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57. *The Structure of Polyisoprenes. Part IV. Double Bond Interaction in Certain Carbalkoxy-substituted* 1 : 5-*Dienes.*

By L. Bateman and G. A. Jeffrey.

A peculiar lack of olefinic reactivity, combined with a facility for cyclisation of methyl and ethyl $\Delta^{1:5}$-hexadiene-1 : 1 : 3 : 3 : 4 : 4 : 6 : 6-octacarboxylates, has been attributed by Ingold, Parekh, and Shoppee to ring-chain mesomerism. A reinvestigation of these and related compounds has now been made by using *X*-ray methods, and it is shown that the crystal structure of the methyl ester is incompatible with the *cis*-configuration required for such interspatial double-bond saturation. A radical disruption of a mesomeric system by crystallisation from solution is improbable and, an earlier formulation incorporating a *bicyclo*butane nucleus being rejected on chemical grounds, it is necessary to seek a new interpretation of the anomalous reactivity. We suggest that the determinative condition is hyperconjugation throughout the carbon framework of the molecule, and discuss this in relation to 1 : 5-dienes generally.

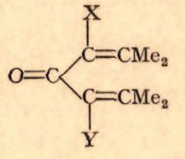
When unsaturated groups are components of a conjugated system it is well known that their individual properties are modified. Quantum mechanics now provides a sound theoretical basis for the extensive factual knowledge and even permits semi-quantitative treatment of the simpler examples (Lennard-Jones and Coulson, *Trans. Faraday Soc.*, 1939, **35**, 811). Much less understood and well defined are electronic interactions of more widely separated unsaturated centres and those in which formally saturated atoms or groups participate.

The latter type has featured prominently in the development of organic theory and is identified with two modes of electronic polarisation, *viz.*, the inductive effect, having its origin in electrostatic forces, and the tautomeric effect, resulting from a tendency to covalency change. As data have accumulated, so the complexity of electron response to environmental demand has become increasingly evident, and this is exemplified in the recognition of hyperconjugation. For some years the co-existence of the two effects acting oppositely has been assumed (*e.g.*, the $-I+T$ character of the halogens $\overset{\curvearrowleft}{\rightarrow}\text{Cl}$; Ingold, *Chem. Reviews*, 1934, **15**, 225) and a similar concept has recently been extended to the typically saturated alkyl groups (Baker and Nathan, J., 1935, 1844; Hughes, Ingold, and Taher, J., 1940, 949; Hughes and Ingold, *Trans. Faraday Soc.*, 1941, **37**, 657; Baker and Hemming, J., 1942, 191). Here, in addition to the commonly displayed inductive response, a tautomeric electron release is assigned to C–H bonds and this conjugation of unsaturated centres with saturated bond electrons—hyperconjugation (Mulliken, Riecke, and Brown, *J. Amer. Chem. Soc.*, 1941, **63**, 41)—is thought to be of wide generality. Fundamentally, the reason for the presence of different polarisations in any one group remains enigmatical, although the respective operative conditions can often be well defined (Hughes and Ingold, *loc. cit.*).

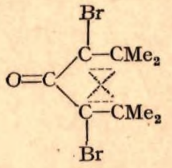
The related problem of double-bond interaction in non-conjugated dienes, which is the theme of this and the following paper, has evoked relatively negligible interest.

Müller (*Ber.*, 1921, **54**, 1466) postulated neutralisation of ethylenic activity across space to account for his observation, which Savard (*Bull. Soc. chim.*, **1929**, **45**, 398) claims to have confirmed, that geraniol is more transparent to ultra-violet light than the corresponding mono-olefin, citronellol. This evidence must be accepted with reserve, however, in view of the well-known difficulty in obtaining pure homogeneous terpenes and their susceptibility to oxidation. A similar condition has been envisaged in certain allylic ketones showing abnormal spectra (Ramart-Lucas, Grignard's " Traité de Chimie Organique," **1936**, II, p. 86) and in support is quoted loss of ketonic function on oxime formation—a doubtful criterion, since this reaction is known to be sensitive to less specific structural changes. The absence of correlation with more general theoretical principles obviates further consideration of these ideas, but it is of interest to note the presumed diagnostic value of absorption spectra for mutual double bond saturation (cf. this vol., p. 216).

Much more significant is the work of Ingold and Shoppee who generalised their conclusions in the theory of ring-chain mesomerism. The attention of these authors (J., **1928**, 365) was attracted by the pronounced change in physical and chemical properties in the series phorone, dibromophorone, bromohydroxyphorone (I, X = Y = H; X = Y = Br; X = Br, Y = OH, respectively). Colour, refractivity, and parachor all decrease markedly, and chemical reactivity parallels the increasing saturation thus revealed. A comprehensive



(I.)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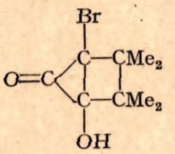
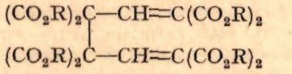
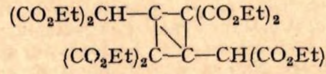

(III.)

investigation indicated that, while bromohydroxyphorone is the saturated dicyclic compound (III), dibromophorone possesses hybrid character and cannot be formulated simply. The state was represented by (II), where two electrons from each double bond are shared over the dotted tracks and thereby effect a degree of bonding across space. In spite of consistent inter-relationships, such as the correlation of the electronic nature of X and Y with the position of the derivative along the (I)→(III) scale, Ingold and Shoppee appreciated the limitations of conclusions derived from these highly tautomeric systems.

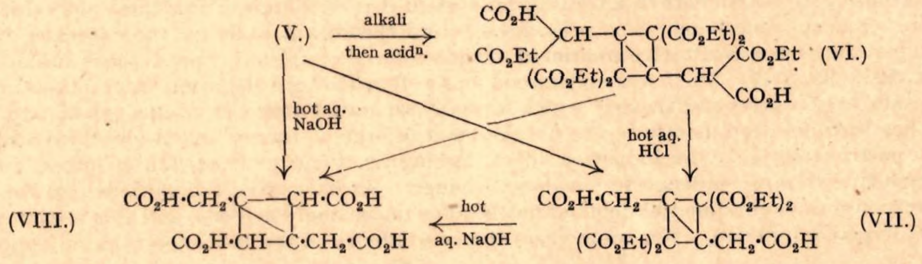
The problem was therefore pursued with a series of compounds first isolated by Guthzeit and Hartmann (*J. pr. Chem.*, **1910**, **81**, 329). Reaction of sodio-dicarbethoxyglutaconic ester with iodine, and similar condensations gave a crystalline solid whose analysis and preparation were consistent with the expected product (IV, R = Et). However, the compound was remarkably resistant to the usual olefinic reagents and Guthzeit and Hartmann concluded that they had actually synthesised the *bicyclo*butane derivative (V). Support for this decision was obtained from hydrolysis, halogenation, and alkylation experiments which indicated

(IV.)


$$\begin{array}{l}(CO_2R)_2C\text{—}CH{=}C(CO_2R)_2\\ \quad\quad\quad\ \ |\\ (CO_2R)_2C\text{—}CH{=}C(CO_2R)_2\end{array}$$


(V.)

that two $-CH(CO_2Et)_2$ groups, each with replaceable hydrogen, were attached to the dicyclic nucleus. Furthermore, it was discovered that substitution at the extra-nuclear carbon atoms, as in (VI) and (VII), left the saturated character unimpaired, whereas products with nuclear hydrogen resulting from decarboxylating



hydrolysis readily reduced permanganate—the inference being that such replacement afforded the means for disruptive nuclear attack.

In their re-investigation, which included the corresponding methyl analogues, Ingold, Parekh, and Shoppee (J., **1936**, 142) confirmed that the octa-esters had all the reputed stability towards permanganate but found equal resistance to halogenation and alkylation. Hydrolytic degradation proceeded in the stages described, but the decarboxylated derivatives all contained a combined molecule of water additional to the reported composition, and the alleged unsaturation of certain acids, *e.g.*, that formulated as (VIII), proved to be fictitious. Because of these discrepancies and to explain ozonolyses, realised with difficulty, in which the octa-esters underwent scission in agreement with formula (IV), the bicyclic formula (V) was rejected in favour of (IX) with resonance interaction of the double bonds, precisely as in dibromophorone.* The hexa-ester diacid

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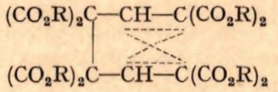
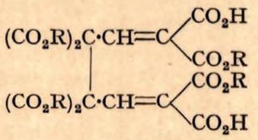
* The only other compounds based on the *bicyclo*butane ring system are described by Beesley and Thorpe, J., **1920**, **117**, 591.

(*ex* VI) was reformulated as (X, R = Et) with similar mesomerism, but the acids supposedly (VII) and (VIII) correspond to the *cyclo*pentane derivatives (XI) and (XII). Slight, but significant differences appeared in the

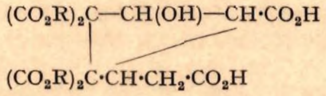
(IX.)

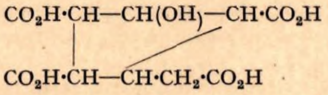




(X.)

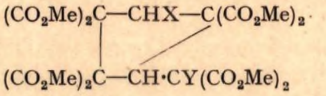
(XI.)

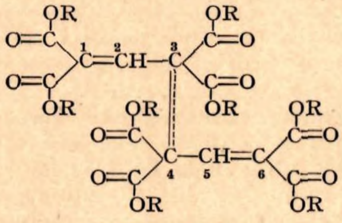




(XII.)

(XIII.)





(XIV.)

methyl series. Dissolution of the octamethyl ester in cold dilute methyl-alcoholic sodium methoxide and subsequent acidification gave, not the hexa-ester diacid (X, R = Me) as in the ethyl series, but a compound of the ester and methyl alcohol (XIII, X = OMe, Y = H). This distilled without decomposition, in common with the other neutral esters containing combined water [*e.g.*, esters of (XI) and (XII)] but in contrast to the parent ester. Finally, electrolytic reduction gave a fully saturated dihydro-derivative, which also distilled unchanged and whose formulation as (XIII, X = Y = H) was further supported by relating its complete hydrolytic degradation product to the acid (XII).

The reactivity of the octa-esters is clearly paradoxical. On the one hand, the ethylenic bonds revealed by ozonolysis are highly resistant to the usual addenda; on the other, *one* molecule of a normally less active reagent combines easily under acid or alkaline conditions with concomitant cyclisation. The double bonds appear to be interconnected in some way, and Ingold, Parekh, and Shoppee identified this with the resonance electron exchange depicted in (IX).

The possibility of an alternative explanation was suggested by a complete *X*-ray structure analysis of the typical straight chain polyisoprene derivative, geranylamine hydrochloride (Jeffrey, *Proc. Roy. Soc.*, in the press; see Bateman and Jeffrey, *Nature*, 1943, **152**, 446), in which the central C–C bond of the 1 : 5-diene system formed by *trans*-linked isoprene units was found to be abnormally short. This feature is commonly associated with single bonds bounded by conjugated unsaturated centres, and although it is not entirely unexpected theoretically (Bateman, *Trans. Faraday Soc.*, 1942, **38**, 367) yet the reason for its existence in a 1 : 5-diene remains obscure. A tentative explanation (Bateman and Jeffrey, *loc. cit.*) in terms of hyperconjugation has yet to receive experimental support and in simple systems this presents some difficulty.

Now the double bonds in the octa-esters are also 1 : 5-spaced, and it is reasonable to enquire whether their peculiar properties originate in similar but more extensive chain hyperconjugation. Superficial resemblances are at once apparent; cyclisation following the addition of one molecule of reagent is common to the acid hydration and other reactions (Bloomfield, J., 1943, 289; 1944, 114) of open-chain terpenes, and the relatively easy thermal breakdown at the central C–C bond (Ingold and Shoppee, J., 1930, 1619; Ingold, Parekh, and Shoppee, *loc. cit.*) suggests facilitation by allylic resonance energy (Huckel, *Z. Elektrochem.*, 1937, **43**, 841).

When the octa-ester is written as (XIV) the molecule is seen to possess high latent conjugation whose development is a function of the electron-conducting capacity of the central C–C bond. Full conjugation will create a system of much lower energy, and the tendency to approach this state will be a driving force offsetting the barriers imposed by single-bond insulation and by normal orbital hybridisation, as is true indeed of any mesomeric system. Although the octa-esters differ from relevant hydrocarbons by the absence of hydrogen at carbon atoms 3 and 4 (XIV), yet Hughes and Ingold (*loc. cit.*; Hughes, Ingold, Masterman, and McNulty, J., 1940, 899) have stressed that all quasi-unsaturated groups have hyperconjugative powers and this will certainly be true of the highly polarisable carbalkoxyl groups. It may be noted that the carbon atoms forming the central bond are flanked by atoms contributing sp^2 bonding orbitals. Hence symmetrical sp^3 hybridisation at the former may not be energetically favoured, but instead a characteristic hybridisation in which the hybrid bond has an added measure of electronic transmission over that of a normal single bond (possibly lower s/p ratio). In this sense, a normal double bond is simulated, but the absence of π electrons in the hybrid bond limits further similarity (*e.g.*, lack of additive function and ultra-violet absorption differences—Bateman and Koch, J., 1944, 600). It is perhaps significant that the octa-esters are labile under conditions of electrical asymmetry where transmissive powers will be invoked to the full.

The consequence of chain hyperconjugation to molecular structure cannot be definitely predicted. In normal conjugation, a *trans*-planar configuration is usual owing to enhancement of the resonance process, and a similar orientation about the hybrid bond, as in geranylamine hydrochloride, might well be anticipated in the octa-esters. Ring-chain mesomerism, on the other hand, necessarily requires a *cis*-arrangement. A discrimination between these theories becomes possible therefore by configuration analysis, and we have undertaken this by *X*-ray methods.

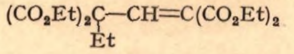
In general, intramolecular symmetry is not revealed by *X*-rays without recourse to a complete crystal structure analysis, but when it is used in symmetry operations effecting translations in the crystal lattice, systematic extinctions occur in the diffraction pattern that permit recognition from readily accessible data. A centre of symmetry can be unequivocally identified providing that the compound crystallise in a particular lattice arrangement and that its molecular complexity be known from an independent source. In practice, the latter condition can nearly always be met, and the success of the method essentially depends on Nature providing the former.

The octaethyl ester was examined first for symmetry character and proved to be an example from which no certain conclusion can be drawn. The crystals are triclinic with one molecule in the unit cell, and *X*-ray diffraction makes no distinction between the space group $P1$, with an asymmetric molecule, and $P\bar{1}$, with a centrosymmetric molecule. The absence of detectable pyroelectric effect indicates the latter but does not provide the decisive evidence required.

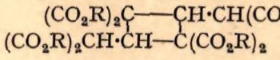
The corresponding octamethyl ester, however, showed the presence of a centre of symmetry unambiguously. The crystal system is monoclinic, and very careful indexing of oscillation photographs revealed the systematic extinctions of the space-group $P2_1/a$. The combination of two-fold screw axis and glide plane requires four asymmetric structures per unit cell, but the observed density limits the number of molecules to two, and hence each molecule must provide two centrosymmetrically related units. A *cis*-configuration is impossible, and ring-chain mesomerism must be rejected as a structural feature of the crystalline state.

In addition to this approach, the unit cells of some derivatives and related compounds were measured in the hope that decisions between *cis*-, *trans*-, and cyclic structures might be made from a study of intermolecular packing. No systematic variations in molecular dimensions could be traced, and inspection of Stuart models makes it plain that the presence of several carbalkoxyl groups, each with some freedom of orientation, swamps the slight differences introduced by rearrangement of the central carbon framework. For example, the symmetrical *trans*-forms of the uncyclised esters fitted the unit cells excellently, but the *cis*- and dicyclic forms were not sufficiently different to make them inadmissible. At the same time, Ingold, Parekh, and Shoppee's experimental record, where repeated, was confirmed in all essential respects, both chemically and by *X*-ray molecular-weight determinations. We also identified three forms of the hexamethyl ester diacid (X, R = Me), one containing acetone of crystallisation, and two forms of the acid esters (XI, R = Me and Et, respectively), one hydrated in each case. *X*-Ray data are given for crystalline methyl αγ-dicarbomethoxyglutaconate, for its *cyclo*butane *dimer* (XVI, R = Me), which proved to be centrosymmetric, and for the two stereoisomeric *dimers* (XVI, R = Et) of ethyl αγ-dicarbethoxyglutaconate. The configurations adduced for the latter on chemical grounds (Ingold, Perren, and Thorpe, J., 1922, 1765) are supported but not conclusively proved.

(XV.)



$$(CO_2Et)_2\underset{Et}{C}—CH{=}C(CO_2Et)_2$$



(XVI.)

The non-existence of ring-chain mesomerism in the crystal raises the question whether this is also true in the liquid phase where the anomalous reactivity is observed. Intramolecular association of the double bonds is considered to induce a state of lower energy owing to the greater freedom of the electrons than when confined to normal bonds. If such a preferred state does exist in solution, a configurational change to the *trans*-structure on crystallisation is possible only if accompanied by similar but intermolecular mesomerism and by improved crystal packing. We see no reason to expect special crystal forces and, in fact, the simple unit cells of the octa-esters, in contrast to the acid esters (XI, R = Me or Et), and particularly their hydrates, where hydrogen bonding is a structural condition, are indicative of nothing more than ordinary van der Waals attractions. The direct examination of the molecular state in solution described in the accompanying paper supports this reasoning.

The *X*-ray data are only compatible with formula (V) if the carbon nucleus is assumed to be planar. This is highly improbable stereochemically, and the rejection of the *bicyclo*-structure on chemical and spectral evidence (this vol., p. 217) is therefore confirmed.

There is then no alternative but to accept the open-chain formula and to seek another explanation of the unusual chemistry. Depression of double-bond activity may be due to the deactivating carbalkoxyl substituents or to steric hindrance. Ethyl αγ-dicarbethoxy-α-ethylglutaconate (XV), where the double bond has the same group environment, is also resistant to additive reagents. Comparative experiments show that it reduces potassium permanganate in acetone solution roughly 15 times as rapidly as the octaethyl ester at the same molar concentration. Although this rate difference, which is half the true comparative value if the double bond is the seat of oxidative attack and if the rate is directly proportional to olefin concentration, might be attributed to the heavier side-chain substitution in the octa-ester, present knowledge indicates that this interpretation is probably inadequate. Although other substituted glutaconic acids show normal, if greatly reduced, olefinic activity (*e.g.*, ααβ-trimethyl-, Perkin and Thorpe, J., 1897, **71**, 1182; ααγ-trimethyl-, Blaise, *Compt. rend.*, 1903, **136**, 1141; Perkin and Smith, J., 1903, **83**, 777), yet Ingold, Parekh, and Shoppee (*loc. cit.*) have isolated the hexa-ester diacid from the action of permanganate on the octamethyl ester, a result which recalls the inertness of the double bond and the lability of the alkyl group in tetraethylethane towards the same reagent (Koch and Hilberath, *Ber.*, 1940, **73**, 1171). Unless it can be shown, contrary to these indications of more profound reactivity difference, that the measured oxidation is initiated at the double bond in both cases, rate comparison has little value. Nevertheless, we think that the common substitutional influences must be reckoned with in assessing additive function in these systems.

Of greater significance is the cyclisation propensity. This is characterised by simultaneous addition of a molecule A–B such that A adds to one olefinic centre, B to the other—a feature clearly similar to 1 : 4-addition to butadiene except that valency redistribution occurs through internal bonding instead of by double-bond shift. As Ingold *et al.* argued, acceptance of partial double-bond interaction seems inevitable, and we suggest that this has now to be identified with chain hyperconjugation. In effect, this result generalises a principle familiar in the aromatic series (*e.g.*, the benzenoid character of pyrrole, furan, and thiophen and perhaps of *cyclo*hexadiene, cf. Bateman and Koch, *loc. cit.*; and the ionicity of the CH_2 group in the series *cyclo*pentadiene, indene, fluorene), *viz.*, that the intervention of a saturated group does not entirely thwart the development of full molecular conjugation.

EXPERIMENTAL.

No original preparations were undertaken, but certain differences were found from the m. p. data of Ingold, Parekh, and Shoppee, whose values are therefore given in parentheses for comparison. The density units are g./c.c.

Methyl αγ-dicarbomethoxyglutaconate. M. p. 50—51° (43°; cf. this vol., p. 221). Large triclinic crystals tabular on (100) with cell dimensions $a = 12·26$, $b = 8·79$, $c = 8·30$ A., $\alpha = 115°$, $\beta = 115°$, $\gamma = 113°$; $V = 666$ A.^{3}. Hence, with 2 molecules in the cell, the observed density of 1·38 gives M, 277 (Calc.: 274).

Octamethyl ester. M. p. 141° (139°) (Found : C, 48·35; H, 4·85; M, by vapour-pressure equilibration of a benzene solution against olive oil, 540 ± 30; cryoscopically in benzene, 530 ± 30. Calc. for $C_{22}H_{26}O_{16}$: C, 48·35; H, 4·8%; M, 546). Crystallises from acetone and a little light petroleum (b. p. 60—80°) in monoclinic prisms with forms {010}, {001}, {110}. Cell dimensions : $a = 10·39$, $b = 14·60$, $c = 8·37$ A., $\beta = 103·5°$; $V = 1234$ A.^{3}. Very careful indexing of oscillation photographs revealed systematic extinctions of $(0k0)$ absent for k odd, and $(h0l)$ absent for h odd with no exceptions. The space-group is therefore $P2_1/a$, requiring 4 asymmetric structure units. The observed density is 1·48 and that calculated for 2 centrosymmetric molecules in the cell is 1·47.

Octaethyl ester. M. p. 86° (Found : C, 54·7; H, 6·45. Calc. for $C_{30}H_{42}O_{16}$: C, 54·7; H, 6·45%). Triclinic crystals with {100}, {102}, {001}, {010}, commonly developed, also occasionally {011} and {101}. Cell dimensions : $a = 12·24$, $b = 8·72$, $c = 8·72$ A., $\alpha = 97·5°$, $\beta = 104·5°$, $\gamma = 107·5°$; $V = 855$ A.^{3}. Absence of pyroelectric effect indicates a space group $P\bar{1}$ with one centrosymmetric molecule. d(obs.) = 1·275, whence $M = 657$ (Calc.: 658).

Comparative Reducing Power of the Octaethyl Ester and Ethyl αγ-Dicarbethoxy-α-ethylglutaconate towards Permanganate.—Attempts to measure the reduction in acetone solution quantitatively by an absorptionmeter were abandoned, partly owing to the development of a brownish tinge as the pink colour faded, with subsequent coagulation of the manganese dioxide, and partly because the octa-ester invariably gave an opaque solution as reaction proceeded. Instead, a deficit of permanganate was used and the time for complete disappearance of colour measured. A trace of acid was added to eliminate adventitious variations due to possible sensitivity to pH conditions (*e.g.*, induction period). In the absence of thermostatic temperature control (2° range) the solutions were maintained under the same conditions throughout the whole of the reaction. A typical experiment was : Solution A : octa-ester, 0·0213M; $KMnO_4$, 0·00052M; HCl, 0·00003N. Solution B : ethylated tetra-ester (p. 214), 0·0215M; $KMnO_4$ and HCl as in A. Solution C : $KMnO_4$ and HCl as in A. A was decolourised in 52 hours, B in 4 hours, and C had faded slightly in 52 hours. Three similar experiments gave a mean reduction time ratio for A/B of 15±4.

Hexamethyl Ester Diacid (X, R = Me).—Difficulty was experienced in obtaining suitable crystals for X-ray work, and crystallisation behaviour was capricious generally. Two apparently isomorphous and visually indistinguishable forms were isolated from acetone : an anhydrous form (1), and an unstable solvated form (2) which lost solvent on standing in air. The former was usually obtained, the latter rarely, and the conditions favouring the formation of either crystals were not discovered. Form (1) had m. p. 225—226° (decomp.) (218°) (Found : C, 46·3; H, 4·5. Calc. for $C_{20}H_{22}O_{16}$: C, 46·3; H, 4·3%); monoclinic plates with $a = 18·4$, $b = 8·55$, $c = 14·3$ A., $\beta = 92°$; $V = 2248$ A.^{3}. The space-group is $C2/c$ with 4 centrosymmetric molecules, or Cc with 8 asymmetric molecules; d(obs.) = 1·55, whence $M = 523$ (Calc. : 518). Form (2) had the same m. p. after loss of solvent; on standing, the crystals became opaque and this change was reflected in the analytical figures (Found : after *ca.* 7 days, C, 48·7; H, 5·15; after *ca.* 10 days, C, 48·3; H, 5·0; after 24 weeks, C, 46·25; H, 4·35; equiv., by titration, 263. $C_{20}H_{22}O_{16},2C_3H_6O$ requires C, 49·2; H, 5·35%; M, 634); cell dimensions : $a = 23·00$, $b = 8·05$, $c = 16·75$ A., $\beta = 93°$, $V = 3100$ A.^{3}. Space-group also $C2/c$ or Cc; d(obs.) = 1·35, whence $M = 629$. The acid was slightly soluble in hot water, the cooled solution depositing a third crystalline form (3) as very small triclinic prisms of the same m. p. (Found : C, 46·05; H, 4·4%); cell dimensions : $a = 10·01$, $b = 8·24$, $c = 8·20$ A., $\alpha = 118°$, $\beta = 109°$, $\gamma = 108°$; $V = 555$ A.^{3}; $n = 1$; d(obs.) = 1·57, whence $M = 524$.

Hexaethyl Ester Diacid (X, R = Et).—M. p. 191—193° (193°). Triclinic prisms with $a = 11·07$, $b = 8·92$, $c = 8·55$ A.; $\alpha = 119°$, $\beta = 106°$, $\gamma = 94°$; $V = 715$ A.^{3}. d(obs.) = 1·385, whence $M = 596$ (Calc.; 620). Absence of pyroelectric effect indicates one centrosymmetric molecule in the cell.

Hexaethyl Ester Diacid Chloride.—M. p. 66·5—67° (65—66°). Monoclinic prisms with $a = 27·86$, $b = 8·73$, $c = 12·96$ A., $\beta = 98·5°$; $V = 3117$ A.^{3}; $n = 4$; d(obs.) = 1·355, whence $M = 635$ (Calc. : 639). Space group $P2/a$.

Dihydro-octamethyl Ester (XIII, X = Y = H).—M. p. 156°, with previous softening (149°) (Found : C, 48·25; H, 5·2. Calc. for $C_{22}H_{28}O_{16}$: C, 48·2; H, 5·15%). Monoclinic prisms with $a = 19·63$, $b = 12·19$, $c = 11·51$ A., $\beta = 109°$, $V = 2603$ A.^{3}; $n = 4$; d(obs.) = 1·40, whence $M = 548$ (Calc.; 548). Space-group $C2/c$.

Methyl cyclo*Pentane Hydroxy-acid Ester* (XI, R = Me).—Anhydrous (1) and hydrated (2) forms were isolated on crystallisation from water. Form (1) had m. p. 248—250°, with previous softening (245°) (Found : C, 45·8; H, 4·85. Calc. for $C_{16}H_{20}O_{13}$: C, 45·7; H, 4·8%). Orthorhombic bipyramids with $a = 26·62$, $b = 18·65$, $c = 16·34$ A.; $V = 7616$ A.^{3}; $n = 16$; d(obs.) = 1·47, whence $M = 421$ (Calc. : 420). Form (2) afforded orthorhombic needles with $a = 62·7$, $b = 26·66$, $c = 12·15$ A.; $V = 20310$ A.^{3}; $n = 32 + 256H_2O$; d(obs.) = 1·47, whence $M = 562$ ($C_{16}H_{20}O_{13},8H_2O$ requires M, 564).

Ethyl cyclo*Pentane Hydroxy-acid Ester* (XI, R = Et).—Again, anhydrous (1) and hydrated (2) forms were isolated. The first, crystallised from ether and ligroin, had m. p. 153—154° (152°) (Found : C, 50·4; H, 5·95. Calc. for $C_{20}H_{28}O_{13}$: C, 50·4; H, 5·9%); orthorhombic pyramids, usually penetration twins, with $a = 29·46$, $b = 19·45$, $c = 16·47$ A.; $V = 9437$ A.^{3}; $n = 16$; d(obs.) = 1·345, whence $M = 478$ (Calc. : 476). The *hydrate* (2) crystallised from water (Found : C, 48·4, 48·5; H, 6·1, 6·15. $C_{20}H_{28}O_{13},H_2O$ requires C, 48·5; H, 6·1%) in monoclinic prisms with $a = 19·08$,

$b = 15{\cdot}61$, $c = 8{\cdot}80$ A., $\beta = 112°$; $V = 2430$ A.^{3}; $n = 4$; d(obs.) $= 1{\cdot}32$, whence $M = 483$ (Calc.: 494). Space-group $P2_1/a$. Guthzeit and Hartmann reported a trihydrate, $C_{20}H_{26}O_{12},3H_2O$, *i.e.*, $C_{20}H_{28}O_{13},2H_2O$, but, in agreement with Ingold, Parekh, and Shoppee, we failed to isolate this. The monohydrate now described is new.

Dimer of Methyl αγ-Dicarbomethoxyglutaconate (XVI, R = Me).—M. p. 222° (Found: C, 48·45; H, 5·25. $C_{22}H_{28}O_{16}$ requires C, 48·2; H, 5·15%); monoclinic prisms with $a = 11{\cdot}00$, $b = 14{\cdot}18$, $c = 8{\cdot}13$ A., $\beta = 99{\cdot}5°$; $V = 1250$ A.^{3}; $n = 2$; d(obs.) $= 1{\cdot}44$, whence $M = 542$ (Calc.: 548). Extinctions correspond to the space-group $P2_1/n$. The molecules must therefore possess a centre of symmetry and their configuration is probably analogous to that of the corresponding ethyl dimer, m. p. 103°, as proposed by Ingold, Perren, and Thorpe (*loc. cit.*).

Dimers of Ethyl αγ-Dicarbethoxyglutaconate (XVI, R = Et).—(1) M. p. 103° (Found: C, 54·4; H, 6·7. $C_{30}H_{44}O_{16}$ requires C, 54·5; H, 6·7%); tabular triclinic crystals with $a = 11{\cdot}81$, $b = 9{\cdot}49$, $c = 9{\cdot}37$ A., $\alpha = 111°$, $\beta = 111°$, $\gamma = 112{\cdot}5°$; $V = 875$ A.^{3}; $n = 1$; d(obs.) $= 1{\cdot}25$, whence $M = 658$ (Calc.: 660). Space-group probably $P\bar{1}$, with centrosymmetric molecule. (2) M. p. 86—87° (Found: C, 54·35; H, 6·8%); short monoclinic needles with $a = 26{\cdot}28$, $b = 12{\cdot}49$, $c = 21{\cdot}42$ A., $\beta = 101{\cdot}5°$; $V = 6890$ A.^{3}; $n = 8$; d(obs.) $= 1{\cdot}27$, whence $M = 660$. Space group $A2/a$.

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