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AZIRINE FORMATION BY DECOMPOSITION OF TERMINAL VINYL AZIDES

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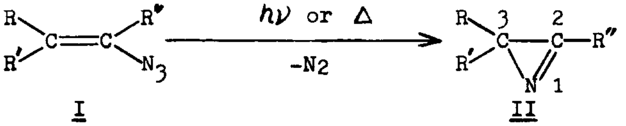
We wish to report that terminal vinyl azides* gave 1-azirines** by both photolysis and thermolysis and some properties of resulted unstable 2-unsubstituted-1-azirines.

It was established that the decomposition of internal vinyl azides* I resulted in the formation of 2-substituted-1-azirines II and has been proved to be general and elegant method for 1-azirine synthesis(1,2,3).



R,R′=Hydrogen, Alkyl, Aryl
R″=Alkyl, Aryl

In the case of terminal vinyl azides, several workers assumed 1-azirine as intermediate for decomposition of the azides(2,3,4,5), but isolation of itself has not been succeeded. Moreover, G.Smolinsky and his coworker concluded that internal vinyl azides formed azirines while terminal vinyl azides did not on thermal decomposition(3). J.H.Boyer and his coworkers reported that β-styrylazide gave phenylacetonitrile in 74% and 8% yield on photolysis and thermolysis respectively(4).

However, recently we found that both cis- and trans-β-styrylazide gave

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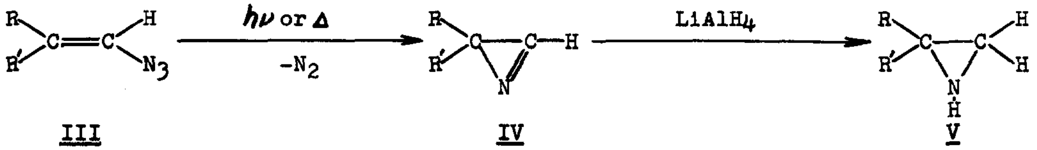
* These terms were proposed by G.Smolinsky(3). Internal vinyl azide is the vinyl azide bearing a substituent other than hydrogen, which is bonded to the carbon bearing the azide group, and terminal vinyl azide is the azide in which a hydrogen atom is bonded to azide bearing carbon.

** The nomenclature of azirine ring system, which A.Hassner proposed(2), is used.

3-phenyl-1-azirine and trace of phenylacetonitrile on both photolysis and thermolysis(6).

In order to make clear the above ambiguity of azirine formation from terminal vinyl azides, we have chosen the following eight azides III and studied their decomposition reaction.



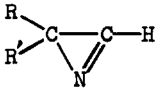
	a	b	c	d	e	f	g	h
R;	$CH_3CH_2CH_2$	$PhCH_2CH_2$	H	CH_3CH_2	Ph	Ph	Ph	H
R';	H	H	$PhCH_3CH_2$	CH_3CH_2	CH_3CH_2	Ph	H	Ph

In each case, photolysis was carried out by irradiation of 3650Å light supplied by 100W high pressure mercury lamp to THF or CCl_4 solution of the azide at -50°C in nitrogen atmosphere. The photolysate was colourless solution but on exposure to air, the solution turned brown. Then immediately after photolysis, the product in THF was reduced by $LiAlH_4$. Nmr spectra of the reduction products were consistent with expected aziridines V respectively. IR spectra of Ve and Vg were identical with independently synthesized corresponding aziridines(7,8). These aziridines have characteristic N-H stretching frequency at about 3200cm^{-1} as usual aziridines have(9). The other reduction products have this IR band. Moreover phenylthiourea derivative of Ve (mp.99°C), showed no melting point depression on admixture with authentic sample(8). These results apparently show that the photolysates of terminal vinyl azides should have three membered ring structure containing one nitrogen atom. This means that azirines are formed on photolysis of terminal vinyl azides.

Azirine formation was also confirmed by IR and nmr spectra. IR (at room temperature) and nmr (at -20°C) spectra of the photolysates were measured in CCl_4 solution immediately after photolyzed in this solvent. The spectral data are shown in Table.

It was reported that the C=N stretching frequency in 2-alkyl- and 2-aryl-azirines occurred near 1775cm^{-1} and 1740cm^{-1} respectively(2). Our compounds, 2-unsubstituted-1-azirines, have no absorption in this region but have their imine absorption at 1650-1665cm^{-1}. This absorption would appear to be anomalous, but is well explained by double bond-single bond mechanical interaction which is derived from bond angle effect and difference of C-C and C-H bond(10). Therefore, this νC=N can be adopted for characteristic band for 2-unsubstituted-1-azirines.

Table. Infrared and Nmr spectra of 2-unsubstituted-1-azirines



	IR(cm^{-1}) C=N stretch	nmr(τ) H on 2-position
IVa	1650	-0.1 (broad)
IVb=IVc	1660	0.3 (broad)
IVd	1665	-0.2 (quintet)
IVe	1650	0.3 (triplet)
IVf	1650	0.1 (singlet)
IVg=IVh***	1655	0.4 (doublet)

*** Reported in our previous paper(6).

Common and characteristic nmr signal, corresponding one proton, of these azirines IV was found at about zero tau. These signals are assigned for the proton on 2-position of 2-unsubstituted-1-azirines. Comparing the chemical shift of strained aldimine proton with that of open chain one, e.g. $CH_3C\underline{\underline{H}}=NCH_2CH_2CH_3$ 2.37τ(11), remarkable deshielding (2.0-2.6ppm) is observed. This phenomenon can be ascribed to anisotropy of azirine ring, because proton on 2-position is situated in the deshielding core of azirine. Similar anisotropy has been observed in cyclopropene series(12) and 3-position proton of azirine(2). Quintet for IVd, triplet for IVe and broad signal for IVa and IVb of this aldimine proton resonance are consequent on long range coupling with methylene on 3-position.

Thermal decomposition of IIIb, IIIc and IIIe was carried out in nitrogen atmosphere by heating the dibutylether solution at 125°C. In each case the azirine IV formation was confirmed by preparation of corresponding aziridine V from decomposition product. G.Smolinsky and his coworker reported that thermolysis of IIIf in boiling xylene gave 3-phenylindole VI and in boiling ethanol gave indole VI and 2,2,5,5-tetraphenyldihydropyrazine VII(3). In our case, in refluxing benzene for one hour the formation of 3,3-diphenyl-1-azirine IVf was confirmed by nmr and IR spectra as shown in Table. Also the presence of indole VI was identified by IR spectrum. This azirine IVf gradually dimerized to dihydropyrazine VII and also gave indole VI on heating in xylene.

Now it comes to conclusion that 1-azirine formation is common and general reaction of terminal vinyl azides as well as internal ones. There is obvious difference in the stability of 1-azirines. The azirines bearing hydrogen on 2-position are so unstable especially for oxygen that it is difficult to isolate them. In 2-unsubstituted-1-azirine series, disubstituted by alkyl or aryl on 3-position azirines IVd, IVe, IVf are more stable than monosubstituted ones IVa, IVb, IVg. Especially 3-alkyl-1-azirines IVa, IVb are so unstable that they decompose exothermically on exposure to air.

The chemistry of these unstable azirines is in progress and will be reported in near future.

REFFERENCES

1. G.Smolinsky, J.Org.Chem.,27,3557(1962). G.R.Harvey and K.W.Rattes, ibid.,31, 3907(1966). A.Hassner and F.W.Fowler, Tetrahedron Letters,1545(1967).
2. A.Hassner and F.W.Fowler, J.Am.Chem.Soc..90,2869(1968).
3. G.Smolinsky and C.A.Pryde, J.Org.Chem.,33,2411(1968).
4. J.H.Boyer, W.E.Krueger and G.J.Mikole, J.Am.Chem.Soc.,89,5504(1967).
5. J.S.Meek and J.S.Fowler, J.Org.Chem.,33,3418(1968).
6. K.Isomura, S.Kobayashi and H.Taniguchi, Tetrahedron Letters, 3499(1968).
7. S.V.Zotova, L.V.Loga and M.Yu.Lukina, Chem.Abst.,64,3447(c)(1966).
8. S.Eguchi and Y.Ishii, Bull.Chem.Soc.Japan,36,1434(1963).
9. A.Lattes, R.Martino and R.M.Noel, Compt.Rend.,c263,49(1966).
10. L.J.Bellamy, Advances in Infrared Group Frequencies, p.21. Richard Clay Ltd., Bungay, Suffolk. (1968).
11. J.F.King and T.Durst, Can.J.Chem.,40,882(1962).
12. K.B.Wiberg and B.J.Nist, J.Am.Chem.Soc.,83,1226(1961).