The Photoaddition of Diphenylacetylene to Norbornadiene

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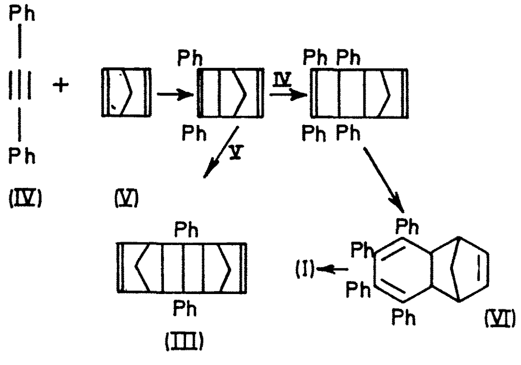
Summary Irradiation of diphenylacetylene and norbornadiene gives 1,2,3,4-tetraphenylbenzene, *p*-terphenyl, and a 2 : 1 adduct of norbornadiene and diphenylacetylene.

LITTLE is known about the reactions of an excited diphenylacetylene,[1–4] although studies have been reported on reactions of diphenylacetylene as a substrate.[5] Diphenylacetylene reacts with 2,3-dihydropyran[2] or tetramethylethylene[3] to give cyclobutene derivatives. We report on the novel photoadditions of diphenylacetylene to norbornadiene.



SCHEME

A mixture of diphenylacetylene (1 g) and norbornadiene (20 g) was irradiated for 45 h through a Pyrex filter with a high-pressure mercury lamp. Chromatography on silica gel gave 1,2,3,4-tetraphenylbenzene (I) (m.p. 189·5—190·5°, 430 mg, 40% yield).† Irradiation of a solution of diphenylacetylene (1 g) and norbornadiene (20 g) in benzene (65 ml) gave 1,2,3,4-tetraphenylbenzene (I) (217 mg, 20% yield), *p*-terphenyl (II) (m.p. 208—209°, 13 mg, 1% yield), and a 2 : 1 adduct of norbornadiene and diphenylacetylene, (III) (m.p. 175—176; 150 mg, 7% yield) after chromatography on silica gel. The structures of (I)[6] and (II) were established by the identity of their i.r. spectra with those of authentic samples, mixed m.ps. Elemental analysis and the mass spectrum (M^+ 362) indicated that (III) is a 2 : 1 adduct of norbornadiene and diphenylacetylene. The n.m.r. spectrum (CCl_4) shows an AB quartet at τ 9·26 and 8·39 (4H, methylene bridge protons, *J* 9 Hz), singlets at 7·80 (4H, cyclobutane protons) and 7·63 (4H, bridgehead protons), a doublet at 4·08 (4H, olefinic protons, *J* 1 Hz), and a multiplet for the aromatic protons at 2·75 (10H). The simple n.m.r. spectrum indicates that (III) has the symmetrical structure. Two *endo–endo*-structures and two *exo–exo*-structures are possible for (III), but its exact stereochemical configuration has not yet been determined.

Compound (I) may be formed (Scheme) by the elimination of cyclopentadiene from intermediate (VI), which has not yet been isolated.‡ *p*-Terphenyl, which may be considered to be formed from (III) by the elimination of two molecules of cyclopentadiene, was not produced on irradiation of (III) under the experimental conditions.

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† Small amounts of (II) and (III) were detected by g.l.c., but these products could not be isolated.

‡ As the dissociation (VI) → (I) is allowed concerted thermal process,[7] it is not surprising that (VI) was not isolated.

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