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PHOTOLYSIS AND THERMOLYSIS OF 3-AZIDO-2-CYCLOHEXEN-1-ONES

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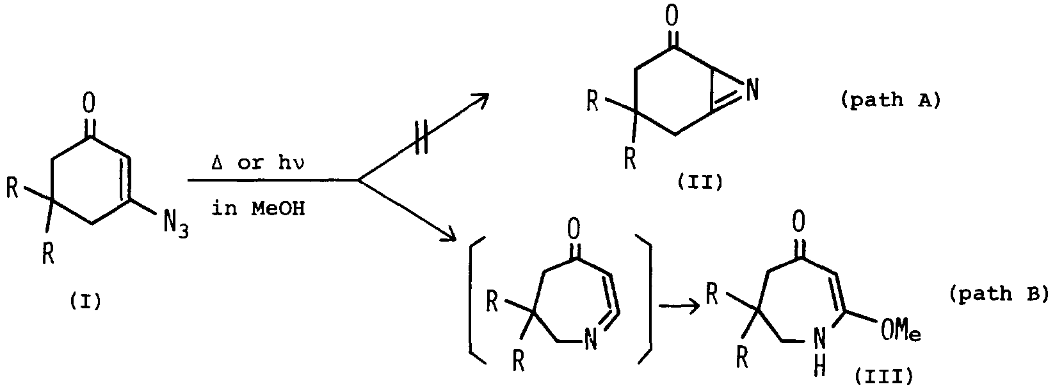
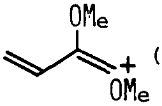
Although photo and thermal decompositions of 3-azido-2-cyclohexen-1-one (I) are expected to proceed in both reaction courses of the azirine formation (path A) and the Curtius-type rearrangement (path B),[1] it has been reported to give no azirine (II) but only a Curtius-type rearrangement product (III).[2,3]



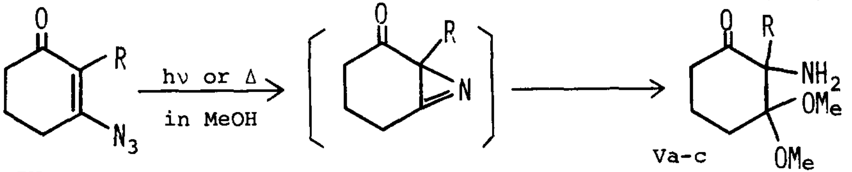
It is of interest to examine whether the reaction giving the azirine (II) does not indeed occur, and further to clarify the factors controlling both reaction courses, path A and B. That the azirine (II) could not be formed in the case of I is assumed to be ascribed partly to a torsional strain[1] of the fused azirine ring, and so, an increase in stability of the azirine ring of II may make the path A possible. We investigated the photo and thermal decompositions of 3-azido-2-cyclohexen-1-one derivatives and found that the introduction of alkyl function at C-2 position of I caused the preferential azirine formation to give 2-amino-2-alkyl-3,3-dimethoxy-cyclohexanone (V).

Irradiation of a methanolic solution of 2-benzyl-3-azido-2-cyclohexen-1-one (IVa) at room temperature with a 450w high pressure mercury lamp in a Pyrex vessel gave 2-amino-2-benzyl-3,3-dimethoxy-cyclohexanone (Va), mp 68-69°, in 50% yield. Thermal decomposition of IVa was performed by heating a methanolic solution in a sealed bomb at 140-150° for 5 hr, giving also Va in 52% yield. The structure of Va was proved by the following spectral data: IR $\nu_{max}^{CCl_4}$ 3375, 3300 (NH_2), 1710 (C=O), 1180, 1150, 1090 and 1060 cm^{-1} (ketal); NMR (in $CDCl_3$) τ 8.72 (2H, b-s, NH_2, disappeared with D_2O), 8.8-7.2 (6H, m, ring methylene), 7.00 (2H, AB quartet, J=14 Hz, benzyl methylene), 6.84 (3H, s, OCH_3), 6.46 (3H, s, OCH_3) and 3.2-2.6 (5H, m, aromatic proton); MS m/e 263 (M^+). The cyclic ketal structure of Va was further confirmed by the characteristic base peak at m/e 101 ascribed to a fragment peak (i).[4]



(i)

m/e 101



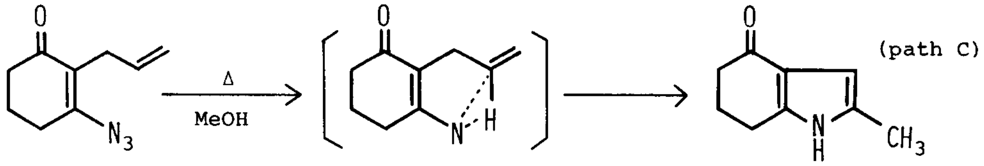
(path A)

IVa-c a; $R=CH_2C_6H_5$, b; $R=CH_3$, C; $R=CH_2CH=CH_2$

Thermolysis and photolysis of 2-methyl- (IVb) or 2-allyl-3-azido-2-cyclohexen-1-one (IVc) similarly gave the α-aminoketal Vb [bp 75-85°/0.045 mmhg (bath temp); IR $\nu_{max}^{CCl_4}$ 3380, 3320, 1720, 1180, 1150 and 1090 cm^{-1}; MS m/e 187 (M^+), 101 (i)] or Vc [bp 100-110°/0.08 mmhg (bath temp); IR $\nu_{max}^{CCl_4}$ 3380, 3320, 1720, 1180, 1150 and 1090 cm^{-1}; MS m/e 213 (M^+) and 101 (i)] as a major product. In the case of pyrolysis of IVc, indole derivative VI [mp 204° (lit. 207°[5]); IR $\nu_{max}^{CHCl_3}$ 3450 (NH) and 1640 cm^{-1} (COC=C-N); NMR (in $CDCl_3$) τ 8.05-7.35 (4H, m, $CH_2\times2$), 7.76 (3H, s, CH_3), 7.20 (2H, t, J=6 Hz, CH_2C=), 3.90-3.70 (1H, m, CH=) and 0.9-0.7 (1H, b-s, NH)] was also obtained along with Vc.

The azirine was not isolated in all these cases, but its presence as a reaction intermediate is inferred from the formation of Va,b,c.[1,6]

The results are summarized in Table. As can be seen in Table substitution of alkyl group at C-2 position in 3-azido-2-cyclohexen-1-ones (I and IV) has



IVc

VI

(path C)

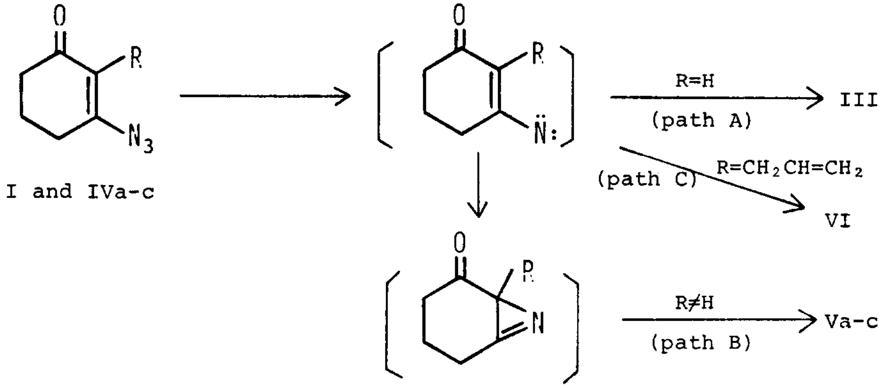
Table

Starting Materials		Reaction Conditions		Yields of Reaction Products			
Compd No.	R	Pyrolysis or Photolysis	Solvent	Azepinone (III)	α-Amino-ketal (V)	Indole (VI)	
I	H	Δ	in MeOH[3]	36			
		hν	MeOH				*
IVa	$CH_2C_6H_5$	Δ	MeOH		52		
		hν	MeOH		50		
IVb	CH_3	Δ	MeOH		53		
		hν	MeOH		71		
IVc	$CH_2CH=CH_2$	Δ	MeOH		30	4	**
		hν	MeOH		27	trace	

*) complex mixture
**) Carbomethoxyethylbenzene was obtained as a minor product.

an important influence on the reaction pathways.

To explain the above results, we propose such a mechanism that decomposition of the 3-azido-2-cyclohexen-1-ones (I and IV) gives, at first, the nitrene intermediate, which changes to the indole (VI), the azepinone (III) via the ketenimine or the α-aminoketal (V) via the azirine as shown in Scheme. In 3-azido-2-cyclohexen-1-one (I), the nitrene causes the Curtius-type rearrangement in preference to the azirine formation. In 2-alkyl-3-azido-2-cyclohexen-1-ones (IV), however, the preferencial azirine formation occurs, giving the α-aminoketal (V), probably because the alkyl function at C-2 stabilizes the produced azirine.[1] The formation of the indole (VI) by the decomposition of IVc strongly suggests[1,7] the existence of the nitrene as the reaction intermediate.



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