

Title	A Photochemically Induced Novel Ring Enlargement Reaction. Reaction of Cation Radical Derived from 7,8-Bis(methoxycarbonyl)-9-(4-methoxyphenyl)-1-phenyl-3,4-benzo-9-azabicyclo[4.2.1]non-3-ene-2,5-dione
Author(s)	Maruyama, Kazuhiro; Ogawa, Takuji
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**A Photochemically Induced Novel Ring Enlargement Reaction.
Reaction of Cation Radical Derived from 7,8-Bis(methoxycarbonyl)-
9-(4-methoxyphenyl)-1-phenyl-3,4-benzo-9-azabicyclo[4.2.1]non-3-ene-2,5-dione**

Kazuhiro MARUYAMA* and Takuji OGAWA

Department of Chemistry, Faculty of Science, Kyoto University, Sakyo-ku, Kyoto 606

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Synopsis. By oxidation with molecular oxygen, photoadducts **2** of 1-(4-methoxyphenyl)-1a-phenyl-1a,7a-dihydro-1H-naphth[2,3-b]azirine-2,7-dione with olefins afforded cation radicals of **2** in acidic media such as $\text{CF}_3\text{CO}_2\text{H}$ or HClO_4 . On irradiation, the cation radicals gave ring enlarged isomers 10,11-bis(methoxycarbonyl)-1-phenyl-3,4-benzo-7,8-(3'-methoxybenzo)-9-azabicyclo[4.3.2]undec-3,7-diene-2,5-dione (**3**).

Photochemical reactions of cation radicals derived from title compound **2a** and its analogues were investigated. The substrate **2a** is a photoproduct of 1-(4-methoxyphenyl)-1a,7a-dihydro-1H-naphth[2,3-b]azirine-2,7-dione (**1**) and dimethyl fumarate.¹⁾ The compound **2a** was inert photochemically in a neutral solvent,^{1,7)} but under aerated conditions in an acidic medium it produced immediately the cation radical. Upon irradiation the cation radical showed a ring enlargement reaction of a novel type unknown so far.

Results and Discussion

Immediately after yellow crystals of **2a** (160 mg) were dissolved into 20 ml of 70% HClO_4 or trifluoroacetic acid the solution became purple coloured and the purple solution showed a strong ESR signal at $g=2.0032$ (Fig. 1). The radical species had a life time of several days at 0 °C. Under deaerated conditions neither purple colour nor ESR signal was observed in the solution. Upon exposure of the solution to air, the purple coloured radical showing ESR signal gradually appeared (Fig. 2). Accordingly, oxygen is responsible for the formation of purple coloured radicals. In a neutral air saturated solvent such as acetonitrile or benzene, **2a—i** did not afford the purple coloured radical.

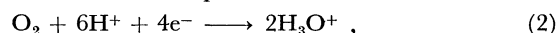
The same purple coloured radicals were produced by electrolysis of **2a** in an acetonitrile solution containing 20 mM (1 M = 1 mol dm⁻³) of triethylammonium perchlorate or in trifluoroacetic acid containing

0.1 M of sodium acetate at platinum anode. (The half wave potentials of **2** were tabulated in Table 1). Consequently, the purple coloured radicals are undoubtedly cation radicals of **2**.

The reason why the cation radical could not be afforded in neutral solvents might be explained in terms of the pH dependence of oxidation reduction potential of oxygen. In acetonitrile the dominant reductive reaction of oxygen is



and the potential is -0.55 V (*vs.* normal hydrogen electrode (NHE)).²⁾ Thus produced super oxide anion affords hydrogen peroxide in a protic solvent.³⁾ In a strong acid such as 85% orthophosphoric acid, the dominant reaction is reported to be



and the potential is $+1.2$ V (*vs.* NHE).⁴⁾ The potential difference between oxygen and **2a** can be calculated to be -1.50 V in acetonitrile and -0.14 V in tri-

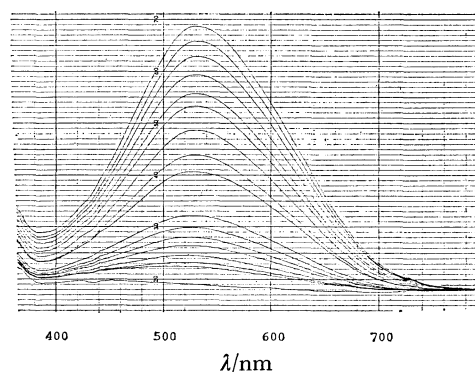


Fig. 2. Time dependent UV absorption change of **2a** in trifluoroacetic acid. Time interval is 5 min.

TABLE 1. STABLE CATION RADICALS

	R ₁ R ₂		X ^{c)}	Generated by oxygen ^{a)}		Half wave potentials/V ^{b)}	
				ESR <i>g</i> -value	UV λ_{max} /nm	CH_3CN (20 mM Et_4ClO_4)	$\text{CF}_3\text{CO}_2\text{H}$ (0.1 M $\text{CH}_3\text{CO}_2\text{Na}$)
2a	H	OCH ₃		2.0032	535	0.95	1.34
2b	H	OCH ₃		2.0032	530	0.82	1.20
2c	H	OCH ₃		2.0032	527	0.88	1.24
2d	H	OCH ₃		2.0032	527	1.22 ^{d)}	0.88 ^{d)}
2e	H	OCH ₃		e)	e)	0.83	1.23
2f	Cl	OCH ₃		2.0032	535	0.98	1.34
2g	Cl	OCH ₃		2.0032	545	0.84	1.21
2h	H	Cl		e)	e)	1.33 ^{d)}	1.66 ^{d)}
2i	H	Cl		e)	e)	1.20	1.53

a) Oxidized in $\text{CF}_3\text{CO}_2\text{H}$. b) Determined by cyclic voltammetry using Ag^+/Ag as a reference electrode, and then converted to those *vs.* NHE by using $E^\circ(\text{Ag}^+/\text{Ag}) = 0.2225$ V. c) $\text{E} = \text{CO}_2\text{CH}_3$. d) Irreversible. e) The cation radical was not observed.

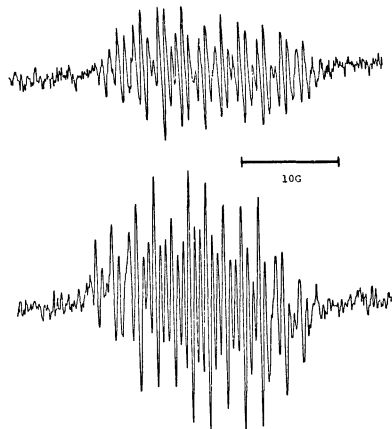
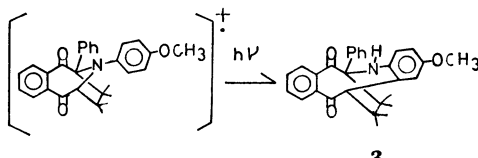


Fig. 1. ESR spectra of the cation radical of **2a** (upper) and **2b** (lower) in air saturated trifluoroacetic acid.

TABLE 2. PHOTOREACTION OF CATION RADICAL OF 2



	Yield %	Mp $\theta_m/^\circ\text{C}$	Characteristic $^1\text{H-NMR}$ chemical shift of 3 (δ)
2a	21	237—239.5	3.06(s, 3H), 3.41(s, 3H), 3.64(s, 3H)
2b	0		
2c	34	Oil	2.96(s, 3H), 3.59(s, 3H)
2d	20	Oil	3.60(s, 3H)

fluoroacetic acid based on the assumption that the reduction potential of oxygen in trifluoroacetic acid is the same as that in 85% orthophosphoric acid. Thus, the electron transfer from **2** to oxygen is far more favourable in the acidic media than in the neutral solvent.⁵⁾

Further, photochemical reactions of cation radicals of **2** were investigated. As a typical example, **2a** (160 mg) was dissolved into 20 ml of 70% HClO_4 and irradiated for 30 h at 0°C with light of longer wavelength than 480 nm using a filter (Toshiba VY-48) in order to irradiate only the cation radical. Colourless crystals crystallized out of the solution by irradiation. The remaining solution changed its colour into pale brown. The crystals were collected, and the solution was diluted with 100 ml of water. The colourless solids precipitated was filtered, washed with water, and then dissolved in dichloromethane. The dichloromethane solution was dried with MgSO_4 and passed through a short column of alumina using dichloromethane as an eluent. On standing the solution over nights at room temperature ($\approx 25^\circ\text{C}$) colourless crystals (mp 237—239.5 $^\circ\text{C}$) were precipitated out. Total yield of the crystals was 21.0%. The remaining was a dark brown tarry matter. The structure of the product was compatible with **3a** depicted in Scheme 1.⁸⁾

Since the HOMO of cation radical of **2a—i** presumably is nitrogen n-orbital and the LUMO might be π^* of *N*-aryl group, an electron at the nitrogen n-orbital may transfer to the π^* of *N*-aryl group on irradiation. As a result the π system of *N*-aryl group is charged in negative and nitrogen is doubly charged in positive. This charge separation is presumably a driving force of the rearrangement.

This type of the photochemical reaction is unique, because the photochemical reaction of cation radical has been scarcely reported.⁶⁾

Experimental

Apparatus. $^1\text{H-NMR}$ spectra were recorded on a JEOL PS-100 spectrometer. Mass spectra were recorded on a Hitachi M-52 mass spectrometer. Infrared spectra were taken on a JASCO-402G spectrometer. UV-spectra were taken on a Shimadzu UV-200. Electron spin resonance spectra were taken on a JEOL PE-3X. Elemental analyses were performed at the microanalytical laboratory of Kyoto

University. Melting points were measured on a Yanagimoto micro melting point apparatus and uncorrected.

Materials. Compound **1** was prepared from 2-phenyl-1,4-naphthoquinone and 4-methoxyphenylazide as reported previously.¹⁾ Photochemical production of **2** is reported elsewhere.⁷⁾ Perchloric acid 70% was purchased from Nakarai Chemicals, LTD., and used without further purification. Trifluoroacetic acid was purchased from Nakarai Chemicals, LTD., and dried over phosphorous pentoxide and distilled.

Physical Properties of 3. **3a:** $^1\text{H-NMR}$ (CDCl_3) δ =3.06(3H, s, CO_2CH_3), 3.41 (3H, s, CO_2CH_3), 3.64 (3H, s, $\text{NC}_6\text{H}_5\text{OCH}_3$), 4.05 (1H, d, $J=7$ Hz), 4.48 (1H, d, $J=7.0$, 8.5 Hz), 4.56 (1H, s, NH), 5.09 (1H, d, $J=8.5$ Hz), 6.54 (2H, d, $J=9.0$ Hz), 6.88 (1H, d, $J=9$ Hz), 7.2—8.0 (9H, m); IR (KBr) 3400 (NH), 1732, 1705, 1682 cm^{-1} ; MS (16 eV) m/e (rel intensity) 501 (M^+ ; 100). Found: C, 69.75; H, 5.32; N, 2.87%. Calcd: C, 69.73; H, 5.05; N, 2.80%. Mp 237—239.5 $^\circ\text{C}$.

3c: $^1\text{H-NMR}$ (CDCl_3) δ =1.56 (1H, s), 2.0 (1H, d, d, ABq, $J=3$, 10, and 15 Hz), 2.7 (1H, D, D, ABq, $J=9$, 5, and 15 Hz), 2.94 (3H, s), 3.60 (3H, s), 3.6 (1H, m), 4.76 (1H, d, d, $J=3$, 9 Hz), 6.4—6.5 (2H, m), 6.8—6.9 (1H, m), 7.1—7.5 (8H, m), 7.7—7.9 (1H, m); IR (CDCl_3) 3500, 2960, 1780, and 1690 cm^{-1} ; MS (16 eV) m/e (rel intensity) 441 (M^+ ; 100). Found: C, 73.27; H, 5.42; N, 3.06%. Calcd: C, 77.46; H, 5.25; N, 3.17%. Colourless oil. Bp ca. 200 $^\circ\text{C}$ (1.3 Pa, the Kugelrohr distillation apparatus).

3d: $^1\text{H-NMR}$ (CDCl_3) δ =1.60 (1H, s), 2.05 (1H, m), 2.70 (1H, m), 3.65 (3H, s), 3.6 (1H, m), 4.80 (1H, d, d, $J=4$, 10 Hz), 6.4—6.5 (2H, m), 6.8—6.9 (1H, m), 7.1—7.5 (8H, m), 7.7—7.9 (1H, m); IR (CDCl_3) 3500, 2200, 1780, and 1690 cm^{-1} ; MS (16 eV) m/e (rel intensity) 408 (M^+ ; 100). Found: C, 76.70; H, 4.82; N, 6.79%. Calcd: C, 76.46; H, 4.94; N, 6.86%. Colourless oil. Bp ca. 200 $^\circ\text{C}$ (1.3 Pa the Kugelrohr distillation apparatus).

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- 7) K. Maruyama and T. Ogawa, *J. Org. Chem.*, to be published.
- 8) None of **3** was detected when the cation radical solution was left in the dark for a week, but only a dark tarry matter was produced.