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The Deamination of 3-Methylenecyclobutylcarbinylamine[1]

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The nitrous acid deamination of 3-methylenecyclobutylcarbinylamine in water gave 2-methylenecyclopentanol and 3-methylenecyclopentanol. The reduction of methyl 3-methylenecyclobutanecarboxylate with lithium aluminum hydride gave 3-methylenecyclobutylcarbinol.

The deamination of small-ring amines has been extensively investigated, especially with respect to the elucidation of the nature of the intermediate cation.[3] We will report here on the deamination of 3-methylene cyclobutylcarbinylamine (I). The carbonium ion, II, formed initially by the deamination of I may give rise to a variety of products. One may consider, *inter alia*, the possible reaction routes shown in Fig. 1. The carbonium ion, II, may give, (a) compound III by a direct attack of a hydroxyl anion upon II, (b) the dienol IV from the resonance-stabilized cation formed by the ring cleavage, (c) the five-membered alcohol, V, by the ring enlargement, or (d) products arising from the methylenecyclobutyl cation, VI, which may be stabilized by a homoallylic resonance.[4]

Results and Discussion

The treatment of 3-methylenecyclobutylcarbinylamine (I) in aqueous acetic acid with sodium nitrite afforded an alcoholic fraction, which was then separated into two components (A and B), with the peak area ratio of 13 to 7, by vapor-phase chromatography (v. p. c.). The infrared spectrum

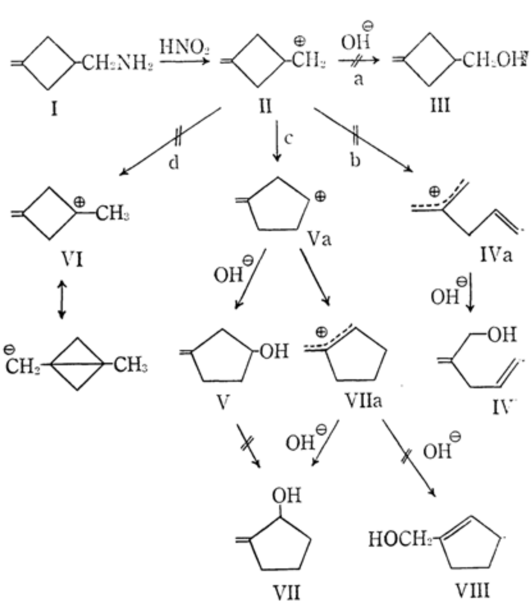

Fig. 1. Possible reaction paths of 3-methylenecyclobutylcarbonium ion (II).

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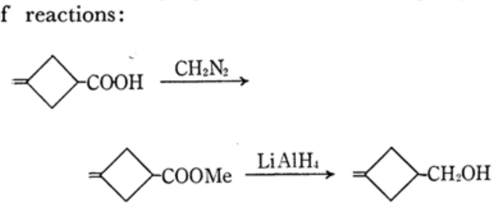
[3] See, for example, R. Breslow, "Molecular Rearrangements," ed. by P. de Mayo, Interscience Publishers, New York (1963), p. 254.

[4] E. F. Kiefer and J. D. Roberts, *J. Am. Chem. Soc.*, **84**, 784 (1962), and the references cited therein.

of the major component (A) shows bands at 3050, 1440 and 885 cm^{-1} and a broad band centered at 3300 cm^{-1}, suggesting the presence of a terminal methylene group and a hydroxyl group. The presence of these groups in compound A is also supported by an examination of its NMR spectrum, which shows a doublet (finely split further by a long-range coupling) at 4.95 (2H), a sharp singlet at 6.75 (1H), and a multiplet at 5.70 τ (1H); these bands can be assigned to the hydrogen atoms of a terminal methylene group, a hydroxyl group, and a methylene group bearing the hydroxyl group respectively. The other NMR bands consist of two broad multiplets centered at 7.7 (2H) and 8.3 τ (4H). These spectral data suggest that component A is 2-methylenecyclopentanol (VII). Confirmative evidence as to the identity of component A with VII could be obtained by a comparison of this substance with an authentic specimen of VII.[5]

The infrared spectrum of component B exhibits bands at 3100, 1420 and 880 cm^{-1} and a broad band centered at 3300 cm^{-1}, showing the presence of a terminal methylene group and a hydroxyl group. The NMR spectrum of this compound shows a pentuplet at 5.15 (2H; terminal methylene), a singlet at 6.70 (1H; hydroxyl proton), and multiplets at 6.4 (1H), 7.6 (4H) and 8.3τ (2H). The band at 6.4τ can be assigned to a hydrogen atom of a methylene group bearing the hydroxyl group; the shift of this band to a higher magnetic field than that of 2-methylenecyclopentanol suggests that the hydroxyl group is not on an allylic position. The bands at 7.6 and 8.3τ suggest the presence of four allylic hydrogen atoms and two methylene hydrogen atoms. These spectral data indicate that the only reasonable structure for component B is 3-methylenecyclopentanol (V). The fact that compound V (or the corresponding carbonium ion Va) is a reasonable precursor to VII gives further support for this structural assignment.

In order to find out whether or not a small amount of 3-methylenecyclobutylcarbinol (III) was formed, III was prepared by the following sequence of reactions:



IX III

The treatment of 3-methylenecyclobutanecarboxylic acid[6] with diazomethane gave the methyl ester (IX), which was then reduced with lithium aluminum hydride to give 3-methylenecyclobutylcarbinol (III). The identification of III is based mainly on spectral data: the infrared spectrum shows bands at 3300 for the hydroxyl group, and at 3050, 1420 and 880 cm^{-1} for the terminal methylene group. The NMR spectrum exhibits a pentuplet at 5.30 (2H; terminal methylene), a singlet at 6.23 (1H; hydroxyl), a multiplet centered at 7.5 (5H; ring hydrogen), and a doublet at 6.45 τ (2H; a methylene group adjacent to the hydroxyl group). A comparison of the v. p. c. of III with those of the deamination mixture proved the absence of III in the mixture.

The formation of V and VII can be explained by considering a rapid Wagner-Meerwein-type ring enlargement of the 3-methylenecyclobutylcarbonium ion (II) to Va, followed by its isomerization to VIIa, which is stabilized by an allylic resonance.

One should also consider another possible route for the formation of VII: 3-methylenecyclopentanol (V) may be in equilibrium with 2-methylenecyclopentanol (VII). This possibility may, however, be rejected by the fact that no isomerization of 3-methylenecyclopentanol (V) occurred under the reaction conditions.

The absence of 1-cyclopentenylcarbinol (VIII) in the reaction mixture was proved by a comparison of the v. p. c. of an authentic sample of VIII[5] with those of the reaction mixture. The absence of VIII is worthy of consideration since the 2-methylenecyclopentyl cation resonates with the 1-cyclopentenylcarbonium ion, and VIII would be thermodynamically more stable than III.[7] The absence of VIII in the reaction mixture further supports the absence of an equilibrium between V and VII under the reaction conditions.

The absence of dienol IV in the reaction mixture is rather surprising. This reaction path (Fig. 1, route b) appears to be the most favorable in view of its gain in the delocalization energy as well as its relief from the strain energy. A closer examination of the geometry of this compound at the transition state shows, however, that the vacant p-orbital of the "allylic cation" at the transition state will be nearly orthogonal to the π-orbital of the methylene group; thus the gain in the delocalization energy in going from II to the cation IVa would not influence the fate of the carbonium ion, II.

From the findings reported above, it may be concluded that compound I follows the general tendency of the ring expansion of a small-ring system, and that the presence of a methylene group on the 3-position of the cyclobutane ring does not

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[5] A. S. Dreiding and J. A. Hartman, *J. Am. Chem. Soc.*, **75**, 939 (1953).

[6] F. F. Caserio, Jr., S. H. Parker, R. Piccolini and J. D. Roberts, *ibid.*, **80**, 5507 (1958).

[7] J. Herling, J. Shabtai and E. Gil-Av, *ibid.*, **87**, 4107 (1965); A. C. Cope, D. Ambross, E. Ciganek, C. F. Howell and Z. Jacura, *ibid.*, **82**, 1750 (1960); O. H. Wheeler, *Chem. Ind.*, **1954**, 900.

influence the carbonium ion, II, except in causing the hydride shift to take place at a later stage.

Experimental

The melting points were measured on a micro hot stage and are not corrected; all boiling points are uncorrected. The infrared spectra of samples as neat liquids were measured on a Hitachi, Model EPI S II, spectrophotometer. The NMR spectra were kindly determined by the Japan Electron Optics Lab. Co. on its Model C-60 at 60 Mc in carbon tetrachloride, tetramethylsilane being used as the internal standard.

The Deamination of 3-Methylenecyclobutylcarbinylamine (I). A solution of 3.6 g. (0.05 mol) of sodium nitrite in 10 m*l* of water was stirred with cooling, into a solution of 2 g (0.03 mol) of I in 10 m*l* of 20% aqueous acetic acid. After it had been stirred for seven hours at room temperature, the reaction mixture was saturated with sodium chloride and then extracted with ether. The ether extract was dried over magnesium sulfate and distilled to give 1.5 g of a fraction boiling at 68—71°C/18 mmHg. The fraction was separated by v. p. c. into two components (A and B) with a peak-area ratio of 13 to 7, using a 375 cm column packed with 10% Silicon D. C. 550 on Shimalite.

The infrared spectrum of component A has bands of a terminal methylene group at 3050, 1440 and 885 cm^{-1} and a broad band of a hydroxyl group centered at 3300 cm^{-1}. The NMR spectrum shows multiplets at 8.3 (4H), 7.7 (2H) and 5.70 (1H), a singlet at 6.75 (1H), and a doublet at 4.95 τ (2H).

Found: C, 68.81; H, 10.18%. Calcd for $C_6H_{10}O$: C, 73.43; H, 10.27%.[8]

The infrared spectrum and the v. p. c. retention time of component A were identical with those of an authentic sample of 2-methylenecyclopentanol (VII).[5] The melting point of its *p*-nitrobenzoate was 84.5—85.5°C; it was not depressed on admixture with an authentic specimen of 2-methylenecyclopentyl *p*-nitrobenzoate.[5]

The infrared spectrum of component B has bands of a terminal methylene group at 3100, 1420 and 880 cm^{-1} and a broad band of a hydroxyl group centered at 3300 cm^{-1}. The NMR spectrum shows multiplets at 8.3 (2H), 7.6 (4H) and 6.4 (1H), a singlet at 6.70 (1H), and a pentuplet at 5.15 τ (2H).

Found: C, 69.90; H, 10.17%. Calcd for $C_6H_{10}O$: C, 73.43; H, 10.27%.[8]

The infrared spectrum and the v. p. c. retention time of this compound were not identical with those of 3-methylenecyclobutylcarbinol (III) or 1-cyclopentenylcarbinol (VIII).

Methyl 3-Methylenecyclobutanecarboxylate (IX). An ether solution of diazomethane (prepared from 0.04 mol of *N*-methyl-*N*-nitrosourea) was added to a solution of 2.2 g (0.02 mol) of 3-methylenecyclobutanecarboxylic acid[6] in 40 m*l* of ether. The mixture was washed with a saturated aqueous solution of sodium chloride and then dried over magnesium sulfate. After the ether had been removed by distillation, the residue was distilled to give 1.8 g of methyl 3-methylenecyclobutanecarboxylate, boiling at 60—61°C/22 mmHg, n_D^{25} 1.4469.

Found: C, 66.44; H, 8.17%. Calcd for $C_7H_{10}O_2$: C, 66.64; H, 7.99%.

3-Methylenecyclobutylcarbinol (III). To a stirred suspension of 1 g (0.03 mol) of lithium aluminum hydride in 100 m*l* of ether, there was slowly added a solution of 2 g (0.02 mol) of methyl 3-methylenecyclobutanecarboxylate in 20 m*l* of ether; the resulting mixture was then stirred for another ten hours at room temperature. The mixture was poured into ice water, and hydrochloric acid was added to dissolve the precipitate. The organic layer was separated, and the aqueous layer was extracted with ether. The combined extract was washed with aqueous sodium bicarbonate and dried over magnesium sulfate. Distillation afforded 0.9 g of IV, boiling at 82—83°C/32 mmHg.

Found: C, 72.36; H, 10.46%. Calcd for $C_6H_{10}O$: C, 73.43; H, 10.27%.

***p*-Nitrobenzoate of III:** mp 60—61°C.

Found: C, 62.97; H, 5.50; N, 5.94%. Calcd for $C_{13}H_{13}O_4N$: C, 63.15; H, 5.30; N, 5.67%.

***p*-Bromobenzenesulfonate of III:** mp 54.5—56.5°C.

Found: C, 45.48; H, 4.11%. Calcd for $C_{12}H_{13}O_3SBr$: C, 45.43; H, 4.13%.

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[8] The elemental analysis, performed only once, agreed poorly with the theoretical values. This deviation is probably due to the presence of a small amount of water, which might have condensed in the cold trap during the v. p. c. fractionation.