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DIPHENYLCARBENE FORMATION IN THE PHOTOLYSIS OF TETRAPHENYLMETHANE

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Whereas phenylated ammonium, phosphonium, and sulfonium salts produce phenyl radicals upon photolysis, such a process has been excluded for tetraphenylborate anion.[1] The behavior of tetraphenylmethane (TPM) has not been reported; some triphenylmethyl derivatives are known to react through cyclization to 5-membered rings.[2]

Irradiation[1a] of a 4×10^{-3} $\underline{M}$ solution of TPM in cyclohexane for 3 days affords biphenyl (I, relative yield 1.0), diphenylmethane (II, 0.15), recovered TPM (0.09), and benzhydrylcyclohexane (III, 0.19).[3] The TPM glc peak may contain traces of sym-tetraphenylethane (IV), but if so an upper limit of 0.02 on the above scale can be established from the mass spectrum. Several other compounds present in trace amounts were not identified. A UV spectrum of the crude reaction solution showed that a 9-phenylfluorene chromophore was present in small amounts, although 9-phenylfluorene itself was shown to be absent. A similar run in cyclooctane showed that benzene was not produced.

In isopropyl alcohol (2×10^{-3} $\underline{M}$), only a trace of benzene could be detected (Porapak QS, 170°). Using dodecane as an internal standard, products and yields were determined to be: I (56%), II (29%), and benzhydryl isopropyl ether (V, 22%). Three other products were formed to the extent of 1% each but were not identified. About 2% of the TPM was still present.

Formation of III and V, coupled with the absence of IV, necessitates the intermediacy of diphenylcarbene. The formation of only trace amounts of benzene in isopropyl alcohol shows that phenyl radicals are not produced to any appreciable extent. Ring closure similar to that observed in triphenylmethyl derivatives[2] is also only a minor path at best.

Although there is no direct evidence concerning the mode of formation of diphenylcarbene, a cyclopropane intermediate, perhaps comparable to that cited by Williams et al.[1d] appears much more likely than a fission-recombination mechanism. Griffin and co-workers have shown that diphenylcarbene is formed in the photolysis of suitably phenylated cyclopropanes and other 3-membered ring

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*Present address: Department of Chemistry, University of North Carolina, Charlotte, N.C. 28213 analogs.[4] In contrast, fission of a phenyl group would result in a triphenylmethyl derivative, which would be expected to form a fluorene.[2]

The formation of diphenylmethane is very unexpected. Since the diphenylmethyl radical is not likely to abstract hydrogen from cyclohexane,[5] it can be ruled out as an intermediate. At present, no alternative path is apparent which can explain the large amounts of II which are observed.

The most striking feature of this reaction is that the diphenylcarbene which is generated differs radically in its behavior from that generated by photolysis of diphenyldiazomethane. The latter compound affords no III in cyclohexane, yielding IV as the main product.[6] This complete turnabout in behavior may be due in part to the use of longer wavelength light in the latter case (an effect recently observed in phenyldiazomethane photolysis[7]). Most likely, the energy-rich TPM-generated diphenylcarbene reacts as a singlet before relaxation to the triplet ground state can occur. Unfortunately, olefin addition reactions are precluded as a reliable test of the singlet character because of the very low quantum efficiency of this reaction and the known photodissociation of molecules similar to the expected products of the addition.[4] Nevertheless, the observations reported here represent the first unequivocal example of diphenylcarbene insertion into a carbon-hydrogen bond.

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