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The Reactivity of Radical Anions Generated by Electron-transfer Reaction of Allyl Acetates

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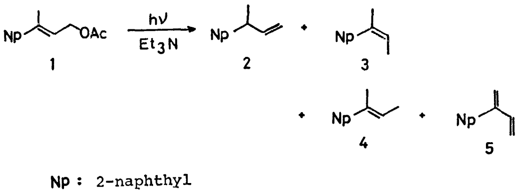
Synopsis. Photoinduced electron-transfer reactions of 3-(2-naphthyl)-2-butenyl acetate gave the reduced products, while the electrochemical and Birch reduction of the acetate furnished (*E*)-2-(2-naphthyl)-2-butene as the sole product. One-electron reduction was suggested by mechanistic studies of the photoreaction on the basis of deuterium incorporation into the products. A similar mechanism can operate in the photoreduction of cinnamyl acetate.

For ten years many photochemists have focused[1] their interest on photoinduced electron-transfer reactions. The reactions involving a system which consists of a pair of donor and acceptor molecules are triggered by irradiation. Now we report the reactivity of the anion radical produced by electron-transfer in the photoinduced reaction of an allyl acetate.[2]

Results and Discussion

Irradiation upon acetonitrile solution of 3-(2-naphthyl)-2-butenyl acetate (**1**) in the presence of triethylamine[3] gave 3-(2-naphthyl)-1-butene (**2**), (*Z*)- and (*E*)-2-(2-naphthyl)-2-butene (**3** and **4** respectively), and 2-(2-naphthyl)-1,3-butadiene (**5**) as hydrocarbon fractions in 14, 2.6, 7.0, and 3.0% yields respectively. When diethylamine and butylamine, which have higher ionization potentials than that of triethylamine, were used as an electron donor, the yields of **2**, **3**, and **4** decreased. The formation of **5**, however, is independent of the ionization potential of the donor, as shown in Table 1. Results which suggest that the photoreaction is proceeding *via* charge transfer in the excited state were also observed in fluorescence quenching of **1** with aliphatic amines, as shown in Table 2.



Scheme 1.

When a mixture of methanol–acetonitrile (1:1) was used instead of acetonitrile as a solvent, a photosolvolytic reaction took place to give 3-methoxy-3-(2-naphthyl)-1-butene (**6**) in 44% yield as a major product.[4] The hydrocarbon products were also isolated. Deuterium incorporation by use of methanol-*d* in place of methanol was observed in the formation of **3** and **4**, while the use of methan-d_3-ol contributed little to the incorporation, as shown in Table 3.

The Birch reduction of **1** in liquid ammonia gave **4** in 49% yield, together with a small amount of dihydro- and tetrahydronaphthalenes. In a reduction similar to the Birch reaction, **1** was reduced on the anode. When an acetonitrile solution of **1** with tetrabutylammonium iodide was electrolyzed in 2.1 F/mol, the product **4** was isolated in 73% yield.

Table 1. Product yields[a)]

Amines	2	3	4	5
Triethylamine	14	2.6	7.0	3.0
Diethylamine	3.3	0.2	1.7	8.6
Butylamine	—	—	—	4.6

a) Yields were measured by GC analyses based on the amount of **1** used.

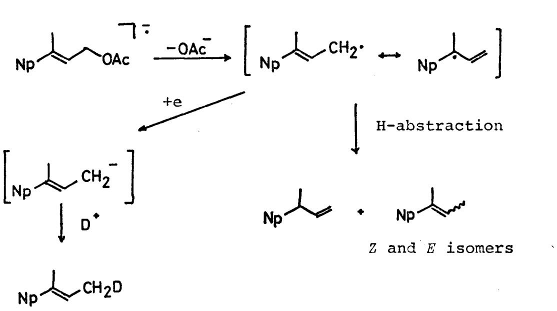
Table 2. Fluorescence quenching ($k_q\tau$/mol^{-1} dm^3) of **1** with aliphatic amines

Solvents	Amines		
	Triethylamine	Diethylamine	Butylamine
Acetonitrile	103	29	3
Cyclohexane	57	22	0

Table 3. Deuterium incorporation for the photoreduction of **1**[a)]

Deuterated solvents	Photoproducts (% of the deuterated)			
	2	3	4	5
CH_3OD	11	24	24	—
CD_3OH	—	—	—	—

a) Experimental errors are within ±3%.



Scheme 2.

Among three kinds of reactions, the photochemical, the Birch, and the electrochemical reduction,[5] the products for the anion radical generated photochemically are different from that of the others. In the photoinduced electron-transfer reaction, the radical which results from the ionic dissociation of the anion radical can hydrogen-abstract from triethylamine to furnish reduction products. On the other hand, the radical generated from the ionic dissociation of the anion radical can be reduced further in the Birch or the electrochemical reaction, resulting in the formation of an anion intermediate which subsequently reacts with the proton added.

In conclusion, the following schematic mechanism is proposed to elucidate the reactivity of the intermediate, as shown in Scheme 2.

According to the reactivity of the radical generated from a photochemical electron-transfer reaction, it is understandable that the photoreaction of cinnamyl acetate with aliphatic amines gave not only 1-phenylpropene (16%) but also allylbenzene (22%).

Experimental

Melting points were obtained with a hot-stage apparatus and are uncorrected. IR spectra were determined on a JASCO IRA-1 spectrometer. NMR spectra were detected by using a Hitachi R-20B 60-MHz instrument. GC-MS analyses were carried out on a Hitachi RMU-6MG instrument. A Pyrex column (0.3 cm i.d. × 1.2 m) packed with Diasolid ZF 80—100 mesh (Nippon Chromato Kogyo Co.) was used for separation. Quantitative and preparative GC were performed on a Shimadzu GC-3BF and on a Varian 90 P-3 instrument, respectively. Fluorescence spectra were recorded on a Hitachi 204 spectrometer.

*Preparation of 3-(2-Naphthyl)-2-butenyl Acetate (**1**).* To a suspension of NaH (5.5 g, 50% oil dispersion) in dry 1,2-dimethoxyethane (70 cm^3, DME) was added a solution of triethyl phosphonoacetate (17.8 g) in dry DME (50 cm^3) at 0 °C under N_2 gas. Then a solution of 2-acetylnaphthlene (10.3 g) in anhydrous DME (70 cm^3) was added dropwise at 0 °C under stirring and the mixture was stirred continuously at room temp for 8 h. After extraction with diethyl ether, the obtained material was chromatographed on a short-column (PF_{254} Merck/10% ether in hexane), and the pure *E*-isomer (7.0 g) was obtained in 48% yield. Mp 45.3—45.7 °C. MS *m/z* 240(M$^+$), ^{1}H-NMR (CCl_4) δ=1.26 (3H, t, *J*=8 Hz), 2.63(3H, d, *J*=1.5 Hz), 4.17(2H, q, *J*=8 Hz), 6.17(1H, q, *J*=1.5 Hz), and 7.2—7.8(7H, m). The *Z*-isomer was also isolated by the chromatography, of which NMR spectrum showed peaks at δ=0.93(3H, t, *J*=8 Hz), 2.16(3H, d, *J*=1.5 Hz), 3.88(2H, q, *J*=8 Hz), 5.86 (1H, q, *J*=1.5 Hz), and 7.1—7.8(7H, m).

To a suspension of $LiAlH_4$ (3.1 g) in anhydrous ether (70 cm^3) was added an etheral solution of the *E*-isomer (7.0 g in 90 cm^3) at room temp under N_2 atmosphere. After stirring for 5 h, the ether extraction afforded crude crystals which were recrystallized from benzene–hexane (1:1). The recrystallized alcohol weighed 4.3 g (74%), mp 85.8—86.5 °C. MS *m/z* 198(100, M$^+$), 180(66, M$-H_2O$), 179(48), 178(21), 165(62). ^{1}H-NMR δ=1.74(1H, s, OH), 2.13(3H, d, *J*=1.5 Hz), 4.40(2H, d, *J*=7 Hz), 6.11(1H, tq, *J*=7 and 1.5 Hz), and 7.3—7.9(7H, m).

To a solution of the alcohol (2.0 g) in anhydrous ether (60 cm^3) was added acetyl chloride (3.0 cm^3) and then triethylamine (6.0 cm^3) at 0 °C. After 90 min, the ether extracted fraction was chromatographed on silica gel (PF_{254}/20% ether in hexane). The obtained crystals weighed 2.3 g(95%); their mp was in the range of 47.8—48.5 °C. MS 241(18), 240(100, M$^+$), 198(38), 197(41), 183(45), 180(55), 179(34), 169(25), and 165(53). Found: *m/z* 240.1152. Calcd for $C_{16}H_{16}O_2$: M, 240.1150. ^{1}H-NMR δ=2.0(3H, s), 2.18 (3H, s), 4.75(2H, d, *J*=8 Hz), 5.96(1H, t, *J*=8 Hz), and 7.2—7.8(7H, m). IR(KBr) 1740 cm^{-1}. UV(CH_3CN) 243 (44000), 274(10000), 284(12000), 295(8900) nm.

*Preparative Photoreaction of **1** with Triethylamine.* A 0.02 M acetonitrile solution (200 cm^3) of **1** with triethylamine (6.0 cm^3) was irradiated with a high-pressure mercury arc for 1.5 h at room temp under N_2 bubbling. After removal of low-boiling point materials, the residue was chromatographed on a precolumn of silica gel (Wako gel Q-50/10% ether in hexane) and rechromatographed on silica gel PF_{254}/hexane). The developed fraction was collected and injected in a GC. Four products showed the following chromatograms: retention time: **2**, 14′; **3**, 12′; **4**, 25′ and **5**, 18′. **2**: MS *m/z* 183(12), 182(69, M$^+$), 181(15), 168(14), 167(100), 166(13), 165(15), and 152(11). Found: *m/z* 182.1071. Calcd for $C_{14}H_{14}$: M, 182.1094. IR 1640 cm^{-1}. ^{1}H-NMR δ=1.40(3H, d, *J*=7 Hz, CH_3), 3.57(1H, qdt, *J*=7, 6, and 2 Hz), 5.05(2H, dd, *J*=17 and 2 Hz and dd, *J*=10 and 2 Hz), 6.05(1H, ddd, *J*=17, 10 and 6 Hz), and 7.4(7H, m). **3**: MS *m/z* 183(22), 182(100, M$^+$), 181(26), 168(17) 167(70), 166(13), and 165(17). ^{1}H-NMR δ=1.65(3H, d, *J*=7 Hz), 2.09(3H, s), 5.75(1H, q, *J*=7 Hz), and 7.5(7H, m). **4**: MS *m/z* 183(20), 182(100, M$^+$), 181(26), 168(16), 167(84), 166(16) and 165(20). Found: *m/z* 182.1079. Calcd for $C_{14}H_{14}$: M, 182.1094. ^{1}H-NMR 1.82(3H, d, *J*=7 Hz), 2.09(3H, s), 5.92(1H, q, *J*=7 Hz), and 7.5(7H, m). **5**: MS *m/z* 181(18) 180(100, M$^+$), 179(77), 178(32), and 165 (41). Found: *m/z* 180.0943. Calcd for $C_{14}H_{12}$: M, 180.0939. ^{1}H-NMR δ=5.2(2H, dd, *J*=17 and 9 Hz), 5.3 (2H, s), 6.7(1H, dd, *J*=17 and 9 Hz), and 7.5(7H, m).

*Photoreaction of **1** with Methanol.* A mixture of methanol–acetonitrile (1:1) was used (80 cm^3) as a solvent for irradiation of **1** (400 mg) in the presence of triethylamine (2.4 cm^3) with a 6 W-low pressure mercury arc for 1.5 h. TLC separation (PF_{254}/10% ether in hexane) gave **2**, **3**, **4**, **5**, and **6** in 20, 1.6, 14, 10, and 44% yields respectively. **6**: MS *m/z* 212(52), 197(43), 182(7), 181(45), 180(100), 179(73), 178(16), 166(18), and 165(59). Found: *m/z* 212.1212. Calcd for $C_{15}H_{16}O$: 212.1200. ^{1}H-NMR δ=1.60(3H, s), 3.12(3H, s), 5.15(1H, dd, *J*=10 and 2 Hz), 5.20(1H, dd, *J*=18 and 2 Hz), 6.00(1H, dd, *J*=18 and 10 Hz), and 7.5(7H, m).

*Electrolytic Reduction of **1**.* An acetonitrile solution (40 cm^3) of **1** (114 mg) with tetrabutylammonium iodide (1.48 g) as a supporting electrolyte was electrolyzed (3.3 V, Pt) under N_2 gas for 1 h. The etheral extraction and TLC separation gave **4** (63 mg).

*Birch Reduction of **1** in Liquid Ammonia.* At −78 °C, an acetonitrile solution (2.0 cm^3) of **1** (105 mg) was dropwise added to a liquid ammonia solution (100 cm^3) of sodium (762 mg). After adding methanol (0.5 cm^3) the mixture was allowed to warm up. The etheral extraction and then TLC separation gave **4** in 49% yield.

Photochemical Reaction of Cinnamyl Acetate with Triethylamine. An acetonitrile solution (350 cm^3) of cinnamyl acetate (1.89 g) with triethylamine (10.9 g) was irradiated with a 12-W low pressure mercury arc under N_2 gas for 2.5 h. The reaction mixture was short-path chromatographed on silica gel with ether. The obtained mixture (190 mg) showed two peaks in GC (10% DEGS on Diasolid 80—100 mesh). Each fraction was preparatively isolated. The first fraction was identified with allylbenzene and the last was 1-phenylpropene by comparison with the spectral data (^{1}H-NMR, IR, and UV). Quantum yields for the formation of the products were 0.22 (allylbenzene) and 0.17 (1-phenylpropene).

References

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