The Synthesis and Reactions of Branched-chain Hydrocarbons. Part VI. The Free-radical Dimerisation of Some Esters and Ketones.*

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A modified procedure for the preparation and use of acetyl peroxide is described and applied to the dimerisation of ethyl *iso*butyrate, methyl αββ-trimethylbutyrate, 3-methylbutan-2-one, 2 : 5-dimethylpentan-3-one, and 2 : 2 : 4-trimethylpentan-3-one. The resulting diones or diesters have been reduced to the corresponding diols.

The discovery by Kharasch *et al.* (*J. Org. Chem.*, 1945, **10**, 386, 394, 401) that the decomposition of acetyl peroxide dissolved in aliphatic acids, esters, or ketones, containing a tertiary α-hydrogen atom (I or III), readily yields compounds containing two or more quaternary carbon atoms (II or IV) offers a route to compounds which are otherwise not readily accessible. A disadvantage of this procedure is the hazard involved in handling acetyl peroxide. We have found, however, that by adapting to our own needs the procedure of Rudolf and McEwen (U.S.P. 2,458,207) acetyl peroxide may be prepared in solution in the compound to be dimerised, thereby minimising the danger of explosion.

$$\underset{\text{(I)}}{\mathrm{R{\cdot}CO{\cdot}CHMe_2}} \qquad \underset{\text{(II)}}{\mathrm{(R{\cdot}CO{\cdot}CMe_2{-})_2}} \qquad \underset{\text{(III)}}{\mathrm{R{\cdot}CHMe{\cdot}CO_2R'}} \qquad \underset{\text{(IV)}}{\mathrm{(R{\cdot}\overset{|}{C}Me{\cdot}CO_2R')_2}}$$

By this method, the ketones (I), in which R = Me, $\mathrm{Pr^i}$, and $\mathrm{Bu^t}$, and the esters (III), in which (*a*) R = Me, R′ = Et, and (*b*) R = $\mathrm{Bu^t}$, R′ = Me, have been dimerised. The diones or diesters produced have been reduced with lithium aluminium hydride to the corresponding diols.

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EXPERIMENTAL

Ethyl Tetramethylsuccinate (IV; R = Me, R′ = Et).—To a well-stirred mixture of ethyl *iso*butyrate (93 g.), acetic anhydride (130·7 g.), and hydrogen peroxide (100-vol.; 77·5 g.), cooled to 0° in ice–salt was added 23% sodium carbonate solution at such a rate that the temperature did not exceed 55°. Addition was continued until the mixture had pH 6. When the mixture had cooled to 10°, the organic layer was separated, dried (Na_2SO_4; 1½ hr.), and filtered, and the filter was washed with ethyl *iso*butyrate. The resulting solution of acetyl peroxide was added during 2½ hr. to well-stirred boiling ethyl *iso*butyrate (97 g.). After further heating and stirring (2½ hr.) the mixture was cooled, washed with 5% sodium carbonate solution, and dried ($CaCl_2$). Distillation at atmosphere pressure gave methyl acetate (1·2 g.), b. p. 55—60°, and ethyl *iso*butyrate (116 g.), b. p. 109·5—111°. The residue was distilled under reduced pressure to yield ethyl tetramethylsuccinate (37·9 g.), b. p. 124—127°/20 mm., n_D^{20} 1·4349—1·4360. A redistilled portion had b. p. 125—127°/20 mm., n_D^{20} 1·4359 (Hudson and Hauser, *J. Amer. Chem. Soc.*, 1941, **63**, 3161, record b. p. 119—121°/15 mm.). Hydrolysis with concentrated sulphuric acid gave tetramethylsuccinic anhydride, m. p. 145—145·5°, which was converted into tetramethylsuccinic acid, m. p. 192° (Hudson and Hauser, *loc. cit.*, record m. p. 147° and 194—196° respectively).

2 : 2 : 3 : 3-*Tetramethylbutane*-1 : 4-*diol*.—A solution of ethyl tetramethylsuccinate (26 g.) in dry ether (50 c.c.) was added dropwise to a well-stirred suspension of lithium aluminium hydride (10 g.) in ether (250 c.c.). The mixture was heated under reflux for 1 hr., then cooled, and water (80 c.c.) slowly added, followed by sufficient 5N-sulphuric acid to remove the aluminium hydroxide. The ethereal layer was separated and the aqueous layer extracted with ether (4 × 30 c.c.). Evaporation of the dried (Na_2SO_4) combined extracts left a solid which on crystallisation from light petroleum (b. p. 60—80°) gave pure 2 : 2 : 3 : 3-*tetramethylbutan*-1 : 4-*diol* (14·2 g.), m. p. 224° (Found: C, 65·6; H, 12·1. $C_8H_{18}O_2$ requires C, 65·7; H, 12·4%). The *bis*-3 : 5-*dinitrobenzoate* was insoluble in most solvents; when washed with ether it had m. p. 186° (Found: C, 49·3; H, 4·0; N, 10·3. $C_{22}H_{22}O_{12}N_4$ requires C, 49·4; H, 4·1; N, 10·5%). The *ditoluene*-p-*sulphonate*, m. p. 109°, formed plates from benzene–light petroleum (Found: C, 58·1; H, 6·8; S, 14·5. $C_{22}H_{30}O_6S_2$ requires C, 58·1; H, 6·7; S, 14·1%). Oxidation of the diol with alkaline permanganate gave tetramethylsuccinic acid, m. p. and mixed m. p. 192°.

3 : 3 : 4 : 4-*Tetramethylhexane*-2 : 5-*dione* (II; R = Me).—A solution of acetyl peroxide in 3-methylbutan-2-one (250 g.), prepared as above from acetic anhydride (260 g.), hydrogen peroxide (100-vol.; 160 g.), and 23% sodium carbonate solution, was added dropwise (4 hr.) to boiling 3-methylbutan-2-one (190 g.). After further heating and stirring (2 hr.) the mixture was cooled, washed with 5% sodium carbonate solution, dried (Na_2SO_4) and distilled at atmospheric pressure to give methyl acetate (2·3 g.), b. p. 55—60°, and 3-methylbutan-2-one (355 g.). The residue was distilled under reduced pressure to yield after a small fore-run 3 : 3 : 4 : 4-tetramethylhexane-2 : 5-dione (47·5 g.), b. p. 108—115°/22 mm., n_D^{20} 1·4539—1·4541 (Kharasch, McBay, and Urry, *J. Amer. Chem. Soc.*, 1948, **70**, 1269, record b. p. 40°/0·5 mm., n_D^{20} 1·4522). The *disemicarbazone*, m. p. 222° (decomp.), was insoluble in most solvents; it was washed with ether (Found: C, 47·3; H, 8·1; N, 26·8. $C_{12}H_{24}O_2N_6,H_2O$ requires C, 47·7; H, 8·7; N, 27·8%). The *bis*-2 : 4-*dinitrophenylhydrazone*, m. p. 192°, formed orange-red crystals from alcohol (Found: C, 50·0; H, 5·1; N, 20·8. $C_{22}H_{26}O_8N_8$ requires C, 49·8; H, 4·9; N, 20·7%), and the tetrabromo-derivative, m. p. 116—117°, white needles from alcohol (Kharasch, McBay, and Urry, *loc. cit.*, record m. p. 117°). Oxidation of the diketone with 50% nitric acid gave tetramethylsuccinic acid, m. p. and mixed m. p. 190—192°.

3 : 3 : 4 : 4-*Tetramethylhexane*-2 : 5-*diol*.—The above diketone (56·9 g.) was reduced as for ethyl tetramethylsuccinate, using lithium aluminium hydride (7 g.), to yield the *diol*, m. p. 71—72° (from light petroleum) (Found: C, 68·9; H, 12·7. $C_{10}H_{22}O_2$ requires C, 68·9; H, 12·7%). Its *bis*-3 : 5-*dinitrobenzoate* had m. p. 171° (from benzene–light petroleum) (Found: C, 51·1; H, 4·8; N, 9·6. $C_{24}H_{26}O_{12}N_4$ requires C, 51·2; H, 4·7; N, 10·0%). The glycol could not be distilled as it decomposed to 2 : 3 : 3 : 4 : 4 : 4-*hexamethyltetrahydrofuran*, b. p. 99·5—100·5°/17 mm., n_D^{20} 1·4424 (Found: C, 76·9; H, 12·8. $C_{10}H_{20}O$ requires C, 76·9; H, 12·9%).

2 : 4 : 4 : 5 : 5 : 7-*Hexamethyloctane*-3 : 6-*dione* (II; R = Pr^i).—A solution of acetyl peroxide in 2 : 4-dimethylpentane-3-one (356 g.) prepared as above from acetic anhydride (390 g.), hydrogen peroxide (100-vol.; 240 g.), and 23% sodium carbonate solution was added dropwise (4 hr.) to boiling 2 : 4-dimethylpentan-3-one (320 g.). After further heating (2 hr.), working

up as in the preceding case gave methyl acetate (2·8 g.), b. p. 56—58°, 2 : 4-dimethylpentan-3-one (563 g.), and 2 : 4 : 4 : 5 : 5 : 7-hexamethyloctane-3 : 6-dione (40 g.), b. p. 108—114°/5·5 mm., n_D^{20} 1·4520—1·4526. Redistillation gave a pure sample, b. p. 108—111·5°/5·5 mm., n_D^{20} 1·4525 (Kharasch, McBay, and Urry, *loc. cit.*, record b. p. 75—77°/1·5 mm., n_D^{20} 1·4520). No carbonyl derivatives could be formed. Oxidation with 60% nitric acid gave tetramethylsuccinic acid, m. p. and mixed m. p. 190°.

2 : 4 : 4 : 5 : 5 : 7-*Hexamethyloctane*-3 : 6-*diol*.—The above diketone (12·2 g) was reduced with lithium aluminium hydride (2 g.) as for ethyl tetramethylsuccinate, to yield the *diol* (7·1 g.) as a viscous liquid, b. p. 119—121°/3·5 mm., which after four months had deposited cubic crystals, m. p. 84° (Found : C, 73·2; H, 13·0. $C_{14}H_{30}O_2$ requires C, 73·0; H, 13·1%). The diol failed to yield any derivatives.

2 : 2 : 4 : 4 : 5 : 5 : 7 : 7-*Octamethyloctane*-3 : 6-*dione* (II; R = Bu^t).—A solution of acetyl peroxide in 2 : 2 : 4-trimethylpentan-3-one (260 g.), prepared from acetic anhydride (260 g.), hydrogen peroxide (100-vol.; 160 g.), and 23% sodium carbonate solution, was added dropwise (6 hr.) to boiling 2 : 2 : 4-trimethylpentan-3-one (80 g.). After further boiling (1 hr.) the mixture was washed with 5% sodium carbonate solution and dried ($MgSO_4$). Distillation gave 2 : 2 : 4-trimethylpentan-3-one (265 g.), b. p. 71—73°/93 mm., followed, after a small intermediate fraction, by 2 : 2 : 4 : 4 : 5 : 5 : 7 : 7-*octamethyloctane*-3 : 6-*dione* (9·0 g.), a viscous liquid, b. p. 108—115°/1 mm., n_D^{20} 1·4572—1·4581. Redistillation gave a pure sample, b. p. 118—122°/1·5 mm., n_D^{20} 1·4581 (Found : C, 75·4; H, 11·8. $C_{16}H_{30}O_2$ requires C, 75·5; H, 11·9%). No carbonyl derivatives could be prepared. Oxidation with 60% nitric acid gave tetramethylsuccinic acid, m. p. and mixed m. p. 192°.

2 : 2 : 4 : 4 : 5 : 5 : 7 : 7-*Octamethyloctane*-3 : 6-*diol*.—The above diketone (11·3 g.) was reduced as above to the *diol* (8·1 g.), a viscous liquid, b. p. 123—128°/3·5 mm., n_D^{20} 1·4750—1·4766. Redistillation gave a pure sample, b. p. 126—128°/3·5 mm., n_D^{20} 1·4765 (Found : C, 74·3; H, 13·0. $C_{16}H_{34}O_2$ requires C, 74·4; H, 13·3%). No derivatives could be obtained.

Dimethyl 2 : 2 : 3 : 4 : 5 : 5-*Hexamethylhexane*-3 : 4-*dicarboxylate* (IV; R = Bu^t, R′ = Me).—A solution of acetyl peroxide in methyl αββ-trimethylbutyrate (300 g.) (Aston, Clarke, Burgess, and Greenberg, *J. Amer. Chem. Soc.*, 1942, **64**, 300) prepared as above from acetic anhydride (360 g.), hydrogen peroxide (100-vol.; 220 g.), and 23% sodium carbonate solution, was added dropwise (4 hr.) with stirring to methyl αββ-trimethylbutyrate (240 g.) at 100°. After further heating and stirring (2 hr.) the mixture was cooled, washed with 5% sodium hydroxide solution, and water, dried ($CaCl_2$), and distilled to remove unchanged methyl αββ-trimethylbutyrate (409·6 g.), b. p. 89—92°/12 mm. The residue was combined with that obtained from another preparation (406 g. ester used; 286·7 g. recovered) and distilled to yield *dimethyl* 2 : 2 : 3 : 4 : 5 : 5-*hexamethylhexane*-3 : 4-*dicarboxylate* (59·1 g.), b. p. 118—127°/5 mm., n_D^{20} 1·4597—1·4604. A redistilled sample had b. p. 124—126°/5 mm., n_D^{20} 1·4602 (Found : C, 67·4; H, 10·9. $C_{16}H_{30}O_4$ requires C, 67·1; H, 10·6%). The ester could not be hydrolysed on boiling with either sulphuric acid or a solution of potassium hydroxide in diethylene glycol.

2 : 3-*Di*-tert.-*butyl*-2 : 3-*dimethylbutane*-1 : 4-*diol* (3 : 4-*Bishydroxymethyl*-2 : 2 : 3 : 4 : 5 : 5-*hexamethylhexane*).—The above ester (20 g.) was reduced with lithium aluminium hydride (3·5 g.) as for ethyl tetramethylsuccinate to give the *diol* (10·6 g.), a viscous oil, b. p. 123—124°/3·5 mm., n_D^{20} 1·4739 (Found : C, 73·4; H, 12·7. $C_{14}H_{30}O_2$ requires C, 73·0; H, 13·1%), giving, with difficulty, a *bis*-3 : 5-*dinitrobenzoate*, m. p. 242°, needles from benzene (Found : C, 54·0; H, 5·8; N, 9·4. $C_{28}H_{34}O_{12}N_4$ requires C, 54·4; H, 5·5; N, 9·1%).

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