

Reactions of Some Dicarboxyl Compounds. Part III.¹ Oxidation of Some β -Diketones with Alkaline Hydrogen Peroxide

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Oxidation of β -diketones ($R^1CO\cdot CR^2R^3\cdot COR^4$) with alkaline hydrogen peroxide affords two types of acid depending upon the nature of R^2 and R^3 . Where both of these are H, the products are R^1CO_2H , R^4CO_2H , and formic acid, which suffers further oxidation. Where R^2 is alkyl, the products are R^1CO_2H , R^2CO_2H , R^4CO_2H , and $R^1R^2CH\cdot CO_2H$ and/or $R^2R^4CH\cdot CO_2H$. Where both R^2 and R^4 are alkyl, the products are $R^1R^2R^3C\cdot CO_2H$ and R^4CO_2H , and $R^2R^3R^4C\cdot CO_2H$ and R^1CO_2H , and this constitutes a useful source of trisubstituted acetic acids. The mechanisms of these reactions are discussed, and an additional oxidative side-reaction of two 2-alkyl-1,3-diketones is described.

DURING another investigation² we ozonised (+)-4 α -acetylcar-2-ene (1) in methanol and decomposed the product with alkaline hydrogen peroxide. The acids so formed were treated with diazomethane to yield a mixture of dimethyl (+)-*cis*-homocarbonate (2) and methyl (+)-*cis*-3-(3-methoxycarbonyl-2,2-dimethylcyclopropyl)-2-methylpropionate (3). At the time, we were surprised at the formation of the latter, but the literature revealed a number of cases in which β -diketones of the type $R^1CO\cdot CR^2R^3\cdot COR^4$ afforded acids of structure $R^1R^2R^3C\cdot CO_2H$ when oxidised with hydrogen peroxide. Thus 2-acetyl-2-methylcyclohexanone (4) affords³ 1-methylcyclopentanecarboxylic acid (5), and 2-acetylcyclohexanone yields a mixture of cyclopentanecarboxylic acid and, in minor amount, 2-methylpimelic acid. Likewise, 3,3-dimethylpentane-2,4-dione (6) yields pivalic acid, but no isobutyric acid was found³ when 3-methylpentane-2,4-dione (7) was similarly oxidised. Oxidation of a number of other 2-acylcycloalkanones with hydrogen peroxide, sometimes in the presence of acetic acid or sodium hydroxide, led⁴⁻⁶ to results similar to those described above.

¹ W. Cocker, P. H. Lawda, T. B. H. McMurry, and M. S. Ntamila, *J. Chem. Soc. (C)*, 1971, 1708.

² W. Cocker, H. St. J. Lauder, and P. V. R. Shannon, *J.C.S. Perkin I*, 1974, 194.

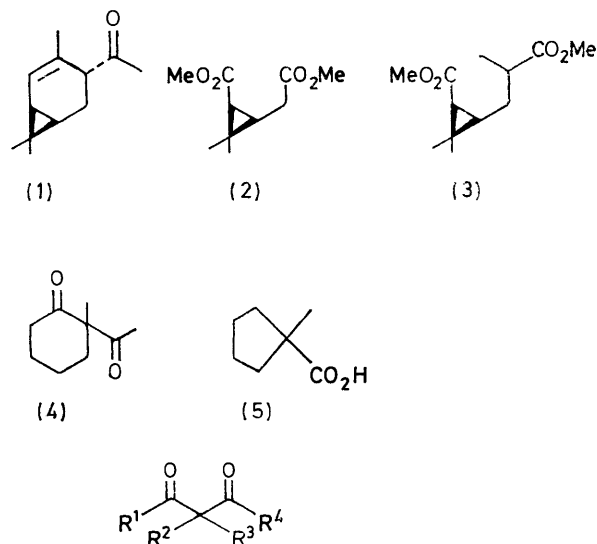
³ G. B. Payne, *J. Org. Chem.*, 1961, **26**, 4793.

⁴ L. P. Vinogradova and S. I. Zav'yalov, *Izvest. Akad. Nauk S.S.S.R., Ser. Khim.*, 1961, 1482 (*Chem. Abs.*, 1962, **56**, 338b).

⁵ L. P. Vinogradova and S. I. Zav'yalov, *Izvest. Akad. Nauk S.S.S.R., Ser. Khim.*, 1961, 2050 (*Chem. Abs.*, 1962, **57**, 12,344c).

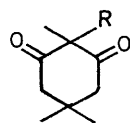
⁶ L. P. Vinogradova, B. A. Rudenko, and S. I. Zav'yalov, *Izvest. Akad. Nauk S.S.S.R., Ser. Khim.*, 1962, 1436 (*Chem. Abs.*, 1963, **58**, 2378g).

Extending these studies, we have oxidised several 1,3-diketones (8)–(21) with alkaline hydrogen peroxide,



- (6) $R^1 = R^2 = R^3 = R^4 = \text{Me}$ (13) $R^1 = R^4 = \text{Me}, R^2 = \text{PhCH}_2, R^3 = \text{H}$
 (7) $R^1 = R^2 = R^4 = \text{Me}, R^3 = \text{H}$ (14) $R^1 = R^2 = \text{Me}, R^3 = \text{H}, R^4 = \text{Ph}$
 (8) $R^1 = R^4 = \text{Me}, R^2 = R^3 = \text{H}$ (15) $R^1 = R^4 = \text{Ph}, R^2 = \text{Me}, R^3 = \text{H}$
 (9) $R^1 = R^4 = \text{Ph}, R^2 = R^3 = \text{H}$ (16) $R^1 = R^2 = R^4 = \text{Me}, R^3 = \text{PhCH}_2$
 (10) $R^1 = R^4 = \text{Me}, R^2 = \text{Et}, R^3 = \text{H}$ (17) $R^1 = R^4 = \text{Me}, R^2 = R^3 = \text{PhCH}_2$
 (11) $R^1 = R^4 = \text{Me}, R^2 = \text{Pr}^n, R^3 = \text{H}$ (18) $R^1 = R^2 = R^3 = \text{Me}, R^4 = \text{Ph}$
 (12) $R^1 = R^4 = \text{Me}, R^2 = \text{allyl}, R^3 = \text{H}$ (19) $R^1 = R^4 = \text{Ph}, R^2 = R^3 = \text{Me}$

isolated the acidic products as their ethyl or methyl esters, and identified them by spectral and g.l.c. comparisons. The results of these experiments are outlined in the Table.

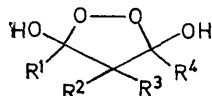
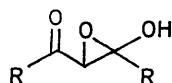


(20) R = H

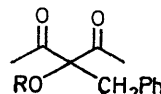
(21) R = Me



(22)

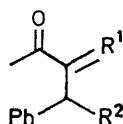
(23) R¹=R⁴=Me, R²=R³=H(24) R¹=R²=R³=R⁴=Me(25) R¹=R²=R⁴=Me, R³=PhCH₂

(26)



(27) R = H

(31) R = Ac

(28) R¹=H, OH, R²=H(29) R¹=O, R²=H(30) R¹=O, R²=OH

The 1,3-diketones fall into three groups, namely those that are unsubstituted at the 2-position [(8) and (9)], those that are mono-2-substituted [(7) and (10)—(15)],

Diketone	Products (%) *
(8)	MeCO ₂ H; HCO ₂ H
(9)	PhCO ₂ H
(7)	Me ₂ CH·CO ₂ H (84); MeCO ₂ H (16)
(10)	MeCHEt·CO ₂ H (49); Pr ⁿ CO ₂ H (42); MeCO ₂ H (9)
(11)	MeCHPr ⁿ ·CO ₂ H (20); Pr ⁿ CO ₂ H (45); EtCO ₂ H (13); MeCO ₂ H (22)
(12)	MeCH(CH ₂ ·CH·CH ₂)·CO ₂ H (40); CH ₂ ·CH·CH ₂ ·CO ₂ H (60)
(13)	PhCH ₂ ·CHMe·CO ₂ H (12); PhCH ₂ ·CO ₂ H (69); PhCO ₂ H (19)
(14)	PhCHMe·CO ₂ H; Me ₂ CH·CO ₂ H; PhCO ₂ H (mainly)
(15)	PhCHMe·CO ₂ H (24); PhCO ₂ H (66); PhCOEt (10)
(6)	Me ₃ C·CO ₂ H (mainly)
(16)	PhCH ₂ ·CMe ₂ ·CO ₂ H
(17)	(PhCH ₂) ₂ CH·COMe; little acidic product
(18)	PhCO ₂ H (56); PhCMe ₂ ·CO ₂ H (17); Me ₃ C·CO ₂ H (27)
(19)	PhCHMe ₂ ·CO ₂ H (50); PhCO ₂ H (50)
(20)	Me ₂ C(CH ₂ ·CO ₂ H) ₂ (34); unchanged diketone (66)
(21)	Me ₂ C(CH ₂ ·CO ₂ H)·CH ₂ ·CO·CHMe ₂

* Owing to losses in methyl acetate during work-up, the quoted yields of acetic acid are probably lower than actual.

and those that are 2,2-disubstituted [(6) and (16)—(19)]. Also oxidised were 2,5,5-trimethyl- and 2,2,5,5-tetramethyl-cyclohexane-1,3-diones [(20) and (21)].

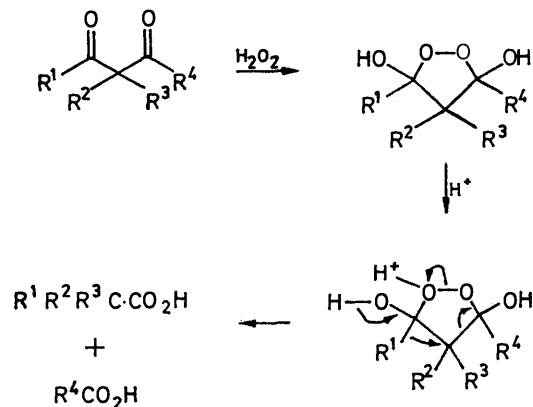
The unsubstituted 1,3-diketones (8) and (9) gave formic acid (from the central carbon atom), and the acid corresponding to the acyl group involved. The isolation

of formic acid is difficult owing to its further oxidation under the reaction conditions, but its reduction of silver ion provides evidence for its formation.

The 2-monosubstituted 1,3-diketones (7) and (10)—(15) undergo two types of reaction, namely (a) an oxidative rearrangement involving migration of an alkyl or aryl group (R¹ or R⁴) from C-1 or C-3 to C-2, yielding either R¹R²CH·CO₂H or R²R⁴CH·CO₂H, and, in addition, R⁴CO₂H or R¹CO₂H, respectively, and (b) an oxidative cleavage similar to that suffered by the unsubstituted β-diketones.

The 2,2-disubstituted 1,3-diketones only undergo the oxidative rearrangement reaction (a), and this can be conveniently used as a method to prepare the difficultly accessible trisubstituted acetic acids R¹R²R³C·CO₂H. For example, 3-benzyl-3-methylpentane-2,4-dione (16) may be converted into 2,2-dimethyl-3-phenylpropanoic acid (22) in ca. 80% yield in this way.

Payne³ has suggested that the addition of hydrogen peroxide to a β-diketone yields a peroxy-compound of the type (23), and that this undergoes acid-catalysed decomposition as shown in Scheme 1. The structure (23) has



SCHEME 1

been suggested⁷ for one of the products of reaction of acetylacetone (8) with hydrogen peroxide. We have confirmed this, and shown that similar peroxy-compounds (24)⁸ and (25) are obtained when 3,3-dimethylpentane-2,4-dione (6) and 3-benzyl-3-methylpentane-2,4-dione (16), respectively, are treated with 1 mol. equiv. of hydrogen peroxide.

The peroxy-compound (23) shows, in Nujol, strong i.r. absorption at 3 350 (OH), 1 420, 1 260, and 1 200 cm⁻¹, but no bands in the carbonyl region. Its 60 MHz n.m.r. spectrum has signals at τ ([²H₄]methanol) 8.52 and 8.50 (ca. 1.2H and 4.8H, 2 CH₃·COH), 7.98 and 7.80 (ca. 1.7H and 0.3H, CH₂), and 7.45 and 7.36 (ca. 0.3H and 1.7H, 2 OH). In [²H₆]acetone, the methyl groups appear as a singlet at τ 8.5, the methylene protons as a pair of signals at 7.46 and 7.36 (ca. 0.3H and 1.7H), and the hydroxyprotons as a broad singlet at 6.70. The compound thus exists as a mixture of *cis*- and *trans*-isomers, as further

⁷ A. Rieche and C. Bischoff, *Chem. Ber.*, 1962, **95**, 77.

⁸ C. Bischoff and H. Brandtstaedter, *Monatsber. Deut. Akad. Wiss. Berlin*, 1966, **8**, 888 (*Chem. Abs.*, 1968, **68**, 68,222h).

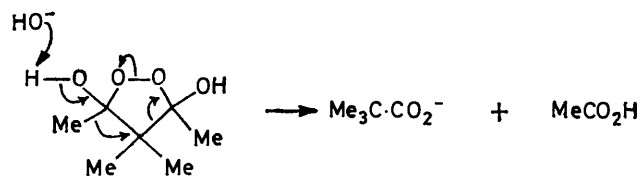
evidenced by its Raman spectrum, which shows two strong bands of unequal intensity at 817 and 839 cm^{-1} which may be ascribed to the O-O groups of the two stereoisomeric structures.

The i.r. spectrum of the second peroxy-compound (24) has characteristics similar to that of (23). The n.m.r. spectrum (solvent $[\text{D}_6]_2$ dimethyl sulphoxide) shows the geminal methyl group signals as two singlets at τ 9.06 (ca. 2H) and 8.98 (ca. 4H), those of the other methyl groups at 8.74 (ca. 4H) and 8.60 (ca. 2H), and that of the hydroxy-protons as a broad singlet at 6.65.

Models show that the *trans*-disposition of methyl and hydroxy-groups is the more stable arrangement in each case. There seems to be little likelihood of intramolecular hydrogen bonding in the *cis*-isomer.

All the peroxy-compounds isolated slowly release iodine from acidulated sodium iodide, and they are reduced to the parent β -diketones with sodium sulphite or with hydrogen over palladised charcoal.

Treatment of the peroxy-compounds with alkali affords, as expected, the same acidic products as formed when the appropriate β -diketone is treated with alkaline hydrogen peroxide. Moreover, the disubstituted peroxy-compounds (24) and (25) slowly become liquid at room temperature either alone or in light petroleum solution, the products being the same as those that are formed with alkali. It is therefore clear that such peroxy-compounds are intermediate in the oxidation of the diketones with alkaline hydrogen peroxide. Cleavage of these with base can be expressed as for (24) (Scheme 2).



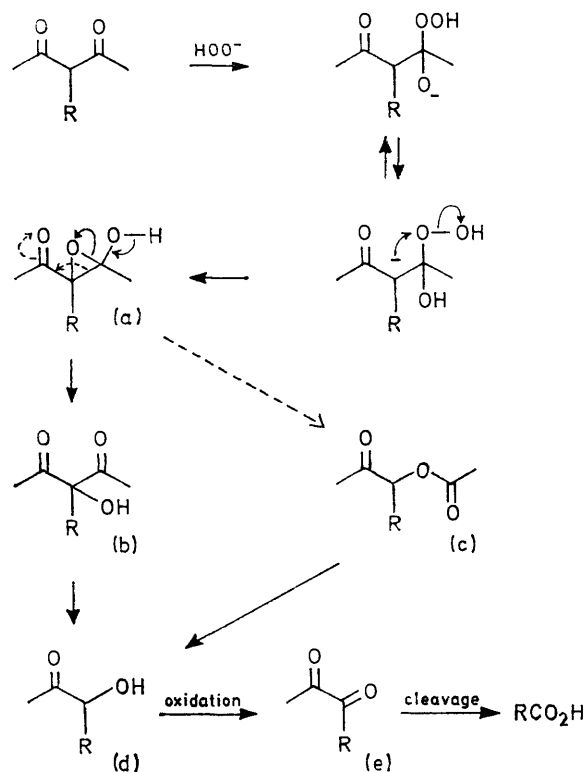
The migratory aptitude of the substituent adjacent to the hydroxy-group will be the inverse of its effect on the latter's acidity. Consequently, oxidation of 2,2-dimethyl-1-phenylbutane-1,3-dione (18) leads to pivalic and 2-methyl-2-phenylpropanoic acids in the ratio 60 : 40.

It is probable that all these peroxy-compounds can undergo a base-catalysed reversal to hydrogen peroxide and the β -diketone. This is certainly the case with (23) which, on brief treatment with alkali, regenerates acetylacetone (8). Cyclic peroxy-compounds could not be formed from 2,2-dimethyl-1,3-diphenylpropane-1,3-dione (19) or either of the cyclohexanediones (20) and (21) owing, presumably, to steric constraints.

The reaction with alkaline hydrogen peroxide may take an additional course if the β -diketone is α -monosubstituted [(7) and (10)–(15)]. This is exemplified by the formation from these compounds of the acid $\text{R}^2\text{CO}_2\text{H}$ (representing oxidation of the central carbon atom), together with the product of the oxidative rearrangement described above. For example, 3-benzylpentane-2,4-dione (13) affords phenylacetic acid *via* oxidative cleavage

and 2-methyl-3-phenylpropanoic acid *via* oxidative rearrangement. The unsubstituted β -diketones (8) and (9) only undergo this oxidative cleavage reaction. Rearrangement products are not observed.

It seems to us that the mechanism of the oxidative cleavage is best represented as outlined in Scheme 3.



Here, the β -diketone is attacked by hydroperoxide ion to form an enol epoxide (a) *via* the route shown. This can then rearrange to the hydroxy-diketone (b) or, perhaps, to the ester (c). Hydrolysis of either (b) or (c) leads to the hydroxy-ketone (d), which is then oxidised to the 1,2-diketone (e). The latter then suffers cleavage to yield the acidic products of the reaction.

Pertinently, Buchi⁹ has reported the oxidation of a 1,3-dicarbonyl system to the 2-hydroxy-compound by treatment of the 2-anion with hydrogen peroxide at low temperature. In this instance, the observed stereochemistry of hydroxylation supports the proposition that an enol epoxide is an intermediate.

Oxidation of 3-benzylpentane-2,4-dione (13) leads not only to the acidic products expected from the oxidative reactions described above but also to benzoic acid and a little benzaldehyde. The last pair may be formed by the route (27) (*cf.* ref. 9) \longrightarrow (28) \longrightarrow (29) \longrightarrow (30). The last can either undergo retroaldol reaction giving benzaldehyde which is further oxidised to benzoic acid, or be directly oxidised to this acid. A similar mechanism can be applied to the formation of propionic acid from (11).

⁹ G. Buchi, K. E. Matsumoto, and H. Nishimura, *J. Amer. Chem. Soc.*, 1971, **93**, 3299.

In fact, alkaline hydrolysis of 3-acetoxy-3-benzylpentane-2,4-dione (31), prepared from (13) and lead tetra-acetate (*cf.* ref. 10), failed to give (27) (*cf.* ref. 11), but afforded the α -ketol (28). Treatment of this (28) with alkaline hydrogen peroxide gave phenylacetic acid and benzoic acid in a similar ratio to that realised when (13) itself was oxidised.

The cyclic dione (21) cannot undergo the oxidative cleavage reaction, and it does not give a peroxy-compound, but it suffers complete hydrolysis, in contrast to the stability¹² of (20), in alkali.

EXPERIMENTAL

I.r. spectra were measured for liquid films (L) or Nujol mulls (N). N.m.r. and u.v. spectra were measured for solutions in carbon tetrachloride and ethanol, respectively, unless otherwise stated. I.r. data for compounds marked with an asterisk (*) and n.m.r. data for those marked with an obelus (†) are available in Supplementary Publication No. 21368 (16 pp., 1 microfiche).* G.l.c. was carried out on a 2 m \times 3 mm, 20% Carbowax 20M on Chromosorb W column at 150 °C.

Diketones.—Compounds (7), (14), and (15) were prepared from commercially available specimens of acetylacetone (8), benzoylacetone, and dibenzoylmethane (9), respectively, by the silver oxide–methyl iodide method.¹³ Compounds (10), (12), and (13) were prepared from the sodio-derivative of acetylacetone and ethyl iodide, allyl bromide, and benzyl chloride, respectively. Compound (11) was prepared by hydrogenation of (12) over palladised charcoal. Compounds (6) and (16) were obtained from (7) by reaction in dimethyl sulphoxide containing potassium *t*-butoxide with methyl iodide and benzyl chloride, respectively. 3,3-dibenzylpentane-2,4-dione (17) was obtained as the major product when acetylacetone was treated in dimethyl sulphoxide with benzyl chloride, with potassium *t*-butoxide as base. The other product was (13). Compound (18) was prepared by acetylation of isobutyrophenone,¹⁴ and (19) by acylation of benzene with dimethylmalonyl dichloride.¹⁵ The substituted dimedones (20) and (21) were made as previously described.¹⁶

Oxidation of 1,3-Diketones with Hydrogen Peroxide Alone.—(a) *Acetylacetone* (8) (*cf.* ref. 7). Acetylacetone (10 g) was cooled to 0 °C and stirred vigorously, and hydrogen peroxide (75%; 4.5 g) was slowly added, the temperature being kept below 10°. The mixture slowly became homogeneous and then solidified. The peroxy-compound* (23) was stirred with cold, damp ether, collected, washed with dry ether, and dried in a desiccator; m.p. 82–84° without crystallisation (*lit.*,⁷ 80–82°).

(b) *3,3-Dimethylpentane-2,4-dione** (6). This had b.p. 16.5–17° at 0.1 mmHg (*lit.*,¹⁷ 57–58° at 10 mmHg), λ_{max} 290 nm (ϵ 83.7), ν_{max} (L) 1 715 and 1 695 cm^{-1} , single peak on g.l.c. The dione (3.3 g) was stirred at 0 °C with hydrogen peroxide (75%; 4.5 g) for 3 h to give the peroxy-compound*

(24) (3 g) as needles (ether–light petroleum), m.p. 78° (decomp.) (Found: C, 51.6; H, 9.0. Calc. for $\text{C}_7\text{H}_{14}\text{O}_4$: C, 51.8; H, 8.7%). It released iodine from acidulated sodium iodide, but did not respond to the chromic acid–sulphuric acid–ether test for hydrogen peroxide.

(c) *3-Benzyl-3-methylpentane-2,4-dione* (16). The following is a more convenient preparation than that described in the literature.¹⁸ Potassium *t*-butoxide (18 g) was slowly added to a stirred solution of 3-methylpentane-2,4-dione (18 g) in dimethyl sulphoxide (50 ml) and benzene (150 ml). After 1 h, benzyl chloride (20 g) was added dropwise and the mixture was stirred at 100 °C for 2 h, and then at 15 °C for 12 h. Two distillations gave 3-benzyl-3-methylpentane-2,4-dione* (16) as a liquid (14.5 g), homogeneous on g.l.c., b.p. 93–94° at 0.4 mmHg (*lit.*,¹⁸ 148–151° at 7 mmHg), ν_{max} (L) 1 710sh, 1 692, 1 595, and 1 490 cm^{-1} , m/e 204 (M^+), 161 ($M - \text{Ac}$), and 43 (100%, Ac) (Found: C, 76.4; H, 7.8. Calc. for $\text{C}_{13}\text{H}_{16}\text{O}_2$: C, 76.4; H, 7.9%).

The dione (16) (2 g) was stirred at 0 °C in methanol (5 ml) with hydrogen peroxide (75%; 2.6 g) for 2 h. Water was added and the solid product was collected and washed with sodium hydrogen carbonate solution (5%) and with light petroleum, to give 4-benzyl-3,4,5-trimethyl-1,2-dioxolan-3,5-diol* (25) (1.4 g) as needles, m.p. 78–79° (benzene–light petroleum), ν_{max} (N) 3 425, 1 196, and 1 118 cm^{-1} , $\tau[(\text{CD}_3)_2\text{SO}]$ 9.10 (3H, s, 4-Me), 8.91 (6H, s, 3- and 5-Me), 7.20 (2H, s, PhCH₂), and 2.76br (5H, s, Ar) (Found: C, 65.2; H, 7.7. $\text{C}_{13}\text{H}_{18}\text{O}_4$ requires C, 65.5; H, 7.6%). Attempted recrystallisation from acetic acid afforded 2-benzyl-2-methylpropanoic acid (see below).

Reduction of the Peroxy-compounds (23) and (24).—(a) The peroxy-compound (23) (0.7 g) in ethyl acetate, was hydrogenated at 1 atm over palladised charcoal (5%; 50 mg). Uptake of hydrogen was rapid, and work-up afforded acetylacetone (8) (0.5 g) as the sole product (g.l.c.). Likewise, the peroxy-compound (24) gave a nearly quantitative yield of 3,3-dimethylpentane-2,4-dione (6).

(b) A suspension of the peroxy-compound (24) (0.3 g) in water (4 ml) covered with a layer of ether (10 ml) was slowly treated at 0 °C with sodium sulphite heptahydrate (0.7 g). The strongly exothermic reaction yielded the dione (6) (0.25 g), homogeneous on g.l.c.

Reaction of the Peroxy-compounds with Alkali.—The peroxy-compound (24) (0.1 g) in methanol (1 ml) was slowly treated with sodium hydroxide solution (30%) to pH 9–10. More alkali was added from time to time to maintain this alkalinity. After 12 h, methanol was removed under reduced pressure, water was added, and the mixture was extracted with ether. The clear aqueous solution was acidified and extracted with ether, and the extract treated with diazomethane giving methyl pivalate (see below) (50 mg), pure by g.l.c. Likewise, the peroxy-compound (25) (0.6 g) gave 2-benzyl-2-methylpropanoic acid (0.3 g), m.p. 57° (*lit.*,¹⁹ 57°).

Spontaneous Decomposition of the Peroxy-compounds.—When kept in a closed tube the peroxy-compound (24) slowly became liquid. After 3 weeks it was diluted with

* For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin I*, 1974, Index issue.

¹⁰ L. F. Fieser and R. Stevenson, *J. Amer. Chem. Soc.*, 1954, **76**, 1728.

¹¹ A. H. Blatt and W. L. Hawkins, *J. Amer. Chem. Soc.*, 1936, **58**, 81.

¹² E. G. Meek, J. H. Turnbull, and W. Wilson, *J. Chem. Soc.*, 1953, 2391.

¹³ R. D. Abel, *J. Chem. Soc.*, 1912, **101**, 989.

¹⁴ A. R. Pinder and Sir R. Robinson, *J. Chem. Soc.*, 1955, 3341.

¹⁵ I. Smedley, *J. Chem. Soc.*, 1910, **97**, 1484.

¹⁶ T. G. Halsall and D. B. Thomas, *J. Chem. Soc.*, 1956, 2431.

¹⁷ A. E. Favorskii and A. S. Onishchenko, *J. Gen. Chem. (U.S.S.R.)*, 1941, **11**, 1111 (*Chem. Abs.*, 1943, **37**, 3735).

¹⁸ I. I. Grandberg, A. P. Krasnoschek, A. N. Kost, and G. K. Faizova, *J. Gen. Chem. (U.S.S.R.)*, 1963, **33**, 2586 (*Chem. Abs.*, 1964, **60**, 515e).

¹⁹ E. Rothstein and R. W. Saville, *J. Chem. Soc.*, 1949, 1946.

ether and extracted with sodium hydrogen carbonate solution (5%). Esterification of the acidic product with diazomethane gave a mixture (g.l.c.) of methyl acetate and methyl pivalate. Likewise, the peroxy-compound (25) became liquid after 2—3 days giving 2-benzyl-2-methylpropanoic acid, identified (g.l.c., i.r.) as its methyl ester. The unsubstituted peroxy-compound (23) is more stable and remains solid for months.

Oxidation of β -Diketones with Alkaline Hydrogen Peroxide.—The diones were dissolved or suspended in 5—6 times their weight of methanol and cooled to 0 °C with stirring, and 4—5 times their weight of hydrogen peroxide (30—34%, or its equivalent of 75%) was carefully added over 0.5 h at 0—5 °C. The mixture was maintained at this temperature while sodium hydroxide solution (30%; an equal volume to the 30% peroxide) was slowly added. After ca. 0.5 h (longer in the case of insoluble diones, which were stirred until a clear solution was obtained), the mixture was shaken with ether to remove neutral substances, and the aqueous layer was acidified and extracted with ether. The extract was treated with diazomethane and the methyl esters so obtained (see Table) were identified by spectral and g.l.c. comparisons.

3-Methylpentane-2,4-dione (7) ²⁰ (2.8 g), b.p. 169—172°, n_D^{25} 1.4420, ν_{\max} (L) 1 720, 1 700 (C=O), and 1 601br cm^{-1} (enol), gave mixed esters (1.67 g).

3-Ethylpentane-2,4-dione (10) ²¹ (3.1 g), b.p. 75—77° at 20 mmHg, $n_D^{24.5}$ 1.4351, λ_{\max} 288 nm (log ϵ 3.38) [302 nm (4.98) on addition of NaOH], ν_{\max} (L) 1 730, 1 695, and 1 590 cm^{-1} , gave mixed esters (1.1 g). Methyl 2-methylbutyrate ²² was obtained *via* the route: diethyl ethylmethylmalonate† \rightarrow ethylmethylmalonic acid* \rightarrow 2-methylbutyric acid.

3-Allylpentane-2,4-dione (12) ²³ (5 g), b.p. 35—42° at 0.15—0.3 mmHg, ν_{\max} (L) 1 720, 1 696 (C=O), 1 638 (C=C), 1 600br (enol), 995, and 992 cm^{-1} , gave mixed esters (2.16 g). Methyl 2-methylpent-4-enoate was prepared as described.²⁴ Diethyl allylmethylmalonate had b.p. 113° at 16 mmHg, ν_{\max} (L) 1 739 (C=O) and 930 cm^{-1} (CH=CH₂), τ 8.8 (6H, t, J 7 Hz, CO₂·CH₂Me), 8.71 (3H, s, Me), 7.51 (2H, d, J 7 Hz, CH₂=CH—CH₂), 5.92 (4H, q, J 7 Hz, CO₂·CH₂Me), 5.02 (2H, m, CH₂=CH), and 4.36 (1H, m, CH₂=CH); 2-methylpent-4-enoic acid had b.p. 98—99° at 15 mmHg, ν_{\max} (L) 2 800br, 1 710 (CO₂H), 1 650, 1 000, and 930 cm^{-1} ; methyl 2-methylpent-4-enoate had b.p. 130° (single peak on g.l.c.), ν_{\max} (L) 1 738, 1 640, 995, and 920 cm^{-1} , τ 8.91 (3H, d, CHMe), 7.68 (3H, m, HC-CO₂Me and CH₂-CH=CH₂), 6.44 (3H, s, CO₂Me), 5.07 (2H, m, CH₂=CH), and 4.33 (1H, m, CH₂=CH).

3-Propylpentane-2,4-dione (11),²⁵ b.p. 81.5—82° at 15 mmHg, ν_{\max} (L) 1 720, 1 692, and 1 610 cm^{-1} (Found: C, 67.9; H, 9.8. Calc. for C₈H₁₄O₂: C, 67.6; H, 9.9%), was obtained by hydrogenation of (12). Oxidation of (11) (3.5 g) gave hexan-2-one (0.68 g) [semicarbazone, m.p. 120° (lit.,²⁶ 125°)] and a crude acid fraction (4 g). Esterification of a sample (0.8 g) with diazomethane gave crude esters (1 g). Methyl 2-methylpentanoate, ν_{\max} (L) 1 730 and 1 170 cm^{-1} , was prepared by hydrogenation of methyl 2-methylpent-4-enoate (see above).

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3-Benzylpentane-2,4-dione (13) ²⁷ (2.3 g), b.p. 153—156° at 18 mmHg, n_D^{20} 1.5328, ν_{\max} (L) 1 720, 1 695, and 1 600 cm^{-1} , homogeneous on g.l.c., gave esters (1.57 g). Methyl 2-benzylpropionate was obtained *via* the following intermediates: diethyl sodiomethylmalonate (35 g ester) with an excess of benzyl chloride in methanol gave dimethyl benzylmethylmalonate (36 g), b.p. 165° at 15 mmHg, needles (light petroleum), m.p. 49—50° (lit.,²⁸ 63°), τ 8.74 (3H, s, Me), 6.89 (2H, s, PhCH₂), 6.38 (6H, s, 2 CO₂Me), and 2.7—3.1 (5H, ArH) (a minor quartet centred at τ 5.9 showed contamination with the ethyl ester); 2-benzylpropionic acid,²⁹ b.p. 165° at 16 mmHg; methyl 2-benzylpropionate, b.p. 120—121° at 15 mmHg, ν_{\max} (L) 1 732, 1 600, and 1 162 cm^{-1} , τ 8.94 (3H, d, MeCH), 7.0—7.6 (3H, ms, CH₂·CHMe), 6.52 (3H, s, CO₂Me), and 2.95 (5H, s, ArH) (single peak on g.l.c.).

2-Methyl-1-phenylbutane-1,3-dione (14) ³⁰ (3.4 g), b.p. 98—102° at 0.7—0.8 mmHg, ν_{\max} (L) 1 713, 1 670, and 1 689 cm^{-1} , gave a mixture of crude acids (4.4 g). Reaction of methyl iodide with methyl phenylacetate in a suspension of sodamide in liquid ammonia [see below for (19)] gave methyl 2-phenylpropionate,³¹ b.p. 108.5—109.5° at 15 mmHg, ν_{\max} (L) 1 737, 1 601, 1 209, 1 164, and 705 cm^{-1} , τ 8.57 (3H, t, J 8.0 Hz, Me), 6.52 (1H, q, J 8.0 Hz, MeCH), 6.46 (3H, s, CO₂Me), and 2.78 (5H, s, ArH).

2-Methyl-1,3-diphenylpropane-1,3-dione (15) (2 g) gave a mixture of acids (2.1 g), m.p. 102—113°, which yielded methyl esters (1.7 g). Propiophenone (0.28 g) was also isolated.

3,3-Dimethylpentane-2,4-dione (6) (3.3 g) gave methyl pivalate ³² * (2.7 g), b.p. 98—99°, ν_{\max} (L) 1 734 cm^{-1} , τ 8.83 (9H, s, 3 Me) and 6.38 (3H, s, CO₂Me).

3-Benzyl-3-methylpentane-2,4-dione (16) (2 g) was converted into its peroxy-compound (25) as earlier described. After collection (1.23 g; m.p. 75°), the mother liquors were acidified and extracted giving 2-benzyl-2-methylpropionic acid ¹⁹ * (0.85 g), m.p. 57°, not raised by recrystallisation from light petroleum, m/e 178 (M^+), 133 (PhCH₂CMe₂⁺), 149 ($M - Et$), and 91 (100%). Methyl 2-benzyl-2-methylpropionate, ν_{\max} (L) 1 738, 1 605, and 1 500 cm^{-1} , τ 8.44 (6H, s, 2 Me), 6.41 (3H, s, CO₂Me), and 2.7—3.0 (5H, ArH), was identical with an authentic specimen.

2,2-Dibenzylpentane-2,4-dione ³³ * (17) was recovered from the residues in the preparation of (13). It had m.p. 111—112°, ν_{\max} (N) 1 690, 1 600, and 1 592 cm^{-1} . The dione (1.4 g) gave 1,1-dibenzylacetone ³⁴ * (0.8 g), b.p. 137° at 0.6 mmHg, ν_{\max} (L) 1 708, 1 599, and 1 493 cm^{-1} , τ 8.41 (3H, s, COMe), 6.9—7.53 (5H, 2 CH₂Ar and CHAc), and 2.7—3.15 (10H, ArH).

2,2-Dimethyl-1-phenylbutane-2,4-dione ¹⁴ (18) (1 g), b.p. 77—78° at 0.1 mmHg, ν_{\max} (L) 1 738, 1 705, 1 665, 1 590, and 1 570 cm^{-1} , gave isobutyrophenone (0.16 g) and acids which afforded mixed esters containing (g.l.c.) methyl acetate, methyl pivalate, methyl benzoate, and methyl 2-methyl-2-phenylpropionate.

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2,2-Dimethyl-1,3-diphenylpropane-1,3-dione ¹⁵* (19) (2.8 g), m.p. 94°, $\nu_{\max}(\bar{N})$ 1 658 (ArCO), 1 595, and 1 576 cm^{-1} , gave solid acids (3 g) and a liquid, neutral product (0.2 g). Methyl 2-methyl-2-phenylpropionate was prepared as follows: methyl 2-phenylpropionate (7.5 g) was added to a stirred suspension of fresh sodamide (1.8 g) in liquid ammonia (80 ml). After 0.25 h, methyl iodide (7.5 g) was slowly added and stirring was continued for 3 h. Work-up gave the required ester* (3.83 g), b.p. 100° at 15 mmHg, n_D^{20} 1.5028, $\nu_{\max}(\text{L})$ 1 735, 1 605, and 1 500 cm^{-1} , τ 8.62 (6H, s, Me₂C), 6.41 (3H, s, CO₂Me), and 2.69 (5H, s, ArH).

2,5,5-Trimethylcyclohexane-1,3-dione (20) ¹⁶* (3.1 g) gave 3,3-dimethylglutaric acid (1 g), m.p. 94–95°, τ 8.86 (6H, s, Me₂C) and 7.5 (4H, s, 2 CH₂). Its methyl ester, b.p. 59–60° at 0.6 mmHg, τ 8.9 (6H, s, Me₂C), 7.57 (4H, s, 2 CH₂), and 6.34 (6H, s, 2 CO₂Me), was indistinguishable on g.l.c. from an authentic specimen.

2,2,5,5-Tetramethylcyclohexane-1,3-dione (21) ¹⁶* (3.4 g), gave an acid fraction (3.84 g), $\nu_{\max}(\text{L})$ 2 700 and 1 710 cm^{-1} , whose methyl ester* had b.p. 58.5–60° at 0.5 mmHg, n_D^{16} 1.4350, λ_{\max} 289 nm (ϵ 27.8), τ 8.93 (6H, d, J 7 Hz, Me₂CH), 8.91 (6H, s, Me₂C), 7.51 (2H, s, CH₂·CO₂Me), 7.43 (1H, q, J 7 Hz, CHMe₂), 7.37 (2H, s, CH₂·CO), and 6.36 (3H, s, CO₂Me), identical with a specimen of methyl 3,3,6-trimethyl-5-oxoheptanoate prepared by alkaline hydrolysis of the dione (21) (Found: C, 66.1; H, 9.8. C₁₁H₂₀O₃ requires C, 66.0; H, 10.1%).

3-Acetoxy-3-benzylpentane-2,4-dione (31).—The diketone (13) (7.6 g) was dissolved in acetic acid (40 ml) and warmed to 40 °C. Lead tetra-acetate (17.6 g) was added in portions, with stirring, so that the temperature did not exceed 50 °C. After 0.5 h, water was added, the product was extracted into ether, and the extract was washed with sodium hydrogen

carbonate solution (5%). Chromatography of the yellow oil (8 g) on silica gel, followed by recrystallisation from pentane gave 3-acetoxy-3-benzylpentane-2,4-dione* as needles, m.p. 42–43°, $\nu_{\max}(\bar{N})$ 1 743, 1 717, 1 603, 1 241, and 1 186 cm^{-1} , τ 7.92 (9H, s, 3 CH₃CO), 6.45 (2H, s, PhCH₂), and 2.89 (5H, m, ArH); addition of benzene caused the acetyl signals to appear at τ 8.10 (3H, s) and 7.99 (6H, s) (Found: C, 67.9; H, 6.5. C₁₄H₁₆O₄ requires C, 67.7; H, 6.5%).

3-Hydroxy-4-phenylbutan-2-one (28).—Sodium hydroxide (1M; 10 ml) was added over 15 min with stirring to the acetoxy-diketone (31) (2.48 g, 10⁻² mol) in methanol (125 ml) and water (25 ml). After a further 10 min, the mixture was diluted with water and extracted with ether yielding the hydroxy-ketone ³⁵* as a pale yellow oil (1.6 g) which was chromatographed on silica gel; $\nu_{\max}(\text{L})$ 3 400, 1 708, and 1 088 cm^{-1} , τ 7.95 (3H, s, MeCO), 7.11 (2H, dd, J 6.0 and 4.5 Hz, CH₂), 6.76br (1H, s, exch. D₂O, OH), 5.80 [1H, t, J 6.0 Hz, CH(OH)], and 2.82 (5H, s, ArH).

Oxidation of the Hydroxy-ketone (28) with Alkaline Hydrogen Peroxide.—The ketol (28) (1 g) was oxidised in the usual way for 5 min at 0 °C. Work-up afforded acidic (0.6 g) and neutral fractions (0.1 g). Esterification of the acids yielded methyl phenylacetate (75%) and methyl benzoate (25%). The neutral fraction contained benzaldehyde together with a little starting material.

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