

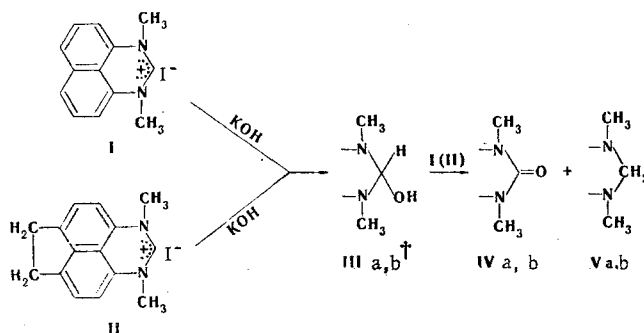
PERIMIDINIUM SALTS: UNUSUAL (IN THE AZOLE SERIES) PRODUCTS OF INTERACTION WITH ALKALI*

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We have found that 1,3-dimethylperimidinium (I) and 1,3-dimethylaceperimidinium (II) salts react with aqueous alkali solution to form a mixture of the corresponding perimidone (IV) and 2,3-dihydro-1,3-dimethylperimidine (V). The reaction proceeds through a step involving the formation of a carbinol pseudo base (III), which then apparently undergoes redox reaction with the starting quaternary salt or it-self undergoes disproportionation.

A portion of the pseudo base is probably converted to the oxo derivative due to autooxidation, since the ratio of the products is not 1:1 but proves to favor the perimidone (55:38%). This sort of direction of the reaction has been described for salts of several azines (for example, isoquinoline [2]), but, as far as we know, this is the first time it has been encountered in the azole series. Five-membered azoles usually



form carbinol pseudo bases, which sometimes exist in the acyclic form [3].

The anomaly may be due to the increased tendency of the perimidines, which are six-membered azoles, to undergo oxidation and reduction.

Dihydro derivatives V, the structure of which was proved by means of IR and PMR spectra, are stable in air and are not oxidized on prolonged storage, in contrast to the analogous compounds of the imidazole series [4].

We apologize for the fact that the N,N-dimethyl-N-formyl-1,8-naphthylenediamine structure [5], was previously erroneously ascribed to IVa on the basis of the results.

EXPERIMENTAL

Action of Alkali on 1-Methylperimidine Methiodide. Methiodide I was obtained as yellow needles with mp 275–276° (alcohol). A suspension of 1.6 g (5 mmole of I in 50 ml of water was heated on a boiling-water bath and treated with 10 ml of 10% KOH solution. The mixture was allowed to stand for 30 min, and

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†The symbol a pertains to the perimidine, while b pertains to the aceperimidine.

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the white precipitate, which was a mixture of IVa and Va, was removed by filtration. To separate the substances, the mixture was treated with 15% HCl (10 ml), and the acid-insoluble 1,3-dimethylperimidone was removed by filtration to give 0.58 g (55%) of colorless needles with mp 209° (alcohol), in agreement with the melting point presented in [6]. The product did not depress the melting point of an authentic sample. IR spectrum: $\nu_{C=O}$ 1675 cm^{-1} (mineral oil).

The hydrochloric acid solution remaining after separation of IVa was neutralized with ammonia, and the precipitated 1,3-dimethyl-2,3-dihydroperimidine was removed by filtration and washed with water to give 0.38 g (38%) of colorless prisms with mp 150° (alcohol). PMR spectrum (12% solution in CDCl_3) δ , ppm: 2.85 (six N-CH₃ protons), 3.97 (two CH₂ protons), 6.38 (quartet, two H_{4,9} protons; $J_{\text{ortho}} = 7\text{ Hz}$, $J_{\text{meta}} = 2.5\text{ Hz}$), 7.16 (center of a complex multiplet, four H_{5,8} and H_{6,7} protons). Found: C 78.8; H 7.1; N 13.9%. C₁₃H₁₄N₂. Calculated: C 78.8; H 7.1; N 14.1%.

Methiodide II, with mp 360° (from alcohol), reacts similarly with alkali.

1,3-Dimethylaceperimidone (IVb). This compound was obtained in 57% yield as yellow needles with mp 212–213° (acetic acid). Found: C 76.0; H 6.1%. C₁₅H₁₄N₂O. Calculated: C 75.6; H 5.9%. IR spectrum: $\nu_{C=O}$ 1670 cm^{-1} (chloroform).

1,3-Dimethyl-2,3-dihydroaceperimidine (Vb). This compound was obtained in 38% yield as sand-colored prisms with mp 152–153° (alcohol). PMR spectrum (12% solution in CDCl_3) δ , ppm: 2.87 (six N-CH₃ protons), 3.22 (four CH₂-CH₂ protons), 3.97 (two CH₂ protons), 6.36 (doublet, two H_{4,9} protons; $J = 7.5\text{ Hz}$), 7.04 (doublet, two H_{5,8} protons, $J = 7.5\text{ Hz}$). Found: C 80.4; H 7.3%. C₁₅H₁₆N₂. Calculated: C 80.3; H 7.2%.

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