HETEROCYCLIC ANALOGS OF PLEIADIENE

X.* REACTION OF 2-SUBSTITUTED QUATERNARY PERIMIDINIUM SALTS WITH ALKALI

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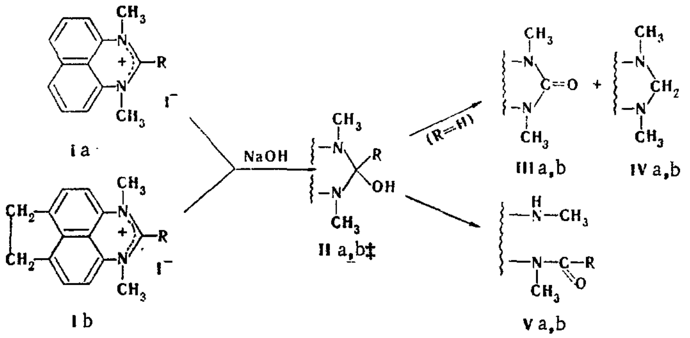
1,2-Disubstituted perimidine and aceperimidine methiodides react with aqueous alkali solutions to give pseudo bases corresponding to the acyclic form.

Recently two of us showed that the carbinol pseudo base (II, R = H) formed initially in the reaction of aqueous alkali solutions with 1,3-dimethylperimidinium and 1,3-dimethylaceperimidinium salts (I, R = H) undergoes redox disproportionation to give a mixture of 2-oxo- (III) and 2,3-dihydroperimidines (IV) [2]:



This direction of the reaction is unusual for quaternary azole salts. For example, imidazolium and benzimidazolium salts, regardless of the substituent in the 2 position, under these conditions form pseudo bases, which exist in an open form of the V type [3]. In the present research we have set out to study the behavior with respect to alkalis of perimidinium and aceperimidinium salts (I), which contain an alkyl or aryl substituent in the 2 position. It is apparent that in this case anomalous reaction to give III and IV was excluded and that one might have expected the formation of either acyclic pseudo bases (V) or (for 2-methyl derivatives) methylene anhydro bases.

The experiments demonstrated that 1,2-dimethylperimidine, 1,2-dimethylaceperimidine, and 1-methyl-2-phenylperimidine methiodides react with aqueous alkali solutions to give high yields of pseudo bases that exist exclusively in acyclic form V in the crystalline state and in solution in chloroform. The following data attest to this: the IR spectra of V contain a ν_{NH} band at 3480 cm^{-1} and a $\nu_{C=O}$(amide) band at 1660 cm^{-1}. The PMR spectrum of Va (R = CH_3) contains signals of the NH proton (δ 5.55 ppm) and three CH_3 groups (δ 1.67, 2.87, and 3.15 ppm), one of which (from the $NHCH_3$ group) is split into a doublet due to spin–spin coupling (J = 6 Hz) with the NH proton (Fig. 1).

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*See [1] for communication IX.

†Deceased.

‡The letters "a" and "b" in formulas I-V pertain, respectively, to the perimidines and aceperimidines.

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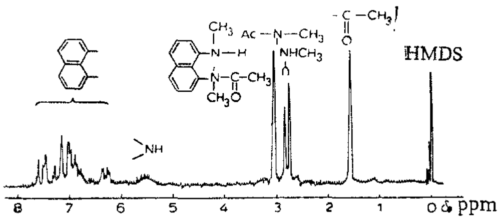

Fig. 1. PMR spectrum of N,N'-dimethyl-N-acetyl-1,8-naphthalenediamine (8% solution in CCl_4).

Thus perimidinium salts that contain a substituent in the 2 position do not manifest any anomalies on reaction with alkalis.

Pseudo bases V are again readily cyclized to perimidinium salts on reaction with hydrochloric acid. Treatment of the resulting methochlorides with potassium iodide gives starting iodides I.

1-Methyl-substituted 2-methyl- and 2-phenylperimidines and 2-methylaceperimidines were obtained by methylation of the corresponding compounds with a free NH group with methyl iodide in dimethylformamide The N-methylated base was isolated by treatment of the resulting quaternary salt with alkali.

This method for methylation gives particularly good results in the case of 2-methyl derivatives of perimidine and aceperimidine. Unlike methylation in alkaline media [4], it does not require the use of an inert atmosphere and is not accompanied by resinification. In addition, the unchanged starting perimidine can be readily regenerated.

EXPERIMENTAL

The IR spectra were measured with a UR-20 spectrometer. The PMR spectrum was measured with a PE-2305 spectrometer (60 MHz). The internal standard was hexamethyldisiloxane (HMDS).

2-Methyl- and 2-Phenylperimidine [6]. These compounds were obtained by the methods in [5, 6], respectively.

2-Methylaceperimidine. This compound was obtained by refluxing 4,5-diaminoacenaphthene [7] with a tenfold amount of acetic anhydride for 30 min. The 2-methylaceperimidine acetate that formed on cooling the reaction mixture was removed by filtration, dissolved in water, and decomposed with ammonia. The yield of 2-methylaceperimidine with mp 230° (from alcohol) was 70%. Found: C 81.0; H 6.1; N 13.2%. $C_{14}H_{12}N_2$. Calculated: C 80.7; H 5.3; N 13.4%.

General Method for the Preparation of 1,2-Disubstituted Perimidines and Aceperimidines. A 0.02-mole sample of methyl iodide was added to a solution of 0.01 mole of 2-substituted perimidine or aceperimidine in 30 ml of dimethylformamide (DMF), and the mixture was heated on a boiling-water bath for 30 min. The yellow crystalline precipitate, which was a mixture of the hydriodides of the starting compound and the reaction product, was separated and dissolved in 100 ml of water. The solution was treated with ammonia, and the precipitated yellow-green crystals were removed by filtration, washed with water, and dried. The crystals were then dissolved in 20 ml of chloroform, and the unchanged perimidine (~20% for the 2-methylperimidines and ~50% for 2-phenylperimidine) was removed by filtration. The filtrate was passed through a column filled with aluminum oxide. The 1,2-disubstituted perimidines and aceperimidines were eluted with chloroform–ether (1 : 1), with collection of the first fraction. This method was used to obtain: 1,2-dimethylperimidine [yield 50-65%, mp 130-131° (from heptane) (mp 159-160° [8]). In view of the discrepancy between our melting point and the literature melting point, we subjected the product to elementary analysis. Found: C 79.9; H 6.8; N 13.2%. $C_{14}H_{14}N_2$. C 80.0; H 6.7; N 13.3%]; 1-methyl-2-phenylperimidine [33% yield, yellow needles with mp 173-174° (from heptane). Found: C 83.3; H 5.4; N 10.8%. $C_{18}H_{14}N_2$. Calculated: C 83.7; H 5.7; N 10.8%]; 1,2-dimethylaceperimidine [77% yield, golden needles with mp 199-200° (from heptane). Found: C 81.4; H 6.3; N 12.5%. $C_{15}H_{14}N_2$. Calculated: C 81.1; H 6.3; N 12.6%].

1,2-Dimethylperimidine Methiodide (Ia, R = CH_3). A solution of 2 g (1 mmole) of 1,2-dimethylperimidine and 0.3 g (2 mmole) of methyl iodide in 5 ml of DMF was heated on a boiling-water bath for 20 min, after which the precipitated yellow methiodide was removed by filtration to give a quantitative yield of a product with mp 262-263° (from alcohol). Found: N 8.1%. $C_{14}H_{15}IN_2$. Calculated: N 8.4%.

A similar method was used to obtain 1-methyl-2-phenylperimidine methiodide (Ia, R = C_6H_5) [yellow plates with mp 274-275° (from alcohol). Found: N 7.4%. $C_{19}H_{17}IN_2$. Calculated: N 7.0%] and 1,2-dimethylaceperimidine methiodide (Ib, R = CH_3) [golden plates with mp 300° (from alcohol). Found: N 7.6%. $C_{16}H_{17}IN_2$. Calculated: N 7.7%].

Reaction of Methiodides I with Alkali. A suspension of the methiodide (5 mmole) in 50 ml of water was heated on a boiling-water bath and treated with 10 ml of 10% KOH. The mixture was held on the bath for 10-15 min, after which it was cooled, and the precipitated pseudo base was removed by filtration. The yield was quantitative. This method was used to obtain N,N'-dimethyl-N-acetyl-1,8-naphthalenediamine (Va, R = CH_3) [colorless needles with mp 116-117° (from hexane). IR spectrum ($CHCl_3$, 10^{-2} M): ν_{NH} 3486, $\nu_{C=O}$ 1663 cm^{-1}. Found: C 73.9; H 7.1; N 12.3%. $C_{14}H_{16}N_2O$. Calculated: C 73.6; H 7.1; N 12.4%], N,N'-dimethyl-N-benzoyl-1,8-naphthalenediamine (Va, R = C_6H_5) [colorless needles with mp 164-165° (from heptane). IR spectrum ($CHCl_3$, 10^{-2} M): ν_{NH} 3465, $\nu_{C=O}$ 1650 cm^{-1}. Found: C 78.9; H 6.0; N 9.5%. $C_{19}H_{18}N_2O$. Calculated: C 78.6; H 6.2; N 9.6%], and N,N'-dimethyl-N-acetyl-4,5-diaminoacenaphthene (Vb, R = CH_3) [yellow prisms with mp 126-127° (from octane). IR spectrum ($CHCl_3$, 10^{-2} M): ν_{NH} 3480, $\nu_{C=O}$ 1660 cm^{-1}. C 75.3; H 7.0; N 10.8%. $C_{16}H_{18}N_2O$. Calculated: C 75.6; H 7.1; N 11.0%].

Reaction of Pseudo Bases V with Hydrochloric Acid. A mixture of 3 mmole of pseudo base V was refluxed with 10 ml of 20% HCl for 3 h, after which the solvent was evaporated, and the precipitated yellow methochloride was crystallized from alcohol. The yields were close to quantitative. This method was used to obtain 1,2-dimethylperimidine methochloride [mp 221-222° (from alcohol). Found: N 11.5%. $C_{14}H_{15}ClN_2$. Calculated: N 11.5%], 1-methyl-2-phenylperimidine methochloride [mp 222° (from alcohol–ether). Found: N 8.7%. $C_{19}H_{17}ClN_2$. Calculated N 9.0%], and 1,2-dimethylaceperimidine methochloride [mp 259-260° (from alcohol). Found: N 10.0%. $C_{16}H_{17}ClN_2$. Calculated: N 10.3%].

Chlorine Exchange in Methochlorides. A solution of 1 mmole of 1,2-dimethylperimidine methochloride in 3 ml of water was treated with a solution of KI (1 mmole) in 1 ml of water, and the resulting precipitate was removed by filtration and washed with 1 ml of cold water. The yield of product with mp 262-263° (from alcohol) was almost quantitative. No melting-point depression was observed for a mixture of this product with a genuine sample of the methiodide.

The remaining experiments on chlorine exchange in methochlorides were carried out as described above.

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