The Photolysis of 4-Bromobiphenyl in Benzene

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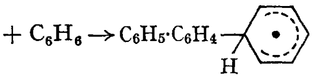
IN earlier work,[1,2] photolysis of iodoaromatic compounds in benzene led to a new general synthesis of biaryls and clarification of certain mechanistic aspects of the reactions. We have now investigated the similar photolyses of other halogenoarenes, using 4-fluoro-, 4-bromo-, and 4-chlorobiphenyl, in benzene, under conditions whereby 4-iodobiphenyl gave 80—90% *p*-terphenyl.

Photolysis of 4-fluorobiphenyl (1 g.) in benzene (170 ml.) for 24 hr., at 2537 Å, caused only 3% decomposition of the substrate, compared to essentially complete photolysis of 4-iodobiphenyl.[1] Gas-chromatographic analysis showed only traces of biphenyl and *p*-terphenyl. Similarly, 4-chlorobiphenyl gave only 1% *p*-terphenyl in 24 hr. Photolysis of 4-bromobiphenyl, for 24 hr., was, however, 70—80% complete, with formation of *p*-terphenyl and biphenyl as the major products. In this case, however, in contrast to that of 4-iodobiphenyl—wherein only about 6% biphenyl is normally formed—the ratio of biphenyl/*p*-terphenyl, in fifteen runs, was 1·0 ± 0·1. Hydrogen bromide (20—30%) and about 1% bromobenzene were also detected, but no bromine was found.

In accord with earlier work, wherein the results were in good agreement with a free-radical mechanism, supported especially by the results of a study of the isomer distribution ratios of the photolysis of iodobenzene in a series of aromatic solvents,[5] we conclude that the photolysis of 4-bromobiphenyl in benzene can be rationalized in terms of the sequence of reactions shown below.

(1) $C_6H_5{\cdot}C_6H_4Br \rightleftharpoons C_6H_5{\cdot}C_6H_4{\bullet} + Br{\bullet}(\tfrac{1}{2}\,Br_2)$

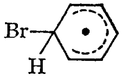
(2) $C_6H_5{\cdot}C_6H_4{\bullet} + C_6H_6 \rightarrow$  (**A**)

(3) $C_6H_5{\cdot}C_6H_4{\bullet} + (\mathbf{A}) \rightarrow C_6H_5{\cdot}C_6H_5 + C_6H_5{\cdot}C_6H_4{\cdot}C_6H_5$

(4) $\tfrac{1}{2}\,Br_2 + (\mathbf{A}) \rightarrow C_6H_5{\cdot}C_6H_4{\cdot}C_6H_5 + HBr$

(5) $C_6H_5{\cdot}C_6H_4{\bullet} + HBr \rightarrow C_6H_5{\cdot}C_6H_5 + Br{\bullet}$

(6) $2\,Br{\bullet} \rightarrow Br_2$

(7) $Br{\bullet} + C_6H_6 \rightarrow$  (**B**)

(8) $Br{\bullet} + (\mathbf{B}) \rightarrow$ addition products (?)

(9) $(\mathbf{B}) + C_6H_5{\cdot}C_6H_4{\bullet} \rightarrow BrC_6H_5 + C_6H_5{\cdot}C_6H_5$

Formation of 4-biphenylyl radicals (*cf.*, Ref. 4) is supported by formation of considerable amounts of 4-iodobiphenyl by photolysis of a solution of 4-bromobiphenyl in benzene, to which iodine was added to trap the radicals.

While we have observed earlier that biphenyl formation in the case of 4-iodobiphenyl photolysis in benzene can be markedly increased by rigorous removal of oxygen from the system,[3] no such procedures are required to observe the high yields of biphenyl in the case of 4-bromobiphenyl. Indeed, the biphenyl/*p*-terphenyl ratio approaches the theoretical limit of unity—showing that hydrogen transfer to the 4-biphenylyl radical, from intermediates (**A**) or (**B**), or possibly from hydrogen bromide, is efficient in the case of the bromine analogue. Equations 3, 5, and 9 represent the possible hydrogen transfer steps, although step 9 is not significant, as shown by the finding of only 1% bromobenzene. As expected, addition of hydrogen bromide to a solution of 4-iodobiphenyl or 4-bromobiphenyl in benzene, raises biphenyl formation on photolysis through step 5. The fate of bromine in the above reactions has yet to be ascertained.

The 4-halogenobiphenyls are thus increasingly resistant to photolysis in the order of the bond strengths of the corresponding substances. While this limits their utility for synthetic purposes, the information here recorded should have general value for predicting results of photolysis of selected mixed dihalogeno-aromatic compounds, which may have synthetic and mechanistic interest. The differences in product distributions in the case of the 4-bromobiphenyl photolysis in benzene, compared to 4-iodobiphenyl, can be rationalized on a free-radical mechanism and on the relative reactivities of bromine atoms *versus* iodine atoms, in the benzene solutions.

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[1] W. Wolf and N. Kharasch, *J. Org. Chem.*, 1965, **30**, 2493.

[2] N. Kharasch, W. Wolf, T. Erpelding, P. G. Naylor, and L. Tokes, *Chem. and Ind.*, 1962, 1760.

[3] N. Kharasch and R. K. Sharma, *Chem. Comm.*, 1966, 106.

[4] J. Szychlinski and L. Litwin, *Roczniki Chem.*, 1963, **37**, 671.

[5] N. Kharasch and P. G. Naylor, unpublished work; *cf.* also Ref. 2.