CHEMISTRY LETTERS, pp. 2015-2016, 1994.

Substituent Effects on the Photosolvolyses of 2-Chloropropiophenones in 2,2,2-Trifluoroethaol

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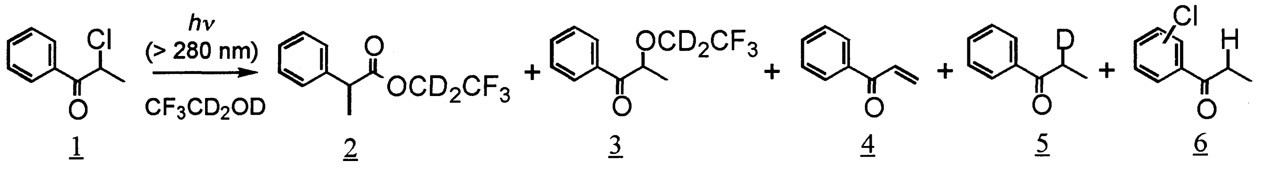
The substituent effects on the product distributions of the photosolvolyses of 2-chloropropiophenones in 2,2,2-trifluoroethanol were investigated. A π-electron-donating methoxy substituent at *p*- and *m*-position enhanced the heterolytic product of the nucleophilic substitution over that of phenyl-rearrangement.

2-Halopropiophenones are known to undergo photochemical loss of halogen atoms involving carbocationic as well as radical species.[1)] Although the carbocationic reactions including phenyl-rearrangement are of great interest on a synthetic viewpoint, the reaction mechanisms are not well understood. In this communication, we describe novel substituent effects on the photosolvolyses of 2-chloropropiophenones 1 in 2,2,2-trifluoroethanol (TFE).

A series of substituted 2-chloropropiophenones was obtained by Friedel-Crafts reactions of substituted benzenes or couplings of aryl magnesium bromides with 2-chloropropionyl chloride. Sample solutions were prepared by dissolving 0.2 μdm^3 of 2-chloropropiophenones into 0.75 mdm^3 of TFE-d$_3$ containing 1 μdm^3 of 2,6-lutidine. Each sample solution was placed in an NMR tube and was irradiated with a 500 W Xe lamp (USHIO XB-50101AA-A) through a pyrex filter at 20 °C. Photolysis products were analyzed by using an HPLC (JASCO PU-980, UV-970) and a ^{1}H-NMR (JEOL EX-270).[2)]

The HPLC and ^{1}H-NMR analyses revealed that the photosolvolysis of 1 in TFE-d$_3$ afforded five products without the thermal solvolysis of 1 as described in Scheme 1. The photosolvolysis products were classified into two types; one is C-Cl bond heterolysis products (2 - 3) and the other is bond homolysis ones (5 and 6). The elimination product (4), can possibly be generated through carbocationic or radical intermediates.[3)] According to the product distributions in Table 1, the photosolvolyses of all substituted derivatives showed excellent material balances of over 95%, and the photosolvolyses products were mainly C-Cl bond heterolysis ones (2 - 3); the *m*-OMe and *m*-Me derivatives resulted in the considerable amount of the C-Cl bond homolysis products (5 and 6). Anyway, it should be emphasized here that the present photosolvolysis of the substituted 1 in a highly polar solvent of TFE afforded the considerably larger amounts of heterolysis products than those obtained for the



Scheme 1.

Table 1. Substituent Dependencies of the Product Distributions (%) of the Photosolvolysis 1 in TFE-d_3 a)

Substituent	1	2	3	4	5 and 6	3/2
p-OMe	66.4	14.0	12.9	5.2	1.0	0.92
p-OMe-*m*-Cl	57.2	12.4	16.9	12.1	1.4	1.4
p-OMe-*m*-Br	39.7	16.2	20.3	20.9	2.4	1.3
p-OMe-*m*-CN	62.9	12.7	11.4	10.6	0.2	0.90
m-OMe b)	30.0	1.8	21.3	11.9	29.8	12
p-Me	67.3	22.6	7.3	2.8	0.0	0.32
m-Me	49.7	26.8	5.8	5.0	11.1	0.22
H	54.7	36.1	3.3	4.2	1.7	0.091
p-Cl	45.6	42.1	5.8	6.5	0.0	0.14
m-Cl	45.1	49.6	3.6	4.1	2.0	0.073
m-CN	51.2	27.6	1.8	12.7	3.3	0.065
m-CF_3	49.1	35.2	0.0	10.9	2.2	0.0

a) After 1 h irradiation, unless otherwise noted. b) After 0.5 h irradiation.

previous photosolvolyses of α-chloroketones.1,4)

Among the heterolysis products (2, and 3), the product ratio between a phenyl-rearrangement product and a nucleophilic substitution one (3/2) apparently suffered from the substituent effect of 1. The increase in the electron-donating ability of the substituent resulted in the increase in the 3/2 ratio, that is contrary to the substituent effects observed for the thermal acetolysis of 3-aryl-2-butyl brosylate.5)

It is also apparent from Table 1 that strong π-donating methoxy substituents facilitated the nucleophilic substitution pathway. The methoxy substituent at the *p*-position resulted in the almost same amount of 2 and 3, and notably, the introduction of electron withdrawing halogen atoms at the *m*-position into the parent *p*-OMe derivative appreciably exalted the 3/2 ratio. The predominance of the nucleophilic substitution by the π-donating substituents became drastic in the case of the *m*-OMe derivative; this novel substituent effect may be reflected to the *meta* electron transmission effect.6)

Thus, the characteristic substituent effects on the photosolvolysis of 1 were demonstrated by the fact that the π-donating substituent exalted the nucleophilic substitution pathway over phenyl-rearrangement one in the TFE solvent. At present, the origin of the novel effect of *m*-OMe substituent is not fully understood, and further investigations are now in progress.

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2) Photolysis products were identified by the comparison of HPLC and ^{1}H-NMR spectra with those of commercially available or synthesized authentic samples. The product distributions were determined by the ^{1}H-NMR signal intensities of $-CH-C\underline{H}_3$ (1, 2, or 3), $-CH=C\underline{H}_2$ (4), $-CH_2-C\underline{H}_3$ (5), and $-CHD-C\underline{H}_3$ (6).

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(Received August 2, 1994)