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The Synthesis and Acid-catalysed Rearrangements of 4-Hydroxycyclohexa-2,5-dienones 1

By (the late) G. F. Burkinshaw, B. R. Davis,* E. G. Hutchinson, and P. D. Woodgate, Chemistry Department, University of Auckland

R. Hodges, Massey University, Palmerston North, New Zealand

Bicyclic unsaturated ketones possessing an angular hydroxy-group are dehydrogenated with 2,3-dichloro-5,6-dicyanobenzoquinone to the corresponding hydroxydienone (p-quinol) this providing a new route to these systems. The boron trifluoride-catalysed rearrangement of a p-quinol has yielded a spiro-diketone, providing the first example of the isolation of a spiran from the acid-catalysed rearrangement of a bicyclic dienone.

In earlier papers 2,3 we have reported on the synthesis and rearrangement of p-quinols (4-hydroxycyclohexa-2,5-dienones). Previously, we have employed known synthetic methods involving oxidation, either with lead tetra-acetate or peracetic acid, of phenols or their methyl ethers. Rearrangement studies have been concerned with the use of acetic anhydride-sulphuric acid² or with light-induced reactions.³ In this paper we report another synthetic route to p-quinols, and their boron trifluoride-catalysed rearrangement. The synthetic route involves, as a final step, the dehydrogenation with 2,3-dichloro-5,6-dicyanobenzoquinone $(DCDCQ)^4$ of a γ -hydroxy $\alpha\beta$ -unsaturated ketone $[e.g. (I) \longrightarrow (II)]$. To date, this dehydrogenation step, has (with one exception ⁵) been limited to compounds whose blocking groups or angular substituents have been alkyl residues.



The p-quinol synthesis therefore required an efficient route for the formation of a γ -hydroxy- $\alpha\beta$ -unsaturated ketone of the general formula (I). Initially, we explored a number of reactions, including the Robinson ring extension of α -hydroxy-ketones^{6,7} and the allylic oxygenation of $\alpha\beta$ -unsaturated ketones^{8,9} but the most successful method involved treatment of a $\beta\gamma$ epoxy-ketone with acid or base, a route that has been used with success in the steroid field.¹⁰ The overall path is illustrated by the synthesis of 6-hydroxybicyclo[4,4,0]deca-1,4-dien-3-one (II) (Scheme 1).

Birch reduction of 6-methoxy-1,2,3,4-tetrahydronaphthalene (III) gave the expected non-conjugated enol ether (IV).¹¹ Mild acid-catalysed hydrolysis with oxalic acid 12 afforded the $\beta\gamma$ -unsaturated ketone (V), which, on treatment with monoperphthalic acid, gave the corresponding epoxide (VI).

Opening of the epoxide was accomplished most readily by chromatography on alumina, although treatment with dilute acid or base also served to produce



the desired γ -hydroxy- $\alpha\beta$ -unsaturated ketone (I), which could be readily purified and was fully characterised by its analytical and spectral properties. Dehydrogenation with DCDCQ in boiling benzene resulted in a smooth conversion into the known p-quinol (II) in 23% overall yield from the methoxytetrahydronaphthalene (III). This yield compared favourably with those recorded for alternative syntheses.²

This route was then applied to the synthesis of the p-quinol (IX; R = H, n = 1) derived from 5-hydroxyindane (VII). It was not necessary to purify intermediates until the penultimate stage, when the γ hydroxy $\alpha\beta$ -unsaturated ketone (VIII; R = H, n = 1) was obtained as a crystalline solid. DCDCO dehydrogenation gave the desired p-quinol, although in lower yield than in the tetralin case. A similar sequence 6-methoxy-7-methyl-1,2,3,4-tetrahydroemploying naphthalene² gave the hydroxy unsaturated ketone (VIII; R = Me, n = 2). One instance is known where a compound of similar structure (X) was not dehydrogenated by DCDCQ,¹³ and in the present instance, too,

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⁴ D. Walker and J. D. Hiebert, *Chem. Rev.*, **1967**, **67**, 153. ⁵ *Chem. Abs.*, **1965**, **62**, 9203b.

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dehydrogenation was not effected. Presumably the hydrogen atom which must be removed from C-4 is in a sterically hindered 1,3-diaxial relationship with the angular hydroxy-group. Dehydrogenation was then attempted with selenium dioxide, but the reaction



product proved to be complex and difficult to purify. One compound isolated in small yield, was tentatively identified as the phenolic aldehyde (XI) from its m.p. and spectral properties. It arises, presumably, by aromatisation followed by benzylic oxidation.

A second compound, also isolated in low yield, was assigned the dimeric structure (XII). Combustion analysis indicated the formula $C_{22}H_{26}O_3$ and the mass spectrum showed the required molecular ion at m/e338. Intense absorptions at 1680 and 1631 cm⁻¹ in the i.r. region were assigned to the carbonyl and olefinic portions of a cross-conjugated cyclohexadienone group. In addition, peaks at 3540 and 1140 cm⁻¹ were characteristic of the hydroxy-group in p-quinols. U.v. maxima at 245 (c 12,100) and 284-291 nm (ε 3380) defined the dienone and aromatic portions of the molecule respectively. The 100 MHz n.m.r. spectrum was also consistent with the formulation (XII). Apart from the methylene resonances in the region δ 1·25-3·15 p.p.m., a broad six-proton peak at δ 2·64 p.p.m. was assigned to the aryl methyl and vinyl methyl groups, the signals being nearly superimposed. The hydroxy-proton resonance at 8 3.58 p.p.m. disappeared on deuteriation, and two aromatic proton singlets occurred at 8 6.45 and 6.74 p.p.m. Finally, the vinyl proton H_a appeared as a doublet of coupling constant 2 Hz at 8 5.77 p.p.m., the observed splitting being due to allylic coupling with H_b. The major fragment ion in the mass spectrum was at m/e 320, due to loss of water from M^{+} . The mechanism of formation of this dimer is regarded as a Michael-type addition 6-hydroxy-7-methyl-1,2,3,4-tetrahydronaphthalene of (produced by dehydration and aromatisation) on pquinol generated in situ, followed by dehydrogenation.

We turn now to the rearrangement of p-quinols catalysed by boron trifluoride. The chemistry of dienones has been reviewed; 14 of particular concern at this juncture is the acid-catalysed rearrangement of bicyclic dienones for which the general mechanism

proposed by Woodward and Singh¹⁵ is illustrated in Scheme 2. Although there is much indirect evidence



to support the intermediacy of a spiran in this reaction such a species has not been isolated previously. However, it was hoped that introduction of an angular hydroxyl group would stabilise the initial spiro carbonium ion; subsequent loss of the alcoholic proton would then trap the spirocyclic intermediate as an isolable compound. This proved to be the case. Treatment of 6-hydroxybicyclo[4,4,0]deca-1,4-dien-3-one (II) with a dilute solution of boron trifluoride in ether, in the dark, gave a product suggested by the n.m.r. spectrum to be a mixture of starting material and spiro[4,5]dec-7-ene-6,9-dione (XIII) in the approximate ratio of **3**:2. Subtraction of the spectrum of starting



material resulted in a spectrum showing a singlet at δ 6.68 p.p.m. assigned to olefinic protons, a singlet at δ 2.80 p.p.m., assigned to the methylene protons α to one carbonyl group, and a series of broad bands between $\delta 1.0$ and 2.4 p.p.m. assigned to the cyclopentane protons.

Treatment of this unstable mixture with zinc in acetic acid afforded a phenolic compound identified as 6-hydroxy-1,2,3,4-tetrahydronaphthalene, and a neutral compound assigned the structure spiro[4,5]decane-6,9-dione (XIV) on the basis of the following evidence. Combustion analysis indicated the formula C₁₀H₁₄O₂ and the required molecular ion was present at m/e 166 in the mass spectrum. The i.r. spectrum showed a strong band at 1710 cm⁻¹; there was no intense absorption maximum in the u.v. region and the n.m.r. spectrum showed resonances only in the region $\delta 1.20$ — 2.90 p.p.m., typical of methylene groups. A six-proton multiplet centred at 8 2.8 p.p.m. was assigned to the protons α to the carbonyl groups, while a series of bands between δ 1·1 and 2·4 p.p.m. was assigned to the

 ¹⁴ A. J. Waring, Adv. Alicyclic Chem., 1966, 1, 131.
 ¹⁵ R. B. Woodward and T. Singh, J. Amer. Chem. Soc., 1950, 72. 494.

cyclopentane protons. The high-resolution mass spectrum also supported the proposed structure. In particular, several fragment ions contain both oxygen atoms, the proposed structures (in the absence of any gross skeletal rearrangements) for which provide good evidence for the existence of a 1,4-dione moiety in the parent molecule. Thus, m/e 125 (C₇H₉O₂) arises directly from M^{+} as indicated by a weak metastable ion at m/e 94·2. Initial cleavage of the α -carbon bond fused to the spirocyclopentane nucleus followed by internal attack ¹⁶ of the oxygen lone pair electrons



generates ion *a*. Subsequent hydrogen atom transfers and cleavage results in expulsion of the stable allylic radical and formation of the oxonium ion m/e 125. The fragment ions of masses 99 and 85 also contain both oxygen atoms, and their production from the same initial α -cleavage ion represented above can be rationalised as follows:



The hydrogen atom transfer from C-2 of the cyclopentane nucleus to the carbonyl carbon atom occurs *via* an eight-membered ring transition state, the existence of which has previously been demonstrated in mass spectrometry.¹⁷ Subsequent allylic cleavage or vinylic cleavage generates the ions m/e 85 and 99 respectively. Further support for the presence of the partial structure COCH₂CH₂CO in the parent molecule was adduced from the presence of ions at m/e 137 and 109. m/e 137 requires the loss of an ethyl radical from the molecular ion: m/e 109 also arises from m/e 138



(itself formed by loss of carbon monoxide from M^{+}) by expulsion of an ethyl radical (m^* 86·1).



Furthermore, a Dreiding model of the spiro-system having the dione ring in a stable chair conformation with the carbonyl groups disposed *trans* to each other, showed that one of the hydrogen atoms on C-2 is suitably oriented to undergo a McLafferty rearrangement to the C-9 carbonyl oxygen atom, and an important fragment of mass 96, $C_{\rm g}H_{\rm g}O$, can be rationalised as follows:



The diketone gave a bisethylene acetal of the required molecular formula, and the mass spectrum showed the expected simplification to give only one major fragment

- ¹⁶ R. T. Gray, R. J. Spangler, and C. Djerassi, *J. Org. Chem.*, 1970, **35**, 1525.
 - ¹⁷ M. Katoh and C. Djerassi, *Chem. Comm.*, 1969, 1385.

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ion, at m/e 155, $C_9H_{15}O_2$. This sequence involves a series of two-electron shifts:



the driving force for the initial cleavage is probably the generation of a stable tertiary carbonium ion. The alternative charge distribution in the first stage generates the well known m/e 99 ion, O·CH₂·CH₂·O.C·-CH:CH₂, and this was also present (7% relative intensity). These two fragments together define the molecular structure. Initial α -cleavage may, however, occur at other sites in the molecular ion and a weak (4%) fragment at m/e 153 may be accounted for as follows:





The behaviour of the hydroxy-dienone (IX; R = H, n = 1) containing a five-membered ring was examined next. The analogue containing an angular methyl group was studied by Bloom ¹⁸ who showed that the acid-catalysed rearrangement involved a 1,2-methyl migration, rather than formation of a strained spiran containing a cyclobutane ring. In the present case, when the hydroxy-dienone was treated with a dilute solution of boron trifluoride in ether, the only product isolated was 5-hydroxyindane. The mode of formation of this phenol is uncertain.

EXPERIMENTAL

For general experimental details, see ref. 2. Mass spectra were measured on an A.E.I. MS-9 spectrometer operating at 70 eV. In all cases the elemental composition of the fragments indicated was confirmed by high resolution measurement.

Synthesis of Hydroxydienones

6-Hydroxybicyclo[4,4,0]deca-1,4-dien-3-one.-Reduction of 6-methoxy-1,2,3,4-tetrahydronaphthalene with lithium in liquid ammonia,11 followed by acid-catalysed hydrolysis of the enol ether,¹² gave bicyclo[4,4,0]dec-1(6)-en-3-one. Monoperphthalic acid in ether was added to this ketone and the solution was set aside at 4° for 4 days, to give 1,6-epoxybicyclo[4,4,0]decan-3-one (VI) as an oil in 90%yield, $\nu_{max.}$ 1713 (C=O), 1258 cm^-1 (epoxide); δ 2.45 and 2.60 p.p.m. (2d, J 17 Hz, 2H, C-2 protons). This epoxide was then allowed to react under the following conditions. (a) The epoxide (VI) (10 g) was adsorbed on deactivated alumina. Benzene-ether (9:1) eluted starting material (1.0 g), while benzene-ether (2:1) eluted 6-hydroxybicyclo-[4,4,0] dec-1-en-3-one (I) (6.4 g, 64%) as rods, m.p. 67–68° (from acetone) (Found: C, 72.0; H, 8.3. $C_{10}H_{14}O_2$ requires C, 72.3; H, 8.5%), v_{max} 3400 (OH), 1680, and 1612 cm⁻¹ (O=C-C=C); δ 1.0–3.0 (12H, methylene protons), 3.96 (s, OH, exchanged with D_2O), and 5.57 p.p.m. (s, 1H, C-2 vinyl H), λ_{max} 233.5 nm (ε 13,500).
(b) The epoxide (2.2 g) was heated under reflux with

(b) The epoxide $(2\cdot 2 \text{ g})$ was heated under reflux with 5% methanolic potassium hydroxide (80 ml) for 1 hr. Chromatography of the product on alumina gave the hydroxy-ketone (I) (1.0 g, 45%) as rods, m.p. 67-68° (from acetone) with identical spectral properties.

(c) The epoxide (1.0 g) in acetone (20 ml) was set aside with 1.5n-aqueous perchloric acid (8 ml) for 24 h to give the same hydroxy-ketone (0.5 g, 50%), identified by mixed m.p., and spectral properties.

6-Hydroxybicyclo[4,4,0]deca-1,4-dien-3-one (II).—The hydroxy-enone (I) (0.30 g) and 2,3-dichloro-5,6-dicyanobenzoquinone (0.64 g) were heated under reflux in dry benzene (50 ml) for 6 h and the cooled solution was poured onto an alumina column. Elution with benzene–ether (2:1) gave 6-hydroxybicyclo[4,4,0]deca-1,4-dien-3-one (0.15 g, 50%), m.p. 124—125° (lit.,² 125°), i.r., u.v., and n.m.r. spectra identical with those of an authentic sample.

5-Methoxyindane (VII; R = Me).—Reaction of indane with acetyl chloride and aluminium chloride gave 5-acetylindane, which on oxidation with perbenzoic acid gave 5-acetoxyindane, b.p. 119—121°/5·5 mm (Found: C, 74·7; H, 6·7. Calc. for $C_{11}H_{12}O_2$: C, 75·0; H, 6·9%), ν_{max} 1750 cm⁻¹ (ArOAc). Basic hydrolysis gave 5-hydroxyindane (VII; R = H), m.p. 54° (lit.,¹⁹ 55°), which, on reaction with methyl iodide and potassium t-butoxide, gave 5-methoxyindane, with correct i.r. and n.m.r. spectra.

6-Hydroxybicyclo[4,3,0]non-1-en-3-one.—Lithium (3.55 g) was added, during 10 min, to a solution of 5-methoxyindane (VII; R = Me) (15.0 g) in ether (60 ml) and liquid ammonia (200 ml). After a further 15 min ethanol was added and the solution was worked up to give 3-methoxybicyclo-[4,3,0]nona-1(6),3-diene (14.3 g, 95%), as an oil, $n_{\rm p}^{20}$ 1.5080, $\nu_{\rm max}$. 1660 (trisubstituted C=C str.), 1220 and 1030 cm⁻¹ (vinyl ether); δ 3.49 (s, OMe) and 4.65 p.p.m. (s, 1H, C-4 vinyl H). Oxalic acid dihydrate (13.4 g) in aqueous ethanol (260 ml) was added to a solution of the methoxy-diene (16.0 g) in ethanol (100 ml) and the solution was stirred at 20° for 2 h. Work-up gave bicyclo[4,3,0]non-1(6)-en-3-one (VIII; R = H, n = 1) (12.1 g, 84%) as an oil, $\nu_{\rm max}$. 1710 (C=O) and 1660 cm⁻¹ (C=C). Monoperphthalic acid (0.3 mol) in ether was added to the unsaturated ketone

¹⁹ 'Elsevier's Encyclopaedia of Organic Chemistry,' ed. E. Josephy and F. Radt, Elsevier, New York, vol. 12A, 182.

¹⁸ S. M. Bloom, J. Amer. Chem. Soc., 1959, 81, 4728.

(12.0 g, 0.09 mol) and the solution was stood at 4° for 5 days. Work-up gave 1,6-epoxybicyclo[4,3,0]nonan-3-one (7.8 g, 60%) as an oil, ν_{max} 1710 (C=O), 1258 cm⁻¹ (epoxide); δ 2.18 and 2.39 p.p.m. (2d, J 18 Hz, 2H, C-2 methylene).

The epoxide (7.8 g) was adsorbed onto deactivated alumina and the column was eluted as follows: (a) benzene eluted unchanged unsaturated ketone (1.2 g, 15%); (b) benzene-ether (10:1) eluted the epoxide (1.1 g, 14%); (c) benzene-ether (3:1) eluted 6-hydroxybicyclo[4,3,0]non-1-en-3-one (4.0 g, 51%) which crystallised as rods, m.p. 66—67° (from acetone) (Found: C, 70.8; H, 7.9. C₉H₁₂O₂ requires C, 71.0; H, 7.9%), ν_{max} 3595, 3350 (OH), 1660 (conj. C=O), 1623 (C=C), and 935 cm⁻¹ (C=C-H o.o.p. def.); δ 2.45 (s, 1H, OH, exchanged with D₂O) and 5.82 p.p.m. (s, 1H, C-2 vinyl H); λ_{max} 233.5 nm (ϵ 13,600).

6-Hydroxybicyclo[4,3,0]nona-1,4-dien-3-one (IX; R = H, n = 1).—The hydroxy-unsaturated ketone (VIII; R = H, n = 1) (0.78 g) and 2,3-dichloro-5,6-dicyanobenzoquinone (1.3 g) were heated under reflux in benzene (100 ml) for 8 h. The cooled solution was adsorbed onto a column of alumina. Elution with benzene-ether (2:1) gave 6-hydroxybicyclo-[4,3,0]nona-1,4-dien-3-one (0.10 g, 13%) as plates, m.p. 68—70° (Found: $M^{+:}$, 150.0681. C₉H₁₀O₂ requires 150.0681), ν_{max} 3580 (OH), 3030 (=CH), 1670 (C=O), 1642, 1610 (C=C), and 845 (C=CH, o.o.p. def.); δ 1.63 (s, 1H, OH, exchanged with D₂O), 5.94 (d, $J_{2.4}$ 2 Hz, 1H, C-2 vinyl H), 6.03 (2d, $J_{4.2}$ 2 Hz, $J_{4.5}$ 9 Hz, 1H, C-4 vinyl H), and 7.00 (d, J 9 Hz, 1H, C-5 vinyl H); λ_{max} 236 nm (ϵ 12,100).

6-Hydroxy-4-methylbicyclo[4,4,0]dec-1-en-3-one (VIII; R = Me, n = 2).—6-Methoxy-7-methyl-1,2,3,4-tetrahydronaphthalene (15.5 g) in dry ether (50 ml) was added to liquid ammonia. Lithium (4.3 g) was added during 10 min and the solution was then stirred for 30 min. Addition of ethanol and work-up gave 3-methoxy-4-methylbicyclo[4,4,0]deca-1(6),3-diene (15.2 g, 95%) as an oil, ν_{max} . 1340 (C-Me) and 1078 cm⁻¹ (=C-O-C str.); δ 1.55 (s, 3H, C-4 Me) and 3.45 p.p.m. (s, 3H, OMe).

Oxalic acid dihydrate (10.6 g) in aqueous ethanol was added to a solution of the methoxy-diene (15.0 g) and the mixture was stirred for 3 h. Work-up gave 4-methylbicyclo[4,4,0]dec-1(6)-en-3-one (13.0 g, 95%) as an oil, $\nu_{\rm max}$. 1710 (C=O) and 1380 cm⁻¹ (C-Me); δ 1.07 p.p.m. (d, J 6 Hz, 3H, C-4 Me).

Reaction of this unsaturated ketone (13.0 g, 0.08 mol.) with monoperphthalic acid (0.09 mol.) in ether for 3 days at 4° gave 1,6-epoxy-4-methylbicyclo[4,4,0]decan-3-one (14.0 g, 97%) as an oil, ν_{max} . 1710 (C=O) and 1220 cm⁻¹ (epoxide), δ 1.16 (d, J 6.5 Hz, 3H, C-4 Me), 2.53 and 2.80 p.p.m. (2d, J 19 Hz, 2H, C-2 methylene protons).

The crude epoxide (14·0 g) was adsorbed onto a column of alumina which was eluted as follows: (a) benzene eluted both unchanged epoxide (2·7 g, 19%) and unreacted unsaturated ketone (0·4 g, 3%); (b) benzene-ether (1:1) eluted the hydroxy-ketone (VIII; R == Me, n = 2) (10·4 g, 70%) which crystallised from acetone as rods, m.p. 91–92° (Found: C, 73·2; H, 8·9. C₁₁H₁₆O₂ requires C, 73·3; H, 8·9%), ν_{max} 3600, 3400 (OH), 1675 (C=O), 1630 (C=C), 1380 (CMe), and 1158 cm⁻¹ (OH), δ 1·08 (d, J 6·5 Hz, 3H, C-4 Me), 2·35 (s, OH, exchanged with D₂O), and 5·70 p.p.m. (s, 1H, C-2 vinyl H); λ_{max} 233·5 nm (ε 13,400). The hydroxy unsaturated ketone was recovered un-

The hydroxy unsaturated ketone was recovered unchanged on attempted reaction with 2,3-dichloro-5,6-dicyanobenzoquinone.

Selenium Dioxide Dehydrogenation .--- The hydroxy un-

saturated ketone (VIII; R = Me, n = 2) (8.6 g) and selenium dioxide (5.6 g) in t-butyl alcohol (120 ml) and glacial acetic acid (3 ml) were heated under reflux (nitrogen) for 27 h. The cooled solution was added to chloroform (100 ml) and filtered. Partial purification was achieved by filtration through alumina and washing of the eluate with ammonium sulphide. Preparative t.l.c. yielded a number of compounds.

One compound was tentatively identified as 7-formyl-6-hydroxy-1,2,3,4-tetrahydronaphthalene (XI), m.p. 52-53° (lit.,²⁰ m.p. 56·5–57·5°), ν_{max} 3030 (aromatic CH), 1660 (hydrogen bonded aromatic aldehyde), 1570 and 1488 cm⁻¹ (aromatic C=C); 81.66-1.95 (m, 4H, methylene protons), 2.58-2.96 (m, 4H, benzylic protons), 6.67 and 7·20 p.p.m. (s, each 1H, aromatic H); λ_{max} 218, 227, and 268 nm (z 17,550, 17,300, and 14,600). A second product was formulated as the dimer (XII), m.p. 170-171° (Found: C, 78.05; H, 7.8. $C_{22}H_{26}O_3$ requires C, 78.1; H, 7.7%), v_{max} 3540, 1680, 1631, 1140, and 1100 cm⁻¹; δ 1.25-2.2 (m, 12H, methylene protons), 2·2-2·5 (m, 3H, methylene protons), 2.64 (broad s, 6H, aryl and vinyl Me), 2.85-3.15 (m, 1H, methylene H), 3.58 (s, OH, exchanged with D₂O), 5.77 (d, J 2 Hz, 1H, vinyl proton), 6.45 (s, 1H, aromatic H), 6.74 p.p.m. (s, 1H, aromatic H); $\lambda_{max.}$ (CHCl₃) 245 and 283-291 nm (ε 12,100 and 3380); $M^+ \cdot 338$.

Boron Trifluoride-Ether Rearrangements

6-Hydroxybicyclo[4,4,0]deca-1,4-dien-3-one.-The dienone (0.20 g) in ether (20 ml) was treated with boron trifluorideether (2 ml) and the solution was kept in the dark for 40 h. The solution was poured into water and the ethereal extract was worked up to yield a pale orange oil (0.15 g). The n.m.r. spectrum of this oil was consistent with its being a 3:2 mixture of starting material and spiro[4,5]dec-7-ene-6,9-dione (XIII). Purification of this unstable product was not attempted; the total product in ether (20 ml) was added to zinc powder (0.20 g) in acetic acid (8 ml) and the mixture was heated under reflux for 3 h. Addition of water, and ether extraction gave both acidic and neutral fractions. The acidic fraction gave 6-hydroxy-1,2,3,4-tetrahydronaphthalene (60 mg), identified by its i.r. spectrum and by t.l.c. The neutral fraction gave needles of spiro[4,5] decane-6,9-dione (from light petroleumether), m.p. $88.5-89.5^{\circ}$ (Found: C, 72.0; H, 8.4%; M^{+} , 166.0998. C₁₀H₁₄O₂ requires C, 72.3; H, 8.5%; M^{++} , 166-0994), ν_{max} . 1710 (C=O), 1440 cm⁻¹ (CH₂CO); δ 1·20-2·90 p.p.m. (CH₂ envelope). The bisethylene acetal was obtained as an oil, by reaction of the diketone with ethanediol and acid (Found: m/e 155.1068. C9H15-O₂ requires m/e 155·1072), v_{max} 1115 cm⁻¹ (C–O–C).

6-Hydroxybicyclo[4,3,0]nona-1,4-dien-3-one.—The dienone (0.20 g) in ether (10 ml) was treated with boron trifluorideether (1 ml) and the solution was set aside in the dark for 60 h. Work-up, as above, and chromatography on alumina gave 5-hydroxyindane (100 mg, 50%) as needles, m.p. 54° (lit.,¹⁹ 55°), identical by i.r. and n.m.r. spectra and t.l.c. behaviour.

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²⁰ R. T. Arnold, H. E. Zaugg, and J. Sprung, J. Amer. Chem. Soc., 1941, **63**, 1314.