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REACTION OF 1-ALKYL-2-FORMYLIMIDAZOLE WITH TRIBENZYLPHOSPHINE OXIDE: AN EXAMPLE OF THE SYNTHESIS OF HETEROCYCLIC ANALOGS OF STILBENE

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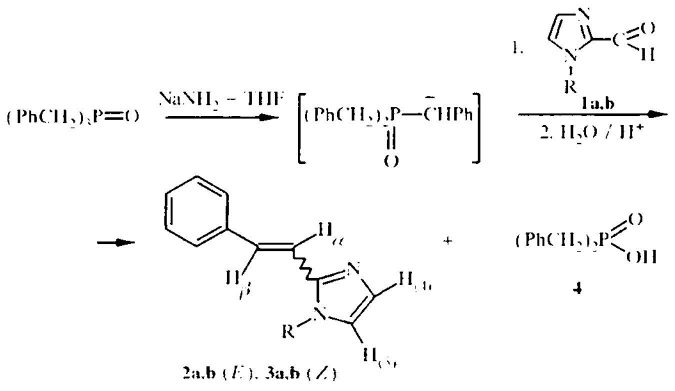
2-Ethenylimidazoles are building blocks for the synthesis of biologically active compounds and are promising ligands for the design of metal-complex catalysts. A method of synthesis of 2-vinylbenzimidazoles by the Wittig reaction from 2-chloromethylbenzimidazoles, triphenylphosphine, and formaldehyde is known [1]. A multistage synthesis of 1-methyl-2-(1-phenylvinyl)-1H-imidazole by the sequential treatment of 1-methyl-1H-imidazole with butyllithium and acetophenone with subsequent dehydration of the resulting hydroxy derivative has also been described [2].

We here briefly report that the reaction of the available 1-alkyl-2-formylimidazoles **1a,b** [3] with tribenzylphosphine oxide, readily available from red phosphorus and benzyl chloride [4], leads to 1-alkyl-2-(2-phenylethenyl)-1H-imidazoles of predominately the *E*-structure **2a,b**. The content of *Z*-isomers **3a,b** did not exceed 14%. The process was effected under the conditions of and according to the Wittig–Horner reaction (system was $NaNH_2$–THF, 60-65°C, 2 h), although examples of the successful implication of symmetrical phosphine oxides and heterocyclic aldehydes in this reaction are not known up to the present time.



1–3 a R = Me, **b** R = Et

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Dibenzylphosphinic acid (**4**) and (*E*)-stilbene, formed from tribenzylphosphine oxide, were also identified in the reaction mixture. A similar reaction was described previously in the case of diphenylbenzylphosphine oxide [5].

The reaction of aldehydes of the azole series with the available tribenzylphosphine oxide may therefore become a convenient method of synthesis of phenylethenylazoles, the heterocyclic analogs of stilbene, which are promising starting compounds for obtaining dyestuffs, optical whiteners, complex-forming agents, and pharmaceuticals (functional derivatives of stilbene possessing fungicidal and insecticidal properties have been isolated from rhubarb, false hellebore, pine trees, and red sandalwood [6]).

1-Methyl-2-(2-phenylethenyl)-1H-imidazole (2a,3a). Yield 42% [ratio of *E*- (**2a**) and *Z*- (**3a**) isomers 7 : 1]. Viscous undistillable liquid. ^{1}H NMR spectrum (CDCl$_3$, 400 MHz) for compound **2a**: 3.69 (3H, s, CH$_3$); 6.85 (1H, d, J_{54} = 1.0 Hz, 5-H); 6.89 (1H, d, $J_{\alpha\beta}$ = 16.2 Hz, α-H); 7.06 (1H, d, J_{45} = 1.0 Hz, 4-H); 7.20-7.52 (5H, m, H$_{arom}$); 7.56 ppm (1H, d, $J_{\beta\alpha}$ = 16.2 Hz, β-H). Compound **3a**: 3.23 (3H, s, CH$_3$); 6.39 (1H, d, $J_{\alpha\beta}$ = 12.2 Hz, α-H); 6.79 (1H, d, J_{54} = 1.2 Hz, 5-H); 6.80 (1H, d, $J_{\beta\alpha}$ =12.2 Hz, β-H); 7.20-7.52 ppm (5H, m, H$_{arom}$). The chemical shift of the 4-H proton was not determined due to overlap by signals of other protons. Found, %: C 77.69; H 7.02; N 14.78. $C_{12}H_{12}N_2$. Calculated, %: C 78.23; H 6.56; N 15.20.

1-Ethyl-2-(2-phenylethenyl)-1H-imidazole (2b,3b). Yield 52% (ratio of *E*- (**2b**) and *Z*- (**3b**) isomers 6 : 1). Viscous undistillable liquid. ^{1}H NMR spectrum (CDCl$_3$, 400 MHz) for compouns **2b**: 1.42 (3H, t, ^3J = 7.3 Hz, CH$_3$); 4.05 (2H, q, ^3J = 7.3 Hz, CH$_2$); 6.87 (1H, d, $J_{\alpha\beta}$ = 15.8 Hz, α-H); 6.90 (1H, d, J_{54} = 1.1 Hz, 5-H); 7.08 (1H, d, J_{45} = 1.1 Hz, 4-H); 7.20-7.52 (5H, m, H$_{arom}$); 7.59 ppm (1H, d, $J_{\beta\alpha}$ = 15.8 Hz, β-H). Compound **3b**: 1.18 (3H, t, ^3J = 7.3 Hz, CH$_3$); 3.65 (2H, q, ^3J = 7.3 Hz, CH$_2$); 6.37 (1H, d, $J_{\alpha\beta}$ = 12.2 Hz, α-H); 6.77 (1H, d, $J_{\beta\alpha}$ = 12.2 Hz, β-H); 6.87 (1H, d, J_{54} = 1.1 Hz, 5-H); 7.20-7.52 ppm (5H, m, H$_{arom}$). The chemical shift of the 4-H proton was not determined due to overlap by the signals of other protons. Found, %: C 78.29; H 7.18; N 14.49. $C_{13}H_{14}N_2$. Calculated, %: C 78.75; H 7.12; N 14.13.

Dibenzylphosphinic Acid (4). Yield 61% (in the reaction with **1a**) and 79% (in the reaction with **1b**); mp 190°C (ethanol) (literature mp 191°C [7]). ^{1}H NMR spectrum (CDCl$_3$, 400 MHz): 2.85 (4H, d, $^2J_{HP}$ = 16.9 Hz, CH$_2$); 7.18-7.28 (10H, m, H$_{arom}$); 9.02 ppm (1H, s, OH). ^{31}P NMR spectrum (CDCl$_3$, 90 MHz): 49.4 ppm. Found, %: C 68.92; H 6.23; P 12.71. $C_{14}H_{15}O_2P$. Calculated, %: C 68.29; H 6.14; P 12.58.

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