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CHANGE IN THE REGIOSELECTIVITY OF THE REACTION OF PERIMIDINE WITH CINNAMIC ACID DEPENDING ON THE CONCENTRATION OF POLYPHOSPHORIC ACID

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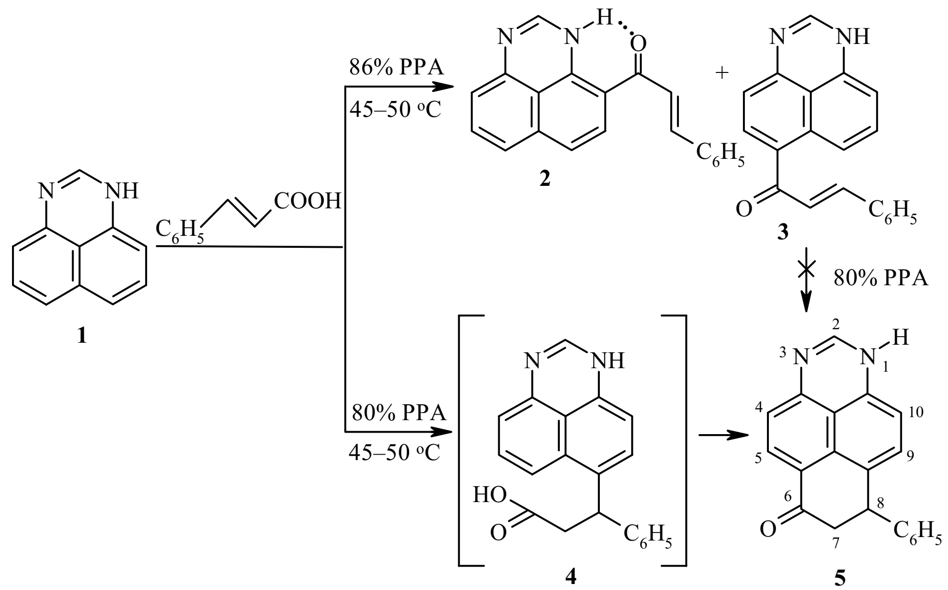
In a continuation of work on the acylation of perimidine **1** in polyphosphoric acid (PPA) [1, 2] we proposed to study its reaction with α,β-unsaturated acids. The reaction of **1** with cinnamic acid occurred readily at 45-50°C, however the results were different depending on the amount of P_2O_5 in PPA. For example in 86% PPA acylation occurred to give 4(9)- and 6(7)-cinnamoylperimidines **2** and **3**, with the latter predominating. With standard 80% PPA the reaction changed to the formation of the pericyclic compound 6(8)-oxo-8(6)-phenyl-1,6,7,8-tetrahydro-1,3-diazapyrene (**5**).



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We have also established that chalcone **3** is not the precursor of compound **5**, since compound **3** is unchanged under the reaction conditions, but undergoes resinification under more vigorous conditions. It means that compound **5** is formed *via* alkylation of perimidine with the ambident cinnamoyl cation with subsequent intramolecular acylation of the intermediate acid **4**, and not *vice versa*. In our view the change in regioselectivity on increasing the concentration of P_2O_5 in PPA is explained by the formation of a mixed anhydride of cinnamic and polyphosphoric acids which may possess only acylating properties.

The reaction was carried out by stirring a mixture of perimidine, a 1.5 molar excess of cinnamic acid and 10-fold excess by weight of PPA of the corresponding concentration at 45-50°C for 1 h. The mixture was then poured into cold water, made basic to about pH 8 with ammonia, the precipitate was filtered off, washed with water, and dried. Isomers **2** and **3** were separated by column chromatography on silica gel. The 4(9)-isomer was eluted with benzene–ethyl acetate, 1:1, the 6(7)-isomer with ethyl acetate. Compound **5** was purified by recrystallization from ethyl acetate.

4(9)-Cinnamoylperimidine (2). Orange crystals; mp 194-196°C (benzene–petroleum ether). ^1H NMR spectrum (acetone-d_6), δ, ppm, J (Hz): 7.1 (1H, br. d, $J_{4,5}$ = 7.7, 4-H); 7.2 (1H, d, $J_{7,8}$ = 9.4, 7-H); 7.4 (1H, br. d, $J_{6,5}$ = 8.2, 6-H); 7.45 (3H, m, *m*- and *p*-H C_6H_5); 7.6 (1H, br. t, 5-H); 7.8 (1H, d, J_{trans} = 15.4, CH=C$\underline{H}$–CO); 7.85 (2H, m, *o*-H C_6H_5); 8.0 (1H, J_{trans} = 15.4, C$\underline{H}$=CH–CO); 8.02 (1H, d, $J_{8,7}$ = 9.4, 8-H); 8.04 (1H, s, 2-H). Found, %: C 80.39; H 4.56; N 9.45. $C_{20}H_{14}N_2O$. Calculated, %: C 80.52; H 4.73; N 9.39.

6(7)-Cinnamoylperimidine (3). Bright red crystals; mp 234-235°C (benzene–ethanol). ^1H NMR spectrum (acetone-d_6), δ, ppm, J (Hz): 6.5 (1H, br. d, $J_{4,5}$ = 8.2, 4-H); 6.8 (1H, dd, $J_{9,8}$ = 7.4, $J_{9,7}$ << 1, 9-H); 7.4-7.5 (4H, m, 8-H and *m*-, *p*-H, C_6H_5); 7.6 (1H, d, J_{trans} = 15.7, CH=C$\underline{H}$–CO); 7.65 (1H, s, 2-H); 7.73 (1H, J_{trans} = 15.7, C$\underline{H}$=CH–CO); 7.8 (2H, m, *o*-H C_6H_5); 8.1 (1H, br. d, $J_{5,4}$ = 8.2, 5-H); 8.4 (br. dd, $J_{7,8}$ = 8.7, 7-H). Found, %: C 80.66; H 4.80; N 9.28. $C_{20}H_{14}N_2O$. Calculated, %: C 80.52; H 4.73; N 9.39.

6(8)-Oxo-8(6)-phenyl-1,6,7,8-tetrahydro-1,3-diazapyrene (5). Orange crystals; mp 98-99°C (ethyl acetate). ^1H NMR spectrum (acetone-d_6), δ, ppm, J (Hz): 3.0 (2H, dd, J = 6.4, C$\underline{H}_2$=CH(*cis*), J = 7.3 C$\underline{H}_2$=CH(*trans*)); 4.5 (1H, br. t, J = 6.8, C$\underline{H}$–CH_2); 6.6 (1H d, $J_{4,5}$ = 8.1, 4-H); 6.7 (1H, d, $J_{10,9}$ = 7.7, 10-H); 7.0 (1H, d, $J_{9,10}$ = 7.7, 9-H); 7.2-7.3 (5H, m, C_6H_5); 7.6 (1H, s, H-2); 7.8 (1H, d, $J_{5,4}$ = 8.1, 5-H). Found, %: C 80.43; H 4.61; N 9.22. $C_{20}H_{14}N_2O$. Calculated, %: C 80.52; H 4.73; N 9.39.

REFERENCES

1. A. F. Pozharskii, I. V. Borovlev, and I. S. Kashparov, *Khim. Geterotsikl. Soedin.,* 543 (1975).
2. I. V. Borovlev and A. F. Pozharskii, *Khim. Geterotsikl. Soedin.,* 1688 (1975).