

Addition of Cycloheptatrienylidene and Diphenylcyclopropenylidene to Tetracyclones

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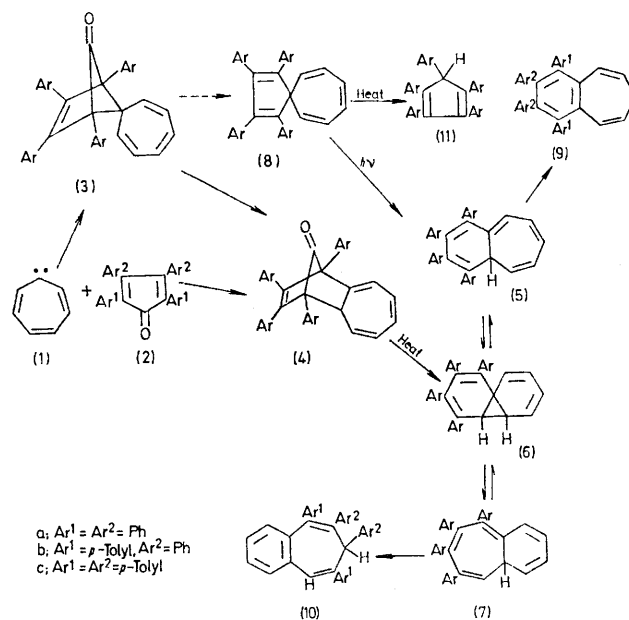
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Summary Addition of cycloheptatrienylidene to tetracyclones gives the benzocycloheptatrienes (**9**) and (**10**) arising from the intermediates (**5**) and (**7**) which are believed to equilibrate through the bis-norcaradiene (**6**); addition of 2,3-diphenylcyclopropenylidene gives products that would be expected of 1,4-addition of the carbene to the diene system.

As a continuation of our interest in the chemical properties of carbenes in which the vacant orbital of the singlet state is an integral component of a carbocyclic aromatic system,¹ we have studied the addition of cycloheptatrienylidene (**1**) to three tetracyclones, dienes which have both the electron deficiency that should be conducive to attack by a nucleophilic carbene and the restricted geometry that should optimize a concerted 1,4-addition.[†]

Cycloheptatrienylidene was generated in the presence of tetracyclones (1:1.5 M) by pyrolysis (diglyme; 100°; 5 h) of the sodium salt of troponone toluene-*p*-sulphonylhydrazone.³ Work-up followed by chromatography on basic alumina gave a mixture of the isomeric benzocycloheptatrienes (**9**) and (**10**)[‡] (isomer ratio 9:10, *ca.* 1:2) in total yield of 30–40% (**9a**) m.p. 238°; (**9b**) 248°; (**9c**) 255°; (**10a**) 102°; (**10b**) 107°; (**10c**) 121°; (**10a–c**) remained as viscous semi-solids after becoming transparent. The isomer (**9a**) was easily separated from ethanol-soluble (**10a**) and

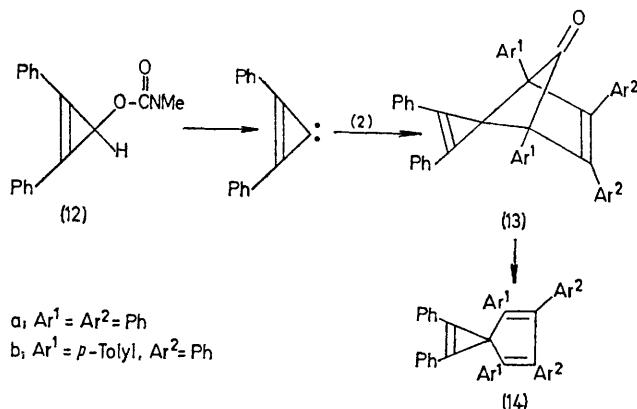
identified by comparison with an authentic sample.⁴ The n.m.r. spectra (CDCl₃) of (**9b**) and (**9c**) showed one and two



[†] Simple orbital symmetry theory² predicts 1,4-addition to be allowed if the attacking carbene assumes a σ -approach. This is the presumed mode of attack of aromatic carbenes on electron deficient double bonds.

[‡] Analytical and mass spectral data of all new products are in accord with their assigned structures.

methyl signals, respectively, [(9b) τ 7.77; (9c) 7.94 and 7.75] further supporting the symmetrical structure of (9). On the other hand, the n.m.r. spectra of (10)§ exhibited an extremely unsymmetrical feature [τ (CDCl₃) (10a) 4.63 (1H, s), 2.5—3.3 (25H, m); (10b) 7.78 (3H, s), 7.72 (3H, s), 4.68 (1H, s), 2.57—3.30 (23H, m); (10c) 7.90 (3H, s), 7.80 (3H, s), 7.77 (3H, s), 7.72 (3H, s), 4.71 (1H, s), 2.57—3.33 (21H, m)]. The u.v. spectrum of (10a) showed λ_{\max} (MeCN) 275 nm (ϵ 34,000); cf. (9a) 250 (48,000).



Formation of (9) and (10) and the complete absence of penta-arylcyclopentadienes from these reactions is compelling evidence against a reaction scheme involving thermal decarbonylation of the 1,4-carbene adduct (3) since it is known that thermolysis of (8) under the conditions of the reaction gives a good yield of the cyclopentadiene (11) and none of (9) or (10).⁶ On the other hand, formation of (9) and (10) in these reactions is interesting in that, not only do they suggest a unique method of entry¶ [via (4)] into the manifold but they also have important bearing on the

§ For unambiguous proof of structure, see ref. 5.

¶ The origin of (4) is not clear. One possibility is thermal rearrangement of 1,2-adducts of (1) and (2). On the other hand, it is not possible at this time to exclude either thermal reorganization of initially formed (3) or even a concerted 1,4-addition of either cycloheptatrienyliene or, possibly, cycloheptatetraene to give (4) directly.

†† When this intermediate was suggested we were unaware of a report of a set of experiments by Gruber and Pomerantz⁷ in which the parent bis-norcaradiene was postulated to explain deuterium scrambling from thermolysis (408°) of benzocycloheptatriene.

¹ W. M. Jones, M. E. Stowe, E. E. Wells, jun., and E. W. Lester, *J. Amer. Chem. Soc.*, 1968, **90**, 1849.

² R. B. Woodward and R. Hoffmann, 'The Conservation of Orbital Symmetry,' Verlag Chemie Academic Press, Weinheim, 1970, p. 70; R. Hoffmann, *J. Amer. Chem. Soc.*, 1968, **90**, 1475; W. Kirmse, 'Carbene Chemistry,' Academic Press, New York, 1971, p. 281.

³ W. M. Jones and C. L. Ennis, *J. Amer. Chem. Soc.*, 1969, **91**, 6391.

⁴ H. Dürr and G. Scheppers, *Angew. Chem. Internat. Edn.*, 1968, **7**, 371.

⁵ H. Dürr, H. Kober, I. Halberstadt, U. Neu, T. Coburn, T. Mitsuhashi, and W. M. Jones, *J. Amer. Chem. Soc.*, 1973, **95**, 3818.

⁶ H. Dürr and H. Kober, *Tetrahedron Letters*, 1972, 1255, 1259.

⁷ G. W. Gruber and M. Pomerantz, *Tetrahedron Letters*, 1970, 3755.

⁸ For other spiro[2,4]heptatriene derivatives, see E. T. McBee, G. W. Calundann, and T. Hodgins, *J. Org. Chem.*, 1966, **31**, 4260; H. Dürr, L. Schrader, and H. Seidl, *Chem. Ber.*, 1971, **104**, 391; H. Dürr, R. Sergio, and W. Comber, *Angew. Chem. Internat. Edn.*, 1972, **11**, 224; H. Dürr and B. Ruge, *ibid.*, p. 225; T. Severin, H. Krämer, and P. Adhikary, *Chem. Ber.*, 1971, **104**, 972.

mechanism of equilibration of (5) and (7) resulting from photolysis of (8).⁵ Thus, it was suggested that (9) and (10) arise from thermal equilibration of (5) and (7) through the bis-norcaradiene (6).^{5††} However, under the conditions of the reaction it was not possible to exclude a photolytically allowed 1,11 sigmatropic interconversion of (5) and (7) by-passing (6). Furthermore, it was not possible to study this reaction in the absence of light since thermolysis of (8) gives only (11).⁶ Formation of (9) and (10) from (4) leaves no question but that the interconversion of (5) and (7) does not require light. Furthermore, (9) and (10) are formed in identical ratios when the (5), (6), (7) manifold is entered at the same temperature from either (8) (photolysis at 100°) or (4) [thermolysis of the tosylhydrazone of (1) at 100°]. Thus, it would appear that the (5) \rightleftharpoons (7) process is thermally induced in both cases.

In contrast to the complex chemistry found in the cycloheptatrienyliene case, addition of diphenylcyclopropenyliene to tetracyclones appears rather straightforward. Thus, when generated from (12)¹ in benzene-*n*-heptane under reflux (8 h) in the presence of (2a) or (2b), the carbene gave ca. 20% (14a) (m.p. 220°) and (14b) (m.p. 213°).⁸ [λ_{\max} (MeCN) (14a) 228 (ϵ 48,000), 236 (50,000), 312 (41,000), 329 (36,000); (14b) 228 (43,000), 237 (43,000), 313 (35,000), 329 nm (32,000)]. The n.m.r. spectrum (CCl₄) of (14a) shows three phenyl multiplets with the same intensity (τ 3.16, 3.03, and 2.64), and that of (14b) has only one methyl signal (τ 7.87) and aromatic multiplets (τ 3.35, 3.01, and 2.61).

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