Photochemical Aromatic Cyclohexylation

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Photolysis of cyclohexyl iodide with aromatic compounds led to aromatic cyclohexylation by a process apparently involving a cationic cyclohexyl species.

Photolysis of simple alkyl iodides has been shown to produce cations *via* electron transfer between an initially formed radical pair (equation 1).[1,2] In light of our interest in aromatic alkylation processes (*e.g.*, acetonylation,[3] nitromethylation,[4] and cyanomethylation[5,6]), we were interested in determining if photolysis of cyclohexyl iodide in the presence of simple aromatic hydrocarbons would lead to aromatic substitution and by what mechanism.

$$RX \xrightarrow{h\nu} [R^{\bullet}\ {}^{\bullet}X] \rightarrow R^+ + X^- \qquad (1)$$

$$C_6H_{11}^+ + ArH \rightarrow \overset{+}{Ar}HC_6H_{11} \xrightarrow{-H^+} ArC_6H_{11} \qquad (2)$$

$$C_6H_{11}^+ + MeCN \rightarrow C_6H_{11}N{=}\overset{+}{C}Me \xrightarrow[-H^+]{+H_2O} C_6H_{11}NHCOMe \qquad (3)$$

$$C_6H_{11}^+ + MeOH \rightarrow C_6H_{11}(\overset{+}{O}\text{-}H)Me \xrightarrow{-H^+} C_6H_{11}OMe \qquad (4)$$

Deoxygenated solutions of cyclohexyl iodide in an excess of the aromatic compound as solvent were photolysed for 14 h at 254 nm using low-pressure mercury lamps. Approximately half of the unchanged alkyl halide was recovered; extended photolysis times did not appreciably improve halide consumption. The products were analysed directly (iodometry, g.c., and g.c.–mass spectroscopy) and results are summarized in Table 1. Most of the iodo moiety from cyclohexyl iodide was accounted for as iodine. Cyclohexene (yield 7—18%) was the major organic product derived from the halide. Arylcyclohexanes were found in moderate amounts from anisole but in smaller quantities with toluene and benzene. Additional minor by-products were found with each aromatic hydrocarbon. Photolysis of cyclohexyl iodide with benzonitrile did not lead to nuclear cyclohexylation but instead produced *N*-cyclohexylbenzamide. This finding indicated that the cyclohexyl radical is not the attacking species since benzonitrile is known to undergo radical cyclohexylation with much greater ease than the other more electron-rich aromatic compounds.[7] Instead the observed Ritter reaction[8] by the cyclohexyl species suggested that the cyclohexyl cation was formed in the photolysis.

The distribution of isomers of the arylcyclohexanes produced upon photolysis was a further indication that the reactions involved the cyclohexyl cation. Primarily, an *ortho–para* distribution typical of that found in Friedel–Crafts alkylations,[9,10] and substantially different from that for the earlier reported free-radical cyclohexylations[7] was observed with anisole and toluene. Furthermore the reactions between anisole and toluene, and with either cyclohexene or cyclohexyl chloride with aluminium chloride gave isomer patterns (*ortho* : *meta* : *para* = 64 : 0.3 : 36 with anisole and *ortho* : *meta* + *para* = 60 : 40 with toluene) fairly similar to those from the photolysis.

Further evidence of cation involvement came from photolyses performed with an aromatic compound in either acetonitrile or methanol as solvent (Table 2). In both cases the amount of alkylbenzene produced was smaller than in the neat photolyses, and additional products were found, the most significant being *N*-cyclohexylacetamide in acetonitrile, and cyclohexyl methyl ether in methanol.

Mechanistically we feel that the cyclohexyl cation is the common intermediate which can explain the products observed. Cyclohexene is formed *via* elimination while the alkylaromatic compound is formed *via* electrophilic substitution (equation 2). In solvents such as acetonitrile or methanol the cyclohexyl cation undergoes additional solvent trapping reactions: the Ritter reaction (equation 3) and nucleophilic

Table 1. Photolysis of $C_6H_{11}I$ in aromatic solvents.[a]

		Products, %[b]			
ArH	% $C_6H_{11}I$ recovered	I_2	C_6H_{10}	$C_6H_{11}Ar$	Other[c]
C_6H_6	58	10	18	1.0	Minor[d]
PhMe	47	38	8	1.8[e]	IC_6H_4Me[f]
PhOMe	50	24	7	11.5[g]	$PhOC_6H_{11}$[h]
PhCN	42	30	8	0	$C_6H_{11}NHCOPh$ (9%)

[a] $C_6H_{11}X$ (5 mmol) in ArH (10 ml), *h*ν for 13—24 h. [b] Based on starting halide. [c] Two unidentified products (M_r about 154 and 156) were detected in all runs (0.5—1%). [d] Not identified. [e] *ortho: meta* + *para* = 60 : 40. [f] PhCHO, $PhCH_2OH$, $PhCH_2I$, and other unidentified products found. [g] *ortho* : *meta* : *para* = 57 : 1 : 42. [h] Phenol, methylanisole, and other unidentified products of M_r *ca.* 190 were found.

Table 2. Solvent effects on $C_6H_{11}I$ photolysis with Ar.

Acetonitrile:[a]

		Products, %			
ArH	% $C_6H_{11}I$ recovered	$C_6H_{11}Ar$	$C_6H_{11}NHCOMe$	C_6H_{10}	I_2
C_6H_6	30	0.5	3.0	19	38
PhMe	20	0.5[b]	2.8	23	39
PhOMe	25	1.0[c]	2.0	18	25
PhCN	27	0.1	5.1	13	35
Methanol:[a]					
			$C_6H_{11}OMe$		
C_6H_6	28	0.5	1.2[d]	12	38
PhMe	22	1.0[e]	2.9	45	38
PhOMe	32	0.8[f]	1.1	29	25
PhCN	24	0.2[g]	2.1	15	36

[a] Solvent (5 ml), ArH (5 ml), $C_6H_{11}I$ (5 mmol), 14 h photolysis. [b] *ortho* : *meta* + *para* = 58 : 42. [c] *ortho* : *meta* : *para* = 55 : 3 : 42. [d] Other products included toluene, phenol, and methoxyiodocyclohexane in small amounts. [e] *ortho* : *meta* + *para* = 53 : 47. [f] *ortho* : *meta* : *para* = 60 : 3 : 37. [g] Isomer pattern could not be determined.

substitution to give the ether (equation 4). Further details of the mechanism of this and related alkyl iodide photolyses are under study.

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