"Tetraphenylcyclobutadiene" from Tetracyclone

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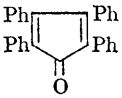
IT has been reported recently[1] that the mass spectrum of tetraphenylcyclobutadienepalladium chloride at 185° shows a very intense peak at *m/e* 356 corresponding to tetraphenylcyclobutadiene (I) less an electron and this was adduced for the formation of monomeric (I) in the gas phase. We report a similar result obtained several years ago.

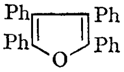
It was suggested by one of us that tetracyclone (II) might readily eliminate the elements of carbon monoxide on electron impact to give the cation of (I), and when the mass spectrum was determined with an M.S.8 mass spectrometer (heated reservoir at 300°) it showed, as expected, intense peaks at *m/e* 384 [molecular ion of (II)] and at *m/e* 356 corresponding to the cation of (I). This result has been briefly mentioned in another context.[2]

However, there was only an extremely weak "metastable peak" at *m/e* 330 corresponding to the transition *m/e* 384 → *m/e* 356 while an unexpected ion *m/e* 372, corresponding to the parent molecular ion of tetraphenylfuran (III), was observed. Measurement of the latter peak at various ionising electron energies showed no evidence that it occurred by the unlikely process of a breakdown from the ketone (II) and it seemed possible that it was formed from the ketone by thermal decomposition to tetraphenylcyclobutadiene and subsequent reaction with residual oxygen or water vapour during the period (90 min.) that the sample was in the reservoir. No significant variation in the equal intensities of the ions of *m/e* 384 and 372 was observed over the period indicated. Cookson[4] *et al.* reported a very similar result and used the occurrence of the furan (III) cation as support for the production of (I) in the gas phase. It appears likely that the same process occurred in the present case and that monomeric (I) was produced in the gas phase by thermal decomposition as well as the cation of (I) by electron impact from the dienone (II).

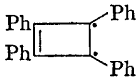
(I)



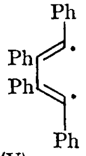
(II)



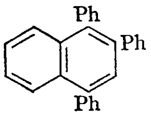
(III)



(IV)



(V)



(VI)

A very intense peak was observed at *m/e* 178. Cookson *et al.*[1] suggested that in their case this could be a Hückel aromatic tetraphenylcyclobutadiene dication or a diphenylacetylene cation radical. It is most probably the latter since in a recent repeat spectrum on the dienone (II) using a direct entry probe and an M.S.9 mass spectrometer we observed a strong "metastable peak" (m^* 89·0) corresponding to the transition *m/e* 356 → *m/e* 178. Under these conditions the peak corresponding to the furan (III) cation was not observed, but a strong "metastable peak", m^* 330, for the transition *m/e* 384 → *m/e* 356 appeared.

Our results show a clear parallelism with those of Cookson *et al.*,[1] and the recent report by Fields and Myerson[3] of the similarities between electron impact and pyrolytic processes in the case of benzyne production from phthalic anhydride may encourage further attempts to prepare (I) by pyrolysis or photolysis. However, pyrolytic experiments in the solid phase with the dienone (II) have been unsuccessful[4] and among other compounds isolated, 1,2,4-triphenylnaphthalene (VI) (*M*, 356) was recorded; it appears unlikely that this is the species detected in our experiments since this would not easily give the most intense breakdown ion of *m/e* 178.

Photolysis of tetracyclone (II) in the presence of oxygen is known to produce *cis*-dibenzoylstilbene with the liberation of one equivalent of carbon monoxide[5] and a photo-oxide has been proposed as an intermediate.[5,6] It is possible that tetraphenylcyclobutadiene (singlet I or triplet IV, or the open-chain tautomer V) is a transient intermediate in this process.

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[1] J. H. Beynon, R. C. Cookson, R. R. Hill, D. W. Jones, R. A. Saunders, and A. E. Williams, *J. Chem. Soc.*, 1965, 7052.

[2] M. St. C. Flett, "Physical Aids to the Organic Chemist", Elsevier, Amsterdam, 1962, p. 341.

[3] E. K. Fields and S. Meyerson, *Chem. Comm.*, 1965, 474.

[4] E. McNelis, *J. Org. Chem.*, **1965**, **22**, 4324.

[5] N. M. Bikales and E. I. Becker, *J. Org. Chem.*, **1956**, **21**, 1405.

[6] C. Dufraisse, A. Etienne, and J. Aubry, *Bull. Soc. chim. France*, 1954, 1201.