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UNEXPECTED PRODUCT OF THE ALKYLATION OF PERIMIDINES BY CHALCONES UNDER MICHAEL REACTION CONDITIONS

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An attempt to effect the N-alkylation of perimidines **1a-c** using α,β-unsaturated ketones (chalcones) under Michael reaction conditions in a neutral medium similar to the reaction with acrylonitrile [1] and also in basic medium in the system KOH–acetone was unsuccessful, perhaps due to steric hindrance. The reaction proceeds under more vigorous conditions at 180-185°C with sodium glycolate in ethylene glycol. However, the corresponding 1,3-diazapyrenes **8a-d** proved somewhat unexpectedly to be the sole products of this reaction along with considerable tar formation. Products **8a-d** were obtained in our previous work from the same reagents in polyphosphoric acid [2, 3]. While the result of this reaction would have been difficult to predict *a priori*, this process undoubtedly occurs according to the mechanism below (Scheme 1).

The ambident nature of perimidine N-anion was also noted earlier in its reaction with allyl and benzyl halides since C-alkylation products at $C_{(4)}$ and $C_{(9)}$ were isolated along with 1-allyl- and 1-benzylperimidines [4]. Anions **2** (R^1 = H, Me, Ph) act as $C_{(6)}$-nucleophiles in reactions with chalcones, i.e., in canonical structure **2b**. The product of the C-alkylation of compound **4** after deprotonation reacts as anion **5b**, undergoing intramolecular addition at the carbonyl group. Phenalene **7** is formed after dehydration. However, as in acid media [2, 3], phenalene **7** readily undergoes aromatization, indicating high thermodynamic stability of the 1,3-diazapyrene molecule. Thus, the C-variant of the Michael reaction occurs in the first step taking account of the likely reversibility of the N-alkylation of the perimidine anion under thermodynamic control conditions. Despite the relatively low yield of compound **8**, this transformation would appear to open new possibilities for the synthesis of this heterocyclic system.

Thus, in the standard procedure, solution is prepared by adding metallic sodium (2.6 mmol) to ethylene glycol (7 ml). Then, perimidine **1** (2 mmol) and benzalacetophenone or benzalacetone (4 mmol) are added and heated to 180-185°C. The mixture is retained at this temperature for 4 h. After cooling, the solution was poured into water (100 ml) and extracted with three 50-ml benzene portions. The combined extract was evaporated to 10 ml and passed through a silica gel column with benzene as the eluent for the first fraction and with ethyl acetate for the second fraction. The first fraction containing a small amount of tarry products was discarded. After distilling off the solvent, the second fraction gave products **8a-d**. The yield of 6,8-diphenyl-1,3-diazapyrene (**8a**) was 35%. The yield of 2-methyl-6,8-diphenyl-1,3-diazapyrene (**8b**) was 29%. The yield of

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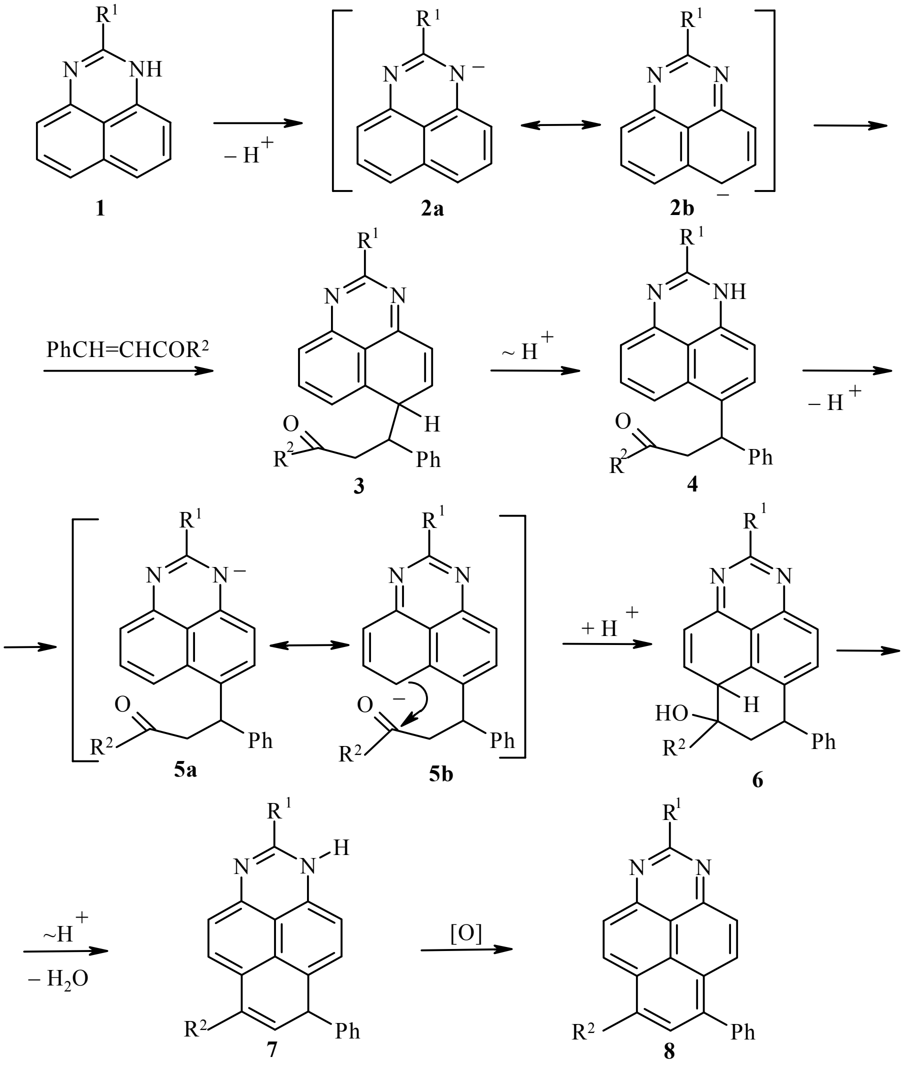
Scheme 1



1 a R^1 = H, **b** R^1 = Me, **c** R^1 = Ph; **8 a** R^1 = H, R^2 = Ph, **b** R^1 = Me, R^2 = Ph, **c** R^1 = R^2 = Ph,
d R^1 = H, R^2 = Me

2,6,8-triphenyl-1,3-diazapyrene (**8c**) was 23%. The yield of 6-methyl-8-phenyl-1,3-diazapyrene (**8d**) was 22%. Mixed probes of products **8a-d** with previously obtained samples of the corresponding compounds [3] did not give a melting point depression.

REFERENCES

1. A. F. Pozharskii, V. V. Dal'nikovskaya, V. M. Mar'yanovskii, and A. A. Konstantinchenko, *Khim. Geterotsikl. Soedin.*, 973 (1981).
2. I. V. Borovlev, A. V. Aksenov, and A. F. Pozharskii, *Khim. Geterotsikl. Soedin.*, 1523 (1997).
3. I. V. Borovlev, O. P. Demidov, and A. F. Pozharskii, *Khim. Geterotsikl. Soedin.*, 796 (2001).
4. A. F. Pozharskii and A. A. Konstantinchenko, *Khim. Geterotsikl. Soedin.*, 954 (1979).