The solid-state interaction of organometallic aldehydes with 1,8-naphthylenediamine

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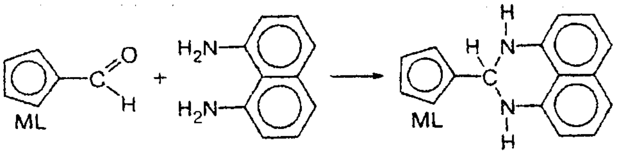
Organometallic derivatives of 2,3-dihydroperimidine were obtained by the solid state interaction of ferrocene-, cymantrene-, and ruthenocenecarbaldehydes with 1,8-naphthylenediamine.

Key words: solid state interaction, organometallic aldehydes, 2,3-dihydroperimidine, 1,8-naphthylenediamine.

Continuing our studies of the solid state interaction of organic and organometallic aldehydes with amines and their derivatives,[1—4] in this work, we synthesized 2-substituted 2,3-dihydroperimidines in the solid state. Perimidine, being an aromatic heterocycle with a high reactivity with respect to both nucleophilic and electrophilic reagents, is a key compound for preparation of many derivatives used in various areas.[5] Compounds containing the perimidine fragment are most widely used as dyes (in particular, the known Sudan Black B). Perimidine derivatives with antistatic properties and biological activity and used as luminophores and additives to liquid crystalline displays are described.

Substituted perimidines are prepared by the reactions of 1,8-naphthylenediamine (**1**) with various aromatic and heteroaromatic carbonyl compounds. The interaction of diamine **1** with aldehydes is traditionally carried out in alcohol solutions at room temperature or in benzene solutions on heating.[5,6] As a result, cyclic products are formed, 2-substituted 2,3-dihydroperimidines, which can easily be transformed into perimidines by dehydrogenation with sodium pyrosulfite.

We established in this work that diamine **1** reacts with crystalline organometallic aldehydes, ferrocenecarbaldehyde (**2a**), ruthenocenecarbaldehyde (**2b**), and cymantrenecarbaldehyde (**2c**), in the solid state at room temperature to form 2-metallocenyl-2,3-dihydroperimidines (**3a—c**).



2a—c **1** **3a—c**

ML = CpFe (**a**), CpRu (**b**), $Mn(CO)_3$ (**c**)

Equimolar amounts of compound **1** and aldehyde were mixed and left in an open flask in the dark with periodical stirring with a glass rod. The reaction course was monitored by the ^1H NMR spectra, comparing integral intensities of the aldehyde protons and H(2) of the perimidine cycle of compound **3**, which is the single reaction product. Conversion of the starting products at room temperature at different durations of interaction is shown in Table 1. Diamine **1** most rapidly reacts with aldehyde **2c**, and its reaction with aldehyde **2b** is the slowest.

Although all aldehydes studied in the work react with diamine **1** in the solid state at room temperature, the reaction rates are sufficiently low. The interaction is substantially accelerated when the reaction mixture is exposed to 70 °C for 1 h. In this case, the reaction mixtures immediately melt, and then for the reactions of ferrocene- and ruthenocenecarbaldehydes, the products are crystallized at the same temperature. When a mixture of cymantrenecarbaldehyde with diamine **1** was heated, the melting of the reaction mixture was accompanied by a noticeable change in color: the mixture

Table 1. Conversion of aldehydes **2a—c** in the reaction with diamine **1** ($T = 20$ °C)

Aldehyde	Duration of interaction/days	Conversion (%)
2a	4	66
	6	75
	10	95
2b	4	32
	6	42
	10	64
	16	90
2c	4	90
	6	100

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became dark-brown; therefore, the heating was continued for 5 min only. Further reaction and crystallization of the product occurred at room temperature for several hours. The ^{1}H NMR spectra of the samples of all three reaction mixtures after the end of the interaction did not contain the signals of the starting 1,8-naphthylenediamine.

As for similar reactions in solutions,[5,6] we failed to detect the formation of intermediate azomethines during the solid state interaction of compound **1** with aldehydes **2a—c**. The use of a double excess of aldehyde **2a** in the solid state reaction also did not result in the appearance of Schiff's bases.

2-Metallocenyl-2,3-dihydroperimidines **3b,c** obtained by us were not described earlier. The 2-ferrocenyl derivative was synthesized[7] by refluxing in benzene for 12 h with the addition of catalyst and distillation of released water.

Experimental

^{1}H NMR spectra were recorded on a Bruker AMX-200 instrument in deuteroacetone. Ferrocenecarbaldehyde,[8] ruthenocenecarbaldehyde,[9] and cymantrenecarbaldehyde[10] were synthesized by previously described procedures. 1,8-Naphthylenediamine (Aldrich Chemical Co.) was crystallized from hexane.

Solid state interaction of aldehydes 2a—c with diamine 1 (general procedure). Aldehyde (0.5 mmol) was mixed with compound **1** (0.5 mmol), and the mixture was left in air in the dark at −20 °C with periodical stirring or was heated at 70 °C for the time indicated in the text. The reaction course was monitored by periodical detection of ^{1}H NMR spectra of solutions of samples of the reaction mixture in deuteroacetone. The conversion of compounds **2a—c** was determined by comparison of the ratio of integral intensities of signals of the aldehyde proton and H(2) of the perimidine cycle. After the end of the interaction, the product was crystallized from an appropriate solvent.

2-Ferrocenyl-2,3-dihydroperimidine (3a). Yellow crystals, yield 0.166 g (94%), m.p. 176—177 °C (hexane) (Ref. 7: m.p. 182—183 °C). ^{1}H NMR, δ: 4.18 (m, 2 H, C_5H_4); 4.29 (s, 5 H, C_5H_5); 4.40 (m, 2 H, C_5H_4); 5.37 (m, 1 H, CH); 5.66 (m, 2 H, 2 NH); 6.57 (m, 2 H, Ar); 7.04 (m, 2 H, Ar); 7.15 (m, 2 H, Ar). Found (%): C, 71.20; H, 5.12; N, 7.91. $C_{21}H_{18}FeN_2$. Calculated (%): C, 71.30; H, 5.23; N, 7.93.

2-Ruthenocenyl-2,3-dihydroperimidine (3b). Colorless crystals, yield 0.173 g (87%), m.p. 203—204 °C (benzene—hexane, 3 : 1). ^{1}H NMR, δ: 4.80 (m, 2 H, C_5H_4); 4.94 (s, 5 H, C_5H_5); 5.05 (m, 2 H, C_5H_4); 5.31 (m, 1 H, CH); 5.71 (m, 2 H, 2 NH); 6.78 (m, 2 H, Ar); 7.29 (m, 2 H, Ar); 7.41 (m, 2 H, Ar). Found (%): C, 63.16; H, 4.30; N, 6.94. $C_{21}H_{18}N_2Ru$. Calculated (%): C, 63.14; H, 4.54; N, 7.01.

2-Cymantrenyl-2,3-dihydroperimidine (3c). Brown lustrous crystals, yield 0.153 g (82%), m.p. 166—168 °C (benzene—hexane, 3 : 1). ^{1}H NMR, δ: 5.10 (m, 2 H, C_5H_4); 5.39 (m, 2 H, C_5H_4); 5.60 (m, 1 H, CH); 6.22 (m, 2 H, 2 NH); 6.84 (m, 2 H, Ar); 7.33 (m, 2 H, Ar); 7.44 (m, 2 H, Ar). Found (%): C, 61.30; H, 3.52; N, 7.53. $C_{19}H_{13}MnN_2O_3$. Calculated (%): C, 61.36; H, 3.38; N, 7.52.

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