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Cyclic *O*-Acyloximes as Novel Photolatent Bases

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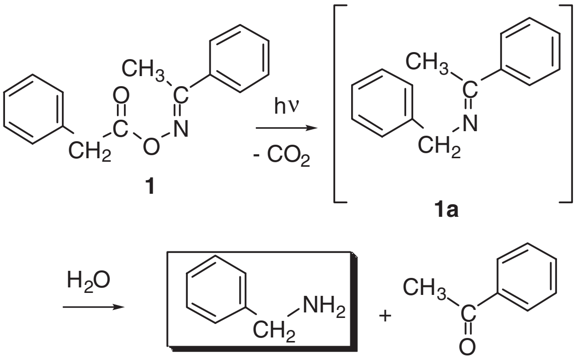
Cyclic *O*-acyloximes were prepared as novel photolatent bases with good photoreactivity and thermal stability. They were transformed into cyclic imines on irradiation at 254 nm and showed higher crosslinking ability for poly(glycidyl methacrylate) compared with an *O*-acyloxime with noncyclic structure.

Photolatent catalysts have been widely used as key materials for imaging and coating technologies.[1,2] Photochemical generation of free-radicals and acids has already been investigated extensively, and compounds that generate basic materials have been increasing recently.[2–5] *O*-Acyloximes are photoreactive compounds with good thermal stability and are known to generate primary amines on UV irradiation.[6,7] For example, acetophenone *O*-phenylacetyloxime (**1**) generates benzylamine on irradiation followed by hydrolysis of resulting imine **1a** as shown in Scheme 1. However, acetophenone is also produced as a by-product. In some applications, the elution or migration of by-products is undesirable. Herein we designed *O*-acyloximes with a cyclic structure, 4,5,6,7-tetrahydro-3-phenyl-8*H*-1,2-oxazocin-8-one (**2a**) and 4,5-dihydro-3-phenyl-7*H*-1,2-oxazepin-7-one (**2b**), which will not release ketones. The cyclic structure is advantageous for the formation of imines after decarboxylation. In this communication, photochemical and physical properties of **2a** and **2b** are clarified, and photocrosslinking behaviors of poly(glycidyl methacrylate) (PGMA) containing these *O*-acyloximes are compared.

2a and **2b** were prepared from 6-hydroxyimino-6-phenylhexanoic acid and 5-hydroxyimino-5-phenylpentanoic acid, respectively. The acids were treated with thionyl chloride in pyridine–diethyl ether mixture at below −5 °C. After purification, cyclic products were isolated and identified by IR, ^{1}H and ^{13}C NMR spectra, and elemental analysis.[8] The yields of **2a** and **2b** were 41 and 10%, respectively.

Thermal and optical properties of *O*-acyloximes are summarized in Table 1. Thermal decomposition temperatures (T_ds) of **2a** and **2b** were higher than 200 °C, showing high thermal stability as well as **1**. UV absorption characteristics of **2a** and **2b** in acetonitrile were similar to **1**. Quantum yield of photolysis at 254 nm (Φ_{254}) for **2a** was found to be essentially the same as **1**.



Scheme 1. Photoreaction of **1**.

Table 1. Physical properties and Φ_{254} of *O*-acyloximes

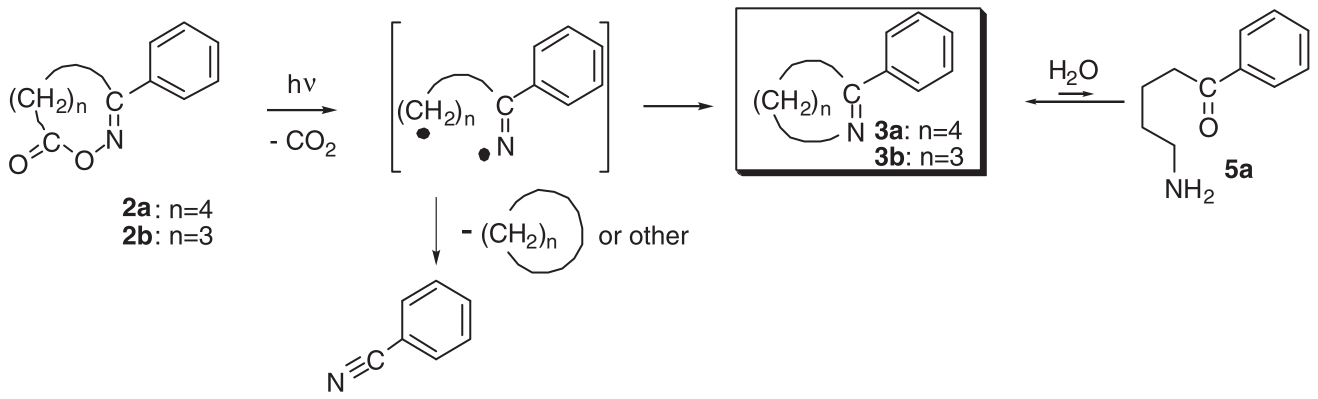
O-Acyloxime	Mp /°C	T_d[a] /°C	λ_{max}[b] /nm	ε at 254 nm[b] /L mol^{-1} cm^{-1}	Φ_{254}[b,c]
1	42–43.5	201	245	14200	0.35
2a	136–137	208	246	13800	0.36
2b	215–216.5	233	252	13300	—[d]

[a]T_d from thermogravimetric analysis. Heating at 10 °C min^{-1} under N$_2$. [b]In acetonitrile. [c]Based on normal phase HPLC analysis of irradiated acetonitrile solution (2 × 10^{-4} M) under N$_2$. [d]Not measured because the solubility of **2b** was too low to prepare 2 × 10^{-4} M.

The acetonitrile solution of **2a** after irradiation with 60 mJ cm^{-2} was analyzed by GC-MS.[9] The GC chromatogram showed peaks at 26 (broad), 24.3, and 9.4 min, which were assigned to 2-phenyl-3,4,5,6-tetrahydropyridine (**3a**) (*m*/*z* 159), 2-phenylpyridine (**4a**) (*m*/*z* 155), and benzonitrile (*m*/*z* 103), respectively. Similarly, **2b** showed GC-MS[9] peaks assignable to **3b** (*m*/*z* 145), 2-phenylpyrrole (**4b**) (*m*/*z* = 143), and benzonitrile. From these results, photoreaction mechanisms are proposed as Scheme 2, where both cyclic imines and benzonitrile were produced from biradical intermediates. It is unclear whether **4a** and **4b** were formed during irradiation or pretreatment for GC-MS.

In general, ketimines are easily hydrolyzed[10] to form ketones and amines in air. Thus, **3a** was prepared authentically[11] from 5-chlorovaleronitrile and phenyllithium as described in the literature,[12] and its stability was investigated. When **3a** having a C=N stretching band at 1635 cm^{-1} in IR spectrum was treated with concd. HCl, yellowish solid having a peak at 1685 cm^{-1} assignable to C=O stretching band was obtained, indicating the formation of hydrochloride salt of **5a**. After treating with NaOH aqueous solution and extraction with chloroform, the solid was turned into brownish oil whose ^{1}H NMR and IR spectra were identical to those of **3a**. These results suggest that **3a** was stable in 6-membered cyclic form and not hydrolyzed immediately to **5a** in contrast to **1a**.

The photocrosslinking of PGMA containing *O*-acyloximes was performed. M_n and glass transition temperature of PGMA were 17000 and 70 °C, respectively. On irradiation followed by heating, the films became insoluble in tetrahydrofuran (THF). Figure 1 shows the changes of insoluble fraction of PGMA films containing 3 mol % of *O*-acyloximes[13] based on the ratio of film thickness before and after soaking in THF. Irradiation energy required for the insolubilization of films containing **2a** and **2b** was less than that containing **1**, showing the high crosslinking ability of **2a** and **2b**.



Scheme 2. Proposed photoreaction mechnisms of cyclic *O*-acyloximes.

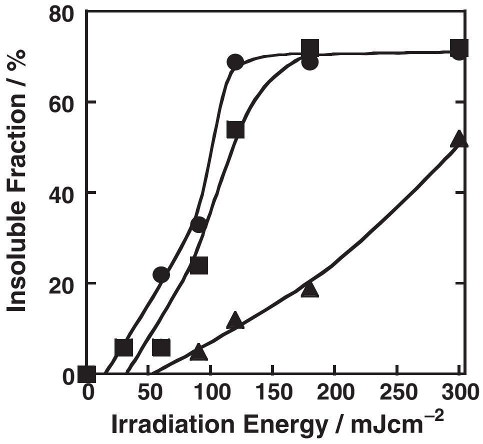


Figure 1. Insolubilization of PGMA films containing 3 mol % of (●) **2a**, (■) **2b**, and (▲) **1** on irradiation followed by heating at 140 °C for 5 min. Film formation: by spin-coating cyclohexanone solutions on silicone substrates followed by drying at 80 °C for 5 min on a hot plate (film thickness: 0.3–0.4 µm). Soaking: THF 10 min at room temperature.

The insoluble fractions of PGMA films containing 5 mol % of **2a** and **2b** were 65 and 67%, respectively, after irradiation at 300 mJ cm^{-2} followed by heating at 120 °C for 5 min. Under the same heating conditions, the insoluble fraction of PGMA film containing 5 mol % of authentically prepared **3a** was 91%. These results suggest that cyclic imines might contribute to the high potentiality of the crosslinking, probably through the nucleophilic attack on epoxy carbon by a lone pair on nitrogen atom of cyclic imine.

In conclusion, novel cyclic *O*-acyloximes showed good photoreactivity and thermal stability. On irradiation, they generated cyclic imines which were not hydrolyzed easily, and caused photocrosslinking of PGMA films more effective than non-cyclic compounds.

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9 Irradiated solutions of *O*-acyloximes (2.0×10^{-4} M) were passed through a pipette holding small amount of silica gel, evaporated under reduced pressure, dissolved into a mixed solution of ethyl acetate and hexane, and conducted to a Shimadzu QP2010plus GCMS with a DB-5MS column and an injection temperature of 200 °C. Oven temperature was held at 50 °C for 5 min, increased by 5 °C min^{-1} to 200 °C, and held at 200 °C for 10 min.

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11 **3a** was unstable and gradually turned into dark liquid even if stored at −20 °C after bubbling argon gas. Therefore, we redistilled before use.

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13 [epoxy unit]:[*O*-acyloxime] = 97:3 (mol/mol).