NOVEL PYRIDAZINIUM ION SYNTHESIS. REACTION OF DIAMINOCYCLOPROPENIUM ION WITH DIAZOALKANES

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The reaction of bis(diisopropylamino)cyclopropenium perchlorate (1) with an excess of $RCHN_2$ (R: H, CH_3) afforded 3,4-bis(diisopropylamino)-6-R-pyridazinium perchlorate (2a, b). This reaction provides a novel synthetic method of pyridazinium compounds.

Recent interest in cyclopropenium ion chemistry has focused on the hetero-atom substituted derivatives. Since the physical and chemical properties of the highly strained 3C-2π ring system are sensitively affected by the substituents on the ring, the investigation of reactivities of cyclopropenium ion possessing hetero-atom substituents is a fascinating problem.[1] So far we have reported such examples,[1-8] and developed the various novel electron systems derived from hetero-atom substituted cyclopropenium ions. As for the reactions of cyclopropenium ions leading to the formation of heterocycles, only a few examples have been known.[9-12] In our inves-

tigation carried out for synthesis of heterocycles using hetero-atom substituted cyclopropenium ions,[12] we have found a novel synthesis of pyridazinium compounds by a reaction of dialkylaminocyclopropenium ion with diazoalkane under mild conditions.

In this communication, we wish to report the reaction of bis(diisopropylamino)cyclopropenium perchlorate (1).[13]

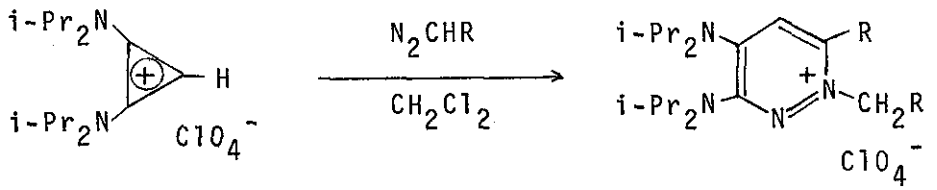
An excess of diazomethane in ether was added to a solution of the salt 1 in dichloromethane at room temperature. The reaction proceeded with gas evoluation. After stirring at room temperature for 3h, work-up with aqueous perchloric acid followed by recrystallization from dichloromethane-ether afforded yellow crystals (2a), mp 133-134.5°, in 75% yield. Elemental analysis was consistent with a $C_{17}H_{33}N_4O_4Cl$ formulation. The infrared spectrum of the product showed an olefinic C-H stretching absorption at 3070 cm^{-1} and a characteristic band assignable to perchlorate ion at 1090 cm^{-1}. The pmr spectrum of the salt (in $CDCl_3$) exhibited two A_6X patterns of the isopropyl protons, singlet of N-CH_3 (δ, 4.18, 3H) and AB quartet centered at δ 7.37 and 8.54 (J=7.2Hz, 1H respectively). The cmr spectrum[14] confirmed the presence of the pyridazinium moiety, of which signals appeared as four singlets at 114.1 (d), 140.4 (d), 146.9 (s) and 150.6 (s), while the N-methyl carbon resonated at 48.2 (q).

Similar treatment of 1 with an excess of diazoethane gave

pyridazinium salt (2b); 108-109.5° (from chloroform-ether), ir (KBr) 3090, 1578 and 1090 cm^{-1}. In the pmr spectrum, one olefinic proton was observed at δ 6.99. The cmr spectrum showed four carbon signals for pyridazinium ring at 115.5 (d), 147.7 (s) 149.5 (s) and 149.8 (s). Nmr spectra of 2b clearly indicate that the methyl group attaches to the 6-position of the pyridazine ring. The structure of the products (2a, b) was confirmed by converting them to 1,6-dihydropyridazine derivatives (3a, b) by means of sodium borohydride.

Reduction of the perchlorates (2) with sodium borohydride in ethanol at room temperature followed by extraction with n-hexane, and removal of the solvent gave slightly yellow liquid, nearly pure (3a, b) in good yield.[15] The oily products were further purified by Kugelrohr distillation at 120-130°/0.1 Torr for 3a, and 110-120°/0.1 Torr for 3b. The mass spectra exhibited molecular ion peak for dihydropyridazine derivatives (M^+: 294 for 3a, 322 for 3b). The pmr spectra of 3 were in accord with the proposed structures. The olefinic proton of 3a appeared at δ 5.54 as a triplet (J = 5.3Hz) and the methylene protons were observed at 2.98 as a doublet (J = 5.3Hz). The pmr spectrum of 3b showed the olefinic proton at δ 5.29 (d, J = 4.6Hz), the methine proton at position 6 as a multiplet, the methyl protons at position 6 as a doublet (J = 6.8Hz) at 1.11, the ethyl protons as an ABX_3 pattern (δ_A = 3.07, δ_B = 2.72, δ_X = 1.17, J_{AB} = 11.8Hz, $J_{AX} = J_{BX}$ = 6.8Hz), besides two isopropyl protons.

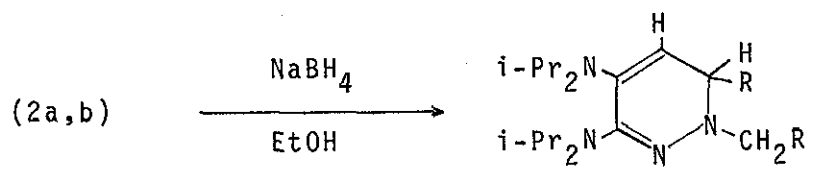
Thus, the structures of the products 2a, b and their dihydro derivatives (3a, b) have been confirmed to be 1-alkyl-3,4-diaminopyridazinium perchlorate and 1,6-dihydropyridazine derivatives, respectively.



1

2a, R=H

2b, R=CH_3

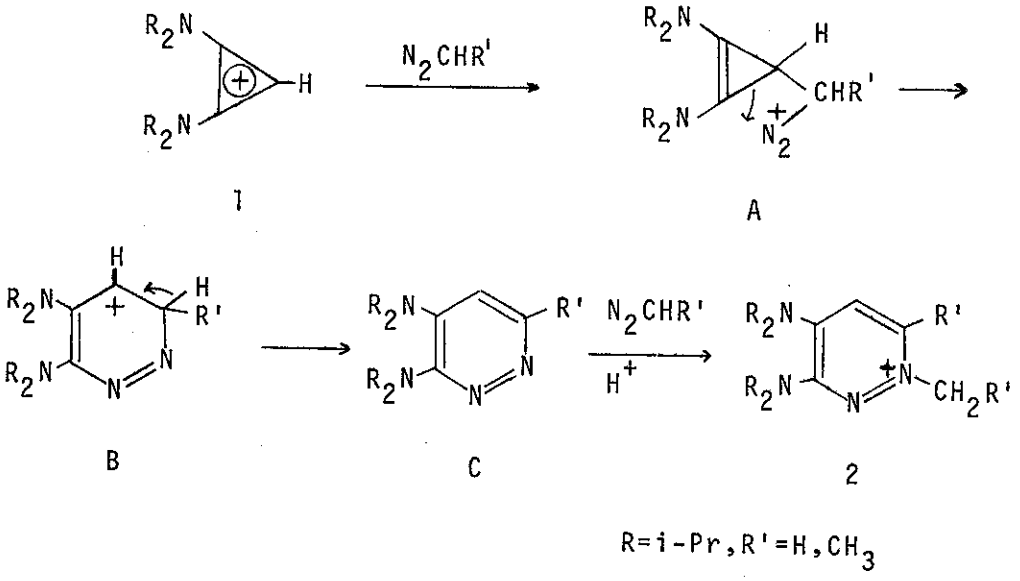


3a, R=H

3b, R=CH_3

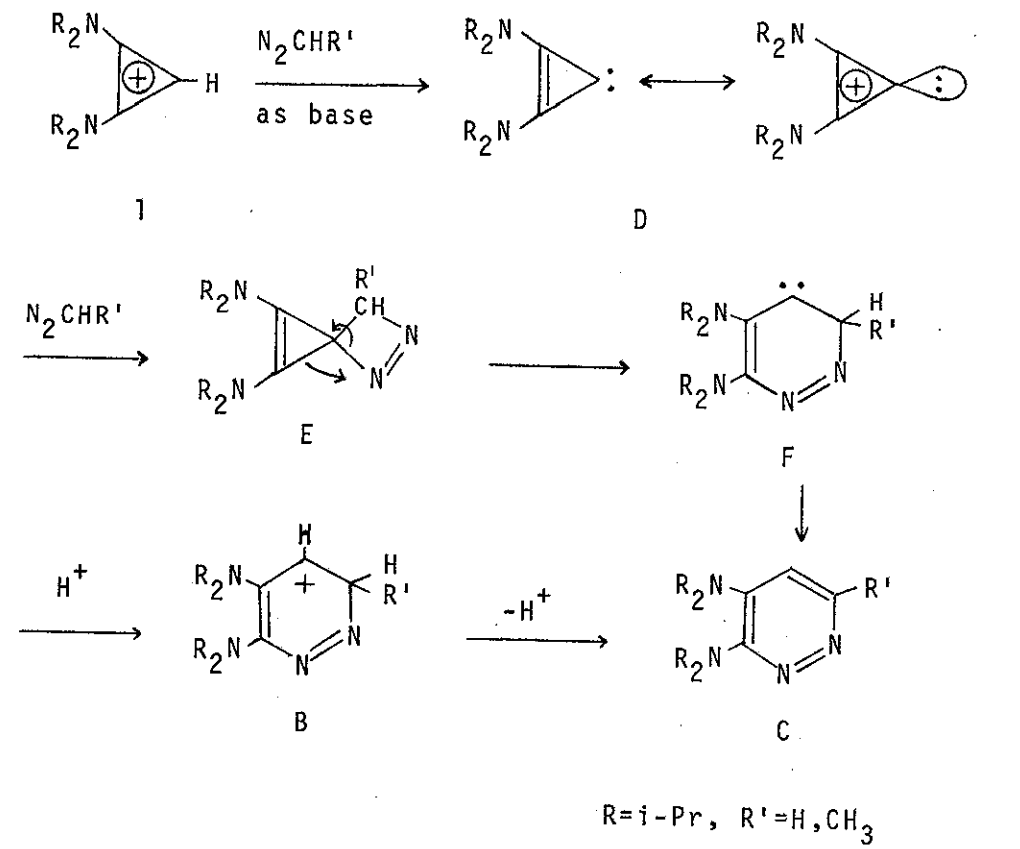
The reaction leading to the formation of pyridazinium ion might be shown as Scheme 1. However, as shown in Scheme 2, another path way of pyridazine (C) formation via diaminocyclopropenylidene (D) could be possible, since several 1,2-diamino-3-X-substituted cyclopropenium perchlorates (X = CH_3, Ph, Cl, SMe etc.) which are unable to generate diaminocyclopropenylidene were unreactive to diazomethane under similar conditions.

Scheme 1



R=i-Pr, R'=H, CH_3

Scheme 2



R=i-Pr, R'=H, CH_3

Extention of this interesting reaction to other 1,2-disubstituted cyclopropenium ions and elucidation of mechanism of the reaction are now under way.

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13. The salt 1 was prepared from bisdiisopropylaminocyclopropenethione by nitric acid oxidation. Z. Yoshida, H. Konishi, H. Ogoshi, to be published elsewhere.

14. The FT-cmr spectra were measured at 15.04 MHz in $CDCl_3$ solution, ^{13}C chemical shifts are in parts per million from internal TMS, the designations in parentheses show the multiplicities in off-resonance spectra.

15. The yield of 3a was 85% based on 2a. While 3b was obtained from unpurified 2b in 66% yield based on 1.

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