INTERMOLECULAR TRAPPING OF VINYL NITRENE EQUILIBRATED WITH AZIRINE

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Abstract–Thermal decomposition of 3–azido–1,2–benzo–1,3–cycloheptadiene (1a) gave the fused azirine (2a), which gave pyrrolobenzocycloheptadiene (3a) on heating with dimethyl acetylenedicarboxylate (DMAD). Thermolysis of 1–azidoindene (1b), did not give the azirine, but gave the fused pyrrole (3b) by decomposition in the presence of DMAD. These results provided firm evidence for intermediacy of vinyl nitrenes.

Thermal intramolecular reactions of azirines have been established to be a versatile method for the synthesis of 6– and 7–membered nitrogen containing heterocycles as well as 5–membered ring compounds.[1] Our recent study on thermal behavior of optically active azirine provided kinetic evidence for the intermediacy of vinyl nitrene,[2] which had been occasionally invoked without firm evidence. However, no intermolecular reactions have been reported. Here, we describe the first example of thermally induced intermolecular reaction of azirine which provides firm evidence for vinyl nitrene.

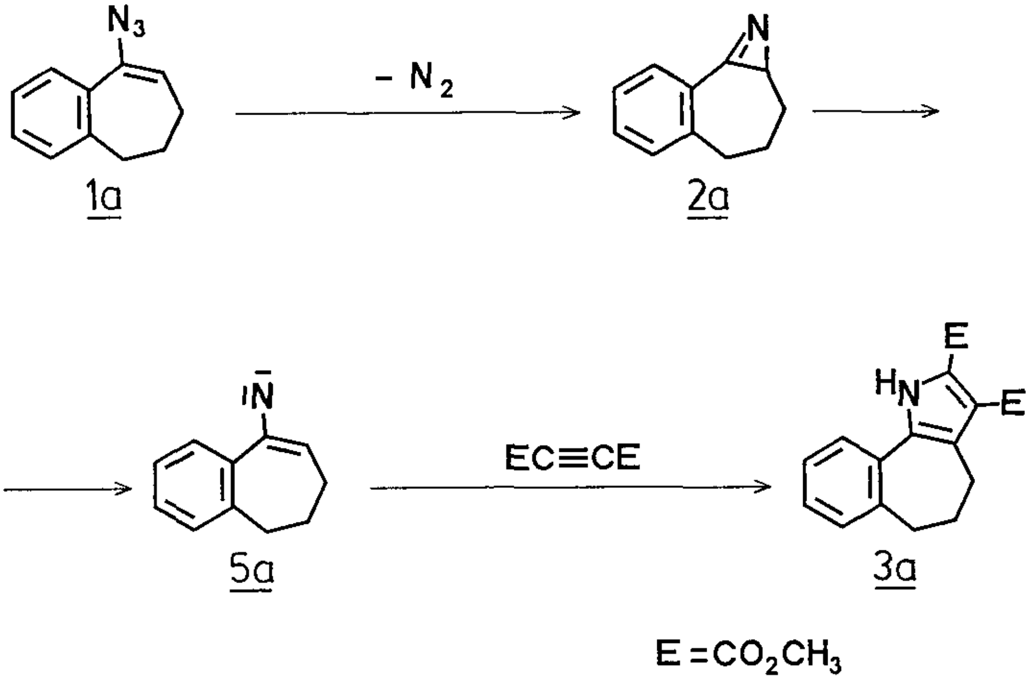
This communication is dedicated to Professor Masatomo Hamana on the occasion of his 75th. birthday.

Heating 2–methy–3–phenyl–2*H*–azirine and 3–methyl–2–phenyl–2*H*–azirine with dimethyl acetylenedicarboxylate (DMAD), dimethyl maleate, or dimethyl fumarate gave no intermolecular reaction products, although formation of vinyl nitrenes was inferred by easy racemization of the optically active specimens of these azirines.[3] The failure would be ascribed to too low concentration of vinyl nitrene to undergo intermolecular reaction.

To increase the equilibrium concentration of vinyl nitrene we chose fused azirines, in which the ground state energy would be raised owing to the additional strain caused by fusing.

In order to obtain strained fused azirine we prepared 1–azidobenzo[1]cyclohepta–1,3–diene (1a) as the precursor by addition of IN_3 to benzocyclohepta–1,3–diene followed by base induced elimination of HI, although azirines fused with rings smaller than cyclooctane and cyclooctene had not been isolated. Thermolysis of 1a in heptane under reflux for 1 h followed by distillation of the resulting pale yellow oil at reduced pressure gave colorless oil. This oil was identified as the expected fused 2*H*–azirine (2a) on the basis of nmr spectrum and sharp ir absorption at 1740 cm^{-1}, characteristic of azirine ring.[4]

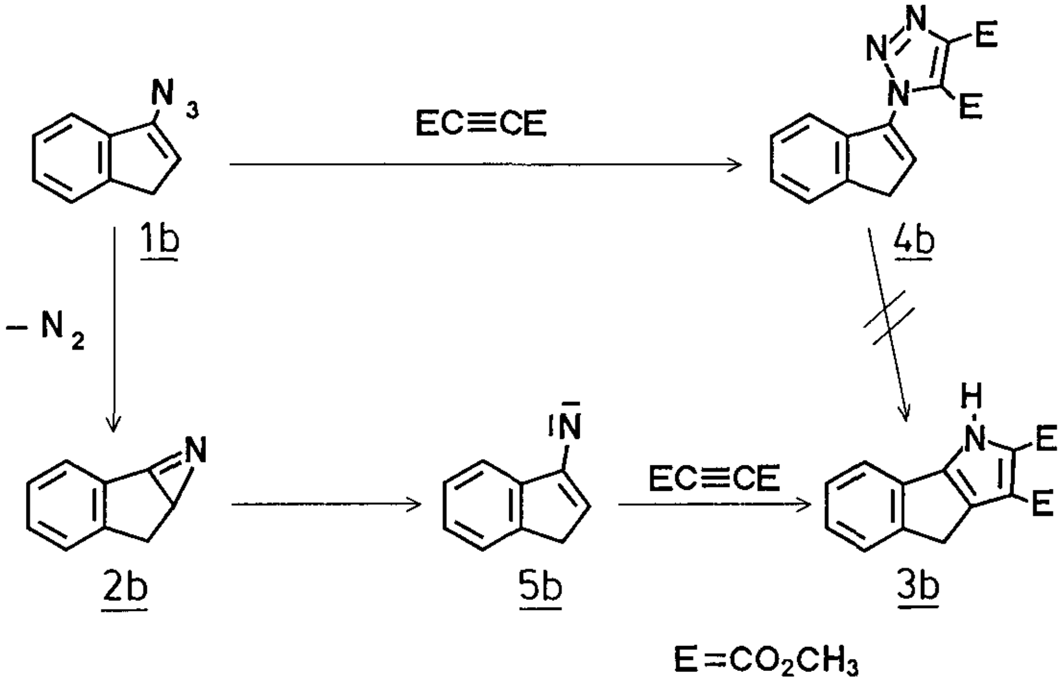
Heating the xylene solution of 2a and DMAD under reflux for 2 h gave a black solution.



Scheme 1

Evaporation of the solvent followed by chromatography on silica gel gave colorless needles (3a), mp 156 – 157°C, in 13% yield. On the basis of spectral data,[4] this compound was assigned as dimethyl pyrrolo[3,2-*b*]benzo-1,3-cycloheptadiene-2,3-dicarboxylate (3a). The structure of 3a was further confirmed by enhancement of an aromatic proton in NOE experiment irradiating the N–H signal.

Attempted isolation of the corresponding azirine (2b) from 1-azidoindene (1b) failed. However, thermal decomposition of 1b by dropwise addition of a xylene solution of 1b into a refluxing DMAD solution of xylene, followed by the same treatment of the resulting black solution as above gave two crystalline compounds. The minor product, mp 244 – 255°C, obtained in 6% yield, had the similar spectral properties[4] as 3a, and was assigned as the fused pyrrole (3b). The other compound, obtained in 41% yield, was easily assigned as the triazole (4b) formed by 1,3-dipolar cycloaddition of the azide with DMAD. Control experiment revealed that the triazole was intact under the conditions of thermolysis of the azide, which showed that the pyrrole (3b) would be formed via 2*H*-azirine (2b) formed in the solution.



Scheme 2

Most plausible mechanism for the formation of pyrroles would be addition of vinyl nitrene (5) to DMAD, as shown in the Schemes 1 and 2. The azirines (2) formed by loss of nitrogen from the vinyl azides are destabilized by fusion to 5- or 7-membered ring. Therefore, on heating the concentration of the vinyl nitrenes (5) equilibrated with azirines (2) becomes high enough to react intermolecularly with acetylene forming fused pyrroles (3).

Formation of fused pyrroles (3a and 3b) furnishes not only the first example of thermally induced intermolecular reaction of azirine but also firm evidence for vinyl nitrene.

REFERENCES AND NOTE

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2. K. Isomura, H. Taguchi, T. Tanaka, and H. Taniguchi, Chemistry. Lett., 1977, 401; K. Isomura, S. Noguchi, M. Saruwatari, S. Hatano, and H. Taniguchi, Tetrahedron Lett., 1980, 21, 3879.
3. K. Isomura, G. Ayabe, S. Hatano, and H. Taniguchi, J. Chem. Soc., Chem. Commun., 1980, 1262.
4. New compounds gave correct analysis. Ir and nmr spectral data of 2a, 3a, 3b, and 4b are listed below;

   2a; Ir (neat, cm^{-1}) 1748

   Nmr (δ in $CDCl_3$) 1.60–2.92 (7H, m), 7.03–7.82 (4H, m)

   3a; Ir (nujol mull, cm^{-1}) 3288, 1730, 1692

   Nmr (δ in $CDCl_3$) 2.02–2.11 (2H, m), 2.77–2.81 (1H, m), 2.87 (2H, t, J=6.0 Hz), 3.89 (3H, s), 3.91 (3H, s), 7.22–7.51 (4H, m), 9.14 (1H, D_2O exchangeable br s)

   3b; Ir (nujol mull, cm^{-1}) 3320, 1740, 1670

   Nmr (δ, in $CDCl_3$) 3.71 (2H, s), 3.92 (3H, s), 3.97 (3H, s), 7.20–7.50 (4H, m), 9.84 (1H, (1H, D_2O exchangeable br s)

   4b; Ir (nujol mull, cm^{-1}) 1738, 1720

   Nmr (δ in $CDCl_3$) 3.65 (2H, d, J=2.4 Hz), 3.90 (3H, s), 4.01 (3H, s), 6.79 (1H, t, J=2.4 Hz), 7.14–7.67 (4H, m)

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