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UNEXPECTED RESULT OF THE CINNAMOYLATION OF PERIMIDINE UNDER FRIEDEL–CRAFTS CONDITIONS

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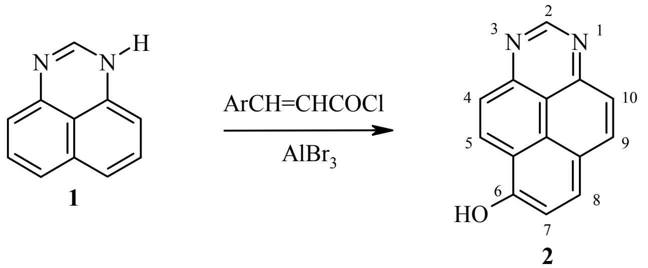
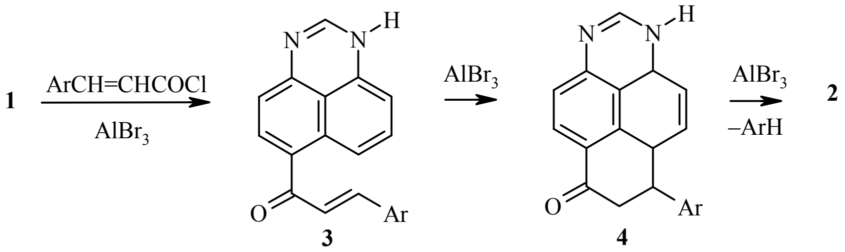
In a continuation of a study of the acylation of perimidine (**1**) [1, 2], we supposed to investigate the cinnamoylation of this compound under Friedel–Crafts conditions. The reaction of **1** with cinnamoyl chloride and *p*-bromocinnamoyl chloride proceeds readily at room temperature in dichloroethane. However, when a large excess of $AlBr_3$ was used, this reaction unexpectedly terminated with the formation of the same compound in both cases, namely, 6-hydroxy-1,3-diazapyrene (**2**):



Ar = C_6H_5, *p*-BrC_6H_4

We propose that this transformation features a tandem process involving acylation to give the corresponding 6(7)-cinnamoylperimidines **3**, intramolecular alkylation leading to 8(6)-aryl-6(8)-oxo-1,6,7,8-tetrahydro-1,3-diazapyrene **4**, and subsequent dearylation:



Two other tautomeric N–H forms are possible for **2** but comparison of the ^{1}H NMR spectrum of this compound with the spectra of acylperimidines [1] and 1,3-diazapyrenes [3] provides evidence for the 6-phenolic form of 1,3-diazapyrene.

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6-Hydroxy-1,3-diazapyrene (2). A solution of cinnamoyl chloride (0.002 mol) or *p*-bromocinnamoyl chloride in dichloroethane (1 ml) was added dropwise with stirring to a mixture of 6 ml dichloroethane, $AlBr_3$ (0.02 mol), and perimidine (0.002 mol) without permitting the reaction mixture to warm above 30°C. At the end of the addition, the mixture was stirred at room temperature for an additional 30 min and then poured carefully into water (10 ml). The precipitate was separated by filtration and dried. The dry mixture was ground and extracted with ethanol in a Soxhlet apparatus. The solution was evaporated to 10 ml and benzene (10 ml) was added. The precipitate was filtered off. The yield of red-brown crystalline **2** was 84% from cinnamoyl chloride and 57% from *p*-bromocinnamoyl chloride; mp 303-305°C (dec., ethanol). ^1H NMR spectrum (DMF-d_7), δ, ppm, J (Hz): 7.84 (1H, d, J_{78} = 8.25, 7-H); 7.99 (1H, d, J_{109} = 8.19, 10-H); 8.12 (1H, d, J_{45} = 9.34, 4-H); 8.56 (1H, d, J_{87} = 8.25, 8-H); 8.68 (1H, d, J_{910} = 8.19, 9-H); 9.00 (1H, d, J_{54} = 9.34, 5-H); 9.63 (1H, s, 2-H); 12.05 (1H, br. s, OH). ^1H NMR spectrum ($CDCl_3$), δ, ppm, J (Hz): 7.58 (1H, d, J_{78} = 8.28, 7-H); 8.05 (1H, d, J_{109} = 9.01, 10-H); 8.15 (1H, d, J_{45} = 9.30, 4-H); 8.30 (1H, d, J_{87} = 8.28, 8-H); 8.46 (1H, d, J_{910} = 9.01, 9-H); 8.92 (1H, d, J_{54} = 9.30, 5-H); 9.67 (1H, s, 2-H). IR spectrum (vaseline mull), cm^{-1}: 1570, 1590, 1605 (ring C=N), 3350 (OH). Found, %: C 76.48; H 3.59; N 12.62. $C_{14}H_8N_2O$. Calculated, %: C 76.35; H 3.66; N 12.72.

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