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Ring-Opening Reaction of 2, 2-*gem*-Diphenylaziridine*

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2, 2-*gem*-Diphenylaziridine의 開環反應

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ABSTRACT

A study of the ring-opening reaction of 2, 2-*gem*-diphenylaziridine by treating with acetic acid has been undertaken. The structure of the ring-opened product was confirmed as 1, 1-diphenyl-2-aminoethyl acetate. It is most likely that the reaction proceeds through the cleavage of a bond between nitrogen and tertiary carbon atoms in the aziridine ring, followed by the formation of a carbonium ion intermediate.

要 約

2, 2-*gem*-Diphenylaziridine의 醋酸에 의한 開環反應에서 反應生成物은 1, 1-diphenyl-2-amino-ethyl acetate임을 알았다. 또한 이 開環反應은 aziridine 環 안에 있는 窒素原子와 tertiary 炭素原子 사이의 結合이 切斷되어 中間體로서 carbonium 이온이 形成되는 過程을 거쳐서 進行됨을 알았다.

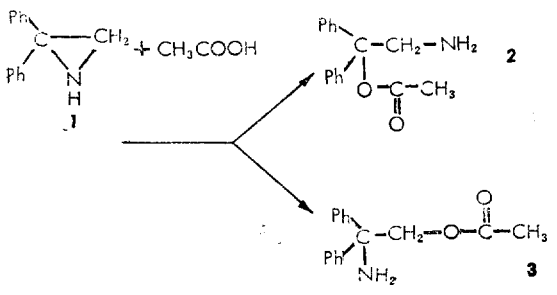
INTRODUCTION

The isomerization of aziridine derivatives has been extensively studied by Heine *et al.*[1] and a group led by Fanta.[2] It is known that most of the isomerization of aziridine compounds proceeds by the scission of a carbon-nitrogen bond, although a few exceptions such as the cleavage of a bond between two carbon atoms in an aziridine ring can be seen in the literature.[1d] Not only the isomerization but various other reactions of aziridine derivatives such as nucleophilic displacement,[3] photochemical reaction,[4] solvolysis,[5] and reaction with organic peracid[6] are also explained by the ring-opening mechanism. Recently, the two groups of Fanta[7] and Sonnett[8] have studied the ring-opening reaction of 1-(*p*-bromophenylsulfonyl)-2, 2-dimethylaziridine and (*p*-2, 2-dimethyl-1-aziridinyl)-N, N, N′, N′-tetramethyl-phosphonic diamide, respectively. Since the compounds they have investigated possess substituents on the nitrogen atom in the aziridine ring and there might be some effects of the substituent bound to the nitrogen atom on the direction of the ring-opening reaction, it seems of interest to investigate the ring cleavage of an aziridine ring which has substituents on the carbon atom and not on the nitrogen atom.

Thus, in this paper, the authors intend to elucidate the direction of the bond cleavage of geminally disubstituted aziridine compound, 2, 2-*gem*-diphenylaziridine

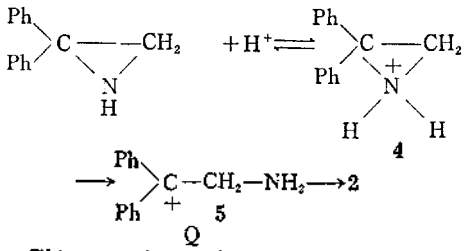
RESULTS AND DISCUSSION

The model compound, 2, 2-*gem*-diphenylaziridine (1) was synthesized by Campbell's method[9] and confirmed by infrared spectrum and elemental analysis. An anhydrous diethyl ether solution of compound 1 was treated with a slight excess of acetic acid at room temperature. The reaction product showed positive to a test for the presence of the amine group by forming Schiff's base with saturated benzene solution of *p*-dimethylaminobenzaldehyde.[10] A strong doublet near 3200 cm^{-1} in the infrared spectrum of the ring-opened product supports the above anticipation for the presence of a primary amine group, and a sharp singlet at 1750 cm^{-1} is ascribed to carbonyl stretching. It is reported[3-8] that aziridine compounds possessing a substituent originally on the nitrogen atom convert into olefinic compounds. Since, however, compound 1 has no substituent on the nitrogen atom, it is not expected that it would form ethylene compounds. This prediction was proved by qualitative tests, that is, the reaction product under investigation was negative to bromine and Baeyer tests, and no bands due to the ethylene group appeared on the infrared spectrum. These facts suggest that the cyclic imine ring was converted into a ring-opened primary amine, although the structure of the ring-opened product is still indistinguishable. Thus, a possible reaction scheme for the ring-opening reaction can be presumed to be as follows:



The proton nmr spectrum of the reaction product is shown in Figure 1. The multiplet centered at 7.48 ppm (δ) is due to the protons bound to the phenyl ring. The sinlet at δ 3.6 can also favorably be assigned to the amine proton.[11] If the lower signal between the two doublets at δ 2.0(J=7.5 cps) and 4.2 (J=6 cps) can be presumed to be due to protons of the acetyl group, the other doublet at δ 4.2 can substantially be referred to methylene protons. It should be noted, however, that the chemical shift ascribed to methylene protons unusually appears at lower fields. If the ring-opened product is assumed to be structure 3 the proton nmr signals due to the methylene protons could hardly be shifted to such an extent as δ 4.2 by only the deshielding effect of the adjacent acetyl group. And since there are no spin-spin interaction of methylene protons in 3, the signal would also be expected to be a singlet, not a doublet. Thus, the possibility of structure 3 as the ring-opened product is unlikely. Therefore, the remaining structure 2 is the only one which is likely for the ring-opened product. In order to examine the above anticipation, the ring-opened product was hydrolized by refluxing in dilute hydrochloric acid solution, which gave crystals melting at 109-110°. It was found that the infrared spectrum and the result of elemental analysis of the obtained compound coincided exactly with those of authentic, 1, 1-diphenyl-2-aminoethanol, and the mixed melting point was not depressed.

Finally, it remains to speculate about the mechanism of the ring-opening reaction. First, it is readily anticipated that a proton would attack the basic center of the nitrogen atom of the secondary imine in acidic media to form an aziridinium ion 4. The possibility of the formation of aziridinium ions is a well known fact.[1b,2c,12] Next, since the small ring of the aziridinium ion must be strained by the compression owing to the larger geminally disubstituted phenyl rings, the aziridinium ion should be easily opened to form the strainless and more stable tertiary carbonium ion 5 as an intermediate to which an acetate anion can join to form 2.



This step-wise mechanism rather than a concerted one is consistent with the conclusion in the study of nucleophilic displacement of 1, 2-diphenyl-3-substituted aziridines done by Deyrup and Greenwald[3] and also with those in solvolysis and thermal rearrangement of substituted aziridine perchlorates and fluoborates investigated by Leonard *et al.*[5]

EXPERIMENTAL SECTION

All chemicals used were Wako (Japanese) special grade and were used without further purification. Infrared spectra were taken on Beckman Model 10 as potassium bromide pressings and are expressed as wave numbers (cm^{-1}). The proton nmr spectrum was measured at 40° with a Varian A-60 spectrometer using $CDCl_3$ as solvent and TMS as the internal standard.

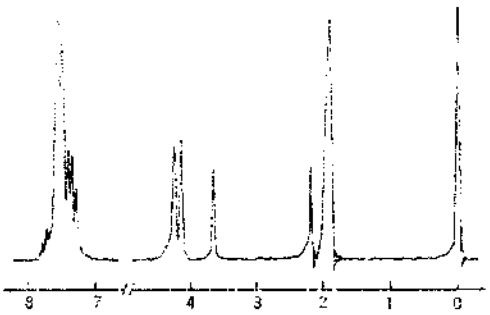
2, 2-Diphenylaziridine(1).

Into an ether solution of phenyl magnesium bromide, freshly prepared from 165 g of phenyl bromide(1. 05 M) and 24. 3 g of magnesium (1M) in 360 ml of ether, was added dropwise 34 g of acetophenon oxime(0. 25 M) in 100 ml of ether. The addition took about 2 hr, keeping the temperature below 50°. The reaction mixture was hydrolized by pouring the mixture into saturated ammonium chloride ice-water solution. The ether layer was separated and the aqueous solution was then extracted from ether. The ether in the combined solution was removed by water suction, and the residue was distiled under *vacuo*, b. p 110-2°(12 mm); colorless pungent liquid; solidified at room temperature, mp 53-6°; obtained 14 g (30%); ir, 3400(s), 305 5-3025(m) 1600, 1540, 1480.

Anal. Calcd. for $C_{14}H_{13}N$: C, 86. 12; H, 6. 71; N. 7. 17. Found: C, 86, 19; H, 6. 71; N, 6. 99

1, 1-Diphenyl-2-aminoethyl acetate(2)

Compound 1(4. 5 g, 0. 023 mole) dissoved in ether was made to react with 2 g of acetic acid(0. 033 mole) at room temperature. Upon removal of the ether and the excess omount of acetic acid, 5. 1 g of white crude crystals were obtained (81%). A small amount of starting material 1 was recovered from the removed solution. The crystals were recrystalized from benzene aceton (1:3) three times, mp 136. 5—137. 5°; ir, 3380, 3220, 1750, 1440, 1060; partial nmr is shown in Figure 1



Anal. Calcd f. or $C_{16}H_{17}NO_2$: C, 75. 27; H, 6. 71; N, 5. 49. Found: C, 75. 58; H, 6. 75; N, 5. 42.

1, 1-Diphenyl-2-aminoethanol.

Compound 2 (10. 2 g, 0. 04 mole) in 60 ml of 20 % aqueous hydrochloric acid solution was heated for 10 min. Cooled to room temperature, the mixture was treated with dilute aqueous sodium hydroxide solution, which gave 8 g of white crystals. Recrystalized from aqueous alcohol, mp 109-110°; ir, 3500-3200 (broad), 1600-1500.

Anal. Calcd. for $C_{14}H_{15}NO$: C, 78. 80; H, 7. 08; N, 6. 52. Found: C. 78. 87; H. 7. 07; N, 6. 67.

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