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PHOTOCHEMICAL (2 + 2) CYCLOADDITION OF AND THERMAL DECOMPOSITION TO N-METHYLACRIDONE AND ACETONE: CHEMILUMINESCENCE AS A PROBE OF POSSIBLE FORMATION OF 1,2-DIOXETANES

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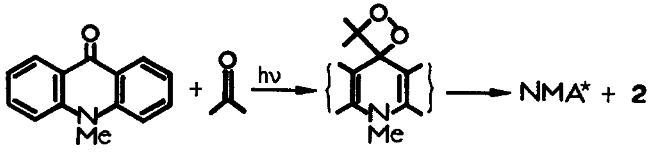
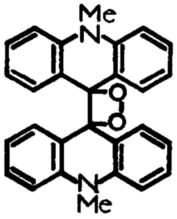
Irradiation of N-methylacridone (NMA) in an acetone solution at -78 °C in the argon atmosphere afforded light emission (Φ_{CL}: 10^{-6} - 10^{-8} einstein/mol) upon warming-up to room temperature. The final products were NMA and acetone exclusively.

Photochemical (2 + 2) cycloaddition reactions between carbonyls and olefins to yield oxetanes,[1] are well known as well as those between two molecules of olefins giving cyclobutanes.[2] Similar cycloaddition reactions between two carbonyl molecules could yield 1,2-dioxetanes and/or 1,3-dioxetanes (cyclic acetals), but there was no literature about the reactions. The reactions are considered as the reverse reactions of the thermal decomposition of 1,2-dioxetanes to the two moles of carbonyls accompanying chemiluminescence (CL). We now describe the first example of such photochemical 1,2-dioxetane formation from two moles of ketones using chemiluminescent light emission as a probe of the formation upon warming-up the photochemical products at -78 °C to room temperature.



NMA (**1**) **2** 1,2-dioxetane (**3**) **1***



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A solution of NMA[3] (**1**: 10^{-2} M) in acetone (Wako Chem. Co.), flushed with O_2, N_2, or Ar for 5 min before irradiation, was irradiated at -78 °C with a 100 W high-pressure Hg lamp (Eikosha: PIH-100) through a Pyrex dewar flask in a Pyrex test tube (ϕ 1.8 cm) for 5-30 min. The irradiated solution gave light emission when warmed up from 77 K to room temperature (Table I).[4] The chemiluminescence (CL) and phosphorescence (PL) spectra of the irradiated solution were identical with PL spectrum of **1** (λ_{max} 525 nm) in acetone under the similar conditions used for CL. Analyses of the spent solution showed that no other compound was detectable than 1 and acetone by GLC[5] and TLC.[5] These data suggest that irradiation of 1 in acetone gave an unstable chemiluminescent compound (probably 1,2-dioxetane, **3**),[6] which decomposed thermally to **1** and acetone exclusively. The emitting species is **1**. NMA, acetone, and irradiation were revealed to be essential. When being irradiated again at -78 °C after CL, the spent solution gave light emission. The irradiation/chemiluminescence were repeatable several times.

Table I shows that presence of O_2 decreased the amounts of CL. It has been known that O_2 quenches radicals or triplet excited states (T_1)[7] and enhances of quantum yield of CL (from S_1 state of the C=O product) (Φ_{CL}) of 1,2-dioxetanes suppressing its non-chemiluminescent, radical decomposition.[8] Thus, O_2 quenches the successive CL reactions at the photochemical cycloaddition stage as well as the thermolysis of **3**. The half life time ($\tau_{1/2}$: *ca.* 60 sec at 0 °C) is in a range of the similar 1,2-dioxetanes derived from substituted 9-methylene-10-methylacridanes appeared in the literatures.[9]

Table I. Quantum Yields of CL[a)] from NMA

solv.	Ar	N_2	O_2
in Me_2CO	1.0×10^{-6}	3.1×10^{-8}	0.7×10^{-8}
in CH_2Cl_2	——	——	0.7×10^{-9}

a) Relative to the Hasting's Standard (see ref. 4).

Similar irradiation of **1** in CH_2Cl_2 gave weaker CL which seems to result from the thermal decomposition of **4**[3] produced photochemically from two molecules of **1**.

The present reaction provides an another general route to synthesize 1,2-dioxetanes.[6b,10] We also aware that the photoirradiation/chemiluminescent light emission system might compose possibly a photo-energy-storage/discharge system, if the reactions would be more effective.

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4) Φ_{CL} values were measured by using a photomultiplier tube (Hamamatsu R-105UH) and are relative to the Hasting's standard [J. W. Hastings and G. Weber, *J. Opt. Soc. Amer.*, **53**, 1410 (1963)].

5) *GLC Conditions*: Yanagimoto Yanaco G-180F (FID), 10% Silicone GE-SE-30 on Diasolid L (60-80 mesh) in a steinless steel column (0.8 m x ϕ 3 mm); Col. temp. 250 °C; inj. temp. 280 °C, carrier gas (N_2) 40.0 ml/min. *TLC Conditions*: Silica gel PF_{254}-gipshaltig (Merck), 0.25 mm ($CHCl_3$).

6)(a) As the referee suggested, the ^{13}C-NMR signal of the quarternary carbons of 3 supposed should appear in the range of δ 89-95 ppm.[6b] However, the solubility limitation at -60∿-80 °C, in that range **3** would be stable, made it difficult to detect the signals and was out of the sensitivety/stability of the instruments available;(b) W. Adam, *Adv. Heterocycl. Chem.*, **21**, 437 (1977).

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