

THE PHOTOLYSIS AND PYROLYSIS OF BIS-2,3-DIPHENYLCYCLOPROPENE

ANHYDRIDES: BENZVALENE

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When the anhydride of triphenyl- $\Delta^{2,3}$ -cyclopropene carboxylic acid, is irradiated, or pyrolysed, hexaphenylbenzene is formed¹. Although a prismane intermediate² could be postulated, the results of the irradiation or pyrolysis of the anhydride of 2,3-diphenyl- $\Delta^{2,3}$ -cyclopropene carboxylic acid (I) indicate a benzvalene intermediate.

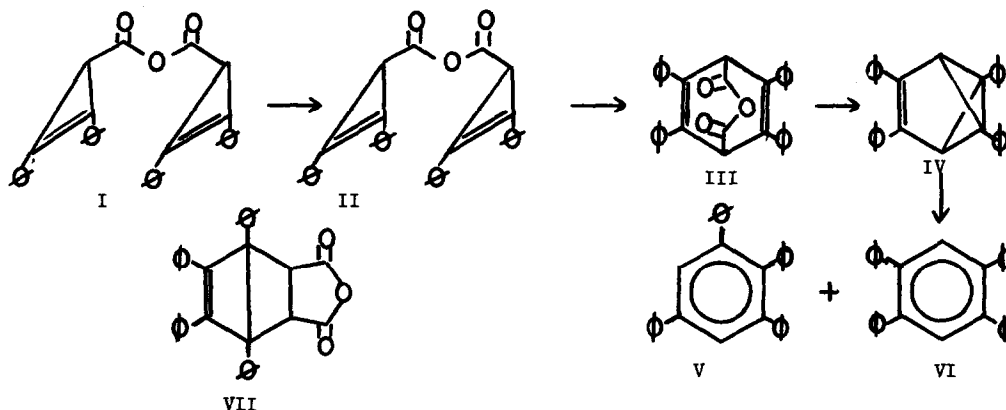
When the anhydride (I) is subjected to photolysis (Hanovia 450 light; ether solution, 45 minutes, with or without a pyrex filter) there is a 72% yield of tetraphenylbenzenes, which consists of a 50-50 mixture of 1,2,3,5-tetraphenylbenzene and 1,2,4,5-tetraphenylbenzene. These were identified by comparison of the Rf's on T.L.C. (SilicAR 7GF, CCl₄ eluent), melting points, the ultraviolet, infrared, and mass spectra with authentic tetraphenyl benzenes. No 1,2,3,4-tetraphenylbenzene is observed in the reaction product. Similar results are obtained when the anhydride is subjected to pyrolysis (sealed tube in vacuo, 175°, 24 hrs.).

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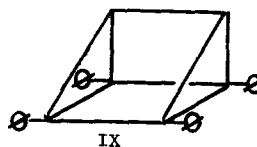
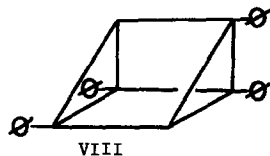
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The photochemical rearrangement was monitored by quantitative ultraviolet determinations. There is no evidence for the build up of any intermediates.



The anhydride may form (II) which, models suggest, is a highly strained species. It then rearranges to (III), a considerably less strained species than (VII). Anhydride (III) may then rearrange to a benzvalene³ which on rearrangement yields 1,2,3,5-tetraphenylbenzene and 1,2,4,5-tetraphenylbenzenes.

An asymmetric tetrasubstituted prismane (VIII), which on rearrangement would yield the observed products, could be formed from (II) or from diphenylcyclopropene dimers obtainable from two diphenylcyclopropene moieties. However it would be reasonable to expect some of the symmetrical prismane (IX) to be formed which on rearrangement would afford some 1,2,3,4-tetraphenyl benzene, none of which is observed. In any event the product distribution² does not support the intermediacy of such a prismane.



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REFERENCES

1. The reaction was first reported in the Ph.D. thesis of Earle B. Hoyt, Jr., Tufts University, (1966)
2. R. Breslow, P. Gal, H.W. Chang, and L.J. Altman. *J. Am. Chem. Soc.* **87**, 5139 (1965)
3. R.N. Warrener and J.B. Bremner. *Tetrahedron Letters* 5691 (1966)