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FRAGMENTATION OF AN ARYLCYCLOHEXADIENYL RADICAL

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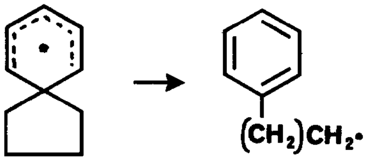
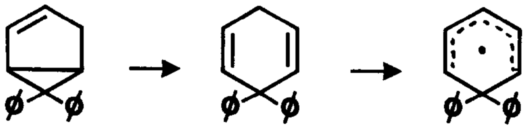
The report by Julia and Mallassine on the rearrangement of the spirocyclohexadienyl radical (I)[1] prompts this preliminary account of observations on the 6,6-diphenylcyclohexadienyl radical (IV). This radical has been generated by hydrogen abstraction from the diene (III), m.p. 35°, which was isolated from the base-catalysed isomerisation of (II).[2]



(I)



(II) (III) (IV)

The major identifiable product of hydrogen abstraction from (III) at temperatures below 100° (by butoxy radicals from di-t-butyl peroxyoxalate) is the dimer (V), m.p. 196-197°. No rearrangement leading to o-terphenyl (or other terphenyl isomers) could be detected unless a one-electron oxidant (O_2, Cu^{++}) was present,[3] nor was there any evidence of significant fragmentation.

Pyrolysis of (V) provided a high temperature source of (IV) (∿130 - 230°). Again terphenyls are not formed in the absence of an oxidising agent. The main products at these temperatures can be rationalised in terms of fragmentation of (IV) with loss of phenyl radicals. For example in chlorobenzene at 230° (6.5mg. in 1.0ml.; sealed tube; N_2) they include biphenyl (0.8 mole/mole), chlorobiphenyls (0.68 mole/mole, in proportions expected for radical phenylation of chlorobenzene), benzene (n.d.)*, and the C_{30} hydrocarbon (VI), m.p. 96-98°, (ca. 25%). These products are rationalised in terms of the reaction scheme shown.

The fragmentation of the 6,6-diphenylcyclohexadienyl radical is probably facilitated by molecular crowding at C-6, and by the absence of alternative reaction pathways. Evidently aryl migration, well known in reactions of unstabilised β-arylethyl radicals, cannot compete with fragmentation in the present system. A previous report[4] of aryl migration in a cyclohexadienyl radical has subsequently been shown to be in error.[5] The o-terphenyl

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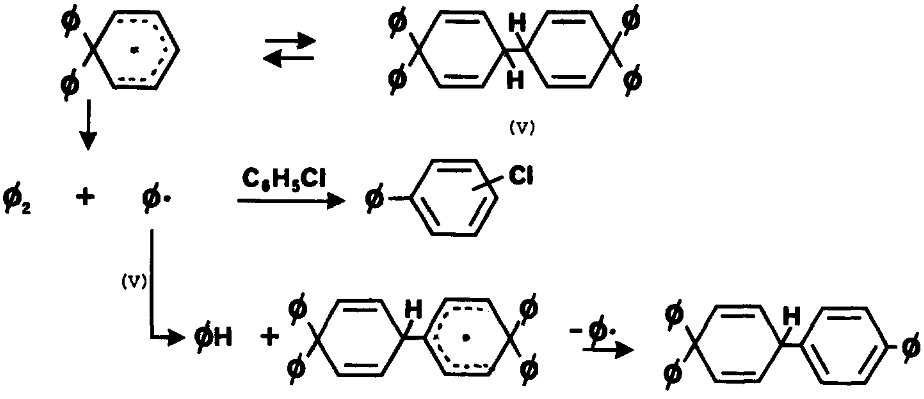
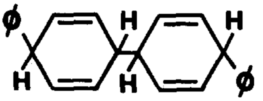
* n.d. = not determined.



(VI)

obtained in the present work under oxidising conditions presumably results from cationic rearrangement.[2,3]

Despite recent claims[6] that addition of aryl radicals to aromatic substrates can be appreciably reversible, we find that disproportionation of monophenylcyclohexadienyl radicals formed by pyrolysis of (VII)[7] is accompanied by very little fragmentation to give phenyl radicals, even in dilute solution at 200°.



(VII)

REFERENCES

1. M. Julia and B. Malassine, Tetrahedron Letters, 987 (1971); see also H. Hart and J.D. DeVrieze, Tetrahedron Letters, 4257 (1968).

2. D.J. Atkinson, M.J. Perkins, and P. Ward, Chem.Comm., 1390 (1969); the isomeric 1,3-diene was removed as its adduct with maleic anhydride.

3. cf. C. Walling and A. Zavitsas, J.A.C.S. **85**, 2084 (1963) but see also footnote in R.B. Bates, D.W. Gosselink and J.A. Kaczynski, Tetrahedron Letters, 199 (1967).

4. D.M. Collington, D.H. Hey, and C.W. Rees, J. Chem. Soc. (C), 1026 (1968).

5. D.H. Hey, G.H. Jones, and M.J. Perkins, Chem.Comm., 1438, (1970).

6. W.A. Henderson, R. Lopresti, and A. Zweig, J.Amer.Chem.Soc., **91**, 6049 (1969); M. Kobayashi, H. Minato, and N. Kobori, Bull.Chem.Soc.Japan, **42**, 2738 (1969).

7. D.F. DeTar, R.A.J. Long, J. Rendleman, J. Bradley, and P. Duncan, J.Amer.Chem.Soc., **89**, 4051 (1967).