Photoreduction of Chlorobiphenyls by $NaBH_4$

By Kazuo Tsujimoto, Shigeru Tasaka, and Mamoru Ohashi*

(*Department of Materials Science, The University of Electro-Communications, Chofu, Tokyo* 182, *Japan*)

Summary Photoreduction of 3- and 4-chlorobiphenyls by $NaBH_4$ is described and a hydride-proton-transfer mechanism is deduced for the former case on the basis of deuterium labelling experiments.

Recently Barltrop and Bradbury reported that photoreduction of halogenated aromatic-compounds by hydride reagents proceeds *via* a radical chain mechanism.[1] We now report that 3- and 4-chlorobiphenyl (I) and (II) are also reduced by $NaBH_4$ on irradiation and the photoreduction of (I) proceeds *via* a hydride-proton-transfer mechanism different from those published.[1,2]

Irradiation of (I) and (II) in the presence of $NaBH_4$ in $MeCN–H_2O$ (10:1) by a low pressure mercury lamp gave biphenyl (III) as the sole product. The quantum yields in the formation of (III) were 0·013 and 0·0024 respectively.

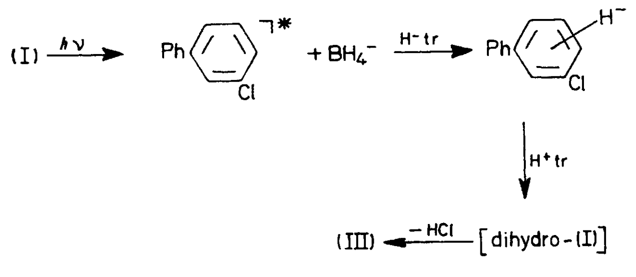
In an attempt to elucidate the mechanism of the reduction, we examined the incorporation of deuterium into (III) obtained by irradiation of (I) and (II) in the presence of deuteriated reagents. The deuterium contents of the resulting products were estimated from analyses of the molecular ions in their mass spectra (see Table).

Table. Deuterium contents of the resulting biphenyls

	$NaBD_4$, H_2O–MeCN		$NaBH_4$, D_2O–MeCN		$NaBH_4$, H_2O–CD_3CN		$NaBD_4$, D_2O–MeCN	
	(I)	(II)	(I)	(II)	(I)	(II)	(I)	(II)
$[^2H_0]$-(III)	43	65	59	92	96	82	28	51
$[^2H_1]$-(III)	49	33	39	8	4	18	40	42
$[^2H_2]$-(III)	8	2	2	0	0	0	32	7

Hydrogen exchange between borohydride and water[3] under the above irradiation conditions was demonstrated by the following experiments; after irradiation of (I) or (II) in the $NaBD_4–H_2O–MeCN$ system, the unchanged $NaBD_4$ was decomposed with excess of benzophenone. The hydrogen content of the resulting deuteriated diphenylmethanol was 16% from n.m.r. and mass spectrometric analyses of its acetate. An accurate estimate of the contribution of each of the different types of hydrogen atom could not be obtained from this result and the results in the Table because of the possible errors in the mass spectrometric analysis of deuterium incorporation[4] and the large hydrogen isotope effect for these hydrogen-transfer reactions.[2] However, the following points are qualitatively clear from the results in the Table. (i) In the case of (I) both hydride (from $NaBH_4$) and proton (from H_2O) are sources of hydrogen in the reduction but not the MeCN hydrogens. (ii) In the case of (II) the $NaBH_4$ hydrogen is transferred efficiently but not the H_2O proton. Hydrogen-transfer from MeCN also occurs.

Although the quantum yield of (III) in the photoreduction of (II) is quite low in comparison with literature values,[1] the deuterium incorporation results are consistent with the Barltrop mechanism. However, for (I) both hydride and proton transfer and the following mechanism in the Scheme, instead of a radical chain mechanism, is proposed as the main process. This mechanism is to some extent similar to that of photoreduction of aromatic compounds by $NaBH_4$.[5]



Scheme. (H^- tr; hydride-transfer, H^+ tr; proton-transfer). The structure of dihydro-(I) is not clear. Structures such as 3-chloro-3,4-dihydrobiphenyl are conceivable.

A difference in behaviour between (I) and (II) is also observed in their photoreduction by Et_3N; *i.e.*, (II) is efficiently reduced on irradiation in the presence of Et_3N through electron transfer to give (III) ($\Phi = 0{\cdot}49$),[6] while the photoreduction of (I) by Et_3N gave 3-chloro-1,4-dihydrobiphenyl ($\Phi = 0{\cdot}1$) in addition to (III) ($\Phi = 0{\cdot}3$).

(*Received, 5th May* 1975; *Com.* 516.)

---

[1] J. A. Barltrop and D. Bradbury, *J. Amer. Chem. Soc.*, 1973, **95**, 5085.
[2] J. T. Groves and J. W. Ma, *J. Amer. Chem. Soc.*, 1974, **96**, 6527.
[3] R. H. Cornforth, *Tetrahedron*, 1970, **26**, 4635.
[4] K. Biemann, 'Mass Spectrometry: Organic Chemical Applications,' McGraw-Hill, New York, 1962, ch. 5.
[5] J. A. Barltrop, *Pure Appl. Chem.*, 1973, **33**, 179.
[6] M. Ohashi, K. Tsujimoto, and K. Seki, *J.C.S. Chem. Comm.*, 1973, 384.