chromatographed with a column filled with aluminum oxide with collection of the first fraction (elution with benzene).

1-Methyl-2-(2,2-diphenyl-2-hydroxyethyl)perimidine (IIIa). This compound was obtained in 74% yield in the form of yellow crystals with mp 134-135°C (from benzene with octane). IR spectrum: 3370 cm^{-1} (OH, broad band of medium intensity). Found: C 82.5; H 5.8; N 7.1%. $C_{26}H_{22}N_2O$. Calculated: C 82.5; H 5.9; N 7.4%.

1-Methyl-2-(2-methyl-2-hydroxypropyl)perimidine (IIIb). This compound was obtained in 68% yield in the form of yellow crystals with mp 107-108°C (from petroleum ether). IR spectrum: 3380 cm^{-1} (OH, broad band of medium intensity). Found: C 76.1; H 7.3; N 10.8%. $C_{16}H_{18}N_2O$. Calculated: C 75.6; H 7.1; N 11.0%.

1,2,2,3-Tetramethyl-2,3-dihydroperimidine (V). A 1.1-g (0.003 mole) sample of 1,2,3-trimethylperimidinium iodide (IV) was added to a solution of methylmagnesium iodide obtained from 0.25 g (0.01 g-atom) of magnesium and 2.65 g (0.015 mole) of methyl iodide in 50 ml of absolute ether, and the suspension was refluxed with stirring until the solution became colorless. It was then cooled and treated with 40 ml of water, and the ether layer was separated and dried with calcium chloride. The ether was removed by distillation to give colorless crystals of V, which were recrystallized from alcohol to give 0.5 g (75%) of a product with mp 59-60°C. PMR spectrum: 1.32 (s, 6H, $C-CH_3$), 2.88 (s, 6H, $N-CH_3$), 6.55 (q, 2H, 4-H, 9-H), and 7.2 ppm (m, 4-H, 5-H, 6-H, 7-H, 8-H). Found: C 78.8; H 8.3; N 12.2%. $C_{15}H_{18}N_2$. Calculated: C 79.2; H 8.0; N 12.4%.

LITERATURE CITED

1. A. F. Pozharskii, L. P. Smirnova, B. A. Tertov, I. S. Kashparov, and V. I. Sokolov, Khim. Geterotsikl. Soedin., No. 12, 1682 (1975).
2. V. A. Anisimova and A. F. Pozharskii, Khim. Geterotsikl. Soedin., No. 1, 137 (1974).
3. S. I. Drusvyatskaya, B. V. Lopatin, A. F. Bekhli, A. I. Krotov, and A. S. Naidenova, Khim.-Farm. Zh., No. 5, 61 (1976).
4. R. F. Smith and M. M. Holmer, J. Chem. Soc., No. 12, 7531 (1965).
5. A. I. Belyashova, N. N. Zatsepina, E. N. Malysheva, A. F. Pozharskii, L. P. Smirnova, and I. F. Tupitsyn, Khim. Geterotsikl. Soedin., No. 11, 1544 (1977).
6. B. A. Tertov, A. S. Morkovnik, and Yu. G. Bogachev, Khim. Geterotsikl. Soedin., No. 12, 1699 (1976).
7. N. N. Zatsepina and I. F. Tupitsyn, Khim. Geterotsikl. Soedin., No. 12, 1587 (1974).
8. N. N. Zatsepina, I. F. Tupitsyn, and L. S. Éfros, The Chemistry and Technology of Isotopes [in Russian], Vol. 56, Khimiya, Leningrad (1967).
9. A. F. Pozharskii and G. G. Yurchuk, Khim. Geterotsikl. Soedin., No. 3, 418 (1979).

HETEROCYCLIC ANALOGS OF PLEIADIENE

44.* AMBIDENT CHARACTER OF THE N ANION OF PERIMIDINE IN REACTIONS WITH BENZYL AND ALLYL HALIDES

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It is shown that the N anion of perimidine displays ambident character in its reactions with benzyl and allyl halides and gives products of C alkylation in the 4 position in addition to N-substituted perimidines.

The N anion (I) of perimidine differs from the N anions of other N-heteromatic systems with respect to its extremely facile oxidizability under the influence of air oxygen, which leads to the formation of an insoluble black substance [2]. There is no doubt that this peculiarity of the N anion of perimidine is a consequence of its exceptionally high π-surplus character, which is characteristic of even the neutral perimidine molecule [3].

* See [1] for communication 43.

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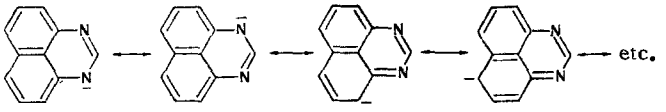
The π-surplus character of the N anion should be manifested in pronounced transfer of the π-electron density from the heteroring to the naphthalene part of the molecule, which can be represented in the form of the superimposition of resonance structures Ia-d:

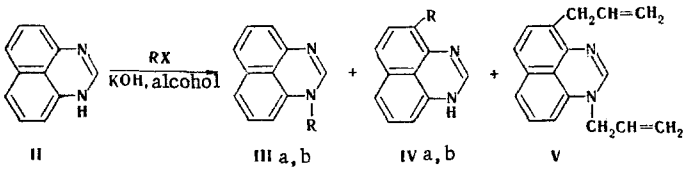


Ia Ib Ic Id

Owing to the contribution of structures of the Ic,d type, the oxidation of the anion most likely begins with the formation of the corresponding radicals as a result of detachment of one electron by oxygen with subsequent reaction of the radicals with oxygen or with one another in the manner in which the oxidative coupling of phenols occurs [4]. This somewhat speculative picture suggests that the perimidine anion should have ambident character. In the present research we obtained evidence for the correctness of this assumption.

It has been shown that anion I is alkylated smoothly in an inert atmosphere by primary alkyl halides to give N-alkylperimidines [2]. However, the benzylation of I proceeds with the formation of a complex mixture of substances, from which 1-benzylperimidine was isolated in low yield [2]. By careful repetition of this experiment with equimolar amounts of perimidine, benzyl chloride, and alkali is alcohol and subsequent chromatography of the resulting mixture of substances on low-activity aluminum oxide we were able to isolate 1-benzylperimidine (10%), the starting perimidine (25%), and the previously unknown 4-benzylperimidine (IVa) in 30% yield.

Under the same conditions I reacts with allyl bromide to give 1-allylperimidine (IIIb) (13%), 4-allylperimidine (IVb) (30%), and 1,4-diallylperimidine (V) (10%). The latter is evidently formed as a result of the subsequent allylation of the 4-allylperimidine anion.



II III a,b IV a,b V

III, IV a R = $C_6H_5CH_2$; III, IV b R = CH_2=CH–CH_2

The structures of all of the compounds obtained are confirmed by the results of elementary analysis, spectroscopic data, and their chemical behavior. In particular, 4-allyl- (IVb) and 4-benzylperimidine (IVa), like other 4-substituted perimidines [5], undergo alkylation to give only the N^1-methyl-substituted compounds (VIa,b, respectively), which do not undergo further quaternization even after prolonged refluxing with methyl iodide. This is a reliable test for the formation of structures of the IV type and is explained by the steric hindrance created by the substituent in the 4 position to alkylation of the adjacent N^3 atom.

We did not detect the other theoretically possible product of C alkylation of the perimidine anion, viz., 6(7)-benzyl(allyl)perimidine, in the reaction mixture. This fact did not exclude the possibility of the formation of IV by a Claisen rearrangement, which, in particular, has been observed for 1-allyl- and 1-benzylpyrroles [6]. However, this possibility was excluded, since III are not converted to IV under the reaction conditions. As expected, perimidine itself is alkylated only at the nitrogen atom when it is heated with allyl bromide in a neutral medium.

We were unable to realize the allylation of the 2-phenylperimidine anion under similar conditions because of pronounced resinfication. However, we did obtain 1-allyl-2-phenylperimidine by recyclization [7] of 1-allylperimidine under the influence of benzoyl chloride.

Thus the results provide evidence for the ambident nature of the perimidine anion. This distinguishes it markedly from the anions of the closely related imidazole systems [8] and other azoles. In the heteroaromatic series pyrrole [9] and indole [10] anions also have ambident character; however, one should note that for them migration of the reaction center occurs within the boundaries of the heteroring, while in the perimidine anion the ambident character encompasses the rings condensed with the heteroring.

EXPERIMENTAL

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

Reaction of Perimidine with Benzyl Chloride in Alcoholic Alkali. A 2.1-g (34 mmole) sample of KOH was added to a suspension of 5.7 g (34 mmole) of perimidine in 100 ml of alcohol, and the mixture was stirred at room temperature until the substances dissolved completely. Benzyl chloride [4.3 g (34 mmole)] was then added to the solution, and the mixture was stirred at room temperature for 20 h. The alcohol was then removed by distillation on a water bath. (All of the preceding operations were carried out in a nitrogen atmosphere.) The residue was dissolved in benzene (100 ml), and the insoluble material was removed by filtration and washed with water to give 1.4 g (25%) of perimidine. The benzene solution was evaporated, and the residual dark oil was dissolved in a small amount of chloroform and chromatographed on aluminum oxide (elution with chloroform). Two fractions were isolated. The first fraction contained 0.9 g (10%) of 1-benzylperimidine (IIIa) with mp 134°C (from octane) (this melting point was in agreement with the melting point in [2]).

The second fraction contained 2.5 g (30%) of 4-benzylperimidine (IVa). The yellow crystals had mp 158-159°C (from octane). IR spectrum (chloroform): ν_{N-H} 3440 cm^{-1}. PMR spectrum (d_4-methanol), δ: 3.8 s (2H, $-CH_2-$), 6.35 q (1H, H_9), 6.95 m (9H, H_5-H_8 + C_6H_5), and 7.22 s (1H, H_2) ppm. Found: C 83.8; H 5.6; N 10.9%. $C_{18}H_{14}N_2$. Calculated: C 83.7; H 5.5; N 10.9%.

Reaction of Perimidine with Allyl Bromide in an Alkaline Medium. A 4.6-g (0.08 mole) sample of KOH was added to a suspension of 11.9 g (0.07 mole) of perimidine in 200 ml of alcohol, and the mixture was stirred until the perimidine and KOH dissolved completely. Allyl bromide [8.6 g (0.07 mole)] was then added, and the solution was stirred at room temperature for 15 h. The alcohol was removed by distillation on a water bath. (All of the preceding operations were carried out in a nitrogen atmosphere.) The residue was treated with benzene (300 ml), and the benzene solution was filtered to remove the precipitated KBr and unchanged perimidine. The filtrate was evaporated, and the residual mixture was separated by chromatography with a column filled with Al_2O_3 (elution with chloroform). Two yellow fractions were isolated. The first fraction contained a mixture of IIIb and V, and the second fraction contained IVb. The yield of IVb was 3.6 g (30%). The light-yellow crystals had mp 169-170°C (from benzene with heptane). IR spectrum (in $CHCl_3$): ν_{N-H} 3442 cm^{-1}. PMR spectrum (d_6-acetone), δ: 3.3 d (2H, $-CH_2-C$ C), 4.01 broad s (1H, N−H), 5.00 m (2H, $=CH_2$), 5.90 m (1H, $-C-CH=C$), 6.36 q (1H, H_9), 7.0 m (4H, H_5-H_8), and 7.31 m (1H, H_2) ppm. Found: C 80.8; H 5.9; N 13.5%. $C_{14}H_{12}N_2$. Calculated: C 80.8; H 5.8; N 13.4%.

The first fraction was rechromatographed with a column filled with Al_2O_3 (elution with benzene). The first compound eluted was V [1.2 g (10%)]. It was initially isolated in the form of a dark-yellow oil that gradually crystallized when it was allowed to stand in a refrigerator. The crystals had mp 61°C (from heptane). PMR spectrum (CCl_4), δ: 3.4 d (2H, $-CH_2-C=C$), 4.00 d (2H, $-CH_2-$), 5.05 m (2H, $2CH_2=C-C-$), 5.82 m (2H, 2-C−CH = C), 6.6 m (1H, H_9), and 6.97 m (5H, H_2, H_5-H_8) ppm. Found: C 82.4; H 6.4; N 11.3%. $C_{17}H_{16}N_2$. Calculated: C 82.2; H 6.5; N 11.3%.

The second compound eluted was IIIb (1.8 g). The light-yellow crystalline compound had mp 78°C (from heptane). PMR spectrum (d_6-acetone), δ: 4.17 d (2H, $N-CH_2-$), 5.23 m (2H, $CH_2=C-C$), 5.70 m (1H, $C-CH=C$), 6.12 q (1H, H_9), 6.70 q (1H, H_4), 7.05 m (4H, H_5-H_8), and 7.30 s (1H, H_2) ppm. Found: C 80.7; H 5.8; N 13.6%. $C_{14}H_{12}N_2$. Calculated: C 80.8; H 5.8; N 13.4%.

Reaction of Perimidine with Allyl Bromide in Dimethylformamide. A 3.4-g (0.02 mole) sample of perimidine was dissolved in 30 ml of dimethylformamide (DMF), 1.2 g (0.01 mole) of allyl bromide was added, and the solution was heated with stirring on a water bath for 6 h. It was then poured into water (250 ml), and the aqueous mixture was made alkaline to pH 8 with 22% ammonium hydroxide. The precipitate was removed by filtration and washed with chloroform (100 ml). The chloroform extract was dried over $CaCl_2$, after which it was evaporated to a volume of 30 ml, and the concentrated solution was chromatographed with a column filled with Al_2O_3 (elution with chloroform). The first fraction was collected, the chloroform was evaporated, and the residual dark oil was crystallized from heptane to give 1 g (50%) of yellow crystals that were identified as IIIb.

1-Methyl-4-allylperimidine (VIb). A 0.5-g (7 mmole) sample of KOH was added to a solution of 1.5 g (7 mmole) of 4-allylperimidine (IVb) in 40 ml of alcohol, and the mixture was stirred until the potassium hydroxide dissolved completely. Methyl iodide [1.02 g (7 mmole)] was added, and the mixture was stirred at room temperature for 1.5 h and was then refluxed for 2 h. All of the preceding operations were carried out in a nitrogen atmosphere. The alcohol was removed by distillation, and the residual oil was dissolved in chloroform

and chromatographed with a column filled with aluminum oxide (elution with chloroform). The first fraction, which was yellow, was collected and worked up to give 0.7 g (43%) of yellow crystals with mp 66°C (from heptane). The IR spectrum did not contain ν_{N-H} absorption in the 3200-3500 cm^{-1} region. Found: C 81.0; H 6.4; N 12.6%. $C_{15}H_{14}N_2$. Calculated: C 81.3; H 6.3; N 12.5%.

1-Methyl-4-benzylperimidine (VIa). This compound was obtained in 70% yield by the method described above for VIb. The light-yellow crystals had mp 105-106°C (from isooctane). Found: C 84.0; H 6.0; N 10.3%. $C_{19}H_{16}N_2$. Calculated: C 83.8; H 5.9; N 10.3%.

1-Allylperimidine Methiodide. A solution of 2 g (0.01 mole) of 1-allylperimidine and a tenfold excess of methyl iodide in 50 ml of acetone was refluxed for 3 h, after which it was worked up to give the product in quantitative yield. The bright-yellow crystals had mp 241°C (from water).

Compounds V, VIa, and VIb did not form methiodides under similar conditions.

N-Allyl-N-formyl-N'-benzoyl-1,8-naphthalenediamine. A solution of 1 g (7 mmole) of benzoyl chloride in 10 ml of ether was added with stirring in the course of 15 min to a solution of 1.5 g (7 mmole) of 1-allylperimidine and 1.4 g (14 mmole) of triethylamine in 40 ml of ether, and the mixture was refluxed for 1 h. The colorless precipitate was removed by filtration and washed with 400 ml of water. The yield of colorless crystals with mp 70°C (from benzene with heptane) was 2.2 g (86%). IR spectrum (in chloroform): 3435 (N–H) and 1680 cm^{-1} (C = O). Found: C 75.8; H 5.4; N 8.7%. $C_{21}H_{18}N_2O_2$. Calculated: C 76.3; H 5.5; N 8.5%.

1-Allyl-2-phenylperimidine. A suspension of 2.2 g (7 mmole) of N-allyl-N-formyl-N'-benzoyl-1,8-naphthalenediamine in 40 ml of 10% NaOH solution was stirred at 100°C for 2 h, after which it was cooled, and the precipitate was removed by filtration, washed with water until the wash waters were neutral, and air dried to give 1.8 g (95%) of bright-yellow crystals with mp 137°C (from isooctane). Found: C 84.3; H 5.7; N 9.9%. $C_{20}H_{16}N_2$. Calculated: C 84.5; H 5.7; N 9.8%.

LITERATURE CITED

1. A. F. Pozharskii, L. P. Smirnova, A. I. Belyashova, N. N. Zatsepina, and I. F. Tupitsyn, Khim. Geterotsikl. Soedin., No. 7, 961 (1979).
2. A. F. Pozharskii and I. S. Kashparov, Khim. Geterotsikl. Soedin., No. 1, 111 (1970).
3. A. F. Pozharskii, I. S. Kashparov, P. J. Halls, and V. G. Zaletov, Khim. Geterotsikl. Soedin., No. 4, 543 (1971).
4. L. M. Strigun, L. S. Vertanyan, and N. M. Émanuél', Usp. Khim., 37, 969 (1968).
5. V. V. Kuz'menko and A. F. Pozharskii, Khim. Geterotsikl. Soedin., No. 7, 977 (1978).
6. T. M. Patterson, J. W. de Haan, M. R. Boyd, and J. D. Ferry, J. Am. Chem. Soc., 94, 2487 (1972).
7. A. K. Sheinkman, A. F. Pozharskii, V. I. Sokolov, and T. V. Stupnikova, Dokl. Akad. Nauk SSSR, 226, 1094 (1976).
8. A. F. Pozharskii, in: Outline of the Chemistry of Azoles [in Russian], Izd. Rostovsk. Univ., Rostov-on-Don (1965), p. 23.
9. P. A. Cauntor and G. A. Vanderwerf, J. Am. Chem. Soc., 80, 970 (1958).
10. M. G. Reinecke, U. W. Johnson, and J. F. Sebastian, Tetrahedron Lett., No. 18, 1183 (1963).