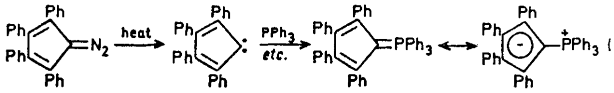
Mode of Formation of Cyclopentadienylides and Cyclopentadienylidenepyrans from Diazocyclopentadienes

By Brian H. Freeman, G. S. Harris, Bryan W. Kennedy, and Douglas Lloyd*
(*Department of Chemistry, Purdie Building, University of St. Andrews, St. Andrews, Fife*)

Summary Thermogravimetric analysis of the reactions between diazotetraphenylcyclopentadiene and a number of substrates containing heteroatoms shows that they proceed *via* a common step, which is taken to be the formation of the carbene, cyclopentadienylidene.

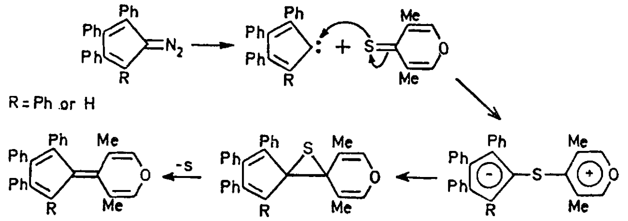
It has been taken for granted that the formation of cyclopentadienylides by thermal decomposition of diazocyclopentadienes in the presence of suitable reactants[1] proceeds *via* formation of a carbene, *e.g.*, reaction (1). An alternative might be that the diazo-compound first added to the other reagent and the resultant adduct then decomposed to provide the ylide. Thus in 1919 Staudinger[2] showed that diazofluorene added to a phosphine to form a phosphazene, which could in turn be decomposed thermally with evolution of nitrogen and formation of the corresponding ylide.



(1)

The decomposition of diazotetraphenylcyclopentadiene in the presence of PPh_3, $AsPh_3$, $SbPh_3$, or $BiPh_3$ has now been followed thermogravimetrically in a modified Stanton model TR I thermobalance. The traces obtained for each of these reactions were identical, quantitative loss of nitrogen occurring at 124° in all cases. It is concluded that the same weight-loss step is involved in each reaction, which indicates that the reactions proceed *via* a common intermediate, namely the carbene tetraphenylcyclopentadienylidene, which then adds to the other reactant.

The reaction between tetraphenyl- or triphenyl-diazocyclopentadienes and a pyranthione or thiinthione to give cyclopentadienylidene-pyrans or -thiins was also postulated to involve a carbene intermediate,[3] because of its similarity to the other assumed carbene-intermediate reactions, and because earlier workers[4] had isolated thiirans as intermediates in related reactions of diazo-compounds with thiones. This reaction might alternatively proceed by dipolar addition of the thione to the diazo-compound to give a thiadiazoline, which could decompose thermally to give successively a thiiran and a cyclopentadienylidene-pyran. Thermogravimetric investigation of the reaction between diazotetraphenylcyclopentadiene and 2,6-dimethylpyran-4-thione was made more difficult by the tendency of the pyranthione to sublime, but when correction was made for this, the trace was again effectively identical with that observed in the other thermal decompositions, with quantitative loss of nitrogen at 124°. Thus in this case the same carbene tetraphenylcyclopentadienylidene intermediate is also implicated.



The cyclopentadienylidene-pyrans had previously been prepared by heating the reactants together in a high-boiling solvent.[3,5] Not surprisingly, in view of the carbene mechanism, yields of these products are greatly increased if the reactants are melted together, without solvent, at 130° for 15 min, as in the method used for the preparation of cyclopentadienylides.[1]

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