Allylic Rearrangements of Cyclo-octatetraenylmethanols

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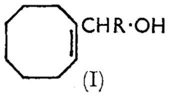
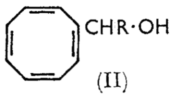
Three alcohols in which the hydroxy-group is allylic to one of the double bonds of a cyclo-octatetraene ring have been prepared by condensation of cyclo-octatetraenyl-lithium with benzaldehyde and acraldehyde, and by reduction of the ketone obtained from cyclo-octatetraenyl-lithium and crotononitrile. In acid solution all three alcohols undergo allylic rearrangements, but only in the case of the alcohol derived from benzaldehyde is the major product formed by migration of the cyclo-octatetraene double bond.

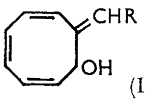
THE preparation and acid-catalysed rearrangement of the cyclo-octenyl alcohols (Ia—c) have been described by Braude *et al.*[1] Here we describe similar work with the cyclo-octatetraenyl analogues (IIa—c).



(I)

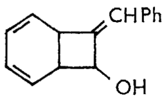


(II)

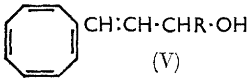


(III)

a; R = Ph
b; R = $CH{:}CH_2$
c; R = CH:CHMe

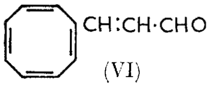


(IV)

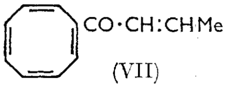


(V)

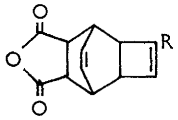
a; R = H
b; R = Me



(VI)



(VII)



(VIII)

a; R = Bz
b; R = CO·CH:CHMe

Treatment of cyclo-octatetraenyl-lithium with benzaldehyde in ether at −70° afforded the known [2] alcohol (IIa). The alcohol was also obtained by reduction of benzoylcyclo-octatetraene with lithium aluminium hydride as described by Cope and Marshall,[2] and was oxidised back to this ketone with the chromium trioxide–pyridine complex. In acidified aqueous acetone the alcohol slowly rearranged to give an isomer which showed u.v. maxima at 260 and 300 mμ and which on catalytic hydrogenation gave 2-benzylcyclo-octanol and a hydrocarbon which was not obtained pure but which was identified as benzylcyclo-octane; oxidation of the 2-benzylcyclo-octanol gave 2-benzylcyclo-octanone, identical with an authentic sample. On these grounds the rearrangement product was assigned the structure (IIIa), although the possibility that the material also contained the valence-bond isomer (IV) was not ruled out. Oxidation of the rearrangement product with chromium trioxide–pyridine afforded an unstable oil from which no pure compounds were isolated, but its i.r. spectrum indicated the absence of benzoylcyclo-octatetraene. This evidence indicates that in acid solution the alcohol (IIa) isomerises completely, and hence in this respect it is similar to α-(cyclopentenyl)-,[3] α-(cyclohexenyl)-,[4] and α-(cycloheptenyl)-[5] benzyl alcohol but is different from α-(cyclo-octenyl)-benzyl alcohol [1] (Ia) which only partly isomerises. Presumably the cyclo-octenyl system is anomalous because in the rearrangement product (2-benzylidenecyclo-octanol) there are non-bonded interactions which are not present in the lower 2-benzylidenecycloalkanols or in the cyclo-octatrienol (IIIa).

In the acid-catalysed allylic rearrangement of the alcohol (Ib) the hydroxy-group migrates to C-2 of the ring rather than to C-3′ of the side-chain.[1] In contrast, the cyclo-octatetraenyl alcohol (IIb), which was obtained from acraldehyde and cyclo-octatetraenyl-lithium, rearranged in acid solution to give the primary alcohol (Va), although both the i.r. and the u.v. spectrum indicated that the rearrangement product also contained at least one of the other two possible allylic isomers which have the hydroxy-group on a ring carbon atom, *e.g.* (IIIb). Oxidation of the rearrangement product with chromium trioxide–pyridine gave the aldehyde (VI), together with a high proportion of polymeric material.

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[1] E. A. Braude, W. F. Forbes, B. F. Gofton, R. P. Houghton, and E. S. Waight, *J. Chem. Soc.*, 1957, 4711.

[2] A. C. Cope and D. J. Marshall, *J. Amer. Chem. Soc.*, 1953, **75**, 3208.

[3] E. A. Braude and W. F. Forbes, *J. Chem. Soc.*, 1951, 1755.

[4] E. A. Braude and J. A. Coles, *J. Chem. Soc.*, 1950, 2014.

[5] E. A. Braude, E. A. Evans, and W. F. Forbes, *J. Chem. Soc.*, 1953, 2202.

In an attempt to prepare the butenol (IIc), crotonaldehyde was treated with cyclo-octatetraenyl-lithium. The product was an unstable oil which showed strong carbonyl absorption (1765 cm.$^{-1}$). The ketone (VII) was therefore prepared from cyclo-octatetraenyl-lithium and crotononitrile, and was purified by way of the silver nitrate complex. Reduction of this ketone with lithium aluminium hydride proceeded largely by 1,4-addition, whereas treatment with potassium borohydride resulted in reduction of both the keto-group and the double bond of the side chain. The alcohol (IIc) was finally prepared by a Meerwein–Ponndorf reduction of the ketone, but the quantity obtained was very small, and although the u.v. and i.r. spectrum of the product which was isolated when the alcohol was kept in acid solution suggested that rearrangement had occurred to give the isomer (Vb), insufficient material was available for confirmation of this by chemical means.

Of the various mono-substituted cyclo-octatetraenes described here, those in which the substituent is conjugated with the ring double bond to which it is attached have u.v. absorption spectra very similar to those of the corresponding 1-substituted cyclo-octenes, whereas those in which the substituent is not conjugated with ring double bond have spectra almost identical to that of cyclo-octatetraene.

Treatment of benzoylcyclo-octatetraene and the ketone (VII) with maleic anhydride afforded adducts which were assigned the structures (VIIIa) and (VIIIb), respectively, on the basis of the i.r. and u.v. evidence and also by analogy with the structure of the maleic anhydride adduct obtained from phenylcyclo-octatetraene.[6]

EXPERIMENTAL

All experiments with cyclo-octatetraene derivatives were carried out under pure, dry nitrogen. I.r. spectra of solids and liquids were recorded for Nujol mulls and liquid films respectively. U.v. spectra were recorded for solutions in ethanol.

Benzoylcyclo-octatetraene.—Cyclo-octatetraenyl bromide [7] (20 g.) in dry ether (25 ml.) was added to n-butyl-lithium [from n-butyl bromide (27 g.)] in dry ether (400 ml.) at −78° and the mixture was stirred at this temperature for 7 hr. Benzonitrile (20 g.) in dry ether (25 ml.) was then added dropwise during 5 min. and the mixture was kept at −78° for a further 15 min. The cooling bath was removed, and the mixture was warmed to −10° and then poured into ice-cold water (400 ml.). The aqueous layer was extracted with ether (2 × 100 ml.), the extracts were added to the ether layer, and the combined organic material was rapidly extracted with ice-cold 0·5N-hydrochloric acid (3 × 200 ml.). The extracts were combined and added to chloroform (200 ml.), and the mixture was heated under reflux for 30 min. and then cooled. The chloroform layer was separated, dried, and fractionated to give the ketone (14·2 g., 63%) as a yellow liquid, b.p. 115—120°/0·1 mm., n_D^{22} 1·6120, which solidified when cooled in ice and then had m.p. 36—37° [from light petroleum (b.p. 40—60°)] (lit.,[2] m.p. 38—39·5°), $\lambda_{max.}$ 250 mμ (ε 12,300), $\nu_{max.}$ 1653 cm.$^{-1}$.

α-(*Cyclo-octatetraenyl*)*benzyl Alcohol* (IIa).—Benzaldehyde (9·0 g.) in dry ether (20 ml.) was added dropwise during 10 min. to a stirred solution of cyclo-octatetraenyl-lithium [from the bromide (9·7 g.)] in dry ether (200 ml.) at −75°. The mixture was stirred for 30 min. at −78°, the cooling bath was removed, and when the temperature of the mixture reached −10°, ice-cold saturated aqueous ammonium chloride (100 ml.) was added. The ether layer was separated, dried, and fractionated to give the alcohol (5·4 g., 47%) as a viscous yellow liquid, b.p. 129—130°/0·3 mm., n_D^{21} 1·5980 [lit.,[2] b.p. 110—120° (bath)/0·1 mm., n_D^{25} 1·5982], i.r. spectrum indistinguishable from that of an authentic sample prepared (90%) by reduction of benzoylcyclo-octatetraene with lithium aluminium hydride as described by Cope and Marshall.[2]

Oxidation of α-(*Cyclo-octatetraenyl*)*benzyl Alcohol.*—The alcohol (1·16 g.) in benzene (10 ml.) was added to the complex [8] prepared from chromium trioxide (1·5 g.) and pyridine (15 ml.), and the mixture was shaken for 18 hr. at room temperature. The solid was filtered off and washed with benzene (20 ml.), and the filtrate and washings were combined and filtered through a short column of alumina (Spence, type H). The column was washed with benzene (20 ml.), and the filtrate and washings were combined and fractionated to give benzoylcyclo-octatetraene (0·76 g., 66%), which was not obtained crystalline, b.p. 110—115°/0·3 mm., n_D^{19} 1·6118, $\lambda_{max.}$ 249 mμ (ε 12,500).

The liquid ketone (0·43 g.), maleic anhydride (0·60 g.), and *o*-dichlorobenzene (10 ml.) were heated together under reflux for 2 hr. to give the *adduct* (VIIIa) (0·44 g. 70%), m.p. 194° (from benzene), $\lambda_{max.}$ 260 mμ (ε 11,300), $\nu_{max.}$ 1849 and 1768 (anhydride CO), 1636 (ketone CO), and 1582 cm.$^{-1}$ (four-membered ring conjugated C⁚C) (Found: C, 74·8; H, 4·7. $C_{19}H_{14}O_4$ requires C, 74·5; H, 4·6%).

2-*Benzylidenecyclo-octa*-3,5,7-*trienol* (IIIa).—α-(Cyclo-octatraenyl)benzyl alcohol (0·12 g.) in a 0·1N solution of hydrogen chloride in 48% (v/v) aqueous acetone was kept for 6 days at room temperature. The mixture was neutralised with saturated aqueous sodium hydrogen carbonate, and the bulk of the acetone was removed under reduced pressure. Extraction of the residual material with ether (2 × 10 ml.) afforded the *alcohol* (0·10 g., 83%), as a viscous orange oil, n_D^{19} 1·6270, $\lambda_{max.}$ 260 and 300 mμ (ε 6900 and 7800 respectively) (Found: C, 85·2; H, 6·95. $C_{15}H_{14}O$ requires C, 85·7; H, 6·7%). The 3,5-*dinitrobenzoate* had m.p. 154—155° [from benzene–light petroleum (b.p. 40—60°)] (Found: C, 65·3; H, 3·9; N, 6·7. $C_{22}H_{16}N_2O_6$ requires C, 65·3; H, 4·0; N, 6·9%).

Hydrogenation of 2-*Benzylidenecyclo-octa*-3,5,7-*trienol* (IIIa).—The alcohol (1·10 g.) in acetic acid (30 ml.) was hydrogenated over Adams platinum (200 mg.) and the reaction was stopped when the theoretical amount of hydrogen (4 mol.) had been absorbed. The catalyst was filtered off and the filtrate was added to water (500 ml.). The mixture was extracted with ether and the extract was washed with saturated aqueous sodium hydrogen carbonate and dried, and the ether was removed by fractionation through a Dufton column (8 in.). The residual liquid was

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[6] R. Huisgen, F. Mietzsch, G. Boche, and H. Seidl, ' Organic Reaction Mechanisms,' *Chem. Soc. Special Publ.* No. 19, 1965, p. 3.

[7] A. C. Cope and M. Burg, *J. Amer. Chem. Soc.*, 1952, **74**, 168.

[8] G. I. Poos, G. E. Arth, R. E. Beyler, and L. H. Sarett, *J. Amer. Chem. Soc.*, 1953, **75**, 422.

chromatographed in light petroleum (b.p. 40—60°) on acid-washed alumina to give an oil (0·12 g.), b.p. 105—115° (bath)/0·1 mm., n_D^{21} 1·5150, which had an i.r. spectrum very similar to that of a sample of benzylcyclo-octane, b.p. 93—98°/0·1 mm., n_D^{18} 1·5140, prepared (67%) by catalytic hydrogenation of α-(cyclo-octatetraenyl)benzyl alcohol as described by Cope and Marshall.[2] Elution of the column with 5% (v/v) ethanol–light petroleum (b.p. 40—60°) afforded 2-*benzylcyclo-octanol* (0·70 g., 62%), b.p. 105—108°/0·1 mm., n_D^{20} 1·5410 (Found: C, 83·0; H, 10·4. $C_{15}H_{22}O$ requires C, 82·5; H, 10·2%).

2-*Benzylcyclo-octanone*.—(*a*) 2-Benzylidenecyclo-octanone[1] (0·80 g.) in acetic acid (25 ml.) was hydrogenated over Adams platinum (10 mg.) until hydrogen (1 mol.) had been absorbed. Isolation of the product in the usual manner afforded the *ketone* (0·72 g., 89%), b.p. 115—120°/0·2 mm., n_D^{23} 1·5375 (Found: C, 83·7; H, 9·6. $C_{15}H_{20}O$ requires C, 83·3; H, 9·3%). The 2,4-*dinitrophenylhydrazone* had m.p. 126—127° (from methanol) (Found: C, 63·3; H, 5·9; N, 14·1. $C_{21}H_{24}N_4O_4$ requires C, 63·6; H, 6·1; N, 14·1%).

(*b*) Chromium trioxide (0·30 g.) in 80% (v/v) aqueous acetic acid (2 ml.) was added to 2-benzylcyclo-octanol (0·56 g.) in acetic acid (5 ml.) and the mixture was kept for 18 hr. and then poured into water (100 ml.). Extraction with ether afforded the ketone (0·40 g., 72%), b.p. 95—100°/0·05 mm., n_D^{19} 1·5300, which had an i.r. spectrum indistinguishable from that of the sample described before, and gave a 2,4-dinitrophenylhydrazone, m.p. and mixed m.p. 125—126°.

1-*Cyclo-octatetraenylprop*-2-*en*-1-*ol* (IIb).—Freshly distilled acraldehyde (4·5 g.) in dry ether (50 ml.) was added dropwise during 10 min. to a stirred solution of cyclo-octatetraenyl-lithium [from the bromide (8·5 g.)] in dry ether (200 ml.) at −75°. The mixture was stirred for 3 min. at −78° and then added to 10% aqueous ammonium chloride (500 ml.). The ether layer was separated, dried, and fractionated to give the *alcohol* (3·53 g., 43%) as a yellow liquid, b.p. 75—77°/0·5 mm., n_D^{19} 1·5560, $\nu_{max.}$ 990s and 925s ($>C=CH_2$) cm.$^{-1}$ (Found: C, 82·6; H, 7·7. $C_{11}H_{12}O$ requires C, 82·45; H, 7·55%).

Acid-catalysed Rearrangement of 1-*Cyclo-octatetraenylprop*-2-*en*-1-*ol* (IIb).—A solution of the alcohol (0·97 g.) in a 0·1N solution of hydrogen chloride in 60% (v/v) aqueous acetone (400 ml.) was kept for 3 days at room temperature. Isolation of the product in the usual manner afforded a yellow-orange liquid (0·54 g., 56%), b.p. 90—94°/0·2 mm., n_D^{21} 1·6215, $\lambda_{max.}$ 235 and 293 mμ (ε 19,900 and 5800), $\nu_{max.}$ 966s (·CH=CH·) and 907s ($>C=CH_2$) cm.$^{-1}$ (Found: C, 82·5; H, 7·7. Calc. for $C_{11}H_{12}O$: C, 82·45; H, 7·55%).

3-*Cyclo-octatetraenylprop*-2-*en*-1-*al*.—The preceding product (0·23 g.) in benzene (5 ml.) was added to the complex prepared from chromium trioxide (0·30 g.) and pyridine (10 ml.), and the mixture was shaken for 24 hr. The solid was filtered off and the filtrate was diluted with ether (250 ml.). The material which precipitated was filtered off and the filtrate was washed with ice-cold N-hydrochloric acid (4 × 250 ml.) and with saturated aqueous sodium hydrogen carbonate, and then dried and fractionated to give the *aldehyde* (91 mg., 40%) as an orange liquid, b.p. 70—80° (bath)/0·3 mm., n_D^{21} 1·6310, $\lambda_{max.}$ 265 mμ (ε 21,800), $\nu_{max.}$ 2791, 2705, 1689 (CO), and 969s ($\cdot CH\overset{t}{=}CH\cdot$) cm.$^{-1}$ (Found: C, 83·2; H, 7·0. $C_{11}H_{10}O$ requires C, 83·5; H, 6·4%). The 2,4-*dinitrophenyl hydrazone* was chromatographed on kieselguhr–bentonite[9] and had m.p. 230—231° (from ethyl acetate), $\lambda_{max.}$ ($CHCl_3$) 395 mμ (ε 43,500) (Found: C, 60·2; H, 4·6; N, 16·4. $C_{17}H_{14}N_4O_4$ requires C, 60·4; H, 4·2; N, 16·6%).

1-*Cyclo-octatetraenyl*-2-*en*-1-*one* (VII).—Crotononitrile[10] (4·2 g.) in dry ether (20 ml.) was added dropwise during 5 min. to a stirred solution of cyclo-octatetraenyl-lithium [from the bromide (6·95 g.)] in dry ether (200 ml.) at −75°. The mixture was stirred at −78° for 20 min. and then added to 10% aqueous ammonium chloride (500 ml.). The ether layer was separated and rapidly extracted with ice-cold N-hydrochloric acid (4 × 100 ml.), and the extracts were combined and heated under reflux for 1 hr. with methylene dichloride (250 ml.). The crude *ketone* (2·42 g.), b.p. 96—104°/0·5 mm., which was obtained when the mixture was cooled and the organic layer was separated, dried, and fractionated, was heated under reflux for 10 min. with silver nitrate (2·42 g.) in ethanol (50 ml.) to give the silver nitrate *complex* (3·67 g., 76%) as a pale yellow solid, m.p. 114—115° (decomp.) (Found: C, 42·1; H, 3·9; N, 4·1. $C_{12}H_{12}AgNO_4$ requires C. 42·1; H, 3·5; N, 4·1%). A suspension of the complex (6·6 g.) in water (150 ml.) was treated with aqueous ammonia (*d* 0·880; 50 ml.) to give the pure ketone (2·48 g., 75%) as an orange-red liquid, b.p. 80—81°/0·1 mm., n_D^{20} 1·5770, $\lambda_{max.}$ 244 mμ (ε 12,900), $\nu_{max.}$ 1667, 1621, and 958 cm.$^{-1}$ (Found: C, 83·3; H, 6·9. $C_{12}H_{12}O$ requires C, 83·7; H, 7·0%).

The *adduct* ((VIIIb) 0·20 g., 41%) which was formed when the ketone (0·31 g.), maleic anhydride (0·80 g.), and *o*-dichlorobenzene (12 ml.) were heated together under reflux for 1·5 hr. had m.p. 176—177° (from methanol), $\lambda_{max.}$ 256 mμ (ε 14,700), $\nu_{max.}$ 1664, 1609, and 1581 cm.$^{-1}$ (Found: C, 71·3; H, 5·15. $C_{16}H_{14}O_4$ requires C, 71·1; H, 5·2%).

Reduction of 1-*Cyclo-octatetraenylbut*-2-*en*-1-*one* (VII).—(a) *With lithium aluminium hydride*. Lithium aluminium hydride (0·15 g.) in dry ether (30 ml.) was added dropwise during 10 min. to a stirred solution of the ketone (1·15 g.) in dry ether (20 ml.) at 0°. Isolation of the product in the usual manner gave impure 1-cyclo-octatetraenylbutan-1-one (0·78 g.), b.p. 76—80°/0·2 mm., n_D^{19} 1·5470, $\nu_{max.}$ 1666 cm.$^{-1}$. The 2,4-*dinitrophenylhydrazone* was chromatographed on kieselguhr–bentonite[9] and then had m.p. 142—143° (Found: C, 60·4; H, 4·8; N, 16·0. $C_{18}H_{18}N_4O_4$ requires C, 61·0; H, 5·1; N, 15·8%).

(b) *With potassium borohydride*. The ketone (1·92 g.), potassium borohydride (1·0 g.), and 75% (v/v) aqueous methanol (55 ml.) were heated together under reflux for 30 min., and then the mixture was cooled and added to water (100 ml.). Extraction with ether afforded 1-*cyclo-octatetraenylbutan*-1-*ol* (1·64 g., 85%) as a yellow liquid, b.p. 75—80°/0·1 mm., n_D^{19} 1·5400 (Found: C, 81·8; 81·6; H, 8·75, 8·6. $C_{12}H_{16}O$ requires C, 81·7; H, 9·15%. Hydrog. no. in ethyl acetate: 44·25. Calc. for 4 double bonds, 44·0).

(c) *With aluminium isopropoxide*. The ketone (0·74 g.) in dry toluene (50 ml.) was added dropwise during 1 hr. to aluminium isopropoxide (1·0 g.) in dry toluene (50 ml.), and then more toluene (300 ml.) was added dropwise during 3 hr. During the additions the volume of the mixture was kept constant by slow distillation. The mixture was cooled. 10% aqueous ammonium chloride (200 ml.) was added, and the organic layer was separated, dried, and fractionated to give a yellow oil (0·20 g.), b.p. 83—85°/0·3 mm., which was

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[9] J. A. Elvidge and M. Whalley, *Chem. and Ind.*, 1955, 589.

[10] R. A. Letch and R. P. Linstead, *J. Chem. Soc.*, 1932, 443.

chromatographed in light petroleum (b.p. 40—60°) on a column of acid-washed alumina. Elution of the second main band afforded 1-*cyclo-octatetraenylbut*-2-*en*-1-*ol* (IIc) (61 mg., 8%), b.p. 80—90° (bath)/0·3 mm., n_D^{20} 1·5470 (Found: C, 82·3; H, 9·0. $C_{12}H_{14}O$ requires C, 82·7; H, 8·1%).

Acid-catalysed Rearrangement of 1-*Cyclo-octatetraenylbut*-2-*en*-1-*ol* (IIc).—The alcohol (54 mg.) was kept in a 0·1N solution of hydrogen chloride in 80% (v/v) aqueous acetone (5 ml.) for 48 hr. Isolation of the product in the usual manner gave a yellow-orange liquid (47 mg.), n_D^{21} 1·5620, $\lambda_{max.}$ 234 mμ (ε 15,500), $\nu_{max.}$ 966s cm.$^{-1}$.

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