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STRUCTURE OF THE POLYPHOSPHORIC ACID DEHYDRATION PRODUCT OF 1,5-DIPHENYL-1-PENTEN-3-OL

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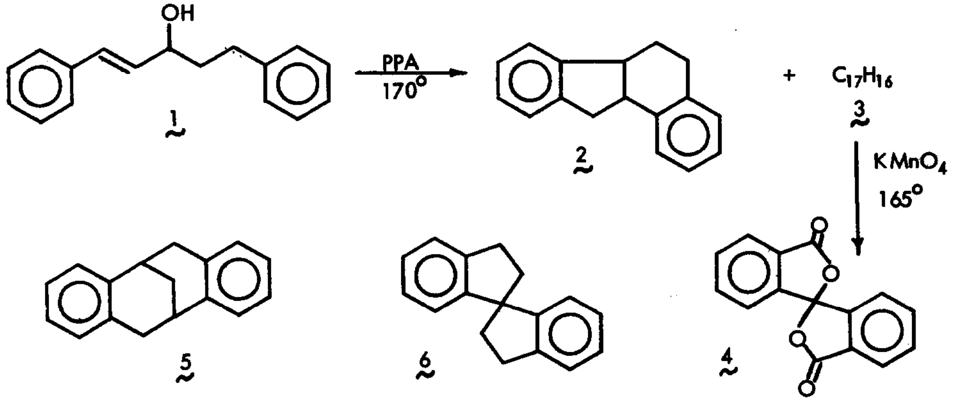
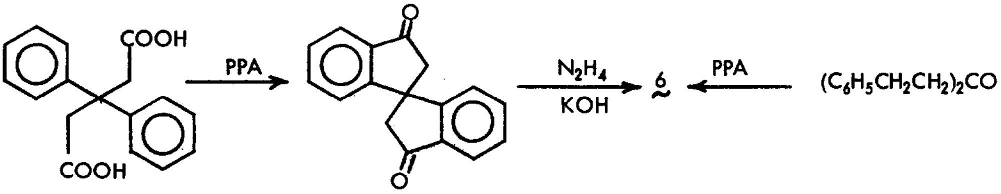
Stetter and Reische[2] reported in 1960 that although 1,5-diphenyl-1-penten-3-ol (**1**) was dehydrated by potassium bisulfate to the expected 1,5-diphenyl-1,3-pentadiene, dehydration with polyphosphoric acid (PPA) was accompanied by cyclization to give a mixture of 6,6a,11,11a-tetrahydro-5H-benzo[a] - fluorene (**2**) and an unknown crystalline hydrocarbon (**3**), $C_{17}H_{16}$, m.p. 120.5-121°. The crystalline product was characterized by the following properties:

(i) It contained no double bonds beyond those present in the two benzene rings and is therefore tetracyclic; (ii) the ir spectrum showed bands (750 and 1100 cm^{-1}) characteristic of *ortho*-disubstituted benzenes but lacked those of mono- and trisubstituted aromatic rings; (iii) vigorous permanganate oxidation gave the known dilactone (**4**) of benzophenone-2,2'-dicarboxylic acid; (iv) the hydrocarbon was not identical with a sample of 2,3,6,7-dibenzobicyclo[3.3.1] nonadiene (**5**) synthesized for comparison.

On the basis of these results Stetter and Reische suggested 1,1'-spirobiindane (**6**) as the probable structure of **3**.



We recently had occasion to prepare authentic 1,1'-spirobiindane (6) by two straightforward methods[3]:

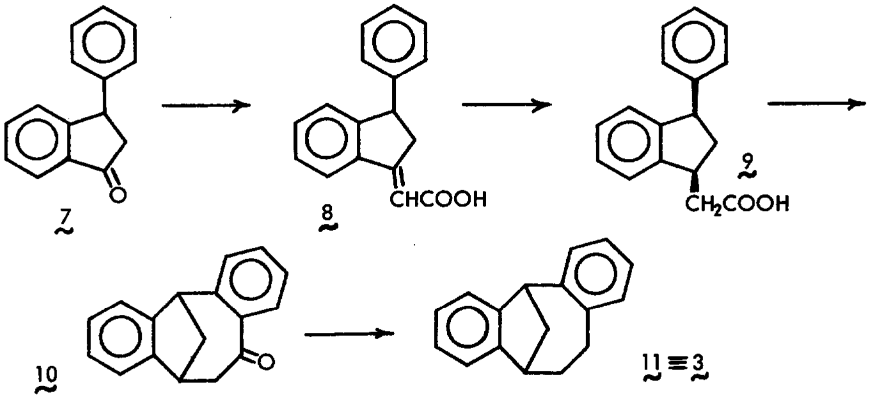


Genuine 6 prepared by these routes is not crystalline at room temperature; moreover its nmr and ir spectra do not agree with those of 3, a sample of which we synthesized by Stetter's method. Using nmr and glc analysis we were unable to detect 6 in the total crude product mixture resulting from PPA dehydration of 1.

Similarities in the nmr spectra of 3 and dibenzobicyclo[3.2.1] octadiene[4] led us to believe that 3 might be 2,3,7,8-dibenzobicyclo[4.2.1] nonadiene (11), a structure which also appeared to be mechanistically more probable than 6. Since this compound has not been reported previously (we could find mention of only one compound with the carbon skeleton of 11[5])we have carried out two independent syntheses of 11 to confirm its identity with 3.

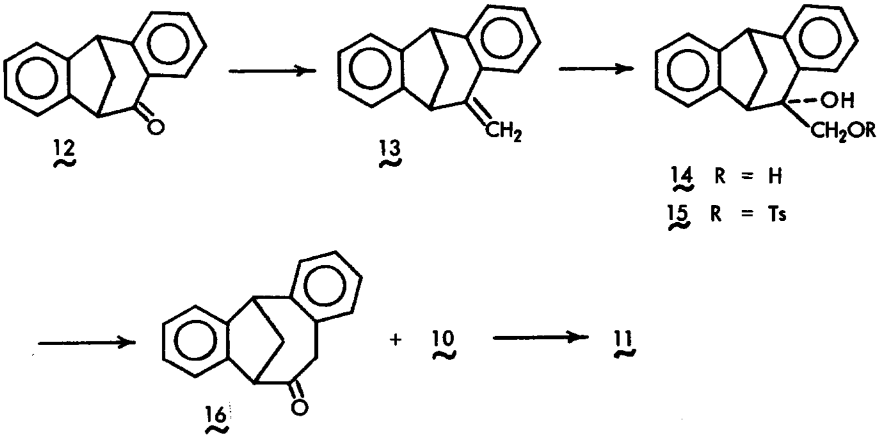
Scheme 1. The starting material was the known[6] 3-phenyl-1-indanone. Emmons reaction with triethylphosphonoacetate (NaH in 1,2-dimethoxyethane, 12 hr, 25°) gave a mixture of conjugated and unconjugated esters (ir 1710, 1740 cm^{-1}). Alkaline hydrolysis gave acid 8, an oily mixture of geometric and double-bond isomers, which was directly reduced (H_2, Pd/C, 50 psi) to the saturated acid[7] 9, m.p. 134° (chloroform-pentane) in 43% overall yield from 7. Alternatively, Reformatsky reaction of 7 with ethyl bromoacetate, followed by dehydration with hot p-toluenesulfonic acid, hydrogenation, and saponification, afforded 9 in 81% overall yield. Pure 9 is a single isomer, undoubtedly cis because of its preparation by catalytic hydrogenation; its methyl ester (CH_2N_2) was homogeneous by glc and showed a sharp methoxy singlet (δ 3.68) in the nmr spectrum. Consonant with its cis configuration, Friedel-Crafts cyclization of 9 (PPA, 140°, 1.5 hr) yielded the bicyclic ketone[7] 10 (81 %), b.p. 175° (0.2 mm), ir 1665, 1600 cm^{-1}, semicarbazone m.p. 230-231°. Huang-Minlon reduction led (77 %) to hydrocarbon 11, m.p. 120-121°. The two bridgehead protons stand out distinctly in the nmr spectra of 10 and 11; H_1 appears as a doublet (J = 8 Hz) at δ 4.1-4.2, while H_6 shows a characteristic five-line peak at δ 3.5. The methylene adjacent to the carbonyl group in 10 appears as a doublet at δ 3.07, and the methylene bridge as a multiplet between 2.1 and 2.8.

SCHEME 1



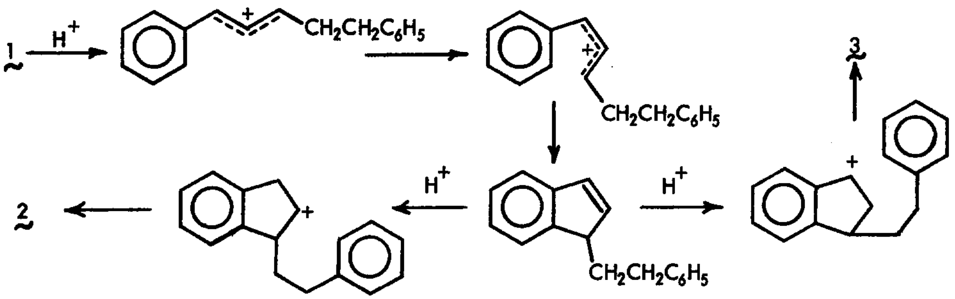
Scheme 2. An alternative preparation of 11 began with the known[8] dibenzobicyclo[3.2.1]-octadien-2-one (12), prepared by Collins oxidation of the corresponding alcohol[9]. Wittig reaction with methylenetriphenylphosphorane gave olefin 13 (83 %), nmr: vinyl singlets at δ 5.03 and 5.30, bridgehead singlets at δ 3.83 and 3.90, converted by osmium tetroxide hydroxylation to diol 14 (70 %) and thence to its monotosylate 15. Pinacolic ring expansion ($CaCO_3$ in DMF, 100°, 24 hr) gave a mixture of two ketones, 10 (ir 1665 cm^{-1}) and 16 (ir 1720 cm^{-1}). This mixture was not separated but converted directly to 11, m.p. 120-121°, by Huang-Minlon reduction (63 % from 14).

SCHEME 2



The samples of 11 synthesized by Schemes 1 and 2 were identical (ir, nmr, mixed m.p.) with each other and with Stetter's dehydration product 3. The oxidation of 3 to 4, which may have been partially responsible for the erroneous proposal 6, is in fact characteristic[10] of the dibenzobicyclo[3.2.1]-octadiene ring system and consequently reasonable for 11.

A plausible mechanism for the formation of 2 and 3 from a common intermediate can be suggested:



Dehydration of 1 as well as the syntheses shown in Schemes 1 and 2 represent short and convenient routes to dibenzobicyclo[4.2.1] nonadiene and functionalized derivatives which make this novel ring system readily available for further study.

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9. We thank Prof. S.J. Cristol, University of Colorado, for his kindness in sending us a sample of this alcohol.
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