Photolysis of Some *ortho*-Methylated Monochlorobiphenyls

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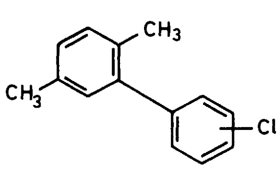
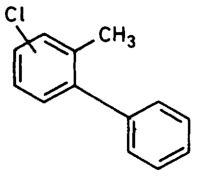
A series of monochloro-*o*-methylated biphenyls was photolysed. Quantum yields of dechlorination lie in between the low values observed for 3- and 4-chlorobiphenyl and the high values obtained for 2-chlorobiphenyl. The results are interpreted in terms of raising the energy of the excited state due to steric crowding of the *ortho*-substituent and relief of strain upon the departure of an *ortho*-chlorine.

Dechlorination, that is the replacement of chlorine by hydrogen, is the major reaction observed when chlorobiphenyls are photolysed in organic solvents. Compounds with *ortho*-chlorine substituents are markedly more photolabile (φ_r usually >0.1) than those without (φ_r usually <0.01), and where both *ortho* and other chlorines are simultaneously present, photolysis leads to the almost exclusive replacement of the *ortho*-substituent.[1,2]

Spectroscopic studies [3-5] have shown that the triplet energy of an *ortho*-substituted biphenyl is higher than that of one lacking *ortho* substitution. For compounds with only one or two *ortho*-chlorines, Wagner and Scheve [3] have shown that the triplet (reactive) excited state is planar, consequently the effect of the *ortho*-substituent is not to force the excited biphenyl out of planarity, but rather to raise its energy by steric crowding. It has been argued that it is this energetic effect which is reponsible for the differences in φ_r between the two classes of compound.[6] In principle, one of two explanations can be advanced for the larger φ_r seen for *ortho*-chlorobiphenyls. Either (i) the effect is purely energetic, and the compounds with the higher triplet energies have more energy available to break the C–Cl bond, or (ii) the effect is at least partly kinetic, where the departure of the *ortho*-chlorine is facilitated by the relief of strain. While recognizing the limitation of quantum yield measurements in answering this kind of question, we have sought to distinguish these two possibilities by studying *ortho*-methylbiphenyls which also contain a chloro-substituent. The substituents chloro and methyl have similar covalent radii, and are acknowledged [3] to affect the electronic spectra of biphenyls similarly. If explanation (i) is correct, then the presence of an *ortho*-methyl group should facilitate the departure of a chlorine atom located elsewhere in the molecule. To this end, we have studied the photochemistry of compounds (1)—(5).



(1) 4-Cl
(2) 3-Cl
(3) 2-Cl



(4) 4-Cl
(5) 3-Cl

Experimental

Preparation of Biphenyl Derivatives.—The chloro(methyl)biphenyls were prepared by Cadogan's method.[7] Compounds (1)—(3) were made by reacting the appropriate chloroaniline (0.05 mol) with *p*-xylene (50 ml) and isopentyl nitrite (7.5 ml) at reflux. Compounds (4) and (5) were prepared similarly from benzene and the chloro-2-methylaniline. Evaporation of the excess arene was followed by chromatography over alumina (eluting with light petroleum) and microdistillation or recrystallization. Reference samples of 2,5-, 3,4-, and 3,5-dimethylbiphenyls were prepared similarly. Although some of these chloro(methyl)biphenyls have been mentioned in the literature, few physical constants have previously been reported; these are given in Table 1.

Relative Rates of Photolysis.—Solutions of the substrate were prepared in spectral grade cyclohexane (*ca.* 2×10^{-3}M) together with a comparable concentration of octadecane, which served as an internal standard for g.l.c. analysis. For photolysis, portions (2.0 ml) of the solution were transferred to quartz ampoules of 8 mm o.d., which were connected to Pyrex tubing by a graded seal. The solutions were evacuated using the freeze–pump–thaw technique (2 cycles at 0.01 mm), and were irradiated at 254 nm, using a Rayonet model RPR photoreactor equipped with RPR 2537 lamps.

After preliminary experiments to determine appropriate irradiation times, eight tubes were photolysed simultaneously using a ' merry-go-round '. Pairs of ampoules were removed at each of four times, and analysed in duplicate by g.l.c. (Carle model 211 gas chromatograph with f.i.d., column 6 ft × 1/8 in 10% OV101 on acid-washed 60–80 Chromosorb W, operated isothermally at 185 °C). Conversion of the chloro-compound was linear with time over the first 20—30% decomposition except for (3), where the rate rapidly dropped off. For compounds other than (3) the rate of reaction was determined as the slope of the line mol l^{-1} reacted ÷ time. For compound (3) the rate of photolysis was determined as the slope of the linear plot of $M_0\ln(M_0/M)$ *versus* time,[12] where M_0 is the initial concentration of (3) and M its concentration after time t. The quantum yields, relative to compound (1), are given in Table 2. They were calculated from the relationship $\varphi^1/\varphi^2 = M_0^1\ln(M_0^1/M^1)/M_0^2\ln(M_0^2/M^2)$.

Absolute Quantum Yields.—The quantum yield of disappearance of (1) was determined using the azoxybenzene actinometer [13] for which $\varphi_r = 0.017$ at 254 nm. The determination was made using the Rayonet photoreactor as follows. Six quartz ampoules of 8 mm o.d. were held vertically in quartz test tubes of 16 mm o.d. The ampoules were filled with 2.0 ml of solution A and the test tubes were filled to at least the same depth with solution B. Duplicates were made of the following sets:

1 A = compound (1) (*ca.* 1.5×10^{-3}M), B = cyclohexane

2 A = azoxybenzene, B = cyclohexane

3 A = azoxybenzene, B = (1) (*ca.* 1.5×10^{-3}M)

Table 1. Physical properties of chloro(methyl)biphenyls

			N.m.r. (CDCl$_3$)						Mass spectrum		
Compd.	(% purity)[a]	M.p (°C)	δ_{CH_3}	δ_{ArH}	Ratio CH$_3$/ArH	$\lambda_{max.}$/nm	$\varepsilon_{max.}$	ε_{254}	Five most intense ions	M^+_{calc}	M^+_{found}
(1)[b]	(>99)	33.5—34	2.2, 2.3	7.1	0.81	244	1 900	1 500	216, 56, 84, 181, 165	216.0707	216.0693
(2)	(>99)	Oil	2.2, 2.3	7.25	0.82	275	2 700	1 800	216, 181, 165, 166, 218	216.0707	216.0693
(3)[c]	(96)	Oil	2.1, 2.3	7.2	0.89	272	840	700	216, 181, 165, 166, 218	216.0707	216.0689
(4)[d]	(>99)	Oil	2.2	7.2	0.35	240	1 800	1 300	202, 167, 164, 82, 83	202.0550	202.0548
(5)[d,e]	(>99)	Oil	2.2	7.35	0.37	235	2 900	1 100	202, 167, 165, 84, 204	202.0550	202.0548

[a] By g.l.c. [b] Low-resolution mass spectrum previously reported.[8] [c] Previously mentioned,[9] but no physical properties were given. [d] I.r. spectrum reported.[10] [e] Completely characterised.[11]

Table 2. Relative and absolute quantum yields of disappearance of chlorobiphenyls

Compound	φ_{rel}	φ_r
(1)	1.0[a]	0.0075[b]
(2)	1.3	0.010
(3)	13	0.097
(4)	0.7	0.005
(5)	1.4	0.010
2-Chlorobiphenyl		0.35,[c] 0.39[d]
3-Chlorobiphenyl		1×10^{-3}[d]
4-Chlorobiphenyl		6×10^{-4}[d]

[a] Assumed. [b] Quantum yield of disappearance of substrate related to the azoxybenzene actinometer, for which $\varphi_r = 0.017$. [c] Ref. 12. [d] Ref. 2.

Following photolysis, the concentration of (1) consumed was determined by g.l.c., and the concentration of the rearrangement product of azoxybenzene was determined by visible spectrophotometry. The difference in absorbance between tubes (2) and (3) allows one to calculate the light intensity absorbed by compound (1). From three duplicate determinations, compound (1) was found to have $\varphi_r = 0.0075 \pm 0.001$.

Product Studies.—These were carried out by g.l.c.–mass spectrometry (Sigma III gas chromatograph interfaced to a VG-7070F mass spectrometer). For each compound, the dechlorination product was the major product observed. Bicyclohexyl (M^+ 166) was observed in all samples. Also detected were traces of both rearrangement products (same M^+ as starting material) and isomers of the dechlorination product. These were investigated further only in the case of compound (1). Comparison of g.l.c. retention times showed that the expected dechlorination product, 2,5-dimethylbiphenyl, was a primary photoproduct. Neither 3,4- or 3,5-dimethylbiphenyl was produced at any stage of the reaction.

Discussion

The relative rate data show that all the compounds studied photodechlorinate with comparable facility, with the exception of the *ortho*-chloro-compound (3) which is much more photolabile. Comparing absolute quantum yields, it is clear that compounds (1), (2), (4), and (5) are more photolabile than their parent compounds 3- and 4-chlorobiphenyl, but they are not as labile as typical compounds having an *ortho*-chlorine substituent. Only (3) has photolability comparable with that of 2-chlorobiphenyl.*

In terms of our original objectives, it would seem that the *ortho*-methyl group is indeed able to enhance the ease of photodecomposition, and we attribute this to raising the energy of the excited triplet state. The extra lability of (3) compared with the other compounds therefore suggests a kinetic effect (relief of strain when the *ortho*-chlorine departs). Consequently, we propose that the striking photolability observed for most *o*-chlorobiphenyls results from a combination of two factors, raising the energy of the excited state by steric compression, and relief of this steric strain when the *ortho*-substituent departs.

Traces of by-products which were isomeric with the starting materials and the dechlorination products were observed in most of these photolyses. Some effort was made to identify them in the case of compound (1); this was unsuccessful. This aspect of the problem was not pursued, since the skeletal rearrangements of simple biphenyl derivatives have already been investigated.[14]

Acknowledgements

We thank the Natural Sciences and Engineering Research Council of Canada for an operating grant for N. J. B. and a summer scholarship to E. J. T. C. T. DeS. thanks the Ontario Ministry of Environment for an Experience '81 grant, and we thank Mr. S. McKinnon for running the mass spectrometer.

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* As observed previously,[2] maximum photolability is observed when there is only one *ortho*-chlorine. Correspondingly, (3), which has two *ortho*-substituents, is less photolabile than 2-chlorobiphenyl.

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Received 23rd *August* 1982; *Paper* 2/1461