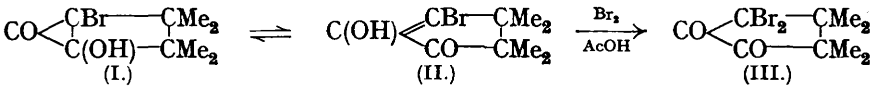
## 59. 1 : 2 : 3-*Triketotetramethyl*cyclo*pentane* : *A Blue Triketone.*

By Charles W. Shoppee.

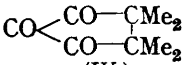
Investigations of cyclic derivatives of phorone (Francis and Willson, J., 1913, **103**, 2238; Ingold and Shoppee, J., 1928, 365, 1868; Shoppee, J., 1928, 1662, 2360) had shown that the orange-coloured compound obtained from the tautomeric bromohydroxy-compounds (I, II) by bromination in an ionising solvent has the structure (III). Its most characteristic reaction is the facile elimination of one bromine atom (cf. Ingold and Shoppee, *loc. cit.*, p. 380) with regeneration of the bromohydroxy-compound (I, II). By treating it with



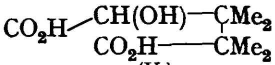
(I.) (II.) (III.)

an excess of hot alcoholic sodium acetate, however, Francis and Willson obtained a colourless bromine-free compound, m. p. 100°, which they regarded as a diacetate, and which afforded a substance, m. p. 68°, also obtained directly from (III), by the action of aqueous potassium hydroxide.

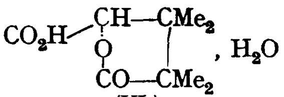
It is now shown that the supposed diacetate is the *hydrate* of 1 : 2 : 3-*triketotetramethyl*cyclo*pentane* (IV), and that the substance, m. p. 68°, is the *lactonic acid monohydrate* (VI) of $\gamma$-hydroxy-$\alpha\alpha\beta\beta$-tetramethylglutaric acid (V).



(IV.)

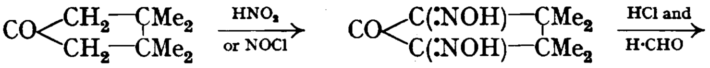


(V.)



(VI.)

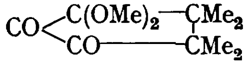
The hydrate of the triketone (IV) was obtained, but not isolated, by the author in 1928 from 3 : 3 : 4 : 4-tetramethyl*cyclo*pentanone (VII) by treatment with nitrous acid or nitrosyl chloride, and subsequent hydrolysis of the dioximino-compound (VIII) with hydrochloric acid and formaldehyde, and was characterised by formation of a trioxime.

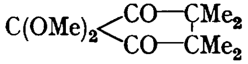


(VII.) (VIII.) (IV)

When the dibromo-diketone is refluxed with sodium or potassium acetate in methyl alcohol, the hydrate of the triketone (IV) or a *molecular compound* of the triketone hydrate and the anhydrous triketone (see below) is obtained. If, however, silver acetate is substituted for sodium or potassium acetate, the product is the crimson-red *dimethoxy*-1 : 2-*diketone* (IX). Further, if the dibromo-diketone is refluxed with absolute methyl-alcoholic potassium hydroxide, the colourless *dimethoxy*-1 : 3-*diketone* (X) is rapidly produced.

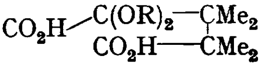
(IX.)



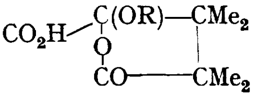


(X.)

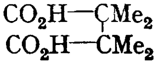
In accordance with the structure of a 1 : 2-diketone suggested by its magnificent crimson-red colour, the compound (IX) readily affords a 2 : 4-*dinitrophenylosazone* (but not a quinoxaline). It is oxidised by hydrogen peroxide in acetone at 0° to give γγ-dimethoxy-ααββ-tetramethylglutaric acid (XI; R = Me), which during isolation loses methyl alcohol to yield the *lactonic acid* (XII; R = Me) of γ-hydroxy-γ-methoxy-ααββ-tetramethylglutaric acid. Oxidation at 15° gives the same products together with tetramethylsuccinic acid (XIII).



(XI.)



(XII.)

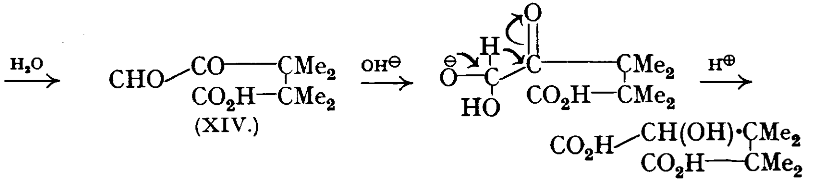


(XIII.)

The dimethoxy-diketone (IX) is stable to warm aqueous potassium hydroxide, but readily hydrolysed by hydrochloric acid in aqueous acetone to the triketone hydrate (IV), which partly recombines with the methyl alcohol produced to give the dimethoxy-1 : 3-diketone (X). The last-named substance yields a 2 : 4-*dinitrophenylhydrazone*, and gives the triketone hydrate by hydrolysis with hydrochloric–acetic acid.

The triketone hydrate, now isolated in a state of purity, is a colourless crystalline substance, m. p. 95°. It reduces Fehling's solution instantaneously in the cold, and rapidly produces silver from cold ammoniacal silver nitrate. When warmed with aqueous solutions of α-amino-acids, it affords deep blue colours analogous to those given by triketohydrindene (Ruhemann, J., 1910, **97**, 2030). It is readily soluble in, and decomposes, sodium carbonate solution (compare the similar acidity of the hydrates of triketopentane and triketohexane; Sachs and Wolff, *Ber.*, 1903, **36**, 3222). The triketone hydrate gives a *hydrate monosemicarbazone* instantaneously, an anhydrous 2 : 4-*dinitrophenylhydrazone*, and a 2 : 4-*dinitrophenylosazone* (which may be alternatively a 1 : 3-*bis*-2′ : 4′-*dinitrophenylhydrazone*); with *o*-phenylenediamine it affords a *quinoxaline*, and by complete oximation the trioxime referred to above. By oxidation with hydrogen peroxide in acetone at 0°, it gives principally tetramethylsuccinic acid, together with traces of the precursor of this, namely, γ-keto-ααββ-tetramethylglutaric acid, isolated as the lactonic acid (XII; R = H) which results by additive ring-closure of the foregoing ketonic acid (Rothstein and Shoppee, J., 1927, 531; Ingold and Shoppee, *loc. cit.*, p. 380). The triketone hydrate is converted almost quantitatively by cold 50% aqueous potassium hydroxide into the lactonic acid hydrate (VI) of γ-hydroxy-ααββ-tetramethylglutaric acid (V). This product undoubtedly arises by the following series of changes (cf. Shoppee, J., 1928, 1662):

(IV)



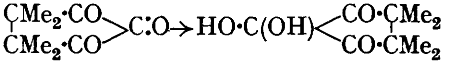
(XIV.) (V.) (VI)

The reaction is precisely analogous to the transformation of triketohydrindene into *o*-carboxymandelic acid (Ruhemann, J., 1910, **97**, 1448, 2026) and explains the isolation of (VI), as recorded by Francis and Willson (*loc. cit.*), by the action of potassium hydroxide on their supposed diacetate or on the dibromo-diketone (III).

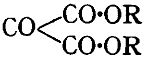
The most striking characteristic of the triketone hydrate (IV) is its behaviour on dehydration; this occurs partially and reversibly (a) when it is melted, the colourless melt rapidly becoming bright green, (b) when its colourless solutions in anhydrous non-hydroxylic media (di-*n*-propyl ether, ligroin, acetone, carbon tetrachloride, benzene, ethylene dibromide, benzonitrile, camphor) are heated, the depth of the blue-green colour developed increasing with temperature up to *ca.* 120—130°. Partial dehydration also occurs on vacuum distillation; complete dehydration, although difficult to attain, is brought about by repeated distillation with phosphoric oxide in a vacuum. The anhydrous triketone obtained by distillation is a solid of intense bright blue-green colour; it crystallises from carbon tetrachloride–ligroin in deep blue prisms, the highest recorded m. p. being 164°. The triketone appears to possess considerable affinity for water, and gradually becomes converted, even in a vacuum in a desiccator, into a colourless molecular compound of triketone and triketone hydrate (probably XV). The triketone naturally exhibits all the reactions of (IV) and (XV).

The blue colour of the triketone must be ascribed to the contiguous association of the three carbonyl groups. The closest analogue yet described, 1 : 2 : 3-triketo*cyclo*pentane, has been obtained only as the colourless hydrate (Reichstein and Oppenhauer, *Helv. Chim. Acta*, 1934, **17**, 390), but all the anhydrous αβγ-tricarbonyl compounds recorded in the literature combine with water to yield colourless hydrates, and, with a single exception, all vary in colour from orange to red. The sole exception is the ester of ketomalonic acid (XVI; R = Me or Et), which is a green liquid giving a colourless crystalline hydrate with great ease (Curtiss and Spencer, *J. Amer. Chem. Soc.*, 1909, **31**, 1053; Curtiss and Stracham, *ibid.*, 1911, **33**, 396).

(XV.)



$$\left.\begin{matrix}\mathrm{CMe_2\cdot CO}\\ |\\ \mathrm{CMe_2\cdot CO}\end{matrix}\right>\mathrm{C{:}O}\rightarrow\mathrm{HO\cdot C(OH)}\left<\begin{matrix}\mathrm{CO\cdot CMe_2}\\ |\\ \mathrm{CO\cdot CMe_2}\end{matrix}\right.$$



$$\mathrm{CO}\left<\begin{matrix}\mathrm{CO\cdot OR}\\ \mathrm{CO\cdot OR}\end{matrix}\right.$$

(XVI.)

The absorption spectra of the blue triketone, and of the red diketone (IX) for comparison, show that the blue colour is due to an absorption band with a maximum at 685 mμ (carbon tetrachloride) and the red colour of the diketone is similarly due to an unsymmetrical band at 510 mμ (alcohol). The ultra-violet absorption spectra of the two compounds are distinctly different (see table).

| | Blue Triketone (IV). | | | Red Diketone (IX). |
|---|---|---|---|---|
| Solvent. | Alcohol. | Chloroform (B.P.).* | Carbon tetrachloride. | Alcohol. |
| Colour of solution. | None | After ½ minute, none | Blue | Red |
| Absorption maxima in mμ.† | 346, 311, (298) | 345, 309, (295) | 685, 367, *ca.* 313, (301) | 510, (482), 322, 309, 294, 283 group of narrow bands |
| ε (at respective wave-lengths). | 61, 54, 36 | 46, 53, — | 8·4, 39, 47, — | 58, —, 36, 55, 58, 64 |
| Active substance present. | Triketone hydrate | Triketone hydrate | Triketone | Diketone |

* Contains alcohol, hence the conversion into the hydrate.

† Inflexions in brackets.

Molar extinction coefficient, ε, = density/(molar concentration × thickness in cm.).

The blue colour of the anhydrous triketone, at first sight somewhat unusual, is only an example of the general rule that conjugation of chromophoric groups tends to displace colour in the direction yellow ⟶ red ⟶ blue; in other words, that conjugation tends to displace the absorption bands towards longer wave-lengths. The fact that this triketone is blue whereas simple tricarbonyl compounds are orange or red may be due to a possible auxochromic action of the two $CMe_2$ group on the three carbonyl groups; alternatively, the cyclic structure may contribute to the observed effect. The green colour of the ketomalonic esters cannot be dependent upon such accessory factors.

The lactonic acid (VI) exists as the monohydrate, which is not dehydrated at 50° in a vacuum over phosphoric oxide and behaves as a monobasic acid on titration. It was first obtained by the author by reduction of the lactonic acid (XII, R = H) with sodium amalgam, during a repetition of Francis and Willson's original experiments; the product had the m. p. and properties described by Francis and Willson and was not analysed. Since, however, the analyses recorded by Francis and Willson indicate the anhydrous lactonic acid, the original specimen, prepared in 1928, a new specimen obtained by the same method, and the specimen furnished by the foregoing pinacolic change have been analysed: in all three cases identical figures are obtained which correspond to those required for the monohydrate.

## EXPERIMENTAL.

1 : 1-Dibromo-2 : 2 : 3 : 3-tetramethyl*cyclo*pentanedione (III) was obtained as described by Francis and Willson (*loc. cit.*; compare Ingold and Shoppee, *loc. cit.*, p. 408). Owing to the extreme ease with which the compound reverts to the parent bromo-hydroxy-ketone, crystallisation is difficult except on the smallest scale. By use of dry di-*n*-propyl ether, the product being in solution for the least time possible, the dibromo-diketone (80 g.) was obtained in large orange rhomboids, m. p. 182°.

1 : 2 : 3-*Triketotetramethyl*cyclo*pentane Hydrate*.—The dibromo-diketone and an equal weight of fused sodium acetate were refluxed with absolute methyl alcohol for 6 hours; the yellow solution was filtered from precipitated sodium bromide, and methyl alcohol largely removed by evaporation. The product, which contained acetic acid, was dissolved in ether, washed with water, dried (sodium sulphate), and recovered as a yellow oil which crystallised after 1—2 weeks. The solid, after draining on porcelain and crystallisation from ether–ligroin (b. p. 40—60°), furnished 1 : 2 : 3-*triketotetramethyl*cyclo*pentane hydrate* in colourless leaflets, m. p. 95° to a colourless liquid which rapidly turned bright green [Found: C, 58·1; H, 7·6; *M* (cryoscopic in glacial acetic acid), 183, 193. $C_9H_{14}O_4$ requires C, 58·1; H, 7·6%; *M*, 186]. Use of fused potassium acetate and/or ethyl alcohol gave the same result.

The triketone hydrate reacted instantaneously with alcoholic semicarbazide acetate to give the *hydrate monosemicarbazone*, which formed colourless plates, m. p. 153° (decomp.), from dilute methyl alcohol (Found: C, 49·3; H, 7·3; N, 17·6. $C_{10}H_{17}O_4N_3$ requires C, 49·4; H, 7·05; N, 17·3%). With 2 : 4-dinitrophenylhydrazine sulphate it furnished the anhydrous 2 : 4-*dinitrophenylhydrazone*, which crystallised from ethyl acetate or ethyl alcohol in clusters of orange prisms, m. p. 219—220° (Found: C, 51·5; H, 4·5; N, 16·2. $C_{15}H_{16}O_6N_4$ requires C, 51·7; H, 4·6; N, 16·6%); the action of excess of the reagent during a longer period afforded the 2 : 4-*dinitrophenylosazone* (?1 : 3-*bis*-2′ : 4′-*dinitrophenylhydrazone*), which separated from much ethyl alcohol as a crystalline brick-red powder, m. p. 268—270° (decomp.) (Found: N, 20·6. $C_{21}H_{20}O_9N_8$ requires N, 21·2%). A *quinoxaline*, readily obtained, crystallised from dilute alcohol in fine yellow prisms, m. p. 108° (Found: C, 74·5; H, 6·7; N, 11·7. $C_{15}H_{16}ON_2$ requires C, 75·0; H, 6·7; N, 11·7%). Complete oximation gave the trioxime, m. p. and mixed m. p. 169°.

The triketone hydrate is stable to potassium permanganate in cold acetone, but is oxidised on warming. It is slightly soluble in cold water, but dissolves in cold aqueous sodium carbonate, and is partly extracted from ethereal solution with this reagent. The observed depressions of m. p. in camphor lead to anomalous molecular weights (Found: *M*, 545, 554, 535, 554). The hydrate stains the skin violet-brown.

*The Molecular Compound* (XV).—In a repetition of the foregoing preparation of the triketone hydrate, the yellow oily product was kept in a vacuum over potassium hydroxide to remove acetic acid, since, owing to the acid nature of the triketone hydrate, washing with sodium carbonate solution cannot be employed. The oil gradually solidified, and the solid crystallised from ether–ligroin (b. p. 40—60°) or from ligroin (b. p. 100—120°) in colourless prisms, m. p. 119—120° to a green liquid. The substance was identified as a *molecular compound* of 1 : 2 : 3-triketotetramethyl*cyclo*pentane (1 mol.) and its hydrate (1 mol.) [Found: C, 61·0; H, 7·4; OMe, 0; *M* (cryoscopic in glacial acetic acid), 340, 343. $C_{18}H_{26}O_7$ requires C, 61·0; H, 7·4%; *M*, 354]. It gave blue colours with hot α-amino-acid solutions, stained the skin, and furnished the hydrate semicarbazone, m. p. 153° (decomp.) (Found: C, 49·6; H, 7·1; N, 17·2%), the osazone, m. p. 268—270°, and the quinoxaline, m. p. 108° (Found: N, 11·6%), described above; in each case, a mixed m. p. exhibited no depression. The compound gave blue-green solutions in hot non-hydroxylic solvents, and furnished anomalous molecular weights by the Rast method (Found : *M*, 497, 475).

*Oxidation of the Triketone Hydrate.*—Use of hydrogen peroxide in acetone at 0° in the presence of solid sodium bicarbonate gave principally tetramethylsuccinic acid, m. p. 193° (gas evolution), mixed m. p. 193°, after crystallisation from ethyl acetate; the ethyl acetate mother-liquors contained a small quantity of a more soluble acid, m. p. 135—138°, which was not identified with certainty, but was probably the lactone of γγ-dihydroxy-ααββ-tetramethylglutaric acid, m. p. 140°.

*Transformation of the Triketone Hydrate into the Lactonic Acid Hydrate* (VI).—When the triketone hydrate (0·5 g.) was treated with 50% aqueous potassium hydroxide (2 c.c.), solution occurred with evolution of heat and the transient appearance of a white crystalline solid; no sequence of colour changes such as those described by Ruhemann (J., 1910, **97**, 1448) for triketohydrindene hydrate was observed. After ½ hour, the solution was acidified with ice-cold 2*N*-sulphuric acid and extracted with ether, and the extract dried (sodium sulphate) and evaporated. A solid acid (0·49 g.) was obtained, which after crystallisation from ethyl acetate–ligroin (b. p. 60—80°) had m. p. 68° and was identified as the *hydrate* of the lactonic acid of γ-hydroxy-ααββ-tetramethylglutaric acid [Found : C, 53·0; H, 8·0; *M*(Rast), 269, 281; *M* (by titration), 205. $C_9H_{14}O_4,H_2O$ requires C, 52·9; H, 7·9%; *M*, 204]. No depression of the m. p. was observed by admixture with a specimen, m. p. 68°, freshly prepared by Francis and Willson's method (*loc. cit.*) (Found : C, 53·1; H, 7·85%), or with the original specimen, m. p. 68°, prepared by Ingold and Shoppee in 1928 (*loc. cit.*) (Found : C, 52·9; H, 7·9%).

1 : 2 : 3-*Triketotetramethyl*cyclo*pentane* (IV).—When the pure triketone hydrate was heated in a vacuum (10 mm.; bath at *ca.* 140°), a blue crystalline solid passed over, which consisted largely of the anhydrous *triketone* (Found : C, 62·3; H, 7·4. $C_9H_{12}O_3$ requires C, 64·3; H, 7·2%). These microanalytical figures indicate the possible presence of 29% of triketone hydrate in the product; the pure triketone hydrate was therefore intimately mixed with phosphoric oxide, and maintained at 140°/760 mm. for ½ hour; then the pressure was reduced to 10 mm., and the blue triketone passed over and was immediately sealed up for microanalysis (Found : C, 62·4; H, 7·3%; in a repetition : C, 62·5; H, 7·25%, corresponding to 73% and 74% dehydration respectively). A specimen, prepared by a two-stage repetition of the distillation with phosphoric oxide in a one-piece all-glass apparatus and crystallised from dry carbon tetrachloride, was obtained in bright blue prisms, m. p. 164° (Found : C, 62·8; H, 7·3%, corresponding to 80% dehydration). (An alternative possibility is that the low carbon values are due to incomplete combustion; cf. Ingold and Shoppee, *loc. cit.*, p. 385.)

1 : 1-*Dimethoxy*-2 : 2 : 3 : 3-*tetramethyl*cyclo*pentanedione* (IX).—The dibromo-diketone (10 g.) silver acetate (20 g.), and absolute methyl alcohol were refluxed for 1 hour. Silver bromide and the excess of silver acetate were removed by filtration, and methyl alcohol by evaporation in a vacuum. The product (*A*) was dissolved in ether, washed with 2*N*-sodium carbonate and with water, dried (sodium sulphate), and recovered; after solidification, two crystallisations from ligroin (b. p. 40—60°) gave 1 : 1-*dimethoxy*-2 : 2 : 3 : 3-*tetramethyl*cyclo*pentanedione* (4 g.) in large rose-red cubes, m. p. 68° [Found : C, 61·6; H, 8·5; OMe, 28·6; *M* (Rast), 236, 239. $C_{11}H_{18}O_4$ requires C, 61·7; H, 8·45; OMe, 29·0%; *M*, 214]. The ketone is slightly volatile in methyl alcohol, but not in ether, and can be distilled in small quantities in a vacuum. With *o*-phenylenediamine in methyl alcohol, the red colour disappeared, but a crystalline quinoxaline could not be obtained. The 2 : 4-*dinitrophenylosazone* formed orange needles, m. p. 266° (decomp.), from much ethyl acetate or from xylene (Found : C, 48·1; H, 4·1; N, 20·5. $C_{23}H_{26}O_{10}N_8$ requires C, 48·1; H, 4·5; N, 19·5%). Small quantities of the triketone are also formed in the reaction, since the product (*A*) stained the skin violet.

On one occasion the reaction after prolongation for 18 hours yielded, not the dimethoxy-diketone, but exclusively the triketone hydrate. The product, a yellow oil, gave the triketone 2 : 4-dinitrophenylhydrazone (m. p. 218—220°; mixed m. p. 219—220°. Found : C, 51·6; H, 4·8; OMe, 0%), and crystallised on keeping; recrystallised from ether–ligroin (b. p. 40—60°), it separated in colourless leaflets of the triketone hydrate, m. p. 95°, mixed m. p. 95° (Found : C, 58·1; H, 7·7; OMe, 0%). This occurrence is believed to be connected with the specimen of silver acetate used, which may have contained sufficient occluded acid to cause hydrolysis of the dimethoxy-diketone, since it was not encountered in many subsequent repetitions in which various specimens of silver acetate and reflux-times up to 72 hours were employed.

*Oxidation with hydrogen peroxide.* To the dimethoxy-diketone (1 g.) in acetone at 0°, perhydrol (1 c.c.) was added drop by drop during stirring in the presence of sodium bicarbonate

(1 g.) and a trace of 2*N*-sodium hydroxide. The red colour of the solution slowly faded, and the colourless oil of peppermint-like odour remaining after removal of acetone by evaporation became crystalline over-night. After draining on porcelain, the product was twice crystallised from ligroin (b. p. 40—60°), the *lactone* of *γ-hydroxy-γ-methoxy-*ααββ-*tetramethylglutaric acid* being obtained as a colourless crystalline powder, m. p. 58°, soluble in sodium bicarbonate solution [Found : C, 56·0; H, 7·45; OMe, 14·9; *M* (Rast), 288, 295. $C_{10}H_{16}O_5$ requires C, 55·6; H, 7·45; OMe, 14·4%; *M*, 216]. Repetition at 15° gave a product, which was worked up into neutral and acidic fractions; the latter gave traces of the above lactonic acid, but consisted mainly of tetramethylsuccinic acid, m. p. 193° (gas evolution) after crystallisation from ethyl acetate–ligroin (Found : C, 55·2; H, 8·1. Calc. for $C_8H_{14}O_4$ : C, 55·2; H, 8·1%). The neutral fraction was too small for examination (Found : C, 60·1; H, 9·3; OMe, 27·2%).

*Hydrolysis.* The dimethoxy-diketone (10 g.), dissolved in acetone (50 c.c.), was heated with concentrated hydrochloric acid (5 c.c.) under reflux. The red colour of the solution gave place to yellow in a few minutes and the liquid was evaporated (4-bulb column). The residual oil was taken up in ether, washed with 2*N*-sodium carbonate, dried (sodium sulphate), and recovered as a yellow oil, which by rapid distillation gave a bright blue distillate, b. p. *ca.* 120°/10 mm. On cooling, blue crystals of the anhydrous triketone separated, which after filtration and washing with ligroin had m. p. 150—153° (Found : C, 62·8, 62·4; H, 7·1, 7·4%). When the filtrate was evaporated and cooled below 0°, large, almost colourless rhombs (2 g.) were deposited : these were identified as 2 : 2-dimethoxytetramethyl*cyclo*pentane-1 : 3-dione (see below), m. p. 62°, mixed m. p. 62°, after two crystallisations from ligroin (b. p. 40—60°). The sodium carbonate washings were acidified with hydrochloric acid, and repeatedly extracted with ether; the extract, after drying (sodium sulphate) and evaporation, gave practically pure triketone hydrate (1 g.), m. p. (crude) 92° (Found : C, 58·2; H, 7·5%).

1 : 1-Diethoxy-2 : 2 : 3 : 3-tetramethyl*cyclo*pentanedione, obtained by refluxing the dibromo-diketone with silver acetate in absolute alcohol, formed a rose-red oil containing more than 30% of ethoxyl (Calc., 37·2%).

2 : 2-*Dimethoxytetramethyl*cyclo*pentane*-1 : 3-*dione* (X).—The dibromo-diketone (3 g.) reacted violently with a warm solution of potassium hydroxide (1·25 g.) in absolute methyl alcohol (25 c.c.) with separation of potassium bromide and formation of a rose-pink solution; after 1 hour's heating on the steam-bath, methyl alcohol was removed by evaporation and the product was dissolved in ether, washed with water, dried (sodium sulphate), and recovered. The resulting oil, which from its red colour contained some of the 1 : 1-dimethoxy-isomeride (IX), and also contained some of the triketone hydrate, since it stained the skin, crystallised readily when cooled below 0°. Draining and washing with a little cold ligroin on porous porcelain removed the red colour, and after two crystallisations from ligroin (b. p. 40—60°) 2 : 2-*dimethoxytetramethyl*cyclo*pentane*-1 : 3-*dione* was obtained in very long, colourless prisms, m. p. 62° [Found : C, 61·6; H, 8·5; OMe, 28·8; *M* (Rast), 200, 201. $C_{11}H_{18}O_4$ requires C, 61·7; H, 8·45; OMe, 29·0%; *M*, 214]. The 2 : 4-*dinitrophenylhydrazone* separated from ethyl acetate–alcohol in brick-red leaflets, m. p. 184° (Found : C, 52·0; H, 5·4; N, 14·5. $C_{17}H_{22}O_7N_4$ requires C, 51·8; H, 5·6; N, 14·2%). Hydrolysis with 50% acetic acid containing a little hydrochloric acid in an open vessel to facilitate the removal of methyl alcohol and/or methyl acetate furnished the triketone hydrate.

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