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$\Delta^{2,6}$-HEXALIN-1,5-DIONE

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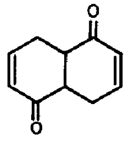
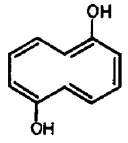
Abstract—$\Delta^{2,6}$-Hexalin-1,5-dione (I) has been prepared from decalin-1,5-dione (III) as follows. The latter substance was converted to the diketal IX($R^1 = R^2 = H$) which, on bromination with phenyltrimethylammonium tribromide in tetrahydrofuran, was transformed into the 2,6-dibromo compound IX($R^1 = R^2 = Br$). Treatment with potassium t-butoxide in t-butyl alcohol gave the diene diketal X, and this substance on mild acid hydrolysis was converted into the highly crystalline diene dione I.

Δ^2-Octalone 1 (VI) has similarly been prepared from the ketal VII($R = H$) of α-decalone *via* the bromo compound VII($R = Br$) and the unsaturated ketal VIII. The product was identical with material prepared by the pyrolysis of 2-acetoxy-1-decalone (V).

The objective of the present study was to prepare the hexalindione I in order to see if in its enolized form it would exhibit any behavior indicative of existence (possibly only intermediary in the course of forming new products) in the cyclodecapentaenediol form II.[1] The present paper describes the synthesis of the diene dione I as well as of Δ^2-octalone-1 (VI). Preliminary enolization experiments have given rather complex results which are not yet amenable to interpretation.



I



II

Since we envisaged synthesizing the diene dione from the known decalin-1,5-dione (III),[2] the model conversion of α-decalone IV ($R = H$) into Δ^2-octalone-1 (VI) was first studied. Direct halogenation of α-decalone gives mainly 9-halo compounds which on dehydrohalogenation yield largely Δ^9-octalone-1, formed along with some of the Δ^8-isomer.[3,4] In the present study, *trans*-9-chlorodecalone IV ($R = Cl$)[3,4] was treated with tetramethylammonium acetate in order to see if displacement would be accompanied by rearrangement to give 2-acetoxy-1-decalone (V).[5] The product, however, was a mixture of Δ^9-octalone-1 and 9-acetoxy-1-decalone (IV, $R = OAc$). The structure of the latter substance was established by its conversion with 2,4-dinitrophenylhydrazine into the 2,4-dinitrophenylhydrazone of Δ^9-octalone-1. In

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[1] For discussions regarding the stability and attempts to synthesize the cyclodecapentaene and related systems, see, *inter alia*, P. W. Schiess, Ph.D. Thesis, University of Basel, Switzerland, 1958; D. Ginsburg, ed., *Non-Benzenoid Aromatic Compounds*. Interscience, New York, N.Y. (1959); C. A. Grob and P. W. Schiess, *Helv. Chim. Acta* **43**, 1546 (1960); F. Sondheimer, R. Wolovsky and Y. Amiel, *J. Amer. Chem. Soc.* **84**, 274 (1962).

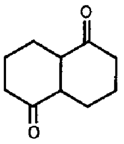
[2] W. S. Johnson, C. D. Gutsche and D. K. Banerjee, *J. Amer. Chem. Soc.* **73**, 5464 (1951).

[3] H. O. House and H. W. Thompson, *J. Org. Chem.* **26**, 3729 (1961).

[4] E. W. Warnhoff, Ph.D. Dissertation, University of Wisconsin (1953).

[5] Cf. K. L. Williamson and W. S. Johnson, *J. Org. Chem.* **26**, 4563 (1961).

contrast, when the mixture of 9-chlorodecalones was treated with potassium acetate in acetic acid, a new isomeric acetoxy decalone, m.p. 73–75·5° after purification, was produced in 47% yield along with some Δ^9-octalone-1. This new substance proved to be the 2-acetoxy compound V since it formed a yellow 2,4-dinitrophenylhydrazone, m.p. 202–202·5°, which was stable on heating in 95% ethanol. On pyrolysis,[6] the 75° acetoxy ketone was converted into Δ^2-octalone-1 (VI), m.p. 71·5–72·5°, λ_{max} 226·3 mμ (ϵ 9,150). This substance has been previously reported[7a] as a liquid, b.p. 114° (5 mm), which was obtained in 30% yield by air oxidation of Δ^2-octalin. The semicarbazone is reported to melt at 203–204°.[7a] Another preparation of the octalone, by hydride reduction of 1-methoxy-*trans*-Δ^1-octalone-3, yielded a semicarbazone, m.p. 210–212°.[7b] This derivative of our material melted at 218–219°.



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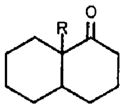
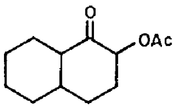
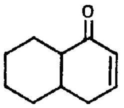


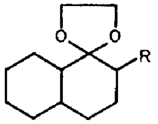
IV



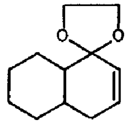
V



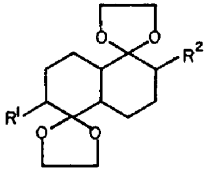
VI



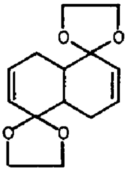
VII



VIII



IX



X

Since it was considered desirable to produce the diene dione under relatively mild conditions which would minimize possible rearrangement *via* the enolized form, another general approach was examined. The ethylene ketal VII (R = H) of α-decalone was brominated by the excellent method of Marquet *et al.*[8] with phenyltrimethylammonium tribromide in tetrahydrofuran for 2 hr at 0° to give in 45%

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[6] The method described for the pyrolysis of 2-acetoxycyclohexanone was used: K. L. Williamson, R. T. Keller, G. S. Fonken, J. Szmuszkovicz and W. S. Johnson, *J. Org. Chem.* **27**, 1612 (1962).

[7(a)] A. H. Cook, *J. Chem. Soc.* 1774 (1938); [(b)] H. Mühle and Ch. Tamm, *Helv. Chim. Acta* **45**, 1475 (1962).

[8] A. Marquet, M. Dvolaitzky, H. Kagan, L. Mamlok. C. Ouannes and J. Jacques, *Bull. Soc. chim. Fr.* 1822 (1961). Recently P. E. Eaton, *J. Amer. Chem. Soc.* **84**, 2344 (1962) has applied a similar scheme to the preparation of tricyclo[5.3.0.0^{2,6}]deca-4,9-diene-3,8-dione from the saturated diketone.

yield the 2-bromoketal VII (R = Br), m.p. 97·5–98° after purification. Dehydrobromination of this substance with potassium t-butoxide in t-butyl alcohol gave the unsaturated ketal VIII, which was converted by mild acid hydrolysis into the octalone VI in 88% yield. Because of the mild conditions under which the unsaturated ketone was thus liberated, this ketal approach was the method of choice for preparing the diene dione.

Szmuszkovicz and Sausen[9] have described the preparation of the diketal IX ($R^1 = R^2 =$ H), m.p. 122·3–122·6°, as the major product of the reaction of ethylene glycol with decalin-1,5-dione (III).[2] Since the *trans*-fused compound would be expected to be more stable as well as more reactive than the *cis*-isomer, this 122° material is tentatively assigned the *trans* configuration. The diketal was brominated as described above, and after a reaction period of 1 hr the only pure product that could be isolated was the monobromo diketal IX (R^1 = H, R^2 = Br), m.p. 168–169°. After a 4 hr treatment, however, the crude dibromo diketal IX ($R^1 = R^2$ = Br) was produced in 72% yield, m.p. 226–227° after purification. This crude product on treatment with potassium t-butoxide and t-butyl alcohol underwent dehydrohalogenation to give the diene diketal X in 73% yield, m.p. 155–156° after purification. When the crude diene diketal was treated at room temperature in aqueous acetone with a trace of *p*-toluenesulfonic acid, it was converted in 87% yield into the desired hexalindione I. The pure material melted at 228·5–230° and exhibited the expected absorption at 5·98 and 6·2 μ in the IR spectrum. The principal maximum in the U.V. spectrum, however, appeared at unusually short wavelength: $\lambda_{\max}^{95\%\mathrm{EtOH}}$ 217 mμ (ϵ 18,000) as compared with the expected value of 226 mμ. This abnormality may be due to one or more of the following influences: (a) a transannular long-range effect caused by interaction of the neighbouring conjugate system; (b) geometrical distortion of the chromophoric system;[10] (c) a relatively weak association of the solvent (ethanol) with the carbonyl groups of the diene dione resulting in less than the usual bathochromic solvent effect on the position of the maximum. In connection with this last factor (c)[11] it was interesting to note that the principal maximum in the U.V. spectrum of the diene dione in cyclohexane solution appeared at 212 mμ, which corresponds to a relatively small (5 mμ) ethanol-to-cyclohexane solvent shift, as compared with the usual value of 11 mμ.[12,13]

In view of the abnormal U.V. spectrum and the extraordinarily high melting point of the diene dione, it was considered necessary to adduce further evidence for the structure which was confirmed as follows. The I.R. spectrum (see above) was unexceptional, and the principal band of the mass spectrum was found at 162 (M. Wt. of I, 162). The N.M.R. spectrum at 60 megacycles of a solution of the substance in deuterochloroform (tetramethylsilane as an internal standard) exhibited a multiplet

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[9] See G. N. Sausen, Ph.D. Dissertation, University of Wisconsin (1953).

[10] Cf. the UV absorption of norcarenone, $\lambda_{\max}^{\mathrm{EtOH}}$ 218 mμ, E. E. van Tamelen, J. McNary and F. A. Lornitzo, *J. Amer. Chem. Soc.* **79**, 1231 (1957).

[11] We wish to thank Professor R. H. Eastman for suggesting this possibility.

[12] H. Dannenberg, *Abhandl. preuss. Akad. Wiss.* **21**, 3 (1939).

[13] This observation suggests the possibility that an improved correlation between calculated (Woodward type rules) and found U.V. maxima for α,β-unsaturated ketones might be realized by using values obtained from solutions of the substrate in an aprotic solvent. Although the largest discrepancies are undoubtedly due to geometrical influences, those that are due to varying degrees of association of the carbonyl group of α,β-unsaturated ketones with active hydrogens of the solvent thus could be minimized.

for 2 protons centered at δ = ca. 7·0 ppm ($2\,\overset{\overset{\textstyle H}{|}}{C}{=}C{-}C{=}O$) and a multiplet for 2 protons centered at ca. 6·0 ppm ($2\,C{=}\overset{\overset{\textstyle H}{|}}{C}{-}C{=}O$). The absorption for the remaining 6 protons was observed between 1·9 and 3·4 ppm as a poorly resolved multiplet. On catalytic hydrogenation over 10% palladium-on-carbon, the diene dione absorbed 2·1 mole-equivalents of hydrogen. The product was identified, by mixed m.p. and I.R. spectral comparisons, with the more stable isomer of decalin-1,5-dione, m.p. 166–167°, which almost certainly has the *trans* configuration.[2] If the likely assumption is made that isomerization did not occur during the hydrogenation step, the diene dione also has the *trans* configuration which is consistent with its mode of formation, its high crystallinity and low solubility suggesting a high degree of symmetry.

The U.V. spectrum of the diene dione was not affected significantly by the addition of acid to its solution in alcohol. However, when a trace of sodium hydroxide was added, a dramatic change ensued in that the peak at 217 mμ disappeared and was replaced by a stronger maximum at 232 mμ (ϵ 32,000). In addition, a triplet appeared at 325, 336 and 347 mμ which, after standing, gradually diminished in intensity while a new absorption developed in the 275–280 mμ region. Preliminary studies on the formation of the dienol acetate of the diene dione I have shown that conventional procedures give complex mixtures of products, which have not yet been identified.

EXPERIMENTAL

Reaction of trans-9-chloro-1-decalone (IV, R = Cl) *with tetramethylammonium acetate*

A mixture of 0·5 g crystalline chloro ketone[3,4] and 0·5 g tetramethylammonium acetate in 50 ml anhydrous acetone was heated under reflux for 17 hr. The suspension containing tetramethylammonium chloride was filtered, and the filtrate diluted with water and extracted with ether. The combined ether layers were washed with water, followed by saturated brine, and dried (Na_2SO_4). The IR spectrum of the oily residue (0·46 g) obtained on evaporation of the solvent indicated that it consisted of approximately equal amounts of Δ^9-octalone-1 and an acetoxy decalone. A 0·09-g sample of this mixture was allowed to react with excess 2,4-dinitrophenylhydrazine reagent, and there was thus produced 0·13 g (90% yield) of red plates, m.p. 262–266°. A single crystallization from xylene gave 0·11 g bright red plates, m.p. 263–263·8° undepressed on admixture with an authentic specimen of the 2,4-dinitrophenylhydrazone of Δ^9-octalone-1.[4]

2-Acetoxy-1-decalone (V). The following is a modification of a previously described procedure.[14] A mixture of 111 g crude 9-chloro-1-decalone,[4] 82 g of freshly fused potassium acetate and 25 ml of acetic anhydride in 1 l. acetic acid was heated under reflux for 16 hr. Most of the acetic acid was removed by distillation at red. press., ether was added to the residue and the mixture filtered to remove the insoluble salts. The filtrate was washed with water, 10% potassium carbonate solution, again with water, followed by saturated brine, and finally dried (K_2CO_3). The residue obtained on removal of the ether was distilled through a 2-ft. column packed with stainless steel saddles. The fraction boiling at 93·5–94° (0·035 mm) amounted to 44 g (47% yield) of liquid which spontaneously crystallized. One recrystallization from 95% ethanol gave colorless plates, m.p. 73–75·5°. Two further recrystallizations raised the m.p. to 74·5–75·5°. (Found: C, 68·2; H, 8·6. $C_{12}H_{18}O_3$ requires: C, 68·54; H, 8·63%).

The *2,4-dinitrophenylhydrazone* was obtained from 95% ethanol as bright yellow needles, m.p. 202–202·5°. This product was stable in boiling 95% ethanol. (Found: C, 55·5; H, 5·6; N, 14·4. $C_{18}H_{22}N_4O_6$ requires: C, 55·38; H, 5·68; N, 14·35%).

1-Ethylenedioxy-2-bromodecalin (VII, R = Br). 1-Ethylenedioxydecalin was prepared from 9·8 g α-decalone, b.p. 98–98·5° (6 mm), by treatment with 4·05 g purified ethylene glycol and 90 mg *p*-toluenesulfonic acid monohydrate in 150 ml benzene. After heating at reflux for 16 hr in a system containing a continuous water separator, the mixture was cooled, washed with saturated sodium

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[14] H. W. Wanzlich, G. Gollmer and H. Milz, *Chem. Ber.* **88**, 69 (1955).

bicarbonate solution, then with water and finally with saturated brine. The solution was dried (Na_2SO_4), and the solvent removed by distillation at red. press. The residual oil was distilled through a 4-in. Vigreux column to give a total of 11·9 g, b.p. 76–84° (0·18 mm). The I.R. spectrum showed weak absorption in the 5·84 μ region, indicating the presence of traces of ketonic material which could be readily removed by filtration of the ketal through a column of alumina. Elution with hexane gave a 91% recovery of ketal showing no absorption in the carbonyl region of the I.R. spectrum. Material of this quality was used in the bromination experiment described below.

A solution of 1·13 g 1-ethylenedioxydecalin (VII, R = H) in 25 ml tetrahydrofuran (purified by distillation from lithium aluminum hydride) was cooled to ice-bath temp; then 2·26 g phenyltrimethylammonium tribromide, m.p. 115·5–116·5°,[15] was quickly added, and the mixture was allowed to stand at ice-bath temp with occasional swirling for 2 hr. During this period colorless crystals of phenyltrimethylammonium bromide precipitated from the red-orange solution. The reaction mixture was poured into a mixture of 25 ml each of 0·1 N sodium thiosulfate and saturated sodium bicarbonate solution, and then extracted with ether. The combined ether layers were washed thoroughly with water, followed by saturated brine and dried (Na_2SO_4). A small amount of benzene was added, and the solution concentrated by distillation at red. press. Crystallization of the residual oil from methanol gave 0·72 g (45% yield) elongated colorless prisms, m.p. 96–97·5°. A specimen was further purified by recrystallization from methanol, sublimation at 78–98° (0·15 mm), and finally recrystallization again from methanol. The first-crop material from this last crystallization, after careful drying, had m.p. 97·5–98°. (Found: C, 52·3; H, 7·1; Br, 28·9. $C_{12}H_{19}O_2Br$ requires: C, 52·37; H, 6·96; Br, 29·04%).

Δ^2-*Octalone*-1 (VI)

(a) *By pyrolysis of* 2-*acetoxy*-1-*decalone* (V). The still pot of the apparatus previously described[6] was charged with 42 g 2-acetoxy-1-decalone, b.p. 93·5–94° (0·035 mm). The oil bath temp was maintained at 180°, the pyrolysis column temp at 425°, and the system press. at 0·03–1·5 mm. The product, which boiled between 83 and 170° (0·08–1·5 mm), collected and solidified in the condenser of the partial take-off head at the top of the fractionating column. The head was therefore periodically heated so that the condensate melted and ran into the receiver. After approximately ½ material had pyrolyzed, the process was interrupted, and the crystalline product in the receiver amounted to 12 g, λ_{max} 227 mμ (ϵ 8,000). One recrystallization from 95% ethanol gave material, m.p. 71–72°. Evaporative distillation at 80° (10 mm) gave colorless plates, m.p. 71·5–72·5°, λ_{max} 226·3 mμ (ϵ 9,150). (Found: C, 80·2; H, 9·4. $C_{10}H_{14}O$ requires: C, 79·96; H, 9·39%).

The semicarbazone was obtained from absolute ethanol as colorless prisms, m.p. 218–219° (in a sealed, evacuated capillary). The reported m.p. is 203–204°.[7]

The 2,4-*dinitrophenylhydrazone* was obtained from xylene as bright red plates, m.p. 211–213°. (Found: C, 58·5; H, 5·7; N, 16·6. $C_{16}H_{18}O_4N_4$ requires: C, 58·17; H, 5·49; N, 16·96%).

(b) *From* 1-*ethylenedioxy*-2-*bromodecalin* (VII, R = Br). To a solution of 1·0 g potassium in 50 ml anhydrous t-butyl alcohol was added 19·4 mg potassium iodide, followed by 0·293 g 1-ethylenedioxy-2-bromodecalin, m.p. 97·3–98·3° (atm of N_2). This mixture was heated with stirring under reflux for 64 hr. Most of the solvent was removed by distillation at red. press. (bath temp 60°), the residue was diluted with water, and the mixture extracted with ether. The combined ether layers were washed with water and then with saturated brine. The residue obtained upon evaporation of the solvent at red. press. was heated at steam-bath temp with a solution of 0·5 ml conc sulfuric acid in 15 ml water. The mixture was neutralized with 15 ml saturated sodium bicarbonate solution, then extracted with ether. The combined ether layers were washed with water, followed by saturated brine and finally dried (Na_2SO_4). The light-brown oily residue obtained upon evaporation of the solvent at red. press. amounted to 0·254 g, $\lambda_{max}^{95\%\ EtOH}$ 226 mμ (ϵ 4,370). This material was dissolved in benzene and the solution distilled to remove traces of water. The residue was evaporatively distilled at 70–80° (7 mm) to give 0·141 g colorless crystals. Crystallization from hexane afforded 17 mg, $\lambda_{max}^{95\%\ EtOH}$ 225·6 mμ (ϵ 9,100), m.p. 70–72° undepressed on admixture with material prepared as described above (section a).

1,5-*Bis-ethylenedioxydecalin* (IX).[9] A solution of 25·0 g of a mixture of *cis*- and *trans*-1,5-decalindione,[2] 37·4 g ethylene glycol, 0·5 g *p*-toluenesulfonic acid, and 140 ml toluene was heated under

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[15] This reagent was prepared by a slight modification of the procedure of D. Vorländer and E. Siebert (*Chem. Ber*. **52**, 283 (1919)). Thus from 378 g dimethylaniline there was obtained, after trituration of the crude product with hot methanol, then cooling and addition of ether, a total of 762 g orange crystals, m.p. 114–115·5 (in an evacuated capillary). A 665-g portion of this material was recrystallized from 1·5 l. glacial acetic acid and then once again from 550 ml methanol to afford, after thorough drying at red. press. 587 g orange crystals, m.p. 115·5–116·5° (in an evacuated capillary). Iodometric determinations showed that 1·0 mole of this material contained 1·0 mole available bromine.

reflux and the water was removed by azeotropic distillation through a continuous water separator. After 27 hr no more water was separating; therefore the solution was cooled and neutralized with 30 ml of 10% sodium carbonate solution. The organic layer was washed with saturated brine and dried (K_2CO_3). The crystalline residue obtained on evaporation of the solvent at red. press. was recrystallized from 60–68° pet. ether–cyclohexane to give 32·7 g (86% yield), m.p. 115·5–121° with previous softening. Repeated recrystallizations from 60–68° pet. ether gave colorless prisms, m.p. 122·3–122·6°. (Found: C, 65·9; H, 8·7. $C_{14}H_{22}O_4$ requires: C, 66·12; H, 8·72%).

For larger-scale preparations, it was found expedient to distill the crude product in a 2-bulb flask at red. press. Crystallization of the distillate gave yields as high as 67% of material, m.p. 121·8–122·8°.

2-*Bromo*-1,5-*bis-ethylenedioxydecalin* (IX, R^1 = H, R^2 = Br). To a cooled (ice bath) solution of 1·00 g 1,5-bis-ethylenedioxydecalin, m.p. 121·8–122·8°, in 40 ml anhydrous tetrahydrofuran was added 3·16 g phenyltrimethylammonium tribromide, m.p. 115·5–116·1.[15] The solution was allowed to stand 1 hr at ice-bath temp with occasional swirling. Then it was poured into a mixture of 25 ml saturated sodium bicarbonate solution and 50 ml 0·1 N sodium thiosulfate solution. Addition of 50 ml ether and 100 ml ethyl acetate resulted in precipitation of a small amount amorphous solid (probably the dibromo compound) which was removed by filtration. The aqueous layer was extracted with ether, and the combined organic layers were concentrated at red. press. (steam-bath temp). Crystallization from methanol gave a white amorphous product which, on evaporative distillation up to 180° (0·13 mm), gave 0·17 g colorless sublimate, m.p. 166–176° with previous softening. A second crop obtained from the methanol crystallization described above yielded, after 2 recrystallizations from methanol, 0·12 g colorless crystals, m.p. 153–173°. This material was combined with the sublimate described above and chromatographed on 20 g of Florisil. Elution with 25% benzene in hexane gave 0·224 g of a mixture of needles and prisms, m.p. 168–178°. Recrystallization from methanol gave 0·107 g fine colorless needles, m.p. 168–169° (in an evacuated capillary). (Found: C, 50·3; H, 6·2; Br, 23·7. $C_{14}H_{21}O_4Br$ requires: C, 50·46; H, 6·35; Br, 23·98%).

2,6-*Dibromo*-1,5-*bis-ethylenedioxydecalin* (IX, $R^1 = R^2$ = Br). To a cold (ice bath) solution of 3·03 g 1,5-bis-ethylenedioxydecalin, m.p. 121·8–122·8°, in 150 ml anhydrous tetrahydrofuran was added with stirring 9·32 g phenyltrimethylammonium tribromide, m.p. 115·5–116·5°.[15] The mixture was allowed to stir for 4 hr at 0° and was then poured into an ice-cold solution of 10 g potassium carbonate in 300 ml water. The voluminous white precipitate that resulted was separated by filtration and washed with water. After drying for 20 hr at 0·07 mm, it amounted to 3·66 g, m.p. about 200° dec (in an evacuated capillary). Trituration with 25 ml of hot absolute ethanol, then with 10 ml ether gave 3·11 g white powder, m.p. 208·5–209° dec (in an evacuated capillary). Material of this quality was quite suitable for the dehydrobromination step described below.

Crude material from another experiment was recrystallized in turn from chloroform–methanol, chloroform and finally from peroxide-free dioxane to give fine colorless needles, m.p. 214–214·5° dec (in an evacuated capillary). On the hot stage these needles turned slightly brown and opaque at about 200° and gradually melted with sublimation above 230°. (Found: C, 40·95; H, 4·9; Br, 39·0. $C_{14}H_{20}O_4Br_2$ requires: C, 40·80; H, 4·89; Br, 38·78%).

1,5-*Bis-ethylenedioxy*-$\Delta^{2,6}$-*hexalin* (X). A total of 35·0 g 2,6-dibromo-1,5-bis-ethylenedioxydecalin (from combined portions m.p. between 194 and 208°) was partially dissolved in 750 ml of purified[16] dioxane by stirring for 1·5 hr at 100°. The temp of the mixture was lowered to 40°, and the system was then evacuated and filled with nitrogen 3 times. The stirred suspension was cooled to 15°, and 865 ml of a solution of 54 g potassium in 1·6 l. anhydrous t-butyl alcohol was added under nitrogen over a 30-min period. The mixture was then warmed to reflux temp over another 30-min period and heated at this temp with stirring for 14 hr. Most of the solvent was removed by distillation at red. press., 150 ml water was added, and distillation was continued for a while longer to remove traces of t-butyl alcohol. The resulting brown mixture was extracted thoroughly with ether. The combined ether layers were washed thoroughly with water, followed by saturated brine and finally dried (K_2CO_3). The residue obtained upon removal of the solvent at red. press. (steam-bath temp) was triturated with hot methanol to yield 15·47 g (73% yield) colorless prisms, m.p. 140–140·7° (in an evacuated capillary) with previous softening. The second crop amounted to 1·68 g, m.p. 103–120° (in an evacuated capillary) with previous softening. A sample of the first-crop material was recrystallized once from 95% ethanol and twice from isopropyl ether to give irregular colorless plates, m.p. 155·2–155·8° (in an evacuated capillary) with previous softening. On the hot stage these crystals turned opaque at 119° and then began to form colorless blades at 148° before melting at 157–158°. (Found: C, 67·3; H, 7·4. $C_{14}H_{18}O_4$ requires: C, 67·18; H, 7·25%).

A 12·8-g portion of the first-crop material on recrystallization from isopropyl ether gave 5·23 g material, m.p. 146–146·5° (in an evacuated capillary), which was used for the hydrolysis experiment described below.

$\Delta^{2,6}$-*Hexalin*-1,5-*dione* (I). A solution of 5·10 g diene diketal, m.p. 146–146·5°, described directly

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[16] L. F. Fieser, *Experiments in Organic Chemistry* (3rd Edition) p. 285. D. C. Heath, Boston (1955).

above, and 1·5 g *p*-toluenesulfonic acid monohydrate in 250 ml acetone and 25 ml water was stirred for 1·5 hr at room temp (atm. of N_2). It is noteworthy that after 30 min a crystalline precipitate separated which later redissolved. Most of the acetone was removed by distillation at red. press. (55°), 50 ml water was added, and the distillation was continued for a few min to remove traces of acetone. The colorless crystalline precipitate remaining was separated by filtration, washed, and triturated with several portions water to give 2·89 g (87% yield) nearly colorless prisms, m.p. 216–217° (in an evacuated capillary) with softening at 214°. Sublimation at 110–180° (0·15–0·2 mm) followed by recrystallization from 95% ethanol gave 2·75 g colorless irregular prisms, m.p. 228·5–230° (in an evacuated capillary) with previous softening; $\lambda_{\max}^{95\%\ \mathrm{EtOH}}$ 217 mμ (ϵ 18,000); $\lambda_{\max}^{\mathrm{cyclohexane}}$ 212 mμ, $\lambda_{\max}^{\mathrm{CHCl_3}}$ 5·98 μ (conjugated C═O), 6·2 (C═C). See discussion for NMR and mass spectral data. (Found: C, 74·1; H, 6·4. $C_{10}H_{10}O_2$ requires: C, 74·06; H, 6·22%).

Hydrogenation of the hexalindione (I). A quantitative micro hydrogenation of the pure diene dione in 95% ethanol over 10% palladium-on carbon (carried out by E. H. Meier) gave an uptake of hydrogen of 2·1 mole equivalents. In a larger scale experiment, carried out by D. M. Bailey, a solution of 0·128 g somewhat impure diene dione I, m.p. 218–226° (vac), in 125 ml absolute ethanol was hydrogenated over 50 mg 10% palladium-on-carbon (American Platinum Works, Inc.). After 10 min the uptake of hydrogen stopped abruptly, 88% of the theoretical amount of gas being absorbed. The residue obtained on evaporation of the filtrate was crystallized from benzene to give 0·085 g (64%) crystals, m.p. 160–165°, undepressed on admixture with authentic *trans*-decalin-1,5-dione.[3] Trituration of the residues from the mother liquors with pet. ether gave an additional 0·020 g crystals, m.p. 154–160°.

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