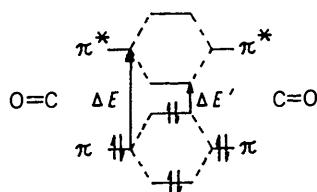


2,2,6,6-Tetramethylheptane-3,4,5-trione

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The preparation of 2,2,6,6-tetramethylheptane-3,4,5-trione, orange needles, m.p. 16°, is described together with some of its properties, and those of its derivatives.

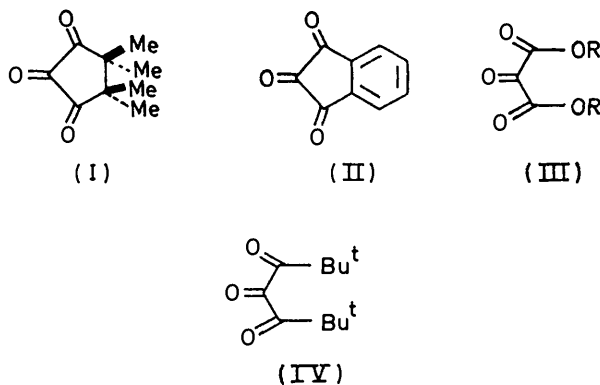
TETRAMETHYLCYCLOPENTANE-1,2,3-TRIONE¹ (I) was prepared as a bright blue crystalline solid, m.p. 164°, λ_{max} 685, 367, and 313 nm, giving blue solutions in non-polar nonhydroxylic solvents. An attempt, made jointly with Professor D. C. Craig, to examine the u.v. spectrum in the vapour phase failed because of the high m.p. and the low vapour pressure of the compound. The blue colour of the triketone (I) may be connected with the enforced planarity of the three carbonyl chromophores forming the cross-conjugated system; it seems possible that the resulting loss of the three-fold degenerate $\pi-\pi^*$ and $n-\pi^*$ transitions ($\Delta E_{\pi-\pi^*} > \Delta E_{n-\pi^*}$), arising from carbonyl group interactions, could produce the absorption maximum in the red at 685 nm responsible for the blue colour. Splitting of the original energy levels of the π orbitals will lead to $\Delta E'_{\pi-\pi^*} < \Delta E_{\pi-\pi^*}$ for the $\pi-\pi^*$ transitions (Figure), whilst a similar situation will arise for the $n-\pi^*$ transitions in the plane normal to the plane of the ring system with $\Delta E'_{n-\pi^*} < \Delta E_{n-\pi^*}$; the overall result will be absorption of radiation at longer wavelength.



FIGURE

The hydrate, m.p. 95°, of the triketone (I) undergoes dehydration¹ (a) when it is melted, the colourless melt becoming bright green, and (b) when its solutions in anhydrous nonhydroxylic media are heated, the initially colourless solutions becoming blue-green.

One of us (C. W. S.) had observed that the above behaviour is paralleled by that of indane-1,2,3-trione (II); the colourless hydrate of this, m.p. 139°, affords the anhydrous compound as red crystals melting at 255° to give a green liquid recrystallising in red needles, and gives initially colourless solutions in benzene, nitrobenzene, and acetic anhydride, which become blue-green when heated. Subsequently, it was found that similar observations had been made independently by Schönberg and Moubacher.² An X-ray crystallographic study by Bolton³ showed the anhydrous tetragonal form of the triketone (II) to be planar. If the geometry of the red tetragonal solid phase is retained in the green liquid phase, the colour of the latter may arise from planarity of the molecule and the resulting carbonyl electron interactions.



The anhydrous mesoxalic esters (III; R = Me or Et), are green liquids,⁴ greenish yellow oils,⁵ and golden

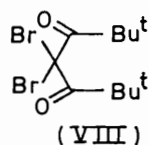
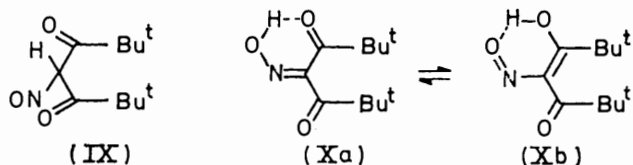
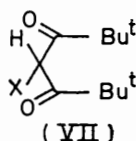
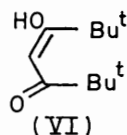
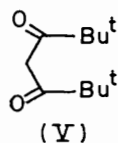
¹ C. W. Shoppee, *J. Chem. Soc.*, 1936, 269.

² A. Schönberg and R. Moubacher, *J. Chem. Soc.*, 1943, 71.

³ W. Bolton, *Acta Cryst.*, 1965, **18**, 5.

yellow liquids;⁶ the homologue $\text{MeO}_2\text{C}[\text{CO}]_2\text{CO}_2\text{Me}$ is an orange-yellow liquid.⁷ These acyclic compounds, which may involve dipolar mesomeric forms, do not provide suitable comparisons with the triketone (I). We have therefore examined the non-enolisable 2,2,6,6-tetramethylheptane-3,4,5-trione (IV) as a simple non-planar acyclic analogue of (I).

Divaloylmethane^{8,9} (V) appears to exist largely, if not exclusively, as the enolic form (VI). Monobromin-

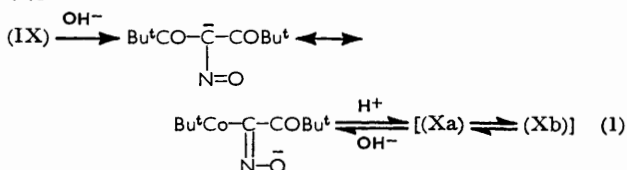


ation in carbon tetrachloride readily yielded 90% of the monobromo-diketone (VII; X = Br), m.p. 45°, ν_{max} . 1725 and 1695 cm^{-1} , which may indicate the existence of two conformers with $\overset{+}{\text{C}}-\overset{-}{\text{O}}$ and $\overset{\delta+}{\text{C}}-\overset{\delta-}{\text{Br}}$ dipoles approximately parallel and antiparallel. Chlorination gave the monochloro-diketone (VII; X = Cl), m.p. ca. 20°, whose i.r. spectra were closely similar to those of bromo-analogue. Iodination with iodine monochloride gave the analogous monoiodo-diketone. All attempts to prepare the dibromo-diketone (VIII), a possible precursor of the triketone (IV), by dibromination of divaloylmethane (V) or further bromination of the monobromo-diketone (VII; X = Br) in chloroform, acetic acid at 110°, or in trifluoroacetic acid failed. However, bromination of the monobromo-diketone (VII; X = Br) in acetic acid at 100° in the presence of excess of anhydrous sodium acetate gave an orange liquid, containing two components by t.l.c., consisting of the unchanged monobromo-diketone (VII; X = Br) (R_F 0.33) and the triketone (IV) (orange spot; R_F 0.66); the unchanged colourless starting material, m.p. 45° (VII; X = Br), separated from a solution of the product in hexane at -30°, whilst column chromatography on silica of the residual orange solution gave the triketone (IV) as an orange oil, which crystallised, m.p. 16°, in long orange needles on keeping at -30° but in only 25% yield. It seems probable that the triketone (IV) is formed

by the reaction sequence $\text{>CHBr} \longrightarrow \text{>CHOAc} \longrightarrow \text{>CBrOAc} \longrightarrow \text{>CO}$.^{10,11}

Divaloylmethane (V) by treatment as such, in ether, or in acetic acid with nitrosyl chloride at 20° gave the colourless dimer of the nitroso-compound (IX) (50%), m.p. 125–126° (decomp.), the isonitroso-compound* [(Xa) \rightleftharpoons (Xb)], m.p. 100°, the orange triketone (IV) (16%), and the monochloro-diketone (VII; X = Cl) (4%).

The dimer of the nitroso-compound (IX) exhibits i.r. and n.m.r. spectra similar to those shown by the monobromo-diketone (VII; X = Br); it is irreversibly converted by cold aqueous potassium hydroxide into a yellow anion, which on acidification affords the colourless isonitroso-compound [(Xa) \rightleftharpoons (Xb)] [equation (1)].



The isonitroso-compound gives an n.m.r. spectrum containing a singlet at τ 0.93 for one proton exchangeable with deuterium. This observation suggests that the hydroxyimino-structure (Xa) is interconvertible with the unsaturated nitroso-structure (Xb); the low field at which this signal appears is consistent with the exchange reaction [(Xa) \rightleftharpoons (Xb)], and with the signals given by exchanging protons (at τ ca. 0) in enolic forms of β -diketones and α -hydroxymethylene-ketones.^{12,13} The volatility and the i.r. spectrum of the isonitroso-compound also suggest hydrogen bonding.

The formation of a small amount of the orange triketone (IV) is due to oxidation of the isonitroso-compound [as (Xa)] by nitrosyl chloride [equation (2)]; a $(\text{Bu}^t\text{CO})_2\text{C}=\text{NOH} + \text{NOCl} \longrightarrow (\text{Bu}^t\text{CO})_2\text{CO} + \text{N}_2\text{O} + \text{HCl}$ (2) similar reaction, in which nitrous acid was the oxidising agent, has been observed by Claisen and Manasse¹⁴ for mono-oximes of α -diketones [equation (3)].



⁸ J. T. Adams and C. R. Hauser, *J. Amer. Chem. Soc.*, 1944, **66**, 1220.

⁹ K. R. Kopecky, D. Nonhebel, G. Morris, and G. S. Hammond, *J. Org. Chem.*, 1962, **27**, 1036.

¹⁰ R. de Neufville and H. von Pechmann, *Ber.*, 1890, **23**, 3375.

¹¹ E. P. Kohler and J. L. E. Erickson, *J. Amer. Chem. Soc.*, 1931, **53**, 2307.

¹² J. L. Burdett and M. T. Rogers, *J. Amer. Chem. Soc.*, 1964, **86**, 2105.

¹³ E. W. Garbisch, *J. Amer. Chem. Soc.*, 1963, **85**, 1696.

¹⁴ L. Claisen and C. Manasse, *Ber.*, 1889, **22**, 526, 530.

* In this paper the term isonitroso refers to a hydroxyimino-ketone-nitroso-enol tautomeric mixture.

⁴ R. S. Curtiss and F. G. C. Spencer, *J. Amer. Chem. Soc.*, 1909, **31**, 1053; R. S. Curtiss and E. K. Stracham, *ibid.*, 1911, **33**, 396.

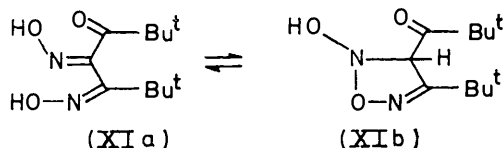
⁵ R. Müller, *Ber.*, 1933, **66**, 1668.

⁶ A. W. Dox, *Org. Synth.*, 1925, **4**, 27; B. B. Corson and R. K. Hazen, *ibid.*, 1930, **10**, 54.

⁷ H. H. Fox, *J. Org. Chem.*, 1947, **12**, 535.

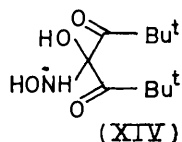
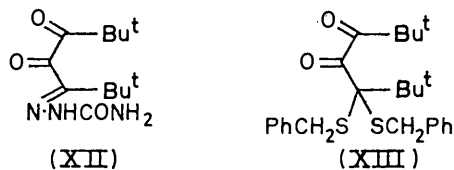
The production of the monochloro-diketone (VII; X = Cl) is unexpected, since the usual mode of polarisation of nitrosyl chloride is $\overset{\delta+}{\text{N}}\text{O}-\overset{\delta-}{\text{Cl}}$; on one occasion when the diketone (V) was treated with nitrosyl chloride in ethereal solution in the presence of calcium carbonate at 20° for 5 days, the principal product appeared to be the monochloro-diketone (VII; X = Cl). Farmer *et al.*¹⁵ record a case in which use of nitrosyl chloride led to formation of both an isonitroso-compound and a chlorinated product.

The isonitroso-compound reacts with hydroxylamine to give the bisoxime [(XIa) \rightleftharpoons (XIb)]; this appears to contain a small proportion of a geometrical isomer because the n.m.r. spectrum in deuteriochloroform shows two singlet signals at τ 8.89 and 8.67 each for *ca.* 9 protons, accompanied by two symmetrically placed minor singlets at τ 8.96 and 8.61 (which are not spinning side-bands), all arising from two t-butyl groups; the spectrum also shows two singlets at τ 1.38 and 6.25, each for one proton and each exchangeable with deuterium, corresponding respectively to the proton of a free hydroxyimino-group (XIa) and to the methine proton of a ring-chain tautomeric form (XIb).



The mass spectrum of the bisoxime (XIa) fails to show the parent peak at m/e 228 owing to a ready McLafferty rearrangement; peaks at m/e 229, 210, 172, 155, 127, 126, 116, 111, 99, 98, 85, 84, and 57 (base peak) are observed.

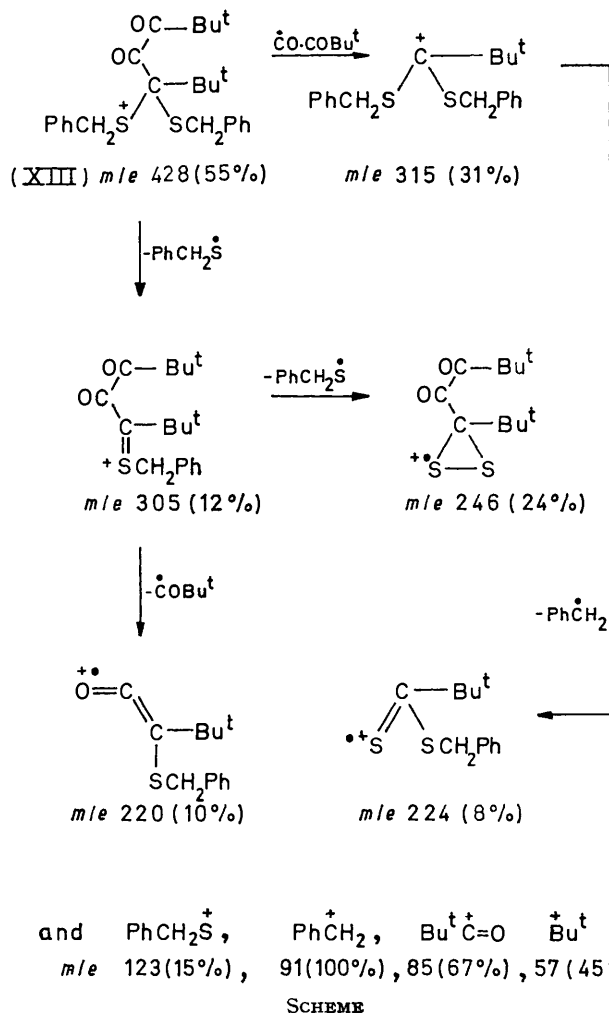
The structure of the orange triketone (IV) follows from the two methods of formation given above, and is supported by the preparation of a yellow semicarbazone, a yellow dibenzyl thioacetal, and a colourless adduct with hydroxylamine.



The yellow semicarbazone gives an n.m.r. spectrum showing two singlets, each for 9 protons, at τ 9.01 and

8.72, for the t-butyl groups. We therefore assign the unsymmetrical α -diketonc formula (XII), which is supported by the mass spectrum. This shows a peak at m/e 256 ($M + 1$)⁺ but no parent peak at m/e 255 owing to the occurrence of a McLafferty rearrangement; peaks at m/e 199, 156 (base peak), 141, 69, 57 (co-base peak, Bu^+), and 41 are observed.

The yellow dibenzyl thioacetal gives an n.m.r. spectrum with a singlet at τ 8.76, a four line signal at τ 6.48, 6.37, 6.13, and 6.02 with τ_{HA} at 6.42 and τ_{HB} 6.09 (J_{AB} 11 Hz), and a multiplet centred at τ 2.98; electronic integration of a 300 MHz spectrum proves the ratio of the signals to be 9 : 2 : 5, so that they correspond to 18 t-butyl protons, 4 non-equivalent methylene protons, and 10 aromatic protons respectively. Unless



an accidental equivalence is being observed, the singlet for the t-butyl protons indicates a symmetrical formula with the two benzylthio-groups attached to the central carbon atom. Such a formula is, however, incompatible with the field ionisation mass spectrum, which shows the parent peak at m/e 428, and a fragmentation pattern containing peaks at m/e 315 and 224 (Scheme)

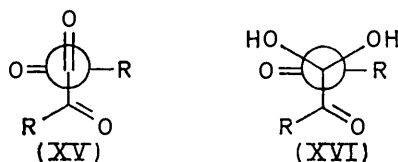
¹⁵ E. H. Farmer, C. K. Ingold, and J. F. Thorpe, *J. Chem. Soc.*, 1922, 121, 128.

that can only be derived from the unsymmetrical α -diketonic structure (XIII).

The electron impact mass spectrum fails to show the parent peak at m/e 428, and, instead of the peak at m/e 315, a peak at 316 arising by hydrogen transfer.

The orange triketone (IV) reacted with hydroxylamine acetate to give a colourless solid, which sublimed without melting, and is regarded as the addition product (XIV). The solution in hexadeuteriodimethyl sulphoxide was colourless and showed a singlet for 18 protons at τ 9.02, but in hexadeuterioacetone the solution quickly became orange in the probe at 35°, and the n.m.r. spectrum changed rapidly. The initial spectrum showed singlets at τ 9.0 and 8.8 in the ratio of 3 : 1, but the ratio 15 min later was 1 : 3; the orange triketone exhibits a singlet signal at τ 8.8, and it appears that hexadeuterioacetone decomposes the adduct to form [$^2\text{H}_6$]acetoxime and to regenerate the triketone (IV).

Although other anhydrous triketones, e.g. tetramethylcyclopentane-1,2,3-trione (I),¹ indane-1,2,3-trione (II),² diphenyl triketone,^{10,11,16,17} readily form colourless hydrates, the triketone (IV) fails to do so. The most probable conformation of the triketone (IV) is that shown as a Newman projection (XV; R = Bu^t) with the dihedral angle between two carbonyl dipoles equal to 90° and dipole interaction equal to zero. Dipolar interaction between the central carbonyl group and the third carbonyl group will not be zero, and Professor A. Hassner has suggested that this is the driving force for hydration of the central carbonyl group, e.g. in diphenyl triketone (XV \rightarrow XVI; R =



Ph), and is insufficient for hydration of (IV) to give (XVI; R = Bu^t) because the t-butyl group is much larger than the phenyl group. A similar effect may be responsible for the instability of the adduct (XIV).

EXPERIMENTAL

For general experimental directions see *J. Chem. Soc.*, 1959, 345. M.p.s were determined with a Köflier hot-stage apparatus and are corrected. U.v. absorption spectra in cyclohexane were measured with a Beckman Acta III spectrometer, whilst i.r. absorption spectra (in carbon tetrachloride solution unless otherwise specified) were measured with Beckman IR 18 and IR 33 spectrometers. N.m.r. spectra were obtained with Varian A60 and XL100 instruments (in deuteriochloroform unless otherwise specified) with tetramethylsilane as internal reference. Mass spectra were measured with an A.E.I. MS9 double-focusing spectrometer coupled to a DS20 data system, at the University of Sydney, or with a Varian-MAT 311 double-focusing spectrometer coupled to an SS102 data system. Column chromatography was performed using aluminum oxide (Woelm; neutral) or

silica gel G (Merck); t.l.c. was carried out using silica gel F (Merck), the plates being developed with iodine after examination in u.v. light.

2,2,6,6-Tetramethylheptane-3,5-dione [(V) \rightleftharpoons (VI)].—This diketone, b.p. 102° at 31 mmHg (P.C.R. Inc.), slowly crystallised; the crystals, m.p. 28–30°, were readily soluble in organic solvents and could not be recrystallised. The i.r. and n.m.r. spectra of the liquid and the solid phase were identical, ν_{max} 3590 (OH), 1600 (C=C-CO), 1390, and 1360 (Bu^t) cm⁻¹, τ 8.76 (18H, s), 4.23 (1H, s), and 3.98 (s, OH). Adams and Hauser⁸ record b.p. 96–97° at 20 mmHg whilst Hammond *et al.*⁹ report b.p. 100–102° at 36 mmHg.

4-Bromo-2,2,6,6-tetramethylheptane-3,5-dione (VII; X = Br).—The diketone [(V) \rightleftharpoons (VI)] (9.2 g), dissolved in carbon tetrachloride (50 ml), was treated dropwise with a solution of bromine (6.3 g) in carbon tetrachloride during 5 min at 20°. The mixture was stirred for 15 min and hydrogen bromide and the solvent were removed in a vacuum. The product, dissolved in ether (150 ml), was washed with water, sodium hydrogen carbonate solution, sodium thiosulphate solution, and water again, dried, and evaporated. The residual solid (12.0 g) by recrystallisation from hexane at -60° gave **4-bromo-2,2,6,6-tetramethylheptane-3,5-dione** (9.2 g) as needles, m.p. 44–45°, which were chromatographically homogeneous [R_F 0.7 and 0.33 in ether-hexane (1 : 9) and (1 : 24) respectively, 0.6 in benzene, 0.05 in hexane], ν_{max} 1725, 1695 (CO), 1390, and 1360 (Bu^t) cm⁻¹, τ 8.76 (18H, s) and 4.40 (1H, s, not exchangeable with deuterium) [Found (after drying at 20° and 0.01 mmHg): C, 50.1; H, 7.3; Br, 29.7. C₁₁H₁₉BrO₂ requires C, 50.0; H, 7.2; Br, 30.4%]. The chloro-diketone (VII; X = Cl), prepared similarly in 91% yield, was a liquid, which crystallised when cooled; recrystallisation from hexane at -60° afforded **4-chloro-2,2,6,6-tetramethylheptane-3,5-dione** (2.9 g), m.p. 19–20°, which was chromatographically pure [R_F 0.15, 0.45, and 0.7 in ether-hexane (1 : 24), (1 : 19), and (1 : 9) respectively, 0.6 in benzene], ν_{max} 1730, 1700 (CO), 1390, and 1360 (Bu^t) cm⁻¹, τ 8.71 (18H, s) and 4.37 (1H, s) [Found: *M* (mass spectrometry), 218, 220. C₁₁H₁₉³⁵ClO₂ requires *M*, 218]. The iodo-diketone (VII; X = I) prepared similarly using iodine monochloride in 66% yield was a viscous liquid, which crystallised when chilled and triturated with hexane and could be recrystallised from pentane at -60° to furnish **4-iodo-2,2,6,6-tetramethylheptane-3,5-dione** (1.6 g), m.p. 13–15°, [R_F 0.7 in ether-hexane (1 : 9)] [Found: *M* (mass spectrometry), 310. C₁₁H₁₉I O₂ requires *M*, 310]. When stored at -30° the iodo-diketone slowly decomposed liberating iodine.

2,2,6,6-Tetramethylheptane-3,4,5-trione (IV).—(a) The monobromo-diketone (VII; X = Br) (1.3 g) was dissolved in acetic acid (20 ml) containing anhydrous sodium acetate (1.65 g) at ca. 100°, and a solution of bromine (1 g) in acetic acid (10 ml) added dropwise during 30 min. The mixture was refluxed overnight, cooled, and poured into a saturated solution of sodium carbonate (150 ml). The resultant orange oil was extracted with ether, and the extract was washed with sodium thiosulphate solution and with water, dried, and evaporated. The product was taken up in hexane (ca. 4 ml) and the solution chilled to -30° when crystals of the unchanged monobromo-diketone (0.8 g), m.p. 44–45°, separated and were collected. T.l.c. of the

¹⁶ H. Wieland and S. Bloch, *Ber.*, 1904, **37**, 1524.

¹⁷ L. A. Bigelow and R. S. Hanslick, *Org. Synth.*, 1933, **13**, 38.

mother liquor in ether-hexane (1:24) showed the presence of two components, R_F 0.33 (starting material) and 0.66 (orange spot). Column chromatography on silica with hexane as eluant resulted in complete separation; removal of solvent gave 2,2,6,6-tetramethylheptane-3,4,5-trione (IV) as an orange oil (1.0 g), which crystallised on keeping at -30° in long orange needles, m.p. 16° , λ_{\max} 440, 340, 325, 285, 273, 248, and 204 nm, ν_{\max} (Nujol) 1705, 1680sh (CO), 1390, 1360 (Bu^b), 862 (?), and 690 (?) cm^{-1} , τ (CCl₄) 8.8 (18H, s) [Found: M (mass spectrometry), 198.1262. C₁₁H₁₈O₃ requires M , 198.1256], which reduced Tollen's reagent on warming, but failed to give a blue colour with glycine and to stain the skin purple.

(b) Nitrosyl chloride was passed into a solution of 2,2,6,6-tetramethylheptane-3,5-dione (V) (4 g) in acetic acid (30 ml) at 20° . The temperature rose to ca. 40° and within 1 min crystals separated from the brown solution. After 5 min, the crystals of 4-nitroso-2,2,6,6-tetramethylheptane-3,5-dione (IX) (1.4 g) (*vide infra*) were collected, washed with hexane, and found by t.l.c. to be homogeneous. The combined mother liquor and washings were concentrated in a vacuum removing most of the hexane, and nitrosyl chloride was again passed into the solution. A second crop of the nitroso-compound (0.6 g) was filtered off and washed with hexane. A third treatment of the united and concentrated mother liquor and washings with nitrosyl chloride failed to yield more of the nitroso-compound; next day the solution was poured into water (200 ml) and an orange oil separated. Hexane was added, in which the orange oil dissolved; a few s later, crystals began to separate from the hexane layer. The mixture was left for 30 min; the colourless crystals of the isonitroso-compound [(Xa) \rightleftharpoons (Xb)] (0.7 g) (*vide infra*) were collected, washed with hexane, and found by t.l.c. to be homogeneous. To the two-phase filtrate (hexane-aqueous acetic acid) hexane (100 ml) was added, and the hexane layer separated; the aqueous layer was extracted with hexane (50 ml) and with ether (2 \times 50 ml). The combined organic extracts were washed with sodium hydrogen carbonate solution and with water, dried, and evaporated to give an orange oil (1.4 g). Column chromatography on silica (35 g) in hexane and elution with hexane (200, 165, and 350 ml) gave respectively no material, the trione (IV) (0.69 g), and 20 mg of material which was discarded. Elution with ether-hexane (1:49) (250 ml) yielded material (90 mg), containing three components by t.l.c. in ether-hexane (1:24): R_F 0.66 [triketone (IV)], 0.2 (unknown), and 0.15 (*vide infra*), which was discarded. Further elution with ether-hexane (1:24) (100 ml) yielded the monochloro-diketone (VII; X = Cl) (0.15 g), R_F 0.15 in ether-hexane (1:24), 0.45 in ether-hexane (1:19), whose i.r. and n.m.r. spectra were identical with those described above; further elution with ether-hexane (1:24) (150 ml) yielded no material. Elution with ether (100 ml) gave no product; further elution with ether (40 ml) gave a pale yellow oil (0.35 g) containing two components (t.l.c. in ether) with R_F 0.7 (major) and 0.6 (minor). Trituration of the yellow oil with hexane gave the isonitroso-compound [(Xa) \rightleftharpoons (Xb)] (0.3 g), m.p. $99-100^\circ$ (*vide infra*); the coloured mother liquor was discarded. Final elution with ether (200 ml) afforded an oil (<0.1 g), which t.l.c. showed to comprise many components and which was discarded.

4-Nitroso-2,2,6,6-tetramethylheptane-3,5-dione (IX).—Prepared as described above, and in 40° yield by the action of

nitrosyl chloride on the neat diketone [(V) \rightleftharpoons (VI)] at 20° , the dimer of 4-nitroso-2,2,6,6-tetramethylheptane-3,5-dione had m.p. $125-126^\circ$ (decomp.) [from chloroform-hexane (3:2)], R_F 0.8 (in chloroform), ν_{\max} (CHCl₃) 1725, 1710 (CO), 1390, 1365 (Bu^b), and 1350 (NO) cm^{-1} , ν_{\max} (Nujol) 1730, 1714, 1400, 1360, and 1350 cm^{-1} , τ 8.74 (18H, s) and 3.06 (1H, s, no exchange with deuterium oxide alone or in trifluoroacetic acid) [Found (after drying at 50° and 0.01 mmHg): C, 62.2; H, 8.9; N, 6.6%; M (mass spectrometry), 213.1363. C₁₁H₁₈NO₃ requires C, 61.9; H, 8.9; N, 6.6%; M , 213.1364].

Isonitroso-compound [(Xa) \rightleftharpoons (Xb)].—Obtained as described above, and by the action of nitrosyl chloride on the diketone [(V) \rightleftharpoons (VI)], neat or in ethereal solution at 20° in ca. 10% yield, the isonitroso-compound formed needles, m.p. $99-100^\circ$ with partial sublimation (from ether-pentane), R_F 0.1 (in chloroform), 0.7 (in ether), ν_{\max} 3580sh, 3370br (OH), 1705, 1695sh (CO), 1665 (C=NOH), 1385, and 1360 (Bu^b) cm^{-1} , τ 8.86 (9H, s), 8.74 (9H, s), and 0.93 (1H, s), exchanged with deuterium oxide [Found (after drying at 50° and 0.01 mmHg (36% loss by sublimation)): C, 61.5; H, 8.8; N, 6.45%; M (mass spectrometry), 213.1367. C₁₁H₁₈NO₃ requires C, 61.9; H, 8.9; N, 6.6%; M , 213.1365]. The bisoxime [(XIa) \rightleftharpoons (XIb)] of the isonitroso-compound [(Xa) \rightleftharpoons (Xb)] was prepared by refluxing the latter (0.53 g) with excess of hydroxylamine acetate in methanol for 1 h; the bisoxime (0.4 g), recrystallised from carbon tetrachloride-hexane, formed small needles, m.p. $139-140^\circ$, with some sublimation and transformation to large prisms, m.p. $149-150^\circ$, R_F 0.9 (in ether), ν_{\max} 3560 (OH), 3240br (H...OH), 1392, and 1361 (Bu^b) cm^{-1} , τ 8.89(s) and 8.96(s) (minor) (9H), 8.61(s) and 8.67(s) (minor) (9H), 6.25 (1H, s), and 1.38 (1H, s), the last two protons exchanging with deuterium [Found (after drying at 50° and 0.01 mmHg): C, 57.95; H, 8.9; N, 12.2. C₁₁H₂₀N₂O₃ requires C, 57.8; H, 8.8; N, 12.3%]; for the mass spectrum see Discussion section.

Conversion of the Nitroso-compound (IX) to the Isonitroso-compound [(Xa) \rightleftharpoons (Xb)].—The nitroso-compound (2.1 g) was suspended in ethanol (10 ml) and *n*-KOH (11 ml) was added; the solid dissolved upon shaking and warming to 40° . The yellow solution was poured into an aqueous solution of citric acid to give an oil, which readily solidified. Extraction with ether afforded the isonitroso-compound (2 g), m.p. 99° (from ether-hexane), mixed m.p. 99° , R_F 0.7 (in ether).

Derivatives of the Trietone (IV).—(a) The orange solution of the trietone (0.15 g) in methanol (2 ml) was treated with an excess of a solution of semicarbazide acetate in methanol and the mixture was heated momentarily to boiling, cooled, and kept for 2 h at 20° . The pale lemon solution was evaporated in a vacuum and the resulting solid was triturated with water, collected, washed with water, dried, and recrystallised from carbon tetrachloride-hexane. The semicarbazone (XII) (0.1 g) formed pale yellow prisms, m.p. ca. 120° with transition to colourless needles, m.p. $149-150^\circ$ (decomp.), ν_{\max} (CHCl₃) 3530, 3410 (NH), 1740 (CO), 1680 (C=N), 1555 (N=C-C=O), 1385, and 1360 (Bu^b) cm^{-1} , τ 9.01 (9H, s), 8.72 (9H, s), a broad multiplet centred at 4.30 (NH₂), with a superimposed singlet at 4.44 (-NH-) removed by deuterium exchange, the whole signal integrating for 3 protons [Found (after drying at 25° and 0.01 mmHg over P₂O₅): C, 56.25; H, 8.15; N, 16.3. C₁₂H₂₂N₃O₃ requires C, 56.45; H, 8.3; N, 16.45%]. For the mass spectrum, see Discussion section.

(b) The triketone (0.1 g), dissolved in toluene- α -thiol (2 ml), was treated with boron trifluoride-ether complex; the mixture was left overnight at 20°, diluted with ether, washed twice with *N*-KOH, twice with water, dried, and evaporated. The residual oil showed two components, R_F 0.75 (yellow spot) and 0.70 [t.l.c. in ether-hexane (1:9)]. Column chromatography on silica (3 g) in hexane and elution with hexane (125 ml) removed all the yellow material; the resultant oil crystallised on cooling to -30°, and the solid was triturated with methanol at -60° and crystallised from methanol to yield the yellow dibenzyl thioacetal (XIII) (50 mg), m.p. ca. 79°, ν_{\max} (CCl₄) 1685 (CO), 1385, 1355 (Bu^t), and 690 (C-S-C) cm⁻¹. For the n.m.r. spectrum and the field ionisation mass spectrum, see Discussion section; the electron impact mass spectrum shows no parent peak at m/e 428 and yields peaks at m/e 319,* 318,* 317,* 316,* 260, 251, 246, 182, 176, 123, 110, 91 (base peak, PhCH₂⁺), 85, 57 (Bu^t), and 56 [Found (after drying at 25° and 0.01 mmHg over P₂O₅): C, 71.0; H, 7.2; S, 15.1, 15.2; O, 6.7%; M (mass spectrometry), 428. C₂₅H₃₂O₂S₂ requires C, 70.1; H, 7.5; S, 15.0; O, 7.45%; M , 428].

(c) The triketone (0.15 g) was shaken, in aqueous suspension or in methanol solution, with an excess of hydroxylamine acetate; the orange colour gradually disappeared and a solid separated. After 30 min, the solid was filtered off and washed with water and with hexane to remove the last traces of triketone (yield, 0.16 g). The adduct (XIV)

did not melt but sublimed; ν_{\max} (Nujol) 3610sh, 3460sh, 3240sh (OH, NH), and 1770 (?CO), τ [(CD₃)₂SO] 9.0 (18H, s), τ [yellow solution in (CD₃)₂CO] 9.0 and 8.8 (ratio 3:1, after 15 min ratio 1:3) [Found (after brief drying at 20° and 0.01 mmHg): C, 57.3; H, 9.2; N, 6.0. C₁₁H₂₁NO₄ requires C, 57.1; H, 9.15; N, 6.05%].

Diphenyl Triketone.^{16,18}—Prepared from dibenzoylmethane by the method of Bigelow and Hanslick,¹⁷ the triketone had m.p. 68–70° (from hexane), λ_{\max} 440 nm.

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* These peaks, of relative intensities 64:16:8:2, probably arise by hydrogen transfer: C₂₅H₃₂O₂S₂ (m/e 428) → $\dot{C}O\cdot COBu^t + Bu^t\dot{C}(SCH_2Ph)_2$ (315) → Bu^tCH(SCH₂Ph)₂ (316) → Bu^tCH(SCH₂Ph)(⁺SHCH₂Ph) (317) → Bu^tCH-(⁺SHCH₂Ph)₂ (318), whilst m/e 319 could be derived from perfluorokerosene.