Photochemical Aromatic Alkylation

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Photolysis of *n*-alkyl iodides (propyl, butyl, pentyl, and hexyl) in neat aromatic compounds (benzene, toluene, and anisole) produced modest amounts of the corresponding *n*-alkylated aromatic products. In addition, varying amounts of isomerized alkylarene were found, and extensive isomerization was noted in the recovered alkyl iodides. All isomerization was suppressed by running the photolyses in the presence of triethylamine, an HI trapping agent. Photolysis of secondary alkyl iodides (isopropyl, *sec*-butyl, and 2- and 3-hexyl) led to very small amounts of the corresponding *sec*-alkylarene. When the photolyses were performed in solvents such as acetonitrile and methanol, solvolysis products (*N*-alkylacetamides or alkyl methyl ethers) were formed at the expense of the aromatic substitution products. These results were indicative of alkyl cation intermediates, presumably formed by way of electron transfer within an initial alkyl radical–iodine atom pair. Of various model cation systems studied for comparison, the photolysis intermediates resembled poorly solvated cation models (i.e. from aprotic alkylamine deaminations) most closely.

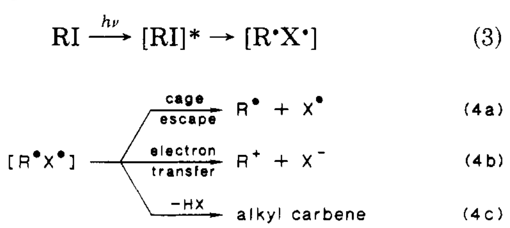
Recently we have shown that the photolytic cyanomethylation resulting upon irradiation of chloroacetonitrile in the presence of aromatics occurred by way of an electron transfer from an excited aromatic species to the halide (eq 1) followed by ultimate radical coupling between the radical cation and cyanomethyl radical (eq 2).[2] Subsequent photolysis of iodo- and bromoacetonitrile with aromatic substrates also led to aromatic cyanomethylation, but the product patterns were different enough from those observed with chloroacetonitrile so as to rule out the electron-transfer scheme (eq 1, 2) in these cases.[3] Furthermore, mechanisms involving direct homolytic substitution by cyanomethyl radicals could be discounted, and there was some inducation that cations might be involved.[3]

$$\mathrm{ArH} \xrightarrow{h\nu} \mathrm{ArH}^* \xrightarrow{\mathrm{ClCH_2CN}} [\mathrm{ArH}^{\bullet+} + {}^{-\bullet}\mathrm{ClCH_2CN}]\ (\mathrm{I}) \qquad (1)$$

$$\mathrm{I} \xrightarrow{-\mathrm{Cl}^-} [\mathrm{ArH}^{\bullet+} + {}^{\bullet}\mathrm{CH_2CN}] \rightarrow \mathrm{Ar}\overset{+}{\mathrm{H}}\mathrm{CH_2CN} \xrightarrow{-\mathrm{H}^+} \mathrm{ArCH_2CN} \qquad (2)$$

In an effort to learn more about this latter iodide reaction, we have instigated photolysis studies with simple alkyl iodides in the presence of aromatic substrates. Condensed-phase photolyses of alkyl iodides are known to generate a rather diverse group of intermediates (including radicals, cations, and carbenes), presumably by way of an initial alkyl radical–halogen atom pair (eq 3 and 4).[4-9] In a few cases, these photolyses were performed in the presence of an aromatic substrate, resulting in some aromatic substitution products (eq 5),[5] but the pathway by which these products arose was not delineated.

$$\mathrm{RI} \xrightarrow{h\nu} [\mathrm{RI}]^* \rightarrow [\mathrm{R}^{\bullet}\mathrm{X}^{\bullet}] \qquad (3)$$



$$\mathrm{ArH} + \mathrm{RX} \xrightarrow{h\nu} \mathrm{ArR} + \mathrm{HX} \qquad (5)$$

Preliminary studies of cyclohexyl iodide photolyzed with aromatic substrates led to modest levels of cycloalkylarenes in addition to cyclohexene as the major product.[10] Yet, despite the fact that the alkyl iodide can competitively undergo excitation and subsequent dissociation to radicals (eq 3), no evidence for homolytic substitution by cycloalkyl radicals or an electron-transfer scheme such as eq 1 and 2 was obtained. Instead, the photochemical aromatic cyclohexylation isomers and relative rates were identical with Friedel–Crafts substitution patterns.[10] When these photolyses were performed in acetonitrile or methanol, solvolysis products (*N*-cyclohexylacetamide or cyclohexyl methyl ether, respectively) were found instead of the cycloalkylarenes.[10] The findings were consistent with a scheme in which an initially formed alkyl radical transferred an electron quickly to the geminate iodine atom resulting in a alkyl cation (eq 4b), which was responsible for aromatic substitution (eq 6) as well as the elimination and solvolysis products.

$$\mathrm{R}^+ \xrightarrow{\mathrm{ArH}} \mathrm{ArHR}^+ \xrightarrow{-\mathrm{H}^+} \mathrm{ArR} \qquad (6)$$

It seemed to us that if alkyl cations were involved as electrophiles in the aromatic substitution process, we ought to be able to more clearly demonstrate this by photolyzing appropriate primary alkyl halides, which could produce cations capable of rearranging. To this end, we have examined the photolytic behavior of a rather extensive series of simple alkyl iodides in the presence of aromatic substrates. We report herein our findings with propyl, butyl, pentyl, hexyl, and heptyl iodides, particularly focusing on whether and how aromatic substitution occurs.

Experimental Section

Materials. The aromatic substrates and alkyl iodides, obtained commercially, were used as is after checking for purity by GC and

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(2) Kurz, M. E.; Lapin, S. C.; Mariam, K.; Hagen, T. J.; Qian, X. Q. *J. Org. Chem.* 1984, *49*, 2728.

(3) Kurz, M. E.; Mariam, K.; Qian, X. Q., unpublished work.

(4) Kropp, P. J. *Acc. Chem. Res.* 1984, *17*, 131.

(5) Kropp, P. J.; Poindexter, G. S.; Pienta, N. J.; Hamilton, D. C. *J. Am. Chem. Soc.* 1976, *98*, 8135.

(6) Kropp, P. J.; Sawyer, J. A.; Snyder, J. J. *J. Org. Chem.* 1984, *49*, 1583.

(7) Kropp, P. J.; Gibson, J. R.; Snyder, J. J.; Poindexter, G. S. *Tetrahedron Lett.* 1978, 207.

(8) Bhalerao, V. K.; Nanjundiah, B. S.; Sonawane, H. R., Nair, P. M. *Tetrahedron* 1986, *42*, 1487.

(9) Sammes, P. G. In *Chemistry of the Carbon-Halogen Bond*; Patai, S., Ed.; Wiley: New York, 1973; Chapter 11.

(10) Kurz, M. E.; Rodgers, M. *J. Chem. Soc., Chem. Commun.* 1985, 1227.

0022-3263/88/1953-0172$01.50/0

Table I. C_3H_7I Photolysis with ArH[a]

			products,[b] %					rcvrd C_3H_7I, %	
C_3H_7I	ArH	additive	*n*-PrAr (*o*/*m*/*p*)	*i*-PrAr (*o*/*m*/*p*)	I_2	ArI	other[c]	1-	2-
1-	C_6H_6		5.5	0.8	24	2.5		15	nd[d]
1-	C_6H_6	Et_3N[e]	5.3		nd			0	0
2-	C_6H_6		0.1	1.3	nd	3.5		0.3	nd
1-	$C_6H_5CH_3$		5.8 (35/28/37)	1.4 (48/20/32)	21	1.2	PhBu-*n* (1.0)	7	12
1-	$C_6H_5CH_3$	Et_3N[e]	5.6 (35/28/37)		nd			0	0
1-	$C_6H_5CH_3$	CH_3CN[f]	0.6 (nd)	0.1 (nd)	nd	0.1	PhBu-*n* (0.2) *n*-$PrNHCOCH_3$ (3.9)	11	5
2-	$C_6H_5CH_3$		2.3	2.9 (47/21/32)	21	1.0		tr	15
2-	$C_6H_5CH_3$	CH_3CN[f]		0.2 (47/27/26)	nd		*i*-$PrNHCOCH_3$ (6.8)	0.1	9
1-	$C_6H_5OCH_3$		2.8 (nd)	24.4 (nd)	18	1.5	HOPhPr-*i* (0.2)	6.1	13.5
1-	$C_6H_5OCH_3$	Et_3N[e]	4.4 (54/23/23)		nd			0	0
2-	$C_6H_5OCH_3$			31.5 (56/10/34)	16	1.3	HOPhPr-*i* (0.2)	0.1	18

[a] C_3H_7I (2.5 mmol) + ArH (10 mL), 254 nm, 20–24 h. [b] Based on mmol/mmol of initial propyl iodide; determined by GC relative to an internal standard. [c] Propene, not accurately quantified, was the major end product of the initial propyl group in all cases. [d] Not determined. [e] Equimolar (2.5 mmol). [f] Used as solvent (10 mL); 1 mL of ArH in these cases.

GC–MS. Some of the 1-iodopropane was vacuum distilled (to rid it of any copper stabilizer) before use, but no difference was observed in photolyses run with this freshly distilled material relative to those using the iodide as supplied. Authentic samples of a number of expected aralkane products were available commercially, while others (isopropyl-, *n*-propyl-, and *n*-butylanisole isomers) were prepared by methylation of the corresponding alkylphenols with dimethyl sulfate.[11]

Analytical Procedures. Qualitative and quantitative gas chromatographic analyses were performed on Hewlett-Packard 5840 gas chromatographs equipped with flame-ionization detectors, capillary inlets (both splitless and split mode), and the following capillary columns: (1) 25 m × 0.25 mm fused silica gel with bonded poly(dimethylsiloxane) (OV-1), (2) 15 m × 0.25 mm fused silica gel with Carbowax 20 M, (3) 15 m × 0.25 mm fused silica gel coated with DB-210 (OV-210). GC–mass spectral analyses were performed on a Hewlett-Packard Model 5790A gas chromatograph [equipped with either a column identical with (1) or with a (4) 12.5 m × 0.25 mm bonded fused silica gel capillary column coated with SP2100] and a 5970B Mass Selective Detector, which were controlled by a Hewlett-Packard Model 59970A workstation. Nuclear magnetic resonance spectra were obtained on a 60-MHz Hitachi Perkin-Elmer Model R-24B NMR spectrometer with tetramethylsilane as a standard. UV absorption spectra were recorded on a Beckman Model 35 UV–vis spectrometer. Routine infrared spectra were obtained as thin films between sodium chloride disks on a Perkin-Elmer Model 710B infrared spectrometer.

Photolyses. Photochemical reactions were carried out in quartz tubes with a Rayonet photochemical reactor equipped with 16 low-pressure mercury vapor lamps emitting greater than 99% monochromatic light at 254 nm. The appropriate halide (generally 2.5 mmol) and aromatic substrate (1 mL) were combined with 10 mL of solvent (neat aromatic, acetonitrile, or methanol), sealed with a rubber septum, degassed with nitrogen, and irradiated or 14–24 h. Photolyses with various additives (e.g., triethylamine) were performed in a similar manner. In many cases, the reaction mixtures were analyzed directly by GC and GC–MS whereas in other cases the iodine produced was quantitatively determined and removed by aqueous sodium thiosulfate before analysis. In some cases, gaseous products (propenes and butenes) were identified by head-space sampling through the septum of the sealed tubes.

Friedel–Crafts reactions were performed by adding alkyl chlorides to a mixture of the aromatic hydrocarbon and aluminum chloride and stirring at room temperature for 0.5 h. These mixtures were quenched with aqueous acid, washed with dilute aqueous base, and dried over sodium sulfate. Products were analyzed quantitatively by GC and in some cases isolated by fractional distillation and characterized by IR, NMR, and MS for comparison with photolyses products.

Aprotic deaminations of *n*-butyl- and *n*-propylamines were performed according to an adaptation of the method of Friedman.[12] The amine was added dropwise to an equimolar (to the amine) mixture of isoamyl nitrite and glacial acetic acid in benzene or toluene as the solvent. After the mixture was stirred for 1 h, a quantitative marker was added, and the product mixture was partitioned between water and ether. The ether layer was then washed with water, aqueous sodium carbonate, and water, dried, and concentrated (if necessary) before analyzing by GC and GC–MS.

Silver nitrate dehalogenations were performed by adding a solution of the alkyl iodide or chloride to equimolar silver nitrate and excess aromatic substrate dissolved in either acetonitrile or ethanol. The mixture was stirred in the dark at room temperature until precipitation was complete (0.5 h to 4 days depending on the alkyl group) and then filtered from the silver halide. The filtrate was analyzed by GC and GC–MS.

Results

Propyl Iodides. Deoxygenated solutions of 1- or 2-iodopropane in excess benzene, toluene, or anisole as solvent were photolyzed at 254 nm with low-pressue mercury lamps for 20–24 h. At the end of this time, significant levels (up to half) of propyl iodides were recovered, much of which had undergone rearrangement in the case of 1-iodopropane (Table I). The major organic product found in all cases was propene, but accurate quantitation of this product was not performed. With 1-iodopropane, significant levels of aromatic alkylation products were observed in all runs. Except for the anisole run, lesser amounts of aromatic substitution resulted from all 2-iodopropane photolyses. Small amounts of iodoarenes were found from both iodides with all three aromatic substrates. Most of the remaining iodo moiety from the propyl iodide consumed was accounted for as iodine. Traces of isopropylphenols were detected in the anisole reactions, indicative of ether cleavage probably by the hydrogen iodide produced.

The nature of the aromatic alkylation products was scrutinized closely. With benzene and toluene, *n*-propylarenes predominated, but with anisole, a much greater amount of isopropylanisoles was found. The addition of an equimolar amount of triethylamine had a significant effect on the course of the *n*-propyl iodide photolysis (Table I). All of the initial alkyl iodide was consumed, and no isomerized alkylbenzene was found even with anisole (which had nearly 25% isopropylanisoles without the amine).

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[11] Hiess, G. S.; Hager, F. D. *Organic Syntheses*; Wiley: New York, 1941; Collect. Vol. I, p 58.

[12] Jurewicz, A. T.; Bayless, J. H.; Friedman, L. *J. Am. Chem. Soc.* **1965**, *87*, 5788.

Table II. C_4H_9I Photolysis with ArH[a]

			products,[b] %					
			ArBu				rcvrd BuI, %	
BuI	ArH	additive	*n*-	*sec*-	other[c]	I_2	1-	2-
1-	PhH		4.3	0.9	$C_4H_8I_2$, 1.1	57	17	33
1-	PhH	Et_3N	6.3				2.7	
1-	$PhCH_3$		4.6	1.1	$C_4H_8I_2$, 0.2	45	14	nd[d]
1-	$PhCH_3$	Et_3N	7.1[e]		$C_4H_8I_2$, 1.0	nd	0.5	0
1-	$PhOCH_3$		2.9	9.7	$C_4H_8I_2$, 0.2	37	17	33
1-	$PhOCH_3$	Et_3N	9.6[f]					
2-	PhH			0.9		58	tr	50
2-	$PhCH_3$			1.8	$C_4H_8I_2$, 1.0	47	tr	nd
2-	$PhOCH_3$			15		33	tr	42
i-	PhH		1.6[g]	0.2		nd	nd	nd
i-	$PhCH_3$		1.2[h]					
i-	$PhCH_3$	Et_3N	1.3[i]		*i*-PenPh, 0.5; $(PhCH_2)_2$, 0.4	nd	nd	nd
i-	$PhOCH_3$		2.1[j]	3.8[k]		nd	nd	nd
i-	$PhOCH_3$	Et_3N	3.6[l]			nd	nd	nd
i-[m]	PhH		0.3[g]		$BuBr_2$, 0.2; $(Ph)_2$, 0.3	nd	nd	nd
i-[m]	$PhCH_3$		0.3[n]		$C_{14}H_{14}$,[o] 2.3	nd	nd	nd
t-	PhH		<0.1[p]			nd	nd	nd

[a] C_4H_9I (2.5 mmol) + ArH (10 mL), 254 nm, 20–24 h. [b] Yields are based on mmol/mmol of initial C_4H_9I; determined by GC relative to an internal standard. [c] Butenes (1-, *cis*-2-, and *trans*-2- from 1- and 2-IC_4H_9 and isobutene from isobutyl and *tert*-butyl iodide) were identified as the major products, but were not quantified. [d] Not determined. [e] *o*/*m*/*p* = 33/31/36. [f] *o*/*m*/*p* = 51/26/23. [g] *i*-BuPh. [h] *i*-$BuPhCH_3$, *o*/*m*/*p* = 30/19/54. [i] *i*-$BuPhCH_3$, *o*/*m*/*p* = 34/18/48. [j] *i*-$BuPhOCH_3$, isomers overlapped with *sec*- and *t*-$BuPhOCH_3$ isomers. [k] *t*-$BuPhOCH_3$, 30%, also formed. [l] *i*-$BuPhOCH_3$, *o*/*m*/*p* = 54/22/24. [m] *i*-BuBr [n] *i*-$BuPhCH_3$. [o] Isomers. [p] *t*-BuC_6H_5.

Relatively nonselective isomeric patterns (typical of either alkyl cations[13] or radicals[14]) were observed for both *n*-propyl- and isopropyltoluene products, neither of which was influenced by triethylamine. The isomerized isopropyltoluenes from the *n*-propyl iodide–toluene photolysis were similar to those found from isopropyl iodide photolysis.

As before,[10] when the photolyses were performed in acetonitrile, the amount of aromatic substitution product was reduced and *N*-alkylacetamides resulted. With both *n*-propyl and isopropyl iodide, the amide was formed without any alkyl group isomerization, just as was the case with the alkylbenzenes produced.

Butyl Iodides. The major products from all photolyses involving *n*- and *sec*-butyl iodide were identified (but not quantitatively determined) as mixtures of 1- and *cis*- and *trans*-2-butenes. The aromatic alkylation products were analogous to those found in the propyl cases: i.e., *n*-butyl iodide photolysis in neat benzene or toluene gave mostly *n*-butylbenzene or *n*-butyltoluenes with small amounts of *sec*-butylarenes. With anisole, nearly 10% of *sec*-butylanisoles were generated in addition to about 3% *n*-butylanisoles. In all three runs, approximately 50% butyl iodide was recovered at the end of 24 h, two-thirds of which had undergone isomerization to 2-iodobutane. Minor amounts of various diiodobutane isomers were detected in these runs.

When photolyses with all three aromatic substrates were performed with added triethylamine, the *sec*-butylated products were not formed, the yields of *n*-butylarenes increased slightly, and all of the butyl iodide was consumed.

Isobutyl halide photochemistry was also investigated. A small amount of *sec*-butylbenzene accompanied a slightly greater amount of the unrearranged isobutylbenzene when isobutyl iodide was photolyzed with benzene. Its photolysis with toluene, alone or with triethylamine, gave only isobutylation, though in the latter case small amounts of probable radical products, bibenzyl and isopentylbenzene, were found. Only in the anisole–isobutyl iodide photolysis was *tert*-butylation observed, and this was totally repressed with added amine (Table II). Photolysis of isobutyl bromide with either benzene or toluene gave lesser amounts of isobutylation and again no *tert*-butylation; biphenyl and isomeric dibromobutanes were also present (Table II).

Studies performed with either *tert*-butyl iodide or *tert*-butyl bromide led to less than 0.2% aromatic *tert*-butylation. Isobutylene was the major product along with biphenyl and many minor unidentified byproducts (Table II).

The photolyses of 1-butyl, 2-butyl, and isobutyl iodide with benzene and anisole were performed in the solvents acetonitrile, methylene chloride, methanol, and ethanol (Table III). In all reactions run with the 1- and 2-butyl iodide in methylene chloride, most, or all, of the aromatic alkylation was inhibited, and about 50% of 2-butyl iodide was recovered or formed. All reactions performed in acetonitrile gave rise to the corresponding alkylacetamide (with no skeletal rearrangement) in 2–12% yields. Aromatic alkylation persisted in most of these runs, but at significantly reduced levels. The photolytic reactions performed in methanol produced only alkyl methyl ethers, whereas those in ethanol gave some aromatic alkylation in addition to alkyl ethyl ethers (Table III).

A number of potential cation model systems for the four butyl and two propyl structures were studied for comparison purposes. Benzene and toluene were reacted with *n*-propyl or isopropyl chloride and *n*-butyl *sec*-butyl, isobutyl, and *tert*-butyl chloride with either aluminum chloride in excess aromatic substrate as solvent or silver nitrate in acetonitrile solution. In addition, deaminations of all four butylamines and both propylamines were carried out by using equimolar amyl nitrite and acetic acid.[12] The results of the aromatic substitution occurring in these systems in comparison to the alkyl iodide photolysis are summarized in Table IV. The photolytic aromatic alkylation behavior was not consistent with cation-producing systems such as the Friedel–Crafts alkylation[13] or of silver nitrate promoted dehalogenation of propyl halides[15] (where

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(13) Olah, G. A.; Olah, J. A.; Ohyama, T. *J. Am. Chem. Soc.* **1984**, *106*, 5284.

(14) Tiecco, M.; Testaferri, L. In *Reactive Intermediates*; Abramovitch, R. A., Ed.; Plenum: New York, 1983; Vol. 3, Chapter 2.

(15) Beak, P.; Transik, R. J.; Moobery, J. B.; Johnson, P. Y. *J. Am. Chem. Soc.* **1966**, *88*, 4288.

Table III. Solvent Effect on Butyl Iodide Photolysis[a]

			products,[b]				
			ArBu			rcvrd BuI, %	
BuI	ArH	solvent	*n*-	*sec*-	solvolysis	1-	2-
1-	PhH	CH_3CN	0.1	0.6	*n*-$BuNHCOCH_3$, 4.3	34	9
1-	PhH	CH_2Cl_2	0.4	0.5	*c*	4	35
1-	$PhOCH_3$	CH_2Cl_2			*c*	2	45
2-	PhH	CH_3CN		0.4	2-$BuNHCOCH_3$, 3.9	16	5
2-	PhH	CH_3OH			2-$BuOCH_3$, 2.3		6
2-	PhH	C_2H_5OH		0.2	2-$BuOC_2H_5$, 11.7		<1
2-	PhH	CH_2Cl_2		0.6			46
2-	$PhOCH_3$	CH_3CN			2-$BuNHCOCH_3$, 5.2	16	9
2-	$PhOCH_3$	CH_3OH			2-$BuOCH_3$, 1.9		tr
2-	$PhOCH_3$	C_2H_5OH		0.2	2-$BuOC_2H_5$, 14		tr
2-	$PhOCH_3$	CH_2Cl_2				tr	50
i-	PhH	CH_3CN	0.4[d]		*i*-$BuNHCOCH_3$, 5.0		
i-	$PhCH_3$	CH_3CN	1.3[d]		*i*-$BuNHCOCH_3$, 4.6		

[a] C_4H_9I (2.5 mmol) + ArH (1 mL) + solvent (10 mL), 254 nm, 20–24 h. [b] Yields were based on mmol/mmol initial C_4H_9I; isomeric butenes were identified as the major products but were not quantified. [c] BuI_2, 1% formed. [d] *i*-BuAr.

Table IV. Photolytic Aromatic Substitution Patterns versus Model Systems

	RI + hr[a]			RNH_2 + *i*-PenONO + HOAc[b]			$RCl + AlCl_3$[c]	
R	C_6H_5R	%	dist[d]	C_6H_5R	%	dist[d]	C_6H_5R[d]	dist[d]
benzene								
n-Pr	*n*-PrPh	5.3	100	*n*-PrPh	0.7	100	*n*-PrPh[e]	40 (28[f])
							i-PrPh	60 (72)
n-Bu	*n*-BuPh	6.3	100	*n*-BuPh	1.0	100	*n*-BuPh	26
							sec-BuPh	74
i-Bu	*i*-BuPh	1.6	89	*i*-BuPh	0.26	87	*t*-BuPh[g]	100
	sec-BuPh	0.2	11	*sec*-BuPh	0.04	13		
toluene								
n-Pr	*n*-$PrPhCH_3$ (*o*/*m*/*p* = 35/28/37)	5.6					*n*-$PrPhCH_3$[f]	47
							i-$PrPhCH_3$	53
n-Bu	*n*-$BuPhCH_3$ (*o*/*m*/*p* = 33/31/36)	7.1		*n*-$BuPhCH_3$ (*o*/*m*/*p* = 32/26/42)	1.2		*n*-$BuPhCH_3$[g] (*o*/*m*/*p* = 28/32/42)	40
							sec-$BuPhCH_3$	60[h]
i-Bu	*i*-$BuPhCH_3$ (*o*/*m*/*p* = 34/18/48)	1.8		*i*-$BuPhCH_3$, (*o*/*m*/*p* = 31/22/47)[i]	1[i]		*t*-$BuPhCH_3$[j]	100

[a] RI (2.5 mmol) + ArH (10 mmol) + Et_3N (2.5 mmol), hr, 24 h. [b] Equimolar amine, isopentyl nitrite, and glacial acetic acid in excess ArH, 20 °C. [c] RCl (2.5 mmol) + $AlCl_3$ (2.5 mmol) + ArH (25 mL), 20 °C. [d] Distribution. [e] Reference 17. [f] Reference 18. [g] Combined yield of 40%. [h] Overlapping isomers, not separable by GC. [i] Approximate. [j] Yield of 50%.

no aromatic substitution was observed). It did, however, resemble the reactivity of poorly solvated cations produced from aprotic alkylamine deaminations.[12,16]

Iodopentane Photolysis. Much the same pattern emerged when 1-pentyl iodide was photolyzed with benzene. *n*-Pentylbenzene was formed primarily along with a mixture of alkenes (mostly isomerized, Table V). Nearly two-thirds of the original amount of alkyl iodide was recovered, of which nearly half had isomerized. The same reaction performed with added triethylamine gave increased amounts of *n*-pentylbenzene and pentene (mostly 1-pentene) as most of the alkyl iodide was consumed (Table V). Analogous behavior was observed when 1-iodopentane was photolyzed with toluene. With triethylamine additive, the radical byproduct 1-hexylbenzene was observed in significant amounts. In all of the 1-iodopentane studies, reasonably good material balances with respect to the pentyl moiety were noted. The photolysis of 3-pentyl iodide with benzene gave a smaller amount (0.4%) of 3-pentylbenzene.

Iodohexane Photolyses. 1-, 2-, and 3-iodohexanes were photolyzed in the presence of benzene at 254 nm. 1-Iodohexane produced the largest amount of hexylbenzenes (about 4%), the majority (>95%) consisting of *n*-hexylbenzene with traces of 2- and 3-hexylbenzene also detected. Hexene (12%), hexene (8.8%), and traces of iodobenzene were also formed. Significant levels of iodohexanes were recovered, but nearly half of it consisted of isomerized 2- or 3-iodohexane.

With 2- and 3-iodohexane, small quantities (0.8%) of a mixture of 2- and 3-hexylbenzenes were found. Hexene and hexane were qualitatively identified, and significant amounts of iodohexanes were recovered in all three cases.

When the 1-iodohexane–benzene photolysis were performed with added triethylamine, a slightly increased yield of *n*-hexylbenzene was noted, and most of the 2- and 3-hexylbenzenes were eliminated. Very little iodohexane was recovered, with virtually no isomerization of the starting material. The yield of hexenes (primarily 1-hexene) increased dramatically, from 8.8% to 60.2%, while the amount of hexane dropped off to 3%. Both dodecane and dodecene (not found in photolyses run without the amine) were detected in small amounts.

Iodoheptane Photolysis. 1-Iodoheptane was also photolyzed in benzene with and without triethylamine (Table V). The results were analogous to the 1-iodohexane experiments. Heptene and heptane were produced but not quantitated. The yield of alkylated benzene, suppression of isomerization, and absence of alkyl halides found after photolysis matched the iodohexane results. Small levels

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(16) Olah, G. A.; Overchuck, N. A.; Lapierre, J. C. *J. Am. Chem. Soc.* **1965**, *87*, 5785.

(17) Ipatieff, V. N.; Pines, H.; Schmerling, L. *J. Org. Chem.* **1940**, *5*, 253.

(18) Smoot, C. R.; Brown, H. C. *J. Am. Chem. Soc.* **1956**, *78*, 6249.

Table V. *N*-Hexyl and *N*-Pentyl Iodide Photolysis in Benzene

		products[a]							
		alkylbenzene		alkenes			rcvrd RI, %		
RI, R =	additive	*n*-	*sec*-	1-	2-*cis*-	2-*trans*-	1-	2-	3-
1-pentyl		2.6	tr	7.8	10.8	3.9	33	28	9
1-pentyl	Et_3N	3.8	tr	59.3	4.9	1.2	14	1	tr
1-pentyl[b]		3.6[c]		17.2[d]	5.7	2.2	51	10	1
1-pentyl[b]	Et_3N	4.1[e]		20.0[d]	6.2	tr	43	1	0
3-pentyl			0.4[f]		30[g]			16	
1-hexyl[h]		3.8	0.2		9[g]		23	25[i]	
1-hexyl	Et_3N	4.4	tr[j]		60[g]		0.5	tr[i]	
2-hexyl			0.8[k]		nd			nd	
3-hexyl			0.8[l]		nd			nd	
1-heptyl		3.4	0.2		nd		33	22[i]	
1-heptyl	Et_3N	4.0			nd[m]		tr	tr	

[a] RI (2.5 mmol) and ArH (10 mL), 254 nm, 24 h; yields based on mmol/mmol of RI determined by GC with an internal standard. [b] Toluene rather than benzene. [c] Tentative *o*/*m*/*p* = 24/16/60. [d] $C_{14}H_{14}$ isomers (1.6–3.0%) other than $(C_6H_5CH_2)_2$. [e] Isomers not determined due to interfering *n*-hexylbenzene (6.1%), which was formed as well. [f] 3-Pentylbenzene. [g] Isomers not determined. [h] Additional runs made with added zinc or in the presence of oxygen showed little difference from these values. [i] Not separable. [j] Dodecane (3%) and dodecene (2%) were also found. [k] 2-Hexylbenzene. [l] 3-Hexylbenzene. [m] Tetradecane (5%) and tetradecene (5%) were also found.

Table VI. Hexyl Iodide Photolysis with Anisole

	products,[a] %					rcvrd iodohexanes, %	
	(methoxyphenyl)hexanes						
iodohexane	1-	2-	3-	hexenes	hexanes	1-	2- + 3-
1-[b]	5.5	7	5.5	6	5	34	34
1- + NEt_3[c]	5.5	trace	trace	40	1.2	tr	tr
2-[b]		14	6	25[d]			54
3-[b]		7.4	4.6	15	7		62
2-[e]		10.2[f]		24[d]			
2-[g]		5.4[f]		33[d]			
2-hexene + HI[h]		13	6.4				

[a] Yields are based on mmol/mmol initial hexyl iodide, determined by GC relative to an internal standard. [b] Other products: methylanisoles (3%), methyl iodide (2%), I_2 (8%), phenol (trace), iodoanisole (trace), diiodohexane (trace). [c] Other products: dodecane (3%), dodecene (2%), *n*-hexylbenzene (0.1%), iodoanisole, and hexylphenol (traces). [d] Includes hexenes and hexane, which dod not separate in some runs. [e] Benzonitrile (2.0 mmol) added. [f] Includes 2- and 3-methoxyphenylhexane, which coeluted on the GC columns used. [g] *m*-Dinitrobenzene (0.65 mmol) added. [h] Equimolar amounts, no hexyl iodide.

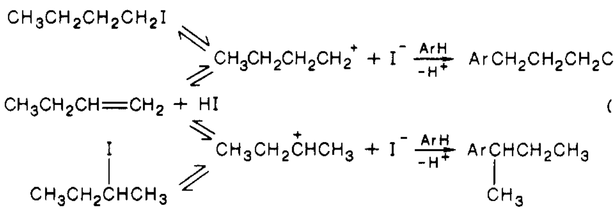
of dimeric products (tetradecane and tetradecene) were formed when the amine additive was used.

Discussion

Generally, the major product observed upon photolysis of simpler alkyl iodides has been the corresponding elimination product, formed from either β- or α-elimination, purportedly involving cationic[4,5,8] and carbene[4,6] intermediates, respectively. In order to get around this dominant reactivity pattern, Kropp purposely used alkyl iodides incapable of simple elimination so as to focus on potential solvolysis behavior.[2,4,5]

The formation of alkenes was also the dominant reaction in our photolyses. Alkyl cations are the intermediates that can best explain the products observed in our studies. The alkylaromatic was formed by way of electrophilic substitution (eq 6) whereas photolyses in acetonitrile and alcohols led to solvolysis products[4,10] (acetamides and ethers, respectively).

Aromatic substitution occurred to the greatest extent with the primary iodides and was a much less favorable reaction with secondary and tertiary iodides, which apparently undergo elimination with more ease. An even more striking aspect of the aromatic alkylation observed with the primary iodides is the lack of rearrangement, which is characteristic of carbocation species.[19] In fact it can be seen (Tables I, II, V, and VI) that rearranged products were found primarily in cases where no triethylamine additive was used. In these reactions, the combination of alkene and HI formed upon elimination would react to form the same or an isomerized alkyl iodide (e.g., eq 7 shown for the butyl system). These equilibria



(7)

nicely account for the extensive isomerization noted in the recovered alkyl iodide as well as the small amount of *sec*-alkylation that occurred (eq 7). With triethylamine present to remove the HI as an ammonium salt, this equilibrium was disrupted, and all the alkyl iodide was consumed. No rearrangement was noted in the alkylarene or alkene produced or in the alkyl iodide recovered.

Further confirmation of these equilibria (eq 7) was gained by observing a similar ratio of the two hexylated anisoles upon irradiation of a mixture of 2-hexene and HI or either 2- or 3-iodohexane in anisole (Table VI).

The lack of the usual rearrangements noted for the proposed carbocation intermediates contrasts with the behavior of alkyl species from the Friedel–Crafts reaction[13] (Table IV). Yet the photolytic alkylation behavior, even the unusual *sec*-butylation observed from isobutyl iodide in the benzene reaction, closely mimicked that observed for cations formed upon aprotic deamination of alkyl amines, both in our work (Table IV) and in that of earlier

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[19] Olah, G. A. *Friedel-Crafts Chemistry*; Wiley-Interscience: New York, 1973.

authors.[12,16] With isobutyl, this may be due to preferential backside migration of methyl from a more stable gauche form of the diazonium ion precursor rather than hydride migration from a more crowded conformer. The unusual behavior of these poorly solvated cations has been attributed to kinetic rather than the usual thermodyanamic factors.[20,21]

That primary unsolvated cations can be formed upon photolysis is not surprising since this method has been used to generate quite a number of high-energy cations difficult to prepare solvolytically, including bridgehead[5] and vinyl[22,23] (but not alkynyl[24]) cations.

The substitution pattern found from alkyl iodide photolysis with toluene also resembles that observed from cationic alkylation systems (Table IV)[12,25] and are somewhat different from alkyl radical substitution patterns.[26] This coupled with the lack of significant products resulting from the common benzylic hydrogen abstraction with toluene in most of the photolyses suggests that free-radical involvement in these reactions is minimal. However, photolysis with triethylamine additive did give rise to some radical coupling products, perhaps due to electron transfer from exited triethylamine to the alkyl iodide followed by loss of iodide.[27]

Conclusions

The alkylation observed upon photolyses of primary alkyl halides in the presence of aromatic substrates is best explained as involving high-energy cations, which are trapped before they can undergo common hydride rearrangements.

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Registry No. PrI, 107-08-4; *i*-PrI, 75-30-9; BuI, 542-69-8; *sec*-BuI, 513-48-4; *i*-BuI, 513-38-2; *t*-BuI, 558-17-8; *i*-BuBr, 78-77-3; *t*-BuBr, 507-19-7; $\mathrm{I(CH_2)_4Me}$, 628-17-1; $\mathrm{Et_2CHI}$, 1809-05-8; $\mathrm{I(CH_2)_5Me}$, 638-45-9; $\mathrm{MeCH(I)(CH_2)_3Me}$, 18589-27-0; PrCHIEt, 31294-91-4; $\mathrm{I(CH_2)_6Me}$, 4282-40-0; PhH, 71-43-2; PhMe, 108-88-3; PhOMe, 100-66-3.

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(20) Bayless, J. H.; Mendicino, F. D.; Friedman, L. *J. Am. Chem. Soc.* **1965**, *87*, 5790.

(21) Froemsdorf, D. H.; McCain, M. E. *J. Am. Chem. Soc.* **1965**, *87*, 3983.

(22) McNeeley, S. A.; Kropp, P. J. *J. Am. Chem. Soc.* **1976**, *98*, 4319.

(23) Suzuki, T.; Kitamura, T.; Sonoda, T.; Kobayashi, S.; Taniguchi, H. *J. Org. Chem.* **1981**, *46*, 5324.

(24) Ioune, Y.; Fununaga, T.; Hakushi, T. *J. Org. Chem.* **1983**, *48*, 1732.

(25) Olah, G. A.; Overchuck, N. A.; *J. Am. Chem. Soc.* **1965**, *87*, 5786.

(26) Kurz, M. E.; Frank, F. J.; Stronach, C., unpublished work.

(27) Latowski, T.; Zelent, B. *J. Org. Chem.* **1979**, *44*, 3559.

Conformational Studies by Dynamic NMR. 33.[1] Possible Applications of the Magic Angle Spinning Technique for Identifying Meso and Racemic Conformers in the Solid State

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The ^{13}C magic angle spinning NMR spectrum of a meso compound in the solid often displays a different number of lines with respect to its racemic isomer. Usually the meso isomers that have a symmetric conformation in the crystal are expected to yield the same spectral multiplicity as in solution (e.g., *meso*-2,3-dimethylsuccinic acid). Exceptions might in principle occur in the few cases when the center of molecular symmetry is not coincident with a center of crystallographic symmetry: examples of this type, however, were not encountered in the present work. On the other hand the isomeric racemic derivatives are normally expected to have solid-state spectra with a larger number of lines than in solution (e.g., *d,l*-2,3-dimethylsuccinic acid). In a very limited number of cases solid-state spectra with unsplit lines can be encountered: an example (*trans*-1,2-cyclohexanedicarboxylic acid) is reported here and discussed. In the case of *N,N'*-diisopropyl-*N,N'*-dimethyl-1,5-naphthyldiamine (1) the ^{13}C solution spectrum at −90 °C does show the existence of two conformers with unequal proportions: one of them being meso, the other racemic. The solid-state spectrum of 1 shows that some of the lines of the major conformer are split into two with respect to the solution spectrum whereas those of the minor conformer are unsplit, as in solution. On this basis the racemic structure has been tentatively assigned to the major conformer and the meso structure to the minor conformer. In favorable circumstances, as those here reported, these features might possibly be helpful in discriminating meso from racemic conformers when they cannot be physically separated nor investigated by X-ray diffraction.

Introduction

Compounds existing in the meso and racemic (*d,l*) forms yield different NMR spectra in solution. The spectra differ in the chemical shifts and, to a lesser extent, in the coupling constants but in most cases display the same number of lines and the same multiplicity. As a consequence the structure often cannot be assigned on the basis of this spectral evidence.

When the meso and racemic compounds can be separated, other methods (e.g., X-ray diffraction) help in obtaining the correct assignment. However if the two forms interconvert rapidly into each other, i.e., when the meso

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[1] Part 31. Bonini, B. F.; Grossi, L.; Lunazzi, L.; Macciantelli, D. *J. Org. Chem.* **1986**, *51*, 517. Part 32. Casarini, D.; Lunazzi, L.; Placucci, G.; Macciantelli, D. *J. Org. Chem.*, in press.

0022-3263/88/1953-0177$01.50/0