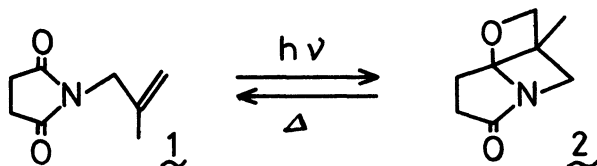


OXETANES DERIVED FROM N-METHYLGLUTARIMIDE
AND THEIR ISOMERIZATION IN ACIDIC MEDIA

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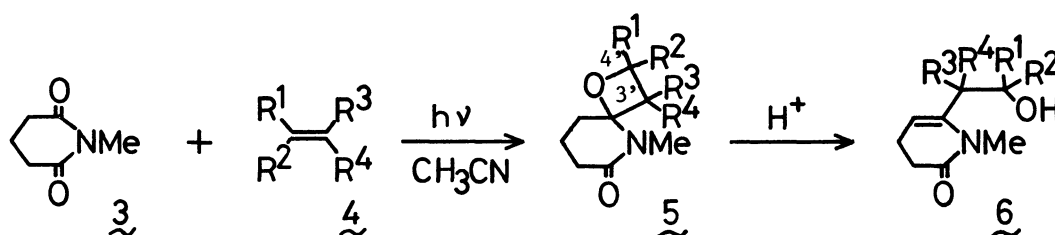
Irradiation of an acetonitrile solution of N-methylglutarimide 3 and an olefin 4 gave oxetanes 5 in a high yield. The oxetanes 5 were converted smoothly to homoallyl alcohols, 3,4-dihydro-6-(2-hydroxyalkyl)-1-methyl-2(1H)-pyridones 6 by refluxing in acidic media.

Some of authors have reported that the irradiation of N-(2-methylallyl)-succinimide 1 underwent an intramolecular Paterno-Büchi reaction to give a tricyclic oxetane 2, but from the latter 2 was regenerated again thermally.¹⁾ Now,



we extended the reaction to N-methylglutarimide 3 and olefins 4a-f. In general, oxetanes were obtained in high yields as shown in Table. The oxetanes were ascertained to isomerize to give 3,4-dihydro-6-(2-hydroxyalkyl)-1-methyl-2(1H)-pyridones by refluxing in acidic media. Thus we confirmed the synthetic potentiality of the intermolecular Paterno-Büchi reaction of glutarimides combined with the acid catalyzed isomerization of the obtained oxetanes to give 3,4-dihydro-6-(2-hydroxyalkyl)-1-methyl-2(1H)-pyridones.

Typically, an acetonitrile solution of N-methylglutarimide 3 (0.4 M) and isobutylene 4a (ca. 1.3 M) was irradiated with a 120-W low-pressure Hg-lamp for approximately 35 hours. At this stage the imide was completely consumed. After evaporation of the solvent and excess isobutylene, distillation of the residue gave a colourless oil of oxetane 5a (85-90 °C / 0.025 Torr, Kugelrohr, 91% yield based on the starting imide), containing a small amount of isomeric oxetane (<5%). 5a; ¹H NMR (CCl₄) δ 1.16 (s, 3H, Me), 1.41 (s, 3H, Me), 2.1-2.8 (m, 6H), 3.04 (s, 3H, NMe), 3.96 and 4.18 (ABq, J=6 Hz, 2H, OCH₂); IR (neat) 1645, 961 cm⁻¹; MS (20 eV), m/e (rel intensity) 183 (M⁺, 14), 166 (18), 153 (100), 138 (30); satisfactory elemental analysis. The oxetane 5a was isomerized to a homoallyl alcohol 6a by refluxing in benzene in the presence of an acid catalyst (formic acid).²⁾ 6a; isolated yield 80%; bp 130-5 °C / 0.012 Torr; ¹H NMR (CCl₄) δ 1.41 (s, 6H, Me), 2.0-2.4 (m, 4H), 3.12 (s, 3H, NMe), 3.58 (s, 2H), 3.8 (s, 1H, OH), 5.57 (t, J=6 Hz, 1H); IR (neat) 3370, 1645 cm⁻¹; MS (20 eV), m/e (rel intensity) 183 (M⁺, 82), 166 (100), 153 (50),



Table

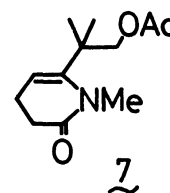
4	R ¹	R ²	R ³	R ⁴	Products			
					Yield(%) ^{a)}	Bp(°C / Torr) ^{b)}	Isomer ratio	
4a	H	H	Me	Me	5a	91	85-90 / 0.025	20 / 1
4b	H	H	Me	n-Pr	5b	79	88-92 / 0.025	1 / 1 ^{c)}
4c	H	Me	Me	Me	5c	91	85-92 / 0.03	20 / 1 ^{d)}
4d	H	Et	Me	Me	5d	73	90-95 / 0.03	
4e	Me	Me	Me	Me	5e	52	60-85 / 0.01 (mp 120-2°C)	
4f	H	-(CH ₂) ₄ -		H	6f	58	120-40 / 0.01 (mp 110-2°C)	

a) Isolated yield. b) Kugelrohr. c) For isomers at C3' position (R³ and R⁴).
d) For isomers at C4' position (R¹ and R²).

152 (50), 124 (54), 110 (59); satisfactory elemental analysis. The alcohol 6a was further converted to its acetate 7 (bp 85 °C / 0.025 Torr).

Other examples are summarized in Table. Cyclohexene 4f also reacted with 3 to give an oxetane which was identified by means of ¹H NMR spectrum. However, distillation of the oxetane resulted in the formation of isomerized homoallyl alcohol 6f.³⁾

6-Alkyl-3,4-dihydro-1-methyl-2(1H)-pyridones have been prepared by dehydration of acyclic δ-oxo-amides only with difficulty.⁴⁾ Since 6 is derived to 6-alkyl-1-methyl-2(1H)-pyridones by treating with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone,⁵⁾ synthetic utility of oxetanes derived from glutarimides *via* simple photochemical procedure should be emphasized.



References and Notes

- 1) K. Maruyama and Y. Kubo, *J. Org. Chem.*, **42**, 3215 (1977).
- 2) The isomerization was observed only by refluxing the oxetane 5a in benzene without acid catalyst. However, in the presence of 1,8-diazabicyclo[5,4,0]-7-undecene the isomerization was completely suppressed.
- 3) Other oxetanes in Table similarly isomerized to the corresponding homoallyl alcohols 6 in the presence of an acid catalyst.
- 4) R. Lukeš and J. Gorocholinskij, *Collection Czech. Chem. Commun.*, **8**, 223 (1936); R. Lukeš and M. Černý, *ibid.*, **23**, 946 (1958); R. Lukeš, A. Fábryová, S. Doležal, and L. Novotný, *ibid.*, **25**, 1063 (1960).
- 5) A. I. Meyers, R. L. Nolen, E. W. Collington, T. A. Narwid, and R. C. Strickland, *J. Org. Chem.*, **38**, 1974 (1973).

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