.<sup>\.</sup>Сн<sub>3</sub>

AZETIDINE-2,4-DIONES VIA PHOTOCYCLIZATION OF N-FORMYL-N-METHYL  $\alpha$ , $\beta$ -UNSATURATED AMIDES

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Upon irradiation N-formyl-N-methylcyclohexene-l-carboxamide (2a) cyclized to give N-methylcyclohexane-l,l-dicarboximide (3a) in a high yield. The reaction proceeds via intramolecular hydrogen abstraction. Similarly, several other alkyl-substituted azetidine-2,4-diones were synthesized.

Recently we reported that N-methylcyclohexane-1,2-dicarboximide (1) photochemically isomerized to N-methylcyclohexane-1,1-dicarboximide (3a), and pointed out that N-formyl-N-methylcyclohexene-1-carboxamide (2a) could be the intermediate in this reaction.<sup>1)</sup> Now we extended the photocyclization of N-formyl-N-methyl  $\alpha,\beta$ unsaturated amides for the synthesis of alkyl-substituted azetidine-2,4-diones.



Typically, N-formyl-N-methylcyclohexene-l-carboxamide (2a, 2.5 mmol) in 25 ml of acetonitrile was externally irradiated with a 120 W low-pressure Hg lamp through quartz after bubbling N<sub>2</sub> gas. After 6 h (conversion ~70%), chromatography of the reaction mixture on silica gel gave N-methylcyclohexane-l,l-dicarboximide (3a, mp 96-97 °C; <sup>1</sup>H-NMR  $\delta$  1.2-2.0 (m, 10 H), 2.89 (s, 3 H); IR (KBr) 1822, 1710, 945 cm<sup>-1</sup>), a cyclized product, in a yield of 85%.<sup>2</sup>) Other examples are summarized in Table.<sup>3</sup>)

Intermediacy of 1,4-biradical  $\frac{4}{\sim}$  which is produced via hydrogen abstraction by enone moiety from formyl group could be reasonably postulated. Similar hydrogen abstraction reaction of N,N-dibenzyl acrylamide has been published.<sup>4)</sup> Table. Azetidine-2,4-diones from N-Formyl-N-methyl  $\alpha,\beta$ -Unsaturated Amides\*

	$\mathbb{R}^{2} \xrightarrow[]{\text{CHO}}_{\mathbb{R}^{2}} \mathbb{N}^{\mathbb{CHO}}_{\mathbb{R}^{3}}$			hu CH <sub>3</sub> CN	$\rightarrow \qquad \begin{array}{c} R^{1}CH_{2} \\ R^{2} \\ R^{2} \\ R^{2} \\ R^{3} \\ R^{3}$				
2	Rl	$R^2$	3	Yield(%)**	2~	$R^1$	R <sup>2</sup>	3~	Yield(%)
2a	– (CH <sub>2</sub>	$(2)_{4}^{-}$	3a	85	2e ~	Н	n-C <sub>3</sub> H <sub>7</sub>	3e ≈	55
2b	– (CH <sub>2</sub>	2) <sub>3</sub> -	3b	81	2f ∼	Н	$iso-C_{3}H_{7}$	3£	50
2c ≫	Н	CH3	3℃	25	2g ∼	Н	n-C4 <sup>H</sup> 9	3g	70***
2d	CH3	CH <sub>3</sub>	3e	29	2h	Н	$\frown$	3h	54

\*Conversions are 70-80%. \*\*Isolated yield and based on the amount of 2 consumed. \*\*\*NMR yield.

As seen from Table, 2a and 2b whose substituents  $(R^1, R^2)$  are ring component result in the better yields than the others (2c-2h). This result may be attributed to their different tendency towards trans-cis



their different tendency towards trans-cis isomerization. That is to say, since the trans-cis isomerization could compete with the intramolecular hydrogen abstraction, the yields in the reactions of 2c-2h would be lowered. In fact, 2d isomerized to its cis isomer 2d' upon irradiation, and 2c-2h needed about two-fold irradiation time compared to 2a and 2b.

Previously some synthetic methods for azetidine-2,4-diones have been reported,<sup>5)</sup> but generally those involve sluggish reactions giving poor yields. The present synthetic approach to azetidine-2,4-diones simply consists of photolysis of N-formyl-N-methyl  $\alpha$ , $\beta$ -unsaturated amides which can be readily prepared from N-methylformamide and  $\alpha$ , $\beta$ -unsaturated carboxylic acid chlorides, and hence will provide a convenient synthetic method for alkyl-substituted azetidine-2,4-diones.

## References and Notes

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- 2) Quantum yield of formation of 3a was  $0.3_1$ .
- 3) All products gave satisfactory elemental analyses and reasonable spectral data.
- 4) T. Hasegawa, M. Watabe, H. Aoyama, and Y. Omote, Tetrahedron, 485 (1977).
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