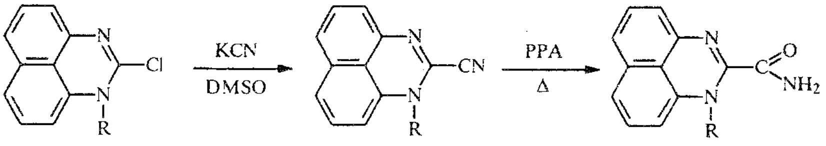
HETEROCYCLIC ANALOGS OF PLEIADIENE
61.* 2-CYANO- AND 2-CARBAMOYLPERIMIDINES

A. N. Suslov, A. F. Pozharskii, and I. V. Borovlev

Treatment of 1-R-2 chloroperimidines with potassium or sodium cyanides in DMSO solution leads to facile substitution of the chlorine atom by the CN group and formation of previously unknown 1-R-2-cyanoperimidines. The latter upon heating in polyphosphoric acid are converted to 1-R-2-carbomoylperimidines in good yield.

Up to the present time, little information has been available on perimidines containing strong electron-acceptor groups in the 2 position, especially −M type groups. The major reason for this is the high positive charge on the C_2 atom, due to which donor groups (NH_2, $NHNH_2$, OH, etc.) are easily introduced at this site of the molecule, but not acceptor groups [2]. Furthermore, individual electron-acceptor substituents introduced into the 2 position have proved to be very labile, undergoing thermal elimination or hydrolytic cleavage. For example, permidine-2-carboxylic acid is easily decarboxylated [3], while perimidine-2-sulfonic acid is converted to permidone upon brief heating in water [4].

We have for the first time accomplished direct introduction of a CN group into the 2 position of the perimidine molecule, which opens up a route to obtaining many other 2-substituted perimidines. We have found that upon treatment of 1-methyl- and 1-ethyl-2-chloroperimidines I with potassium or sodium cyanides in DMSO, even at room temperature facile nucleophilic exchange of the chlorine atom for the CN group occurs, as a result of which the previously unknown 2-cyanoperimidines II are formed in good yield. We could not obtain 2-cyanoperimidine unsubstituted at the 1 position in this way, probably because under these conditions 2-chloroperimidine is converted to the N-anion and then does not undergo nucleophilic substitution.



Ia,b IIa,b IIIa,b

a R = Me, b R = Et

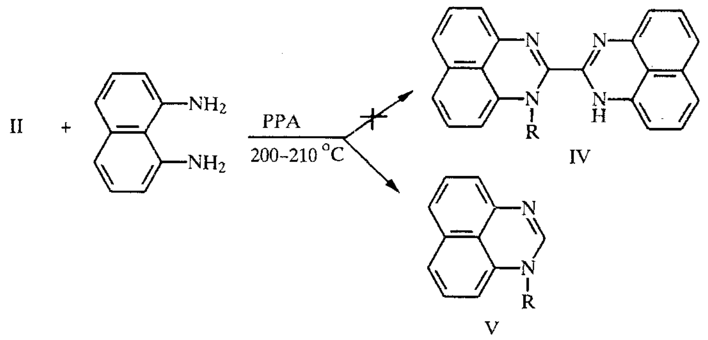
Compounds II upon brief heating in polyphosphoric acid at 120-140°C are smoothly converted to 1-R-2-carbomoylperimidines III. However, in an attempt to react cyanides II with 1,8-diaminonaphthalene (PPA, 200-210°C, 3 h) with the goal of obtaining previously unknown N-monosubstituted 2,2′-diperimidines IV as the sole reaction product, we isolated 1-R-2-perimidines V. Obviously under these conditions, hydrolysis of the nitrile group to carboxyl followed by decarboxylation occurs more easily than condensation with 1,8-diaminonaphthalene (see top of following page).

An interesting feature of compounds II is their bright red color, distinguishing them from the yellow perimidines V and the yellow-orange 2-carbamoylperimidines III. The color is due to the low-intensity absorption band in the 460 nm region with the absorption limit continuing almost up to 540 nm. An analogous band is found at 400 nm in simple perimidines, while in 2-

---

*For Communication 60, see [1].

Rostov State University, Rostov-na-Donu 344006, Russia. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 804-806, June, 1993. Original article submitted May 18, 1993.



carbamoylperimidines it is found at 400-405 nm with the absorption limit all the way up to 470 nm. The nature of this absorption band and the characteristics of its shift as a function of substituents were discussed earlier in [5, 6].

EXPERIMENTAL

The electronic absorption spectra were recorded on the Specord M 40 spectrophotometer in methanol solution. The IR spectra were recorded on the UR-20. The PMR spectra were recorded on the Bruker WH-90 (compounds IIa and IIIa) and the Unity-300 (compounds IIb and IIIb).

1-Ethyl-2-chloroperimidine (Ib). A mixture of 1.06 g (5 mmoles) 1-ethylperimidone [7] and 10 ml phosphorus oxychloride were boiled for 3 h, after which the excess $POCl_3$ was driven off and the residue was ground with 50 g ice and then carefully neutralized with ammonia. The precipitated crystals of compound Ib were filtered, washed with ice water (30 ml), and dried under vacuum over calcium chloride. Yield, 0.7 g (61%). Yellow crystals with T_{mp} 82-83 °C (from octane).

1-Methyl-2-cyanoperimidine (IIa). A 0.7 g portion (9.2 mmoles) of potassium cyanide was added to a solution of 1.74 g (8 mmoles) compound Ia [8] in 25 ml DMSO. The mixture, which rapidly acquired a red color, was stirred at room temperature for 1 h, after which it was poured into 100 ml water. The precipitated residue was filtered and washed with water. Yield, 1.61 g (97%). Bright red needles with T_{mp} 145-146 °C (from ethanol). UV spectrum, λ_{max} (log ε): 232 (4.61), 330 (4.03), 342 (4.04), 460 (3.09). IR spectrum (CCl_4): 2250 cm^{-1} (CN). PMR spectrum ($CDCl_3$): 3.23 (3H, s, CH_3-N); 6.08 (1H, dd, 9-H); 6.81 (1H, dd, 4-H); 7.21 ppm (4H, m, 5-H...8-H).

1-Ethyl-2-cyanoperimidine (IIb). Obtained analogously to compound IIa from 1-ethyl-2-chloroperimidine (Ib). Yield, 88%. Red crystals with T_{mp} 129-130 °C (from alcohol), UV spectrum, λ_{max} (log ε): 232 (4.71), 330 (4.06), 344 (4.12), 462 (3.12). PMR spectrum (DMSO-D_6): 1.33 (3H, t, $CH_2\underline{CH_3}$); 3.90 (2H, q, $\underline{CH_2}CH_3$); 6.52 (1H, dd, 9-H); 6.78 (1H, dd, 4-H); 7.25 ppm (4H, m, 5-H...8-H).

1-Methyl-2-carbamoylperimidine (IIIa). A mixture of 1.03 g (5 mmoles) 1-methyl-2-cyanoperimidine and 10 g polyphosphoric acid were stirred at 120-140 °C for 30 min, after which they were added to cold water (50 ml) and made alkaline with ammonia up to pH ~8. The precipitated amide residue was filtered, washed with water, and dried. Yield, 1 g (89%). Yellow-orange crystals with T_{mp} 192-193 °C (from aqueous ethanol or a 1:1 benzene–heptane mixture). UV spectrum, λ_{max} (log ε): 233 (4.63), 331 (4.16), 400 (3.15). IR spectrum, ($CHCl_3$): 3505, 3385 (NH_2), 1695 (C=O), 1625, 1585 cm^{-1} (arom.). PMR spectrum ($CDCl_3$): 3.45 (3H, s, CH_3-N); 5.60 (2H, br.s, NH_2); 6.30 (1H, dd, 9-H); 6.84 (1H, dd, 4-H); 7.20 (4H, m, 5-H...8-H). PMR spectrum (DMSO-D_6): 3.17 (1H, s, CH_3-N); 6.40 (1H, dd, 9-H); 6.73 (1H, dd, 4-H); 7.15 (4H, m, 5-H...8-H); 7.83 (1H, br.s, NH_2); 8.16 (1H, br.s, NH_2).

1-Ethyl-2-carbamoylperimidine (IIIb). Obtained from nitrile IIb analogously to compound IIIa. Yield, 86%. Yellow crystals with T_{mp} 216-217 °C (from a toluene–octane mixture). UV spectrum, λ_{max} (log ε): 234 (4.60), 335 (4.16), 400 (3.04). IR spectrum ($CHCl_3$): 3505, 3390 (NH_2), 1695 (C=O), 1620, 1580 cm^{-1} (arom.). PMR spectrum (DMSO-D_6): 1.30 (3H, t, $CH_2\underline{CH_3}$; 3.74 (2H, q, $\underline{CH_2}CH_3$); 6.48 (1H, dd, 9-H); 6.72 (1H, dd, 4-H); 7.21 (4H, m, 5-H...8-H); 7.75 (1H, br.s, NH_2); 8.16 ppm (1H, br.s, NH_2).

REFERENCES

1. A. F. Pozharskii, E. V. Tsarevskaya, and M. I. Rudnev, Khim. Geterotsk. Soedin., No. 6, 827 (1988).
2. A. F. Pozharskii and V. V. Dal'nikovskaya, Usp. Khim., **50**, 1559 (1981).
3. A. F. Pozharskii, L. P. Smirnova, B. A. Tertov, I. S. Kashparov, and V. I. Sokolov, Khim. Geterotsikl. Soedin., No. 12, 1682 (1975).
4. J. M. Herbert, P. D. Woodgate, and W. A. Denny, Heterocycles, **26**, 1043 (1987).
5. A. F. Pozharskii, Theoretical Principles of Heterocyclic Chemistry [in Russian], Khimiya, Moscow (1985), p. 95.
6. W. Thiel, J. Fabian, and B. Friebe, J. Prakt. Chem., **328**, 812 (1986).
7. I. S. Kashparov and A. F. Pozharskii, Khim. Geterotsikl. Soedin., No. 1, 124 (1971).
8. A. F. Pozharskii and I. S. Kashparov, Khim. Geterotsikl. Soedin., No. 8, 1129 (1970).