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Synthesis of 2,5-Diphenylbicyclo[4.2.0]octa-2,4-diene. Exclusive Existence in the Bicyclic Form and a Correction of the Reported Structure of 2,5-Diphenyl-1,3,5-cyclooctatriene

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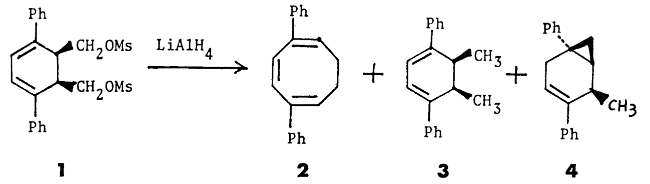
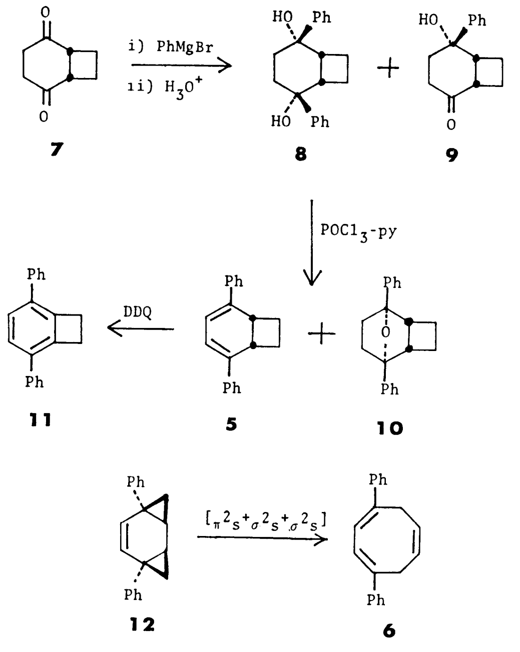
Synopsis. 2,5-Diphenylbicyclo[4.2.0]octa-2,4-diene has been found to exist exclusively in the bicyclic form, giving rise to questioning the reported structure of 2,5-diphenyl-1,3,5-cyclooctatriene. The structure of 1,4-diphenyl-1,3,6-cyclooctatriene is proposed for the compound.

Courtot and Rumin reported that reduction of the dimesylate of *cis*-5,6-bis(hydroxymethyl)-1,4-diphenyl-1,3-cyclohexadiene (**1**) with lithium aluminum hydride gives 2,5-diphenyl-1,3,5-cyclooctatriene (**2**) along with 5,6-dimethyl-1,4-diphenyl-1,3-cyclohexadiene (**3**) and 1,4-diphenyl-5-methylbicyclo[4.1.0]hept-3-ene (**4**).[1]

In the course of studies on unsaturated eight-membered ring compounds, we prepared 2,5-diphenylbicyclo[4.2.0]octa-2,4-diene (**5**), a valence isomer of **2**, and found that compound **5** exclusively exists in the bicyclic form at room temperature to 100 °C. This gave rise to questioning the reported structure of **2**. A reasonable alternative structure for the compound of Courtot and Rumin seems to be 1,4-diphenyl-1,3,6-cyclooctatriene (**6**) for several reasons.



Scheme 1.



Scheme 2.

Reaction of bicyclo[4.2.0]octane-2,5-dione (**7**)[2] with phenylmagnesium bromide (five equivalents) gave 2,5-diphenylbicyclo[4.2.0]octane-*r*-2,*c*-5-diol (**8**) and 5-hydroxy-5-phenylbicyclo[4.2.0]octan-2-one (**9**). The stereochemistry of these compounds was assigned from a steric point of view. Dehydration of **8** with phosphoryl chloride in pyridine gave **5** and 1,6-diphenyl-9-oxatricyclo[4.2.1.0^{2,5}]nonane (**10**).

The ^{1}H-NMR spectrum of **5** (CCl_4) exhibits signals at δ 2.3—2.8 (4H, m, H-7,8), 3.92 (2H, m, H-1,6), 6.38 (2H, s, H-3,4), and 7.0—7.5 (10H, m, aromatic protons), in line with the bicyclic structure. The spectrum did not change even after heating the solution at 100 °C for 4 h. Treatment of **5** with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone readily gave 2,5-diphenylbicyclo[4.2.0]-octa-1,3,5-triene (**11**).

The results indicate that between the bicyclic structure (**5**) and the ring-opened structure (**2**), the former is thermodynamically favorable. Thus, the reported structure of **2** is questionable. The reasonable structure of Courtot's compound is probably 1,4-diphenyl-1,3,6-cyclooctatriene (**6**) for the following reasons: (i) The methylene protons of **2** appear at δ 3.20 in the ^{1}H-NMR spectrum. The chemical shift is 0.77 ppm lower than that of 1,3,5-cyclooctatriene itself (δ 2.43),[3] being nearer to that of 1,3,6-cyclooctatriene (δ 2.70).[4] In structure **6**, the phenyl group would exert relatively large down-field anisotropy effect on the adjacent methylene protons, whereas, in structure **2**, no such large effect is expected. (ii) Similar reduction of the *trans* isomer of **1** was reported to give a *trans*-bis-σ-homobenzene derivative as the main product.[1] Therefore, it would be highly probable that Courtot's compound was obtained from the *cis*-bis-σ-homobenzene derivative (**12**) by $[_{\pi}2_s+_{\sigma}2_s+_{\sigma}2_s]$ cycloreversion. *cis*-Bis-σ-homobenzenes have been reported to undergo cycloreversion readily.[5]

The reason for compound **5** exclusively existing in the bicyclic form should be noted. 1,3,5-Cyclooctatriene itself is at equilibrium with bicyclo[4.2.0]octa-2,4-diene with free energy difference of only 1.1 kcal mol^{-1} (89.2: 10.8 at 60 °C).[6] The ratio is largely affected by introduction of substituents.[6,7] Since the cyclohexadiene moiety of **5** should be almost planar, the gain of conjugative energy by the introduction of the phenyl groups at C-2 and -5 might be sufficient to favor the bicyclic form. Such an effect by phenyl has also been observed in cycloheptatriene-norcaradiene equilibrium.[8]

Experimental

Melting points were determined with a Thomas-Hoover apparatus and are uncorrected. IR, UV, and ^{1}H-NMR spectra were recorded with a Hitachi 215, a Hitachi 323, and a JEOL PMX 60 spectrometer, respectively. Microanalyses were performed at the Microanalytical Laboratory in this department.

Reaction of Bicyclo[4.2.0]octane-2,5-dione (7) with Phenylmagnesium Bromide. An ethereal solution (20 ml) of **7** (1.38 g, 10 mmol) was added dropwise at room temperature over a period of 15 min to an ethereal solution (*ca.* 100 ml) of phenylmagnesium bromide prepared from bromobenzene (7.85 g, 50 mmol) and magnesium (1.21 g, 50.4 mmol).[9] Dry tetrahydrofuran (150 ml) was added and the mixture was stirred under nitrogen for 16 h. 1 M Sulfuric acid (20 ml) and then water (200 ml) was added. The products were extracted ethyl acetate (2 × 50 ml). The extracts were washed with water, and brine, and dried over $MgSO_4$. After removal of the solvent the residue was chromatographed on silica gel. Elution with dichloromethane gave, in the order of elution, 2,5-diphenylbicyclo[4.2.0]octane-*r*-2,*c*-5-diol (**8**) (0.640 g, 20.5 %) and 5-hydroxy-5-phenylbicyclo[4.2.0]octan-2-one (**9**) (1.18 g, 54.6%). (**8**): colorless crystals from benzene–dichloromethane; mp 140—142 °C; IR (KBr) ν 3300, 1498, 1453, 1006, 753, 703 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.9—2.4 (8H, m), 3.03 (2H, m), 3.57 (2H, s, OH), 7.2—7.6 (10H, m). Found: C, 81.69; H, 7.78%. Calcd for $C_{20}H_{22}O_2$: C, 81.60; H, 7.53%. (**9**): colorless crystals from benzene–dichloromethane; mp 162—162.5 °C; IR (KBr) ν 3350, 1695, 967, 752, 698 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.9—2.7 (8H, m), 3.0—3.5 (2H, m), 7.2—7.5 (5H, m). Found: C, 77.71; H, 7.65%. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46%.

Dehydration of the Diol (8). A solution of the diol (**8**) (318 mg, 1.08 mmol) and phosphoryl chloride (1.67 g, 11 mmol) in pyridine (5 ml) was heated under nitrogen at 50 °C for 3.5 h. The cooled mixture was poured into cold 6 M hydrochloric acid (15 ml) and extracted with benzene (2 × 20 ml). The extracts were washed with water and dried. The solvent was removed and the residue was chromatographed on silica gel. Elution with benzene–hexane gave, in the order of elution, 2,5-diphenyl-bicyclo[4.2.0]octa-2,4-diene (**5**) (120 mg, 43%) and 1,6-diphenyl-9-oxatricyclo[4.2.1.0^{2,5}]nonane (**10**) (45.6 mg, 15%). (**5**): yellow needles from ethanol–dichloromethane; mp 131—133 °C; IR (KBr) ν 1590, 1546, 1495, 1450, 850, 765, 745, 684 cm^{-1}; UV (cyclohexane) λ 233 (log ε 4.06), 358 (4.36), 366 nm (sh. 4.34). Found: C, 92.84; H, 7.32%. Calcd for $C_{20}H_{18}$: C, 92.98; H, 7.02%, (**10**): colorless crystals from hexane; mp 83—84 °C; IR (KBr) ν 1600, 1010, 967, 754, 700 cm^{-1}; ^{1}H-NMR (CCl_4) δ 1.5—1.9 (4H, m), 1.97 (4H, s), 2.97 (2H, m), 7.0—7.5 (10H, m). Found: C, 86.81; H, 7.38%. Calcd for $C_{20}H_{20}O$: C, 86.92; H, 7.29%.

Dehydrogenation of the Diene (5). A mixture of the diene (**5**) (30.3 mg, 0.117 mmol) and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (28.3 mg, 0.124 mmol) in benzene (2 ml) was stirred at room temperature for 40 h. Filtration gave 2,3-dichloro-5,6-dicyanohydroquinone (22.5 mg). The filtrate was chromatographed on silica gel, eluted with benzene, to give 2,5-diphenylbicyclo[4.2.0]octa-1,3,5-triene (**11**) (17.7 mg. 59%); colorless crystals from hexane–dichloromethane; mp 182—183 °C; IR (KBr) ν 3050, 1590, 1472, 1451, 1067, 1021, 777, 759, 752 cm^{-1}; UV (cyclohexane) λ 289.5 nm (log ε 4.47); ^{1}H-NMR ($CDCl_3$) δ 3.45 (4H, s), 7.2—7.8 (12H, m). Found: C, 93.43; H, 6.48%. Calcd for $C_{20}H_{16}$: C, 93.71; H, 6.29%.

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4) Measured in our laboratory.

5) a) G. Kaupp and K. Rosch, *Angew. Chem. Int. Ed. Engl*, **15**, 163 (1976); b) H. Prinzbach, D. Stusche, J. Markert, and H. H. Limbach, *Chem. Ber.*, **109**, 3505 (1976).

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9) An appreciable amount of white solids separated out, hindering completion of the reaction.