NOTES Bull. Chem. Soc. Jpn., 67, 2348—2350(1994) [Vol. 67, No. 8

Photosensitized Electron-Transfer Reaction of 3-Aryl-2-methyloxaziridine: Direct Deoxygenation from the Isomeric Arylnitrone

Yasunori Iwano, Yasuhiko Kawamura,* Hiroki Miyoshi, Toshifumi Yoshinari, and Tokunaru Horie
Department of Chemical Science and Technology, Faculty of Engineering, The University of Tokushima,
Minamijosanjima, Tokushima 770

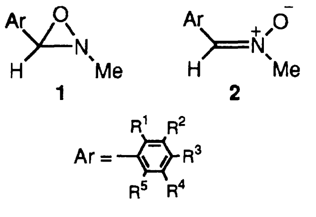
(Received March 30, 1994)

Synopsis. Photosensitized electron-transfer reactions of 3-aryl-2-methyloxaziridines gave mainly the corresponding benzaldehydes, whereas the isomeric nitrones gave imines as well as aldehydes. Deoxygenation of the nitrone occurred via the nitrone cation radical under the reaction conditions. An aryl substituent effect on the reaction and isomerizations of both cation radicals are also discussed.

Nitrone deoxygenation has long been of interest, since it is a supplementary case of the *N*-oxide deoxygenation which has been recognized to be the best model of microsomal oxidation.[1] One of the remarkable features of this biological process is an N. I. H. shift, which is a para-to-meta rearrangement of a label when a labeled benzene derivative is subjected to oxidation.[2] Furthermore, it is still disputed whether an *N*-oxide or an isomeric oxaziridine releases an active oxygen species.[3] In relation to this, we found a deoxygenation reaction of an arylnitrone induced by a photosensitized electron transfer (PET).[4] It also seems to be controversial whether the deoxygenation occurs from the nitrone or from the isomeric aryloxaziridine under PET conditions. A study of the isomeric oxaziridines should be crucial for clarifying this point. The stability of the oxaziridines, however, depends on the structural factors; they are not always easily handled. We, therefore, planned to study the PET reactions of some stable 3-aryl-2-methyloxaziridines (**1**) compared with those of the isomeric arylnitrones (**2**).

Results and Discussion

Methoxylated arylnitrones (**2**) were prepared by a known procedure.[5] The isomeric oxaziridines (**1**) were prepared by the photoirradiation (Pyrex filter) of **2** in CD_3CN (Chart 1). Then, a CD_3CN solution of 9,10-dicyanoanthracene (DCA) as a photosensitizer was added to a sample which was purged with argon prior to irradiation.



	R¹	R²	R³	R⁴	R⁵
a	OMe	H	H	H	H
b	H	H	OMe	H	H
c	OMe	H	OMe	H	H
d	H	OMe	H	OMe	H
e	OMe	H	OMe	H	OMe

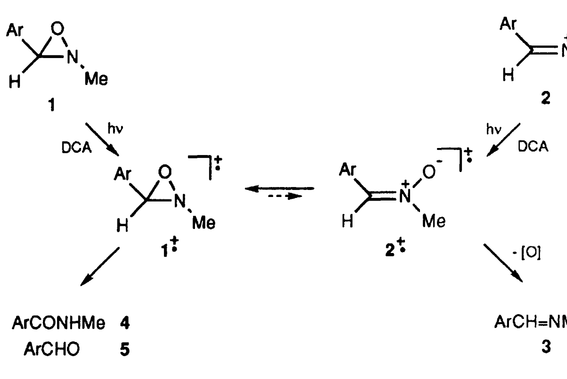
Chart 1.

The fluorescene of DCA was effectively quenched upon the addition of **1** or **2** (Table 1). The quenching rate constants (k_q) favorably support a single electron transfer (SET) in the singlet manifold as the fluorescence quenching mechanism. The value correlates well with the free energy for the SET (ΔG_{SET}) estimated by the Rehm–Weller equation.[6] The photoreactions of

Table 1. Oxidation Potentials of Aryloxaziridines and Nitrones and Kinetic Data of Quenching of the DCA Fluorescence with Them[a]

Oxaziridine and Nitrone	$k_q\tau$	k_q[b] $\times 10^{-10}$	$E^{ox}_{1/2}$	ΔG_{SET}[c]
	M^{-1}	$M^{-1}s^{-1}$	V vs. SCE	$kJ\,mol^{-1}$
1a	120	0.784	1.57	−46
1b	127	0.830	1.65	−39
1c	149	0.972	1.30	−72
1d	138	0.902	1.53	−50
1e	132	0.861	1.23	−79
2a	228	1.49	1.22	−80
2b	247	1.61	1.16	−86
2c	260	1.70	1.06	−95
2d	170	1.11	1.28	−74
2e	215	1.41	0.99	−100

a) Quenching data were obtained in dry MeCN under air at room temperature. Oxidation potentials were measured in dry MeCN under Ar at room temperature. Supporting electrolyte was $Et_4N^+ClO_4^-$. b) Calculated by using τ=15.3 ns[10] for the lifetime of $^1DCA^*$. c) Free energy change of the single electron transfer from **1** or **2** to $^1DCA^*$ in MeCN.



Scheme 1.

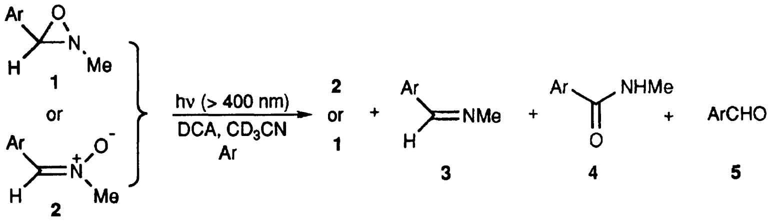
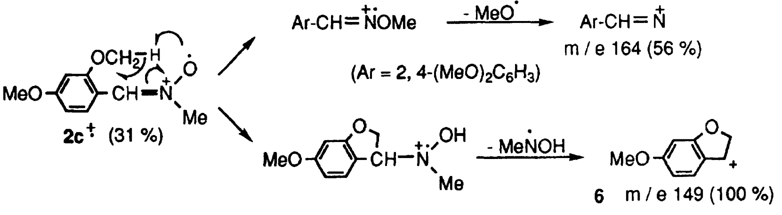


Chart 2.



Scheme 2.

1 and **2** in the presence of a much easier oxidizable compound, 1,2,4,5-tetramethoxybenzene,[7] and those without DCA were retarded (Chart 2). These facts suggest that the photoreactions proceed by the SET mechanism.

The results of the photoreactions (Table 2) are summarized as follows: (1) Oxaziridines **1** and nitrones **2** with the same substitution pattern showed adverse reactivities to each other. (2) In the reaction of **1**, imines (**3**) were not given at all, whereas **2** gave **3**, except for the reaction of arylnitrones (**2c** and **2e**) with the 2-methoxyphenyl group. (3) In all cases, benzaldehydes (**5**) were given as a major product. (4) Isomerization of **1** to **2**, and vice versa, were observed, depending on the substrates.

A mechanism which takes all of the observations into account is proposed in Scheme 1. A general trend for the formations of **4** and **5**, although there are some exceptions for the formation of **4** from **1**, suggests that a cation radical conversion from **2** into **1** occurred, and eventually **4** and **5** were formed from the cation radical of **1**. The oxaziridine formations from **2a**, **2b**, and **2c** also support this consideration. The reversal process, i.e., isomerization from **1** to **2** in the cation radical state, however, does not seem to exist, or proceeds very slowly if any, except for the case of **1e**. Benzaldehydes **5** were formed generally in the reaction, whereas imines were not. The participation of the disproportionation of a nitrone cation radical and that of trace amounts of water for the formation of **5** can be excluded, as mentioned in a previous paper.[4] The above fact, therefore, suggests that the formation of an aldehyde occurs via an oxaziridine cation radical, and deoxygenation occurs via a nitrone cation radical exclusively. It is of interest to note that **2c** and **2e** with the 2-methoxy group on the aryl moiety did not give the corresponding imines at all. Although a clear explanation for the reason is presently difficult, the mass spectral fragmentation pattern of **2** is suggestive. That is, only **2c** and **2e** gave an ion assignable to a dihydrobenzofuran cation (**6**)[9] (Scheme 2 for **2c**). Although such dihydrobenzofurans or related compounds were not detected in a reaction mixture of **2c** or **2e**, this characteristic fragmentation mode seems to be correlated with their peculiar reactivities in the PET reaction.

Table 2. Photosensitized Electron-Transfer Reactions of Aryloxaziridines (**1**) and Nitrones (**2**)[a]

Oxaziridine and Nitrone	Conv./%	Yield/%				
		1	**2**	**3**	**4**	**5**
1a	27	73	0	0	2	17
1b	6	94	0	0	0	6
1c	28	72	Tr[b]	0	Tr	12
1d	14	86	0	0	3	5
1e	100	0	21	0	0	53
2a	85	5	15	4	15	61
2b	100	39	0	21	6	34
2c	72	28	28	0	0	44
2d	92	0	8	21	9	62
2e	36	0	64	0	19	17

a) Data were obtained by the ^{1}H NMR analysis employing cyclododecane as an internal standard. b) Tr=trace.

In order to characterize the released oxygen from the nitrones and to gain insight into the potential energy difference of both interchangeable cation radicals, trapping of the released oxygen, kinetic experiments, and PET reactions of sterically constrained oxaziridines are now underway.

Experimentals

Preparations of Aryloxaziridines (1) and the Corresponding Nitrones (2). Methoxylated **2** were prepared by the condensation of substituted benzaldehydes and methylamine hydrochloride in the presence of sodium hydroxide.[5] Oxaziridines **1** were prepared by the photoirradiation of **2** with a high-pressure mercury lamp (Riko, 400 W) through a Pyrex filter in CD_3CN just before conducting the PET reactions. The purity was assured by ^{1}H NMR (400 MHz).

Preparations of Authentic Photoproducts. Imines **3** were prepared by the condensations of benzaldehydes with methylamine in the usual way. Benzamides were prepared by the condensations of freshly prepared benzoyl chlorides with methylamine.

General Method for the Quantitative Analysis for the Photoreaction. Arylnitrones **2** were dissolved in CD_3CN. The concentrations of **2** (10^{-3} M; 1 M=1 mol dm^{-3}) were adjusted so that 75% of the fluorescence quenching of 9,10-dicyanoanthracene (DCA) occurred. The photoreactions of **2** in the presence of DCA (10^{-4} M) were performed with a high-pressure mercury lamp through a glass filter (Toshiba L-42; >400 nm) for 6 h under Ar at <15 °C. The reaction was monitored by ^{1}H NMR (400 MHz); the conversion of **2** and the product yields were calculated based on the integration of cyclododecane as an internal standard. To a CD_3CN solution (10^{-2} M) of the corresponding aryloxaziridines (**1**) prepared by the above-mentioned method was added a saturated CD_3CN solution of DCA under Ar; the mixture was again irradiated with the lamp through an L-42 glass filter for 6 h. The conversions and product yields were calculated in the same way as those of **2**. The presence of all major products in a reaction mixture was verified by GC-MS and ^{1}H NMR.

This work was supported by Grant-in-Aid for Scientific Research No. 04640506 from the Ministry of Education, Science and Culture.

References

1) A. G. Rowely and J. R. F. Steedmann, *Chem. Ind.* (*London*), **1981**, 365; M. N. Akhtar, D. R. Boyd, J. D. Neil, and D. M. Jerrina, *J. Chem. Soc., Perkin Trans. 1*, **1980**, 1693.

2) J. W. Daly, D. M. Jerina, and B. Witkop, *Experimentia*, **28**, 1129 (1972); J. P. Ferris, M. J. Fasco, F. H. Stylianopoulou, D. M. Jerrina, J. W. Daly, and A. M. Jeffrey, *Arch. Biochem. Biophys.*, **156**, 97 (1973).

3) A. Albini and M. Alpegiani, *Chem. Rev.*, **84**, 43 (1984), and references cited therein.

4) Y. Kawamura, Y. Iwano, Y. Shimizu, Y. Tokai, and T. Horie, *Chem. Lett.*, **1994**, 707.

5) R. G. Pews, *J. Org. Chem.*, **32**, 1628 (1967).

6) D. Rehm and A. Weller, *Isr. J. Chem.*, **8**, 259 (1970).

7) Half-wave oxidation potential is reported as +0.81 V vs. SCE (standard caromel electrode).[8]

8) C. K. Mann and K. K. Barnes, "Electrochemical Reactions in Nonaqueous Systems," Marcel Dekker, New York (1970), p. 252.

9) B. Søgaard larsen, G. Schroll, S. -O. Lawesson, J. H. Bowie, and R. G. Cooks, *Tetrahedron*, **24**, 5193 (1968).

10) J. Eriksen and C. S. Foote, *J. Phys. Chem.*, **82**, 2659 (1980).