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DECOMPOSITION OF 1-AZIDO-1,3-BUTADIENES

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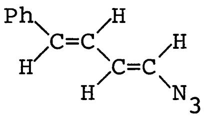
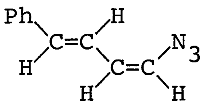
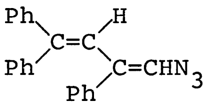
The photolysis and the thermolysis of the title compounds (I) were studied. The photolysis of (I) at low temperature gave 3-alkenyl-1-azirine (II) but at room temperature gave (II), pyrrole (III) or butenonitrile (IV) depending on the nature of the substituents of (I). The thermolysis of (I) gave (III), (IV) or 2H-pyrrole (V).

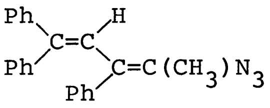
Both the thermolysis and the photolysis of terminal as well as internal vinyl azides gave 1-azirines,[1-3] while β-aryl-vinyl azides and 3-aryl-1-azirines gave indoles accompanied with acetonitrile derivatives when subjected to high temperature.[2,3] On the other hand, 3-alkyl-1-azirines gave nitriles, but no ring expansion products (Δ^2-pyrrolines) were obtained.[3] We now report the decomposition of 1-azido-1,3-butadienes (I) and of 3-alkenyl-1-azirines (II).

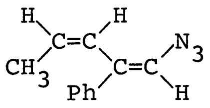
Azides (Ia~Ie) were synthesized by the methods which were previously developed for the synthesis of terminal vinyl azides.[4]


(Ia)


(Ib)


(Ic)


(Id)


(Ie)

Irradiation of the n-hexane solution of (Ia) and (Ib) at room temperature with a 100W high pressure mercury lamp gave 2-phenylpyrrole (IIIa) quantitatively, which was confirmed by mixed melting point with an authentic sample.[5] The fact that the same compound was obtained from both the azide isomers, suggested the existence of a common intermediate such as 3-styryl-1-azirine (IIa). The photolysis at room temperature was monitored by UV spectroscopy. The appearance of isosbestic points (233mμ, 247mμ, 280mμ) indicated that no intermediate could be detected under these reaction conditions.

However, the photolysates of the same azides at lower temperatures (-42~-45°C) showed identical spectra, but different from that of (IIIa), which changed into that of (IIIa) when the solution was warmed to room temperature. The nmr spectrum of this labile photo-product was taken at -32°C in $CDCl_3$ immediately after photolysis at -82°C and shown in figure 1. The doublet at 0τ was assigned to the proton at the 2-position of 1-azirine.$^{3)}$ The chemical shifts and the splitting patterns of the other signals are all consistent with the structure of 3-(trans-styryl)-1-azirine (IIa).

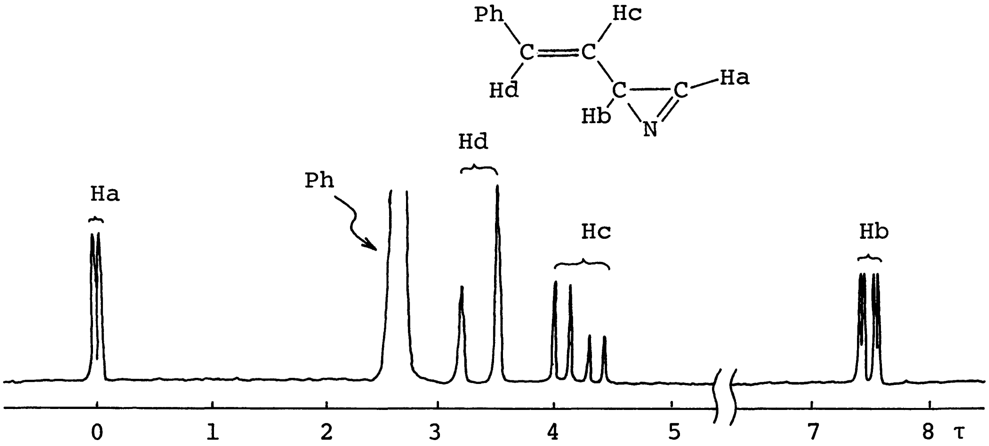


Fig. 1. Nmr spectrum of (IIa) at -32°C in $CDCl_3$.

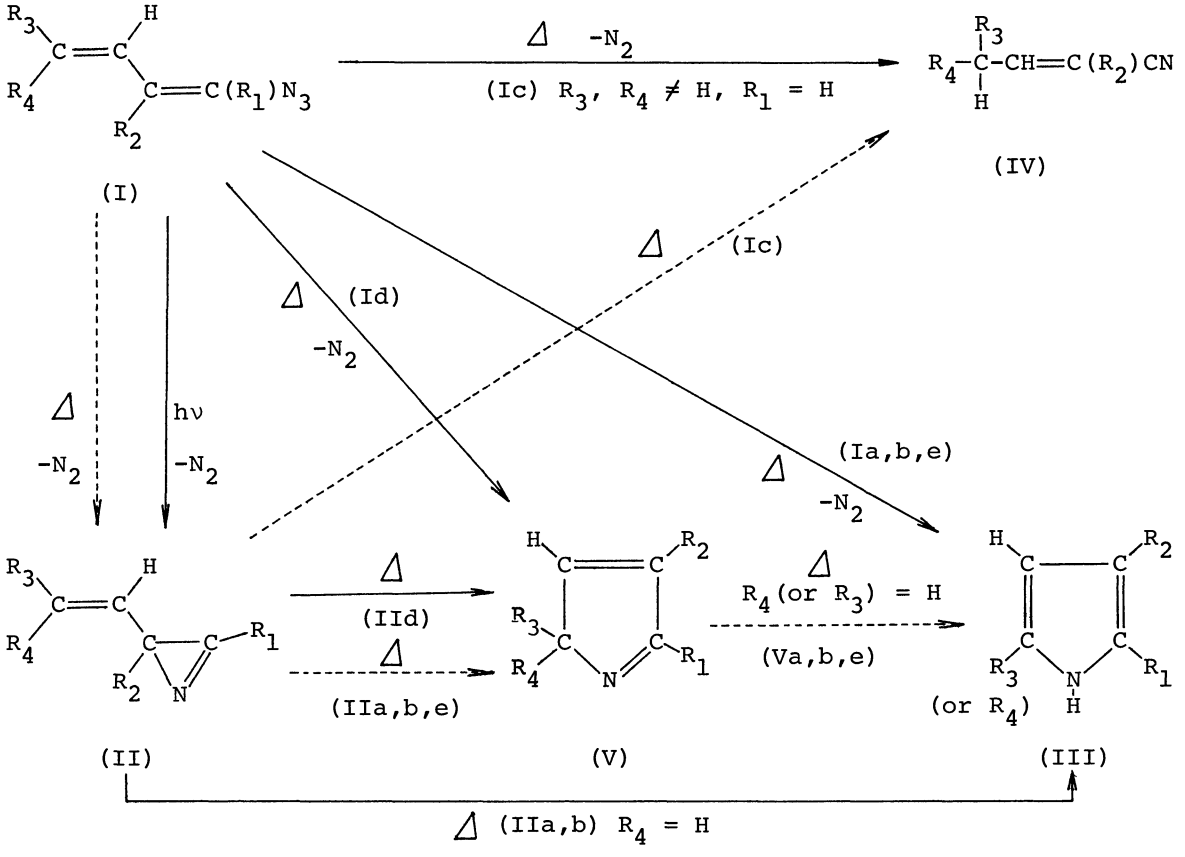
Thermal decomposition of (Ia) and (Ib) was performed by refluxing the n-hexane solution of each azide, and again pyrrole (IIIa) was obtained quantitatively.

However, different compounds were obtained by the photolysis and the thermolysis of (Ic) and (Id), which had two phenyl groups at the 4-position of 1-azido-1,3-butadiene.

On irradiation at room temperature and on refluxing of the n-hexane solution of (Ic) gave white crystalline solids quantitatively, mp 124.0~126.0°C from ethanol; ν max (nujol) $2240cm^{-1}$; λ max (cyclohexane) 262mμ (ε=16,400); m/e 295 (M^+). Catalytic hydrogenation of this compound gave 2,4,4-triphenylbutyronitrile and ozonolysis gave diphenylacetaldehyde and benzoic acid. Therefore, the structure of this compound were established as 2,4,4-triphenyl-2-butenonitrile (IVc).

Photolysis of (Id) gave 1-azirine (IId), which was the only azirine isolable at room temperature in this study. The structure was assigned by the characteristic IR band (1780cm^{-1}) of 2-substituted-1-azirine.$^{1)}$ The thermolysis of (Id) and (IId) by refluxing the n-hexane solution gave the same white crystalline solids quantitatively, mp 113.0~115.5°C from ethanol; ν max (nujol) 1640cm^{-1}. This compound was confirmed to be 5-methyl-2,2,4-triphenyl-2H-pyrrole (Vd) by catalytic hydrogenation to 2-methyl-3,5,5-triphenylpyrrolidine.

Therefore, the decomposition reaction sequence of 1-azido-1,3-butadienes can be summarized as follows;



	R_1	R_2	R_3	R_4	
(Ia)	H	H	Ph	H	(trans-trans)
(Ib)	H	H	Ph	H	(trans-cis)
(Ic)	H	Ph	Ph	Ph	
(Id)	CH_3	Ph	Ph	Ph	
(Ie)	H	Ph	H	CH_3	

We were able to confirm the azirine formation for photolysis but not for thermolysis of all azides examined in this study. This is probably because 3-alkenyl-1-azirines are thermally less stable than 3-alkyl- and 3-aryl-1-azirines. Azirine (IId) was isolated on photolysis at room temperature; this is consistent with the fact that 2-substituted-1-azirines were much more stable than 2-unsubstituted ones.$^{6)}$

Furthermore, quantitative formation of pyrrole (IIIe) was observed for the thermolysis of 1-azido-4-methyl-2-phenyl-1,3-butadiene (Ie). On the other hand, 2,4,4-triphenyl-derivatives (Ic, Id) did not give the corresponding pyrroles. The formation of 2H-pyrrole (Vd), but not pyrrole, from azide (Id) and azirine (IId) may be explained by the fact that 2,2-disubstituted-2H-pyrroles are not so unstable to rearrange to pyrrole derivatives under these reaction conditions.$^{7)}$ In the decomposition of azide (Ic), more stable nitrile (IVc) turned out to be the product preferred to 2H-pyrrole (Vc), the cyclization product, i.e. rearrangement involving hydrogen shift takes place on azirine (IIc), which is produced in the course of the decomposition of azide (Ic).

These typical but versatile reactions of 1-azido-1,3-butadienes may well be attributed to the various fates of 1-azirines on thermal reactions.$^{8)}$

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