of the



treatment with alkali), followed by oxidation of the resulting enol to the corresponding dione by active oxygen derived from decomposing  $\cdot OOH$  groups. In the case of the dimethylcyclohexene hydroperoxide, the corresponding triol contains the pinacolic grouping,  $\cdot CMe(OH)\cdot CMe(OH)\cdot$ , which is able to liberate both methyl and hydroxyl groups in the manner characteristic of pinacolones. Of the two possible courses of reaction, viz., to give the pinacolone,  $R\cdot CMe\cdot CO\cdot R'$ , or (by elimination of  $MeOH$ ) the enol,  $\cdot CMe:C(OH)\cdot$ , the latter is found in practice to be preferred.

#### EXPERIMENTAL.

**1 : 2-Dimethylcyclohexene Hydroperoxide.**—1 : 2-Dimethylcyclohexene (75 g.), prepared by the dehydration of 1 : 2-dimethylcyclohexan-1-ol in the presence of iodine (Signaigo and Cramer, *J. Amer. Chem. Soc.*, 1933, **55**, 3326), was oxidised at 35° in a quartz flask illuminated by a Hanovia U.V.S. 500 lamp. During 210 minutes oxygen (6 litres) was absorbed. After removal of unchanged hydrocarbon (*ca.* 30 g.) and other easily volatile products by gentle heating (bath below 45°) the residue was fractionally distilled at <1 mm. The main peroxide fraction (12.2 g.), distilling at 70–75°/0.5 mm., had  $n_D^{20}$  1.4908 (Found : C, 68.75; H, 10.1. Calc. for  $C_8H_{14}O_2$  : C, 67.55, H, 9.9%). It was a colourless oil which (when determined immediately for peroxide by the colorimetric method of Bolland *et al.*, *loc. cit.*), gave P.O.C. 28.4% (calc. for pure peroxide : P.O.C., 22.2%), but after being kept for 5 days at 0° gave P.O.C. 21.4% by the colorimetric method but only 14.4% by the potassium iodide method of Dastur and Lea (*loc. cit.*). On refractionation, the main distillate (b. p. 72–74°/0.5 mm.; 11.5 g.) then had C, 69.15; H, 10.15; P.O.C. (colorimetric) 29.7; P.O.C. (potassium iodide method) 17.7%.

**Hydrogenation of the Hydroperoxide.**—The re-fractionated hydroperoxide (10.8 g.) was dissolved in absolute alcohol (100 c.c.) and hydrogenated in the presence of 0.4 g. of freshly prepared Adams's platinum catalyst. Rapid absorption of 1470 c.c. (N.T.P.) of hydrogen occurred, but then no more gas was taken up even after a further 0.4 g. of catalyst had been added and the reaction mixture warmed to 55°. The filtered mixture was distilled; the main (alcoholic) oxidation product (7.2 g.) had b. p. 52°/0.1 mm.,  $n_D^{20}$  1.4790 (Found : C, 74.9; H, 11.6. Calc. for  $C_8H_{14}O$  : C, 75.0; H, 12.5%), and was, therefore, incompletely saturated. This product was dissolved in pure ethanol (125 c.c.) and shaken in hydrogen at 65° with a mixture of 0.4 g. each of Adams's platinum and palladium catalysts. A further slow uptake of hydrogen set in, and continued until saturation was substantially complete. The distilled reduction product consisted mainly of an alcoholic product (5.7 g.) having b. p. 50–54°/0.1 mm.,  $n_D^{20}$  1.4647 (Found : C, 73.75; H, 12.35%).

**Composition of Hydrogenation Product.**—The almost saturated reduction product (3.4 g.) was heated with a few small crystals of iodine at 180–190° for 30 minutes and the dehydrated material allowed to distil. The oily distillate (1.8 g.) was well washed with water, dried over calcium chloride and distilled over sodium. The product was a slightly impure hydrocarbon (1.1 g.) having  $n_D^{20}$  1.4598 (Found : C, 85.6; H, 12.7. Calc. for  $C_8H_{14}$  : C, 87.2; H, 12.8%). This was converted into the corresponding bromo-adduct by dissolving it in pure chloroform (2 c.c.) and adding to the solution at 0° bromine (1.8 g.) dissolved in chloroform (2 c.c.). The adduct, when worked up, consisted of a mixture of oily and crystalline dibromides; the solid (1.0 g.), after being twice crystallised from dry alcohol, had m. p. 151° and was identified as pure 1 : 2-dimethyl- $\Delta^1$ -cyclohexene dibromide (Found : Br, 59.35. Calc. for  $C_8H_{14}Br_2$  : Br, 59.35%). Repetition of the bromination using pure 1 : 2-dimethylcyclohexene gave an exactly similar result, 1.2 g. of the dibromide being obtained. Thus, the hydrocarbon formed by the dehydration consisted almost wholly of 1 : 2-dimethyl- $\Delta^1$ -cyclohexene.

The portion of the hydrogenation product which remained undehydrated by the iodine-treatment gave on distillation an alcohol (0.9 g.) having b. p. 68–72°/12 mm. This alcohol, crude 1 : 2-dimethylcyclohexan-3-ol, gave, when heated at 110–120° for 30 minutes with  $\alpha$ -naphthyl isocyanate (1.3 g.), a crude urethane (0.6 g.), m. p. 134–137°, which, after recrystallisation from ligroin (b. p. 100–120°), formed colourless prisms, m. p. 141° (Found : C, 76.55; H, 7.6; N, 4.75.  $C_{14}H_{23}O_2N$  requires : C, 76.75; H, 7.8; N, 4.7%). The same  $\alpha$ -naphthyl urethane (m. p. 140°) could also be formed, although in poor yield, from the unfractionated hydrogenation product (Found : C, 76.75; H, 8.0; N, 4.7%); the diminished yield is probably due to some dehydration of the tertiary alcohol by the isocyanate, since Bickel and French (*J. Amer. Chem. Soc.*, 1926, **48**, 747) have observed that free water has an adverse effect on the reaction of  $\alpha$ -naphthyl isocyanate with secondary alcohols. The urethane showed no depression of melting point when mixed with an authentic specimen (below).

**Synthesis of 1 : 2-Dimethylcyclohexan-3-ol.**—*o*-Xylene (200 g.) was nitrated by the method of Emerson and Smith (*loc. cit.*) and converted into 3-nitro-*o*-xylene (118 g.). The latter was converted *via* the corresponding amine (85 g.) and then the iodide (124 g.) into crude 2 : 3-dimethylphenol (56 g.). The crude phenol melted at 44–47° (Smith and Opie record m. p. 65–66°), but, after several crystallisations from ligroin (b. p. 40–60°) a fraction was isolated having m. p. 71–73° (Short, Stromberg and Wiles, *J.*, 1936, 322, record 73.5–74.5°; Kruber and Schmidt, *Ber.*, 1931, **64**, 2274, record 75°); the residue doubtless contained isomers of the desired 2 : 3-dimethylphenol, formed by nitration occurring elsewhere than at the 3-position. Hydrogenation of the compound, m. p. 71–73°, was conducted in ethanol (100 c.c.) at 180°/100 atm., using Raney nickel as catalyst, this procedure being more satisfactory than that employed by Sabatier and Mailhe (*Compt. rend.*, 1906, **142**, 553) for 3 : 4-dimethylphenol. The hydrogenation gave a product from which 1 : 2-dimethylcyclohexan-3-ol (13 g.) was isolated by fractional distillation; this had b. p. 77–79°/12 mm. and  $n_D^{20}$  1.4662 (Found : C, 74.65; H, 12.55.  $C_8H_{16}O$  requires C, 75.0; H, 12.5%). The synthetic alcohol (1 g.) gave when heated with  $\alpha$ -naphthyl isocyanate (1 g.) at 110–120° for 30 minutes the corresponding urethane, m. p. 130–133° (0.6 g.) which on recrystallisation melted at 138–140° (Found : C, 76.65; H, 7.8; N, 4.60%).

**Composition of 1-Methyl- $\Delta^1$ -cyclohexene-5-hydroperoxide with Alkali.**—1-Methylcyclohexene hydroperoxide (12.5 g.), prepared as described by Farmer and Sundralingam (*loc. cit.*), was mechanically shaken with 300 c.c. of *N* sodium hydroxide. The aqueous product was thoroughly extracted with ether, then acidified with 6*N* sulphuric acid, and finally continuously extracted with ether for 7 hours. The dried ether extract gave, on evaporation, an oily liquid containing some suspended crystals, m. p. 196–199°. The latter, recrystallised from 96% alcohol, had m. p. 205–207° (0.2 g.) (Found : C, 66.75; H, 8.2. Calc. for  $C_7H_{10}O_2$  : C, 66.65; H, 8.0%), the same as that recorded by Butz (*J. Org. Chem.*, 1943, **8**, 515) for 2-methylcyclohexan-1 : 3-dione. The absorption spectrum of this material, kindly determined for us by Dr. H. P. Koch,

had the characteristics: Max. A., 2620;  $\Sigma$ , 17,000 (0.001 molar solution used). Butz (*loc. cit.*) records for methylcyclohexandione: max. 2610 A.;  $\Sigma$ , 17,000 (0.000606 molar solution used).

*Purification of 1:2-Dimethyl- $\Delta^1$ -cyclohexene.*—The hydrocarbon, prepared as described above by dehydration of 1:2-dimethylcyclohexan-1-ol in presence of a little iodine (95 g.), was dissolved in chloroform (150 c.c.) and treated, while cooled in ice-salt, with bromine (138 g.) dissolved in chloroform (150 c.c.) during 3½ hours with rapid stirring. The solvent was removed under reduced pressure (below 50°) and the residual mixture of solid and liquid dibromides filtered. The liquid dibromide was not used, but the solid was collected and crystallised several times from dry ethanol, the dissolution on each occasion being conducted with the minimum of heating (owing to the ready interaction of the bromide and alcohol to form ethoxy compounds) and the crystallisation each time rapidly promoted by rapidly cooling the solution to -5°. At best, only 85 g. of solid dibromide having m. p. 145—148° together with 17 g. of somewhat impure dibromide (m. p. 140—145°) survived this extremely wasteful crystallisation.

The hydrocarbon was regenerated from the pure solid dibromide (97 g.) by dissolving the latter in pure acetone containing a trace of zinc chloride and debrominating it with zinc. For this purpose, the solution, contained in a flask provided with a gas inlet tube and a reflux condenser, was treated with granulated zinc (50 g.) in portions, the reaction mixture being warmed at the beginning to promote reaction. When ebullition had ceased the reaction product was cooled, poured into water and the oily hydrocarbon taken up in ether. The ether extract was dried over potassium carbonate and the ether removed through a column; the residual dimethylcyclohexene was twice distilled over sodium in an atmosphere of pure nitrogen, and the product (14.0 g.) had b. p. 134°, and  $n_D^{15}$  1.4616 (Found: C, 87.1; H, 12.8. Calc. for  $C_8H_{14}$ : C, 87.2; H, 12.8%). Dimethylcyclohexene, ordinarily obtained by the iodine dehydration method, has  $n_D^{15}$  1.4610.

*Peroxidation of Pure 1:2-Dimethyl- $\Delta^1$ -cyclohexene.*—The pure hydrocarbon obtained by debromination of solid dimethylcyclohexene dibromide was oxidised in U.V. light and the oxidation product rectified and finally hydrogenated all exactly as described above. The behaviour throughout, and the products of peroxidation and of hydrogenation, agreed so closely with those described above for "ordinary" dimethylcyclohexene, that further description is unnecessary. Clearly, both a primary and a tertiary dimethylcyclohexene can be obtained by hydrogenation of the hydroperoxidation product of homogeneous 1:2-dimethylcyclohexene.

This work forms part of a programme of fundamental investigation on rubber undertaken by the Board of the British Rubber Producers' Research Association.

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