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PHOTOCHEMICAL ARYLATION BY OXIME ESTERS IN BENZENE AND PYRIDINE: SIMPLE SYNTHESIS OF BIARYL COMPOUNDS

Masato Hasebe, Koichi Kogawa, and Takashi Tsuchiya*
School of Pharmacy, Hokuriku University,
Kanagawa-machi, Kanazawa 920-11, Japan

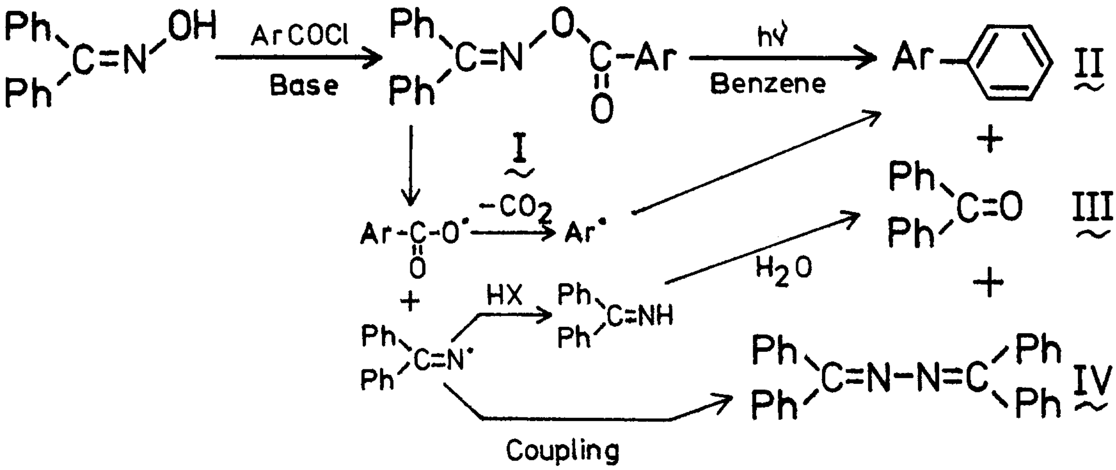
Summary: Irradiation of benzophenone O-arenecarbonyloximes in benzene and pyridine affords the corresponding arylbenzenes and arylpyridines, respectively, in high yields.

Aryl radicals are generated by various ways among which thermal decomposition of arenecarbonyl peroxides,[1] arenediazonium salts,[2] acylarylnitrosoamines,[3] and aryl triazenes[4] which are used as efficient precursors for radical reactions. Although they may be useful compounds to generate aryl radicals, their stability and preparation give some difficulties to their utilities. Photolysis of some haloaromatic compounds in benzene also produces aryl radicals under appropriate conditions.[5,6] Aryl substituted benzenes are formed by those thermal and photochemical reactions in benzene.

We report here that benzophenone O-arenecarbonyloximes are quite useful synthetic precursors for photochemical arylation reactions of aromatic and aza-aromatic compounds.

The effective radical precursors, benzophenone O-arenecarbonyloximes (Ia-g), were prepared easily from benzophenone oxime and arenecarboxylic acid chlorides in the presence of a base such as pyridine in 75-95% yields.

The oxime esters (Ia-f, 5-10 mmol) were irradiated (Pyrex filter, 400 W high pressure Hg lamp) in benzene under N_2 gas flow at room temperature. The products were isolated by silica gel column chromatography and identified by comparison of their spectral data with those of authentic samples. In each case, expected biphenyls (IIa-c) and phenylpyridines (IId-f) were obtained in



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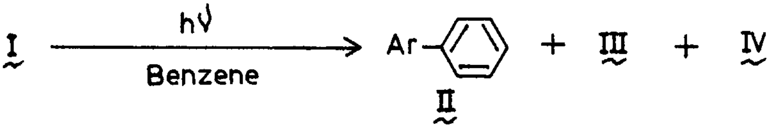


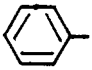
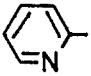
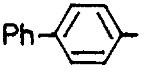
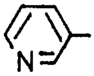
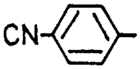
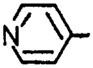
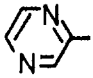
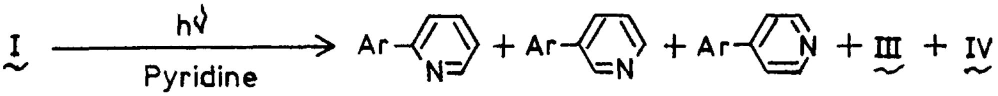
I	Ar	II(%)	I	Ar	II(%)
a.		70	d.		75
b.		47	e.		80
c.		62	f.		85
			g.		73

Table I

good yields together with benzophenone (III, 70-85%) and benzophenone azine (IV, 8-18%) (Table I). Any evidence of arenecarboxylation on benzene ring was not observed under the present reaction conditions.[7]

Irradiation of those simple oxime esters (Ia,d-f, 20-25 mmol) in pyridine was also very effective one-step synthesis of bipyridyls (Vd-f, VId-f, VIId-f) and phenylpyridines (Va, VIa, VIIa) (Table II). The photolysis of Ia,d-f in pyridine gave three isomers of arylpyridines in high total yields (80-87%) together with III (81-92%) and IV (4-12%) and the formation of α-isomers was predominant.[8] The isomer distribution of products depends strongly on the



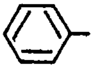
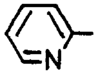
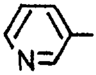
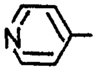
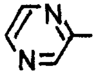
I	Ar	V(%)	VI(%)	VII(%)
a.		37	24	19
d.		45	25	15
e.		44	21	18
f.		44	23	20
g.		41	30	15

Table II

reactivity of the generated radicals, since " hot " radicals have shown less selectivity.[6] Those isomers of bipyridyls were separated by fractional recrystallization of their picrates successfully.

The arylation of pyrazine was also successful by the photolysis of the oxime ester (Ig) in benzene and pyridine; giving phenylpyrazine (IIg) and three pyrazylpyridines (Vg, VIg, VIIg) in good yields, respectively (Table I,II).

The evidence of any rearrangement of generated aryl radicals was not observed through the reaction and arylation always took the position vacated by the carboxyl group of starting compounds selectively.[6,9] Moreover, heating those oxime esters (Ia-g) in benzene and pyridine did not afford any biaryl derivatives and starting compounds were recovered.

The homolytic cleavage of the weak N-O bond of the oxime ester (Ia) may proceed from its excited triplet state under the presented photolytic conditions.[10] Then decarboxylation of the formed arenecarboxylyl radical generates an aryl radical which reacts with benzene and pyridine to produce biaryl compounds (Scheme I). Benzophenone (III) and benzophenone azine (IV) might be derived from the iminyl radical as shown in the Scheme.

Those photochemical arylation reactions show that simple oxime esters

(Ia-g) are quite effective radical precursors under mild photlytic conditions and afford arylated products in good yields. For a typical example, photolysis of the oxime ester (Ie) in benzene gave 3-phenylpyridine (IIIe), which required long laborious work to make by ordinary methods,[11] over 80% yields in one step. The oxime esters of quinoline- and naphthalene-carboxylic acids were also found to produce the corresponding arylated compounds under similar photolytic conditions.

Further synthetic applications of this reaction to other systems are in progress.

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