Dechlorination of 4-Chlorobiphenyl mediated by Aromatic Photo-catalysts

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4-Chlorobiphenyl was effectively dechlorinated by near u.v.–visible light in the presence of both an aliphatic amine as an electron donor and anthracene or a derivative as a photo-catalyst.

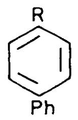
In 1973 we reported that irradiation of 4-chlorobiphenyl (**1**), a type of polychlorinated biphenyl (PCB), with u.v. light (254 nm) in the presence of triethylamine led to dechlorination to give biphenyl (**2**) in excellent quantum yield.[1] This photoreaction does not occur with light in the near u.v. or visible region because of the transparency of (**1**). However, we found that on adding anthracene (**3**) as a photo-catalyst the dechlorination did proceed effectively.

In the present work, a solution of (**1**) (3.02×10^{-2} M), NEt_3 (1.02 M), and (**3**) (8.0×10^{-3} M) in MeCN (2 ml)–dimethylformamide (DMF) (1 ml) was irradiated through a filter (>310 nm) with a 1 kW Xenon arc lamp under nitrogen. The

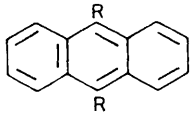
Table 1. Conditions and yields.[a]

Entry	Catalyst	10^{-3} Conc./M	Solvent	Irrad. time/h	% (**2**)	% (**1**)[c]	% Catalyst[c]
1	(**3**)	3.2	MeCN	2.0	11 (2.4)[b]	87	65
2	(**3**)	8.0	MeCN–DMF (2:1)	1.0	59 (0.9)	41	65
3	(**3**)	8.0	,,	2.0	79 (2.5)	21	61
4	(**3**)	8.0	,,	4.0	91 (5.3)	8.1	58
5	(**4**)	4.3	,,	2.0	43 (2.4)	55	6.0
6	(**5**)	4.0	,,	2.0	5.8 (2.5)	94	25
7	(**6**)	2.7	,,	1.5	1.8 (2.0)	98	—
8	(**7**)	2.8	MeCN	2.0	5.4 (2.4)	93	85

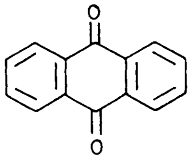
[a] The photo-products were identified by gas chromatography–mass spectrometry and high-resolution mass spectrometry. Quantitative analyses were carried out on an H. P. 5890 capillary g.c. with methylsilicone at 150—300 °C using naphthalene as an internal standard.[6] [b] Yields in the absence of photo-catalyst are in parentheses. [c] Recovered yields.



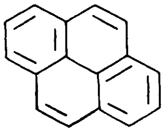
(1) R = Cl
(2) R = H



(3) R = H
(4) R = Ph
(5) R = Me



(6)



(7)

anthracene derivatives (4)—(6) and pyrene (7) were also examined as catalysts. Results are summarized in Table 1. In entries 1—4 the yield of (2) increased with increasing concentration of photo-catalyst (3) and with longer irradiation time. In entry 4, a 91% yield of (2) was achieved using the photo-catalyst (3), although only 58% of (3) was recovered and 9,10-dihydroanthracene and tetrahydrobianthryl were obtained. In the case of (4) large amounts of its dihydroderivative and no dimer were obtained together with a small amount of recovered (4) (entry 5). Compounds (5) and (7) showed low photocatalytic efficiency and (6) none at all (entries 6—8).

Since the photo-induced electron transfer from NEt_3 to excited aromatic hydrocarbons is well documented,[2] electron transfer from NEt_3 to excited (3) to give the radical anion of (3) is conceivable. The next stage would be a thermodynamically unfavourable electron transfer from the radical anion of (3) [$E_{\frac{1}{2}}$ (3)/(3)$^{\bullet-}$ −1.91 V *vs.* standard calomel electrode (S.C.E.)] to (1) [$E_{\frac{1}{2}}$ (1)/(1)$^{\bullet-}$ −2.37 V *vs.* S.C.E.][3] to give the radical anion of (1) which would decompose spontaneously to furnish biphenyl radical and Cl^-, as occurs in the photochemical dechlorination of (1) in the presence of NEt_3.[1,4] The endothermic electron transfer from (3)$^{\bullet-}$ to (1) observed here is similar to that observed electrochemically where electron transfer in solution can often be carried out even with redox reagents whose potentials are up to 0.6 V lower than that of the substrate.[5] These endothermic electron transfers can take place if a thermodynamically unfavourable electron transfer equilibrium is followed by a fast and irreversible step.

Thus, an efficient photocatalytic dechlorination of 4-chlorobiphenyl was achieved using near u.v.–visible light in the presence of an aliphatic amine and a mediator.

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