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AZETIDINE-2,4-DIONES VIA PHOTOCYCLIZATION OF N-FORMYL-N-METHYL α,β-UNSATURATED AMIDES

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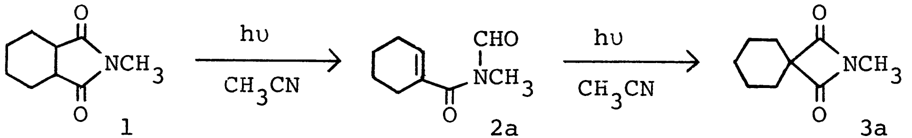
Upon irradiation N-formyl-N-methylcyclohexene-1-carboxamide (2a) cyclized to give N-methylcyclohexane-1,1-dicarboximide (3a) in a high yield. The reaction proceeds via intramolecular hydrogen abstraction. Similarly, several other alkyl-substituted azetidine-2,4-diones were synthesized.

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.[1)] Now we extended the photocyclization of N-formyl-N-methyl α,β-unsaturated amides for the synthesis of alkyl-substituted azetidine-2,4-diones.



1 2a 3a

Typically, N-formyl-N-methylcyclohexene-1-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$_2$ gas. After 6 h (conversion ∼70%), chromatography of the reaction mixture on silica gel gave N-methylcyclohexane-1,1-dicarboximide (3a, mp 96-97 °C; ^{1}H-NMR δ 1.2-2.0 (m, 10 H), 2.89 (s, 3 H); IR (KBr) 1822, 1710, 945 cm^{-1}), a cyclized product, in a yield of 85%.[2)] Other examples are summarized in Table.[3)]

Intermediacy of 1,4-biradical 4 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.[4)]

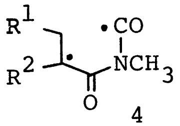


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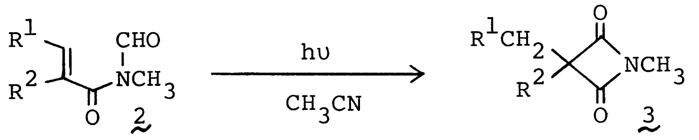
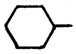
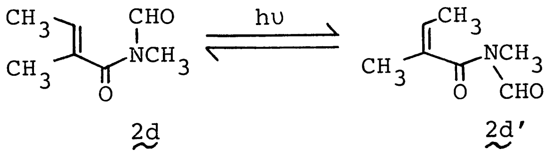
Table. Azetidine-2,4-diones from N-Formyl-N-methyl α,β-Unsaturated Amides*



2	R^1	R^2	3	Yield(%)**	2	R^1	R^2	3	Yield(%)
2a	$-(CH_2)_4-$		3a	85	2e	H	n-C_3H_7	3e	55
2b	$-(CH_2)_3-$		3b	81	2f	H	iso-C_3H_7	3f	50
2c	H	CH_3	3c	25	2g	H	n-C_4H_9	3g	70***
2d	CH_3	CH_3	3e	29	2h	H		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 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,[5] 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 α,β-unsaturated amides which can be readily prepared from N-methylformamide and α,β-unsaturated carboxylic acid chlorides, and hence will provide a convenient synthetic method for alkyl-substituted azetidine-2,4-diones.

References and Notes

1) K. Maruyama, T. Ishitoku, and Y. Kubo, J. Am. Chem. Soc., 101, 3670 (1979). Kanaoka et al. independently reported α-cleavage reaction of cyclic imides. Y. Kanaoka, H. Okajima, and Y. Hatanaka, J. Org. Chem., 44, 1749 (1979).
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).
5) A. C. Poshkus and J. E. Herveh, J. Org. Chem., 30, 2466 (1965), and references are cited therein.

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