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PHOTOLYSIS OF TETRASUBSTITUTED CYCLOHEXADIENE ANHYDRIDES
EXPERIMENTAL SUPPORT FOR
BENZVALENE - BENZVALENE PHOTOISOMERISATION*

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It was reported earlier(1), that photolysis of 1,2,4,5-tetramethyl-3,5-cyclohexadiene-cis-1,2-dicarboxylic anhydride, unlike the parent diene anhydride,** afforded durene as well as bicyclo(2.2.0)-hexene isomers. In order to define the generality of this photoaromatisation reaction, in particular the influence of substituents, both steric and/or electronic, on the 1,3-dienoid system, we have investigated the photoreactions of some 3,4,5,6-tetrasubstituted derivatives (I).

The photoaromatisation was considered to arise from a cycloelectronic redistribution(2) of the initially excited diene system, which resulted in the fragmentation of the anhydride into CO and CO_2. The isolation of 3',6'-dimethyl-o-terphenyl (IIb) in 78% yield upon irradiation(3) of (Ib)

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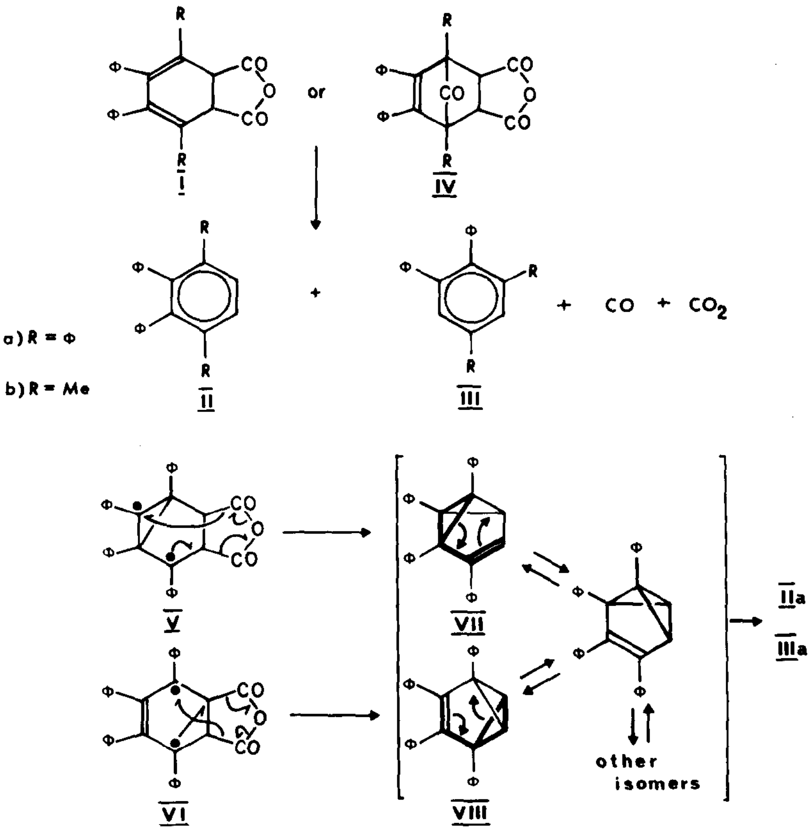
* Considered as Part II of the series, "Excited State Reactions of Imides and Anhydrides".

** In this case, the anti-bicyclo(2.2.0)hex-5-ene-2,3-dicarboxylic anhydride was formed, proved by conversion to cis, trans, cis-tetracarbomethoxycyclobutane.

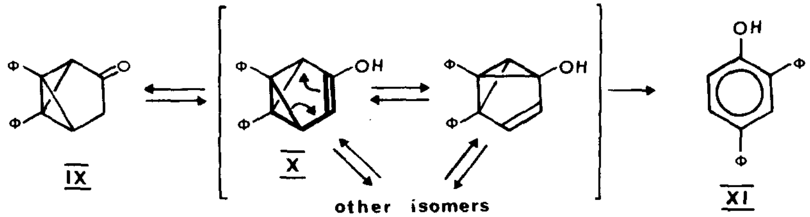
supported this reaction pathway. The same hydrocarbon was also formed (40% yield) on irradiation of the bicyclic ketone (IVb), indicating that photodecarbonylation to the diene(4) was a major decomposition route.



In contrast, however, isolation and separation of the hydrocarbon fraction from irradiation of the tetraphenyl derivative (Ia) showed that only a small amount (0.5%) of the expected isomer (IIa) was obtained. The major hydrocarbon (20%) was the isomeric 1,2,3,5-tetraphenylbenzene (IIIa)(5). No 1,2,4,5-tetraphenylbenzene was observed. Similar results were again obtained from the related ketone (IVa).

Control photolyses confirmed that (IIIa) did not result from photoisomerisation of (IIa). We consider that (IIIa) is formed from the diene (Ia) via an intramolecular process, and that the rearrangement can be explained on the basis of benzvalene intermediates(6),(7),(8). The stabilised benzylic diradicals (V) and (VI) may be involved as intermediates in the formation of the benzvalenes (VII) or (VIII), both of which would collapse only to (IIa). However, photoisomerisation of the vinyl cyclopropane moiety allows ready benzvalene - benzvalene interconversion of the initially formed benzvalene(s) to a mixture of isomers (seven in this tetrasubstituted series). The non-statistical ratio of tetraphenylbenzene isomers produced in this reaction indicates that a high degree of selectivity operates either in the benzvalene - benzvalene interconversion or in their subsequent collapse to the aromatic hydrocarbon. Viehe(9) has discussed the theoretical significance of benzvalene - benzvalene isomerisation, and these results may constitute an experimental verification of this concept.

A precedent for this type of isomerisation is found in the photolysis of the tricyclic ketone (IX) reported by Masamune(10). The enolic form (X) of (IX) is a hydroxybenzvalene, isomerisation of which, together with aromatisation leads to the observed 2,4-diphenylphenol (XI). Direct opening of (IX) would be expected to form the isomeric 3,4-diphenylphenol.



Acknowledgement

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Note Added Prinzbach et al.(11) have found that no isomerisation occurred on irradiation of (Ia). We have repeated this experiment under their conditions in ether solution at -10°C and found only trace amounts of (IIIa) in the hydrocarbon fraction, while at 25°C this isomer was present in significant amounts.

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