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HETEROCYCLIC ANALOGS OF PLEIADIENE.

47.* N-AMINATION OF PERIMIDINES

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N-Aminoperimidinium salts were obtained by the action of O-mesitylsulfonylhydroxylamine on perimidine and its 1- and 2-substituted derivatives, and some transformations of the salts (reaction with p-nitrobenzaldehyde, reduction with sodium borohydride, and the synthesis of 2,4-dimethylpyrazolo[1,5-a]perimidine) were realized.

Of the amines of the perimidine series, most study has been devoted to 2-aminoperimidines, which are readily obtained via the Chichibabin reaction [2]. The available data on perimidines that contain an amino group in the naphthalene ring are meager [3], and N-aminoperimidines were unknown up until now. We have established that the N-amination of perimidines can be easily accomplished by means of O-mesitylsulfonylhydroxylamine (MSHA), which is an electrophilic aminating agent that has recently found extensive application [4]. The reaction of perimidine and its 1- and 2-substituted derivatives (Ia-e) with MSHA in methylene chloride at room temperature is complete in a few minutes, and salts IIIb-e are obtained in 72-100% yields. The amination of perimidine itself is somewhat less successful (the product is obtained in 42% yield).

The structure of N-aminoperimidinium salts II is confirmed by the results of elementary analysis from them of derivatives of a new heteroaromatic system, viz., pyrazolo[1,5-a]perimidine. Thus, 2,4-dimethyl-3-acetylpyrazolo[1,5-a]perimidine (III) is formed in quantitative yield by the action of acetic anhydride in the presence of potassium hydroxide on the 1,2-dimethyl-3-aminoperimidinium salt (IIc). Compound III is readily deacetylated to give 2,4-dimethylpyrazolo[1,5-a]perimidine (IV) by refluxing with concentrated HCl. Compound IV in turn can be reconverted to III by heating with acetic anhydride in the presence of potassium carbonate.

*See [1] for Communication 46.

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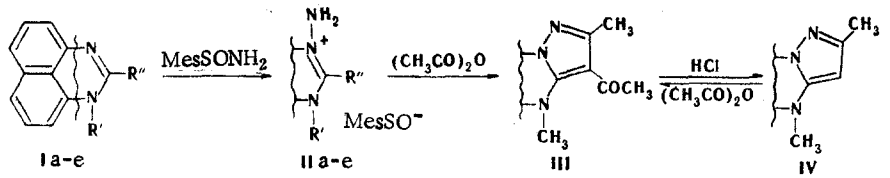
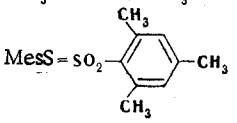


Ia-e IIa-e III IV

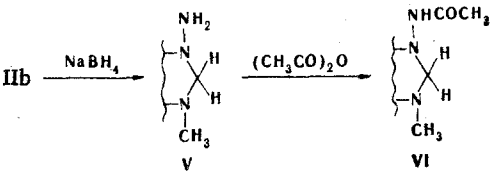
I-II a R′=R″=H; b, d, e R′=CH3; c R′=R″=CH3; b R″=H; d R″=C6H5, e R″=o-C6H4OCH3;



Dark red 1-benzylideneaminoperimidine is formed when an alcohol solution of salt IIa and p-nitrobenzaldehyde is refluxed.

The N-amination of perimidine by means of hydroxylamine-O-sulfonic acid [5] is hindered because of the low solubility of Ia in aqueous alkali; however, 1-aminoperimidine and perimidine itself, which we were unable to separate, are isolated from the reaction mixture when an aqueous alcohol solution of alkali is used.

The reduction of salt IIb with sodium borohydride in water leads to 1-methyl-3-amino-2,3-dihydroperimidine (V), the structure of which was confirmed by means of IR and PMR spectroscopy and by synthesis of its N-acetyl derivative VI by treatment with acetic anhydride.



V VI

EXPERIMENTAL

The IR spectra of the compounds were recorded with a UR-20 spectrometer. The PMR spectra were recorded with a Tesla BS-467 spectrometer (60 MHz) with hexamethyldisiloxane as the internal standard.

1-Aminoperimidinium Mesitylenesulfonate (IIa). A solution of 1.3 g (5 mmole) of MSHA in 5 ml of chloroform was added dropwise at 20°C to a solution of 0.85 g (5 mmole) of perimidine in 20 ml of alcohol (the selection of the solvents was determined by the solubility of perimidine), and the mixture was stirred for 1 h. The precipitate was removed by filtration and washed with alcohol and ether to give 0.8 g (42%) of yellow-green prisms with mp 237-238°C (dec., from water). IR spectrum (in mineral oil): 3155, 3260, and 3320 cm^{-1} (NH_2). Found: C 62.4; H 5.5; N 10.8; S 8.0%. $C_{20}H_{21}N_3O_3S$. Calculated: C 62.6; H 5.5; N 11.0; S 8.3%.

1-Methyl-3-aminoperimidinium Mesitylenesulfonate (IIb). A solution of 2.6 g (10 mmole) of MSHA in 15 ml of methylene chloride was added dropwise with stirring at 0-5°C in 15 min to a solution of 1.82 g (10 mmole) of 1-methylperimidine in 30 ml of methylene chloride, and the mixture was stirred at room temperature for 15 min. The precipitate was removed by filtration to give 3.7 g (93%) of light-green prisms with mp 225-226°C (dec., from water). IR spectrum (in mineral oil): 3170, 3250, and 3320 cm^{-1} (NH_2). Found: C 63.7; H 5.6; N 10.8; S 8.1%. $C_{21}H_{23}N_3O_3S$. Calculated: C 63.5; H 5.8; N 10.6; S 8.0%.

1,2-Dimethyl-3-aminoperimidinium Mesitylenesulfonate (IIc). The experiment was carried out by the method indicated above. Workup gave yellow prisms, with mp 223-224°C (dec., from alcohol), in 83% yield. IR spectrum (in mineral oil): 3130 and 3235 cm^{-1} (NH_2). Found: C 64.5; H 5.8; N 9.9; S 7.4%. $C_{22}H_{25}N_3O_3S$. Calculated: C 64.2; H 6.1; N 10.2; S 7.8%.

1-Methyl-2-phenyl-3-aminoperimidinium Mesitylenesulfonate (IId). A solution of 1.8 g (7 mmole) of MSHA in 15 ml of methylene chloride was added dropwise to a cooled (to 0-5°C) solution of 1.8 g (7 mmole) of 1-methyl-2-phenylperimidine in 15 ml of methylene chloride in 20 min, during which a yellow-green precipitate formed. The precipitate was removed by filtration after stirring at room temperature (20 min) to give 3.3 g (quantitative yield) of prisms with mp 232-233°C (dec., from alcohol). IR spectrum (in mineral oil): 3180, 3290, and 3450 cm^{-1} (NH_2). Found: C 68.6; H 5.8; N 9.0; S 6.9%. $C_{27}H_{27}N_3O_3S$. Calculated: C 68.5; H 5.7; N 9.0; S 6.8%.

1-Methyl-2-(o-methoxyphenyl)-3-aminoperimidinium Perchlorate (IIe). A solution of 2.6 g (10 mmole) of MSHA in 10 ml of methylene chloride was added dropwise to a cooled solution of 1.2 g (4 mmole) of 1-methyl-2-(o-methoxyphenyl)perimidine in 10 ml of methylene chloride, and the mixture was stirred at 20°C for 1 h. Ether (50 ml) was added, and the ether layer was separated from the pasty dark-red mass. The residue was treated with 50 ml of hot water, 5 ml of 30% perchloric acid was added, and the precipitate was removed by filtration to give 1.2 g (72%) of yellow-green prisms with mp 248-250°C (dec., from alcohol). IR spectrum (in mineral oil): 3235 and 3335 cm^{-1} (NH_2). Found: C 56.4; H 4.6; Cl 8.8; N 10.5%. $C_{19}H_{18}ClN_3O_5$. Calculated: C 56.5; H 4.5; Cl 8.8; N 10.4%.

2,4-Dimethyl-3-acetylpyrazolo[1,5-a]perimidine (III). A mixture of 1.0 g (2.5 mmole) of 1,2-dimethyl-3-aminoperimidinium mesitylenesulfonate and 1.4 g (10 mmole) of potassium carbonate in 5 ml of acetic anhydride was refluxed for 1 h, during which the yellow-green solution became colorless. The mixture was cooled and treated with 25 ml of water, and the aqueous mixture was neutralized to pH 7-8 with sodium bicarbonate. The resulting precipitate was removed by filtration and washed with water to give 0.7 g (quantitative yield) of colorless needles with mp 206°C (from butanol). IR spectrum (in chloroform): 1660 cm^{-1} (C=O), PMR spectrum (in CF_3COOH), δ: 2.4 (6H, s, C–CH_3 and $COCH_3$), 3.05 (3H, s, N–CH_3), 6.45 (1H, m, 5-H), and 6.75-7.2 ppm (5H, m, 6-H to 10-H). Found: C 73.6; H 5.3; N 15.1%. $C_{17}H_{15}N_3O$. Calculated: C 73.6; H 5.4; N 15.2%.

2,4-Dimethylpyrazolo[1,5-a]perimidine (IV). A solution of 0.28 g (1 mmole) of III in 7 ml of concentrated HCl was refluxed for 2 h, after which it was cooled, neutralized with 22% ammonium hydroxide, and extracted with chloroform. The product was purified by chromatography on Al_2O_3 (elution with chloroform) to give 0.23 g (quantitative yield) of slightly yellow prisms with mp 142-143°C (from heptane). Found: C 76.8; H 5.3; N 18.0%. $C_{15}H_{13}N_3$. Calculated: C 76.6; H 5.5; N 17.9%. The hydrochloride was obtained as yellowish needles with mp 208-209°C (from alcohol with ethyl acetate).

1-(p-Nitrobenzylidene)aminoperimidine. A mixture of equimolar amounts of salt IIa and p-nitrobenzaldehyde in alcohol was refluxed for 1 h, after which it was cooled, and the precipitate was removed by filtration and washed with water to give dark-red needles, with mp 198-199°C (from DMF), in quantitative yield. Found: C 68.6; H 3.8; N 17.5%. $C_{18}H_{12}N_4O_2$. Calculated: C 68.4; H 3.8; N 17.7%.

1-Methyl-3-amino-2,3-dihydroperimidine (V). A suspension of 0.7 g (1.8 mmole) of salt IIb in 20 ml of water was treated with 0.19 g (5 mmole) of $NaBH_4$ in portions, during which a colorless precipitate was formed. The precipitate was removed by filtration, washed with water, and purified by chromatography with a column filled with Al_2O_3 (elution with chloroform) to give 0.35 g (quantitative yield) of slightly yellow prisms with mp 151-152°C (from alcohol). IR spectrum (chloroform): 3365 cm^{-1} (NH_2). PMR spectrum (in $CDCl_3$), δ: 2.88 (3H, s, N–CH_3), 3.52 (2H, s, N–NH_2), 4.22 (2H, s, –CH_2–), 6.43 (1H, q, J_{meta} = 7.5 Hz, J_{ortho} = 2 Hz, 9-H), 6.83 (1H, q, J_{meta} = 7.0 Hz, J_{ortho} = 2 Hz, 4-H), and 7.23 ppm (4H, m, 5-H to 8-H). Found: C 72.5; H 6.3; N 21.0%. $C_{12}H_{13}N_3$. Calculated: C 72.4; H 6.5; N 21.1%.

1-Methyl-3-acetamido-2,3-dihydroperimidine (VI). A 0.45-g (2.2 mmole) sample of V was dissolved in the cold in 6 ml of acetic anhydride, and the precipitate that formed after 10 min was removed by filtration after 30 min and washed with water to give 0.45 g (85%) of colorless needles with mp 201-202°C (from alcohol). IR spectrum (in mineral oil): 3280 (N–H) and 1680 cm^{-1} (C=O). Found: C 69.8; H 6.0; N 17.2%. $C_{14}H_{15}N_3O$. Calculated: C 69.7; H 6.2; N 17.4%.

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