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PROOF OF INTERMEDIACY OF AZIRINE OLIGOMERS FOR DIHYDROPYRAZINE FORMATION FROM 1-AZIRINE. THE STRUCTURES OF THE OILGOMERS

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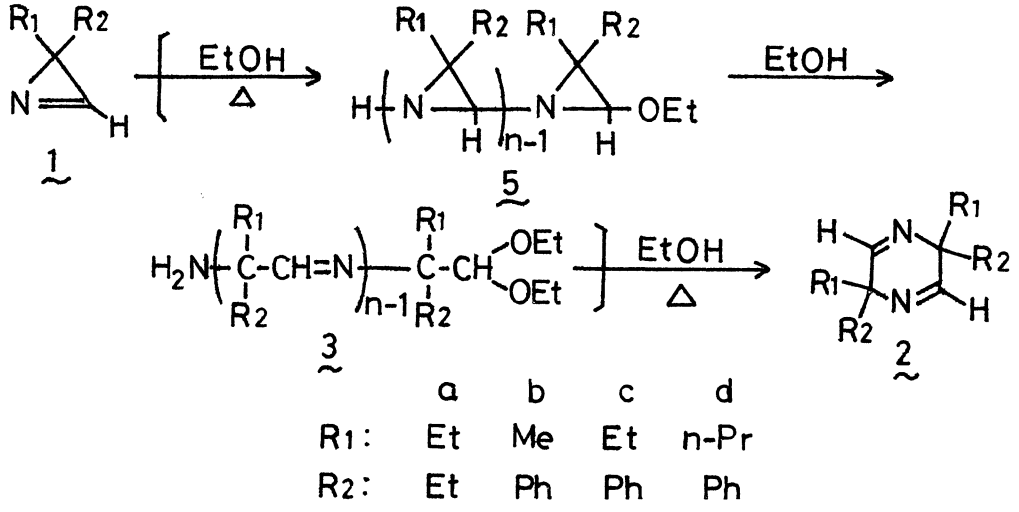
Two kinds of azirine oligomers were isolated as intermediates in dihydropyrazine formation from 1-azirine, and the structures of these oligomers were determined by ir, ^{1}H nmr, and ^{13}C nmr as polyaziridine and polyimine. Polyaziridine rapidly changed into polyimine by addition of ethanol, and heating of the ethanol solution of polyimine gave dihydropyrazine and aminoacetal, which proved the intermediacy of these oligomers for dihydropyrazine formation from 1-azirine.

It is known that 1-azirine 1 often gives its dimer, dihydropyrazine, 2 under various conditions, e.g., by only standing for a long time,[1] by heating,[2] by passing through an alumina column,[3] by action of metal carbonyl,[4] and by treatment with alcoholic HCl.[5] In the case of hydrolysis,[5] the reaction was explained by self-condensation of resulting aminoketone. Possible routes of dimerization were cited in the literatures as follows: (1) dimerization of the intermediate (·C=C-N· or ·C=N-C·) formed in thermal reaction of 1-azirine by C-N or C-C bond fission,[2] (2) dimerization of aza-analogue of π-allylmetal intermediate,[4] but no convincing evidences were stated.

We found the existence of two kinds of oligomers as relatively stable intermediates in the same dimerization reaction of several 3,3-disubstituted-1-azirines 1a-1d. From the interest in these phenomena, azirine oligomers were isolated and its structures were determined.

Scheme 1



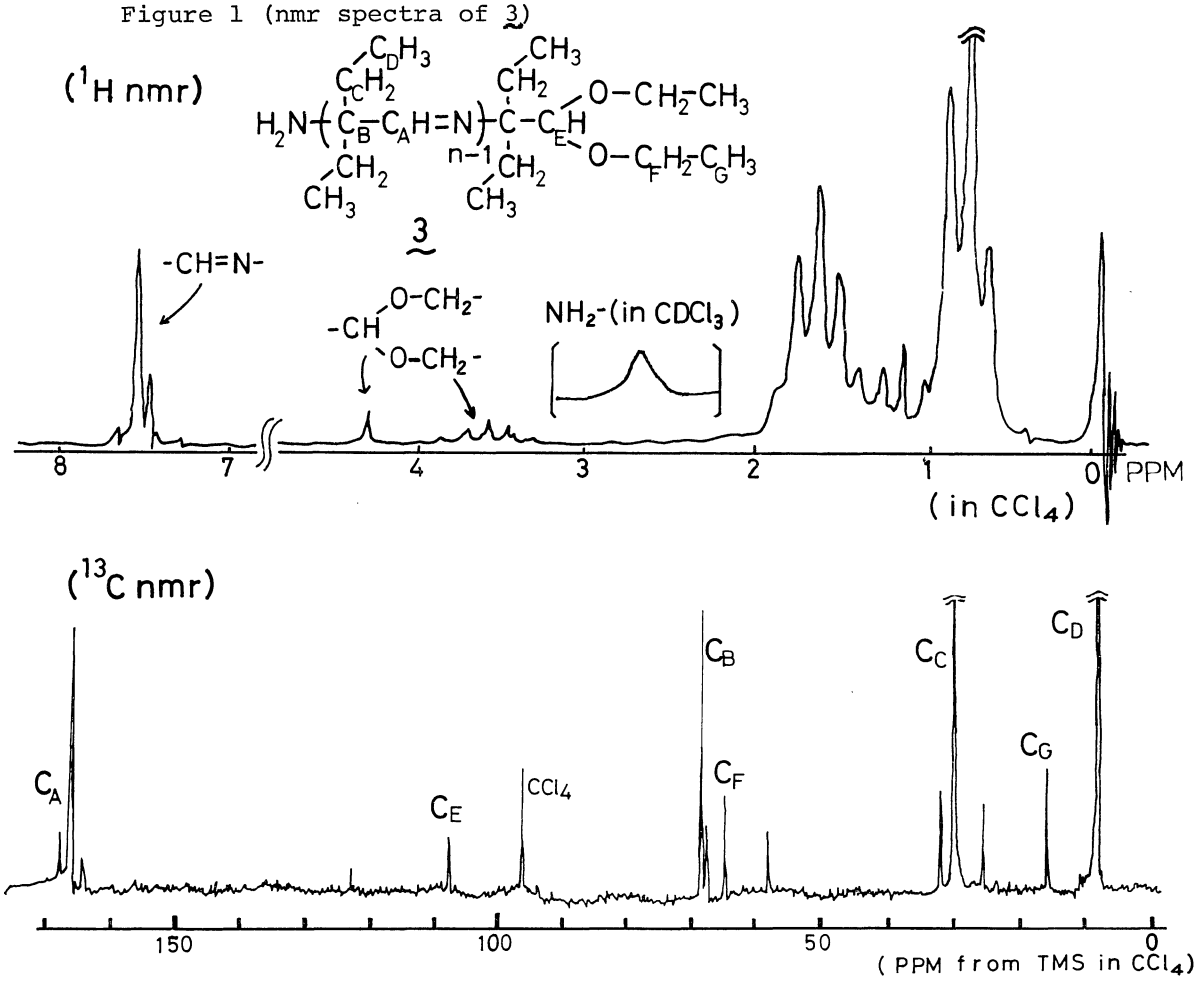
	a	b	c	d
R1:	Et	Me	Et	n-Pr
R2:	Et	Ph	Ph	Ph

An ethanol solution of 3,3-diethyl-1-azirine 1a (0.10g, in 2ml of ethanol) was heated at 80°C for 3 hr in a sealed tube under nitrogen atmosphere. Evaporation of the solvent gave colorless oil 3 of molecular weight 700 (by vapor pressure osmometric method in benzene), which indicates the formation of an oligomer of 1a.

The ir spectrum [a strong band at 1650 cm^{-1} for C=N, and four strong bands at 1020, 1060, 1110, and 1150 cm^{-1} for acetal group] suggested the polyimine structure for this oligomer 3 as shown in Scheme 1. Proton (^1H nmr) and carbon-13 nmr spectra (^{13}C nmr) are shown in Figure 1. The signals at ca. δ 7.5 (^1H nmr) and ca. δ 166.7 (^{13}C nmr) strongly support the presence of imino linkage (-CH=N-). Splitting of these signals into a few peaks can be explained by the difference in positions of -CH=N- in the polymer chain. One end group, diethyl acetal group, was assigned by comparison with the ^1H nmr and ^{13}C nmr of the acetal group of 2-amino-2-ethylbutyraldehyde diethyl acetal 4. [^1H nmr, δ: 4.02(s, methine proton), ABX_3 pattern centered at 3.60(methylene protons), 1.18(t, methyl protons). ^{13}C nmr, δ: 108.2 (methine carbon), 65.1(methylene carbons), 15.5(methyl carbons).] The broad signal at δ 2.67 (^1H nmr in $CDCl_3$) was assigned as NH_2- by the D_2O exchange technique and attributed to the other end group. These results definitely showed the structure of 3 as polyimine as shown in Scheme 1.

Average number of degree of polymerization for 3, $\bar{n}$, was calculated to be 6.8 from molecular weight, and to be 7.2 from the ^1H nmr area ratio of imine proton to

Figure 1 (nmr spectra of 3)



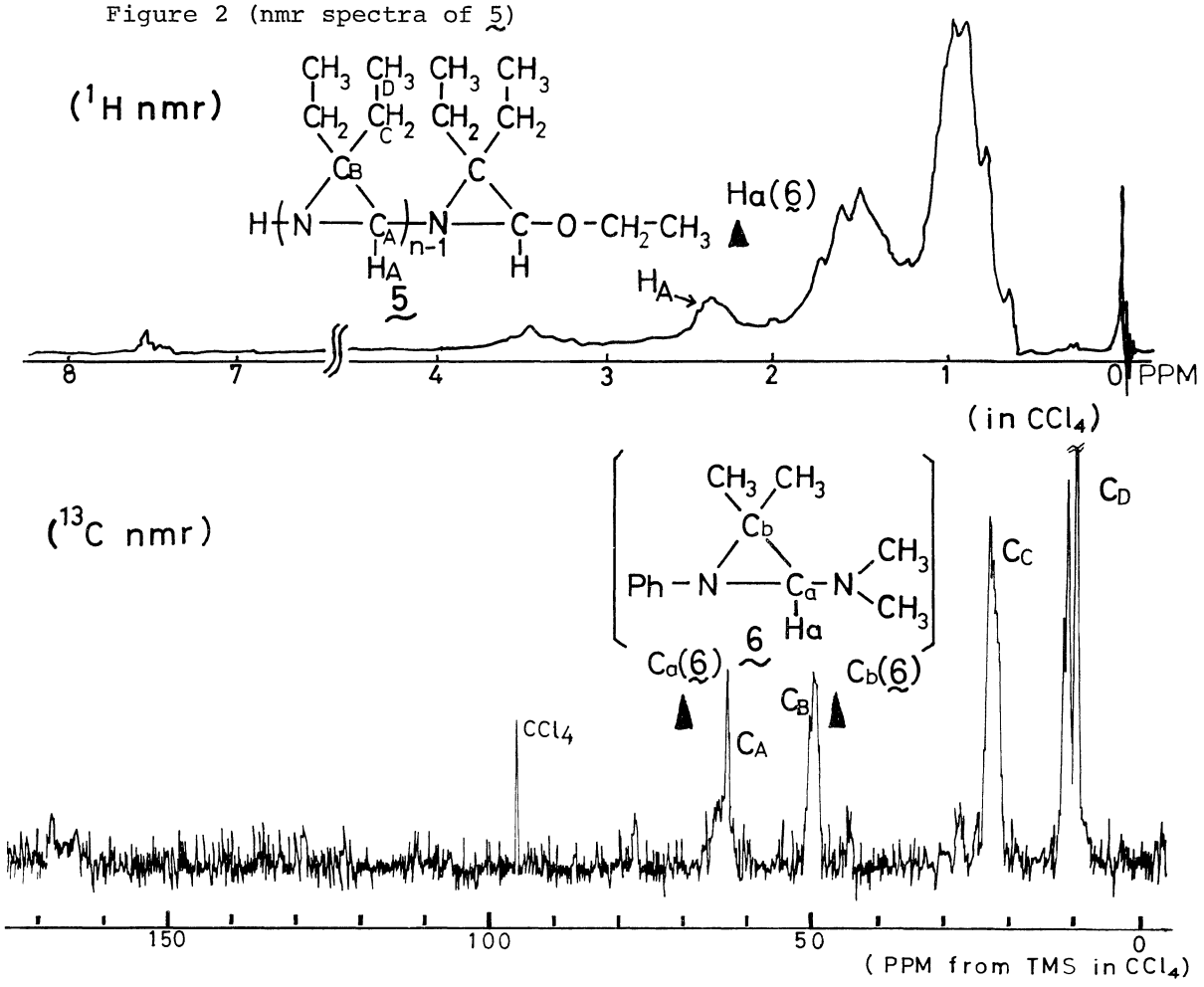
methine proton of acetal group. The agreement of these two calculated $\bar{n}$ values further supports the structural assignment of 3.

Since 3 has NH_2- and diethyl acetal end groups, one may rationalize the formation of 3 by opening of the imino linkage of 1a. One possible pathway to give 3 might be polymerization of 1a utilizing its imino linkage to form polyaziridine 5 followed by ring opening by addition of ethanol across both end positions. An analogous polymerization was reported in the case of cyclopropene.[6]

In an attempt to trap 5, the mixture of 1a and 1/6 mole equivalent of ethanol was heated at 80°C for 6 hr. The resultant viscous product mixture showed quite different ir and ^1H nmr spectra from those of 3, although the presence of a trace of 3 was detectable. The ir spectrum showed a sharp band at 1250 cm^{-1} which was assigned as the ring breathing absorption of aziridine ring.[7] This result suggests the product to be polyaziridine 5. This structure was further confirmed by ^1H nmr and ^{13}C nmr spectra which were shown in Figure 2. Ring proton H_A and ring carbons C_A and C_B were reasonably assigned by comparing these spectra with those of 3,3-dimethyl-2-dimethylamino-1-phenyl-aziridine 6.[8] The broad nmr signals of 5 would be ascribed to the presence of asymmetric carbons C_A and the restricted free rotation of the whole molecule by its crowded structure.

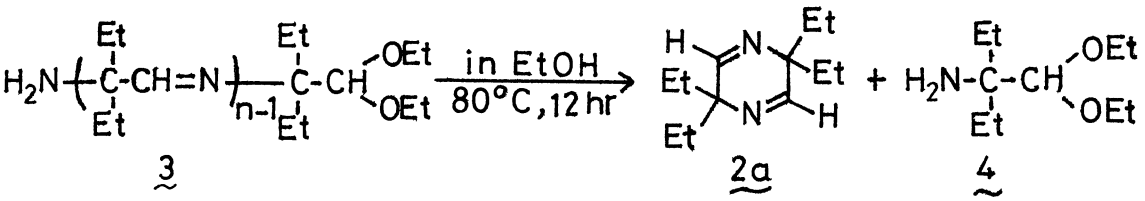
Formation of these two types of oligomers had been postulated for the resinous materials obtained from 1-azirines without final proof.[9] Now, we have fully es-

Figure 2 (nmr spectra of 5)



tablished the structures of these oligomers, by making clear the structures of the end groups as well as the repeating units.

By addition of an excess amount of ethanol to 5 followed by immediate evaporation, 5 completely changed into 3. Heating of the ethanol solution of 3 ($\bar{n}$=7) at 80°C for 12 hr gave 2,2,5,5-tetraethyl-2,5-dihydropyrazine 2a and aminoacetal 4 in the ratio 3:1. This ratio appears reasonable in view of the structure and degree of polymerization of polyimine 3; for the transformation of aminoacetal 4 into dihydropyrazine 2a does occur but very slowly under the conditions of depolymerization.



3 2a 4

Other 1-azirines, 3-methyl-3-phenyl- 1b, 3-ethyl-3-phenyl- 1c, and 3-n-propyl-3-phenyl-1-azirine 1d, also gave oligomers by heating in ethanol, which by prolonged heating in ethanol gave corresponding dihydropyrazine.

From these results, we suggest that there is a pathway from 1-azirine to dihydropyrazine in which two types of oligomers are formed successively as the intermediates.

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