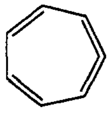
benzocyclobutadiene. Indeed **11** has been suggested as an intermediate in the room temperature conversion of octa-3,5-diene-1,7-diyne to benzocyclobutadiene and, ultimately, its dimers.[19] It seems very likely to us that **1**, **11**, and perhaps dicarbene **12** will all be accessible under our conditions.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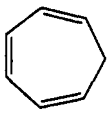
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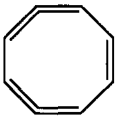
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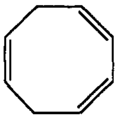
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Registry No. 2, 6926-49-4.

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Photoinduced Electron-Transfer Fragmentation of Amino Alcohols: Stereochemical Effects and Connectivity between One- and Two-Electron Events

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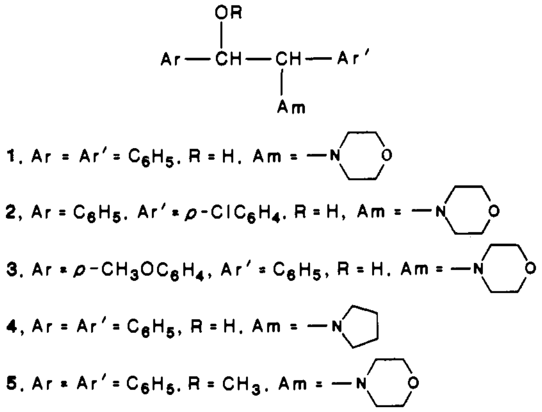
Reactions of radical ions or radical ion pairs formed by photoinduced electron transfer are of considerable current interest.[1-15] Among the possible fates of ions formed by heteroatom oxidations is C–C bond fragmentation.[16-21] Recently we reported that certain tertiary amines suffer C–C bond cleavage when oxidized by acceptors excited by visible light.[22] For amino ketones this reaction was indicated to proceed via homolytic cleavage of the bond between the carbonyl and C_α of the amine to efficiently yield free radicals. Herein we report studies with several β-amino alcohols (**1–4**) which demonstrate that photoredox-induced cleavage of the C_α–C_β bond can be a clean and efficient reaction having close analogy to two-electron solvolytic fragmentations.[23,24] Noteworthy features of the amino alcohol fragmentation are the high chemical specificity of the cleavage, the connectivity between one- and two-electron bond reorganization, and a remarkably large stereochemical effect on reactivity.



1, Ar = Ar′ = C_6H_5, R = H, Am = —N

2, Ar = C_6H_5, Ar′ = p-ClC_6H_4, R = H, Am = —N

3, Ar = p-$CH_3OC_6H_4$, Ar′ = C_6H_5, R = H, Am = —N

4, Ar = Ar′ = C_6H_5, R = H, Am = —N

5, Ar = Ar′ = C_6H_5, R = CH_3, Am = —N

The amino alcohols used in this study were synthesized either by reaction of a secondary amine with the appropriate epoxide (*threo*- and *erythro*-**1** and **4**) or by a sequence of benzoin condensation and chlorination followed by amine substitution and reduction[25] to yield **2** and **3**. The erythro ether **5** was prepared by reaction of *erythro*-**1** with sodium hydride and methyl iodide. The visible light-absorbing electron acceptors, thioindigo (TI) and $Ru[5,5'\text{-}CO_2Et(bpy)]_3(PF_6)_2$ (RuL_3^{2+}), were prepared and purified as reported elsewhere;[26-28] photolyses were carried out with either a 200-W mercury lamp or a tungsten lamp with filters to restrict the exciting light to wavelengths (400–500 nm) absorbed only by the acceptors. Solutions containing the amino alcohol, electron acceptor, and solvent (benzene, methylene chloride, acetonitrile, or acetonitrile–water) were vacuum degassed by freeze–pump–thaw cycles; product analyses of irradiated samples were by HPLC (for amino alcohols and their photolysis products), UV–vis absorption spectroscopy (TI, RuL_3^{2+}, and their reduction products), and gas chromatography. Infrared spectra were obtained on a FT-IR Matson Series 100 spectrometer. NMR studies of photoreacting solutions were carried out on vacuum degassed samples in CD_3CN or C_6D_6 to which a small amount of D_2O (3%) had been added; spectra were measured on a GE-NMR QE-300 spectrometer.

A detailed study of the reaction of **1–3** with TI as the light-absorbing electron acceptor shows an especially clear example of a net two-electron redox fragmentation process occurring according to eq 1. When **1** and TI are irradiated in a NMR tube new proton signals due to the aldehyde hydrogen of benzaldehyde and α_{C-H} of morpholine (ratio 1:2) appear as the photolysis proceeds. When TI is irradiated with **2** or **3**, proton signals for benzaldehyde, Ar′CHO, and the C–H of morpholine appear in the ratio 1:1:4; in all cases no signals due to *N*-benzylmorpholine or other products from the amine can be detected.[29] Irradiation of either RuL_3^{2+} or TI with **2** and **3** in acetonitrile–water or benzene–water leads to the two aldehydes (eq 1) in equal amounts as detected by HPLC.[30] The yields of benzaldehyde from **1** and conversion of

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[29] *N*-Benzylmorpholine exhibits proton signals which are clearly detectable under the reaction conditions.
[30] Although a thorough investigation of solvent effects has not yet been completed, preliminary results indicate that increase in solvent polarity is accompanied by a decrease in reactivity and an increase in diastereomeric selectivity.

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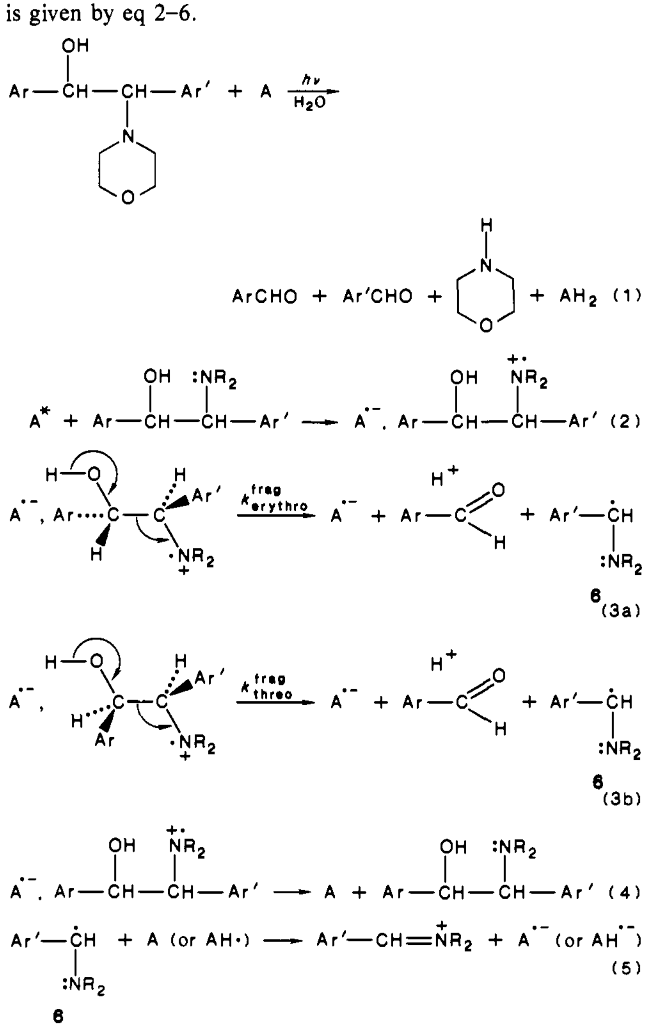
Table I. Reactivity of Stereoisomers of **1** and **4** with Electron Acceptors

tertiary amine isomer	overall reactivity[a]		k_q[c], $M^{-1}\ s^{-1}$	k_q(erythro)/ k_q(threo)	OH stretching ν, cm^{-1}[d]	reactvity after correction for differential quenching[e]			
	$\phi_{Ru^{2+}}$[b]	ϕ_{TI}[b]				ϕ_{TI}	$ArCHO^{rel}$	erythro/threo reactivity	
erythro-**1**	0.10	0.03	2.9×10^9	2.1	3428.6	0.04	1.2	3.3[f]	4.0[g]
threo-**1**	0.02	0.005	1.4×10^9		3308.3	0.01	0.3		
erythro-**4**	0.14	0.04	9.1×10^9	1.7	3436.4	0.17	3.4	4.2[f]	3.1[g]
threo-**4**	0.03	0.006	5.3×10^{-9}		3244.9	0.04	1.1		
5		0.006	2.5×10^9			0.002	0		

[a] Using same concentrations of different isomers (0.1 M). The concentrations of $Ru(5,5'\text{-}COOEt)_3(PF_6)_2$ and TI are 1×10^{-4} M. All the samples are vacuum degassed. For both cases, the reactions were monitored by measuring the $Ru(5,5'\text{-}COOEt)_3(PF_6)_2$ and TI absorbance with a HP-8451 spectrometer at the absorbance maximum, i.e., 502 and 544 nm, respectively. Plots of absorbance (λ_{max}) vs. time provided straight lines for less than 10% conversion; the slopes of the plots are proportional to the quantum yields for the reaction after correction for incomplete light absorption. Quantum yields were determined relative to a secondary actinometer which was irradiated in parallel with the solutions. [b] $\phi_{Ru^{2+}}$: Quantum efficiency for reductio nof $RuL_3^{2+} \rightarrow RuL_3^{+}$ in purified CH_3CN solvent. ϕ_{TI}: quantum efficiency for reduction of TI → TIH_2 in purified C_6H_6 solvent. [c] Fluorescence quenching of TI by different quenchers in benzene solvent. [d] O–H stretches were measured in purified CH_2Cl_2 solvent with the same amine concentration as that in photolysis experiment. [e] Quenching correction. Vary concentration of quenchers to obtain same percentage of TI quenched in different stereoisomer system. [f] From thioindigo conversion. [g] From benzaldehyde production.

TI to TIH_2 (1.9:1) are consistent with the stoichiometry of eq 1;[31] thus the oxidations of alcohol and amine functions to carbonyl and iminium ions via C–C bond cleavage (two net one-electron redox processes) is accompanied by the two-electron reduction of the acceptor.[31] A reasonable mechanism for the overall reaction is given by eq 2–6.



The diastereomers of **1** and **4** have been individually studied; as summarized in Table I, there is a striking preference for reaction of erythro over threo isomers for reaction with both electron acceptors. A portion of the difference in reactivity can be ascribed to the quenching step; for both pairs the erythro diastereomer is a more efficient quencher than the threo by ca. 2:1. These differences appear to be controlled, at least in part, by intramolecular hydrogen bonding as indicated by the O–H stretching frequencies listed in the table. The threo isomer has a lower frequency O–H stretch that can be attributed to facile intramolecular hydrogen bonding which renders the amine a less effective electron donor.[32] Such hydrogen bonding is stereochemically restricted for the erythro isomer; hence it is a better donor and more effective quencher.

More significant factors in the differential erythro/threo reactivity are the net product formation ratios, after correction for quenching (Table I). For reduction of both acceptors as well as oxidation of the donor there is a net 3–4-fold reactivity difference favoring erythro in each case. Quenching should produce a radical ion pair (eq 2) from which the fragmentation (eq 3) should ensue; the differences in reactivity most reasonably reflect competition between fragmentation (eq 3a and 3b) and back electron transfer (eq 4). As illustrated, a likely explanation for the measured differences is the requirement for a coplanar antiparallel relationship between alcohol, C–C bond, and amine cation radical. This geometry is much more easily attained by erythro isomers of **1** and **4** than for the corresponding threo compounds. The stereochemical effects observed here closely resemble those observed for heterolytic two-electron "synchronous" fragmentations occurring in solvolysis and related reactions.[23,24] A remarkable feature of the present results is the merging of one- and two-electron processes in the fragmentation step (eq 3). Although fragmentation clearly occurs for other substituted amines concurrent with or subsequent to electron-transfer photooxidation, the reactivity of alcohols **1–4**, where the two-electron fragmentation is possible, is substantially enhanced (compare erythro ether **5** vs. *erythro*-**1**). That a moderately long-lived radical (**6**) is produced is indicated by our finding that the erythro isomers of **1** and **4** are excellent photoinitiators with electron acceptors in photopolymerization reactions.[22,33]

The magnitude of the stereochemical effect observed in these photofragmentations is noteworthy, particularly in view of the fact that the fragmentation step must be very rapid to compete with reverse electron transfer. The details of the photoredox-induced fragmentations elucidated here suggest that selective and yet relatively efficient C–C cleavage processes can be induced by single electron transfer reactions for a wide variety of substrates.

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[31] The yield of isolated benzaldehyde from TI–1 irradiation is 180% of reacted **1**; the addition of water (or D_2O) drives the iminium ion to aldehyde but does not affect the quantum yields for photoreduction at the levels used.

[32] The IR spectra of the erythro isomers vary with concentration; in dilute (0.03 M) solution the band is very weak and sharp, indicative of a free O–H. As the concentration is increased there is a decrease in the stretching frequency together with a decrease in sharpness. In contrast, the IR spectra of the threo isomers are relatively broad, compared to those of the dilute erythro isomers, and nearly independent of concentration.

[33] Ci, X.; Lee, L. Y. C., unpublished results.

Acknowledgment. We are grateful to the U.S. Department of Energy (Grant DE-FG02-86ER13504) and the L. D. Caulk Dentsply Corp. for support of this research. We thank Professors F. D. Lewis and G. W. Griffin for valuable suggestions concerning this work. Xiaohong Ci is grateful for a DeRight Fellowship.

Polarized ESR Spectra of the Triplet Enols Generated from *o*-Methylacetophenone and Related Compounds

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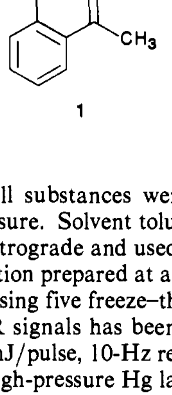
Reaction sequence of the photoenolization of *o*-methylacetophenone has been proposed on the basis of the nanosecond flash photolysis.[1] Intramolecular hydrogen transfer in the photoexcited $^3n\pi^*$ state of this molecule leads to the formation of a short-lived biradical which decays to produce the unstable enol. Although a 1,4-biradical is a key intermediate in this reaction, no direct observation of the intermediate by ESR technique has been reported, to our best knowledge.

In this communication, we present the results of application of a time-resolved ESR technique to the photochemistry of *o*-methylacetophenone (**1**) and the related compounds, 2,4,6-trimethylbenzaldehyde (**2**) and 5,8-dimethyl-1-tetralone (**3**),[2] in glassy matrix. Generation of the transient species during the photoenolization and chemical quenching of the biradical in the presence of an electron acceptor in solution have been demonstrated.



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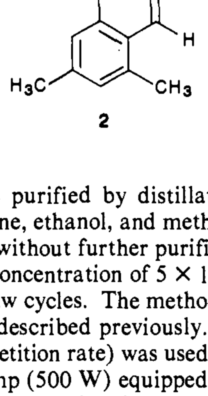

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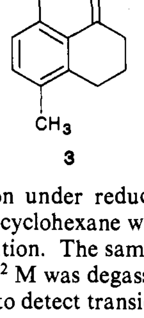

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All substances were purified by distillation under reduced pressure. Solvent toluene, ethanol, and methylcyclohexane were spectrograde and used without further purification. The sample solution prepared at a concentration of 5×10^{-2} M was degassed by using five freeze–thaw cycles. The method to detect transient ESR signals has been described previously.[3] A nitrogen laser (5 mJ/pulse, 10-Hz repetition rate) was used for the light source. A high-pressure Hg lamp (500 W) equipped with a UV-31 glass filter was used for continuous irradiation.

Continuous irradiation of each solution containing **1**–**3** in the mixed solvent of toluene/ethanol (1:1, v/v) at 77 K showed no ESR signal except a small one due to free radical. On the other hand, the transient species in the photoreaction was detected by applying the time-resolved ESR method. Figure 1a shows the ESR spectrum observed for the solution of **1** at 1 μs after the light pulse irradiation. The weak emission signal at about 1500 G corresponds to the $|\Delta M_S| = 2$ transition of the triplet molecule. The $|\Delta M_S| = 1$ transitions show the phases of AEA at the low-field half and of EAE at the high-field half (A, absorption; E, emission). The estimated zero-field parameters, $|D|$ and $|E|$, are 0.060 and 0.0025 cm^{-1}, respectively. These values are different from those of the excited triplet states of acetophenone derivatives.[4,5] Similar polarized spectra were also obtained in nonpolar solvents such as methylcyclohexane and toluene/ethanol (10:1, v/v), though the additional E-polarized lines due to the transient free radicals appeared at the $g = 2$ region.

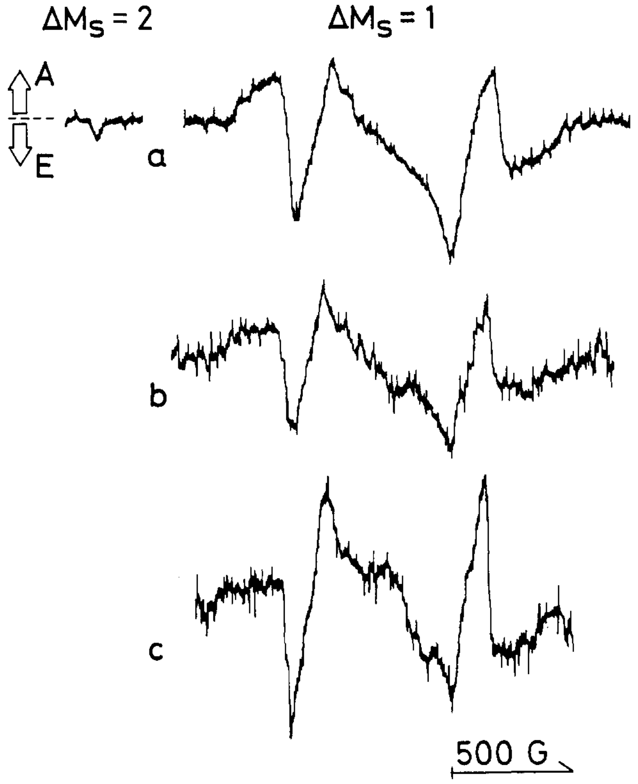

Figure 1. Transient ESR spectra of the intermediate biradicals generated by the laser pulse irradiation of **1** (a), **2** (b), and **3** (c) in toluene/ethanol (1 : 1) at 77 K. The spectra were taken at 1 μs after the laser pulse.

In order to certify the above transient species, measurements were performed for **2** and **3**, both having a similar structural situation between the carbonyl and methyl groups to that of **1**. The compound **3** has a fixed structure, while **1** and **2** form syn and anti conformations. Light pulse irradiation to the solutions of **2** and **3** afforded the spin-polarized spectra shown in Figure 1b and 1c, respectively. The polarization patterns and zero-field parameters of these spectra agreed well with those of Figure 1a. Thus, the results clearly indicate the generation of triplet biradical species in these photochemical reactions. A similar examination carried out for 2-methylbenzophenone (**4**) gave only a spectrum similar to those of the excited triplet states of benzophenone derivatives.[6] The short reported lifetime of the biradical generated from the syn form of **4**[7] would make the detection by our time-resolved ESR system difficult, while the excited triplet state has a relatively long lifetime.

Spin polarization of excited triplet states usually arises from the anisotropic intersystem crossing (ISC) to the triplet sublevels.[8] According to the qualitative consideration to the phase of CIDEP at the $|\Delta M_S| = 1$ region, two physically realizable situations are necessary to interpret the AEA/EAE pattern with the signs of D and E regarding the manner of ISC. We assume simply the same signs of D and E. Then the zero-field energies W_x, W_y, and W_z are in the order $W_y > W_x > W_z$ for $D > 0$ and $W_z > W_x > W_y$ for $D < 0$. When the highly populated state in the sublevels is T_z and T_y for $D > 0$ or T_x for $D < 0$, the phase pattern of the

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