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PHOTOLYSIS OF CHLOROBENZENE.
PHENYLATION OF CHLOROBENZENE WITH ANOMALOUS ORIENTATION

Masanobu KOJIMA, Hirochika SAKURAGI, and Katsumi TOKUMARU*
Department of Chemistry, The University of Tsukuba, Sakura-mura, Ibaraki 305

Photolysis of chlorobenzene as neat and in concentrated solutions gives a mixture of o-, m-, and p-chlorobiphenyls in an anomalous ratio, with the highest ratio of the p-isomer. However, on dilution with solvent, the isomer ratio tends to approach the normal ratio as obtained from the usual phenylation of chlorobenzene with the highest ratio of the o-isomer. A mechanism is proposed in which a triplet excimer of chlorobenzene arising in concentrated solutions favours the production of the p-isomer.

Although photolyses of iodobenzene and bromobenzene are known to generate phenyl radicals,1) photolysis of chlorobenzene had not actively been investigated until Lemal and coworkers postulated a π-complexed pair of a chlorine atom and a phenyl radical to account for their experimental observation.2) Since their work much attention has been paid to the mechanism for the photolytic cleavage of the carbon-chlorine bond in chlorobenzene. Arnold and Wong explained Lemal's result in terms of a simple homolytic cleavage of the carbon-chlorine bond of the excited chlorobenzene.3) Bunce and coworkers proposed that irradiation of chlorobenzene leads cleavage from the triplet state and its singlet excimer, if produced in higher concentrations of chlorobenzene, deactivates without undergoing the cleavage in contrast with 1-chloronaphthalene which dissociates through the excimer.4) Recently, Soumillion and De Wolf reported that photolysis of chloroaromatic compounds in methanol proceeds through electron transfer from their triplet to their ground state to generate their ion radicals which react with the solvent.5) These reports have prompted us to present our findings that photolysis of chlorobenzene results in phenylation of chlorobenzene with an orientation different from the usual phenylations, which indicates that the photolysis will take place through the interaction of the excited chlorobenzene molecules with the ground-state chlorobenzene molecules.

Irradiation of neat chlorobenzene (6 cm^3) in a quartz vessel with a 160-W low pressure mercury lamp under nitrogen atmosphere at room temperature for 5 h afforded o-, m-, and p-chlorobiphenyls as main products (nearly 0.1 mmol) in a ratio of 25 : 30 : 45 accompanied by a small amount of biphenyl. As Table 1 indicates, the above ratio of the chlorobiphenyl isomers clearly differs from the "normal" ratio obtained from reactions of chlorobenzene with phenyl radicals generated from their well-known sources, which most favour the formation of the o-isomer.

Table 1. Typical Results for Phenylation of Chlorobenzene

Radical Source (mol/dm^3)		Distribution of Chlorobiphenyl Isomers (%)		
		o-	m-	p-
PhCl photolysis	(neat)	25	30	45
PhI photolysis	(3.86)	59	26	15
$(PhCO_2)_2$ photolysis	(0.06)	55	28	17
$(PhCO_2)_2$ thermolysis	(0.05)	57	27	16

Control experiments by irradiating the respective chlorobiphenyl isomers rule out the possibility that these isomers would photoisomerize to each other and show that biphenyl arises from prolonged irradiation of o-chlorobiphenyl. Furthermore, the isomer ratio was not practically changed in the presence or absence of radical scavengers like oxygen, phenol, or 2,6-di-t-butyl-4-methylphenol.

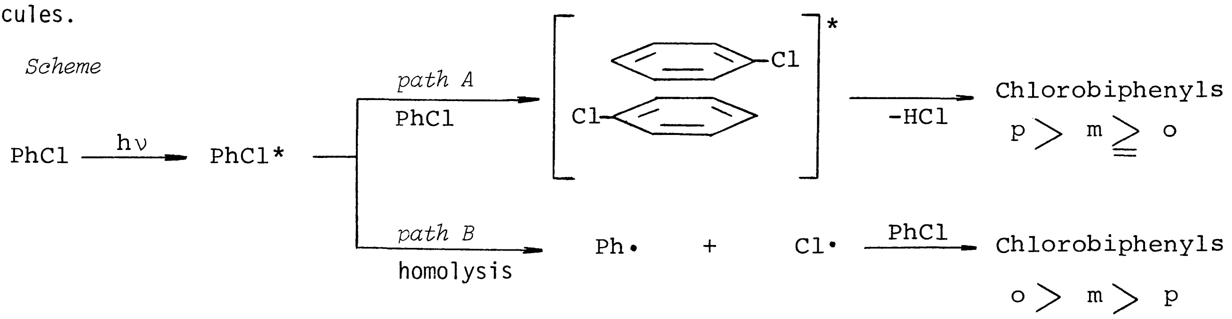
Irradiation was carried out for different concentrations of chlorobenzene in 1,1,2-trichlorotrifluoroethane (200 cm^3) with a 400-W high pressure mercury lamp for 10 h and typical results for duplicate or triplicate runs are summarized in Table 2. Chlorobenzene in more than 5 x 10^{-1} mol/dm^3 concentration gave the isomeric chlorobiphenyls in a similar ratio to that from the neat substrate, in the highest ratio of the p-isomer.[6] However, decrease in chlorobenzene concentration altered the isomer ratio to give the highest ratio of the o-isomer approaching to the "normal" value.

Table 2. Photolysis of Chlorobenzene in CCl_2FCClF_2 (200 cm^3) with a 400-W high pressure mercury lamp (10 h)

Concentration of PhCl (mol/dm^3)	Product Distribution (%)				Yield (mmol)
	Ph$_2$	chlorobiphenyl			
		o-	m-	p-	
5 x 10^{-1}	2	34	25	39	0.2
5 x 10^{-2}	-	41	33	26	0.02
5 x 10^{-3}	-	51	25	25	0.002

These results suggest that in dilute solutions free phenyl radicals generated from photolysis of chlorobenzene act on chlorobenzene to give the normal ratio of isomeric chlorobiphenyls; on the other hand, in concentrated solutions the excited chlorobenzene would interact with ground-state chlorobenzene with a configuration favorable for affording the p-isomer after the cleavage of the C-Cl bond. In view of the report on a triplet excimer of chlorobenzene,[7] it is reasonable to suppose that this is responsible for the formation of p-chlorobiphenyl, while in dilute solutions the excited chlorobenzene molecules will undergo cleavage into phenyl radicals before their encounter with the ground-state molecules.

Scheme



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