Monatshefte für Chemie 116, 777—787 (1985)

Monatshefte für Chemie
Chemical Monthly

Diisophorone and Related Compounds. Part 15[1] 2,7-Epoxydiisophoranes: Oxirane Cleavage by *Grignard* Reagents

Anthony A. Allen and **Frederick Kurzer***

Royal Free Hospital School of Medicine (University of London),
London NW3 2PF, England

(Received 6 September 1984. Accepted 3 October 1984)

Grignard reagents cleave the oxirane ring of 2,7-epoxydiisophoran-1-ol producing diisophor-7-ene-1,2-diol, the formulation of which is in accord with its ^{13}C-nmr spectrum, and its further reactions. It yields a 1,2-cyclic sulphite ester, a 7,8-epoxide, and is converted into 1-acetoxydiisophora-2,7-diene by acetic anhydride, and into diisophor-2(7)-en-1-ol by successive dehydration and hydrogenation. Its allylic hydroxylation by selenium dioxide is attended by dehydration, producing moderate yields of diisophora-2,7-diene-1,6-diol.

(Keywords: 2,7-Epoxydiisophoran-1-ol, action of Grignard reagents on; Diisophora-2,7-dienes, ^{13}C-nmr spectra thereof; Tricyclo[7.3.1.0^{2,7}]tridecanes)

Diisophoron und verwandte Verbindungen. 15. Mitt.
2,7-Epoxydiisophorane: Oxiranspaltung mittels Grignard-Verbindungen

2,7-Epoxydiisophoran-1-ol wird von *Grignard*-Verbindungen unter Spaltung des Oxiranringes in Diisophor-7-en-1,2-diol umgewandelt, dessen Struktur durch sein ^{13}C-Kernresonanz-Spektrum und seine weiteren Umsetzungen bewiesen wird: Es bildet einen cyklischen 1,2-Sulphit-Ester, ein 7,8-Epoxyd, und wird von Essigsäureanhydrid in 1-Acetoxydiisophora-2,7-dien sowie durch aufeinanderfolgende Wasserabspaltung und katalytische Hydrierung in Diisophor-2(7)-en-1-ol umgewandelt. Hydroxylierung in Allyl-Stellung durch Selendioxyd ergibt unter gleichzeitiger Wasserabspaltung geringe Ausbeuten von Diisophora-2,7-dien-1,6-diol.

Introduction

In continuation of our examination[2,3] of possible methods for the removal, from the diisophorone structure, of the inert 2,7-olefinic bond joining its condensed cyclohexane rings A and B[4], we have studied the action of *Grignard* reagents on the readily accessible 2,7-epoxydiisophoran-1-ol[2]. The reaction has proved effective for the intended purpose, though in a manner different from that envisaged.

Results and Discussion

Oxiranes undergo several types of conversions with *Grignard* reagents[5–8]. The precedents, especially those in the sterol series[6], suggested that the reaction might introduce angular alkyl (or aryl) substituents into the diisophorane structure at C-2 or C-7, with retention of a saturated bond in this position. In order to confine the action to the oxirane moiety, a representative lacking keto-groups, viz. 2,7-epoxydiisophoran-1-ol[2] (**1**) was selected as the model compound. In the event, the reaction took an unexpected course, resulting irrespective of the *Grignard* reagent employed, in the same net isomerisation.

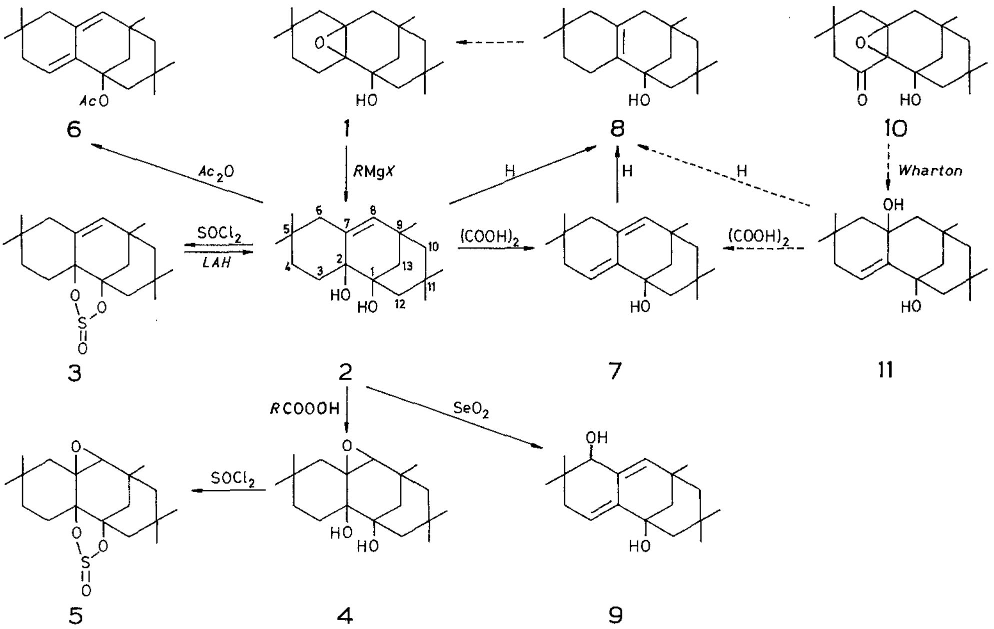
Thus, the interaction of **1** with methyl, ethyl or phenyl magnesium halide gave the same product, $C_{18}H_{30}O_2$, which is formulated, in accordance with its properties, as diisophor-7-ene-1,2-diol (**2**). It was produced most conveniently in 60–70% yield by the use of ethylmagnesium bromide. Its formation in moderate yield from **1** by the action of nascent aluminium hydride has already been briefly mentioned[2].

The ir spectrum of this diolene (**2**) contains, in addition to the usual alkane absorptions[4], strong peaks (at 3450, 3285 cm^{-1}) attributable to two hydroxy-groups. A band of moderate intensity at 845 cm^{-1} is possibly associated with a trisubstituted olefinic bond allylic to a hydroxy-group, the presence of which is also consistent[9] with the location and intensity of the uv absorption maximum (205 nm, $\log \varepsilon$ 3.68).

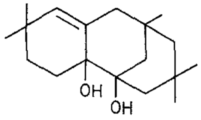
The structural assignment (to **2**) is based on its chemical behaviour and is in accord with ^{13}C-nmr spectral data (see below). The distinctness of the diolene (**2**) and the known[2] isomeric diisophor-2-ene-1,7-diol (**11**) immediately excluded this possible formulation.

On treatment with thionyl chloride in pyridine at 0°, the diolene (**2**) gave a cyclic sulphite ester (**3**), from which the starting material was recoverable by the action of lithium aluminium hydride (but not of lithium borohydride, the reagent normally preferred[10] for this purpose). This observation shows the close proximity of the two hydroxyl functions and suggests, in conjunction with other evidence (see below), that the newly introduced hydroxyl-group occupies the C-2 β-position. The olefinic bond in **2** was readily oxidised by 3-chloroperoxybenzoic acid[2]; the resulting 7,8-epoxide (**4**) gave, as did its precursor, a cyclic sulphite ester (**5**).

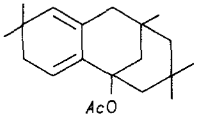
The action of boiling acetic anhydride on **2** produced, by simultaneous acetylation and dehydration, good yields of the conjugated diolefin, 1-acetoxydiisophora-2,7-diene (**6**). The heteroannular character of its diene-system is shown by the position of its uv absorption maximum (λ_{max} 246 nm) which agrees with the calculated value (244 nm)[11]. The isomeric homoannular diene structures (**6a**, **6b**), associated with a base value of 253 nm, are thus eliminated. The conjugated double bonds can be distributed in only one way over rings A and B in diisophoran-1-ols (viz. as 2,7-dienes, e.g. **6**, **9**), other alternatives being excluded by the presence of substituents.



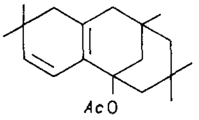
In the absence of migration of the double bond during the acetic anhydride treatment (**2**→**6**), the 7,8-olefinic bond is also present in **2**, a consideration which eliminates the possible formulation of the original diol as **2a**.



2a



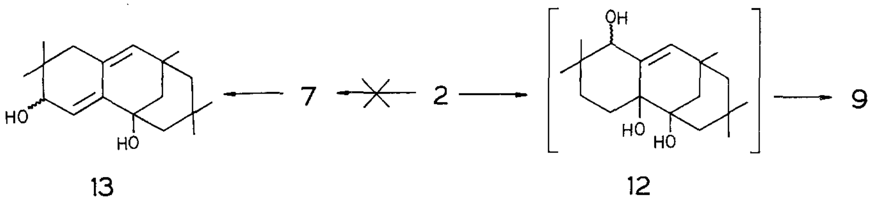
6a



6b

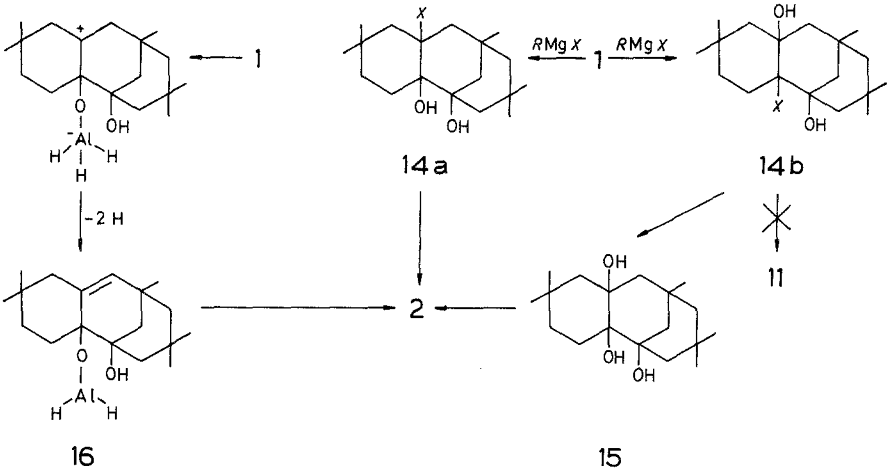
Anhydrous oxalic acid at 200°[12] dehydrated the diolene (**2**) to the known[2] low-melting non-crystalline diisophora-2,7-dien-1-ol (**7**), which was identified by its catalytic reduction to diisophor-2(7)-en-1-ol (**8**)[13,14] and by its identity (ir, tlc) with material previously obtained by the comparable dehydration of diisophor-2-ene-1,7-diol (**11**), the structural isomer of **2** originating from 2,7-epoxydiisophoran-1-ol-3-one (**10**) in the *Wharton* reaction[2]. Catalytic hydrogenation of **2** in glacial acetic acid occurred with simultaneous dehydration giving **8** directly in one operation. The results of this hydrogenation (**2** → **8**) and the dehydration (**2** → **7**) provide further support for the formulation of **2**, and establish, moreover, a link between 2,7-epoxides that contain a 3-keto-group (e.g. **10**) and those that do not (e.g. **1**), by their conversion into products common to both series.

The action of selenium dioxide in ethanol on **2**, performed with the object of introducing a hydroxyl group allylic to the 7,8-double bond (at C-6)[15], occurred with simultaneous dehydration affording low yields of diisophora-2,7-diene-1,6-diol (**9**), presumably by way of the intermediate triolene **12**. Its formulation is in accord with the presence of a heteroannular conjugated diene system (λ_{max} 243 nm), its ^{13}C-nmr spectrum (see below), and with its distinctness from the known[16] 1,4-dihydroxy-isomer (**13**) that might have possibly arisen by the alternative sequence **2** → **7** → **13**.



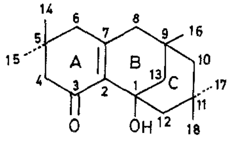
The mechanism of the present conversion of 2,7-epoxydiisophoran-1-ol (**1**) into the olefinic diol **2** by *Grignard* reagents must account for the fact that the hydrocarbon moiety of the organometallic reagent does not participate in the overall reaction. It is known[5] that epoxides may interact with *either* of the entities that are regarded[17] as the proximate reactive species of *Grignard* reagents, viz. dialkyl magnesium, and magnesium halide. If the conditions and relative reaction rates favour interaction with the latter, simple halohydrin formation predominates[5,8,18,19]. In the present example, initial halohydrin formation, followed by dehydrohalogenation of the intermediate 2-hydroxy-7-halogeno-compound **14a** is a likely reaction sequence by which **2** may be formed. The alternative 2-halogeno-7-hydroxy-isomer **14b** would yield a different known[2] product (**11**) on dehydrohalogenation, and could produce **2** only after an additional hydrolytic step (to **15**); the former simpler interpretation is therefore preferred.

The conversion of **1** into **2** under the influence of nascent aluminium hydride[2], on the other hand, may be represented by an ionic mechanism (involving **16**), which is based on *Kirchhof*'s proposal[20] for the formally comparable isomerisation of 1,2-epoxycyclododecane to 1-hydroxycyclododec-2-ene by the action of diisobutyl aluminium hydride.



^{13}C-*NMR Spectra*

An examination of the ^{13}C-nmr spectra of the key diolene (**2**), and of two of its transformation products (**6**, **9**) provided further evidence in support of the suggested structures. The spectra consisted in each case of the appropriate number of singlets and multiplets, and were interpreted on the basis of assignments recently deduced for ketols[21] and carboxylic acids[1] of the diisophorone series. Table 1 records the proton noise decoupled chemical shifts and first order multiplicities of the compounds concerned (**2**, **6**, **9**), displayed in accordance with their proposed assignments. The spectra of the parent ketol [**A**, diisophor-2(7)-en-1-ol-3-one][21] and of the 4-hydroxy-isomer **13**[16,21] of **9** are included for comparison.



A

Doublets: Information concerning the doublets provides the clearest structural evidence and is expediently considered first. The diolene (**2**), diene acetate (**6**) and dienediol (**9**) each give rise to a doublet near 133 ppm, the two dienes (**6**, **9**) to an additional doublet at 120 ppm, and the dienediol (**9**) to a third doublet, at 77 ppm. The first of these signals, being the only doublet of the diolene (**2**), is attributed to its C-8 carbon atom, and hence

Table 1. ^{13}C-*NMR spectra of compounds* **2**, **6** *and* **9** *and their proposed assignments (ppm downfield from TMS)*

Compound[a]	A	2	6	9	13[b]
C-1	71.4 s	*73.2 s	82.9 s	72.0 s	71.8 s
C-2	135.4 s	*74.5 s	132.8 s	136.3 s	131.8 s
C-3	200.7 s	26.0 t	120.0 d	119.1 d	121.1 d
C-4	51.8 t	34.1 t	39.9 t	38.9 t	73.4 d
C-5	*32.2 s	31.8 s	30.0 s	34.6 s	34.2 s
C-6	45.7 t	*44.7 t	*44.2 t	76.9 d	39.6 t
C-7	157.5 s	136.7 s	136.9 s	140.9 s	143.9 s
C-8	44.6 t	133.7 d	132.5 d	132.1 d	135.3 d
C-9	*32.4 s	36.5 s	36.2 s	36.5 s	36.6 s
C-10	52.1 t	48.8 t	51.9 t	53.1 t	53.0 t
C-11	31.4 s	31.2 s	31.5 s	31.7 s	31.7 s
C-12	50.3 t	*46.3 t	48.5 t	50.4 t	50.6 t
C-13	46.6 t	*45.3 t	*44.3 t	48.5 t	48.0 t
C-14	26.8 q	25.9 q	26.0 q	20.0 q	25.8 q
C-15	29.7 q	30.0 q	29.1 q	27.1 q	24.5 q
C-16	28.2 q	31.3 q	30.4 q	29.4 q	29.3 q
C-17	32.7 q	33.0 q	30.7 q	30.4 q	30.2 q
C-18	37.1 q	37.4 q	37.4 q	37.4 q	37.4 q
C-19			169.2 s		
C-20			22.7 q		

[a] For numbering, see structure **A**.

[b] The assignments for **13** differ from those previously given[21] by two minor interchanges, made possible by comparisons with the newly available compounds (**2**, **6**, **9**), and by the correction of a printing error.

* Signals may be vertically interchanged.

to the same position in compounds **6** and **9** by analogy. Conversely, the near identity of the chemical shifts of this signal in **6**, **9**, and **13** (in which the conjugated double bond system spans necessarily carbon atoms C-3, 2, 7 and 8, see above), and in **2** provides a plausible argument in favour of the postulated 7,8-position of the double bond in **2**, rather than the 6,7-alternative (**2a**, see also above). The chemical shift of this low-field doublet (133 ppm) is appropriate for a cycloaliphatic methine carbon[22]; it lies between numerical values established for cyclohexenes (127 ppm)[23a] and comparable diisophora-2,7-dienes (ca. 140 ppm)[21].

The spectrum of the diene acetate (**6**) contains one additional doublet (δ, 120 ppm); this is clearly associated with the 3-methine carbon both in this compound, and by analogy in the comparable dienediol (**9**; δ, 119 ppm). Its consistency with the corresponding signal of the 4-hydroxy-isomer (**13**, δ, 121 ppm) is also noteworthy. The remaining doublet of **9** is attributable to the carbon bearing the secondary hydroxyl-group. Of the possible positions, C-4 or C-6, the former is eliminated by the non-identity of **9** with the known[16] 1,4-dihydroxydiene **13**. The resonance (76.9 ppm) of this doublet is in good accord with comparable figures for both cyclohexanols[23b,24] and hydroxydiisophorones[1,21].

Singlets: A signification observation concerning this group of signals is the presence, in the spectrum of **2**, of two distinct singlets near 74 ppm, confirming the presence of *two tert.*hydroxyl-groups. Being very closely spaced, they are assigned collectively to C-1 and C-2 (of **2**); the possible alternative location of one of the *tert.*hydroxyl-groups at C-7 is excluded by the distinctness of **2** from its known[2] isomer **11**. The dienes **6**, **9** and **13** display, in this range, only the familiar bridgehead C-1 singlet, its chemical shift being appropriate to the 1-substituent (OH or O*Ac*[21]). The low-field singlets associated with the double bond systems are allotted, in accordance with previous reasoning[21], so as to reflect the higher shielding of C-2 relative to C-7.

In the high-field region, each of the compounds gives rise to the usual[1,21] singlet near 32 ppm, attributed to the C-11 carbon remote from structural changes in rings A and B. The C-9 carbon, located in an unchanging structural environment, is thought to be associated with the singlet appearing constantly near 36 ppm; its small downfield displacement from the usual value (32 ppm[21]) implies a slight deshielding of this centre by the adjacent unsaturated system. The remaining high-field singlet of the C-5 carbon is seen to be subject to small fluctuations with changes in the structure of its surroundings.

Triplets: The dienediol (**9**) generates only four triplets, three of which are immediately assignable (to C-10, 12, 13) by comparison with the parent ketol **A**. The C-4 triplet, resonating at 52 ppm in ketols[21], is displaced upfield (to 39 ppm) in accordance with its altered structural environnment: its chemical shift (in **9**) coincides with the estimate based on the effect of its adjacent structural moieties [viz. 28 (cyclohexane methylene) + 13 (adjacent C*Me*$_2$) − 2 (adjacent olefinic bond) = 39 ppm]. The 4-methylene carbon of the diolene **2** unaccountably resonates further upfield (34 ppm). The remaining suggested assignments, based on analogies and comparisons, are not sufficiently consistent to provide further structural arguments.

Quartets: In agreement with previous findings[1, 21] the quartet of the C-18 eq methyl carbon resonates in each case near 37 ppm, and that of the 17 ax-methyl group at 30 or 33 ppm, when the latter subtends a system of double bonds (in **6**, **9**, **13**), or an isolated olefinic bond (in **2**), respectively. The 15 eq methyl carbon produces the usual quartet at ca. 29 ppm, except in **13**, where the adjacent 4-hydroxy-group, presumably in α-axial configuration[1], causes a marked upfield displacement of this signal (to 24.5 ppm). The C-14 ax quartet, normally emerging at 26 ppm, is similarly affected by the neighbouring 6-hydroxy-group in **9**; this 6-substituent appears to assume the β-equatorial configuration, occupying a position in space approximately midway between the 14- and 15-methyl-groups, a fact that is indicated by a (somewhat smaller) simultaneous upfield shift of the C-15eq signal (29→27 ppm). The narrow range (near 30 ppm) covered by the quartets, that remain to be allocated to C-16 reflects the identical structural environment of the 16-methyl-group in the compounds concerned. The small downfield displacement of these signals relative to those of comparable ketols indicates a deshielding of C-16 similar to that of the adjacent 9-position.

Experimental

General information is given in Part 1[4] concerning standard procedures, apparatus, reagents, solvents and abbreviations. Catalytic hydrogenations were performed at room temperature and atmospheric pressure. Light petroleum had bp. 60–80° unless otherwise stated.

The ^{13}C-nmr spectra were determined on a Bruker WM 250 *Fourier* Transform instrument operating at 62.89 MHz, and the broad band proton noise decoupled and DEPT spectra recorded. The internal standard was tetramethylsilane, and the solvent deuteriochloroform.

Diisophor-7-ene-1,2-diol (**2**)

To a solution of ethylmagnesium bromide [prepared under dry nitrogen from magnesium (1.94 g, 0.08 g atom) and bromoethane (24 g, 0.22 mol) in ether (300 ml)] was added 2,7-epoxydiisophoran-1-ol[2] (**1**) (4.40 g, 0.016 mol) in dry ether (200 ml), and the stirred mixture boiled under reflux for 1 h. The liquid was slowly treated with 3 *N* hydrochloric acid (ca. 50 ml), the product exhaustively extracted with more ether, and the combined washed extracts evaporated in a vacuum. The remaining solid gave, on crystallisation from light petroleum (ca. 30 ml per g, removal of a small insoluble fraction, 0.1–0.2 g), needles (2.65–3.2 g, 60–72%) of the 1,2-diol-7-ene (**2**), m.p. 151–153°. Lit.[2] m.p. 151–153°. [Found: C 77.4, H 10.7. *M* (mass-spectrometrically) 278. Calc. for $C_{18}H_{30}O_2$: C 77.7, H 10.8%. *M* 278]. Ir spectrum, see Ref.[2]. λ_{max} 205 nm ($\log \varepsilon$ 3.68).

The use of phenylmagnesium bromide or methylmagnesium iodide in the above procedure gave the same product (identified by ir) in 62% and 48% yields, respectively.

Cyclic 1,2-Sulphite Ester (**3**) (of **2**)

(a) *Preparation.* A solution of **2** (1.39 g, 0.005 mol) in pyridine (18 ml) at 0° was treated dropwise, with external cooling, with thionyl chloride (3.0 g, 0.025 mol), kept at 0° for 1 h (some darkening), then stirred into ice-water (150 ml) – concentrated hydrochloric acid (18 ml). The resulting precipitate gave massive prisms (0.65 g, 40%) of **3**, m.p. 151–155° (from light petroleum). (Found: C 66.5, H 8.55, S 9.1. $C_{18}H_{28}O_3S$ requires C 66.7, H 8.6, S 9.9%). ν_{max} 2 950 vs, 2 920 vs, 2 865 vs, 1 470 s, 1 455 s, 1 435 m (CH_3, CH_2), 1 395 s, 1 370 s (.C*Me*$_2$); 1 220 vs, 1 200 vs (SO) cm^{-1}. *m*/e: 324 (M^+), 260 ($M^+ - SO_2$), 189 ($M^+ - SO_2 - 71$).

(b) *Reconversion into Diisophor-7-ene-1,2-diol* (**2**). A stirred solution of lithium aluminium hydride (0.15 g, 0.004 mol) in anhydrous ether (30 ml) was treated with one of **3** (0.32 g, 0.001 mol) in the same solvent (30 ml), and the mixture boiled under reflux for 2 h. The product, isolated by the usual procedure[2], was **2** (0.13 g, 47%), identified by mixed m.p. and ir.

The sulphite ester **3** was substantially recovered after treatment (of 0.001 mol) with lithium borohydride[10] (0.002 mol) in ethanol (10 ml) at room temperature for 12 h, followed by boiling (10 min), as well as after attempted catalytic hydrogenation over *Adams'* catalyst[25] in glacial acetic acid.

7,8-Epoxydiisophorane-1,2-diol (4)

Interaction of **2** (2.78 g, 0.01 mol) and 3-chloroperoxybenzoic acid (1.9 g, 0.011 mol) in dichloromethane (60 ml) at room temperature for 12 h, followed by the usual work-up[2] produced a crystalline solid, which gave lustrous prisms (1.9–2.05 g, 64–70%) of **4**, m.p. 118–120° (from light petroleum) [Found: C 73.15, H 10,2. *M* (mass-spectrometrically) 294. $C_{18}H_{30}O_3$ requires C 73.5, H 10.2. *M* 294]. ν_{max} 3 490 vs (OH); 2 950–2 940 vs, 2 860 sh, 1 477 m, 1 460 m (CH_3, CH_2); 1 395 m, 1 380 s, 1 370 s (.C*Me*$_2$); 1 035 s (C—O of OH); 920 m (C—O—C, epoxide) cm^{-1}.

Cyclic 1,2-Sulphite Ester (5) (of 4)

The foregoing epoxide **4** (0.3 g, 0.001 mol) gave, on treatment with pyridine—thionyl chloride (as described for **3**), the 1,2-sulphite ester **5** as massive prisms (0.24 g, 72%), m.p. 115–122° (from light petroleum). (Found: C 63.3, H 8.4, S 9.1. $C_{18}H_{28}O_4S$ requires C 63.5, H 8.2, S 9.4%). ν_{max} 2 960 s, 2 885 s, 1 475 m, 1 460 m (CH_3, CH_2); 1 393, 1 390 m d, 1 370 m (.C*Me*$_2$); 1 210 vs (SO); 925 s (C—O—C, epoxide); 913 s, 890 s, 810 s, 690 s cm^{-1}.

1-Acetoxydiisophora-2,7-diene (6)

A solution of **2** (0.56 g, 0.002 mol) in acetic anhydride (8 ml) was boiled under reflux for 4 h, then stirred into warm water. The resinous product solidified slowly on storage at 0° and gave, on crystallisation from a little ethanol, small prisms (0.48 g, 80%) of **6**, m.p. 56–58° (Found: C 79.7, H 9.8. $C_{20}H_{30}O_2$ requires C 79.5, H 9.9%). λ_{max} 246 nm (log ε 4.10). ν_{max} 2 960 vs, 2 935–2 900 vs br, 2 870 vs, 1 480 m, 1 460 m, 1 440 m (CH_3, CH_2); 1 393 m, 1 370 s (.C*Me*$_2$); 1 650 w, 1 620 w (C=C, conjug. diene); 1 740 vs (C=O); 1 235–1 223 vs br (C—O, acetate); 820 s (CH of trisub. olefin); 1 360 m, 1 255 s, 1 025 s, 1 020 s, 990 m, 800 m cm^{-1}.

Catalytic Hydrogenation of 2

A solution of **2** (0.56 g, 0.002 mol) in glacial acetic acid was hydrogenated over *Adams'* catalyst[25] (0.2 g) (uptake, 90 cc; 45 min, Calc.: 40 + 45 cc at NTP). The solvent was removed in a vacuum, the residual oil taken up in ether, the washed neutral dried solution evaporated, and the residue dissolved in light petroleum (5 ml). The resulting crystals (0.39 g, 75%) were diisophor-2(7)-en-1-ol (**8**), identified by mixed m.p. 82–83° (Lit. m.p. 84–85°[13], 88–90.5°[14]) and ir spectrum, and by its conversion (48%) into 2,7-epoxydiisophoran-1-ol[2], mixed m.p. 154–156°[2].

Dehydration and Catalytic Hydrogenation of 2

A mixture of finely powdered **2** (0.56 g, 0.002 mol) and anhydrous oxalic acid (0.9 g, 0.01 mol) was kept at ca. 195° for 3 h. The resulting viscous mass was extracted with ether (3 × 30 ml) and the washed neutral extracts evaporated. The residual diisophora-2,7-dien-1-ol (**7**) (yellow oil, identified by ir[2]) gave, on catalytic hydrogenation in glacial acetic acid as described immediately above, diisophor-2(7)-en-1-ol (**8**) in 70% yield.

Diisophora-2,7-diene-1,6-diol (**9**)

A solution of **2** (0.56 g, 0.002 mol) in ethanol (12 ml), treated with selenium dioxide (0.45 g, 0.004 mol) was boiled under reflux for 12 h. During the last hour, the excess of the reagent was converted into selenium by the addition of acetone. The finely divided black precipitate was filtered off, and the yellow filtrate added to water. The resulting solidified oil was extracted with ether and gave a viscid resin affording minute prisms (0.12–0.17 g, 22–30%) of **9**, m.p. 144–145° (from light petroleum, 20–30 ml, followed by partial evaporation). [Found: C 77.8, H 9.5. *M* (mass-spectrometrically) 276. $C_{18}H_{28}O_2$ requires C 78.3, H 10.1. *M* 276]. λ_{max} 243 nm (log ε 4.25). ν_{max} 3 400 vs (OH); 2 950 vs, 2 905 vs, 2 885 s, 1 465 s (CH_3, CH_2); 1 390 m, 1 370 s (.CMe_2); 1 717–1 620 w mult (C = C); 1 030 vs (C – O of OH); 847 ms, 820 ms (CH of trisub. olefin); 1 340 m, 1 180 s, 1 100 s, 1 085 s, 1 050 m, 925 m, 910 m, 770 m cm^{-1}.

Acknowledgement

We are indebted to Mrs. *J. E. Elliot* and Miss *F. B. Mills*, of the University of London NMR Spectroscopy Service at King's College London, for the production of the ^{13}C-nmr spectra.

References

[1] Part 14: *Kurzer F., Patel J. N.*, Monatsh. Chem. **115**, 825 (1984).

[2] *Allen A. A., Kurzer F.*, Tetrahedron **34**, 1261 (1978).

[3] *Allen A. A., Kurzer F., Morgan A. R.*, J.C.S. Perkin I **1980**, 733.

[4] *Allen A. A., Duffner R. C., Kurzer F.*, Tetrahedron **34**, 1247 (1978).

[5] *Rosowsky A.*, in: Heterocyclic Compounds with Three or Four Membered Rings (*Weissberger A.*, ed.), Part I, p. 394. New York: Interscience. 1964. *Winstein S., Henderson R. B.*, in: Heterocyclic Compounds (*Elderfield R. C.*, ed.), Vol. I, p. 1. New York: Wiley. 1950.

[6] *Phillips J. G., Parker V. D.*, in: Steroid Reactions (*Djerassi C.*, ed.), p. 631. San Francisco: Holden Day. 1963.

[7] *Kharasch M. S., Reinmuth O.*, Grignard Reactions of Non-metallic Substances, p. 181. New York: Prentice-Hall. 1954.

[8] *Gaylord N. G., Becker E. I.*, Chem. Rev. **49**, 413 (1951).

[9] *Bladon P., Henbest H. B., Wood G. W.*, J. Chem. Soc. **1952**, 2737.

[10] *Fieser L. F., Okumura Y.*, J. Org. Chem. **27**, 2247 (1962); *Okumura Y.*, ibid. **28**, 1075 (1963).

[11] *Dannenberg H.*, Abhandl. Preuss. Akad. Wiss. **21**, 3 (1939); *Woodward R. B.*, J. Amer. Chem. Soc. **63**, 1123 (1941), ibid. **64**, 76 (1942); *Dorfman L.*, Chem. Rev. **53**, 47 (1953); *Fieser L. F., Fieser M.*, Steroids, pp. 15–21. New York: Reinhold. 1959.

[12] *Carlin R. B., Constantine D. A.*, J. Amer. Chem. Soc. **69**, 50 (1947).

[13] *Kabas G., Rutz H. C.*, Tetrahedron **22**, 1219 (1966).

[14] *Furth B., Kossanyi J., Morizur J. P., Vandewalle M.*, Bull. Soc. chim. France **1967**, 1428.

[15] *Guillemonat A.*, Ann. chim. **11**, 143 (1939); *Wiberg K. B., Nielsen S. D.*, J. Org. Chem. **29**, 3353 (1964).

[16] *Davies P. R., Kurzer F., Morgan A. R.*, Monatsh. Chem. **111**, 1097 (1980).

[17] *Schlenk W., Schlenk Jr. W.*, Ber. Dtsch. Chem. Ges. **62**, 920 (1929); *Schlenk Jr. W.*, ibid. **64**, 734, 736 (1931).

[18] *Blaise E. E.,* Compt. rend. **134**, 551 (1902).

[19] *Newth F. H.,* Quart. Rev. **13**, 30 (1959).

[20] *Kirchhof W.,* Chem. Ber. **93**, 2712 (1960).

[21] *Davies P. R., Morgan A. R., Kurzer F.,* Monatsh. Chem. **114**, 739 (1983).

[22] *Wehrli F. W., Wirthlin T.,* Interpretation of Carbon-13 NMR Spectra. London: Heyden & Son Ltd. 1976. Chart at end: Range for $-\mathrm{CH}=$, 113–144 ppm, centred at 129 ppm.

[23] *Johnson L. F., Jankowski W. C.,* Carbon 13 NMR Spectra. A Collection of Assigned Coded and Indexed Spectra. New York: Wiley-Interscience. 1972. (a) Chemical shift of $-\mathrm{CH}=$ in 4-methylcyclohexene, 126.6 ppm. (b) Range for cyclohexanols (Compounds 191, 267, 271, 272, 360) 67–76 ppm.

[24] *Roberts J. D., Weigert F. J., Kroschwitz J. I., Reich H. J.,* J. Amer. Chem. Soc. **92**, 1338 (1970).

[25] *Adams R., Voorhees V., Shriner R. L.,* Org. Synth., Coll. Vol. 1, p. 463. New York: Wiley. 1941.