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Diisophorone and Related Compounds. Part 18 [1] Ring Contraction in Diisophorone by the *Favorski* Reaction

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The action of strong alkalis or alkoxides on 4,8-dibromo-1-carboxydiisophor-2(7)-en-3-one produces 1,3-dicarboxyneodiisophora-2,7-diene (or its esters) by a ring-contraction of the *Favorski*-type; the products are derivatives of tricyclo[6.3.1.$0^{2,6}$]dodecane. Hydriodic acid converts the dienedioic acid by partial saturation of the conjugated 2,7-diene system into the 2(7)-mono-olefinic dioic acid; the carboxyl groups of both series of compounds undergo esterification, anhydride formation and reduction in the normal manner. The ^{13}C nmr spectra of the novel ring-contracted compounds are interpreted, chiefly by reference to those of their diisophorone-precursors, as are their fragmentation patterns under electron impact.

(Keywords: Diisophorone, Favorski ring contraction thereof; "Neodiisophorones"; Tricyclo[6,3,1,$0^{2,6}$]dodecanes; 4,8-Methano-1H-cyclopentacyclooctenes)

Diisophoron und verwandte Verbindungen, 18. Mitt.: Ringverengung in Diisophoron mittels Favorski Reaktion

4,8-Dibromdiisophor-2(7)-en-3-on-1-carbonsäure wird von Alkalien oder Natriumalkoholaten durch eine *Favorski*-artige Ringverengung in Neodiisophora-2,7-dien-1,3-dicarbonsäure (oder deren Ester) verwandelt; die Reaktionsprodukte sind Abkömmlinge des Tricyclo[6.3.1.$0^{2,6}$] dodekans. Partielle Sättigung der konjugierten Doppelbindungen mittels Iodwasserstoffsäure ergibt die entsprechenden 2(7)-Mono-olefine. Veresterung, Anhydridbildung und Reduktion der Carboxylgruppen beider Verbindungsreihen verlaufen normal. Die ^{13}C-Kernresonanz- und Massenspektren der neuen Strukturen werden auf Grund bekannter Spektren der verwandten Diisophoron-Reihe gedeutet.

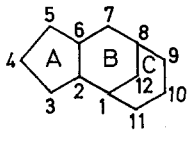
Introduction

The action of nucleophilic reagents on halogenated diisophorones is a versatile method of modifying the substituents, configuration, and degree of unsaturation in this molecular pattern. The diversity of the trans-

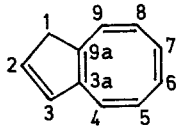
formations that may be performed is exemplified by the nucleophilic reactions undergone by 1-chloro-, 4- and 8-monobromo- and 4,8-dibromo-diisophorones (for references, see Part 17 [1]). In all these examples the ring-system of the reacting species is preserved.

We now describe a reaction of this category which features a rearrangement of the carbon skeleton by a ring-contraction of the *Favorski* type [2–4]. It occurs when 4,8-dibromodiisophor-2(7)-en-3-one-1-carboxylic acid (**2**) is acted upon by strong alkali or alkoxides and involves the conversion of the tricyclo[7.3.1.$0^{2,7}$] tridecane structure of the reactant into the tricyclo[6.3.1.$0^{2,6}$]dodecane ring-system (**A**) of the products. It thus differs strikingly from comparable nucleophilic reactions [1], especially from that of the closely related 4,8-dibromoketol (**1**), which yields the 3,4-diketone (**15**) with retention of the diisophorone ring-structure [5].

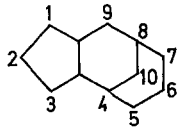
Nomenclature. According to *Baeyer's* nomenclature [6] of bridged polycyclic ring-systems, the rearranged parent hydrocarbon is named tricyclo[6.3.1.$0^{2,6}$]dodecane and is numbered as shown (**A**). The IUPAC notation [7], favoured for abstracting purposes, selects the fully unsaturated hydrocarbon, 1*H*-cyclopentacyclooctene (**B**), as the root of the systematic name and, employing a different order of numbering, designates **C** as 2,3,3a,4,5,6,7,8,9,9a-decahydro-4,8-methano-1*H*-cyclopentacyclooctene. With the further addition of five methyl-substituents and the functional groups, both systematic names are excessively unwieldy and unsuitable for any but archival use. Following our proposals [8] for diisophoranes, we therefore adopt a trivial name, *neodiisophorane,* for the present ring-system, with *inclusion* of the five peripheral methyl groups (**D**), and adjust the numbering so as to preserve maximum comparability of the ring-contracted structures and their diisophorone precursors, especially for the purpose of collating their assigned ^{13}C-nmr spectra. For indexing, the systematic IUPAC names of two key-compounds (**4**, **9**) are included (see Experimental).



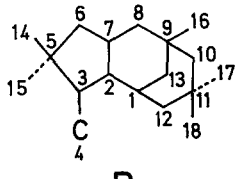
A



B



C



D

Stereochemical Aspects. The cyclopentene-ring of the neodiisophor-2(7)-ene molecule (e.g. **9**, **11**) may assume two conformations, in which its 5-carbon (bearing the 14- and 15-methyl groups) appears above or below the plane of rings A/B*: the two stereoisomers are interconvertible by the displacement ("flipping") of the C-5 apex of their five-membered ring A. As in diisophorones [1, 9], the former is likely to be the preferred conformation, the latter being disfavoured by the close approach of its 15α-quasi-ax-methyl to the 17-methyl group. In the prevalent stereoisomer, a 3-substituent (as in **9**, **11**) thus appears in the 3α-quasi-ax [10] or 3β-quasi-eq, and the components of the 5-gem-dimethyl-group in the 14β-quasi-ax and 15α-quasi-eq configuration, respectively. In the 2,7-dienes (e.g. **4**, **12**), the conjugated double bond system extends the planarity of rings A/B to include carbon atom C-5 as well, so that the 14β- and 15α-methyl groups now assume spatial positions virtually equivalent with respect to the cyclopenteno-ring.

Results and Discussion

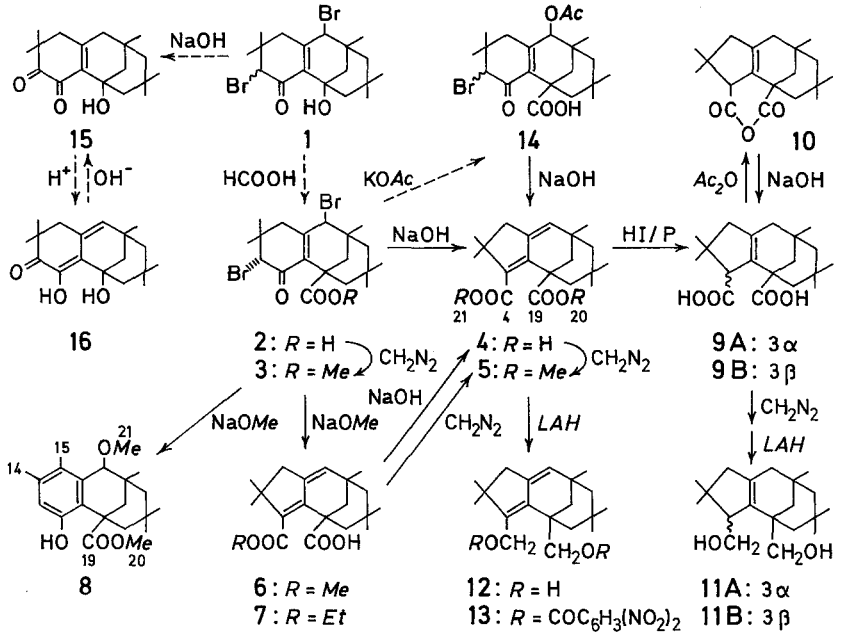
The action of sodium hydroxide on 4,8-dibromo-1-carboxydiisophor-2(7)-en-3-one (**2**) gave a product ($C_{19}H_{26}O_4$) arising by the net replacement of the halogen by two hydroxyl-groups and simultaneous loss of the elements of water. The action of sodium methoxide or ethoxide yielded the corresponding homologues. Their formulation as tricyclo[6.3.1.$0^{2,6}$]dodecanes (**4–7**) is based partly on their spectral and chemical properties, and partly on a systematic reasoning eliminating possible structures retaining the tricyclo[7.3.1.$0^{2,7}$]tridecane carbon skeleton of the starting material.

The alkaline hydrolysis product (**4**) of the 4,8-dibromo-acid (**2**) had the following properties: On treatment with an excess of diazomethane it gave a dimethyl-homologue, from which the starting material was recoverable by alkaline hydrolysis. This observation, and the fact that alcohols are inert towards diazomethane except in the presence of *Lewis* acid catalysts [11], suggest strongly that the methylation product is the diester **5** of the dicarboxylic acid **4**. The non-hydroxylic character of this parent acid is confirmed by the absence, in its ir spectrum, of a strong peak near 3 500 cm^{-1} characteristic of 1- [8], 4- [12] and 8-hydroxydiisophorones [13] and by its inability to yield acyl-derivatives under standard conditions. The removal of the keto-function during its formation is indicated by its failure to form a dinitrophenylhydrazone.

The action of hydriodic acid and red phosphorus on the 2,7-diene-1,3-dicarboxylic acid (**4**) converted its heteroannular 2,7-diene system into the isolated bridged double bond (of **9**), which in accordance with its demonstrated inertness [8], resisted further attack. The concomitant introduction of a new centre of asymmetry at C-3 accounts for the pro-

* In this and the ensuing discussion, rings A/B serve as the plane of reference, the position of ring C being specified as *below* this plane.

Scheme 1



duction of two stereoisomers (**9 A**, **B**). The minor 1,3 β-eq-epimer (**9 B**, m.p. 248–250°) was readily converted into the anhydride (**10**, 75%), from which the starting material was recoverable by alkaline hydrolysis. The dehydration is facilitated by the spatial disposition of the 1- and 3-carboxyl-groups, which emerge parallel to one another ca. 2.7 Å apart, and are almost co-planar with rings A/B. The major epimer (**9 A**, m.p. 202–204°), bearing its 3 α-ax-carboxyl-group in the conformation unfavourable for anhydride formation, failed to undergo dehydration.

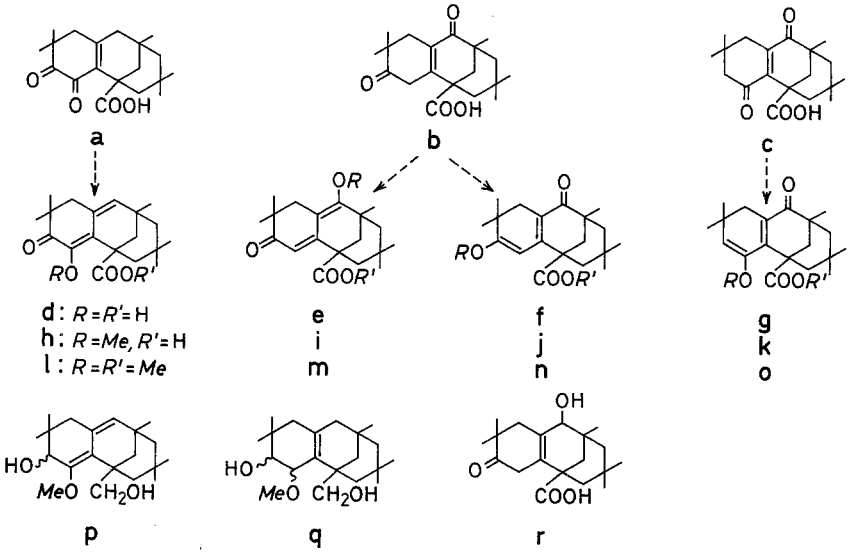
The reduction by lithium aluminium hydride of both the 2,7-diene-1,3-dicarboxylic acid (**4**) and its mono-olefinic analogue (**9**) provides information for rejecting their possible tricyclo[7.3.1.$0^{2,7}$]tridecane structures (see below). The key-compound of the series (**4**, used in the form of its dimethyl ester, **5**) gave the 1,3-bis-hydroxymethyl-compound (**12**), from which a diacyl-derivative (**13**) was obtainable. The epimeric mono-olefinic dicarboxylic acids (**9 A**, **B**) similarly gave the corresponding stereoisomeric primary alcohols **11 A** and **B**. The reagent thus conforms, as in the diisophorone series [14–16] to its usual action pattern of reducing carbonyl groups selectively, without affecting unsaturated carbon-carbon bonds [17].

The action of sodium alkoxides on the 4,8-dibromo-acid (**2**) was comparable to that of alkali in yielding the dicarboxylic acid mono-esters **6** and **7**. The methyl-homologue (**6**) was identified by its alkaline hydrolysis to the parent diacid (**4**), and by its conversion by one mole of diazomethane into the diester (**5**). The expectation that the diester **5** might therefore be directly accessible by methanolysis of the 4,8-dibromo-1-carboxylic methyl ester (**3**) was not realised, however: the reaction proceeded differently to yield the ring A-aromatised diisophorone **8**. The action of alkali on **3** gave only intractable resins.

The ^{1}H- and ^{13}C-nmr spectra, as well as the fragmentation patterns under electron impact of all the foregoing tricyclododecanes are compatible with their proposed structures, and indeed contributed to their adoption. For the sake of brevity, these data are discussed collectively below.

Since the available evidence for the proposed ring-contracted structures (**4**–**7**; **9**–**13**) does not amount to an incontrovertible proof, further support is adduced by the exclusion of any possible diisophorone structures for the compounds. This is particularly desirable, because the comparable action of alkali on 4,8-dibromodiisophor-2(7)-en-1-ol-3-one (**1**) proceeds by an SN 2″-mechanism without ring-contraction to yield 3,4-diketodiisophor-2(7)-en-1-ol (**15**), or the isomeric 4-keto-2,7-diene-1,3-diol (**16**) isolable in acid media [5]. The 4,8-dibromo-1-carboxylic acid (**2**) might therefore similarly produce the 3,4-diketo-acid **a** and thence its isomer **d**. Other feasible mechanisms can be devised (not detailed here) leading

Scheme 2

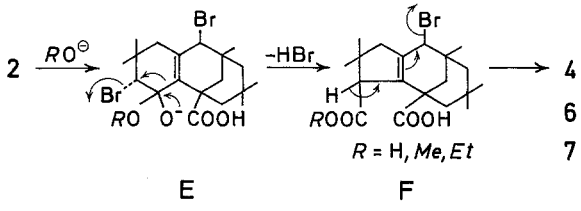


to structures **b** and **c** (and hence **e–g**) for the free acids, and **h–k** for their methyl-, and **l–o** for their dimethyl-homologues. *Each of these potential structures is compatible* with the observed molecular formulae and the first order multiplicities of the ^{13}C nmr signals of the compounds concerned.

That they are in fact inadmissible is shown by the results of the lithium aluminium hydride reductions. The arguments employed depend for their validity on the well-established fact [17], that methoxy-groups are not dealkylated by this reagent. The approach is exemplified by reference to the putative structures **d**, **h** and **l** derived from the 3,4-diketo-acid **a**: reduction of the dimethyl-homologue **l** of the diene **d** would yield **p** ($C_{20}H_{32}O_3$), in accord with the known reduction of cyclic keto- to secondary hydroxyl-groups in diisophorones [14–16]. Since its molecular formula differs from that of the reduction product actually obtained ($C_{19}H_{30}O_2$), structure **l** (and with it **d**) are rejected. Furthermore, on successive hydriodic acid and lithium aluminium hydride reduction (via the dimethyl-derivative), the diene **d** would yield **q**, differing again from the actual reaction product ($C_{19}H_{32}O_2$). Finally, the non-identity of authentic 3,4-diketodiisophor-2(7)-ene-1-carboxylic acid (**a**) [12] and the present hydrolysis product excludes structure **a** for the latter.

The same reasoning eliminates formulations derived from **b** and **c** (Scheme 2). An additional argument for rejecting all structures derived from **b** is their lack of a suitable 3-substituent capable of participating in the observed reversible dehydration of the tentative 2,7-mono-ene **r** (and its 4-hydroxy-8-keto-isomer).

Scheme 3



The reaction now described is an example of the ring-contraction undergone by alicyclic α-haloketones under basic conditions by the general *Favorski* rearrangement [2–4] and bears the closest resemblance to precedents in the steroid field [3, 18]. The observations are unified by a mechanism (Scheme 3, **2**→**E**→**F**) based on the well-documented semi-benzilic pathway [4]. Its adoption, rather than that of the more widely applicable symmetrical (cyclopropanone) pathway [4, 19] is dictated by the absence of an α-hydrogen atom at C-2 in the reactants (**2**, **3**), and thus identifies the present variant as a quasi-*Favorski* reaction [4]. The postulate that the α-halogen substituent of the reactant needs to be in the axial configuration for the operation of the mechanism [4, 20] may possibly be met by a transient conformational change in ring A. The simultaneous introduction of a second double bond (**F**→**4**) by the loss

of the 3-hydrogen- and 8-substituent (from **2** or **14**) appears to be an integral component of the process, without which ring-contraction is not effected.

In contrast, methanolysis of the 4,8-dibromo-1-carboxylic methyl ester (**3**) produced moderate yields of the ring A—aromatised product **8**. The location of its methoxy-substituent at C-8 is consistent with the superior reactivity of the 8- over the 4-bromo-substituent [1] and is confirmed by the appearance of two doublets in the ^{13}C-nmr spectrum of the product which would be absent in that of its 4-methoxy-isomer. The aromatisation is visualised to follow closely the mechanism proposed for the conversion of 8-bromodiisophor-2(7)-en-1-ol-3-one into 6-methyl-5-nordiisophora-2(7)-3,5-triene-1,3-diol [21].

The remarkably divergent course of the reactions of 4- and 8-mono- and 4,8-dibromo-diisophorones with alkalis under comparable conditions (for references, see Part 12 [12]), resulting in replacements with or without migration, aromatisation, or contraction of ring A, must ultimately be ascribed to the substitution pattern in the reactant. The limited information so far obtained suggests that a free 1-carboxy- and a suitable leaving group at C-8 promote the present ring contraction: changes in the former (e.g. to .COO*Me*, .OH), and absence of the latter divert the reaction into different mechanistic channels. An assessment of these effects in terms of their electronic, steric, and related factors is deferred until more examples are available for evaluation.

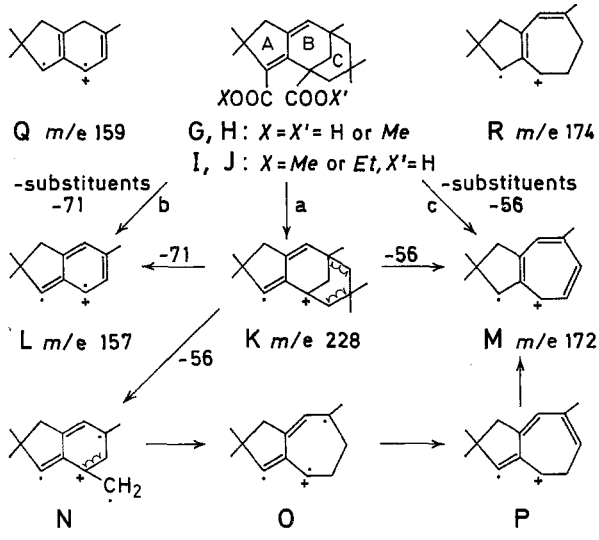
Mass Spectra

The fragmentation of the neodiisophoranes under electron impact conforms to a general pattern involving essentially the stepwise removal of the extranuclear substituents and loss of ring C. Although the sequence of these changes varies in detail for the individual compounds, a prominent feature common to all fragmentations is the emergence of the radical ions **K**, **L** and **M**. Their production by pathways **a–c** is traced, for the sake of brevity, in outline only (Scheme 4), but a more detailed sequence may in each case be constructed by reference to the mass-spectra of the individual compounds (see Experimental).

The formation of intermediate radical ions retaining the intact neodiisophorone structure, but stripped partly or wholly of its substituents (e.g. **K**), is indicated by the appropriate high intensity signals. The removal of ring C occurs by two separate pathways: the familiar [1, 22] loss from the dienes (**G–J**) of the neopentyl-radical (.CH_2CMe_3, *m*/e 71) results in the bicyclic fragment **L**, while extrusion of isopropylidene (*m*/e 56) produces the condensed tropylium species **M** (*m*/e 172), probably by successive homolytic ring cleavages and recyclisation (via **N**, **O**, **P**) of the

type suggested in Scheme 4. The same reaction sequences convert the 2(7)-mono-olefins (**9**, **10**, **11**) into the corresponding dihydro-analogues **Q** (*m*/e 159) and **R** (*m*/e 174); the latter is the predominating fission product in all examples, as shown by the maximum intensity of its signal. Since no peak corresponding to the exclusive loss of the neopentyl radical or isopropylidene ($M^{+\cdot}$—71 or 56) is found in any of the mass spectra, the removal of ring C occurs evidently in the later stages of the fragmentation. Except for the absence of the third alternative mode of ring C-degradation (by elimination of gem-dimethylcyclopropane, *m*/e 70), the behaviour of the neodiisophorones under electron impact thus resembles in its chief aspects that of the diisophorones.

Scheme 4



The proximity to each other of the two carboxyl-groups (in **4**) and the hydroxymethylene-groups (in **11**, **12**) promoted a dehydrative cyclisation of the molecular ions to internal anhydrides or ethers. Steric changes may attend this process, since surprisingly, the mono-unsaturated 1,3 β-dicarboxylic acid (**9 B**) did not produce a dehydrated radical ion, in spite of having its carboxyl-groups favourably disposed for cyclisation, and readily yielding an isolable anhydride (**10**) by chemical means (see above). This anhydride (**10**) displayed, incidentally, the least complex fragmentation pattern by a mass-spectrum comprising few but intense peaks. Attention is finally drawn to the near-identical fragmentation of epimer-pairs of both the 1,3-dicarboxylic acids (**9 A**, **B**) and the 1,3-di(hydroxymethyl)-derivatives (**11 A**, **B**) of the 2(7)-mono-olefins.

^{13}C-*Nmr Spectra*

The fully assigned ^{13}C-nmr spectra of the diisophorones [1, 9, 23, 24] provide guidelines for the interpretation of the spectra of the ring-contracted compounds, especially in respect of the bicyclo[3.3.1]nonane-moiety common to both structures. The numerical data are displayed in the usual manner [23, 24] in accordance with their proposed assignments (Table 2).

Singlets.—One of the low-field singlets (δ, ca. 176 ppm) matches that of the 1-carboxy-carbon (C-19) in diisophorones [24] and is assigned accordingly. Another singlet in this range (170 ppm) is similarly allotted to the 3-carboxy-carbon (C-4). The remaining low-field singlets associated with the carbon atoms flanking the double bonds in the 2(7)mono-olefins and 2,7-dienes are assigned as usual [23, 24], so as to reflect decreasing electron densities associated with C-3, C-2 and C-7. The singlets of C-1, C-9, and C-11 are identified by their close correspondence in chemical shift to those of diisophorone [23, 24].

The singlet of the bridgehead carbon (C-1) appears as expected [24] at 45 ppm in the spectra of the 1-carboxylic acids, and at 40 ppm in those of the 1-hydroxymethyl-compounds (**11**, **12**): the shielding of C-1 by the substituents .OH, .COOH, and .CH_2OH in both diisophorones and neo-diisophorones thus diminishes in the same order as in aliphatic quaternary carbon centres [25] in general, as is illustrated by the data for compounds **S** [26], **T** [27] and **U** [26].

	$Me_3\overset{*}{C}\cdot$ OH	$EtMe_2\overset{*}{C}\cdot$ COOR	$Me_3\overset{*}{C}\cdot$ CH_2OH
δ_{C^*}	68.7	R = H 42.7 R = *Me* 43.0	32.9
	S	**T**	**U**

In its altered structural environment, the C-5 carbon produces its signal at lower field (δ, 40–47 ppm) than in diisophorones (δ, 32–37 ppm [23, 24]). Its deshielding is ascribed chiefly to electron-withdrawal by the adjacent 3-carboxyl-group, reinforced by the conjugation in the 2,7-dienes; it recalls the comparable deshielding influence of the 4-keto-group in 3,4-diketodiisophorones [23, 24].

Doublets.—The sole doublet of the 2,7-dienes (due to C-8) appears near 133 ppm as expected [28]. In the 2(7)-mono-olefins (**9**, **11**), C-3 gives rise to its doublet at 58–64 ppm, implying a deshielding of this ring-carbon in the fused cyclopentene- compared with the cyclopentane-moiety (δ 43 ppm [29]); the configuration of the 3-substituent has only little effect.

Triplets.—Although the triplets are grouped within two narrow ranges of the spectrum, they can be assigned with some confidence as follows.

In the bicyclo[3.3.1]nonane moiety, the signals of C-12 (at 44–45 ppm), C-13 (42–44 ppm) and of C-10 (52–54 ppm) in the mono-olefins (**9**, **11**) are identifiable by their close match with those of corresponding diisophorone-1-carboxylic acids [24]. In the conjugated dienes (**4–7, 12**), the C-10 signal appears at slightly higher field (49 ppm). This leads, by exclusion, to the assignment of the remaining triplet to the C-6 ring carbon [at 47 and 51 ppm for the 2,7-dienes and 2(7)-mono-olefins, respectively]. In the 2(7)-mono-unsaturated series, a fifth triplet remains to be allocated to C-8; its appearance at higher field (ca. 40 ppm) in comparison with diisophorone-1-carboxylic acids (ca. 45 ppm [24]) is attributed to shielding due to the altered substitution pattern of the contracted ring A.

Of the two triplets of the extranuclear hydroxymethylene groups (of **11**, **12**), the one appearing constantly at ca. 71 ppm is clearly associated with the 19-methylene-carbon; its chemical shift matches that of the comparable 1-methylene-centre in 2,2-dimethylpropanol (δ, 73 ppm) [26, 30]. The resonance of the other triplet varies with the saturation of the C-3 ring-carbon, to which the CH_2OH-group is attached. The known chemical shift of the side-chain methylene-carbon in hydroxymethylpentane (δ, 66.7 ppm [31]) supports the assignment.

Quartets.—Three of the five quartets of the neodiisophorones are assignable to the extranuclear methyl groups (C-18, C-17 and C-16) on the basis of established precedents in the diisophorones [23, 24]. The general observation [23, 32] that equatorial methyl carbons of condensed cyclohexane systems resonate at lower field than axial ones, provides a means of provisionally identifying the remaining quartets associated with the 14 β-quasi-ax- and 15 α-quasi-eq-methyl groups. Their nearly equivalent position in the 2,7-dienes (**4–7, 12**) with respect to the more planar cyclopentene-ring (A) is reflected in the very small difference (1–1.5 ppm) in the chemical shifts of their quartets; these are assigned, albeit arbitrarily, to ensure maximum consistency within the series.

The quartets of the ester methyl-groups (in **5**, **6**) appear in the expected range [33]. Of the two very closely spaced signals of the diester **5**, that of the 3-methoxycarbonyl-group is traceable by the identity of its resonance and that of the singular quartet of the mono-ester **6**.

Conclusion

Information concerning tricyclo[6.3.1.$0^{2,6}$]dodecanes is sparse: the first member of this series, described in 1956 [34], remained the sole representative until 1967 [35]. More frequent encounters of this structure during the past 10 years have continued to be incidental rather than systematic, occurring generally in the course of wider studies of spectral [36], physical [37], and synthetic aspects [38] of related alicyclic systems, including ophiobolin-analogues [39]. In addition to its intrinsic interest,

the ring-contraction of diisophorones now described provides ready access to tricyclo[6.3.1.$0^{2,6}$]dodecanes, and a convenient entry for the further study of this ring-system.

Experimental

Standard procedures, reagents, solvents, and details of the spectroscopic equipment used are as given in Parts 17 [1], 12 [12], and previously [8]. Unassigned peaks of the i.r. spectra are not recorded except for some key-compounds.

2,7-Dienes

1,3-Dicarboxyneodiisophora-2,7-diene, 2,4,5,6,7,8-Hexahydro-2,2,6,6,8-pentamethyl-4,8-methano-1H-cyclopentacyclooctene-3,4-dicarboxylic acid (**4**)

(a) A solution of **2** (9.24 g, 0.02 mol) in 3 *N*-sodium hydroxide (27 ml, 0.08 mol)—water (81 ml) was boiled under reflux for 3 h. The yellow liquid gave, on acidification with 3 *N* hydrochloric acid, a granular precipitate, which was collected, washed with water (to neutrality) and air-dried (m.p. 190–200°, 5.7 g, 90%). Crystallisation from acetone (100 ml per g, recovery ca. 40%) gave white opaque granules of **4**, m.p. 215–218° (Found: C 71.4; H 8.6. $C_{19}H_{26}O_4$ requires C 71.7; H 8.2%). Soluble in cold *N* sodium hydroxide and reprecipitated by mineral acid. λ_{max} 291 nm (log ε 4.12); 204 (3.62). ν_{max} 3 460, 3 410 ms d, 965 w, 940 w br (? HO of COOH); 2 960 vs, 2 850 s br, 1 470 m, 1 425 ms (CH_3, CH_2); 2 650 m d (COOH); 1 710 vs, 1 670 vs, 1 645 m (CO of COOH); 1 595 ms br (C=C conjug); 1 300–1 275 s mult, 1 250 ms, 1 225 m br, 740 w cm^{-1}. *m/e* 318 w ($M^{+\cdot}$), 301 mw (*M*-17, OH), 300 s (*M*-18, H_2O), 285 ms (*M*-2 × 17 + 1), 272 mw (*M*-45, COOH-1), 257 mw (*M*-45 — 17 + 1), 256 mw (*M*-45 — 17), 230 s (*M*-71, C_5H_{11}-17), 216 s (*M*-56, C_4H_8-1), 201 s (*M*-71 — 45 — 1), 200 vs max (*M*-56 — 45 — 17), 172 ms (*M*-56 — 2 × 45), 157 vs (*M*-71 — 2 × 45).

The compound did not yield acyl-derivatives (benzoyl, 3,5-dinitrobenzoyl), or a 2,4-dinitrophenylhydrazone under standard conditions. It was unaffected when subjected to the *Koch-Haaf* carboxylation [13].

(b) *From 8-acetoxy-4-bromo-1-carboxydiisophor-2(7)-en-3-one* (**14**)

When **14** (0.88 g, 0.002 mol) was subjected to the action of boiling *N* sodium hydroxide (0.008 mol, 3 h), the crude product contained, according to its u.v. spectrum, much aromatised material. Crystallisation from acetone gave **4** (12–15%), identical with material obtained in (a). The non-uniform material from the crystallisation filtrate resinified, failing to afford any identifiable product.

1,3-Di(methoxycarbonyl)neodiisophora-2,7-diene (**5**)

(a) A suspension of (crude) **4** (6.35 g, 0.02 mol) in ether (150 ml) was slowly treated with etheral diazomethane (ca. 200 ml, from toluene-p-sulphonylmethylnitrosamide [11], "Diazald", 0.07 mol), when the reactant dissolved with brisk effervescence. After 3 hours' storage at room temperature, the excess of the reagent was destroyed with 3 *N* acetic acid, the ethereal phase washed neutral with 1.5 *M* sodium carbonate, then water, evaporated under reduced pressure, and the residual solidified oil dissolved in light petroleum (b.p. 40–60°). Successive crops of massive crystals (m.p. 106–110°, up to 4.8 g, 70%) gave, on recrystal-

Table 1. ^{1}H-Nmr *spectra of representative neodiisophorones*[a]

Compound	Signals			
5	5.54 s (1 H, —CH=)	3.67 s (3 H, O*Me*)	2.44 q (2 H, CH_2)	1.37 s (3 H, *Me*)
		3.59 s (3 H, O*Me*)	1.98 q (2 H, CH_2)	1.18 s (3 H, *Me*)
			1.77 (1 H, $\frac{1}{2}CH_2$)[b]	1.01 s (3 H, *Me*)
			1.72	0.94 s (3 H, *Me*)
				0.83 s (3 H, *Me*)
6	10.8 br (1 H, OH)	3.62 s (3 H, O*Me*)	2.42 q (2 H, CH_2)	1.38 s (3 H, *Me*)
	5.59 s (1 H, —CH=)		2.01 q (2 H, CH_2)	1.23 s (3 H, *Me*)
			1.78 (1 H, $\frac{1}{2}CH_2$)[b]	1.02 s (3 H, *Me*)
			1.73	0.94 s (3 H, *Me*)
				0.83 s (3 H, *Me*)
4	12.0 br (2 H, 2 OH)	—	2.32 q (2 H, CH_2)	1.28 s (3 H, *Me*)
	5.51 s (1 H, —CH=)		1.88 q (2 H, CH_2)	1.12 s (3 H, *Me*)
			1.64 (1 H, $\frac{1}{2}CH_2$)[b]	0.98 s (3 H, *Me*)
			1.5	0.88 s (3 H, *Me*)
				0.79 s (3 H, *Me*)

[a] Chemical shifts are in ppm (δ) from *TMS* as internal standard. Spectra of **5**, **6** determined in $CDCl_3$, of **4** in *DMSO-*d_6

[b] One half of the signal of the third methylene, and the whole signal of the fourth methylene group are obscured by the range of intense methyl singlets

Table 2. *Chemical shifts of* ^{13}C-nmr *signals of neodiisophorones and their assignments*

Compound[a]	C 1	C 2	C 3	C 4	C 5	C 6	C 7	C 8	C 9	C 10
4	45.3 s	144.9 s	140.8 s	168.8 s	47.4 s	47.2 t*	150.6 s	132.0 d	34.0 s	49.2 t
6[b]	44.7 s	144.0 s	137.4 s	171.7 s	47.2 s	46.3 t*	154.3 s	134.3 d	33.9 s	48.7 t
7[b]	44.7 s	143.8 s	137.3 s	171.3 s	47.0 s	46.3 t*	154.1 s	134.1 d	33.9 s	48.6 t
5[b]	44.8 s	143.7 s	137.9 s	166.0 s	46.9 s	46.2 t*	150.8 s	132.9 d	33.8 s	48.7 t
12	40.8 s	145.2 s	140.5 s	56.2 t	45.6 s	47.3 t*	145.4 s	126.9 d	33.4 s	49.4 t
9 A	47.0 s	134.8 s	64.1 d	175.6 s	41.4 s	50.8 t	140.6 s	40.0 t	31.0 s*	53.6 t
9 B	46.7 s	134.8 s	64.2 d	176.0 s	40.3 s	51.5 t	140.1 s	39.8 t	32.6 s	53.1 t
10	44.4 s$^+$	128.6 s	55.0 d	167.1 s	43.8 s$^+$	50.4 t	140.2 s	38.5 t	31.8 s	52.4 t
11 A	40.6 s$^+$	139.3 s	58.3 d	63.1 t	39.7 s$^+$	49.3 t	139.7 s	40.3 t	31.0 s*	53.9 t
11 B	41.1 s$^+$	135.3 s	57.7 d	61.6 t	39.8 s$^+$	51.6 t	141.6 s	40.7 t	30.6 s*	53.0 t

Compound[a]	C 11	C 12	C 13	C 14	C 15	C 16	C 17	C 18	C 19	C 20
4	30.7 s	45.2 t*	44.6 t*	27.8 q	29.3 q$^+$	29.9 q$^+$	30.4 q	38.1 q	178.3 s	
6[b]	30.4 s	45.0 t*	43.2 t*	27.3 q	28.9 q$^+$	29.2 q$^+$	30.0 q	37.7 q	176.2 s	
7[b]	30.4 s	44.9 t*	43.0 t*	27.2 q	28.9 q$^+$	29.2 q$^+$	30.0 q	37.7 q	175.5 s	
5[b]	30.3 s	44.7 t*	43.4 t*	27.3 q	28.9 q$^+$	29.2 q$^+$	30.0 q	37.7 q	176.2 s	50.4 q
12	30.9 s	46.8 t*	43.6 t*	27.8 q	28.8 q$^+$	29.4 q$^+$	30.5 q	37.7 q	71.3 t	
9 A	31.0 s*	45.8 t	42.0 t	25.6 q	31.2 q	29.4 q	33.5 q	38.1 q	178.6 s	
9 B	31.1 s	44.6 t	43.4 t	26.8 q	32.6 q	30.1 q	33.5 q	37.8 q	178.0 s	
10	30.9 s	42.6 t*	41.9 t*	24.4 q	27.9 q	28.2 q	32.7 q	36.9 q	172.1 s	
11 A	30.7 s*	45.3 t	42.8 t	24.2 q	31.9 q	28.7 q	33.6 q	37.6 q	70.9 t	
11 B	30.4 s*	43.6 t°	42.1 t°	26.1 q	31.6 q	30.3 q	33.1 q	37.2 q	71.1 t	

*+° Signals may be exchanged horizontally

[a] Spectra were determined in deuteriochloroform except those of **4**, **9 A**, **9 B**, and **10**, for which deuteriopyridine was used

[b] Additional signals: **6:** C 21, 51.8 q. **7:** C 21, 60.9 t; C 22, 14.0 q. **5:** C 21: 51.7 q

lisation from the same solvent, lustrous prisms of **5**, m.p. 112–114° (Found: C 72.6; H 8.7. $C_{21}H_{30}O_4$ requires C 72.8, H 8.7%). λ_{max} 295 nm (log ε 4.06), 204 (3.49). ν_{max} 2 950 vs–2 850 s, 1 460–1 440 vs (CH_3, CH_2), 1 735 vs, 1 715–1 705 vs d (CO of COO*Me*), 1 390 s, 1 360 s (.C*Me*$_2$), 1 250, 1 245, 1 225 vs br (C—O of ester), 1 585 ms (C=C conjug.), 1 300 vs, 1 280 vs, 1 155 vs, 1 120 vs, 1 065 vs cm^{-1}. *m/e* 346 m (M^+), 331 s (*M*-15, ?*Me*), 315 m (*M*-31, *Me*O), 287 vs (*M*-59, COO*Me*), 259 s (*M*-56, C_4H_8-31), 244 vs (*M*-71, C_5H_{11}-31), 243 s (*M*-71 — 31 — 1), 231 ms (*M*-56 — 59), 228 ms (*M*-2 × 59), 227 vs max (*M*-2 × 59 — 1), 216 vs (*M*-71 — 59), 215 vs (*M*-71 — 59 — 1), 171 s (*M*-56 — 2 × 59 — 1), 157 s (*M*-71 — 2 × 59), 288 m, 271 s, 229 s.

(b) Treatment of a solution of the monomethyl ester **6** (see below, 3.32 g, 0.01 mol) in ether (150 ml) with ethereal diazomethane (from "Diazald", 0.05 mol), and isolation as described for (a) gave **5** as massive prisms (2.8 g, 80%), identical (mixed m.p. 112–114°, i.r.) with material prepared in (a).

(c) *Alkaline hydrolysis of* **5**. A solution of **5** (1.73 g, 0.005 mol) in hot ethanol (35 ml), treated with 5 *N* aqueous sodium hydroxide (10 ml, 0.05 mol) was boiled under reflux for 1.5 h. The deep yellow liquid was distilled to half volume and added to ice—hydrochloric acid (0.05 mol). The precipitate gave, on crystallisation from ethanol—light petroleum, microcrystalline **4**, identified by its i.r. spectrum (see above) (total, 0.67 g, 42%). Spontaneous evaporation of the final mother liquors gave an orange sticky resin.

(d) *Attempted acid hydrolysis*. A solution of **5** (1.73 g, 0.005 mol) in hot glacial acetic acid (15 ml) was slowly treated with concentrated hydrochloric acid (8 ml) and boiled under reflux for 2 h. Addition of the orange-yellow solution to ice-water (200 ml) gave a yellow soft precipitate which solidified when suspended in water. This was mostly unchanged starting material (by i.r., recovery 75%), but gave, on dissolution in light petroleum (b.p. 40–60°, with addition of a little acetone), a small first crop (0.1 g, 6%) of **4** (identified by mixed m.p. 205–208° and i.r.). Spontaneous evaporation of the filtrates gave glass-like prisms of **5**. It is noteworthy that **5** shows behaviour opposite to that of 1-methoxycarbonyl-diisophor-2(7)-en-3-one [12] which is readily hydrolysed under the above acid [40] but not under alkaline conditions.

1-Carboxy-3-methoxycarbonylneodiisophora-2,7-diene (**6**)

(a) *Preparation*. A solution of **2** (4.62 g, 0.01 mol) in warm methanol (60 ml) was treated with one of sodium (1.0 g, 0.044 g · atom) in methanol (40 ml). The pale-yellow liquid was boiled under reflux for 6 h, distilled to one third bulk under reduced pressure and stirred into ice (300 g)—concentrated hydrochloric acid (10 ml). The soft precipitate, hardening to a white mass (m.p. 128–135°, above 3 g, 90%), gave on crystallisation from light petroleum (15–20 ml per g, recovery ca. 60%), lustrous massive prisms of **6**, m.p. 160–163° (Found: C 72.5; H 9.0. $C_{20}H_{28}O_4$ requires C 72.3; H 8.4%).

λ_{max} 291 nm (log ε 4.12), 205 (3.57). ν_{max} 3 500 m, 960–945 s br (? HO of COOH); 2 980 vs (centre of v br peak), 1 465, 1 440, 1 420 vs br mult (CH_3, CH_2) 2 660, 2 580 s br (COOH), 1 740–1 720 vs br (CO of COO*Me*), 1 680–1 660 vs br (CO of COOH), 1 585 vs (C=C conjug.), 1 390, 1 365 s (.C*Me*$_2$), 1 300–1 285 vs br, 1 250–1 220 vs br mult, 755 vs cm^{-1}. *m/e* 332 vs (M^+), 317 vs (*M*-15, ?*Me*), 301 w (*M*-31, *Me*O), 300 s (*M*-31 — 1), 287 w (*M*-45, COOH), 273 vs (*M*-59, COO*Me*), 257 s (*M*-45 — 31 + 1), 245 s (*M*-56, C_4H_8-31), 244 vs max (*M*-71, C_5H_{11}-17), 230 vs (*M*-71 — 31), 229 vs (*M*-71 — 31 — 1), 217 s (*M*-56 — 59), 216 s (*M*-71 — 45), 215 vs (*M*-71 — 45 — 1), 171 vs (*M*-56 — 59 — 45 — 1), 157 vs (*M*-71 — 59 — 45), 314 w, 239 s.

(b) *Alkaline hydrolysis.* A solution of **6** (1.66 g, 0.005 mol) in ethanol (35 ml)—5 *N* aqueous sodium hydroxide (0.05 mol) was boiled under reflux for 1.5 h, the pale-yellow liquid distilled to half volume under reduced pressure and stirred into ice-water containing concentrated hydrochloric acid (5 ml). The white gelatinous precipitate gave, on dissolution in acetone (50 ml), successive crops (1.05–1.2 g, 66–75%) of microcrystalline **4**, identical (i.r.) with material obtained from **2**.

1-Carboxy-3-ethoxycarbonylneodiisophora-2,7-diene (**7**)

A solution of **2** (4.62 g, 0.01 mol) in warm ethanol (60 ml) was treated with one of sodium (1.0 g, 0.044 g · atom) in ethanol (45 ml), and boiled under reflux for 6 h (separation of white solid and severe "bumping"). The crude product was isolated as a resinous precipitate (as described for **6**) and afforded small prisms (above 75%) of **7**, m.p. 164–166° (from light petroleum). (Found: C 72.5; H 8.6. $C_{21}H_{30}O_4$ requires C 72.8; H 8.7%). λ_{max} 292 nm (log ε 4.15); 204 (3.63). ν_{max} 3 450 m, 950, 965 mw (? HO of COOH), 2 950 vs (centre of v br peak), 1 470–1 445 ms, 1 420 s mult (CH_3, CH_2), 2 650–2 550 ms (COOH), 1 730 vs (CO of COO*Et*), 1 670 vs br (CO of COOH), 1 585 vs (C=C conjug.), 1 390, 1 365 m (.CMe_2), 1 295, 1 275, 1 235, 1 220 vs mult cm^{-1}.

m/e: 346 m ($M^{+\cdot}$), 331 m (*M*-15, ?*Me*), 301 w (*M*-45, *Et*O), 300 ms (*M*-45 — 1), 286 w (*M*-45, COOH-15), 285 ms (*M*-45 — 15 — 1), 273 ms (*M*-73, COO*Et*), 256 m (*M*-73 — 17, OH), 215 s (*M*-71, C_5H_{11}-45 — 15), 213 m (*M*-71 — 45 — 17), 201 s (*M*-56, C_4H_8 — 2 × 45 + 1), 200 vs max (*M*-56 — 2 × 45), 172 m (*M*-56 — 73 — 45), 171 m (*M*-56 — 73 — 45 — 1), 157 s (*M*-71 — 73 — 45). The initial loss of 45 mass units (*m*/e = 301) is assigned to *Et*O rather than COOH because of the subsequent appearance of a fragment (*m*/e 273) retaining COOH.

3-Hydroxy-8-methoxy-1-methoxycarbonyl-6-methyl-5-nordiisophora-2(7)-3,5-triene (**8**)

A solution of **3** (4.76 g, 0.01 mol) in methanol (60 ml) was treated with one of sodium (0.5 g, 0.022 g·atom) in methanol (40 ml) and boiled under reflux for 4 h. The yellow liquid was evaporated to half volume and stirred into ice-water containing 3 *N* hydrochloric acid (10 ml). The (air-dried) white precipitate (m.p. 136–154°, 3.5 g) gave, after two crystallisations from acetone-light petroleum (12 and 4 ml per g), needles (0.85–1.05 g, 25–30%) of **8**, m.p. 203–204° (filtrates, F) (Found: C 73.3; H 8.8. $C_{21}H_{30}O_4$ requires C 72.8; H 8.7%). λ_{max} 214 nm (log ε 4.02), 288, 293 (3.48, 3.49), λ_{infl} 225 (3.86). ν_{max} 3 330, 3 270 vs (OH), 2 950–2 850 vs, 1 475, 1 450, 1 435, 1 420 m mult (CH_3, CH_2), 1 735 vs (CO of COO*Me*), 1 250 s–1 240 vs (C—O of COO*Me*) cm^{-1}. For ^{13}C nmr and mass spectra, see Part 19, forthcoming. Filtrate F gave only sticky orange resins from which no identifiable derivatives could be isolated.

1,3-Di(hydroxymethyl)neodiisophora-2,7-diene (**12**)

To a stirred suspension of lithium aluminium hydride (3.80 g, 0.1 mol) in anhydrous ether (250 ml) was added dropwise during 30 min a solution of **5** (3.46 g, 0.01 mol) in anhydrous ether (120 ml) at room temperature, and the mixture boiled under reflux for 2 h. The excess of the lithium aluminium hydride was destroyed by the successive addition of ether saturated with water (250 ml), and 3 *N* hydrochloric acid (150 ml, to acidity). The aqueous phase was extracted twice more with ether, the ethereal solution washed to neutrality with 1.5 *M*

sodium carbonate and water, and dried over anhydrous sodium sulphate. Removal of the solvent gave a nearly colourless oil, solidifying on storage, which produced on crystallisation from light petroleum, massive prisms (2.1 g, 72%) of **12**, m.p. 115–117°. (Found: C 78.6; H 10.5. $C_{19}H_{30}O_2$ requires C 78.6; H 10.3%). λ_{max} 260 nm (log ε 4.15, broad), λ_{infl} 208 (3.55). ν_{max} 3 235 vs br (OH), 2 950–2 870 vs, 1 465 vs–1 435 s mult (CH_3, CH_2), 1 395 w, 1 370 ms (.C*Me*$_2$), 1 060 vs br, 1 040 vs, 995 vs cm^{-1}. *m*/e 290 vs max ($M^{+\cdot}$, unusually intense), 272 ms (*M*-18, H_2O), 259 ms (*M*-31, CH_2OH), 242 ms (*M*-31 — 17, OH), 228 ms (*M*-2 × 31), 201 mw (*M*-71, C_5H_{11}-18), 186 s (*M*-56, C_4H_8-31 — 17), 173 m (*M*-56 — 2 × 31 + 1), 171 s (*M*-71 — 31 — 17), 157 ms (*M*-71 — 2 × 31), 275 ms, 257 m, 244 ms, 187 m, 185 m, 159 s.

1,3-Bis-3′,5′-dinitrobenzoate (**13**). A solution of **12** (0.29 g, 0.001 mol) in pyridine (8 ml), treated with 3,5-dinitrobenzoyl chloride (0.58 g, 0.0025 mol) was kept at 100° for 1 h, then stirred into ice-water containing concentrated hydrochloric acid (8 ml). The collected precipitate was rinsed with 1.5 *M* sodium bicarbonate, then water (to neutrality) and gave yellow prisms (50–60%) of **13**, m.p. 166–168° (from acetone-ethanol, 1 : 2) (Found: C 58.5; H 5.3; N 7.9. $C_{33}H_{34}N_4O_{12}$ requires C 58.4; H 5.0; N 8.3%). ν_{max} 2 970 vs–2 880 s, 1 490 m, 1 465 s (CH_3, CH_2), 1 740 vs br (CO, diester), 1 635 s (C=C conjug.), 1 555 vs br, 1 350 vs, 730, 720 vs d (NO_2), 1 290–1 280 vs br (C—O of diester) cm^{-1}.

2(7)-Monoolefins

1,3-Dicarboxyneodiisophor-2(7)-ene; 2,3,4,5,6,7,8,9-Octahydro-2,2,6,6,8-pentamethyl-4,8-methano-1H-cyclopentacyclooctene-3,4-dicarboxylic acid (**9**)

A solution of **4** (crude, 4.80 g, 0.015 mol) in hot glacial acetic acid (60 ml), treated with red phosphorus (1.4 g, 0.045 g·atom) and 66% hydriodic acid (24 ml), was refluxed for 5 h. The undissolved dark purple solid was filtered off at the pump and the dark-red filtrate stirred into ice-water (750 ml). The collected pale-yellow precipitate was washed with water and air-dried (3.6–4.1 g, 75–85%). Its solution in ethanol-light petroleum (ca. 30 and 10 ml respectively) deposited 4–5 successive crystalline crops.

The first 2 or 3 fractions (m.p. 240–248°, 0.95–1.20 g, 20–25%) gave minute prisms of the *1,3 β-dicarboxylic acid* (**9 B**), m.p. 248–250° (from acetone—ethanol) (Found: C 70.9; H 8.75. $C_{19}H_{28}O_4$ requires C 71.25; H 8.75%). λ_{max} 209 nm (log ε 3.67). ν_{max} 3 450 ms, 935 ms vbr (?HO of COOH), 2 965–2 890 vs, 1 470 ms, 1 445 ms, 1 425 ms (CH_3, CH_2), 2 680, 2 560 ms br (COOH), 1 725 vs, 1 705 sh vbr (CO of COOH), 1 395 m, 1 370 ms (.C*Me*$_2$), 1 350 ms, 1 285 s br, 1 250 s, 1 230, 1 220 ms d, 830 mw, 750 w, 730 ms, 695 w, 680 w cm^{-1}. *m*/e 320 vw ($M^{+\cdot}$), 303 w (*M*-17, OH), 275 m (*M*-45, COOH), 231 s (*M*-2 × 45 + 1), 215 m (*M*-71, C_5H_{11}-2 × 17), 187 w (*M*-71 — 45 — 17), 174 vs max (*M*-56, C_4H_8-2 × 45), 159 m (*M*-71 — 2 × 45), 260 mw.

The final 2 or 3 fractions (m.p. ca. 200°, 1.70–2.15 g, 35–45%) gave white opaque microprisms of the *1,3 α-dicarboxylic acid* (**9 A**), m.p. 202–204° (from ethanol) (Found: C 70.5; H 8.5%). λ_{max} 210 nm (log ε 3.51). ν_{max} 3 460–3 420 m, 935 ms vbr (?HO of COOH), 2 965–2 900 vs, 1 465 ms, 1 425 ms br (CH_3, CH_2), 2 660, 2 540 m br (COOH), 1 715 vs vbr (CO of COOH), 1 395 m, 1 370 ms (.C*Me*$_2$), 1 290, 1 280 s d, 1 230–1 220 ms br, 725–710 mw br, 685 w cm^{-1}. *m*/e 320 vw ($M^{+\cdot}$), 303 s (*M*-17), 275 s (*M*-45), 231 ms (*M*-2 × 45 + 1), 216 m (*M*-71-2 × 17 + 1), 204 m (*M*-71 — 45), 174 vs max (*M*-56-2 × 45), 159 m (*M*-71-2 × 45), 260 ms, 218 s.

The ultimate filtrates gave on spontaneous evaporation at room temperature

clear yellow resins, from which no further solid was directly isolable. Successive esterification with diazomethane and reduction with lithium aluminium hydride of this resin by the procedure given below afforded small additional yields (3–5%), in the form of **11 A**, m.p. 154–157°, the bulk of the residues remaining an intractable resin.

The use of smaller proportions of red phosphorus (1.5 g·atom) and shorter times of refluxing (1 h) gave essentially similar but less satisfactory results: the products were darker in colour and fractionation into **9 A** and **9 B** was less clear-cut.

1,3β-Dicarboxylic acid (**9 B**): *Anhydride formation.* A solution of **9 B** (1.6 g, 0.005 mol) in glacial acetic acid—acetic anhydride (15 ml each) was boiled under reflux for 2 h, and the pale-yellow liquid stirred into warm water (200 ml). The solidified oil gave, on crystallization from methanol—water (8 and 1 ml), hexagonal platelets (1.12 g, 75%) of the *1,3β-anhydride* (**10**), m.p. 74–75° (Found: C 75.0; H 8.9. $C_{19}H_{26}O_3$ requires C 75.5; H 8.6%). ν_{max} 2 965–2 910 vs vbr mult, 1 475–1 450 s mult (CH_3, CH_2), 1 815–1 805 vs br, 1 770–1 760 vs (CO of CO.O.CO), 1 390, 1 370 s (.CMe_2), 1 240–1 230 vs br (?C—O of CO.O.CO) cm^{-1}. *m/e* 302 w ($M^{+\cdot}$), 274 m (*M*-28, CO), 259 mw (*M*-44, COO + 1), 231 vs (*M*-72, CO.O.CO + 1), 215 s (*M*-71, C_5H_{11}-16), 175 s (*M*-56, C_4H_8—72 + 1), 174 vs max (*M*-56 — 72), 159 s (*M*-71 — 72). The filtrates deposited unchanged starting material (up to 12%).

The 1,3α-epimer (**9 A**) failed to yield an anhydride under the identical conditions, being partly recovered (ca. 30%) and partly converted into intractable colourless resins.

Reconversion into the 1,3β-dicarboxylic acid (**9 B**). A solution of **10** (0.60 g, 0.002 mol) in ethanol (4 ml)-3 *N* sodium hydroxide (4 ml) was boiled under reflux for 1 h, then stirred into ice-water acidified with 3 *N* hydrochloric acid (8 ml). The white precipitate, coagulating on warming, was **9 B**, m.p. 246–252° (from ethanol) (80%), identified by i.r.

1,3β-Di(hydroxymethyl)neodiisophor-2(7)-ene (**11 B**)

A suspension of **9 B** (1.60 g, 0.005 mol) in ether (30 ml, in which it is sparingly soluble) was treated with ethereal diazomethane (from "Diazald" [11] 0.04 mol), when the reactant dissolved with effervescence. The usual work-up (see above) gave the crude methyl ester as a colourless viscous oil, tending to solidify to a low-melting solid on prolonged storage, but reverting to the liquid state on contact with solvents. Accordingly, it was dissolved in anhydrous ether (60–80 ml), and added dropwise at room temperature during 15–20 min to a stirred suspension of lithium aluminium hydride (1.9 g, 0.05 mol) in ether (150 ml), which was then boiled under reflux for 2 h. The usual isolation procedure (see **12** above) gave a white solid affording, on crystallisation from light petroleum (60–80 ml, in portions) silky felted needles (1.25 g, 85%) of **11 B**, m.p. 114–116° (Found: C 78.0; H 11.0. $C_{19}H_{32}O_2$ requires C 78.1; H 11.0%). λ_{max} 211 nm (log ε 3.64). ν_{max} 3 355, 3 325, 3 295 vs (OH), 2 955–2 850 vs, 1 475–1 440 s mult (CH_3, CH_2), 1 370 s (.CMe_2), 2 835 s sh, 1 230 m, 1 060 vs, 1 025 vs, 1 010 vs, 985 m, 940 w, 910 w, 675 m cm^{-1}. *m/e* 292 vw ($M^{+\cdot}$), 274 vs (*M*-18, H_2O), 262 vs (*M*-31, CH_2OH + 1), 261 vs (*M*-31), 244 s (*M*-31 — 17), 243 s (*M*-31 — 17 — 1), 230 m (*M*-2 × 31), 187 s (*M*-71, C_5H_{11}-2 × 17), 174 vs max (*M*-56, C_4H_8—2 × 31), 172 s (*M*-56-2 × 31 — 2), 159 s (*M*-71-2 × 31), 232 m, 185 vs.

1,3α-Di(hydroxymethyl)neodiisophor-2(7)-ene (**11 A**)

The use of the 1,3α-dicarboxylic acid (**9 A**) (0.005 mol, which was readily ether-soluble) in the foregoing two-stage process (diazomethane uptake faster)

gave a residual solid which produced, on crystallisation from acetone-light petroleum (ca. 20 and 40 ml), fluffy felted needles (1.25 g, 85%) of **11 A**, m.p. 155–157° (Found: C 79.2; H 11.6%). λ_{max} 211 nm (log ε 3.57). ν_{max} 3 305 vs br (OH), 2 955–2 865 vs mult, 1 485–1 460 ms (CH_3, CH_2), 1 390 w, 1 375 ms (CMe_2), 1 305, 1 275, 1 255 m (diagnostic peaks absent in 1,3 β-isomer), 2 820 s, 1 230 m, 1 055 s, 1 020 vs, 920 mw, 685 mw cm^{-1}. *m/e* 292 vw ($M^{+\cdot}$), 275 m (*M*-17), 274 vs max (*M*-18), 262 vs (*M*-31 + 1), 244 s (*M*-31 — 17), 230 vw (*M*-2 × 31), 204 w (*M*-71 — 17), 187 ms (*M*-71-2 × 17), 174 s (*M*-56 — 31), 159 ms (*M*-71-2 × 31), 246 ms, 232 w and very numerous strong to medium peaks below 159.

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