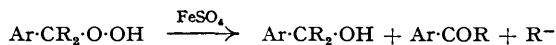


542. *Reactions of Organic Peroxides. Part V. Reaction of Ferrous Sulphate with Methylcyclopentyl and Methylcyclohexyl Hydroperoxides.*

By E. G. E. HAWKINS and D. P. YOUNG.

Reaction of methylcyclopentyl hydroperoxide with ferrous sulphate solution gives mainly dodecane-2:11-dione. Similarly methylcyclohexyl hydroperoxide forms tetradecane-2:13-dione, although in poorer yield. Catalytic aerial oxidation of the C₁₂ diketone affords suberic acid and keto-acids.

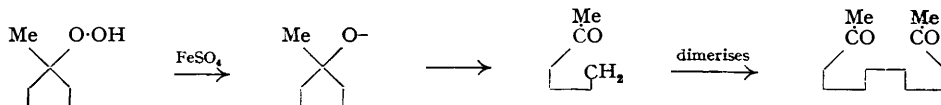
THE reaction with ferrous sulphate generally leads to decomposition of hydroperoxides with an ease which depends on the structure of the latter. Although decomposition of secondary hydroperoxides by this means may well be catalytic, yielding the corresponding ketone by loss of water (Hartmann and Seiberth, *Helv. Chim. Acta*, 1932, 15, 1390; Hock and Lang, *Ber.*, 1942, 75, B, 1051; 1943, 76, B, 169, 1130), the reaction with tertiary hydroperoxides appear to be more complex. With the tertiary hydroperoxides derived from the *sec.*-alkylbenzenes, a mixture of alcohol and ketone is normally formed (see Part II), and a stoichiometric quantity of ferrous sulphate appears to be consumed; ferric compounds are produced.



When a ferrous sulphate solution is shaken with 1-methylcyclopentyl hydroperoxide an exothermic reaction ensues, with formation of a brown, insoluble ferric compound, dodecane-

2 : 11-dione (up to 60%), methyl butyl ketone, 3-methylcyclopentanol (probably derived from a small proportion of the 3-hydroperoxide present in the 1-hydroperoxide), and unidentified minor products. The diketone was unequivocally identified (see Experimental section) and its properties accord with those recorded by Bowden, Heilbron, Jones, Sargent, and Sondheimer (*J.*, 1947, 1579), and by Cason and Prout (*J. Amer. Chem. Soc.*, 1944, **66**, 46).

The reaction of methylcyclopentyl hydroperoxide evidently involves the formation and dimerisation of the free radical $\text{Me}\cdot\text{CO}\cdot[\text{CH}_2]_4\cdot$:



Ferrous lactate, dissolved in potassium citrate solution, also converted the hydroperoxide into diketone, whereas ferrous chloride gave mainly the ketone-carbinol mixture.

Unsuccessful attempts were made to improve the yield of diketone. The presence of sulphuric acid at least equivalent to the basic ferric salt formed improved the yield slightly, and was helpful in that the inorganic precipitate was avoided. Addition of a mutual solvent (methanol or ethanol) also improved the yield, but other organic solvents reduced it, probably because of their reactivity with free radicals. The reaction could be carried out with a fairly crude hydroperoxide, but the product from methylcyclopentane (Part III) containing a large proportion of unchanged hydrocarbon and by-products gave a poor yield. The best yields were obtained by slow addition of the hydroperoxide to the agitated ferrous salt. Temperature had little effect, except that strong cooling (-10°) inhibited the reaction; the optimum temperature appeared to be about that of the room. A fairly wide range of concentration of reactants could be employed, although at high concentrations the yield decreased. Even under a combination of the most favourable conditions, however, the yield of diketone fluctuated between 45 and 59%; probably a factor of the variation was the purity of the hydroperoxide used.

A similar reaction with ferrous sulphate takes place with 1-methylcyclohexyl hydroperoxide, but the yield of tetradecane-2 : 13-dione (Work, *J.*, 1940, 1318) is only *ca.* 12%. Catalytic oxidation of dodecane-2 : 11-dione with oxygen gave suberic acid and a keto-acid, presumably 9-ketodecanoic acid * although the latter and its derivatives could not be obtained pure.

EXPERIMENTAL.

M. p.s are uncorr. Elementary analyses are by Drs. Weiler and Strauss.

Reaction of 1-Methylcyclopentyl Hydroperoxide with Ferrous Sulphate.—(a) The hydroperoxide (5 g.) and ferrous sulphate heptahydrate (12 g.) in water (20 c.c.) were shaken together; the mixture became warm. Extraction with ether followed by distillation of the extract gave fractions (i) b. p. $120-180^\circ$ (1.3 g.) and (ii) $180-270^\circ$ (mainly $250-270^\circ$) (2.3 g.) (residue, 0.2 g.). Fraction (i) consisted mainly of a mixture of ketones (*ca.* 55%) and alcohols (*ca.* 40%) and gave the same derivatives as in (b) below. Fraction (ii) solidified in the receiver. Recrystallisation from ether or benzene-light petroleum gave dodecane-2 : 11-dione, m. p. $67.5-68.5^\circ$ (Found: C, 72.5; H, 11.25. Calc. for $\text{C}_{12}\text{H}_{22}\text{O}_2$: C, 72.7; H, 11.1%).

(b) Two experiments were carried out, in each of which the hydroperoxide (50 g.; 95% pure) was added during $1\frac{1}{2}$ hours to a vigorously stirred solution of crystallised ferrous sulphate (150 g.) in 10% (w/v) sulphuric acid (350 g.), the mixture being cooled to 20° . The organic material was extracted with ether, washed, and dried; the combined products of the two experiments were freed from solvent and distilled under reduced pressure to give low-boiling material, b. p. $<140^\circ/20$ mm. (60 g.), and diketone, b. p. $146^\circ/20$ mm. (32 g.; 39%, calc. on pure hydroperoxide). The first fraction was redistilled at atmospheric pressure through a Vigreux column (3 plates). This provided some ether and material, b. p. 71° (2.3 g.) and $87-88^\circ$ (2.5 g.) (probably hydrocarbons), followed by a series of fractions, b. p. $128-157^\circ$ (30.9 g.), without any well-marked plateaux. A small residue consisted of diketone. The distillates were mixtures of C_6 alcohols and ketones. The lowest-boiling fractions yielded methyl butyl ketone 2 : 4-dinitrophenylhydrazone, m. p. 108° ; the highest-boiling material gave the same dinitrophenylhydrazone, m. p. 107° , and an orange-yellow dinitrophenylhydrazone, m. p. $126-129^\circ$ (Found: C, 52.2; H, 5.1; N, 18.0. Calc. for $\text{C}_{12}\text{H}_{14}\text{O}_4\text{N}_4$: C, 51.6; H, 5.0; N, 20.0%), probably of a cyclic C_6 ketone. The higher fractions also yielded 3-methylcyclopentyl phenylurethane, m. p. $76-78^\circ$, and 1-naphthylurethane, m. p. $97-98^\circ$ (Found: C, 76.0; H, 6.9; N, 5.15. $\text{C}_{17}\text{H}_{19}\text{O}_2\text{N}$ requires C, 76.0; H, 7.1; N, 5.2%), identical (mixed m. p.s) with authentic samples (see below); m. p.s were strongly depressed by admixture with the corresponding derivatives of 1-methyl- and 2-methylcyclopentanol.

(c) The hydroperoxide (10 g.; 87% pure), dissolved in ethanol (10 c.c.), was added to a solution of ferrous sulphate (30 g.) in 10% w/v sulphuric acid (70 c.c.) and ethanol (40 c.c.). The diketone was extracted with ether and distilled, the yield being 4.4 g. (59%, calc. on the pure hydroperoxide).

* Geneva numbering.

(d) Rapid mixing depressed the yield, whilst addition of the ferrous salt solution to the hydroperoxide led only to one quarter of the normal yield of diketone.

Structure of the Diketone.—The product, m. p. 67.5—68.5°, contained no active hydrogen. Besides the elementary analysis given above, it had a ketone equiv. (by hydroxylamine titration) of 101, and a mol. wt. (cryoscopic in benzene) of 204 (Calc. for $C_{12}H_{22}O_2$: ketone equiv., 99; *M*, 198). It gave a strong iodoform reaction, and yielded a 2:4-dinitrophenylhydrazone, m. p. 181.5—182°, and a *dioxime*, m. p. 124° (Found: N, 11.8. $C_{12}H_{24}O_2N_2$ requires N, 12.3%); both derivatives were difficult to purify.

Dodecane-2:11-dione has been reported as having m. p. 67° (Bowden *et al.*, *loc. cit.*) and 67.4—67.8° (Cason and Prout, *loc. cit.*). The identity of the product was confirmed by the following reactions:

(i) *Hypobromite oxidation.* Sodium hydroxide (33 g.) was dissolved in water (200 c.c.), and the solution cooled; bromine (48 g.) was added slowly with stirring, the temperature being kept at 0—10°. Finely powdered diketone (10 g.) was added, and stirring continued for a further 2 hours at the same temperature and overnight at room temperature. The bromoform and carbon tetrabromide were removed in steam, and unchanged diketone (0.4 g.) extracted with ether. Acidification followed by ether-extraction and evaporation gave a product (8.1 g.) which solidified on storage. Recrystallisation from ether gave sebacoic acid, m. p. 130—131° (Found: acid equiv. 100.7. Calc. for $C_{10}H_{18}O_4$: acid equiv., 101).

(ii) *Wolff-Kishner reduction.* The diketones (8.5 g.), potassium hydroxide (10 g.), ethylene glycol (40 c.c.), and hydrazine hydrate (90—95%; 8 c.c.) were heated together under reflux for 1½ hours, and then allowed to evaporate until the liquid temperature reached 180°. Refluxing was then continued for 4 hours. The distillate and residue were combined and extracted with ether. The extract yielded a liquid, b. p. ca. 200°, which after being heated over sodium, was redistilled to give a distillate (3.0 g.), b. p. 206—208°, n_D^{20} 1.4209. Infra-red examination, carried out by Mr. A. R. Philpotts, showed this to be almost entirely *n*-dodecane.

(iii) *Grignard reaction.* To the Grignard reagent [from methyl iodide (12 g.) and magnesium (2 g.) in ether (150 c.c.)] was added the diketone (6 g.) in ether; a solid complex settled out. On working-up of the material in the usual way, the product consisted of a thick syrup which was crystallised from ether-light petroleum. Distillation of the sticky product gave 2:11-dimethyldodecane-2:11-diol which, crystallised from ether-light petroleum, had m. p. 57—58.5° (Found: C, 73.25; H, 12.8; active H, 0.91%. $C_{14}H_{30}O_2$ requires C, 73.0; H, 13.0; active H, 0.87%). Interaction of diethyl sebacate with methylmagnesium iodide gave the same alcohol, m. p. 57—58.5°.

(iv) *Hydrogenation.* The diketone (5 g.) in dioxan (150 c.c.) was hydrogenated at room temperature and pressure over Raney nickel. Absorption was slow, but slightly more than the calculated quantity of hydrogen was taken up in 24 hours, and the product on distillation yielded dodecane-2:11-diol (4.1 g.), b. p. 165—170°/14 mm.; this solidified, and after recrystallisation from aqueous alcohol and then light petroleum had m. p. 54° (Found: C, 69.9; H, 12.9. Calc. for $C_{12}H_{26}O_2$: C, 71.4; H, 13.0%). Bowden *et al.* record m. p. 54—55° for this diol.

(v) *Synthesis.* An ethereal solution of methylmagnesium bromide (1 mol.) was converted into dimethylcadmium by addition of anhydrous cadmium chloride (92 g., 1 equiv.), the reaction being completed by refluxing the mixture for several hours under nitrogen. Sebacyl chloride (96 g., 0.4 mol.) was added slowly with cooling, and the solution finally heated under reflux for 5 hours and decomposed with water and dilute hydrochloric acid. The washed ethereal layer, after removal of the solvent, left solid dodecane-2:11-dione, m. p. 68°, not depressed by the compound obtained from methylcyclopentyl hydroperoxide. It gave a 2:4-dinitrophenylhydrazone, m. p. 182°, identical with that obtained previously.

Effect of Various Conditions on the Ferrous Sulphate Reaction.—The results obtained by carrying out the reaction under a variety of conditions are shown in the Table.

Replacement of the ferrous salt by cobaltous, stannous, or cuprous salts or by lead tetra-acetate or potassium permanganate gave no diketone, although some reaction occurred. The hydroperoxide did not appear to react at all with manganous or cerous salts under similar conditions.

Reaction of 1-Methylcyclohexyl Hydroperoxide with Ferrous Sulphate.—The hydroperoxide (20 g.) was added, with shaking, to ferrous sulphate (50 g.) in water. The peroxide did not react as readily as methylcyclopentyl hydroperoxide at room temperature, so the mixture was heated on the water-bath for 3 hours. Ether-extraction yielded a product which on distillation gave fractions: (i) b. p. 146—156° (13.7 g.); (ii) 80—130°/20 mm. (1.3 g.); (iii) above 130°/20 mm. (1.6 g.); and a residue (0.2 g.). Fraction (i) by analysis was shown to consist of ketones and alcohols. It provided impure 2:4-dinitrophenylhydrazones, and after several recrystallisations a small quantity of a derivative was obtained with m. p. 91—92°, undepressed on admixture with the derivative of methyl *n*-amyl ketone. The semicarbazone had m. p. 120.5—121.5°, identical with methyl *n*-amyl ketone semicarbazone. The alcoholic component of this fraction (ca. 50%) was not identified. Fraction (ii) was a similar mixture of ketone and alcohol. Fraction (iii) solidified in the receiver; recrystallisation yielded tetradecane-2:13-dione, m. p. 76—77° (Work, *loc. cit.*, found m. p. 75°) (Found: C, 73.7; H, 11.0. Calc. for $C_{14}H_{26}O_2$: C, 74.3; H, 11.5%).

Derivatives of the Methylcyclopentanols.—The following derivatives were prepared for comparison: 1-Methylcyclopentanol (Zelinsky and Namjetkin, *Ber.*, 1902, 35, 2683) gave a *phenylurethane*, m. p. 88—89° (Found: C, 71.0; H, 7.7; N, 6.35. $C_{13}H_{17}O_2N$ requires C, 71.2; H, 7.8; N, 6.4%), and a 1-naphthylurethane, m. p. 84° (Found: C, 75.9; H, 7.0; N, 5.2. $C_{17}H_{19}O_2N$ requires C, 75.8; H, 7.1; N, 5.2%). 2- and 3-Methylcyclopentanol were prepared by reduction of the corresponding ketones (Chavanne, *Bull. Sci. Acad. Roy. Belg.*, 1926, [v], 12, 105; van Rysselberge, *ibid.*, p. 171). The 2-isomer yielded a phenylurethane, m. p. 92—94° (cf. Godchot and Bedos, *Compt. rend.*, 1926, 182, 393), and a

1-naphthylurethane, m. p. 116—117° (Found : C, 75.6; H, 7.0; N, 5.1. $C_{17}H_{15}O_2N$ requires C, 75.8; H, 7.1; N, 5.2%). The 3-isomer afforded a phenylurethane, m. p. 78—79° (cf. Godchot, Cauquil, and Calas, *Bull. Soc. chim.*, 1939, **6**, 1366), and a 1-naphthylurethane, m. p. 100—101° (see above).

The peroxide was added to the ferrous salt, except where otherwise stated.
"Room" temp. denotes that no special temperature control was applied.

Ferrous salt.		Hydroperoxide.		Reaction conditions.		Yield of diketone, %.	
Wt., g.	Solvent.	Purity, %.	Wt., g.	Temp.	Rate of addition.		
<i>Ferrous sulphate</i> (7H ₂ O).							
100	H ₂ O, 250 c.c.	86	29	None	Room	Slow	55
30	" 60 c.c.	95	6.5	"	"	"	55
36	" 72 c.c.	98.4	10.8	"	0°	2 Hr. ¹	46—48
30	" 300 c.c.	?	10	"	Room	1.5 Hr.	39
30	" 40 c.c.; EtOH, 20 c.c.	89	10	EtOH, 10 c.c.	"	Slow	42
30	" 60 c.c.	?	10	COMeBu ¹ 10 g.	0°	"	35
40	" 2 c.c.; C ₆ H ₆ , 100 c.c.	?	10	None	10—25°	"	14
30	" 80 c.c.	?	10	"	Room	" ²	47
150	350 c.c.	95.3	50	"	20°	" ³	39
30	10% H ₂ SO ₄ , 70 c.c.; EtOH, 40 c.c.	93.2	10	EtOH, 10 c.c.	-10°	5 Sec.	13
30	" " "	87	10	"	rising <10°	Slow	48
30	" " "	89	10	"	20 → 40	" ⁴	59
30	" " "	89	10	"	40	"	46
30	" " "	93	10	"	80	"	41
30	" " "	93.2	10	"	15 → 60	5 Sec.	36
30	" " "	93.2	10	"	15 → 45	30 Sec.	31
30	" " "	93	10	"	10	Slow ⁵	13
60	6% H ₂ SO ₄ , 120 c.c.; EtOH, 50 c.c.	95—98	10	EtOH, 20 c.c.	10	0.5 Hr.	24
30	20% H ₂ SO ₄ , 35 c.c.; EtOH, 20 c.c.	95—98	10	EtOH, 10 c.c.	10	Slow	15
30	10% H ₂ SO ₄ , 70 c.c.; MeOH, 40 c.c.	89	10	MeOH, 10 c.c.	20 → 40	"	50
30	10% H ₂ SO ₄ , 70 c.c.; COMe ₂ , 40 c.c.	89	10	COMe ₂ , 10 c.c.	20 → 40	"	28
30	10% H ₂ SO ₄ , 70 c.c.; dioxan, 40 c.c.	95—98	10	Dioxan, 10 c.c.	10	"	38
30	H ₂ O, 100 c.c.	98.6	10	10% NaOH, 35 c.c.	0—5	"	34
<i>Ferrous chloride</i> (4H ₂ O).							
15	H ₂ O, 100 c.c.	87.2	10	None	20 → 40	5 Mins.	9
<i>Ferrous lactate</i> .							
31	H ₂ O, 100 c.c.; K citrate, 100 g.	?	10	"	0	0.5 Hr.	32

¹ Under N₂. ² Reaction mixture kept just acid during reaction with H₂SO₄. ³ See (b) on p. 2805.

⁴ See (c) on p. 2805. ⁵ FeSO₄ added to peroxide.

Oxidation of Dodecane-2 : 11-dione.—This work was interrupted before completion, but the following experiment illustrates the salient features of the reaction.

The apparatus consisted of a closed system comprising a flask with "recycle" stirrer, oxygen inlet, a reflux condenser leading to the gas outlet with a sodium hydroxide trap, and a device for sampling without disturbing the gas flow. The whole was immersed in a thermostatically-controlled electrically-heated oil-bath. The gas absorption was measured by means of inlet and outlet wet gas meters.

A solution of dodecane-2 : 11-dione (50 g.) in glacial acetic acid (100 c.c.) containing as catalyst manganese acetate tetrahydrate (0.1 g.), was agitated at 90°, in the above apparatus, in a slow stream of oxygen. After 3½ hours the temperature was raised to 100° to maintain the rate of absorption and after 7 hours a further addition of catalyst (0.1 g.) was made. Oxidation was discontinued after 19½ hours, 17.9 l. of oxygen having been absorbed and 0.25 mol. of carbon dioxide having collected in the exit trap. During the reaction the acidity of the solution increased, whilst the ketone content decreased by over 80%. Acetic acid was removed from the oxidate at 20 mm. pressure, and the residue was esterified with methanol and sulphuric acid. The crude ester (29 g.) was fractionally distilled at 2 mm., yielding a series of ill-defined fractions, b. p. 106—140°/2 mm. (21 g. in all). All these gave positive tests for a carbonyl group, but this appeared to be most highly concentrated in the highest-boiling fractions. The lowest fraction on hydrolysis yielded suberic acid, m. p. 138—140° (Found : equiv., 89. Calc. for C₈H₁₄O₄ : equiv., 87), giving a *p*-nitrobenzyl ester, m. p. 80—81°. The recorded values are 141° and 85° respectively. The higher fractions were separately hydrolysed and examined for other dicarboxylic acids, but only suberic acid was isolated from them. Acidification of the sodium salts from the highest fractions to pH 4, however, yielded a product, which after recrystallisation from ether-light petroleum (by cooling to -10°) had m. p. 28—32° and acid equiv. 159. This acid readily gave a yellow 2 : 4-dinitrophenylhydrazone, m. p. 97—100° (from benzene-light petroleum), soluble in aqueous alkali to give a

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deep-red solution (Found: C, 52.9; H, 5.9; N, 14.7. $C_{16}H_{22}O_6N_4$ requires C, 52.4; H, 6.1; N, 15.3%). The *p*-phenylphenacyl esters could not be recrystallised to beyond m. p. 63—66°. This keto-acid was probably impure 9-ketodecanoic acid, for which Barger, Robinson, and Smith recorded m. p. 47.5—48.5° (*p*-phenylphenacyl ester, m. p. 68—70°).

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