Two Allyl-isomeric Dibenzocyclononatetraenes

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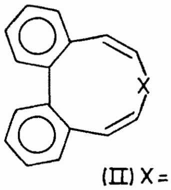
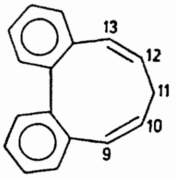
Summary 11*H*-Dibenzo[*a,c*]- and 9*H*-dibenzo[*a,c*]-cyclononatetraene, (IV) and (V), have been synthesised and proved to be much more stable than cyclononatetraene (I).

CYCLONONATETRAENES have been the subject of calculations and experimental research.[1] Although there has been indirect evidence for their existence since 1963, they have been isolated only recently.[2,3] The parent compound cyclononatetraene (I) proved to be unstable,[2] and even the anions of its derivatives tend to isomerize to bicyclic systems.[1b,4] As in other "pseudoaromatic" systems[5] such an electron reorganization would be suppressed in the *benzologues* of cyclonatetraene since it would involve disruption of the benzenoid structures. In the series of benz-annelated conjugated nine-membered-ring systems only derivatives of oxonin and thionin have been prepared *viz.* 4,5;6,7-dibenzoxonin (II) and 4,5;6,7-dibenzothionin (III).[6]

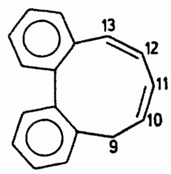
(I)



(II) X=O
(III) X=S



(IV)



(V)

We report the preparation and some properties of the first benz-annelated carbocyclic nine-membered-ring system, 11*H*-dibenzo[*a,c*]cyclononatetraene (IV) and its isomerization to 9*H*-dibenzo[*a,c*]cyclononatetraene (V). The Wittig reaction between biphenyl-2,2′-dialdehyde and the bisphosphorane derived from trimethylene bromide[7] in the presence of sodium methoxide in $HCONMe_2$ (50°, 3 h, argon atmosphere) gave after chromatography on silica gel a 5% yield of 11*H*-dibenzo[*a,c*]cyclononatetraene (IV), m.p. 40°. The spectral properties [i.r. (Nujol) 1660, 1630, 1460, 1430, and 760 (strong) cm^{-1}; u.v. (EtOH) 217 (20,000), 243 (7000), and 293 nm (sh) (ϵ 280)] are in accord with the assigned structure. The band at 760 cm^{-1} and the absence of any absorption between 900 and 1000 cm^{-1} in the i.r. indicate *cis*-configuration of the double bonds in (IV) (cyclononatetraene shows an absorption at 700 cm^{-1}).[2a] The u.v. spectrum is almost identical with that reported for 4,5;6,7-dibenzoxonin (II).[6] The n.m.r. spectrum (100 MHz, $CDCl_3$) confirms the structure of (IV). It exhibits a multiplet at δ 7·0—7·3 p.p.m. (8H, aromatic), two broad singlets at 5·3 and 6·5 p.p.m. (2H, vinylic 9-H and 13-H), five sharp lines centred at 5·5 p.p.m. (2H, vinylic 10-H and 12-H), and a triple triplet centred at 2·67 p.p.m. (2H, methylene 11-H). Irradiation at 2·67 p.p.m. transformed the vinylic absorptions into an AB spectrum of four sharp lines: δ_A 6·0, δ_B 5·75 p.p.m., J_{AB} 12 Hz (supporting the all-*cis*-configuration). The n.m.r. spectrum did not change at low temperatures (−60°).

11*H*-Dibenzo[*a,c*]cyclononatetraene (IV) is rather stable: heating for 7 h at 70° or 1 h at 160°, or prolonged standing in the air, left its spectral properties unchanged.

Attempts to characterize the dibenzo[*a,c*]cyclononatetraenyl anion from (IV) have failed so far. However, reaction of 11*H*-dibenzo[*a,c*]cyclononatetraene (IV) with dimethyl sulphoxide anion in dimethyl sulphoxide, followed by the usual work-up, caused isomerization to another hydrocarbon which remains an oil after chromatography on silica gel. The i.r. spectrum is very similar to that of (IV). The n.m.r. spectrum (100 MHz, $CDCl_3$) exhibits a multiplet at 6·9—7·4 p.p.m. (8H, aromatic), a complex multiplet at 5·4—6·1 p.p.m. (4H, vinylic 10-, 11-, 12-, and 13-H) and a broad band (multiplet) at 3·1 p.p.m. (2H, methylene 9-H_2). The methylene protons (9-H_2), being benzylic, appear at lower field as compared with the respective protons (11-H, allylic) of (IV), and as expected the absorption of the vinylic hydrogens is complex. Irradiation at 3·10 p.p.m. did not cause any significant change in the vinylic region, thus supporting structure (V).

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