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Reactions of syn- and anti-Benzylideneaniline Radical Anions

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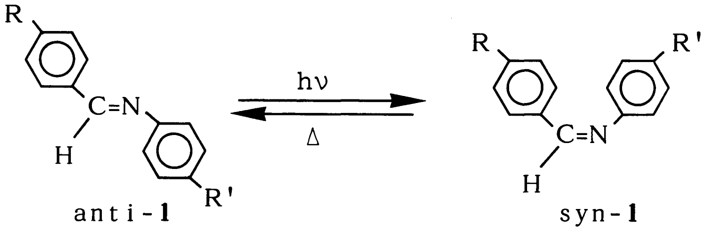
Reactions of a benzylideneaniline radical anion have been studied by spectral and product analyses, in which successive irradiation of uv-light and ionizing radiation at low temperature have been applied to the production of the unstable syn-radical anions.

Imine is a very useful intermediate in the creation of valuable compounds. Even though a radical anion of imine is an important intermediate in electrochemical and photochemical reactions, it has not been studied by time-resolved spectroscopic methods. In this paper, we report one electron reduction of benzylideneaniline and its derivatives (**1**) studied by the combination use of photochemical and radiation chemical methods, which enables to produce very unstable syn-**1** radical anions.



anti-**1** syn-**1**

	R	R'
1a;	H	H
1b;	MeO	H
1c;	Me	H
1d;	CN	H
1e;	H	Me
1f;	H	MeO
1g;	H	CN

Photoirradiation of 0.5 mmol dm^{-3} anti-**1a** in a 77 K MTHF (2-methyltetrahydrofuran) matrix by use of a 150 W Xe-lamp for 5 minutes resulted in a blue shift of the UV absorption maximum of **1a** from 325 nm to 250 nm, and upon melting of the matrix the original spectrum was recovered. Other derivatives also gave a similar spectral change as shown in Table 1. This spectral change was explained in terms of a photoinduced isomerization of anti-**1** to syn-**1** and a thermal inverse reaction.$^{1)}$

Radical anion of anti-**1** was produced by γ-ray irradiation of 0.5 mmol dm^{-3} anti-**1** in a 77 K MTHF matrix.$^{2)}$ An absorption maximum of **1a**$^{\cdot-}$ was observed at 455 nm (Fig. 1; curve A) and agreed with that reported by Shida et al.$^{3)}$ On the other hand, γ-ray irradiation of syn-**1a** isolated in a 77 K MTHF matrix by photoirradiation provided a different absorption spectrum. After γ-ray irradiation at 77 K, it has an absorption maximum at 455 nm with a shoulder around 485 nm (Fig. 1; curve B). Slight annealing of the matrix induced rapid decrease of the band at 485 nm followed by a simultaneous rise of the band at 455 nm with an isosbestic point at 475 nm (Fig. 1; curve C). A newly observed absorption maximum around 485 nm was assigned to syn-**1a** radical anion. Other derivatives also gave absorption spectra of syn-radical anions and the absorption maxima are summarized in Table 1. A pulse radiolytic measurement was carried out by use of photoproduced syn-**1g** at 120 K, in which a transient absorption of syn-**1g** radical anion and its time dependent isomerization (k_i=3.5x10^6 s^{-1}) were clearly observed (Fig. 2). From these results, it is clear that syn-**1** radical anion is also very unstable and rapidly isomerizes to anti-**1** radical anion.

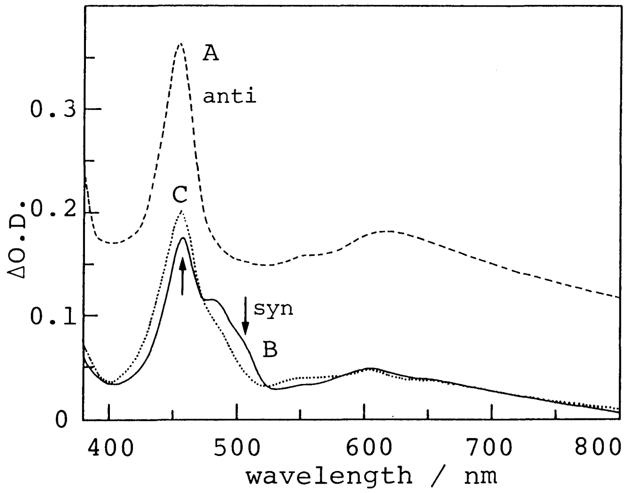


Fig. 1. An absorption spectrum observed upon γ-ray irradiation of 0.5 mmol dm^{-3} **1a** in MTHF at 77 K (curve-A); absorption spectra observed upon photoirradiation and successive γ-ray irradiation of 0.5 mmol dm^{-3} **1a** in MTHF at 77 K (curve-B) and after annealing to 83 K (curve-C).

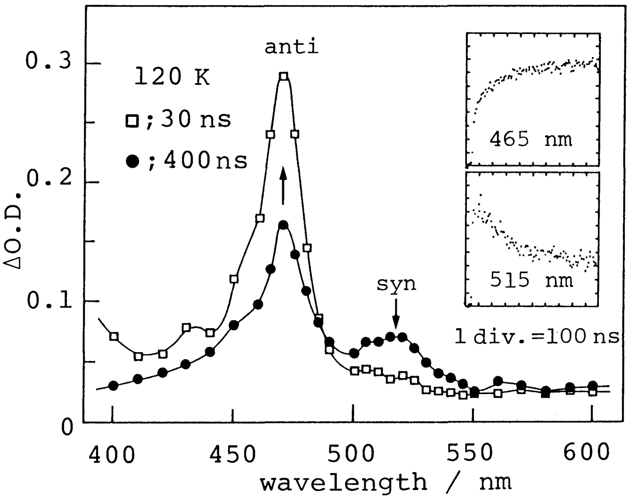


Fig. 2. Transient absorption spectra observed upon electron beam (28 MeV, 8 ns) irradiation of 5 mmol dm^{-3} **1g** in MTHF which had been photoirradiated at 120 K by use of a 450 W Xe lamp through a H_2O filter; insets show time dependent profiles at 465 nm and 515 nm.

Table 1. Absorption Maxima for Benzilideneanilines (**1**) and Their Radical Anions$^{a)}$

Substrate	R	R'	λmax/nm neutral anti	syn$^{c)}$	radical anion$^{b)}$ anti	syn$^{d)}$
1a	H	H	325	250	455	485, 510
1b	MeO	H	295	275	450	480 (broad)
1c	Me	H	280	260	455	490 (broad)
1d	CN	H	295	265	490	530 (broad)
1e	H	MeO	330	250	455	500
1f	H	Me	330	250	455	500
1g	H	CN	295	275	470	520

a) Measurement conditions; [**1**]=0.5 mmol dm^{-3}, MTHF, 77 K.
b) γ-Ray irradiation was carried out at 77 K by a ^{60}Co source for 15 min.
c) The syn isomers were produced by photoirradiation of the anti isomers at 77 K by a 150 W Xe lamp through a H_2O filter for 5 min.
d) The syn-radical anions were produced by successive γ-ray irradiation after the photoirradiation.

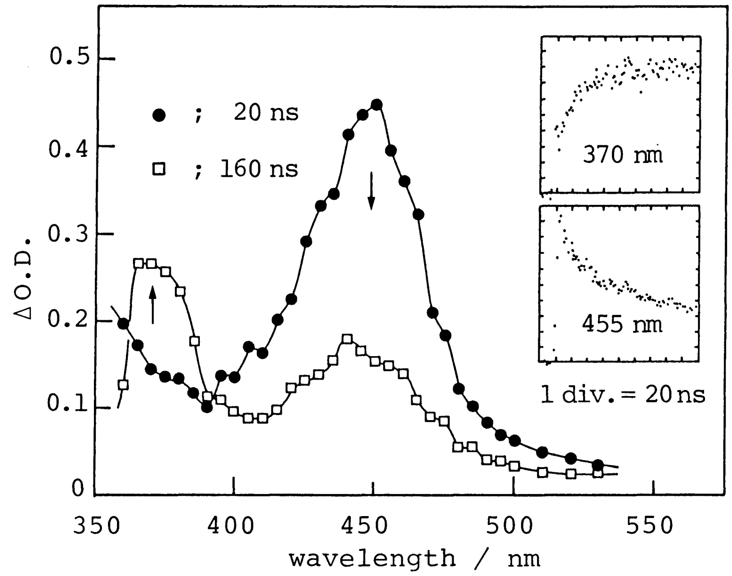


Fig. 3. Transient absorption spectra observed upon electron beam (28 MeV, 8 ns) irradiation of 5 mmol dm^{-3} anti-**1a** in THF at room temperature; insets show time dependent profiles at 370 nm and 455 nm.

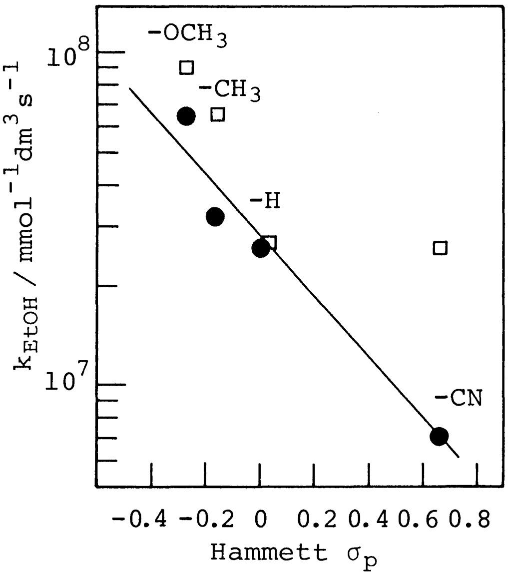
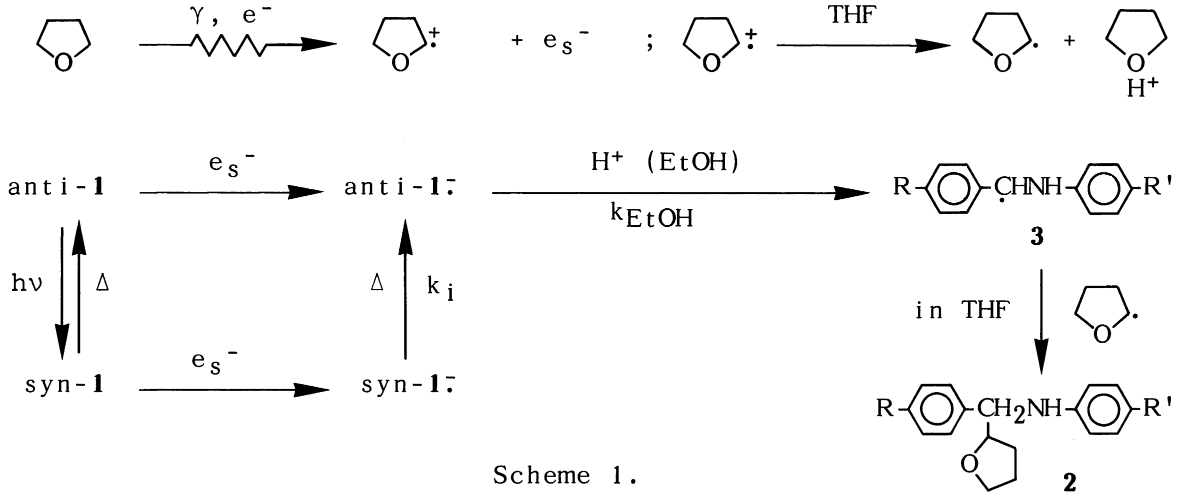


Fig. 4. Relationships between k_{EtOH}'s observed for a series of anti-**1** (4-substituted; □, 4'-substituted; ●) and Hammett σ_p values for the substituents.

Reactions of anti-**1** radical anions were studied by pulse radiolysis. Fig. 3 shows transient absorption spectra obtained by pulse radiolysis of 5 mmol dm^{-3} anti-**1a** in THF at room temperature. The initially observed absorption band with a maximum at 455 nm is the radical anion of anti-**1a**, decrease of which leads to another absorption band with a maximum at 370 nm. In EtOH, this absorption band at 370 nm was observed even immediately after pulse irradiation (<20 ns). Rapid protonation of anti-**1a** radical anion was supposed to induce the formation of a neutral radical, which was confirmed by kinetic measurements. Pseud-first-order decay rates of the radical anion were observed in a series of THF-EtOH mixture solvents, which depended on the concentration of EtOH; the second-order plot gave a straight line, from which a reaction rate constant of the radical anion and EtOH, k_{EtOH} was obtained. The rate constant strongly depends on the substituent. A Hammett plot of k_{EtOH} against σ_p of R' gives almost linear relationship with a negative slope as shown in Fig. 4. This result suggests that a protonation site of the radical anion is the N atom, the electron density of which depends on polar effect of R'. A MNDOC calculation also supports this estimation.

In order to identify the structure of the radical, a product analysis was carried out. γ-Ray irradiation of anti-**1a** in THF at room temperature afforded a THF adduct, N-[(2-tetrahydrofuranyl)-benzyl]-aniline (**2a**) in a yield of 47% (conv. 57%, G=2.5$^{4)}$),$^{5)}$ which is supposed to be derived from the benzyl-type radical (**3a**).$^{6)}$ In THF, the proton source is supposed to be a radical cation of THF. A total reaction scheme of the syn- and anti-radical anions is summarized as follows.



Scheme 1.

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2) Benzylideneaniline (**1a**) was commercially available and purified by column chromatography. Other derivatives were synthesized by coupling of respective aniline and benzaldehyde by a reported procedure.[7] MTHF was stirred with NaOH pelets for removing stabilizer and distilled over $LiAlH_4$. For spectral measurement, a sample solution was degassed by freez-pump-thaw cycles and sealed in a Suprasil cell. Steady state γ-ray irradiation was carried out with a ^{60}Co source (2.6×10^{14} Bq, dose rate 6.3×10^{2} Gy/h). Absorption spectra of low temperature matrices were measured with a multichannel spectrophotometer (Otsuka Electronix, MCPD-1100) and a quartz Dewar vessel. Pulse radiolysis was carried out by electron beam (28 MeV, 8 ns) from ISIR linac. Low temperature irradiation was carried out in a cryostat (Oxford D-1704).

3) T. Shida, "Electronic Absorption Spectra of Radical Ions," Elsevier, New York (1988), p. 192.

4) G value is a molecular amount at energy absorption of 100 eV.

5) **2a**; colorless oil; MS m/e (relative intensity); 253 (M^+,7), 182 (100), 104 (11), 91 (3), 77 (15), 51 (3); ^1H NMR ($CDCl_3$) δ=1.7-1.9 (m, 4H), 3.90 (ddd, 1H, J=7.0 Hz), 4.05 (ddd, 1H, J=6.3 Hz, J=7.0 Hz), 4.23 (ddd, 1H, J=3.9 Hz), 4,42 (d, J=3.9 Hz, 1H), 6.5-7.5 (m, 10H); ^{13}C NMR ($CDCl_3$) δ=25.45, 25.63, 25.78 (t, $-\underline{C}H_2-$), 27.18, 28.73 (t, $-\underline{C}H_2-$), 60.72, 61.96, 62.02 (d, Ph-$\underline{C}$H), 68.50, 68.68 (t, $-\underline{C}H_2-O-$), 81.97, 82.93 (d, $-\underline{C}H-O$), 113.77-114.08 (d, Ph), 117.34-117.46 (d, Ph), 127.19-127.68 (d, Ph), 127.92-129.18 (d, Ph), 139.99 (s, Ph), 141.62 (s, Ph), 147.34 (s, Ph), 147.34 (s, Ph), 147.77 (s, Ph).

6) G. Porter and E. Strachan, Trans. Faraday Soc., **54**, 1595 (1958).

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