Generation of an Aliphatic Methyleneketen. Photolysis of *N*-Methyl-4,4-dimethyl-3-isopropylideneazetidin-2-one

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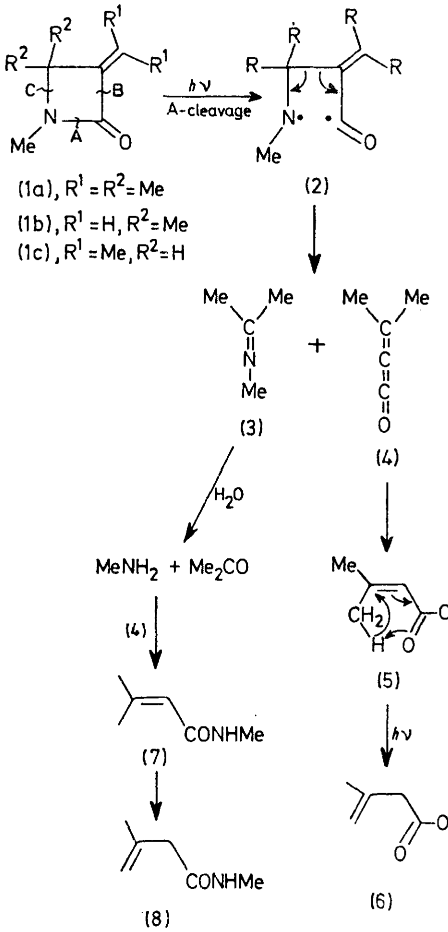
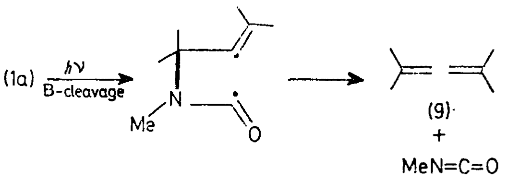
Summary The photofragmentation of *N*-methyl-4,4-dimethyl-3-isopropylideneazetidin-2-one gives exclusively dimethylmethyleneketen and isopropylidene-*N*-methylamine.

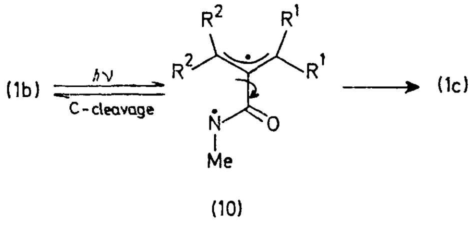
ALTHOUGH ketens are known to be involved in numerous reactions and have proven to be valuable synthetic intermediates, attempts at preparing methyleneketens have been largely unsuccessful.[1] The photochemical generation of a series of phenylmethyleneketens[2] represents a singular success in this area although an attempt to generate a purely aliphatic member of this class of compounds was not successful.[2a]



In view of the fact that lactams are known to undergo photochemical C–N bond cleavage (Norrish Type I) much more efficiently than γ hydrogen abstraction (Norrish Type II),[3] the β lactam system (**1**) appeared to be a suitable precursor to aliphatic methyleneketens.

Irradiation of (**1a**) in methanol solution with 254 nm light led to the isolation of the ester (**6**) (56%, distillation) in addition to a small quantity of the amide (**8**) which was isolated by preparative g.l.c. on the distillation residue.





G.l.c. analysis on the reaction mixture showed that (**6**) was a secondary product from photoisomerization (deconjugation) of the initial photoproduct which was subsequently isolated and identified as the ester (**5**). The, obvious precursor to (**5**) is the novel methyleneketen (**4**) which is trapped by methanol under the reaction conditions. Initial[4,5] bond A cleavage in (**1a**) followed by cleavage of the transannular bond explains the formation of (**4**) and the imine (**3**) which was also detected, whereas (**7**) presumably results from reaction of (**4**) with a small amount of methylamine formed from partial hydrolysis of (**3**). G.l.c. analysis showed that the allene (**9**), which would result from bond B cleavage,[4,6] was not present in the reaction mixture. A reaction initiated by bond C cleavage[4] could also result in the formation of (**9**), or lead to starting material isomerization *via* rotation around the C(O)–C bond in the biradical (**10**) followed by reclosure. A similar process has been reported,[2] and it should be detectable as a (**1b**) → (**1c**) isomerization if it occurs. When (**1b**) was irradiated until only 25% of the starting material remained† no evidence was found for the formation of (**1c**), indicating that if bond C cleavage occurs at all, reclosure is much faster than C(O)–C bond rotation.

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† The expected product of this reaction, methyl acrylate, was not detected but it was shown that methyl acrylate was unstable to the reaction conditions. Similar results were obtained by Hart and his co-workers (ref. 2a) who also failed to observe methylacrylate as a product in their system. The photodeconjugation of (**5**) is perhaps fortuitous since the product, (**6**), has ϵ *ca.* 0 at 254 nm and is not subject to further photodegradation.

[1] D. Borrmann in 'Methoden der Organischen Chemie', Vol. III, Georg Thieme Verlag, Stuttgart, 1968.

[2] (a) H. A. Hart, D. L. Dean, and D. N. Buchanan, *J. Amer. Chem. Soc.*, 1973, **95**, 6294; (b) D. L. Dean and H. A. Hart, *ibid.*, 1972, **94**, 687; a series of methyleneketens have been generated by flash pyrolysis techniques: R. F. C. Brown, F. W. Eastwood, and G. L. Mullen, *ibid*, 1976, **98**, 7421; R. F. C. Brown, F. W. Eastwood, and K. J. Harrington, *Austral. J. Chem.*, 1974, **27**, 2373.

[3] C. H. Nicholls and P. A. Leermakers, *J. Org. Chem.*, 1970, **35**, 2754; P. H. Mazzocchi and M. Bowen, *ibid.*, 1976, **41**, 1279; P. H. Mazzocchi, J. Thomas, and F. Danisi, *J. Polymer. Sci.*, Part B, 1975, **13**, 737.

[4] M. Fisher, *Chem. Ber.*, 1968, **101**, 2669.

[5] H. L. Ammon, P. H. Mazzocchi, W. J. Kopecky, H. J. Tamburin, and P. H. Watts, *J. Amer. Chem. Soc.*, 1973, **95**, 1968.

[6] Only C(O)–N bond cleavage occurs in the homologous pyrollidones: P. H. Mazzocchi and J. J. Thomas, *J. Amer. Chem. Soc.*, 1972, **94**, 8281.