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THE PYRIDYL CATION AS A REACTIVE INTERMEDIATE IN THE PHOTOREACTION OF IODOPYRIDINES WITH BENZENES [1)]

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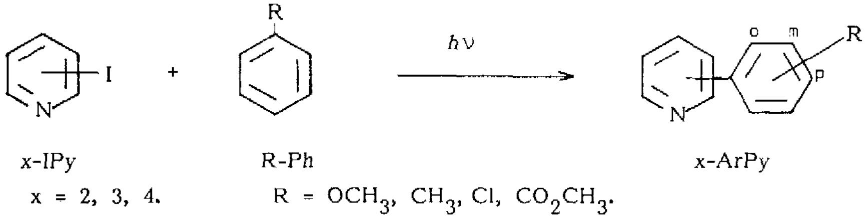
Abstract. The electrophilic behavior of the reactive entity in the photosubstitution of benzenes with 2-iodopyridine was found to be ascribable to the intermediary 2-pyridyl cation, rather than to the electrophilic 2-pyridyl radical.

It has been recognized that heteroaryl radicals in the homolytic heteroarylation of aromatic compounds are electrophilic in character.[2)] Previously we reported the synthesis of 2-arylpyridines by the photoreaction of 2-iodopyridine (2-IPy) and substituted benzenes in dichloromethane, wherein 2-IPy was electrophilic in its reactivity.[3)] However, it remained unclear whether the electrophilic radical or the cation was the reactive entity in the reaction. In the present paper, we provide evidence that the reactive entity is 2-pyridyl cation, rather than the radical.

In order to investigate the general feature of the photo-induced pyridinylations of aromatic compounds, we carried out photolysis of 2-, 3- and 4-IPy in substituted benzenes (R-Ph)(Chart 1).[4)] As shown in Table I, the patterns of the isomer distributions of 3- and 4-arylpyridines (3- and 4-ArPy) were analogous to those of arylbenzenes obtained by homolytic phenylation (photolysis of iodobenzene).[5)] On the other hand, the isomer distribution ratios of 2-arylpyridines seemed closer to those of arylbenzenes obtained by cationic phenylation[6)] (Table II), implying that a cationic species is involved in the photoreaction of 2-IPy.



x = 2, 3, 4.
R = OCH_3, CH_3, Cl, CO_2CH_3.

Chart 1

Table I. Isomer Distribution of Arylpyridines Obtained by Photolyses of Iodopyridines in Substituted Benzenes

	Photolysis of Iodopyridine								
R of RPh	2-ArPy			3- ArPy			4-ArPy		
	o	m	p	o	m	p	o	m	p
OCH_3	52	13	35	72	13	15	71	14	15
CH_3	54	21	25	63	19	18	64	21	16
Cl	41	31	28	69	16	15	58	23	19
CO_2CH_3	28	38	34	57	13	30	50	21	29

Table II. Reported Isomer Distributions of Arylbenzenes Obtained by Homolytic[5)] and Cationic[6)] Phenylation

	Homolytic Phenylation			Cationic Phenylation		
R of RPh	Arylbenzene			Arylbenzene		
	o	m	p	o	m	p
OCH_3	71.5	15.0	13.5	56.4	12.2	31.4
CH_3	65.5	20.0	14.5	47.3	21.1	31.6
Cl	58.0	26.5	15.5	48.2	24.0	27.8
CO_2CH_3	54.0	19.0	27.0	43.1	43.5	13.4

Kropp et al. reported that the alkyl radicals formed by the photolysis of alkyl halides exhibited a dual behavior: 1) direct hydrogen abstraction from solvents; and 2) electron transfer within the radical pairs to generate the corresponding ion pairs, followed by a nucleophilic attack by solvents on the alkyl cations.[7)] In the similar approach, 2-, 3- and 4-IPy in solvents(methanol and dichloromethane) were examined (Chart 2).[4)] In methanol, 2-IPy afforded 2-methoxypyridine (2-MeOPy) as a major product, while 3- and 4-IPy gave the radical product, pyridine (PyH), exclusively and no detectable nucleophilic substitution products (Table III). Similar photolysis of 2-IPy in dichloromethane afforded nearly equal amounts of 2-chloropyridine (2-ClPy) and PyH, while 3- and 4-IPy furnished PyH predominantly with small amounts of 3- and 4-chloropyridine (3-ClPy, 4-ClPy), respectively (Table III)[8)]. These suggest the involvement of the cationic intermediate in the photolysis of 2-IPy.

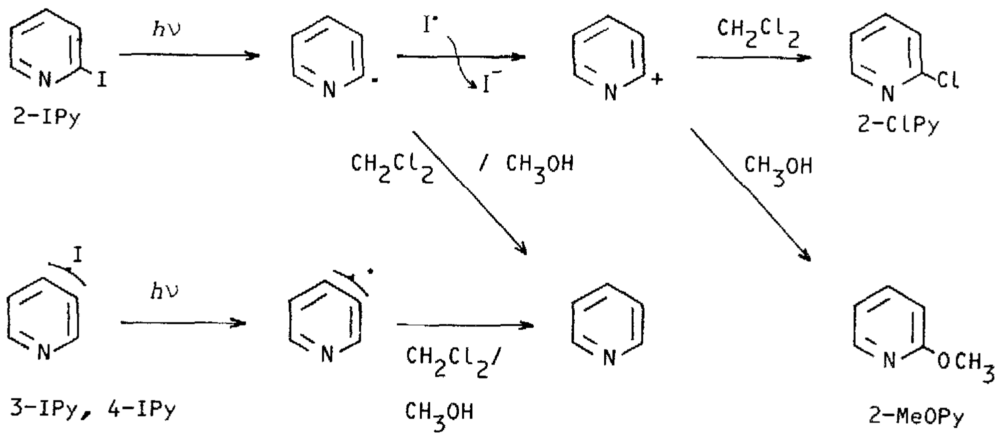


Chart 2

Table III. Photolysis of Iodopyridines in Methanol and in Dichloromethane

		Yields (%) of			
Solvent	IPy	MeOPy	ClPy	PyH	Consumed IPy
Methanol	2-IPy	27		15	49
	3-IPy	0		62	62
	4-IPy	0		65	65
CH_2Cl_2	2-IPy		16	14	31
	3-IPy		7	54	61
	4-IPy		4	40	44

Furthermore, the isomer distribution of 2-(x-carbomethoxyphenyl)pyridines (x = 2, 3, and 4) obtained by the thermolysis of a solution of dibenzoylperoxide and 2-IPy in methyl benzoate[9] (Chart 3) was found to be similar (2: 3: 4 = 50: 13: 37) to that of the homolytic phenylation of methyl benzoate[5] (Table II); under these conditions, the 2-pyridyl radical should be generated without formation of radical pair and hence ion pair. This also supports the assumption that the cation participates in the photolysis of 2-IPy in benzenes.

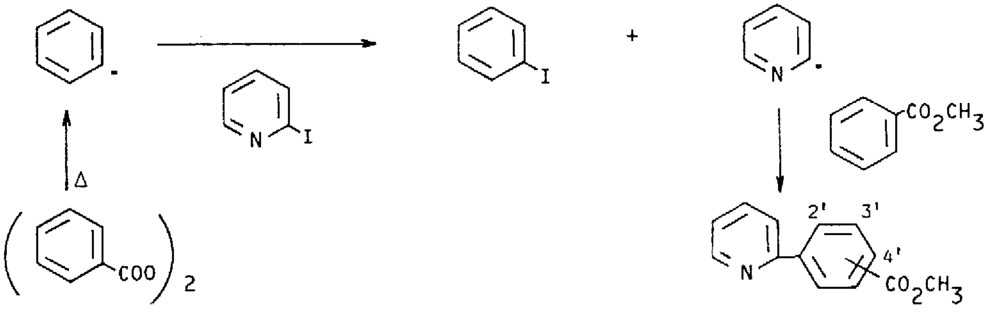
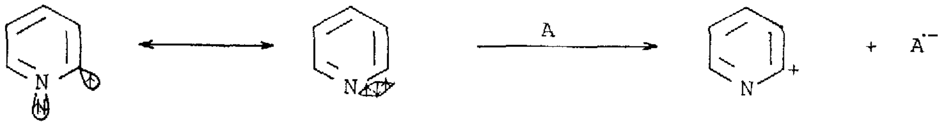


Chart 3

Based on the electronic structure of the 2-pyridyl radical proposed by Bower et al.,[10] it would be reasonably recognized that the 2-pyridyl radical would readily release its unpaired electron from the antibonding orbital of the pseudo π-orbital to an electron acceptor (I• or others), probably in the cage, to form the cation species (Chart 4).

While the electrophilic nature of the heteroarylating agents has been hitherto explained only in terms of the electrophilic radicals,[2] the present study provides a new aspect to homolytic aromatic heteroarylation.



A = Electron acceptor: I$^\bullet$ or others.

Chart 4

References and Notes

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4) UV irradiation (IPy, 0.1 mmol; Solvent, 10 ml) was carried out with a 60 W low-pressure mercury lamp (Eiko-sha) argon atmosphere using a merry-go-round apparatus at room temperature (1h), and the reaction mixtures were determined on a gas chromatograph.
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8) From the fact that irradiation of iodobenzene in dichloromethane afforded a mixture of benzene and a small amount of chlorobenzene (30 : 1), it can be concluded that ClPys from 3- and 4-IPy were derived by competitive radical abstraction from dichloromethane, rather than by nucleophilic substitution.
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