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THE FORMATION OF ACETYLENIC AND BENZENOID COMPOUNDS IN THE PHOTODECOMPOSITION OF 1,2,4,7-TETRAPHENYLCYCLOOCTATETRAENE

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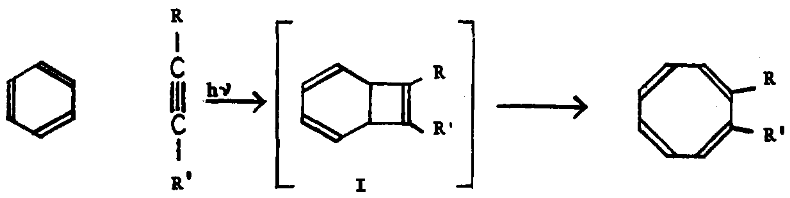
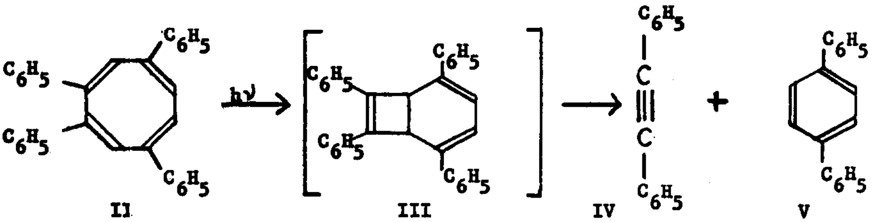
The photochemical synthesis of cyclooctatetraenes from benzene and various substituted acetylenes has been reported recently (1,2); the bicyclooctatriene I is presumed to be an intermediate in this reaction.



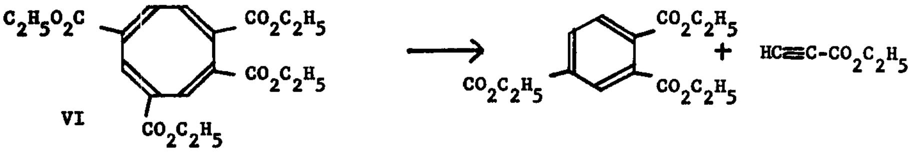
a, R = R' = CO_2CH_3
b, R = H; R' = CO_2CH_3
c, R = H; R' = C_6H_5

We wish to report here the first example of the formal reverse of this reaction, the photochemical decomposition of a cyclooctatetraene into derivatives of benzene and acetylene. The irradiation of 1,2,4,7-tetraphenylcyclooctatetraene (3) (II) in dilute, oxygen-free heptane solutions with a 275 watt General Electric sunlamp for 44 hours yielded a complex mixture of compounds from which para-terphenyl (IV) and diphenylacetylene (V) were isolated in 25% and 20% yields, respectively.


II III IV V

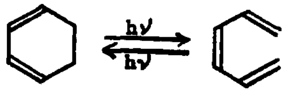
The diphenylacetylene and terphenyl were identified by means of their melting points, appropriate mixed melting points, ultraviolet and infrared spectra, and rfs on thin-layer chromatography. Compound III would seem to be a reasonable intermediate in the photodecomposition.

One example of a pyrolytic reaction leading to similar products has appeared in the literature (4); the pyrolysis of 1,2,4,6-tetracarbethoxycyclooctatetraene (VI) at 300° was reported to yield principally 1,2,4-tricarbethoxybenzene and ethyl propiolate.


VI

Cyclooctatetraene II is also thermally labile, but no terphenyl or diphenylacetylene could be isolated from the mixture of compounds formed on pyrolysis.

The reversible nature of the photoreactions of the cyclooctatetraenes is not without precedent, since it is known that in certain cases, cyclohexadiene and hexatriene compounds are equilibrated by light (5).



When the irradiation of cyclooctatetraene II was carried out in concentrated solutions, an isomeric compound (VII) crystallized from the reaction mixture in 60% yields.

$$\mathrm{II} \underset{\Delta}{\overset{h\nu}{\rightleftarrows}} \mathrm{VII} \xrightarrow{h\nu} \mathrm{IV} + \mathrm{V}$$

Compound VII is thermally labile, and it reverts cleanly to cyclooctatetraene II at 60° with a half-life of about one hour. Compound VII is also photolabile, and it yields, on irradiation, compounds II, IV, and V, among others. The physical properties of VII are not completely consistent with those expected of a compound with structure III, and work on the structure of this intermediate is in progress.

Attempts to extend the photodecomposition reaction to an isomer of compound II, 1,3,5,7-tetraphenylcyclooctatetraene (3) were unsuccessful. The irradiation of this compound yielded a bright red intermediate (which was highly reactive to oxygen), and full decomposition of the cyclooctatetraene was prevented by the filter action of this colored species. The photodecomposition reaction may prove useful for determining the structures of complex cyclooctatetraenes, and other members of this class of compounds are being examined to determine the scope of the photodecomposition.

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References

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