Organic Peroxides Containing Functional Groups. Part I. The Preparation and Properties of Some α-Oxo-hydroperoxides †

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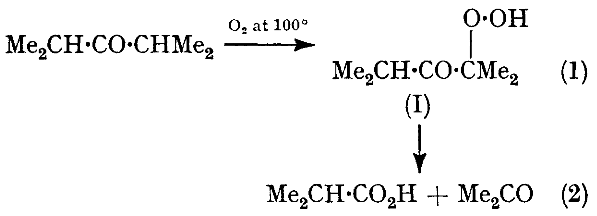
α-Oxo-hydroperoxides have been prepared by the low-temperature base-catalysed autoxidation of methyl isopropyl ketone, di-isopropyl ketone, and 2-methylcyclohexanone. The effect of variations of solvent and base on these autoxidation reactions has been studied. The α-oxo-hydroperoxide structure has been confirmed, and derivatives of both the hydroperoxide and carbonyl functions have been prepared. The product of the decomposition of 2-hydroperoxy-2-methylcyclohexanone has been isolated and identified as 6-oxoheptanoic acid. This product has been shown to result from both the base-catalysed and the uncatalysed thermal decomposition, and the mechanism of its formation is discussed.

α-OXO-HYDROPEROXIDES have been prepared by the autoxidation of aliphatic ketones at 100° in the absence of catalysts[1], and by autoxidation in the presence of strong bases at or below 0°.[2,3] Sharp[1] has shown that the high temperature autoxidation of di-isopropyl ketone takes place according to reactions (1) and (2). At the high temperatures necessary for uncatalysed autoxidation, only low yields of the hydroperoxide intermediate (I) were obtained. The autoxidation of di-n-propyl ketone follows a similar course, but in this case the secondary α-oxo-hydroperoxide could not be isolated.[4] However, the secondary α-oxo-hydroperoxide, 2-hydroperoxycyclohexanone, has been isolated[5] from



$$Me_2CH{\cdot}CO{\cdot}CHMe_2 \xrightarrow{O_2\text{ at }100^\circ} Me_2CH{\cdot}CO{\cdot}\overset{O\cdot OH}{\overset{|}{C}}Me_2 \quad (1)$$

(I)

$$\downarrow$$

$$Me_2CH{\cdot}CO_2H + Me_2CO \quad (2)$$

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[1] D. B. Sharp, L. W. Patton, and S. E. Whitcomb, *J. Amer. Chem. Soc.*, 1951, **73**, 5600.

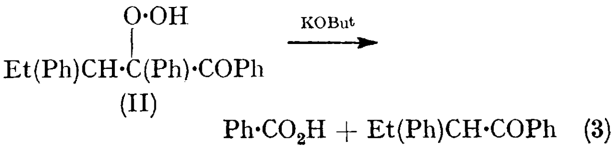
[2] H. R. Gersmann, H. J. W. Nieuwenhuis, and A. F. Bickel, *Proc. Chem. Soc.*, 1962, 279.

[3] F.P. 1,358,288.

[4] D. B. Sharp, L. W. Patton, and A. D. Moorhead, *J. Amer. Chem. Soc.*, 1952, **74**, 1802.

[5] W. Pritzkow, *Chem. Ber.*, 1954, **87**, 1668.

the autoxidation of cyclohexanone in the presence of manganese salts at 100°. Adipaldehydic acid and adipic acid were also formed in the oxidation. Thus, it is well established that oxidation of aliphatic ketones takes place at the positions α to the carbonyl group. In the high-temperature autoxidations very low yields of α-oxo-hydroperoxide are obtained because of the thermal decomposition of these hydroperoxides to yield an acid and a ketone or aldehyde. In this work, we have investigated the preparation of tertiary α-oxo-hydroperoxides by base-catalysed autoxidation at 0° and below. Under these conditions thermal decomposition of the α-oxo-hydroperoxides does not intrude, and consequently much higher yields of the hydroperoxides might be expected than in the high-temperature autoxidation. We were able to confirm this expectation, although in the base-catalysed autoxidation there is some loss of α-oxo-hydroperoxide by base-catalysed decomposition. von Doering and Haines[6] have shown that the α-oxo-hydroperoxide (II) is cleaved by base to give products analogous to those expected from the thermal decomposition reaction (3).



$$\underset{\text{(II)}}{Et(Ph)CH\cdot \overset{O\cdot OH}{\overset{|}{C}}(Ph)\cdot COPh} \xrightarrow{KOBu^t} Ph\cdot CO_2H + Et(Ph)CH\cdot COPh \quad (3)$$

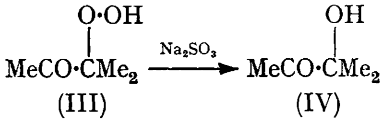
Hydroperoxides were isolated in high yields from the autoxidation of methyl isopropyl ketone, di-isopropyl ketone, and 2-methylcyclohexanone in the presence of an excess of potassium t-butoxide in t-butyl alcohol–dimethoxyethane[2,3] (see Table). Only the mono-hydroperoxide (I) was detected in the autoxidation of di-isopropyl ketone although previous workers[3] have reported a dihydroperoxide. An examination of the reaction variables showed that the following factors favoured high yields of the hydroperoxides: (i) short reaction times, (ii) low reaction temperature (<−8°), (iii) the polar aprotic solvents dimethoxyethane and *NN*-dimethylformamide, and (iv) an excess of base (mole ratio of potassium t-butoxide : ketone >2). The relevance of these factors to the mechanism of the autoxidation is discussed later.

The effect of solvent and temperature on the maximum yields of hydroperoxide attained in the autoxidation of various ketones in the presence of potassium t-butoxide–t-butyl alcohol

Ketone	Solvent *	Temp.	Time to max. yield (min.)	Max. yield of hydroperoxide (wt. %)
MeCOPr^i	DMF	−8°	4	87
	DME	−8	10	80
	HPT	−8	7	72
	THF	−8	7	66
	MeCN	−8	8	56
	PhMe	−8	11	48
	EtOAc	−8	13	38
Pr$^i_2$CO	DMF	−8	5	93
2-Methylcyclohexanone	DMF	−8		10
		−50	20	70
	DME	−50	20	85

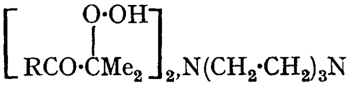
* DMF = Dimethylformamide, DME = dimethoxyethane, HPT = hexamethylphosphoric triamide, THF = tetrahydrofuran.

The structure of the hydroperoxide derived from methyl isopropyl ketone was established as (III) by reduction to 3-methyl-3-hydroxybutan-2-one (IV). The



$$\underset{\text{(III)}}{MeCO\cdot \overset{O\cdot OH}{\overset{|}{C}}Me_2} \xrightarrow{Na_2SO_3} \underset{\text{(IV)}}{MeCO\cdot \overset{OH}{\overset{|}{C}}Me_2}$$

hydroperoxides (I) and (III) were also characterised by the preparation of triethylenediamine adducts (V).[7] These derivatives are prepared under very mild conditions and thus provide a useful method for characterising hydroperoxides. A dialkyl peroxide (VI) was prepared from (I) by reaction with triphenylmethanol in acid solution, and more conveniently from triphenylmethyl chloride.[8] No peresters were isolated from the reaction of the α-oxo-hydroperoxides with acid chlorides in the presence of bases. The α-oxo-hydroperoxides were found to be effective initiators of polymerisation in the presence of cobalt naphthenate; in this respect they resemble *gem*-dihydroperoxides rather than alkyl hydroperoxides.[9]



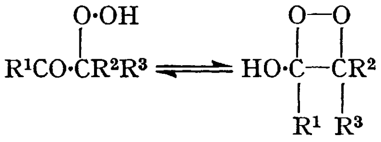
$$\left[RCO\cdot \overset{O\cdot OH}{\overset{|}{C}}Me_2\right]_2,N(CH_2\cdot CH_2)_3N$$

(V) R = Me, Pr^i

$$Me_2CH\cdot CO\cdot CMe_2\cdot O\cdot O\cdot CPh_3$$

(VI)

In earlier work[10] on α-oxo-hydroperoxides it was suggested that the four-membered ring structure (VII) was formed. However, in a recent detailed spectroscopic study[11] of 2-hydroperoxy-2,4-dimethylpentan-3-one (I) no evidence was found for equilibrium (4), or the cyclic structure (VII). In fact, the hydroperoxide (I) exists in solution principally as a hydrogen-bonded dimer, with some intramolecular hydrogen bonding. We obtained similar results for the hydroperoxide (III). These results indicate that the carbonyl group in these hydroperoxides should have the normal reactivity, and we were able to prepare a 2,4-dinitrophenylhydrazone, a



(VII) (4)

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[6] W. von E. Doering and R. M. Haines, *J. Amer. Chem. Soc.*, 1954, **76**, 482.

[7] U.S.P. 3,236,850.

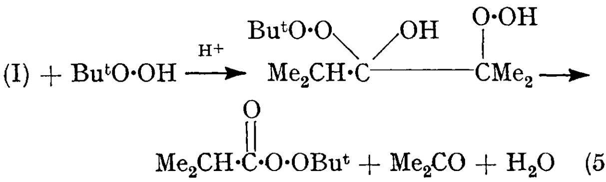
[8] N. A. Milas, R. J. Klein, and D. G. Orphanos, *Chem. and Ind.*, 1964, 423.

[9] G. R. Svoboda, *J. Polymer Sci.*, 1964, **2A**, 2713.

[10] E. P. Kohler and R. B. Thompson, *J. Amer. Chem. Soc.*, 1937, **59**, 887.

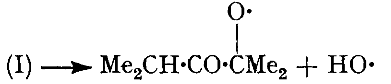
[11] W. H. Richardson and R. F. Steed, *J. Org. Chem.*, 1967, **32**, 771.

semicarbazone, and a liquid oxime from (III). The possibility of forming a peracetal by the reaction of t-butyl hydroperoxide with the carbonyl group of (I) was also investigated. The reaction did not follow the expected course and the main product was t-butyl perisobutyrate. The perester might arise from the decomposition of the hemiperacetal [reaction (5)].



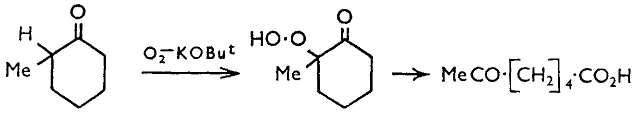
$$(\text{I}) + \text{Bu}^t\text{O·OH} \xrightarrow{\text{H}^+} \text{Me}_2\text{CH·C}(\text{O·OBu}^t)(\text{OH})\text{–CMe}_2(\text{O·OH}) \longrightarrow \text{Me}_2\text{CH·C(=O)·O·OBu}^t + \text{Me}_2\text{CO} + \text{H}_2\text{O} \quad (5)$$

The α-oxo-hydroperoxides (I) and (III) proved to be effective initiators of polymerisation at 110°, thus showing that free radicals are produced in the thermal decomposition. The kinetics of decomposition of 2-hydroperoxy-2,4-dimethylpentan-3-one in chlorobenzene at 110° were studied. Linear plots of log [peroxide] *vs.* time were obtained, but the apparent first-order rate constant was dependent on the initial peroxide concentration. The decomposition is thus clearly not first order, and the homolysis of the peroxide bond [reaction (6)] cannot be the rate-determining step. This is not unexpected, because many hydroperoxides decompose by free-radical-induced chain reactions.[12] A further complication with the α-oxo-hydroperoxides is introduced by the possibility of simultaneous decomposition by the non-radical reaction (2).

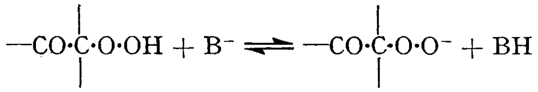


$$(\text{I}) \longrightarrow \text{Me}_2\text{CH·CO·}\overset{\text{O·}}{\overset{|}{\text{C}}}\text{Me}_2 + \text{HO·} \quad (6)$$

The α-oxo-hydroperoxides are also susceptible to a base-catalysed decomposition. The nature of this decomposition was established by a study of the base-catalysed autoxidation of 2-methylcyclohexanone. At −8° the principal product of the autoxidation was found to be 6-oxoheptanoic acid, and only low yields of hydroperoxide (VIII) were isolated (Table). The pure oxo-hydroperoxide (VIII) decomposed very slowly to 6-oxoheptanoic acid over a period of several weeks at room temperature. This indicates that the decomposition is base catalysed and suggests that the reaction takes place by nucleophilic attack of the peroxy-anion on the carbonyl group. The faster rate in the presence of base reflects the greater nucleophilic power of the peroxy-anion compared with the hydroperoxy-group. A cyclic

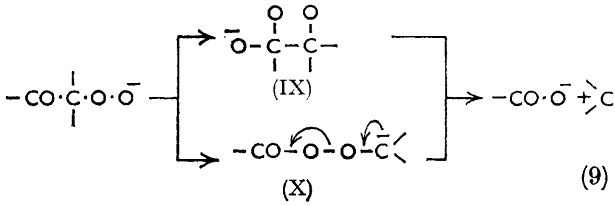


(VIII) (7)



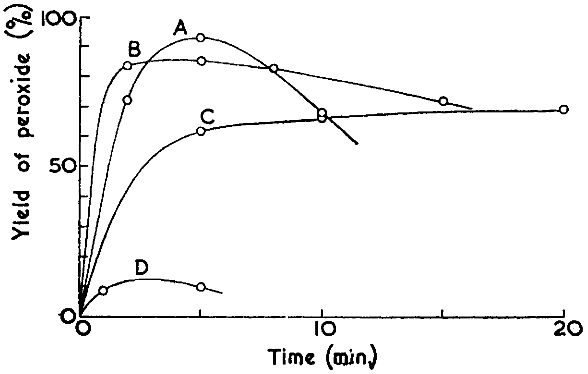
$$-\text{CO·}\overset{|}{\underset{|}{\text{C}}}\text{·O·OH} + \text{B}^- \rightleftharpoons -\text{CO·}\overset{|}{\underset{|}{\text{C}}}\text{·O·O}^- + \text{BH} \quad (8)$$

transition-state (IX) has been proposed by von Doering and Haines[6] to account for the oxidative cleavage of cyclohexanone in the presence of alkoxides, while Elkik[13] has suggested the linear-transition state (X).



(9)

The Base-catalysed Autoxidation.—The factors affecting the yield of hydroperoxide from the autoxidation reaction were investigated in some detail. The Figure shows the effect of reaction time (*i.e.* passage of oxygen) on the yield of hydroperoxides. The yields of α-oxo-hydroperoxides pass through a maximum value, and thus under a given set of experimental conditions the reaction time is an extremely important factor. The kinetic behaviour can be accounted for by a rapid autoxidation, followed by a decomposition to non-peroxidic products. The maximum yield of hydroperoxide is thus governed by the ratio of the rates of formation and decomposition. The high yields of hydroperoxide obtained from di-isopropyl ketone and methyl isopropyl ketone show that under the conditions employed the autoxidation step was very much more rapid than the decomposition reaction. In fact, the rate-controlling step in the autoxidation of these ketones could well have been the rate of delivery of oxygen.



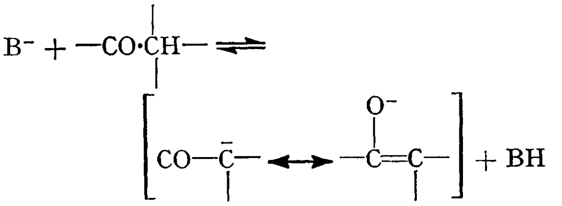
Autoxidation of ketones in 60 : 40 dimethylformamide–t-butyl alcohol: A, di-isopropyl ketone (−8°); B, isopropyl methyl ketone (−8°); C, 2-methylcyclohexanone (−50°); and D, 2-methylcyclohexanone (−8°)

The autoxidation of 2-methylcyclohexanone shows rather different characteristics. At −8°, autoxidation led to the formation of 6-oxoheptanoic acid as already discussed, and only low yields of hydroperoxide were isolated. Clearly in this case the rate of autoxidation must be only slightly greater than the rate of decomposition by reaction (9). At lower temperatures much higher yields of 2-hydroperoxy-2-methylcyclohexanone (VIII) were obtained (see Table), indicating that reaction

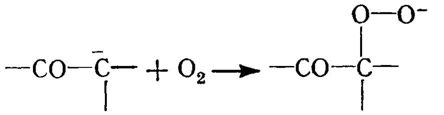
[12] S. W. Benson, *J. Chem. Phys.*, 1964, **40**, 1007.
[13] E. Elkik, *Bull. Soc. chim. France*, 1959, 933.

(9) has a higher activation energy than the autoxidation. These results show that 2-hydroperoxy-2-methylcyclohexanone undergoes the base-catalysed decomposition much more readily than the acyclic hydroperoxides (I) and (III).

The kinetics of autoxidation followed the same general pattern in a number of different solvents, and the times required to reach the maximum yield of hydroperoxide are summarised in the Table. The highest yields of hydroperoxides were obtained in the polar aprotic solvents *NN*-dimethylformamide and dimethoxyethane. This can be accounted for in terms of the carbanion mechanism which has been proposed for these autoxidations.[6-15] The carbanion intermediates are



$$\mathrm{B^- + -CO{\cdot}\overset{|}{\underset{|}{C}}H- \rightleftharpoons \left[CO-\bar{C}- \longleftrightarrow -\overset{O^-}{\overset{|}{C}}=C-\right] + BH} \quad (10)$$



$$\mathrm{-CO-\bar{C}- + O_2 \longrightarrow -CO-\overset{O-O^-}{\overset{|}{C}}-} \quad (11)$$

weakly solvated in the polar aprotic solvents and are thus in a particularly reactive state.[16] This could result in an increase in the rate of formation of the hydroperoxide [reaction (10)] relative to the rate of decomposition, provided that the decomposition reaction is less sensitive to the nature of the solvent. An excess of strong base is required to force the equilibrium (10) to the side of the carbanion. The precise mechanism of reaction (11) has been subject of some controversy.[6,14,15] Gersmann [14] has put forward evidence for the direct addition of oxygen to the carbanion as written in reaction (11). Thus it would appear that the principal features of the autoxidation can be described qualitatively by reactions (10) and (11) together with the decomposition mechanism (8) and (9).

EXPERIMENTAL

Analyses.—Available oxygen determinations were carried out by Method A of reference 17.

Chromatography.—T.l.c. was carried out on Kieselgel G (30 μ) with toluene–ethyl acetate (6 : 1) as the moving phase. The peroxidic spots were detected with hydrogen iodide in acetic acid (1 : 1) or *o*-tolidine in 20% acetic acid.

Spectra.—I.r. spectra were measured as Nujol mulls or in solution in carbon tetrachloride with a Perkin-Elmer Model 237 spectrophotometer. The ^{1}H n.m.r. spectrum of t-butyl perisobutyrate was measured on a Varian A60 spectrometer made available by Dr. J. Feeney of Varian Associates Ltd.

3-*Hydroperoxy*-3-*methylbutan*-2-*one.*—This compound was prepared by a published method.[3] The compound, m.p. 28—30°, was obtained in 58% yield (Found: available oxygen, 12·6%. Calc. for $C_5H_{10}O_3$: available oxygen, 13·6%), $\nu_{max.}$ (CCl_4), 3555var (free OH), 3425br (hydrogen-bonded OH), and 1730s cm.$^{-1}$ (CO). The compound was shown to be homogeneous by t.l.c.

2-*Hydroperoxy*-2,4-*dimethylpentan*-3-*one.*—The compound, prepared by a published method,[3] m.p. 43—44°, was obtained in 63% yield (Found: C, 58·2; H, 10·2; available oxygen, 11·0. Calc. for $C_7H_{14}O_3$: C, 57·6; H, 9·7; available oxygen, 11·0%), $\nu_{max.}$ (CCl_4) 3550var (free OH), 3440br (hydrogen bonded OH), 1730s, and 1720s cm.$^{-1}$ (CO), homogeneous by t.l.c.

Attempted Preparation of 2,4-*Dihydroperoxy*-2,4-*dimethylpentan*-3-*one.*[3]—Di-isopropyl ketone (0·2 g., 0·0017 mole) was dissolved in dimethoxyethane (10 ml.) and the solution was cooled to −2·5°. Potassium t-butoxide (0·9 g., 0·008 mole) was added and oxygen passed through the stirred solution. After a reaction time of 1 min., a small portion of the reaction mixture was examined by t.l.c., and the remainder was poured into acetic acid (30 ml.; 0·005% ferric chloride added), excess of sodium iodide was added, and the liberated iodine was titrated with sodium thiosulphate solution. T.l.c. showed the presence of 2-hydroperoxy-2,4-dimethylpentan-3-one but no second peroxidic species was detected with either hydrogen iodide–acetic acid or *o*-tolidine. The available oxygen estimation corresponded to a 45·6% yield of the monohydroperoxide (*cf.* ref. 3 where a 60% yield of dihydroperoxide—120% yield based on monohydroperoxide is reported). Two further runs with reaction times of 0·5 and 5 min. gave yields of the monohydroperoxide of 51·8 and 57·8% respectively.

2-*Hydroperoxy*-2-*methylcyclohexanone.*—Potassium (7·0 g., 0·18 mole) was dissolved in a mixture of t-butyl alcohol (200 ml.) and dimethoxyethane (300 ml.), and 2-methylcyclohexanone (10·0 g., 0·09 mole) was added. The mixture was cooled to −50° and oxygen passed into the stirred solution through a sintered Polythene gas-dispersion tube at a rate of 15 l./hr. After a reaction time of 20 min. the rate of oxygen uptake decreased rapidly, and the flow of oxygen was stopped. The reaction mixture was added to ice–water (500 g.), the aqueous solution was extracted with ether (400 ml.) to remove unchanged starting material, and the ether extract was discarded. Orthophosphoric acid (4 ml.) diluted with ice–water was stirred into the aqueous solution, which was extracted with ether (2 × 300 ml.). The ether extracts were combined, dried (Na_2SO_4), and evaporated at room temperature. The residue was taken up in ether–pentane (1 : 1) and stored at −20°. Crystals of 2-*hydroperoxy*-2-*methylcyclohexanone* were deposited; the compound is liquid at room temperature. T.l.c. showed the presence of only one peroxidic species (Found: C, 58·6; H, 8·1; available oxygen, 10·8. $C_7H_{12}O_3$ requires C, 58·3; H, 8·3; available oxygen, 11·1%).

Autoxidation of 2-*Methylcyclohexanone at* 10°.—Sodium methoxide (54·0 g., 1·0 mole) suspended in a mixture of methanol (200 ml.) and dimethoxyethane (500 ml.) was cooled to 10°. Oxygen was passed into the stirred solution through a sintered Polythene tube at a rate of 15 l./hr. 2-Methylcyclohexanone (56·0 g., 0·5 mole) was added during 1 hr., the temperature being maintained at 10° by means of an ice-bath. An orange precipitate was formed.

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[14] H. R. Gersmann, H. J. W. Nieuwenhuis, and A. F. Bickel, *Tetrahedron Letters*, 1963, 1383.

[15] G. A. Russell, A. J. Moye, and K. Nagpal, *J. Amer. Chem. Soc.*, 1962, **84**, 4154.

[16] A. J. Parker, *Quart. Rev.*, 1962, **16**, 163.

[17] Laporte Industries Limited, Publication LC4 (Rev.), 1966, pp. 10—14.

The mixture was stirred for a further 15 min. at 10° with the flow of oxygen maintained. The reaction mixture was then poured into water (150 ml.) and extracted with ether (3 × 100 ml.) to remove unchanged starting material. The ether extracts were discarded, and the aqueous layer was acidified (5N-sulphuric acid) and extracted with ether (4 × 200 ml.). The ether extracts were combined, dried (Na_2SO_4), and evaporated at room temperature. The residue, a viscous, red liquid (38 g., 51%) was distilled under reduced pressure to give 6-oxoheptanoic acid, b.p. 122—124°/1 mm., m.p. 33—36° (26 g., 36%) (lit.,[18] b.p. 122—123°/1 mm., m.p. 34—35°) (Found: C, 58·4; H, 8·0; Equiv. wt. 145. Calc. for $C_7H_{12}O_3$: C, 58·3; H, 8·3; Equiv. wt., 144). 6-Oxoheptanoic acid was further characterised by way of its semicarbazone, m.p. 145—148° (lit.,[19] m.p. 144—146°) (Found: C, 47·8; H, 7·3. Calc. for $C_8H_{15}N_3O_3$: C, 47·8; H, 7·5%), and through its reduction by hydrogenation (Raney nickel catalyst), or by sodium borohydride in aqueous solution, to give 6-hydroxyheptanoic acid (Found: C, 57·6; H, 9·1. Calc. for $C_7H_{14}O_3$: C, 57·5; H, 9·6%), which in turn was characterised by its self-condensation in the presence of mineral acids to give 2-methyl-ε-caprolactone b.p. 98°/5 mm. (Found: C, 65·6; H, 9·5. Calc. for $C_7H_{12}O_2$: C, 65·6; H, 9·4%).

Kinetic Runs.—The sample of ketone (*ca.* 0·2 g.) was accurately weighed out in a stoppered test tube, the solvent (7·5 ml.) was added, and the solution was cooled to the required temperature. Potassium t-butoxide solution (5 ml. of 1·8M-solution in t-butyl alcohol) was added and the stoppered reaction tube was placed in a cooling bath for a few minutes before the introduction of the oxygen dispersion tube. Oxygen was passed through the solution for a measured time, the contents of the tube were rapidly transferred (rinsed out with absolute ethanol) to a flask containing acetic acid (30 ml., containing 0·005% ferric chloride). This effectively stopped the reaction by neutralising the base. The yield of hydroperoxide was then determined by analysing the solution for available oxygen.

Reduction of 3-*Hydroperoxy*-3-*methylbutan*-2-*one*.—A solution of 3-hydroperoxy-3-methylbutan-2-one (1·5 g., 0·0127 mole) in water (5 ml.) was added dropwise to a stirred solution of sodium sulphite (4·0 g., 0·032 mole) in water (30 ml. at 0°). After 3 hr., examination of the reaction mixture by t.l.c. showed that all of the hydroperoxide had reacted. The reaction mixture was extracted with ether (2 × 50 ml.), dried (Na_2SO_4), and evaporated to give a colourless liquid. Reaction with 2,4-dinitrophenylhydrazine in aqueous sulphuric acid [20] gave an orange solid which was crystallised from aqueous methanol to give the 2,4-dinitrophenylhydrazone of 3-hydroxy-3-methylbutan-2-one, m.p. 71·5—72° (lit.,[21] m.p. 71—72°) identical (mixed m.p. and comparison by t.l.c.) with an authentic sample.

2,4-*Dimethyl*-2-*triphenylmethylperoxypentan*-3-*one*.—2-Hydroperoxy-2,4-dimethylpentan-3-one (2·0 g., 0·0137 mole) and triphenylmethyl chloride (3·8 g., 0·0137 mole) were heated together at 70° for 2·5 hr. in a flask attached to a rotary evaporator. Evolution of hydrogen chloride ceased after 2·5 hr., and the solid residue was recrystallised from light petroleum (b.p. 60—80°) to give 2,4-*dimethyl*-2-*triphenylmethylperoxypentan*-3-*one*, m.p. 97—98° (1·2 g., 23%) (Found: C, 83·1; H, 5·2; available oxygen 4·1.[22] $C_{26}H_{28}O_3$ requires C, 81·5; H, 6·9; available oxygen, 3·9%).

3-*Hydroperoxy*-3-*methylbutan*-2-*one*, *Triethylenediamine Salt*.—A solution of 3-hydroperoxy-3-methylbutan-2-one (5·2 g., 0·04 mole) in toluene (5 ml.) was added slowly to a solution of triethylenediamine (0·02 mole) in toluene (8 ml.) at room temperature. An exothermic reaction occurred and after 10 min. the white crystalline precipitate was filtered off, washed with light petroleum (b.p. 40—60°; 3 × 20 ml.) and dried *in vacuo* to give the *salt*, m.p. 85° (6·8 g., 92%) (Found: C, 55·0; H, 9·4; available oxygen, 9·0. $C_{16}H_{32}N_2O_6$ requires C, 55·2; H, 9·3; available oxygen, 9·2%).

2-*Hydroperoxy*-2,4-*dimethylpentan*-3-*one*, *Triethylenediamine Salt*.—A solution of 2-hydroperoxy-2,4-dimethylpentan-2-one (8·5 g., 0·058 mole) in toluene (10 ml.) was added to a stirred solution of triethylenediamine (3·25 g., 0·029 mole) in toluene (12 ml.) at room temperature. When the exothermic reaction had subsided, the solution was cooled in an acetone–solid carbon dioxide bath to give a white crystalline precipitate which was washed with light petroleum (b.p. 40—60°) and dried *in vacuo* to give the salt m.p. 58—59° (11·5 g., 98%) (Found: available oxygen, 7·8. $C_{20}H_{40}N_2O_6$ requires available oxygen, 7·9%).

3-*Hydroperoxy*-3-*methylbutan*-2-*one* 2,4-*Dinitrophenylhydrazone*.—2,4-Dinitrophenylhydrazine (1·0 g., 0·005 mole) was suspended in methanol (20 ml.) and sulphuric acid (36N; 2 ml.) was added. The solution was filtered, the filtrate was added to 3-hydroperoxy-3-methylbutan-2-one (0·6 g., 0·005 mole), and sulphuric acid (2N) was added to give a yellow precipitate. Recrystallisation from aqueous methanol gave the 2,4-*dinitrophenylhydrazone*, m.p. 101° (Found: C, 44·6; H, 5·4; N, 18·5; available oxygen, 4·8. $C_{11}H_{14}N_4O_6$ requires C, 44·3; H, 4·7; N, 18·8; available oxygen, 5·3%), $\nu_{max.}$ (Nujol) 1620 and 1590 cm.$^{-1}$ (C=N–).

Reaction of 2-*Hydroperoxy*-2,4-*dimethylpentan*-3-*one with t-Butyl Hydroperoxide*.—t-Butyl hydroperoxide (90%) (1·67 g., 0·0167 mole) was dissolved in toluene (5 ml.), sulphuric acid (50%, 0·05 ml.) was added and the mixture was cooled to 0°. A solution of 2-hydroperoxy-2,4-dimethylpentan-3-one (1·0 g., 0·007 mole) in toluene (5 ml.) was added during 15 min.; the reaction mixture was allowed to warm up to room temperature and then stored for 1 week. At the end of this time, the two phases which had formed were separated and the lower, non-peroxidic, layer was discarded. The upper layer was taken up in benzene, washed with 5% sodium hydroxide, dried (Na_2SO_4), and evaporated. The residue, a colourless liquid, was identified as t-butyl perisobutyrate by comparison of its i.r. and ^{1}H n.m.r. spectra with those of an authentic sample prepared by the method of Milas.[23,24] I.r. spectroscopy alone cannot distinguish between t-butyl perisobutyrate and per-n-butyrate but the ^{1}H n.m.r. spectra showed the characteristic septet of the methine group (τ 7·38) and the doublet of the methyl groups (τ 8·79) associated with the isopropyl group.

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