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Photolysis of *N*, *N*-Dimethylimidazolidinetrione: A Two Nitrogens–Three Carbonyls System[1]

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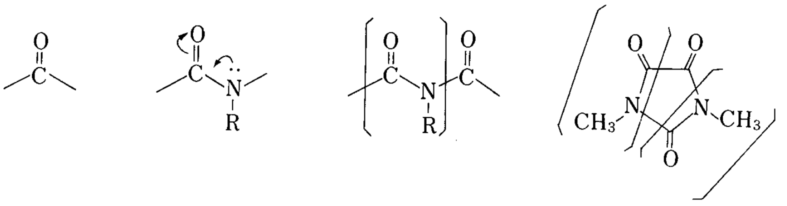
Photolysis of *N*,*N*-dimethylimidazolidinetrione in hydrogen-donating solvents affords hydrogenated and solvent-addition products *via* the Norrish type II process.

Keywords——*N*, *N*-dimethylimidazolidinetrione; hydrogen abstraction; Norrish type II reaction; hydantoin; triplet state; photochemistry

In our systematic study on the photochemistry of nitrogen–carbonyl system, it has been found that the imide carbonyl of aromatic and aliphatic cyclic imides behaves photochemically like a carbonyl group of simple ketone systems undergoing well-known types of reactions such as Norrish type I and II, and Paterno–Büchi reactions.[2] It is worth noting that amides **2** in which the nitrogen deactivates the carbonyl group are essentially inert in photoreactions. Thus, in going from ketones **1** to imides **3** by way of the amides the effects of the nitrogen and one carbonyl appear to compensate for each other in the imide systems **3**, and to a simple approximation, the imides **3** resemble their parent ketones due to the survival of the second carbonyl (Chart 1). As a result, the photochemical behavior of imides in many ways parallels that of ketones.

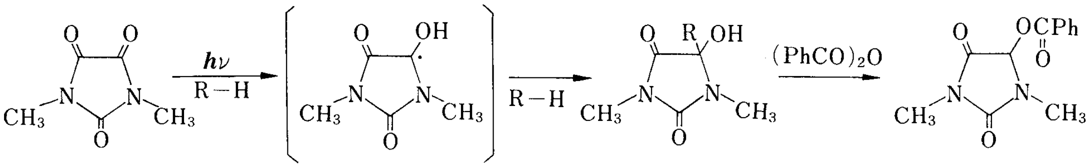


1 **2** **3** **4**

Chart 1

Such a very simple additive rule would be useful in estimating the photoreactivities of complex chromophore systems as well as in designing new photoreactive systems by combining several chromophoric units. Aoyama *et al.* have recently reported the photolysis of α-oxoamide or α-keto acid amide,[3] an α-dicarbonyl–nitrogen system. *N*,*N*-Dimethylimidazolidinetrione (**4**) is a ring system in which an amide and an imide are conjugated, and some carbonyl photoreactivity can be anticipated. In the present paper we wish to report that compound **4** does show such reactivity.

Irradiation of **4** in a hydrogen-donating solvent such as toluene, 2-propanol, methanol or cyclohexane with a high-pressure mercury arc through a Pyrex filter gave hydrogenated (**5b**) and solvent-addition (**5a**, **c**, **d**) products (Chart 2). The results of the photolysis are summarized in Table I. Instrumental and elemental analyses were all consistent with the assigned structures of these photoproducts **5a**, **5c** and **5d**. The structure of product **5b** was



4 7 5 6

a: R = CH_2Ph
b: R = H
c: R = CH_2OH
d: R = cyclohexyl

Chart 2

TABLE I. Photolysis of **4**

Solvent (H-Donor)	Irrad. time (h)	Yield (%)				
		5a	**5b**	**5c**	**5d**	**4** (Recov.)
Toluene	24	50	10	—	—	15
2-Propanol	3	—	23	—	—	30
Methanol	12	—	—	30	—	27
Cyclohexane–acetonitrile	6	—	5	—	24	5

further confirmed by benzoylation and direct comparison with an authentic sample (**6**).

Electronic and spectroscopic properties of imidazolidinetriones have been reported.[4] The lowest energy transition is assigned as n–π*. Since the photoreaction of **4** was sensitized efficiently with benzophenone or acetone, and quenched with 1,3-pentadiene, the reaction appears to proceed from the n–π* triplet state like those of simple ketones by way of hydrogen abstraction (**7**). The above results indicate that an imidazolidinetrione system, consisting of two nitrogens and three carbonyl groups, behaves photochemically like a simple ketone system, as suggested from the additivity rule, and undergoes a Norrish type II reaction leading to the introduction of a hydroxy group into the hydantoin ring. Other photochemical reactions of this system are being explored.

Experimental

Melting points were taken on a Yamato melting point apparatus model MP-21 and are uncorrected. Vacuum distillation was carried out by using a Büchi Kugelrohr apparatus, and boiling points are the uncorrected bath temperatures. Nuclear magnetic resonance (NMR) spectra were taken on a Hitachi R-20B NMR spectrometer with tetramethylsilane (TMS) as an internal standard. Mass spectra (MS) were obtained with a JEOL JMS-Q10A mass spectrometer. Infrared spectra (IR) were recorded with JASCO IRA-1 infrared spectrometer. Preparative layer chromatography (PLC) was carried out on silica gel plates (Kieselgel 60 PF_{254}, Merck, 20 × 20 cm). The light source was a UM-105B (Ushio) 100 W high-pressure mercury lamp.

General Procedure for the Photolysis of 4——A solution containing *N*,*N*-dimethylimidazolidinetrione (**4**)[5] (142 mg, 1.0 mmol) in 250 ml of solvent was irradiated for 3 to 24 h with a 100 W high-pressure mercury arc through a Pyrex filter sleeve under an argon atmosphere. The solvent was removed under reduced pressure and the residue was purified by silica gel thick-layer chromatography, using a CH_2Cl_2–AcOEt mixture (3 : 1, v/v) followed by distillation, recrystallization or derivatization.

5-Benzyl-5-hydroxy-*N*,*N*-dimethylhydantoin (5a)——Colorless oil; bp 210 °C (bath temp.) (0.4 mmHg); 118 mg (50%). IR $\nu_{\max}^{\text{neat}}$ cm^{-1}: 3340 (OH), 1770, 1705 (C=O). NMR ($CDCl_3$) δ: 2.50 (3H, s, $-CH_3$), 3.00 (3H, s, $-CH_3$), 3.10 (1H, d, J = 14 Hz, $-CH_2-$), 3.35 (1H, d, J = 14 Hz, $-CH_2-$). 4.55 (1H, s, −OH), 7.23 (5H, b, aromatic). MS *m/z*: 216 ($M^+ - H_2O$), 143, 131, 116, 92. *Anal.* Calcd for $C_{12}H_{14}N_2O_3$: C, 61.52; H, 6.02; N, 11.96. Found: C, 61.25; H, 6.24; N, 11.72.

5-Hydroxymethyl-5-hydroxy-*N*,*N*-dimethylhydantoin (5c)——Colorless needles; mp 145—146 °C, recrystallized from AcOEt; 52 mg (30%). IR $\nu_{\text{max}}^{\text{Nujol}}$ cm^{-1}: 3430, 3260 (OH), 1760, 1690 (C=O). NMR ($CDCl_3$–DMSO-d_6) δ: 2.90 (3H, s, $-CH_3$), 2.98 (3H, s, $-CH_3$), 3.65 (1H, dt, J=12, 6 Hz, $-C\underline{H}_2OH$), 3.90 (1H, dt, J=12, 6 Hz, $-C\underline{H}_2OH$), 4.60 (1H, t, J=6 Hz, $-CH_2O\underline{H}$), 6.37 (1H, s, –OH). MS *m*/*z*: 156 ($M^+ - H_2O$), 143. *Anal.* Calcd for $C_6H_{10}N_2O_4$: C, 41.38; H, 5.79; N, 16.09. Found: C, 41.20; H, 5.78; N, 15.98.

5-Cyclohexyl-5-hydroxy-*N*,*N*-dimethylhydantoin (5d)——Colorless prisms; mp 113—115 °C, recrystallized from AcOEt–*n*-hexane; 54 mg (24%). IR $\nu_{\text{max}}^{\text{Nujol}}$ cm^{-1}: 3340 (OH), 1760, 1690 (C=O). NMR ($CDCl_3$) δ: 1.70—2.30 (11H, m, cyclohexyl), 2.90 (3H, s, $-CH_3$), 3.00 (3H, s, $-CH_3$), 5.10 (1H, b, –OH). MS *m*/*z*: 226 (M^+), 208, 143. *Anal.* Calcd for $C_{11}H_{18}N_2O_3$: C, 58.39; H, 8.02; N, 12.38. Found: C, 58.17; H, 8.17; N, 12.25.

5-Benzoyloxy-*N*,*N*-dimethylhydantoin (6)——**5b** was heated at 100 °C for 5 h with 1.5 eq of benzoic anhydride, and purified by silica gel thick-layer chromatography using a CH_2Cl_2–AcOEt mixture (10 : 1, v/v) followed by recrystallization from AcOEt–*n*-hexane. Colorless needles; mp 120—122 °C. The melting point of this compound was unchanged on admixture with a sample obtained by the Zn–H_2SO_4 reduction$^{6)}$ of **4**. The IR spectra of the two were superimposable.

References

1) *a*) Photochemistry of Conjugated Nitrogen–Carbonyl Systems. 3. Part 2: E. Sato, Y. Ikeda and Y. Kanaoka, *Chem. Pharm. Bull.*, **31**, 1362 (1983); *b*) Photoinduced Reactions. 74. Part 72: K. Seki, K. Ohkura, M. Terashima and Y. Kanaoka, *Heterocycles*, **22**, 2347 (1984); Part 73: M. Terashima, K. Seki, C. Yoshida, K. Ohkura and Y. Kanaoka, *Chem. Pharm. Bull.*, **33**, 1009 (1985).
2) Y. Kanaoka, *Accounts Chem. Res.*, **11**, 407 (1978).
3) H. Aoyama, M. Sakamoto, K. Kuwabara, K. Yoshida and Y. Omote, *J. Am. Chem. Soc.*, **105**, 1958 (1983), and references cited therein.
4) D. B. Larson, J. F. Arnett and S. P. McGlynn, *J. Am. Chem. Soc.*, **95**, 6928 (1973).
5) Y. Otsuji, S. Wake and E. Imoto, *Tetrahedron*, **26**, 4139 (1970).
6) H. Biltz and D. Heidrich, *Ber.*, **54B**, 1829 (1921).