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CHARGE-TRANSFER-INDUCED PHOTOLYSIS OF BENZYL ACETATES WITH ALIPHATIC AMINES

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Photolysis of benzyl acetates proceeds reductively in the presence of aliphatic amines via electron-transfer followed by proton-transfer. The reaction is appropriately included in the category of the photo-induced Birch reduction.

Although many studies have been reported on photolytic solvolysis of benzyl acetates,1) photo-induced reductive cleavage of benzylic C-O bonds by electron donors has scarcely been examined. Recently Ullman et al. revealed that intramolecular charge-transfer-induced photosolvolysis of benzyl alcohol proceeds through a carbonium ion mechanism.2) In the course of an investigation on charge-transfer-induced alkylation of dicyanobenzene-triethylamine systems, we found that the benzylic C-N bonds were cleaved reductively upon irradiation.3) We now wish to report that some benzyl acetates undergo reductive cleavage of the benzylic C-O bond when irradiated with aliphatic amines via electron-transfer followed by proton-transfer, which suggests that, in contrast with Ullman's results, intermolecular charge-transfer-induced photolysis of benzyl acetates belongs to the photo-induced Birch reduction.

Irradiation of a mixture of p-cyanobenzyl acetate(I, 0.005 M) and triethylamine (0.06 M) in acetonitrile under a nitrogen atomosphere with a low pressure mercury arc for 6h gave p-tolunitrile(II) in 26% yield together with 4,4'-dicyanobibenzyl(III, 16%). The quantum yields in the formation of II and for the consumption of I were 0.2 and 1.2 respectively. The yield of II was a little affected by solvent; under similar conditions II was obtained in 22% yield both in methanol and in tetrahydrofuran. Effects of primary, secondary, and tertiary amines on the quantum yield for the consumption of I and the chemical yield of II are summarized in the Table. The quantum yields seem to depend on the ionization potential of the amine used. It is, therefore, suggested that the reaction proceeds through electron-transfer.4)

The yields of II did not show such a tendency, probably because the Birch reduction or amination of the benzene ring occurred competitively.$^{5)}$ Similarly, irradiation of 1-(p-cyanophenyl)ethyl acetate(IV) in the presence of triethylamine gave p-cyanoethylbenzene(V) in 35% yield together with 2,3-di-(p-cyanophenyl)butane(VI, 9%).

Irradiation of 9-acetoxyfluorene(VII) under similar conditions gave fluorene(VIII), 9-methylfluorene(IX), and 9,9'-bifluorene(X). The yields of the products vary with the nature of amines, and they are also summarized in the Table. The major products were IX and X through radical reactions in the absence of amine,$^{1)}$ while in the presence of amines a Birch type reduction product(VIII) was the major. In this case the yields of the reduction and radical coupling products depend on the ionization potential of the amine used. Prolonged irradiation resulted in the Birch type reduction of aromatic rings with formation of dihydro- and tetrahydrofluorene.$^{5)}$

A reaction of I with triethylamine in the presence of MeOD(MeOD:MeCN=1:1) resulted in incorporation of 1D in the reduction product(II), which was demonstrated by mass spectrometry(d_0 44%, d_1 56%),$^{6)}$ suggesting the participation of a proton transfer step. Examination of the NMR spectra of the deuterated product revealed that the deuterium is located mainly(>90%) in the methyl group.

By these observations we conclude that the present reaction must be classified in the photo-induced Birch type reduction.

Table. Effects of amines

Amine	Φ(con. of I)	Yield, %*			
		II	VIII	IX	X
-	0.03	-	-	38	21
butylamine	0.3	7	19	18	5
diisopropylamine	0.6	42	23	16	6
triethylamine	1.2	26	47	5	-

* Caluculated from GC-MS analyses.

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6) It was confirmed by GC-MS analyses that under similar conditions no hydrogens of II were replaced by deuterium.

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