

NOVEL ALKALINE HYDROLYSIS OF TRIAMINOCYCLOPROPENIUM ION.

NEW ROUTE TO DIAMINOCYCLOPROPENONE AND DIAMINOCYCLOPROPENETHIONE

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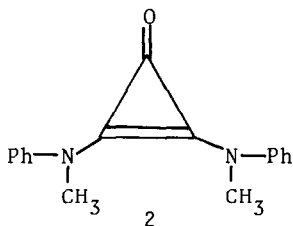
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Cyclopropenones are one of interesting electron systems.<sup>1-6</sup> Especially the physical and chemical properties of the carbonyl group involved in the cyclopropenone ring system propound intriguing problems. As one such example, the marked  $\pi$  conjugative stabilization has been noticed for the parent ketone, its alkyl and aryl derivatives in relation to their chemical properties. To find out further unique properties of cyclopropenones it would be desirable to synthesize the heteroatom-substituted derivatives other than dialkoxy<sup>7</sup>, dimercapto<sup>8</sup> and dichlorocyclopropenones<sup>9</sup> which have so far been reported.

On the other hand, it is of considerable interest that how behaves triaminocyclopropenium ion towards aq. alkali, because the triaminocyclopropenium ion is stable even in hot water.<sup>12</sup> We have found that triaminocyclopropenium salt undergoes the hydrolysis by aq. alkali at room temperature to give diaminocyclopropenone and acrylamide derivative. To 340 mg of 1,2,3-tris-

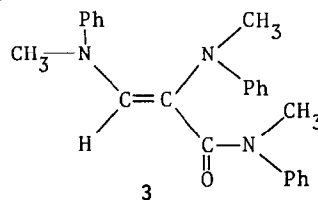


(N-methylanilino)cyclopropenium perchlorate (1) in 40 ml of methanol was added 90 ml of 0.3 % aq. KOH, and stirred at room temperature for 40 hr. Filtration of the precipitate and subsequent recrystallization from acetone gave white needle crystals (2) in 22 % yield. mp 183°. Anal. Calcd for C<sub>17</sub>H<sub>16</sub>N<sub>2</sub>O: C, 77.25; H, 6.10; N, 10.60.

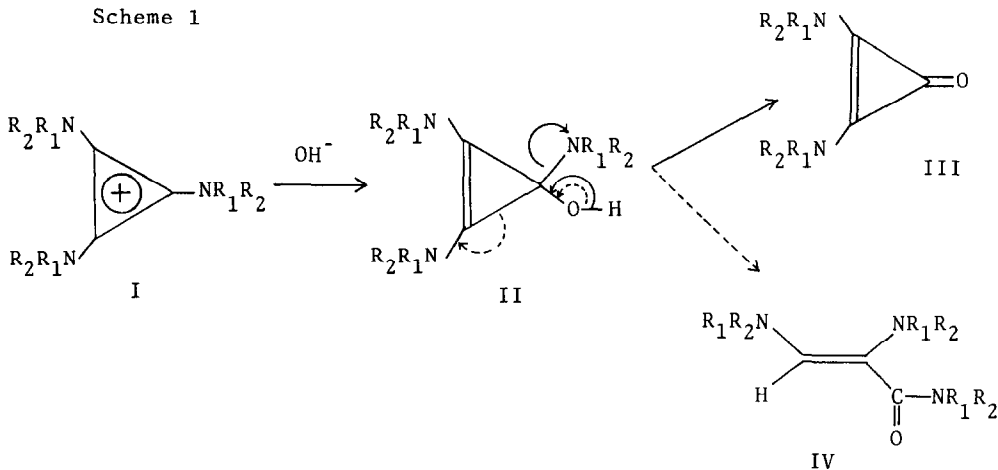
Found: C, 77.00; H, 5.95; N, 10.25. mass spectrum (parent peak) m/e 264.

The compound 2 shows the characteristic absorptions of cyclopropenone at

1920  $\text{cm}^{-1}$  and 1902  $\text{cm}^{-1}$ . The  $\nu_{\text{CO}}$  band appears at 1610  $\text{cm}^{-1}$ . The ultraviolet spectrum in methanol appears at 281 nm ( $\log \epsilon$  4.45) and 290 nm ( $\log \epsilon$  4.42). The nmr in  $\text{CDCl}_3$  shows a multiplet (10 H, aromatic) at  $\tau$  2.57-3.17 and a single (6 H, methyl) at  $\tau$  6.62. The filtrate separated from the above precipitate was concentrated in vacuo. Recrystallization from methanol afforded colorless crystals (3) in 65 % yield. mp 152°. The nmr spectrum of 3 shows three different singlets due to methyl groups at  $\tau$  6.90 (3 H), 7.02 (3 H) and 8.14 (3 H) and multiplet at  $\tau$  2.60 ~ 3.68 (15 H, aromatic and 1 H, olefinic). The infrared spectrum shows strong bands at 1642, 1590, and 1489  $\text{cm}^{-1}$ . The absorption maxima of the UV spectrum appear at 255 nm ( $\log \epsilon$  4.23), 304 (4.14) and 346 (4.20). mass spectrum (parent peak) m/e 371. These spectral data and elemental analysis clearly indicate the compound 3 to be N-methyl, N-phenyl- $\alpha,\beta$ -bis(N-methylanilino)acrylamide. Reaction of 1 with relatively conc. aq. alkali led to quantitative formation (yield 97 %) of 3. On the other hand tris(diphenylamino)cyclopropenium perchlorate (4) was exclusively hydrolyzed to acrylamide derivative even with dil. NaOH (<2%). The distribution of both products (III and IV in Scheme 1) seems to depend upon

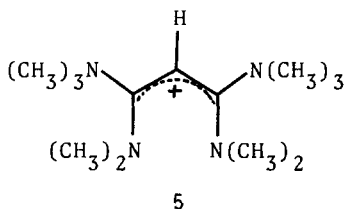


Scheme 1

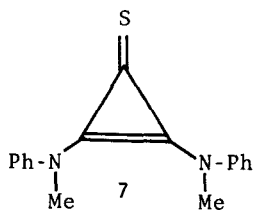


the basicity of amino group attached to cyclopropenium ring, the kind of alkali used and its concentration. The formation of diaminocyclopropenone (III) and acrylamide derivative (IV) might be considered to occur via the common intermediate, triaminocyclopropenol (II) as shown in Scheme 1.

It is extremely interesting that the alkaline hydrolysis of tris(dimethylamino)cyclopropenium perchlorate at room temperature has afforded 1,1,3,3-tetrakis(dimethylamino)allyl perchlorate (5) (yield, 9 %) other than bis-



(dimethylamino)cyclopropenone (6) (yield, 65 %). The compound 5 ( $C_{11}H_{25}N_4ClO_4$ , mp  $173^\circ$  dec) was identified by the spectral (ir, uv, nmr) data of the authentic sample prepared from dichloromethylene dimethylammonium chloride and N,N-dimethylacetamide.<sup>10</sup> Compound 6,  $C_7H_{12}N_2O$ , mp  $45^\circ$ , ir ( $CCl_4$ ) 1936, 1888, 1614  $cm^{-1}$ , uv ( $CH_3CN$ )  $\lambda_{max}$  232 nm (log  $\epsilon$  4.03), 265 (sh, 3.33); nmr ( $CDCl_3$ )  $\tau$  7.01 (singlet,  $CH_2$ ), m/e 140 ( $M^+$ , 4) 112 (M-CO, 76), 97 (73), 56 (100). Although the formation mechanism of 5 is now under investigation, it is deduced that 5 might be formed via disproportionation of the ether produced by the reaction of I ( $R_1, R_2 = CH_3$ ) with II ( $R, R_2 = CH_3$ ). The treatment of 1 with 1 %  $Na_2S$  aqueous-methanol solution at room temperature for 24 hr yielded the white precipitate which was recrystallized from methanol to give colorless crystals (7) in 96 % yield. mp  $189^\circ$ . The nmr spectrum of 7 appears at  $\tau$  2.50 ~ 3.00 (multiplet, 10 H, aromatic) and 6.50 (singlet, 6 H, methyl).



methyl). The mass spectrum shows a parent peak at 280 (m/e). A weak ir absorption at  $1875\ cm^{-1}$  is assigned to the characteristic ring deformation of the cyclopropenethione.<sup>11</sup> From these spectral data and elemental analysis the compound 7 is assigned to bis(N-methylanilino)cyclopropenethione. Novel physical and chemical properties of diaminocyclopropenone and diaminocyclopropenethione will be reported elsewhere.

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