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

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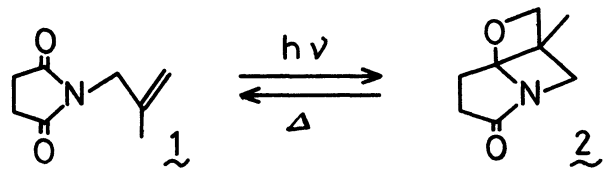
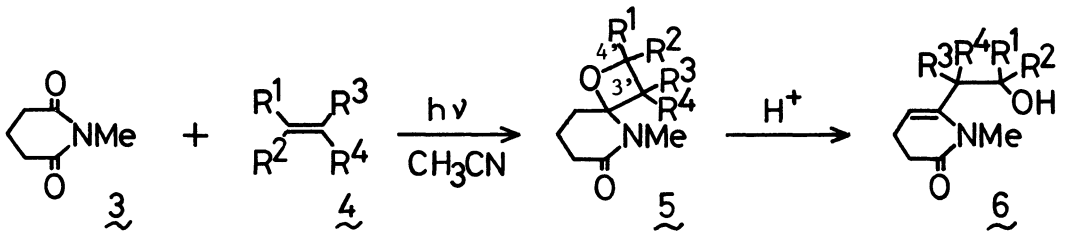
Irradiation of an acetonitrile solution of N-methylglutarimide 3 and an olefin 4 gave oxetanes 5 in a high yield. The oxetanes 5 were converted smoothly to homoallyl alcohols, 3,4-dihydro-6-(2-hydroxyalkyl)-1-methyl-2(1*H*)-pyridones 6 by refluxing in acidic media.

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 1 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(1*H*)-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(1*H*)-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; ^{1}H NMR (CCl_4) 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, OCH_2); 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; ^{1}H NMR (CCl_4) 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),

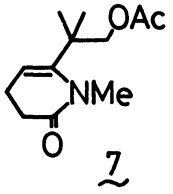


Table

4	R¹	R²	R³	R⁴	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	-(CH₂)₄-		H	6f	58	120-40 / 0.01 (mp 110-2°C)	

a) Isolated yield. b) Kugelrohr. c) For isomers at C3′ position (R^3 and R^4). d) For isomers at C4′ position (R^1 and R^2).

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 ^{1}H 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(1*H*)-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(1*H*)-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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