Photo-induced Reduction of Fluoren-9-ol and its Acetate by Aliphatic Amines

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Irradiation of fluoren-9-ol and its acetate in the presence of an aliphatic amine gave fluorene as the major product. The yield of fluorene depended upon the character of amine and increased in the order of primary < secondary < tertiary amines. By the use of deuteriated reagents ([²H₁]methanol and [²H₃]acetonitrile) it was revealed that the major process was electron transfer followed by proton transfer. A radical reaction also participated as a minor process. A possible reaction mechanism similar to the photo-induced Birch reduction was proposed.
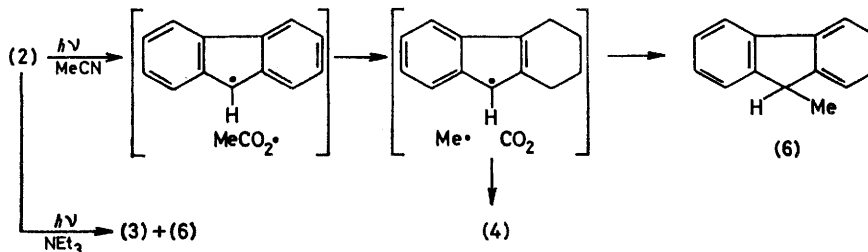
DURING the course of an investigation on charge-transfer-induced alkylation of dicyanobenzene–triethyl-amine systems, we found that the benzylic C–N bonds were cleaved through a photo-induced Birch-type reduction.[1,2] As a logical extension of this new reaction we have investigated the photo-induced reductive cleavage of benzylic C–O bonds.[3] We now report the photo-induced reduction of fluoren-9-ol (1) and its acetate (2) as a typical example.

RESULTS AND DISCUSSION

Upon irradiation in an acetonitrile solution with a low-pressure mercury arc (1) decomposed and fluorene (3) and 9,9'-bifluorene (4) were obtained in 2 and 7% yields, respectively.† However, when a similar reaction was
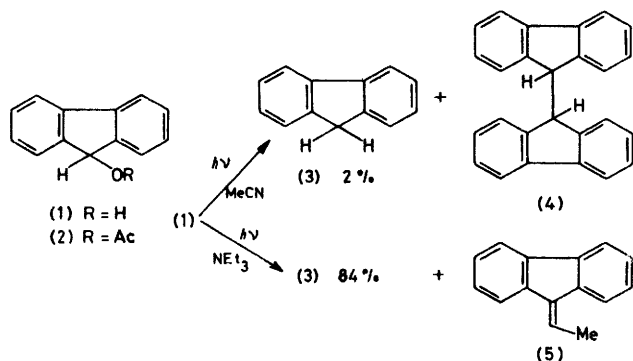
carried out in the presence of triethylamine (TEA), (3) was obtained as the major product in 84% yield together with a small amount of 9-ethylidenefluorene

Similarly, in the photolysis of (2), a radical reaction, decarboxylation, was the main process and 9-methyl-fluorene (6) along with (4) was obtained as the major product. Similar decarboxylation has been observed in the photolysis of various benzhydryl esters.[4] On the other hand, when a similar photolysis was carried out in the presence of an aliphatic amine, the yields of the products (3), (4), and (6) changed depending upon the ionization potential of the amine and the reduction product (3) became the major product. Table 1

Amine	Conversion (%)	Products (%)		
		(3)	(4)	(6)
None	56	<1	12	38
BuNH₂	80	19	5	18
Pr$^i_2$NH	86	23	6	16
TEA	81	36	<1	5
DMF	98	31	2	15

* Conversion and yields of the products were estimated by gas chromatography–mass spectrometry.

summarizes the result of the photochemical reduction by butylamine, di-isopropylamine, and triethylamine under the same conditions. Irradiation of (2) in dimethyl-formamide (DMF) also gave (3) as the major product.

In order to clarify the reaction processes leading to the reduction product (3), deuterium incorporation experiments were carried out. Irradiation of (1) (0.03M) in a mixture of [²H₁]methanol and acetonitrile (1 : 2) in the presence of TEA with a low pressure-mercury arc for 2 h gave (3) in 44% yield, for which mass spectra demon-

(5) (9%). When di-isopropylamine was used in place of triethylamine, a similar reaction gave (3) in 26% yield.

† A small amount of another product, probably (9-cyanomethyl)-fluorene, was also detected in the reaction mixture.

strated that the product incorporated 0.79 atoms of deuterium. The n.m.r. spectra also indicated that most of the deuterium incorporated was located at the 9-position because the relative intensity of the peaks in the aromatic region to the singlet peak at δ 3.82 [assigned

to the methylene group at the 9-position of (3)] was 8 to 1.28. On the other hand, when a mixture of (1) and TEA in [²H₃] acetonitrile was irradiated under similar conditions, the resulting (3) incorporated 0.27 atoms of deuterium. These results clearly indicate that a radical process as a minor path, as well as a proton-transfer step as the major process, participated in the reaction.

Similarly, in the presence of [²H₁]methanol, irradiation of (2) in the presence of TEA for 20 min gave deuteriated (3) which consisted of various deuteriated compounds; [²H₀] 21%, [²H₁] 71%, and [²H₂] 8%. Since the n.m.r. spectrum exhibited that the relative intensity of the aliphatic to the aromatic protons was 1.13 to 8, the incorporated deuterium was located mainly at the 9-position. When (2) was irradiated in [²H₃]acetonitrile in the presence of TEA, 0.18 atom of deuterium was found in the resulting (3) by gas chromatography–mass spectrometry. Those results are summarized in Table 2.

TABLE 2

Deuterium incorporation into (3) in the photolysis under various conditions ^{a}

Compound	Solvent	Irradiation time/h	Deuterium incorporation (%)		
			[²H₀]	[²H₁]	[²H₂]
(3)	MeCN–MeOD	2	74	22	4
(1)	MeCN–MeOD	2	20	79	1
(1)	[²H₃]MeCN	2	71	27	2
(2)	MeCN–MeOD	0.33	21	71	8
(2)	MeCN–MeOD	17	21	48	28 ^{b}
(2)	[²H₃]MeCN	2.5	81	18	1

^{a} TEA was used as the electron donor. ^{b} 3% of the [²H₃]-compound was also detected.

As shown in Table 2, prolonged irradiation of (3) in the presence of TEA in MeOD–MeCN caused H–D exchange and (3) was deuteriated to some extent, probably due to the Birch reduction of the aromatic ring.[4] Contribution of this exchange, however, to the photolysis of (1) or (2) is small, and does not affect the arguments in favour of participation of a proton-transfer step in the formation of (3).

The following reaction mechanism is similar to the photo-induced Birch reduction reported by Barltrop,[5] but somewhat modified to account for the results of the deuterium labelling experiments. Since the fluorescence of (1) and (2) underwent self-quenching, exciplex formation between the singlet excited state of (1) or (2) with amines could not be confirmed from the fluorescence quenching experiments. However, exciplexes between aromatic hydrocarbons and aliphatic amines are well known,[6] and it would be reasonable to assume that the initial step is electron transfer from the amine to the aromatics to form a radical cation–radical anion (a) pair. Proton transfer from the amine radical cation to the OR group or the aromatic moiety of (a), and then elimination of water or acetic acid from the protonated (a), gives an intermediate radical (b) and the amine radical (c), from which two reduction processes will proceed; one, as the major process, is electron transfer from (c) or the amine

to (b) to give a cation (e) and a carbanion (d) which then takes up a proton furnishing (3); the other minor path is uptake of hydrogen by (b), from the solvent or (c), affording (3). On the other hand, when radical coupling between (b) and (c) takes place, an addition product (f) is formed, from which elimination of diethylamine furnishes (6). This process corresponds to the major route in the case of dicyanobenzene–amine systems.[1]
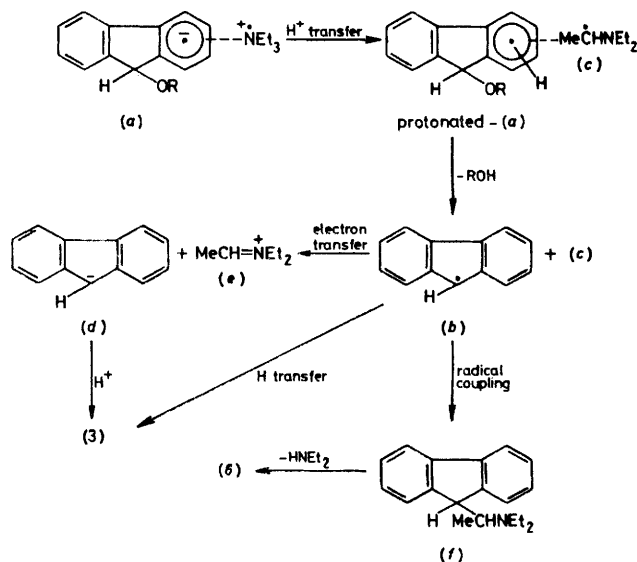
On the basis of those arguments we conclude that although Ullman et al. recently showed that intramolecular charge-transfer-induced photolysis of benzyl esters proceeds through a carbocation mechanism,[7] our results indicate that intermolecular charge-transfer-induced photolysis of fluoren-9-ol and its acetate proceeds through a carbanion mechanism similar to the Birch reduction of an aromatic ring.

EXPERIMENTAL

U.v. spectra were recorded with a Hitachi 124 spectrophotometer. I.r. spectra were recorded with a JASCO IRA-1 grating spectrophotometer. N.m.r. spectra were measured with a Hitachi R-20B or R-24 instrument. Mass spectra were recorded with a Hitachi RMU-6MG spectrometer. G.l.c. analyses were performed with a Shimadzu GC-3BF (DEGS 1.5% on Diasolid, 2-ft column) instrument with flame-ionization detection.

Fluoren-9-ol (1) was prepared from fluoren-9-one purchased from Tokyo Kasei Co. by treatment with NaBH₄ in the usual way. Acetylation with Ac₂O–pyridine in the usual way gave the starting specimen of fluoren-9-yl acetate (2).

[²H₁]Methanol and [²H₃]acetonitrile were purchased from Stohler Isotope Chemicals and their isotopic purities were both 99%.

Photolysis of (1).—(a) In acetonitrile. A solution of (1) (545 mg, 0.037 mol) in acetonitrile (80 ml) was irradiated with a low-pressure mercury arc (6 W) for 2 h under nitrogen. The solvent was removed and the residue was chromatographed on silica gel to give (3) (13 mg, 2%) and (4) (43 mg, 7%) whose structure was confirmed by comparison

of the n.m.r. spectrum with that reported.[8] A small amount (34 mg) of another product, which was not fully identified but was probably 9-cyanomethylfluorene from the following spectral data, $\nu_{max.}$ 2 240 cm^{-1}; δ(CCl$_4$) 2.79 (2 H, d, J 7 Hz), 4.17 (1 H, t, J 7 Hz), and 7.2—8.0 (8 H, m); m/z 205 (M^+, 50%), 178 (12), 166 (17), and 165 (100), was obtained. Starting material (196 mg, 36%) was also recovered.

(b) *In the presence of amines.* A mixture of (1) (539 mg, 0.038 mol) and TEA (2.45 g, 0.3 mol) in acetonitrile (80 ml) was irradiated with a low-pressure mercury arc (6 W) for 2 h under nitrogen. The solvent and the amine were removed *in vacuo* and the residue was chromatographed on silica gel to give (3) (251 mg, 84%), a trace amount of (4), and (5) (36 mg, 9%), whose structure was confirmed by comparison of the i.r. spectrum with that reported.[9] The starting material (157 mg, 29%) was recovered.

An acetonitrile solution containing (1) (112 mg, 0.04 mol) and di-isopropylamine (492 mg, 0.33 mol) was irradiated externally with a low-pressure mercury arc (10 W) by use of a merry-go-round apparatus for 2 h under nitrogen. The solvent and the amine were removed *in vacuo,* and the residue dissolved in CDCl$_3$ and analysed by the n.m.r. spectroscopy using durene as internal standard. The amounts of the starting material (52%) and (3) (12.5%) were estimated from the integral intensities of peaks at δ 5.58 and 3.82 respectively.

(c) *In the presence of* [^{2}H$_1$]*methanol.* A solution of (1) (87 mg, 0.03 mol) and TEA (490 mg, 0.33 mol) in a mixture of [^{2}H$_1$]methanol (5 ml) and acetonitrile (10 ml) was irradiated externally with a low-pressure mercury arc (10 W) under nitrogen for 2 h. After removal of the solvent and the amine, the residue was separated by preparative t.l.c. and (3) (14 mg, 44%) and the starting material (53 mg, 61%) were obtained. The mass spectrum of the resulting (3), m/z 166 (32%) and 167 (100%), indicated that 0.76 atoms of deuterium had been incorporated. The n.m.r. spectrum also indicated that the relative intensity of peaks in the aromatic and aliphatic regions was 8 to 1.26, which indicated that at least 0.74 atom of deuterium was located at the 9-position.

(d) *In* [^{2}H$_3$]*acetonitrile.* A solution of (1) (22 mg, 0.03 mol) and TEA (125 mg, 0.3 mol) in [^{2}H$_3$]acetonitrile (4 ml) was irradiated with a low-pressure mercury arc (6 W) for 2.5 h under nitrogen. The reaction mixture was analysed by gas chromatography–mass spectrometry. The mass spectrum of the fluorene obtained, m/z 166 (100), 167 (53) and 168 (8), indicated that the deuterium contents were [^{2}H$_0$] 71%, [^{2}H$_1$] 27%, and [^{2}H$_2$] 2%.

Photolysis of (2).—(a) *In the presence of amines.* Solutions each containing (2) (102 mg, 0.03 mol) and an amine [butylamine (333 mg, 0.3 mol), di-isopropylamine (323 mg, 0.3 mol) or TEA (461 mg, 0.31 mol] in acetonitrile (15 ml) were irradiated with a low-pressure mercury arc (10 W) by means of a merry-go-round apparatus for 15 h, and the resulting solutions were analysed by gas chromatography–mass spectrometry. The results are summarized in Table 1.

In another photolysis, solutions of (2) (0.03 mol) in acetonitrile, with and without TEA (0.3 mol), were irradiated by use of the same apparatus and the products were analysed by gas chromatography–mass spectrometry after irradiation for 0.5, 3, and 16 h, respectively. The results are summarized in Table 3, which indicates that the yields of products are sensitive to the reaction conditions. From the reaction mixture, (6) was isolated by gas chromatography

and the structure was confirmed by comparison of the mass spectrum with that reported,[10] and the n.m.r. spectrum; δ 1.47 (3 H, d, J 7 Hz), 3.90 (1 H, q, J 7 Hz), and 7.0—7.8 (8 H, m).

TABLE 3

Reaction times and yields of the products

	In MeCN			With TEA		
Irradiation time/h	Conversion (%)	(3) (%)	(6) (%)	Conversion (%)	(3) (%)	(6) (%)
0.5	18		4	22	1	4
3	27		18	32	66	21
16	74		25	92	52	5

(b) *In the presence of* [^{2}H$_1$]*methanol.* A solution of (2) (526 mg, 0.03 mol) and TEA (4.6 g, 0.3 mol) in a mixture of acetonitrile (135 ml) and [^{2}H$_1$]methanol (10 ml) was irradiated with a low-pressure mercury arc (6 W) for 20 min. The solvent and the amine were removed and the resulting (3) was separated by preparative t.l.c. and purified by preparative gas chromatography. The mass spectrum exhibited peaks at m/z 166 (28%), 167 (100), 168 (26), and 169 (3), which indicated that the deuterium incorporation was [^{2}H$_0$] 21%, [^{2}H$_1$] 71%, and [^{2}H$_2$] 8%. The n.m.r. spectrum showed that the relative intensity of the aromatic and aliphatic protons was 8 to 1.13.

(c) *In the presence of* [^{2}H$_3$]*acetonitrile.* A solution of (2) (27 mg, 0.03 mol) and TEA (127 mg, 0.3 mol) in [^{2}H$_3$]-acetonitrile (4 ml) was irradiated with a low-pressure mercury arc (6 W) for 2.5 h. The resulting (3) was analysed by gas chromatography–mass spectrometry. The mass spectrum exhibited peaks at m/z 166 (100%), 167 (37), and 168 (5), which indicated that the deuterium incorporation was [^{2}H$_0$] 81% and [^{2}H$_1$] 18%.

(d) *In DMF.* A solution of (2) (101 mg, 0.03 mol) in DMF (15 ml) was irradiated by means of a merry-go-round apparatus with a low-pressure mercury arc (10 W) for 21 h. The solvent was removed *in vacuo* and the residue was analysed by gas chromatography–mass spectrometry and n.m.r. spectroscopy, using durene as internal standard. Peaks of δ 1.47 (3 H, d), 3.82 (2 H, s), 4.85 (2 H, s) and 6.56 (1 H, s) correspond to (6), (3), (4), and (2), respectively. The results are in Table 1.

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