

SYNTHESIS OF MULTICYCLIC KETO LACTAMS BY THE PHOTO-
RING-EXPANSION OF N-(1-ADAMANTYL)SUCCINIMIDES¹

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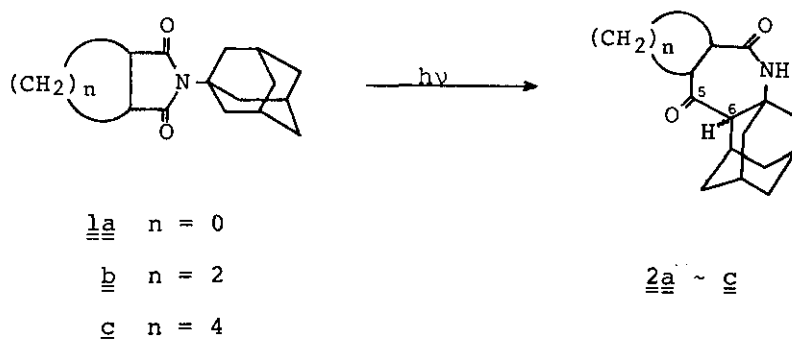
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Upon irradiation N-(1-adamantyl)succinimides with carbocyclic substituents on the imide ring undergo the ring-expansion reaction in fairly good yields affording various multicyclic keto lactam systems.

In our recent reports,^{2,3} it has been shown that N-substituted alicyclic imides undergo photocyclization with ring-expansion to afford medium ring-sized keto lactams which could be synthesized only with difficulty by conventional methods. For an extensive application of this novel synthetically useful reaction to construct multicyclic heterocycles, we now wish to report the photocyclization of N-(1-adamantyl)succinimides (1), which have a typical cage-substituent on imide nitrogen.

The imides (1a-c) used were prepared by condensation of 1-

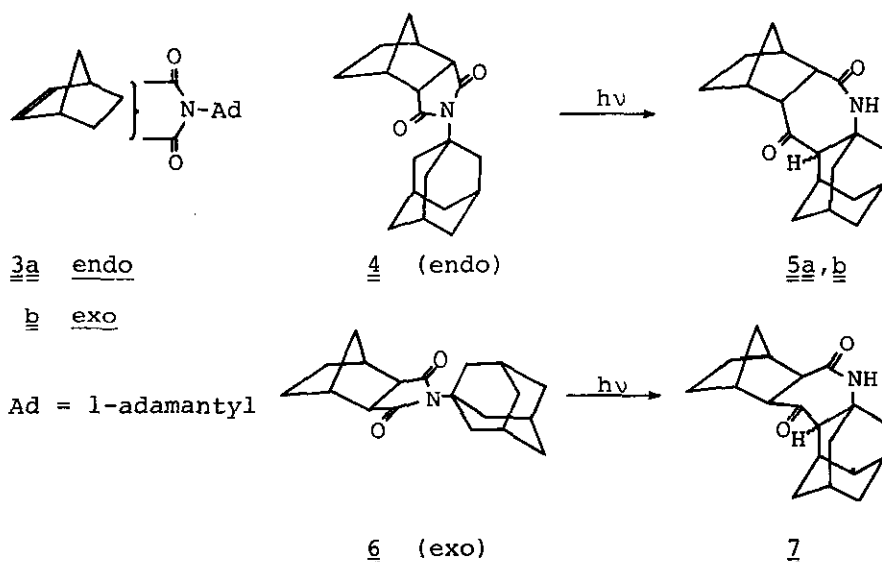
adamantanamine and the appropriate anhydride. A solution of imides (1a~1c) in acetonitrile (10 mM) was irradiated with a 60 W low-pressure mercury lamp at room temperature for 3 hr under a nitrogen atmosphere. Expected cyclization products were obtained in fairly good yield (2a : 78%, mp 209-210°; 2b : 74%, mp 177.5-182.5°; 2c : 57%, mp 203-7°), after purification of photo-



products by column-chromatography (silica gel) followed by recrystallization. The structural assignment of keto lactams (2) were deduced from their spectra and elemental analyses.⁴ In a representative example, identification of 2c was based on the elemental analysis and the spectral data [ir(Nujol) 3270, 3200, 3070 cm^{-1} (NH), 1690 cm^{-1} (C=O), 1645 cm^{-1} (amide); nmr(CDCl_3) δ 5.84, 5.36(broad, NH), 3.62, 3.44(broad-s, $\text{C}_6\text{-H}$); mass m/e 287 (M^+)]. Keto lactams obtained from 1b and 1c were evidenced to be approximately 1 : 1 epimeric mixture from their nmr spectra, respectively.

Further exploration of the reaction for syntheses of complex keto lactams were demonstrated by the photolysis of compounds 4

and 6, obtained from the catalytic hydrogenation of bicyclic imides (3a,b), which were prepared by thermal condensation of corresponding anhydride⁵ and 1-adamantanamine, respectively.



Irradiation of an acetonitrile solution of 4 and 6, in the similar manner as described for 1, gave 5a,b and 7 in moderate yield [5a: 17%, mp 235-7°; 5b: 12%, mp 219-221°; 7: 47%, mp 272-3.5° (in sealed tube)], respectively.⁴ As mentioned in the previous communication,^{1c} it was reasonably assigned that endo and exo configurations of the starting imides (4,6) were retained in the products (5a,b,7) during the reaction. Only in the case of 4, separable stereoisomeric products (5a,b) were obtained by successive recrystallization.

In all cases described none of the elimination product was detected from the photo-product of N-(1-adamantyl)succinimides,

indicating the prominent utilities of this reaction for syntheses of multicyclic keto lactams.

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