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PHOTOCHEMICAL CYCLIZATION OF ACRYLIMIDE DERIVATIVES

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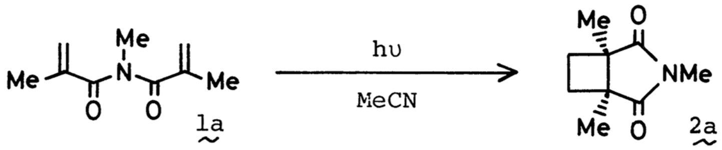
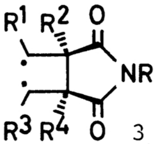
Upon irradiation N-methylmethacrylimide (**1a**) cyclized to give cis-1,3,5-trimethyl-3-azabicyclo[3.2.0]heptane-2,4-dione (**2a**) in a yield of 66%. **2a** gave 1,2-dimethylcyclobutane-cis-1,2-dicarboxylic acid by alkaline hydrolysis. Several other acrylimide derivatives were found to give similar results upon irradiation.

Photochemical cyclization of N-methylmethacrylimide and other analogs was investigated. Interestingly, this photocyclization gave only one of possible stereoisomers, i.e., cis isomer, enabling this reaction to have a high synthetic utility. Thus, we extended the photocyclization of acrylimide derivatives for synthesizing alkyl substituted cis-3-azabicyclo[3.2.0]heptane-2,4-diones. Once Lalonde and Davis reported photolysis of trans-cinnamimide to afford β-truxinimide and cinnamamides,[1)] but their reaction was limited to the compound.



Typically, N-methylmethacrylimide (**1a**, 1.3 mmol) in 25 cm^3 of acetonitrile was irradiated in a quartz tube with a 120 W low-pressure Hg lamp after bubbling N_2 gas. After 3 h (conversion ~90%), chromatography on silica gel gave cis-1,3,5-trimethyl-3-azabicyclo[3.2.0]heptane-2,4-dione (**2a**, mp 95-96 °C), a cyclized product, in a yield of 66%. The structure of **2a** was deduced from its spectroscopic properties: ^{1}H NMR ($CDCl_3$) δ 1.28 (s, 6 H), 1.98 (dd, 2 H, J = 2,7 Hz), 2.34 (dd, 2 H, J = 2,7 Hz), 3.05 (s, 3 H); IR (KBr) 1737, 1670 cm^{-1}; m/e (%, rel intensity) 167 (M^+, 20), 139 (M^+-C_2H_4, 50), 80 (100). Other examples are summarized in Table.



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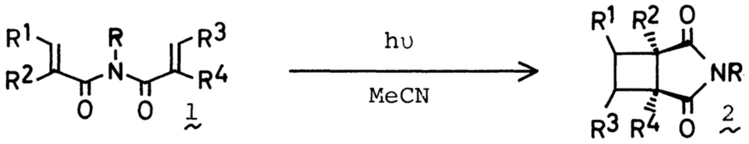
Srinivasan et al. suggested that in the photocyclization of dienes the initial step was the formation of a five membered ring.[2)] According to the result, in this reaction 1,4-biradical **3** which has

Table.



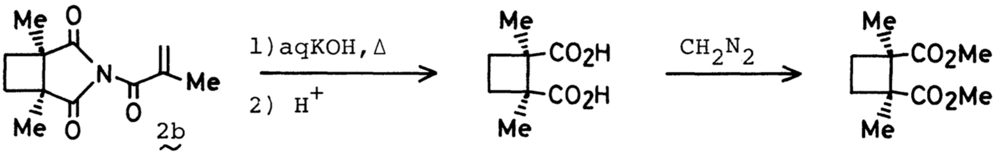
1	R^1	R^2	R^3	R^4	R	Irra.Time(h)	Yield(conv.%)*
1a	H	Me	H	Me	Me	3	66(90)
1b	H	Me	H	Me	$COC(Me)=CH_2$	23	82(100)
1c	H	Me	H	Me	Ph	7	30(88)**
1d	H	Me	H	i-Pr	Me	7	51(95)**
1e	H	i-Pr	H	i-Pr	Me	7	72(86)**
1f	H	Me	H	n-Hex	Me	7	45(90)**
1g	H	n-Hex	H	n-Hex	Me	15	60(100)
1h	$-(CH_2)_4-$		$-(CH_2)_4-$		Me	10	50(100)***

* Yield was calculated on the basis of the consumed amount of **1**.

** NMR yield.3) *** A mixture of three stereoisomers.

a five membered ring of succinimide would be initially produced and bond to give cyclobutane ring. This assumption could explain the stereorandomization at C-6 and C-7 positions of **2** in the reaction of **1h**.4)

This photocyclization gives a good synthetic method for alkyl substituted cis-3-azabicyclo[3.2.0]heptane-2,4-diones, and in addition the products can be transformed to cyclobutane-cis-1,2-dicarboxylic acid derivatives. After hydrolysis in alkaline solution and treatment with diazomethane, **2b** gave 1,2-dimethylcyclobutane-cis-1,2-dicarboxylic acid dimethyl ester (68%).5) Now, scope and limitation are being studied.



References and Notes

1) R. T. Lalonde and C. B. Davis, Can. J. Chem., 47, 3250 (1969).
2) R. Srinivasan and K. H. Carlough, J. Am. Chem. Soc., 89, 4932 (1967).
3) Determined from the relative intensities of NMe proton signal of **2d**, **2e**, and **2f** and OMe proton signal of 1,4-dimethoxybenzene (internal standard).[in case of **2c** done from Me(R^2,R^4) proton signal]
4) The structures of these isomers are under investigation. Photochemical reaction of β,β'-dialkyl substituted **1** was studied for the several imide derivatives to give the mixtures of stereoisomers at C-6 and C-7 positions of 3-azabicyclo[3.2.0]heptane. Details on the distribution of these isomers will be reported elsewhere.
5) This acid was synthesized from methacrylonitrile in a poor yield. C. J. Albisetti, D. C. England, M. J. Hogsed, and R. M. Joyce, J. Am. Chem. Soc., 78, 472 (1956).

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