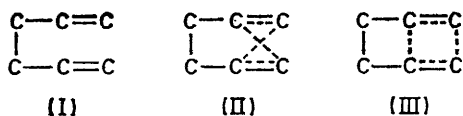


## Structures of Some Hexa-1,5-diene-1,1,3,3,4,4,6,6-octacarboxylic Esters

By C. W. Shoppee\* and N. W. Hughes, Department of Chemistry, Texas Technological University, Lubbock, Texas 79409

The structures of the octamethyl ester, m.p. 139°, and the octaethyl ester, m.p. 86°, obtained by condensation of two molecules of methyl or ethyl sodiodicarboxylglutaconate, as derivatives of hexa-1,5-diene have been proved. The complete lack of normal electrophilic olefinic reactivity shown by these esters cannot be explained by intramolecular cyclisation to isomeric derivatives of bicyclo[2,1,1]hexane or bicyclo[2,2,0]hexane, and is regarded as arising from adverse polar and steric factors. The experimental work recorded by Ingold, Parekh, and Shoppee in 1936, where repeated, has been confirmed and the structures then assigned, with a single exception, proved by n.m.r. spectroscopy and mass spectrometry.

In 1936 Ingold, Parekh, and Shoppee<sup>1</sup> considered the hexa-1,5-diene system (I) in connection with the possibility of the  $\pi$ -electronic interactions exemplified in formulae (II) and (III). We have re-examined the reactions of a derivative of hexa-1,5-diene (I) in the light of orbital symmetry considerations and using modern spectroscopic techniques.

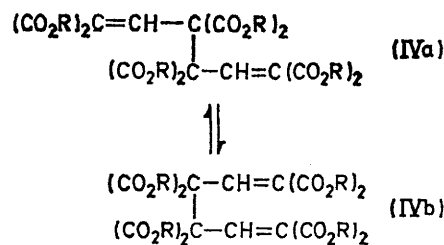


A compound, apparently of type (I), octaethyl hexa-1,5-diene-1,1,3,3,4,4,6,6-octacarboxylate was prepared in 1910 by Guthzeit and Hartmann<sup>2</sup> by the action of

<sup>1</sup> C. K. Ingold, M. M. Parekh, and C. W. Shoppee, *J. Chem. Soc.*, 1936, 142.

<sup>2</sup> M. Guthzeit and E. Hartmann, *J. prakt. Chem.*, 1910, **81**, 329; cf. M. Guthzeit, *Ber.*, 1907, **40**, 4043.

iodine on ethyl sodio-1,3-dicarboxylglutaconate; this octaethyl ester was also obtained by Ingold and Shoppee<sup>3</sup>

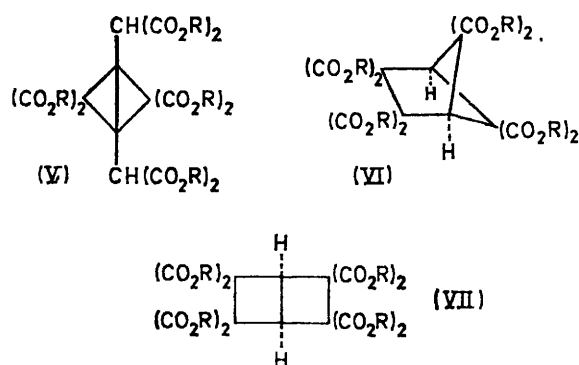


by the action of silver on ethyl bromo-1,3-dicarboxylglutaconate, and by Ingold, Parekh, and Shoppee<sup>1</sup> by a variety of allied methods, e.g. the action of the sodio-ester on the bromo-ester. All these preparative methods suggest a structure (IV) of which conformations (IVa,

<sup>3</sup> C. K. Ingold and C. W. Shoppee, *J. Chem. Soc.*, 1930, 1619; cf. F. Faltis and J. Pirsch, *Ber.*, 1927, **60**, 1621.

IVb; R = Et) represent extremes derived by rotation about the central C-C bond.

However, as Guthzeit and Hartmann observed, and as Ingold, Parekh, and Shoppee confirmed, the octaethyl ester, m.p. 86°, is completely resistant to chlorine, bromine, permanganate, and chromium trioxide in boiling acetic acid. The octamethyl ester, m.p. 139° (IVa or IVb; R = Me), prepared by Ingold, Parekh, and Shoppee, exhibited similar stability to halogens, permanganate, and chromium trioxide; it gives no colour with tetranitromethane in chloroform, and is unchanged by *m*-chloroperbenzoic acid in chloroform for 2 weeks. Guthzeit and Hartmann rejected formula (IVb; R = Et) and proposed a bicyclo[1,1,0]butane structure (V; R = Et), which they supported by an extensive series of experimental results that were shown to be imaginary by Ingold, Parekh, and Shoppee and completely discredited. Such a bicyclo[1,1,0]butane structure (V; R = Me, Et) is excluded by the observation<sup>1</sup> that the octamethyl and octaethyl esters are broken down by ozone to give methyl (or ethyl) ethane-tetracarboxylate and oxalic acid, the products to be expected from compounds of formulae (IVa, IVb).



Ring-chain mesomerism (I)  $\leftrightarrow$  (II) and (I)  $\leftrightarrow$  (III), involving (VI; R = Me, Et) and (VII; R = Me, Et) as contributory structures, was suggested in 1936 by Ingold, Parekh, and Shoppee,<sup>1</sup> to account for the abnormal stability of the octaesters. However, bicyclo[2,1,1]hexane,<sup>4-6</sup> m.p. 20–24°, and numerous derivatives<sup>7-11</sup> are now known as stable individuals; likewise, bicyclo[2,2,0]hexane,<sup>6,12,13</sup> b.p. 80°, is also known as a stable individual. Bateman and Koch<sup>14</sup> concluded from u.v. spectroscopic evidence that ring-chain mesomerism in the octaesters is non-existent in solution.

<sup>4</sup> K. B. Wiberg, B. R. Lowry, and T. H. Colby, *J. Amer. Chem. Soc.*, 1961, **83**, 3998; K. B. Wiberg, B. R. Lowry, and B. J. Nist, *ibid.*, 1962, **84**, 1594; K. B. Wiberg and B. R. Lowry, *ibid.*, 1963, **85**, 3188.

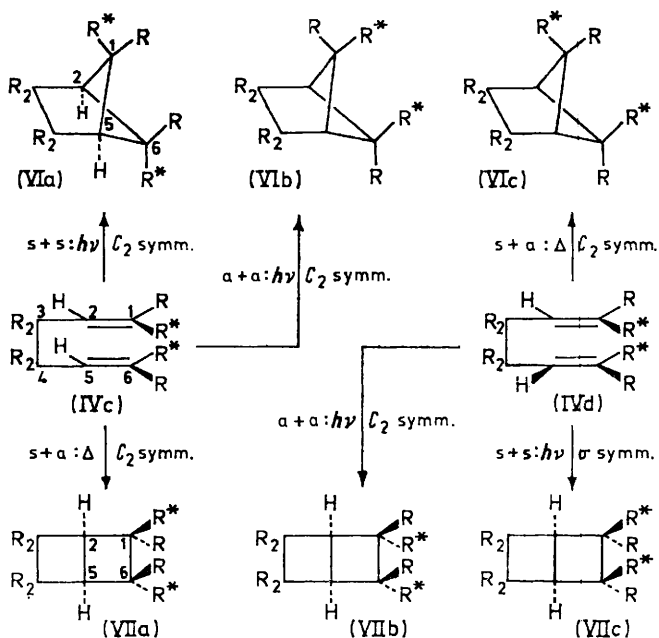
<sup>5</sup> R. Srinivasan, *J. Amer. Chem. Soc.*, 1961, **83**, 4923; *J. Phys. Chem.*, 1963, **67**, 1367.

<sup>6</sup> R. Srinivasan and F. I. Sonntag, *J. Amer. Chem. Soc.*, 1967, **89**, 407.

<sup>7</sup> J. Meinwald and P. G. Gassman, *J. Amer. Chem. Soc.*, 1960, **82**, 2857, 5445; J. Meinwald and J. K. Crandall, *ibid.*, 1966, **88**, 1292; J. Meinwald and W. Szkrybalo, *Tetrahedron Letters*, 1967, 731.

<sup>8</sup> J. L. Charlton, P. de Mayo, and L. Skattebol, *Tetrahedron Letters*, 1965, 4679.

A possible alternative explanation of the reduced reactivity observed is that the octaesters (IVb; R = Me, Et), initially formed by union of two 1,3-dicarboxyglutaconate residues, have already undergone an intramolecular electrocyclic reaction, and that the octaesters isolated have the structures (VI; R = Me, Et) or (VII; R = Me, Et). Intramolecular electrocyclic 'crossed' addition of a *cis*-conformer (IVc; R = CO<sub>2</sub>Me, CO<sub>2</sub>Et) and of a *trans*-conformer (IVd; R = CO<sub>2</sub>Me, CO<sub>2</sub>Et) of an initial octaester can occur theoretically in three ways to give three *cis*-fused products (VIa, b, c), and three geometrically improbable *trans*-fused products. Similarly, intramolecular electrocyclic 'direct' addition of (IVc, IVd; R = CO<sub>2</sub>Me, CO<sub>2</sub>Et) can occur theoretically in three ways to give three *cis*-fused products (VIIa, b, c) and three geometrically improbable *trans*-fused products:



The cyclisations leading to (VIa, b, c) and (VIIa, b) all require the olefinic centres to approach one another orthogonally by deformation of a chair-like conformation. Models suggest that the thermal ground-state reactions (IVd  $\rightarrow$  VIc) and (IVc  $\rightarrow$  VIIa) should be stereochemically difficult, and terminal substitution of hexa-1,5-dienes greatly reduces the efficiency of cyclisation and may suppress cyclisation completely.<sup>15</sup>

<sup>9</sup> F. T. Bond, H. L. Jones, and L. Skerbo, *Tetrahedron Letters*, 1965, 4685.

<sup>10</sup> R. H. S. Liu and G. S. Hammond, *J. Amer. Chem. Soc.*, 1967, **89**, 4936.

<sup>11</sup> C. Yamada, M. J. Pahk, and R. H. S. Liu, *Chem. Comm.*, 1970, 882.

<sup>12</sup> S. Cremer and R. Srinivasan, *Tetrahedron Letters*, 1960, **21**, 24.

<sup>13</sup> C. Steel, R. Zand, P. Hurwitz, and S. G. Cohen, *J. Amer. Chem. Soc.*, 1964, **86**, 679.

<sup>14</sup> L. Bateman and H. P. Koch, *J. Chem. Soc.*, 1945, 216.

<sup>15</sup> R. H. S. Liu, personal communication (letter of Sept. 4, 1970).

Org.

Structures (VI and VII; R = Me, Et) for the octaesters are thus improbable, and are excluded by an X-ray crystallographic study made by Bateman and Jeffery:<sup>16</sup> the octaethyl ester is triclinic and crystallographically awkward, but the octamethyl ester is monoclinic and unambiguously centrosymmetric (*cf.* IVa; R = Me), whereas structures (VI) and (VII) have no centre of symmetry.

The photochemical cyclisations (IVc  $\rightarrow$  VIa) and (IVd  $\rightarrow$  VIIc: from a boat-like conformation) were examined. Irradiation of the octamethyl ester, m.p. 139°, in diphenyl ether solution with or without the presence of acetophenone as sensitiser, with t.l.c. and n.m.r. monitoring, failed to show any conversion during 7 days. Here again the four terminal methoxycarbonyl substituents may suppress cyclisation; thus 2-phenylhexa-1,5-diene photocyclises readily,<sup>11</sup> whereas 1-phenylhexa-1,5-diene with a single terminal substituent fails to react.<sup>15</sup>

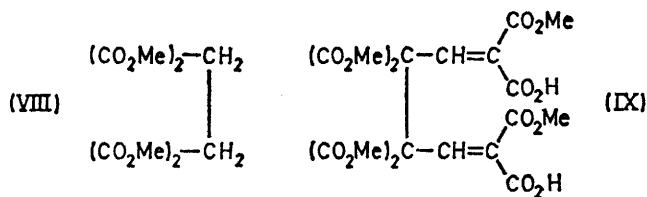
The original structures [(IVa; R = Me) solid state; (IVb; R = Me) solution] are supported by our n.m.r. observations. The octamethyl ester in deuteriochloroform solution at 20° exhibits a sharp singlet signal for two vinyl protons at  $\tau$  2.85. For comparison, the bridge-head protons in bicyclo[2,1,1]hexane [*cf.* (VI)] give rise to a multiplet signal centred at  $\tau$  7.51,<sup>4</sup> 7.47;<sup>5</sup> similarly, the signal for the bridgehead protons of bicyclo[2,2,0]hexane [*cf.* (VII)] appears as part of a very wide multiplet centred at  $\tau$  7.66.<sup>12</sup> There are also visible three singlet signals for 6, 12, and 6 protons respectively at  $\tau$  6.195, 6.22, and 6.24. We assign the 12-proton signal to the 3,3,4,4-methoxycarbonyl groups, one 6-proton signal to one *cis*-pair of 1,6-methoxycarbonyl groups,\* and the other 6-proton signal to the second *cis*-pair of 1,6-methoxycarbonyl groups.† This assignment is supported by the n.m.r. spectra of methyl ethane-1,1,2,2-tetracarboxylate (VIII), which shows a singlet for 12 protons at  $\tau$  6.22. The hexamethylester-diacid<sup>1</sup> (IX), m.p. 218° (decomp.), now prepared from the octaester by partial hydrolysis with potassium carbonate in aqueous acetone at 25° and reconvertible to the octamethylester by acid-catalysed esterification, also shows a singlet signal for 12 protons at  $\tau$  6.23 together with a singlet signal for 6 protons at  $\tau$  6.27 derived from the remaining pair of terminal methoxycarbonyl groups. This observation confirms the assumption of Ingold, Parekh, and Shoppee<sup>1</sup> that hydrolysis is initiated in those methoxycarbonyl groups which may be presumed to be least sterically protected.

The n.m.r. spectrum of the octamethyl ester in deuteriochloroform (*vide-supra*) was unchanged at 70°; in diphenyl ether at 40° the three singlet signals for the eight methoxy-groups were shifted upfield to  $\tau$  6.96, 6.98, and 7.21, undoubtedly on account of the formation of a  $\pi$ -complex between the solvent and the double bonds of the methoxycarbonyl groups, but even at 180° the signals did not coalesce into one (or two) peaks.

\* Also *cis* to the 2- and 5-protons in (IVb; R = Me).

† *trans* To the 2- and 5-protons in (IVb; R = Me).

We believe that the octaesters are correctly formulated as (IVa, IVb; R = Me, Et), and that their stability to electrophilic addition and to oxidation arises from



adverse polar and steric factors. Ethyl 1,3-dicarboxyglutaconate adds bromine in chloroform at 0° (in sunlight) to give ethyl 1,2-dibromo-1,3-dicarboxyglutarate, which spontaneously eliminates hydrogen bromide to furnish ethyl 1-bromo-1,3-dicarboxyglutaconate;<sup>2,17</sup> deactivation of the double bonds in the octaesters by the electron attraction of the terminal *gem*-ethoxycarbonyl groups is thus not a sufficient explanation, and steric hindrance must be a contributory factor. Activation of a double bond to electrophilic addition and oxidation by the electron repulsion of large alkyl groups may be inadequate to overcome steric hindrance; the olefin  $\text{CH}_2=\text{C}(\text{CHMeBu}^t)\text{CMe}_3$  does not add bromine although attacked by perbenzoic acid by ozone,<sup>18</sup> and Professor R. B. Woodward has drawn our attention to the case of 1,1-dineopentylethylene,  $\text{CH}_2=\text{C}(\text{CH}_2\text{CMe}_3)_2$ , which serenely resists the action of hot permanganate.

Ingold, Parekh, and Shoppee<sup>1</sup> were unable to reduce the octamethyl ester (IVa, IVb; R = Me) with zinc-acetic acid or by hydrogenation with platinum or palladium catalysts. They, however, were able to obtain by electrolytic reduction in acid solution a dihydro-octamethyl ester, m.p. 149° (XII), hydrolysed in turn by hydrochloric acid to a hexaester-diacid, m.p. 252°, and by sodium hydroxide to a tetra-acid, m.p. 225°. These three compounds are stable to permanganate, and are cyclopentane derivatives. The ester (XII) arises by an intramolecular Michael-type addition reaction of the intermediate (X), and the marked change in structural type that follows addition of one molecule of hydrogen to the octamethyl ester was verified spectroscopically by Bateman and Koch.<sup>14</sup>

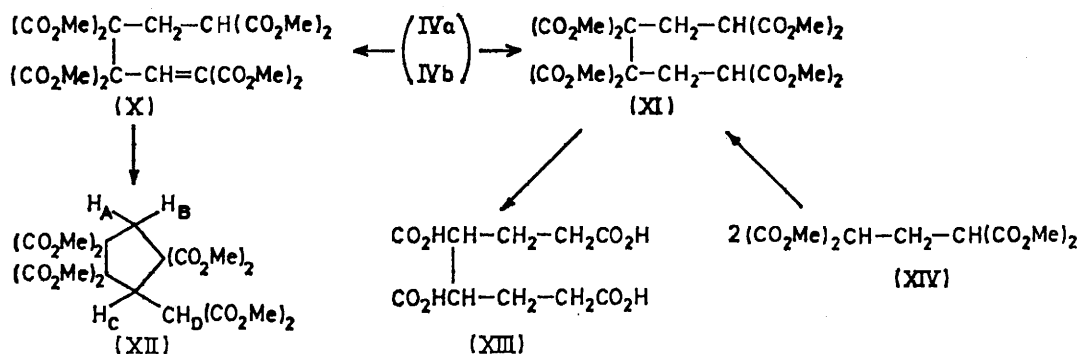
We have been able to obtain the dihydro-octamethyl ester, m.p. 149°, (XII) by hydrogenation of the octamethyl ester (IVa, IVb) with Adams' catalyst in methanol. The structure (XII) has been confirmed by mass spectrometry [ $M^+ = 548$ ], and by the n.m.r. spectrum; this showed an AB quartet signal centred at  $\tau$  6.82 ( $J$  19, 15 Hz) for two protons [ $H_A, H_B$ ], two doublet signals at  $\tau$  5.94, 5.53 ( $J$  11 Hz) each for one proton [ $H_C, H_D$ ], together with singlet signals for three protons each at  $\tau$  6.62, 6.34, 6.305, 6.275, and 6.265, and for nine protons at  $\tau$  6.25 derived from the eight methoxycarbonyl groups. Hydrogenation of the octamethyl ester (IVa, IVb) with Adams' catalyst in acetic acid gave the tetrahydro-octamethyl ester, m.p. 111—

<sup>16</sup> L. Bateman and G. A. Jeffery, *J. Chem. Soc.*, 1945, 211.

<sup>17</sup> Y. Urushibara, *Bull. Chem. Soc. Japan*, 1928, 3, 200.

<sup>18</sup> H. J. Backer, *Rec. trav. Chim.*, 1939, 58, 652.

112° (XI). The structure (XI) has been confirmed by mass spectrometry [ $M^+ = 550$ ], and by the n.m.r. spectrum; this showed a doublet signal at  $\tau$  7.14 ( $J$  4.5 Hz) for four AB protons of two ABX systems, a large poorly resolved doublet signal at  $\tau$  6.26 with some small peaks at *ca.*  $\tau$  6.33, together integrating for 26 protons, and thus representing the eight methoxycarbonyl groups overlaying the two X protons of the

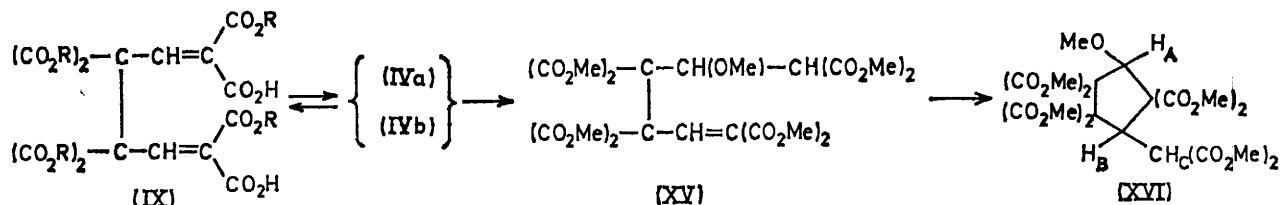


ABX systems. Finally, structure (XI) is proved by complete alkaline hydrolysis to the known 3,4-dicarboxysuberic acid (XIII),<sup>19,20</sup> m.p. 216°, and by synthesis from two molecules of methyl 1,3-dicarboxylglutarate (XIV) [= (XIX)] by coupling of two molecules of the monosodio-derivative with iodine, or by condensation of one molecule of the monosodio-derivative with one molecule of methyl bromo-1,3-dicarboxylglutarate.

Ingold, Parekh, and Shoppee<sup>1</sup> observed that the octamethyl ester (IVa, IVb; R = Me) did not react with methanol, but was converted by cold methanolic sodium methoxide into a methoxyoctamethyl ester, m.p. 193° (XVI). This was in contrast to the behaviour

The formation of the methoxyoctamethyl ester (XVI) has been confirmed and its structure verified by the n.m.r. spectrum and the mass spectrum. The mass spectrum showed the parent peak at  $M^+ 578$  ( $\text{C}_{23}\text{H}_{30}\text{O}_{17}$ ). The n.m.r. spectrum exhibited a singlet signal for one proton at  $\tau$  4.46 ( $\text{H}_A$ ), two doublet signals each for one proton at  $\tau$  5.91, 4.95 ( $J$  9 Hz) ( $\text{H}_B, \text{H}_C$ ), a singlet signal for three protons at  $\tau$  6.53 (OMe), and six singlet

signals at  $\tau$  6.34 (3H), 6.32 (6H), 6.31 (3H), 6.27 (3H), 6.25 (6H), and 6.21 (3H) derived from the eight methoxycarbonyl groups. The mode of formation of the methoxyoctamethyl ester (XVI) seems clearly to involve a base-catalysed nucleophilic addition to one ethylenic centre, facilitated by the electron attraction of two methoxycarbonyl groups, to give a hypothetical intermediate *cf.*<sup>1</sup> (XV), which undergoes a base-catalysed internal nucleophilic addition of Michael type to furnish (XVI). We have observed that methyl 1,3-dicarboxylglutaconate (XVIII) adds methanol to give the methoxytetramethyl ester (XVII) on attempted hydrogenation with Adams' catalyst in methanol, whereas use of



of the octaethyl ester (IVa, IVb; R = Et), which with cold ethanolic sodium ethoxide underwent, not addition of a molecule of ethanol, but partial hydrolysis to the hexaethylester-diacid, m.p. 192° (decomp.) (IX; R = Et). Both the hexamethylester-diacid, m.p. 218° (decomp.) (IX; R = Me), which was isolated<sup>1</sup> in attempted oxidations of the octamethyl ester (IVa, IVb; R = Me) with permanganate in alkaline aqueous acetone and with ferricyanide in aqueous potassium carbonate, and the hexaethylester-diacid (IX; R = Et) by acid-catalysed esterification with the appropriate alcohol regenerated the appropriate octaester.

<sup>19</sup> L. Ruzicka, A. Borges de Almeida, and A. Brack, *Helv. Chim. Acta*, 1934, **17**, 183.

<sup>20</sup> C. T. Blood and R. P. Linstead, *J. Chem. Soc.*, 1952, 2256; *cf.* O. Silberrad, *ibid.*, 1904, **85**, 611; W. J. Sell and T. H. Easterfield, *ibid.*, 1894, **65**, 828; W. J. Sell and A. Jackson, *ibid.*, 1899, **74**, 507.

Adams' catalyst in acetic acid gives methyl 1,3-dicarboxylglutarate (XIX). The n.m.r. spectrum of the methoxytetramethyl ester (XVII) is in perfect agreement with the structure; in particular the doubling-up of the methoxycarbonyl singlet signals is in accord with the symmetry of the molecule.<sup>21</sup>

Ingold, Shoppee, and Parekh<sup>1</sup> found that hydrolysis with mineral acids of the octamethyl ester (IVa, IVb; R = Me), or of the hexamethylester-diacid (IX; R = Me) yielded carbon dioxide and a tetramethylester-diacid,  $\text{C}_{16}\text{H}_{20}\text{O}_{13}$ , m.p. 245°, formulated as (XX; R = Me) and characterised by a hexamethyl ester,  $\text{C}_{18}\text{H}_{24}\text{O}_{13}$ , m.p. 168°. Corresponding observations were made for hydrolysis of the octaethyl ester (IVa, IVb;

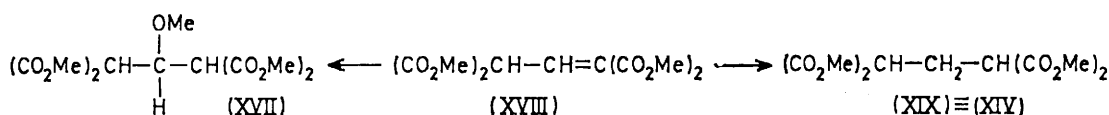
<sup>21</sup> L. M. Jackman and S. Sternhell, 'Applications of NMR Spectroscopy in Organic Chemistry; Pergamon Monographs on Organic Chemistry,' 1969, **5**, 375, especially footnote 2.



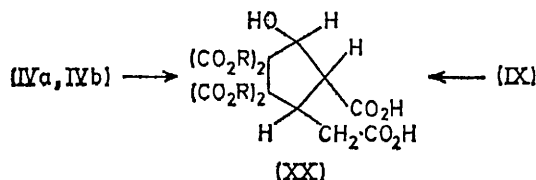
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R = Et) and the hexaethylester-diacid (IX; R = Et), which gave the tetraethylester-diacid, C<sub>20</sub>H<sub>28</sub>O<sub>13</sub>, m.p. 152°, formulated as (XX; R = Et) and characterised as the hexaethyl ester, C<sub>24</sub>H<sub>36</sub>O<sub>13</sub>, m.p. 71°.<sup>2</sup>

The tetramethylester-diacid, m.p. 245°, was stable to

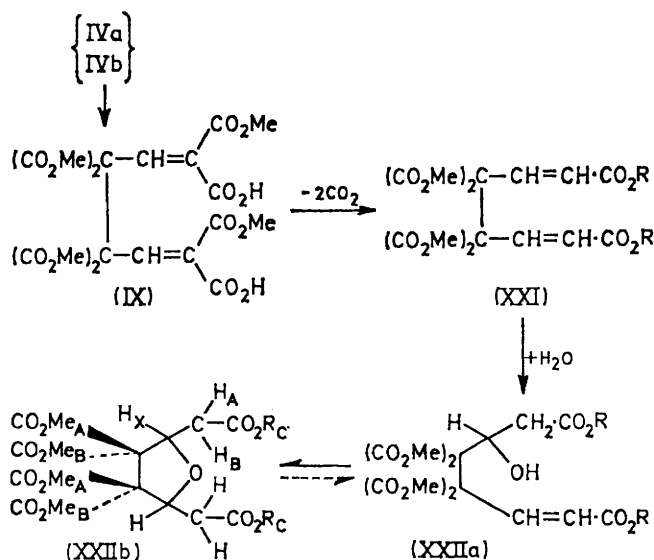


hot chromic acid, boiling conc. nitric acid, and ozone; similarly the hexamethyl ester, m.p. 168°, failed to react with acetic anhydride, acetyl chloride, thionyl chloride, and diazomethane, and we have confirmed that it is unaffected by acetic anhydride-pyridine at 100° for 16 hr., and by Jones' reagent. The hexamethyl ester,



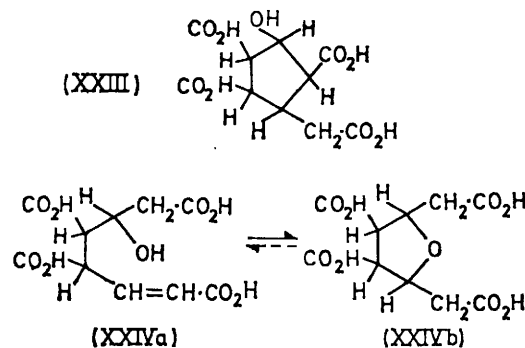
m.p. 168°, could be obtained from the tetramethylester-diacid, m.p. 245°, by simple recrystallisation from methanol; it was unattacked by ozone, and attempts to oxidise it with hot chromic acid regenerated the tetramethyl ester-diacid, m.p. 245°. The presumed presence of a secondary hydroxy-group in these four compounds [as (XX)] was based on the formation of *ca.* 1 mol. of methane by the hexamethyl and hexaethyl esters with the Tschugaeff-Zerewitinoff reagent.<sup>1</sup>

The correct formulae for these four compounds are, however, as (XXIIb). The probable sequence of reactions in the acid hydrolysis of the octa-esters (IVa, IVb; R = Me, Et), involves the acid-catalysed hydration of the acrylic ester or acid (XXI; R = Me, H), and is exemplified for the methyl ester series as follows:



The symmetrical structures (XXIIb; R = H) for the tetramethyl ester-diacid, and (XXIIb; R = Me) for the hexamethyl ester, follow from the mass and n.m.r. spectra. The mass spectrum of the tetramethyl ester-diacid (XXIIb; R = H) showed no parent peak

[M<sup>+</sup> 420] but a base peak at 403 (loss of OH!) and peaks at 389, 361, and 329; the mass spectrum of the hexamethyl ester (XXIIb; R = Me) furnished a parent peak at 448, with peaks at 431 (loss of OH!), 417, 403, and 389. In deuteriochloroform the hexamethyl ester shows an ABX system of nominal intensity for three protons (actually six protons) at  $\tau_A$  7.27,  $\tau_B$  7.69, and  $\tau_X$  4.63; as  $\Delta_{AB} = 42$  Hz and  $J_{AB} = 16$  Hz, this can be considered as an AMX system thus making  $J_{AX} = 2.5$  Hz and  $J_{BX} = 10$  Hz; the methoxycarbonyl signals appear as two singlets, one at  $\tau$  6.29 of nominal intensity for three protons (actually 6 protons), and the other at  $\tau$  6.23 of nominal intensity for six protons (actually 12 protons). In hexadeuteriobenzene, the methoxycarbonyl signals appear as three singlets at  $\tau$  6.67, 6.62, and 6.53, of equal intensity for six protons each; these are assignable to



the three stereochemically different pairs of methoxycarbonyl groups [CO<sub>2</sub>Me<sub>A</sub>, CO<sub>2</sub>Me<sub>B</sub>, CO<sub>2</sub>R<sub>C</sub> (R = Me)], which occur in both the *cis*- and *trans*-isomers. The high degree of symmetry displayed by (XXIIb; R = H) is reflected in the equal facility of esterification of the two acetate carboxy-groups. The n.m.r. spectrum of the hexamethyl ester (XXIIb; R = Me) in deuteriochloroform shows a very weak hydroxy-group signal at  $\tau$  7.30 (maximum intensity *ca.* 0.03 of a proton), which exchanges with deuterium and a correspondingly small signal for vinyl protons at  $\tau$  2.70; the i.r. spectrum in chloroform likewise shows a weak hydrogen-bonded hydroxy-absorption at *ca.* 3450 cm<sup>-1</sup>. These observations, together with the mass spectra (*vide supra*), suggest that traces of the open-chain tautomer (XXIIa; R = Me) are present in solution, and may be responsible for the production of methane by treatment with the Tschugaeff-Zerewitinoff reagent.<sup>1</sup>

We have not re-examined the hydrolysis of the octamethyl ester (IVa, IVb; R = Me), the hexamethyl

ester-diacid (IX), the tetramethyl ester-diacid (XXIIb; R = H), the hexamethyl ester (XXIIb; R = Me), or any of the corresponding ethyl esters with hot 10% aqueous-alcoholic potassium hydroxide. All these reactions yielded<sup>1</sup> one and the same product, a tetracarboxylic acid, C<sub>10</sub>H<sub>12</sub>O<sub>8</sub>, m.p. 193°, giving a yellow colour with ferric chloride, formulated as (XXIII), but stable to permanganate, chromium trioxide in acetic acid at 30°, and lead peroxide in acetic acid at 118°. There can, however, be little doubt that the correct formula for this tetracarboxylic acid is (XXIVb) by analogy with the parent compound (XXIIb). The yellow colour with ferric chloride,<sup>1</sup> the production of methane with the Tshugaëff-Zerewitinoff reagent,<sup>1</sup> and dehydration with potassium hydrogen sulphate at 180°<sup>1</sup> may be explicable in terms of the tautomeric formula (XXIVa).

#### EXPERIMENTAL

For general experimental directions see *J. Chem. Soc.*, 1959, 345. M.p.s were determined with a Kofler hot-stage apparatus. I.r. absorption spectra (solutions in carbon tetrachloride) were measured with Perkin-Elmer 221 and Beckman IR 33 spectrophotometers. N.m.r. spectra were measured with Varian A60 and HA 100 instruments, with deuteriochloroform as solvent and tetramethylsilane as internal reference. Mass spectra were measured with an A.E.I. MS9 double-focus spectrometer.

**Methyl Sodio-1,3-dicarboxylglutaconate.**—Methyl malonate (23 ml.) was added to a solution of sodium (7 g.) in methanol (80 ml.), and followed by chloroform (8 ml.). After refluxing for 30 min., the hot yellow solution was filtered and cooled to yield methyl sodio-1,3-dicarboxylglutaconate (16 g.), m.p. 270–272° (lit.,<sup>1</sup> m.p. 247–249°,<sup>16</sup> m.p. 264°); n.m.r. spectrum, in D<sub>2</sub>O:  $\tau$  6.42 (12H, s), 1.84 (1H, s).

**Octamethyl Hexa-1,5-diene-1,1,3,3,4,4,6,6-octacarboxylate (IVa, IVb; R = Me).**—Methyl sodio-1,3-dicarboxylglutaconate (6.3 g.) suspended in methanol (200 ml.) was stirred with a solution of iodine (3.2 g.) in methanol at 25° for 48 hr. Acetic acid (1 ml.) was added followed by zinc dust and the reaction mixture was stirred until colourless. After filtration and removal of most of the methanol *in vacuo*, the product was dissolved in chloroform and worked up in the usual way: the resultant yellow oil by crystallisation from acetone gave octamethyl hexa-1,5-diene-1,1,3,3,4,4,6,6-octacarboxylate (1.1 g.) m.p. 139–140° (lit.,<sup>1</sup> m.p. 139°,<sup>16</sup> m.p. 141°),  $\nu_{\max}$  1742 (C=O), 1644 (C=C), and 1248 (C-O) cm.<sup>-1</sup>;  $\nu_{\max}$  (in Nujol) 1770, 1725, 1710 (C=O), 1640 (C=C), and 1260 (C-O) cm.<sup>-1</sup>; n.m.r. spectrum,  $\tau$  6.24 (6H, s), 6.22 (12H, s), 6.195 (6H, s), and 2.85 (2 vinyl H, s) [Found: *M* (mass spectrometry), 546. Calc. for C<sub>22</sub>H<sub>28</sub>O<sub>16</sub>: *M*, 546]. The octamethyl ester gave no colour with tetranitromethane in chloroform, and was unchanged, m.p. and mixed m.p. 139–140° (from acetone) after treatment with *m*-chloroperbenzoic acid at 6° for 2 weeks, with periodic addition of further quantities of the peracid.

**Hexamethyl 1,6-Dihydrogen Hexa-1,5-diene-1,1,3,3,4,4,6,6-octacarboxylate (IX; R = Me).**—The octamethyl ester (IVa, IVb; R = Me) (154 mg.), dissolved in acetone (10 ml.), was treated with a solution of potassium carbonate (14 mg.) in water (3 ml.) at 25° for 4 days. Partial removal of the solvents gave the hexamethyl dihydrogen ester (45 mg.), m.p. 218° (decomp.) from acetone [(lit.,<sup>1</sup> m.p. 218° (decomp.)], n.m.r. spectrum, in D<sub>2</sub>O:  $\tau$  6.27 (6H, s), 6.23

(12H, s), and 2.84 (2 vinyl H, s). Esterification with methanol (10 ml.) containing conc. sulphuric acid (0.05 ml.) at 64° for 1 hr. regenerated the octamethyl ester, m.p., and mixed m.p. 139–140°.

**Catalytic Reduction of the Octamethyl Ester (IVa, IVb).**—(a) The octamethyl ester (100 mg.), in methanol (10 ml.) was hydrogenated with platinum oxide at 20° for 24 hr. The catalyst was filtered off, and the filtrate was evaporated *in vacuo*. The residue by recrystallisation from acetone-ether gave dimethyl 2,2,4,4,5,5-hexamethoxycarbonylcyclopentane-1-malonate (XII) (45 mg.), m.p. 150–151° (lit.,<sup>1</sup> m.p. 149°),  $\nu_{\max}$  (in CHCl<sub>3</sub>) 1738 (C=O) and 1260 (C-O) cm.<sup>-1</sup>; n.m.r. spectrum:  $\tau$  6.34, 6.305, 6.275, 6.265, 6.22 (each 3H, s), 6.25 (9H, s), 6.82 (2H, q, *J* 19 and 15 Hz), 5.94 (1H, d, *J* 11 Hz), and 5.53 (1H, d, *J* 11 Hz) [*M* (mass spectrometry), 548.1378. Calc. for C<sub>22</sub>H<sub>28</sub>O<sub>16</sub>: *M*, 548.1377].

(b) The octamethyl ester (2 g.) in acetic acid (100 ml.) containing acetic anhydride (0.5 ml.), was hydrogenated with platinum oxide (200 mg.) for 4 hr. The catalyst was filtered off, and the filtrate evaporated *in vacuo*. The product by recrystallisation from ether yielded octamethyl hexane-1,1,3,3,4,4,6,6-octacarboxylate (XI) (1.8 g.), m.p. 111–112°,  $\nu_{\max}$  (in Nujol) 1750, 1720 (C=O), and 1240 (C-O) cm.<sup>-1</sup>; n.m.r. spectrum:  $\tau$  7.14 (4H, d, *J* 4.5 Hz), 6.25, 6.26 with shoulder doublet (*J* 4.5 Hz) total integral 26H [Found: C, 47.85; H, 5.45%; *M* (mass spectrometry), 550. C<sub>22</sub>H<sub>30</sub>O<sub>16</sub> requires C, 48.0; H, 5.5%; *M*, 550]. This octaester (XI) (500 mg.) was heated under reflux with 10% aqueous potassium hydroxide solution (10 ml.) for 40 hr. The solution was cooled and extracted with ether; the solution was then acidified with 2*N*-hydrochloric acid and extracted with ether. These ether extracts by evaporation afforded no product; the aqueous solution was therefore evaporated completely *in vacuo*, and the resulting solid was triturated with acetone. The acetone extracts by evaporation furnished a colourless solid, which by recrystallisation from acetone-benzene gave 3,4-dicarboxy-suberic acid (XIII), m.p. 215° (lit.,<sup>19,20</sup> m.p. 216–217°) [Found: *M* (mass spectrometry), 262. Calc. for C<sub>10</sub>H<sub>14</sub>O<sub>8</sub>: *M*, 262].

**Partial Synthesis of Octamethyl Hexane-1,1,3,3,4,4,6,6-octacarboxylate (XI).**—The glutaconate (XVIII) (4.5 g.), m.p. 49–50° from ether (lit.,<sup>1</sup> m.p. 43°,<sup>16</sup> m.p. 50–51°),  $\nu_{\max}$  (in Nujol) 1750, 1720 (C=O), 1640 (C=C), 1265, 1230 (C-O) cm.<sup>-1</sup>; n.m.r. spectrum:  $\tau$  6.22 (6H, s), 6.18 (6H, s), 5.28 (1H, d, *J* 9.5 Hz), and 2.78 (1 vinyl H, d, *J* 9.5 Hz), in acetic acid (60 ml.) containing acetic anhydride (0.5 ml.) was hydrogenated with platinum oxide (200 mg.) at 20° for 1 hr. to give, after the usual isolation procedure, dimethyl 1,3-dimethoxycarbonylglutarate (XIV) (2.2 g.), m.p. 47–48° from ether,  $\nu_{\max}$  (in Nujol) 1730 (C=O) and 1220 (C-O) cm.<sup>-1</sup>, n.m.r. spectrum:  $\tau$  7.51 (2H, t, *J* 7 Hz), 6.47 (2H, t, *J* 7 Hz), and 6.23 (12H, s) [Found: C, 47.85; H, 6.0%; *M* (mass spectrometry), 276. C<sub>11</sub>H<sub>16</sub>O<sub>8</sub> requires C, 47.8; H, 5.85%; *M*, 276]. The glutarate (XIV) (500 mg.) was dissolved in methanol (10 ml.) containing sodium (45 mg.) and bromine (290 mg.) was added gradually. The resulting solution of dimethyl 1-bromo-1,3-dimethoxycarbonylglutarate was treated with a solution of the glutarate (XIV) (500 mg.) in methanol (10 ml.) containing sodium (45 mg.), and the mixture was heated under reflux for 4 hr. The cooled reaction mixture was filtered and the filtrate was evaporated *in vacuo*; the residual oil was dissolved in ether and the product was worked up in the usual way to give octamethyl hexane-

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1,1,3,3,4,4,6,6-octacarboxylate (XI) (5 mg.), m.p. and mixed m.p. 111—112° from ether, identical spectroscopically with the preparation described above. The octamethyl ester (XI) was also synthesised by stirring a solution of the glutarate (XIV) (500 mg.) in methanol (10 ml.) containing sodium (45 mg.) with iodine (500 mg.) at 25° for 48 hr., adding acetic acid (1 ml.) with zinc dust until decolourisation, and working up the ether extracts of the reaction product in the usual way.

*Dimethyl 3-Methoxy-2,2,4,4,5,5-hexamethoxycarbonylcyclopentane-1-malonate* (XVI).—The octamethyl ester (IVa, IVb; R = Me) (100 mg.) was dissolved in methanol (10 ml.) containing sodium (200 mg.); after 4 hr. at 25°, the reaction mixture was acidified with 2N-hydrochloric acid, filtered, and cooled to give the malonate (XVI), m.p. 198—200° from acetone (lit.,<sup>1</sup> m.p. 193°); n.m.r. spectrum:  $\tau$  6.53 (3H, s), 6.34 (3H, s), 6.32 (6H, s), 6.31 (3H, s), 6.27 (3H, s), 6.25 (6H, s), 6.21 (3H, s), 5.91 (1H, d,  $J$  9 Hz), 4.95 (1H, d,  $J$  9 Hz), and 4.46 (1H, s) [Found:  $M$  (mass spectrometry), 578. Calc. for  $C_{23}H_{30}O_{17}$ :  $M$ , 578].

*3,3,4,4-Tetramethoxycarbonyltetrahydrofuran-2,5-diacetic Acid* (XXIIb; R = H).—The octamethyl ester (IVa, IVb; R = Me) (1 g.) was heated under reflux with 2N-hydrochloric acid (25 ml.) for 24 hr.; the solution when cooled yielded the acid (XXIIb; R = H) (340 mg.), m.p. 255—257° (lit.,<sup>1</sup> m.p. 245°). This acid (200 mg.) was refluxed with methanol (5 ml.) containing conc. sulphuric acid (0.05 ml.) for 1 hr.; the solution on cooling afforded the diacetate (XXIIb; R = Me) (150 mg.), m.p. 168° from methanol (lit.,<sup>1</sup> m.p. 168°),  $\nu_{\max}$  (in  $CHCl_3$ ), 3450 (OH), 1740 (C=O), and 1250 (C—O)  $cm^{-1}$ ;  $\nu_{\max}$  (in Nujol) 1730 (C=O), 1290, 1245, and 1225 (C—O)  $cm^{-1}$ ; n.m.r. spectrum:  $\tau$  6.29 (6H, s), 6.23 (12H, s), 7.69 (2H, q,  $J$  10 and 16 Hz), 7.27 (2H, q,  $J$  2.5 and 16 Hz), 6.63 (2H, q,  $J$  2.5 and 10 Hz), with a very weak signal at  $\tau$  7.30 (0.03H) readily exchangeable with  $D_2O$  and a correspondingly weak signal at  $\tau$  2.70 [Found:  $M$  (mass spectrometry), 448.  $C_{18}H_{24}O_{13}$  requires  $M$ , 448]. This hexamethyl ester was unchanged by treatment with Jones' reagent, or by pyridine-acetic anhydride at 100° for 16 hr.

<sup>22</sup> H. R. Ing and W. H. Perkin, jun., *J. Chem. Soc.*, 1924, 125, 1814.

*Attempted Photocyclisation of Octamethyl Hexa-1,5-diene 1,1,3,3,4,4,6,6-octacarboxylate* (IVc).—The octamethyl ester (150 mg.) in diphenyl ether (10 ml.) was irradiated in a Pyrex flask for 1 day with a 250 W Hanovia medium-pressure ultraviolet lamp, but the n.m.r. spectrum and t.l.c. on silica (Merck GF-254) in ether-cyclohexane (1 : 4) (viewed after spraying with 36N-sulphuric acid and baking at 140°) of an aliquot, both showed that no reaction had occurred. Acetophenone (0.25 ml.) was added as a sensitiser, and irradiation continued with n.m.r. and t.l.c. monitoring for 7 days; apart from formation of a little brown tar, the starting material was unchanged.

*Tetramethyl Ethane-1,1,2,2-tetracarboxylate* (VIII).—Methyl malonate (13.2 g.) was added to a solution of sodium (2.3 g.) in methanol (30 ml.), followed by bromine (*ca.* 8 g.) until decolourisation ceased. The product, isolated in the usual way, was recrystallised from benzene to give the tetracarboxylate (10 g.), m.p. 135—136° (lit.,<sup>1,22</sup> m.p. 135°, 138°),  $\nu_{\max}$  (in Nujol) 1740 (C=O), 1310 and 1270 (C—O)  $cm^{-1}$ , n.m.r. spectrum:  $\tau$  6.20 (12H, s) and 5.81 (2H, s).

*Dimethyl 2-Methoxy-1,3-dimethoxycarbonylglutarate* (XVII).—Methyl 1,3-dicarboxylglutaconate (XVIII) (m.p. 49—50°; 2 g.) was shaken in hydrogen with platinum oxide (200 mg.) in methanol (50 ml.) at 20° for 4 hr. The catalyst was filtered off, and the methanol removed *in vacuo*; the residue by recrystallisation from ether afforded the glutarate (250 mg.), m.p. 79—81°,  $\nu_{\max}$  (in Nujol) 1725 (C=O), 1260, and 1220 (C—O)  $cm^{-1}$  n.m.r. spectrum:  $\tau$  6.53 (3H, s), 6.24 (6H, s), and 6.225 (6H, s), with signals at  $\tau$  6.02 (2H, d), and 5.42 (1H, t) forming an  $AX_2$  system ( $J_{AX}$  6.5 Hz) [Found: C, 47.05; H, 6.1%;  $M$  (mass spectrometry), 306.  $C_{12}H_{18}O_9$  requires C, 47.05; H, 5.9%;  $M$ , 306].

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