Approaches to the 6,6-Diphenylcyclohexadienyl Radical: Some New Rearrangements

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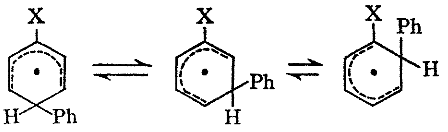
Summary In the course of an investigation directed towards production of 6,6-diphenylcyclohexadienyl radicals, three new rearrangements have been found, including an example of the electrocyclic transformation of a cyclopentenyl anion into a pentadienyl anion.

FOR some time we have entertained the possibility that aryl migration in arylcyclohexadienyl radicals (Equation i) might be a general phenomenon not previously recognised because of the inaccessibility of such radicals with a specified substitution pattern [*e.g.* (**1**) in the absence of (**2**) and (**3**)].†



(**1**) (**2**) (**3**) (i)

The identification of this type of rearrangement would have an important bearing on our understanding of homolytic arylation reactions.[1] Although several approaches to this problem have now been examined,[2] no clear evidence favouring such a rearrangement has emerged. However, we report here some interesting results which have come to light in the course of one aspect of this work.

It was considered that 6,6-diphenylcyclohexadienyl (**8a**), should be a suitable radical with which to discern the rearrangement described, and plausible routes to this species included hydrogen abstraction from any of the three isomeric hydrocarbons (**4**), (**5**), or (**6**). The most accessible of these appeared to be (**4**),‡ hydrogen abstraction from which should give an allyl radical (**7a**) which might rearrange to (**8a**). Formation of (**8a**) from (**5**) or (**6**) would be unexceptional. Occurrence of the conjectured aryl migration in (**8a**) should lead to the three terphenyl isomers.

In the event, radical reactions with (**4**) and (**5**)§ yielded

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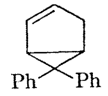
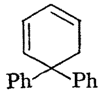
† Following a suggestion by us, one example of this type of rearrangement may have been realised at elevated temperature. D. M. Collington, D. H. Hey, and C. W. Rees, *J. Chem. Soc.* (*C*) 1968, 1017; see also ref. 1.

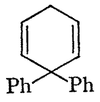
‡ The diphenylbicyclohexene was obtained by photolysis of diphenyldiazomethane in the presence of cyclopentadiene. Details of an identical synthesis were given recently by H. E. Zimmerman, D. S. Crumrine, H. Döpp, and T. S. Huyffer, *J. Amer. Chem. Soc.*, 1969, **91**, 434.

§ The conjugated diene was obtained in 15—25% yield by dehydration of 4,4-diphenylcyclohex-2-en-1-ol (over alumina in the presence of pyridine to avoid cationic rearrangement; E. von Rudloff, *Canad. J. Chem.*, 1961, **39**, 1860). An alternative route from the corresponding cyclohexenone was communicated recently, and apparently gives a superior yield of diene; W. G. Dauben, M. E. Lorber, N. D. Vietmeyer, R. H. Shapiro, J. H. Duncan, and K. Tomer, *J. Amer. Chem. Soc.*, 1968, **90**, 4762.

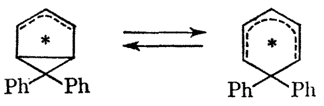
no identifiable products except under mechanistically ambiguous conditions. With *N*-bromosuccinimide (NBS), (**4**) was dehydrogenated to 6,6-diphenylfulvene and partially brominated derivatives thereof,¶ and the conjugated diene (**5**) gave *o*-terphenyl in fair yield (50%). No *m*- or *p*-terphenyl was formed.†† Diphenylfulvene was also a major product (*ca.* 30%) from the reaction of (**4**) with t-butyl perbenzoate in the presence of copper(I) chloride Whilst free radicals almost certainly participate in these reactions, they are not necessarily involved in the rearrangement steps. In the first system heterolysis of an intermediate allylic bromide, and in the second oxidation of radicals by Cu^{II}, could produce carbonium ions.


(**4**)


(**5**)


(**6**)

The non-conjugated diene (**6**) was obtained after isomerisation of either of the isomeric hydrocarbons (**4**) or (**5**), using potassium t-pentoxide in boiling t-pentyl alcohol, This gave an equilibrium mixture containing approximately equal proportions of the two dienes and these were separated by chromatography over silica gel impregnated with silver nitrate. No bicyclohexene (**4**) was detectable (n.m.r., g.l.c.) in the equilibrium mixture. The isomerisation of (**4**) under basic conditions presumably constitutes a new example of the general cyclopentenyl $\rightleftarrows$ pentadienyl anion transformation discussed recently.[3] Orbital symmetry considerations dictate a disrotatory mode for such a process. This is permissible for (**7b**) $\rightleftarrows$ (**8b**), but it is of interest that corresponding cationic rearrangenent, (**7c**) $\rightleftarrows$ (**8c**), which should be conrotatory, is prohibited by the constraining influence of the cyclopropane ring. This might explain the preferential opening to a fulvene structure in the NBS and perbenzoate–copper reactions. The radical rearrangement (**7a**) $\rightleftarrows$ (**8a**) is allowed, and this type of isomerisation may possibly occur in the oxidation of α-thujene to *p*-cymene;[4] it is similar to the "bond alteration" in the photoexcited triplet state of cross-conjugated cyclohexadienones.[5]


(**7**) a, * = • (**8**)

b, * = —

c, * = +

Hydrogen abstraction by butoxy-radicals from the non-conjugated diene (**6**) does constitute a source of the elusive 6,6-diphenylcyclohexadienyl radical (**8a**), and the chemistry of this radical will be the subject of a future report.

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¶ Detailed product analysis on this reaction mixture has not been carried out; however, combination of chromatographic and spectroscopic examination suggested that *ca.* 40—50% of (**4**) had been converted into fulvenes by reaction with 1 equiv. of NBS. Diphenylfulvene was shown to be brominated by reaction with NBS.

†† A 1% yield of either *m*- or *p*-terphenyl would have been readily detected.

[1] M. J. Perkins, *Ann. Reports*, 1968, **65**, *B*, 181.
[2] D. J. Atkinson, Ph.D. Thesis, London, 1969.
[3] R. B. Bates and D. A. McCombs, *Tetrahedron Letters*, 1969, 977; H. Kloosterziel, J. A. A. Van Drunen, and P. Galama, *Chem. Comm.*, 1969, 885.
[4] F. Petru and J. Kovar, *Coll. Czech. Chem. Comm.*, 1950, **15**, 478; K. Sugathan and J. Verghese, *Indian J. Chem.*, 1964, **2**, 497.
[5] H. E. Zimmerman and J. S. Swenton, *J. Amer. Chem. Soc.*, 1967, **89**, 906.