PHOTOLYSIS OF DIARYLIODONIUM SALTS IN AQUEOUS ALKALINE SOLUTION
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The carbon-halogen bond is readily cleaved by ultraviolet radiation. <sup>1</sup> Several groups have investigated the photochemical decomposition of diaryliodonium salts in a variety of solvents. Photochemical decomposition of diphenyliodonium iodide in chloroform gave benzene, iodobenzene, iodine and diphenyliodonium triiodide. <sup>2</sup> When diphenyliodonium iodide is photolysed in labelled benzene the major products are biphenyl in which one ring is labelled, and unlabelled iodobenzene. <sup>3</sup>

The recent publication of Knapezyk and co-workers<sup>4</sup> prompted us to report our results concerning the photolysis of diaryliodonium salts in aqueous alkali. In particular we were interested in the prospect of a biaryl synthesis.

Photolysis of diphenyliodonium hydroxide in aqueous sodium hydroxide solution with a high pressure mercury vapour lamp gave as the major products 4-iodobiphenyl and biphenyl (ca.10% of each). The minor products were terphenyls and iododerivatives of terphenyls (mass spec.). No phenols were formed.

Photolysis of 4-methoxydiphenyliodonium hydroxide<sup>5</sup> in aqueous sodium hydroxide solution gave 4-methoxybiphenyl and 4-methoxy-4-iodobiphenyl (ca.10% of each). Traces of biphenyl and 4,4-dimethoxybiphenyl were also present.<sup>b)</sup>

The mechanism proposed by Knapezyk is in agreement with our results and is summarised in the reaction scheme.

$$Ar^{-1} Ar^{1} + OH^{-} = Ar^{-1} Ar^{1} \xrightarrow{hy} \begin{bmatrix} Ar^{-1} - Ar^{1}, OH \\ & & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ &$$

The biphenyl and the 4-methoxybiphenyl are readily accounted for by pathway (i), whereas the <u>para-iodobiphenyl</u> derivatives may be produced from the intermediate radical  $Ar-I-Ar^1$  before it decomposes to Ar and  $Ar^1$  through a radical cage intermediate  $\begin{bmatrix} Ar \ I-Ar^1 \end{bmatrix}$ , pathway (ii). It seems unlikely that the Ar radicals would react with iodobenzene to give exclusively p-iodobiphenyls.

p-Iodobiphenyls have not previously been observed as products from the photolysis of diaryliodonium salts.

## Footnotes.

- a) Author to which enquires should be addressed.
- b) All products were characterised by n.m.r., mass spec. and in some cases by comparison with authentic samples.

## REFERENCES

- 1). R.K. Sharma and N. Kharasch, Angew. Chem. Int. Ed., 7,36,(1968).
- 2). H.Irving and R.W.Reid, J.Chem.Soc., 2078, (1960).
- 3). G.A.Razuvaez, G.G.Petukhov and B.G.Zateev, Dok.Nauk.Acad.Sci.S.S.R., 27, 803, (1959).
- 4). J.W.Knapezyk, J.J.Labinowski and W.E.McEwen, Tetrahedron Letters, 3739, (1972).
- 5). F.M.Beringer, M.Drexler, E.M.Gindler and C.C.Lumpkin, <u>J.Amer.Chem.Soc.</u>, <u>75</u>, 2705, (1953).