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SYNTHESIS OF FORMYL DERIVATIVES OF 2-HETARYLIMIDAZOLES ANNELATED WITH NAPHTHALENE AND PHENANTHRENE RINGS

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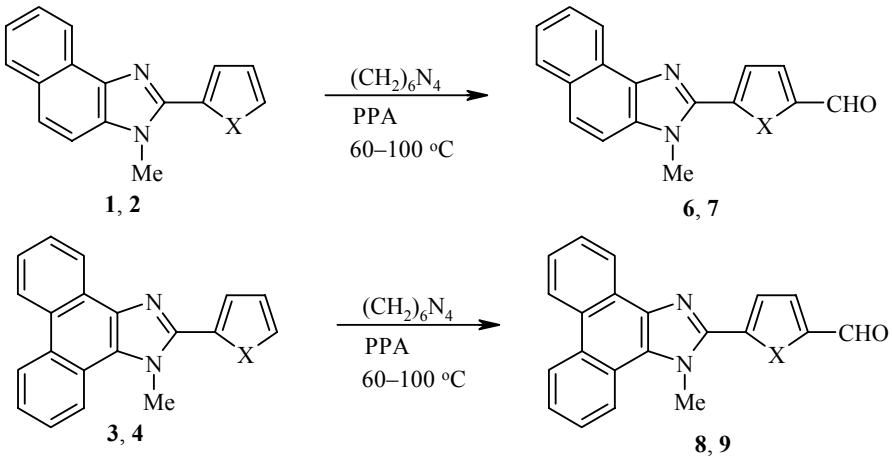
The formylation reaction of a series of 2-hetarylimidazoles, annelated by naphthalene and phenanthrene rings, using hexamethylenetetramine in PPA and the Vilsmeier reagent has been studied. The furyl and thienyl derivatives form principally the 5-formyl-substituted and the pyrrolylimidazoles were found to give a mixture of the α- and β-formyl derivatives.

Keywords: hetarylimidazoles, formylation.

The introduction into the structure of spiropyrans of heterocyclic fragments having luminophoric properties give the potential for the use of similar compounds in utilizing systems of preserving optical information with separate recording and read out channels. The recording of information can be brought about by the action on the molecule of activating UV irradiation and its read out correlated with the change in the luminescence spectrum of the photoinduced form when compared with the cyclic. In this case the very topical question is the preparation of novel heterocyclic aldehydes which are functionalized at the formyl group and which readily allow the introduction of the corresponding hetarene fragment into the spiropyran structures.



1, **3**, **6**, **8** X = O; **2**, **4**, **7**, **9** X = S

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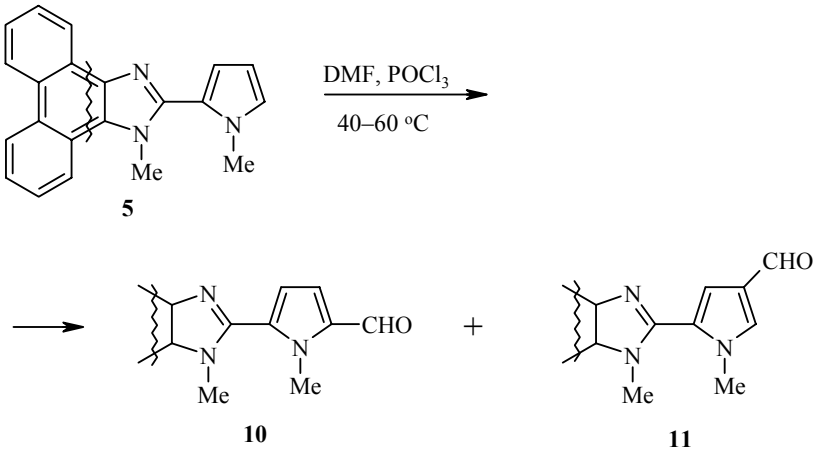
Up to this time the formylation of five-membered π-excessive heterocycles and their derivatives has been successfully carried out by a Vilsmeier reaction. However, according to data in [1], this method does not always prove expedient in most hetarylimidazoles. We have attempted to carry out the direct introduction of an aldehyde group into 2-hetarylimidazoles annelated with the naphthalene and phenanthrene rings using this method.

However, the reaction only took place for compound **5** under these conditions. Compounds **1-4** proved inert to the action of the Vilsmeier reagent even under quite forcing conditions and so for these compounds hexamethylenetetramine in PPA at 60-100°C was used as the formylation method. The 5-formyl derivatives on the hetaryl ring **6-9** were obtained as the formylation products and were separated in 60-75% yields.

A study of the formylation reaction of compound **5** using the Vilsmeier reagent gave unexpected results. In contrast to the similar benzimidazole pyrrolyl derivatives [2], which are characterized by the formation of exclusively the 4'-formyl derivatives on the pyrrole ring under these conditions, we observed the formation of a mixture of α- and β-substituted products. Separation of the isomers gave a 15-20% yield identified as 1-methyl-2-(2'-[5'-formyl-1'-methylpyrrolyl])phenanthro[9,10]imidazole (**10**), an isomer of compound **11**.



This points to a weaker electron acceptor effect of the phenanthro[9,10]imidazole substituent when compared with the corresponding benzimidazole fragment.

Concurrent reactions are observed when the 5 position of the hetaryl ring is occupied by a phenyl substituent. Hence, from ^{1}H NMR data, the formylation of compound **12** using hexamethylenetetramine in PPA medium gives a mixture of 1-methyl-2-(3-formyl-2-phenylfuryl)- (**13**) and 1-methyl-2-(5'-[*o*-formylphenyl]furyl)phenanthro[9,10]imidazoles (**14**).

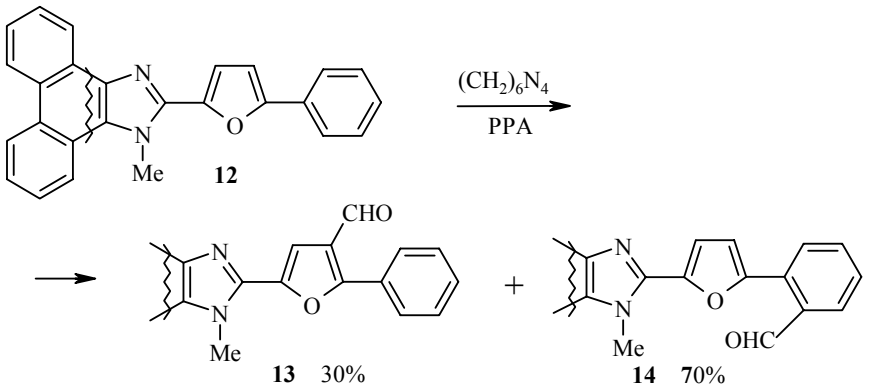


TABLE 1. Parameters for the Formyl 2-Hetarylimidazoles

Compound	Empirical formula	Found, % / Calculated, %			mp, °C	^{1}H NMR spectrum($CDCl_3$), δ, ppm (*J*, Hz)	Yield, %
		C	H	N			
6	$C_{17}H_{12}N_2O_2$	73.83 / 73.92	4.32 / 4.34	10.04 / 10.11	144-145	9.78 (1H, s, CHO); 8.63 (1H, d, *J* = 8.0, H-9); 7.90 (1H, d, *J* = 8.0, H-6); 7.77 (1H, d, *J* = 8.8, H-4); 7.62 (1H, t, *J* = 16.0, H-7); 7.52 (1H, d, *J* = 8.8, H-5); 7.48 (1H, t, *J* = 15.8, H-8); 7.45 (1H, d, *J* = 3.7, H-3'); 7.42 (1H, d, *J* = 3.7, H-4'); 4.22 (3H, N–CH_3)	62
7	$C_{17}H_{12}N_2OS$	70.14 / 69.92	4.13 / 4.11	9.63 / 9.66	180-181	9.98 (1H, s, CHO); 8.68 (1H, d, *J* = 8.2, H-9); 7.92 (1H, d, *J* = 8.2, H-6); 7.82 (1H, d, *J* = 4.0, H-4'); 7.74 (1H, d, *J* = 4.0, H-3'); 7.72 (1H, d, *J* = 8.8, H-4); 7.64 (1H, t, *J* = 16.0, H-7); 7.50 (1H, t, *J* = 16.0, H-8); 7.48 (1H, d, *J* = 8.8, H-5); 4.12 (3H, s, N–CH_3)	60
8	$C_{21}H_{14}N_2O_2$	75.93 / 75.39	4.33 / 4.29	8.25 / 8.28	198-199	9.76 (1H, s, CHO); 8.80 (1H, d, *J* = 8.0, H-7); 8.78 (1H, d, *J* = 8.1, H-8); 8.66 (1H, d, *J* = 7.7, H-4); 8.46 (1H, d, *J* = 7.7, H-11); 7.70 (4H, m, H-5, H-6, H-9, H-10); 7.52 (1H, d, *J* = 3.3, H-3'); 7.44 (1H, d, *J* = 3.3, H-4'); 4.60 (3H, s, N–CH_3)	52
9	$C_{21}H_{14}N_2OS$	72.66 / 73.13	4.03 / 4.09	7.83 / 7.69	207-208	9.96 (1H, s, CHO); 8.80 (1H, d, *J* = 8.0, H-7); 8.75 (1H, d, *J* = 8.0, H-8); 8.68 (1H, d, *J* = 7.7, H-4); 8.44 (1H, d, *J* = 7.7, H-11); 7.88 (1H, d, *J* = 3.9, H-4'); 7.68 (4H, m, H-5, H-6, H-9, H-10); 7.60 (1H, d, *J* = 3.9, H-3'); 4.45 (3H, s, N–CH_3)	60
10	$C_{22}H_{17}N_3O$	76.25 / 76.91	4.94 / 5.01	12.16 / 12.18	227-228	9.83 (1H, s, CHO); 8.82 (1H, d, *J* = 7.7, H-4); 8.72 (1H, d, *J* = 8.8, H-7); 8.68 (1H, d, *J* = 7.7, H-11); 8.50 (1H, d, *J* = 8.1, H-8); 7.65 (4H, m, H-5, H-6, H-9, H-10); 7.51 (1H, d, *J* = 4.2, H-4'); 7.00 (1H, d, *J* = 4.2, H-3'); 4.32 (3H, s, N–CH_3); 4.05 (3H, s, N–CH_3)	65
11	$C_{22}H_{17}N_3O$	76.52 / 76.91	4.91 / 5.05	11.92 / 12.18	215-216	9.70 (1H, d, CHO); 8.82 (1H, d, *J* = 7.7, H-4); 8.72 (1H, d, *J* = 8.8, H-7); 8.55 (1H, d, *J* = 7.7, H-8); 8.68 (1H, d, *J* = 7.7, H-11); 7.68 (4H, m, H-5, H-6, H-9, H-10); 7.08 (1H, s, H-4'); 6.62 (1H, s, H-3'); 4.30 (3H, s, N–CH_3); 4.16 (3H, s, N–CH_3)	17
13	$C_{27}H_{18}N_2O_2$	80.04 / 80.58	4.39 / 4.48	7.22 / 6.69	209-210	10.05 (1H, s, CHO); 8.74 (1H, d, *J* = 8.0, H-8); 8.68 (1H, d, *J* = 7.7, H-4); 8.47 (1H, d, *J* = 7.7, H-11); 7.93 (1H, s, H-3'); 7.65 (4H, m, H-5, H-6, H-9, H-10); 7.56 (4H, m, H_{arom}); 4.62 (3H, s, N–CH_3)	15
14	$C_{27}H_{18}N_2O_2$	80.93 / 80.58	4.68 / 4.51	6.92 / 6.69	204-205	10.22 (1H, s, CHO); 8.72 (1H, d, *J* = 8.0, H-8); 8.68 (1H, d, *J* = 7.7, H-4); 8.48 (2H, d, *J* = 6.3, H_{arom}); 8.47 (1H, d, *J* = 7.7, H-11); 7.65 (4H, m, H-5, H-6, H-9, H-10); 7.26 (1H, d, *J* = 3.0, H-3'); 7.05 (1H, d, *J* = 3.0, H-4'); 4.50 (3H, s, N–CH_3)	40

EXPERIMENTAL

^{1}H NMR spectra were recorded on a Varian Unity-300 (300 MHz) spectrometer using HMDS internal standard. The course of the reaction was monitored chromatographically on Brockmann activity grade II alumina plates (revealed using iodine vapor) in chloroform or on Silufol-250 plates in chloroform.

Synthesis of 1-Methyl-2-(5-formyl-2-furyl)naphtho[1,2-*d*]imidazole (6). 1-Methyl(2-furyl)naphtho-[1,2-*d*]imidazole **1** (2.98 g, 10 mmol) and hexamethylenetetramine (5.6 g, 40 mmol) were stirred in PPA (40 g) at 90-100°C for 4-6 h and the reaction was followed chromatographically. The reaction product was diluted with cold water (150 ml) and carefully neutralized using a 20% solution of ammonia. The product was extracted with chloroform (3 × 100 ml). The extract was evaporated and the residue was chromatographed on an alumina column with chloroform eluent. The product was recrystallized from heptane.

Compounds, 7, 8, 13, 14 were prepared similarly.

Formyl Derivatives 10, 11 were prepared under classic Vilsmeier conditions. The isomer mixture was separated by column chromatography on alumina with chloroform eluent.

The physicochemical and spectroscopic parameters for the compounds obtained are given in Table 1.

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REFERENCES

1. M. M. El'chaninov, L. Ya. Oleinikova, and A. M. Simonov, *Khim. Geterotsikl. Soedin.*, 1047 (1979).
2. M. M. El'chaninov, A. M. Simonov, and L. Ya. Oleinikova, *Khim. Geterotsikl. Soedin.*, 71 (1980).