

# Photochemical Reaction of Polynitrobenzenes with Adamantylideneadamantane: the X-Ray Structure Analysis and Chemical Properties of the Dispiro *N*-(2,4,6-Trinitrophenyl)-1,3,2-dioxazolidine Product

Keiji Okada,\* Yukinori Saito and Masaji Oda\*

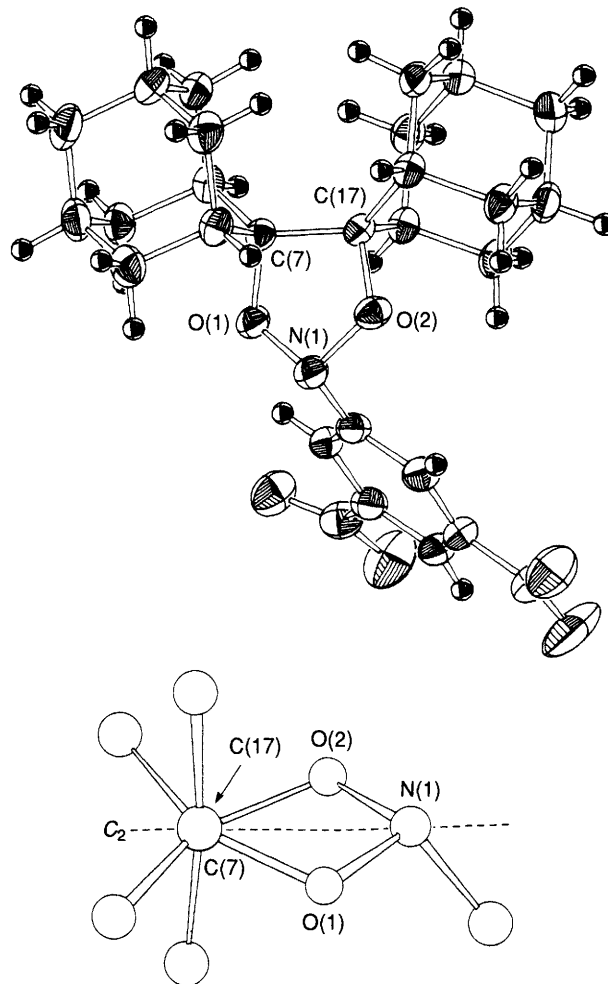
Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan

Photoreaction of polynitrobenzenes (1,3- or 1,4-dinitrobenzene; 1,3,5-trinitrobenzene) with adamantylideneadamantane gave stable dioxazolidine derivatives; X-ray structure analysis together with thermal and acid-catalysed reactions have been examined for one of the dioxazolidines.

The photochemistry of nitrobenzene in cyclohexene and 2-methylbut-2-ene was reported by Buchi and Ayer in 1956.<sup>1</sup> They observed the formation of carbonyl compounds, azobenzene and other substances, and rationalised these fragmentation products by assuming the presence of 1,3,2-dioxazolidine intermediates. Later, de Mayo and coworkers carried out these reactions at low temperature ( $-78^{\circ}\text{C}$ ),<sup>2</sup> and succeeded in recording the NMR spectra of these unstable intermediates. Such structures were also supported by their hydrogenolysis at low temperature to give anilines and *cis*-1,2-dihydroxy compounds. Dioxazolidines thus produced were unstable at room temperature. Hitherto, structural data of these novel heterocyclic compounds have not been reported, and their chemical properties are not well characterised. We report (i) the formation of the stable dioxazolidines **3a–c** in the photoreactions of polynitrobenzenes [1,3- (**1a**) or 1,4-dinitrobenzene (**1b**) or 1,3,5-trinitrobenzene (**1c**)] with bulky adamantylideneadamantane (**2**), (ii) the X-ray structure analysis of **3c**, and (iii) the thermal and acid catalysed reactions of **3c**.

Irradiation of a mixture of polynitrobenzenes **1a–c** (200 mg) and **2** (1 equiv.) in dichloromethane (100 ml) through a Pyrex filter using a 100 W Hg lamp for 5 h under a nitrogen atmosphere produced a yellow solution. Usual work-up followed by chromatographic separation gave dioxazolidines

**3a–c**† in the yields shown in Table 1. 1,3,5-Trinitrobenzene **1c** is more reactive than the dinitrobenzenes **1a,b**. Under similar

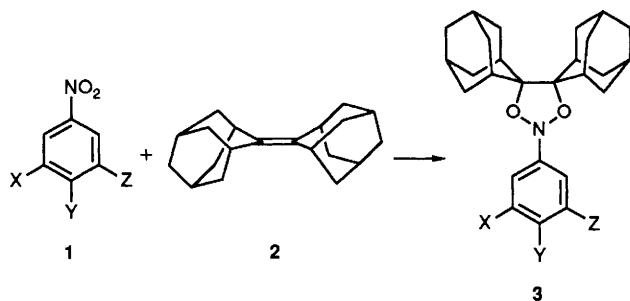


**Fig. 1** ORTEP view of **3c** showing 50% thermal ellipsoids and the Newman projection of the dioxazolidine ring. Bond lengths and angles: C(7)–C(17) 1.577(2), C(7)–O(1) = C(17)–O(2) = 1.466(2), N(1)–O(1) 1.430(2), N(1)–O(2) 1.438(2) Å; C(17)–C(7)–O(1) 97.7(1), C(7)–C(17)–O(2) 97.4(1), C(7)–O(1)–N(1) 106.8(1), C(17)–O(2)–N(1) 108.6(1), O(1)–N(1)–O(2) 105.0(1); torsion angle O(1)–C(7)–C(17)–O(2) 46.7(1).

**Table 1** Formation of the dioxazolidines **3** by photoreaction of polynitrobenzenes **1** with adamantylideneadamantane

Compd.	Solvent	Conditions	Yield (%) of <b>3</b>	Recovery of <b>1</b> (%)
<b>1a</b>	CH <sub>2</sub> Cl <sub>2</sub>	N <sub>2</sub>	9	79
<b>1b</b>	CH <sub>2</sub> Cl <sub>2</sub>	N <sub>2</sub>	6	79
<b>1c</b>	CH <sub>2</sub> Cl <sub>2</sub>	N <sub>2</sub>	32	69
<b>1c</b>	CH <sub>2</sub> Cl <sub>2</sub> –MeCN(1:1)	N <sub>2</sub>	13	61
<b>1c</b>	CH <sub>2</sub> Cl <sub>2</sub>	Aerated	13	67
<b>1c</b>	Acetone <sup>a</sup>	N <sub>2</sub>	13 <sup>a</sup>	57
<b>1c</b>	C <sub>6</sub> H <sub>6</sub>	N <sub>2</sub>	8	85
<b>1c</b>	Dioxane <sup>b</sup>	N <sub>2</sub>	6 <sup>b</sup>	17

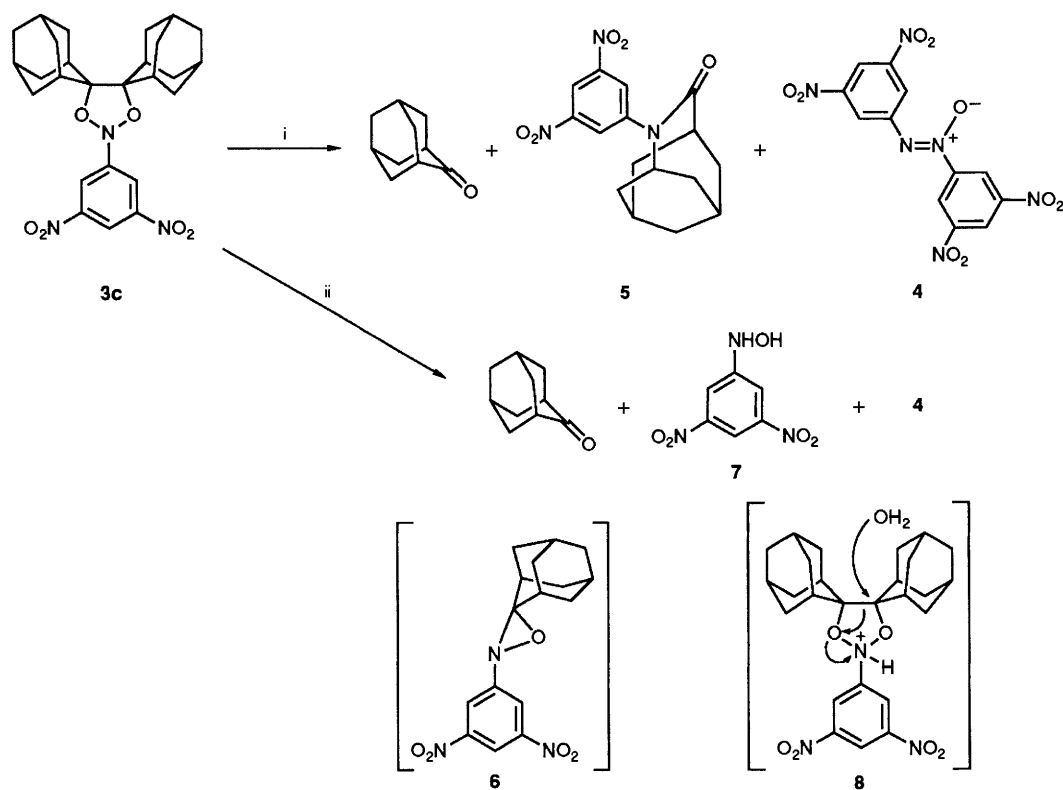
<sup>a</sup> Irradiated through an aqueous K<sub>2</sub>CrO<sub>4</sub>–K<sub>2</sub>CO<sub>3</sub> filter. <sup>b</sup> The azoxybenzene **4** was produced in 11% yield.



a: X = NO<sub>2</sub>, Y = Z = H  
 b: X = Z = H, Y = NO<sub>2</sub>  
 c: X = Z = NO<sub>2</sub>, Y = H

Conditions: *hν* (Pyrex filter), solvent, 5 h at room temp.

† Spectral data: **3a**: yellow prisms, m.p. 104 °C, <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>) δ 1.50–2.60 (m, 28H), 7.48 (t, 1H, *J* 8.2 Hz), 7.68 (ddd, 1H, *J* 8.2, 2.2, 1.0 Hz), 7.99 (ddd, 1H, *J* 8.2, 2.2, 1.0 Hz) and 8.19 (t, 1H, *J* 2.2 Hz); MS (FAB) *m/z* 437 (M + H<sup>+</sup>); UV (n-hexane) λ<sub>max</sub>/nm (log ε) 328 (3.00), **3b**: yellow prisms, m.p. 100 °C, <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>) δ 1.50–2.60 (m, 28H), 7.44 (d-like, 2H, *J* 9.2 Hz) and 8.19 (d-like, 2H, *J* 9.2 Hz); MS (FAB) *m/z* 437 (M + H<sup>+</sup>); UV (n-hexane) λ<sub>max</sub>/nm (log ε) 330 (4.00), **3c**: yellow prisms, m.p. 137 °C, <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>) δ 1.50–2.60 (m, 28H), 8.45 (d, 2H, *J* 2.2 Hz) and 8.79 (t, 1H, *J* 2.2 Hz); MS (FAB) *m/z* 482 (M + H<sup>+</sup>); UV (n-hexane) λ<sub>max</sub>/nm (log ε) 311 (3.37).



**Scheme 1** Reagents and conditions: i, toluene, reflux for 3 h, ii, *p*-MeC<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>H·H<sub>2</sub>O in CH<sub>2</sub>Cl<sub>2</sub> for 2 h at room temperature

conditions, nitrobenzene does not react with **2**. Table 1 also shows the results of photolysis under several other conditions. Dichloromethane is the most suitable solvent for this reaction and in other polar or nonpolar solvents the reaction is slower. When the reaction was carried out in dioxane, the starting nitrobenzene **1c** was extensively consumed, probably by the known hydrogen abstraction path<sup>3</sup> giving a complex mixture from which the dioxazolidine **3c** (6%) and the azoxybenzene **4** (11%) were obtained (see Scheme 1). The reaction also proceeds under aerated conditions in dichloromethane as well as under a nitrogen atmosphere in acetone by irradiation using 313 nm light which is selectively absorbed (>95%) by acetone. These results indicate that the reactive state of **1** is the short-lived triplet excited state. Neither flash photolysis nor time-dependent ESR studies gave evidence for putative long-lived radical ion intermediates.

Fig. 1 shows the X-ray structure of **3c**.<sup>‡</sup> The conformation of the 1,3,2-dioxazolidine skeleton is close to the C<sub>2</sub> (half chair) rather than C<sub>s</sub> (envelope).<sup>4</sup> The nitrogen atom has sp<sup>3</sup> hybridization. The small bond angles C(17)–C(7)–O(1) and C(7)–C(17)–O(2) are probably due to steric repulsion between the bulky adamantyl groups.

Although the stability of dioxazolidines has been qualitatively investigated by de Mayo and coworkers, no isolable product was obtained.<sup>2</sup> Using **1c** as a model compound, the thermal and acid-catalysed decomposition was examined

(Scheme 1).<sup>§</sup> The dioxazolidine **1c** is stable in refluxing benzene. However, it decomposes in refluxing toluene to produce adamantan-2-one (90%), the amide **5** (9%) and the azoxybenzene **4** (13%). The amide **5** would be formed *via* the oxaziridine intermediate **6**, followed by Beckmann-type rearrangement. The azoxybenzene **4** may be produced by the oxidation of the azobenzene with the oxaziridine intermediate **6** or by the reaction of the nitrene intermediate with the dioxazolidine **3c** as de Mayo pointed out.<sup>2</sup> In contrast to the thermal reaction, the acid-catalysed reaction proceeds at room temperature and gives adamantan-2-one (78%), the hydroxylamine **7**<sup>5</sup> (71%) and the azoxybenzene **4** (7%). The hydroxylamine **7** can be derived by successive protonation and fragmentation as indicated in **8** in which a small amount of water (in the CH<sub>2</sub>Cl<sub>2</sub> or the water of hydration of *p*-MeC<sub>6</sub>H<sub>4</sub>-SO<sub>3</sub>H) would participate.

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<sup>‡</sup> Crystal data for **3c**: C<sub>26</sub>H<sub>31</sub>O<sub>6</sub>N<sub>3</sub>, triclinic, space group *P* $\bar{1}$  (No. 2), *a* = 10.619(3), *b* = 11.523(2), *c* = 10.565(2) Å,  $\alpha$  = 110.54(2),  $\beta$  = 92.60(2),  $\gamma$  = 68.12(2)°, *V* = 1117.9(5) Å<sup>3</sup>, *Z* = 2, *D*<sub>c</sub> = 1.430 g cm<sup>-3</sup>; Rigaku AFC5R; Mo-K $\alpha$  radiation ( $\lambda$  = 0.71069 Å); 3° < 2 $\theta$  < 60.0°; 6553 unique reflections, of which 3949 were treated as observed [*F*<sub>o</sub><sup>2</sup> > 3 $\sigma$ (*F*<sub>o</sub><sup>2</sup>)]; *R* = 0.043, *R*<sub>w</sub> = 0.046. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

<sup>§</sup> Spectra data: **4**: colourless needles, m.p. 188 °C, <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>)  $\delta$  9.16 (t, 1H, *J* 2.0 Hz), 9.35 (t, 1H, *J* 2.0 Hz), 9.41 (d, 2H, *J* 2.0 Hz) and 9.55 (d, 2H, *J* 2.0 Hz); MS (FAB) *m/z* 378 (M<sup>+</sup>); **5**: colourless needles, m.p. 172 °C, <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>)  $\delta$  1.70–2.30 (m, 12H), 3.07 (t, 1H, *J* 6.1 Hz), 3.92 (m, 1H) 8.38 (d, 2H, *J* 2.3 Hz) and 8.88 (t, 1H, *J* 2.3 Hz); MS (EI) *m/z* 236 (M<sup>+</sup>); IR (KBr)  $\nu_{\max}$  1661 cm<sup>-1</sup>.