SYNTHESIS OF DERIVATIVES OF CONDENSED IMIDAZOLE SYSTEMS FROM 2-HALOIMIDAZOLES AND 8-HALOXANTHINES

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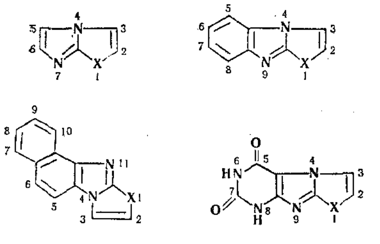
By methods known in the literature for closing imidazole [1] and thiazole [2] rings, we have performed the synthesis of derivatives of a number of condensed imidazole systems. By the reaction of 2-bromo-4,5-diphenylimidazole, 2-chlorobenzimidazole, and 2-chloronaphth[1,2-d]imidazole with α-halo ketones we have obtained the corresponding N-acylmethyl-2-haloimidazoles (**I–IV**). By heating **I–IV** and also 8-bromo-7-phenacyltheophylline (V) [3] with ammonia and amines we have obtained **VI–IX**. The reaction of **I–V** with thiourea or sodium hydrosulfide and subsequent cyclization of the intermediate mercapto compounds under the action of HBr, H_2SO_4, or $POCl_3$ has given **X–XIII**.



VI-IX X=NH; X-XIII X=S

2-Bromo-1-phenacyl-4,5-diphenylimidazole (I). Mp 180–181° C (methanol). Found, %: C 66.05; H 4.04; Br 19.57; N 6.99. Calculated for $C_{23}H_{17}BrN_2O$, %: C 66.19; H 4.11; Br 19.15; N 6.71. **2-Chloro-2-phenacylbenzimidazole (II).** Mp 168–170° C (methanol). Found, %: C 66.29; H 3.89; Cl 13.54; N 10.38. Calculated for $C_{15}H_{11}ClN_2O$, %: C 66.55; H 4.10; Cl 13.10; N 10.35. **3-Acetonyl-2-chloronaphth[1,2-d]imidazole (III).** Mp 133–134° C (aqueous ethanol). Found, %: C 64.75; H 4.18; Cl 14.08; N 10.97. Calculated for $C_{14}H_{11}ClN_2O$, %: C 64.99; H 4.29; Cl 13.71; N 10.83. **3-Phenacyl-2-chloronaphth[1,2-d]imidazole (IV).** Mp 200–201° C (aqueous methanol). Found, %: C 71.55; H 4.27; Cl 11.06; N 8.83. Calculated for $C_{19}H_{13}ClN_2O$, %: C 71.14; H 4.08; Cl 11.05; N 8.73. **1,2,5,6-Tetraphenylimidazo[1,2-a]imidazole (VI).** Mp 252–253° C (aqueous methanol). Found, %: C 84.37; H 5.30; N 10.16. Calculated for $C_{29}H_{21}N_3$, %: C 84.64; H 5.14; N 10.21. **2-Phenylimidazo[1,2-a]benzimidazole (VII).** Mp 285–287° C (decomp., acetic acid). Found, %: C 77.32; H 4.86; N 18.14. Calculated for $C_{15}H_{11}N_3$, %: C 77.23; H 4.75; N 18.02. **1-(p-Methoxyphenyl)-2-phenylnaphth[1,2-d]imidazo[3,2-b]imidazole (VIII).** Mp 266–267° C (ethanol). Found, %: C 80.34; H 4.99; N 10.61. Calculated for $C_{26}H_{19}N_3O$, %: C 80.18; H 4.92; N 10.79. **6,8-Dimethyl-2-phenylimidazo[1,2-f]xanthine (IX).** Decomp. p. > 320° C (acetic acid) [4]. **2,5,6-Triphenylimidazo[2,1-b]thiazole (X).** Mp 175–177° C (dioxane). Found, %: C 78.36; H 4.67; S 8.97. Calculated for $C_{23}H_{16}N_2S$, %: C 78.38; H 4.58; S 9.09. **2-Phenylthiazolo[3,2-a]benzimidazole (XI).** Mp 166–167° C (aqueous ethanol). Found, %: C 72.14; H 3.91; N 10.91. S 12.73. Calculated for $C_{15}H_{10}N_2S$, %: C 71.97; H 4.03; N 11.19; S 12.81. **2-Methylnaphth[1,2-d]imidazo[3,2-b]thiazole (XII).** Mp 184–185° C (decomp., ethanol). Found, %: C 70.54; H 4.25; N 12.04; S 13.66. Calculated for $C_{14}H_{10}N_2S$, %: C 70.56; H 4.23; N 11.75; S 13.46. **6,8-Dimethyl-2-phenylthiazolo[3,2-f]xanthine (XIII).** Mp 260–261.5° C (dimethylformamide). Found, %: C 57.44; H 4.01; N 17.83; S 10.40. Calculated for $C_{15}H_{12}N_4O_2S$, %: C 57.67; H 3.87; N 17.94; S 10.26.

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THE EXISTENCE OF A TRANSANNULAR BOND BETWEEN THE SILICON ATOM AND THE NITRO GROUP IN THE MOLECULE OF 5-NITRO-2,2,5-TRIMETHYL-2-SILA-1,3-DIOXANE

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In the PMR spectra of 2,2-dimethyl-2-sila-1,3-dioxane (I) and its derivatives **II–III** (see table), the resonance of the methylene protons has a singlet nature right down to the freezing temperature of solutions in methylene chloride (~70° C). In contrast to this, the PMR spectrum of 2,2,5-trimethyl-5-nitro-2-sila-1,3-dioxane (**IV**) contains a well-defined AB multiplet of CH_2 protons and two singlet signals of the protons of the trimethylsilyl groups even at room temperature. On this basis, it may be concluded that the molecules **I–III** undergo rapid conformational transitions while **IV** exists as a single conformer.

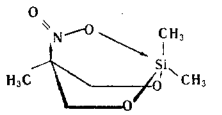
Chemical Shifts in the PMR Spectra of 2, 2-Dimethyl-2-sila-1, 3-dioxanes

Compound	Formula	τ, ppm			
		$C_{4,5}$—H	C_5—CH_3	C_5—H	CH_3
I	$(CH_3)_2SiOCH_2CH_2CH_2O$	6.03	—	8.24	9.91
II	$(CH_3)_2SiOCH_2C(CH_3)_2CH_2O$	6.44	9.05	—	9.91
III	$(CH_3)_2SiOCH_2C(CH_3)(NH_2)CH_2O$	6.40	8.99	—	9.87
IV	$(CH_3)_2SiOCH_2C(CH_3)(NO_2)CH_2O$	5.95 and 5.41 $^3J_{H-H} = 12$ Hz	8.60	—	9.88 and 9.81

It has been stated in a lecture [1] that the experimental value of the dipole moment of **IV** may agree with the theoretical calculations in two cases: 1) if the molecules of **IV** pass rapidly from one chair form to another; 2) if they exist in the boat form. The PMR results thus confirm the correctness of the second of these hypotheses.

According to Urbanski et al. [1], the carbon analog of **IV** exists in the chair form with the nitro group in the axial position.

The existence of the molecule of **IV** in the boat form, a conformer in any case less energetically favorable than the chair structure, can be assessed as a manifestation of the specific influence of the silicon atom on the structure of the heterocycle. The gain in energy of the given conformer of **IV** apparently consists in the formation of a transannular bond between one of the oxygen atoms of the nitro group and the silicon atom, which possesses unfilled 3d orbitals.



The given structure of **IV** is remarkably stable: raising the temperature of the sample to ~180° C does not change the nature of its PMR spectrum. This fact shows the considerable energy of interaction between the silicon atom and the nitro group.

The method of synthesis and the physical constants of the compounds that we studied have been described previously [2]. The PMR spectra were obtained on a YaMR-553 TsLA spectrometer (40 MHz). The chemical shifts were measured for 20% solutions of the substances in carbon tetrachloride containing cyclohexane as internal standard. At low temperatures, the PMR spectra of solutions in methylene chloride were recorded.

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A NEW METHOD FOR THE SYNTHESIS OF 2, 6-DIARYL-SUBSTITUTED PYRYLIUM SALTS BY THE ACYLATION OF PHENOL ETHERS WITH GLUTARIC ACID IN THE PRESENCE OF POLYPHOSPHORIC ACID (PPA)

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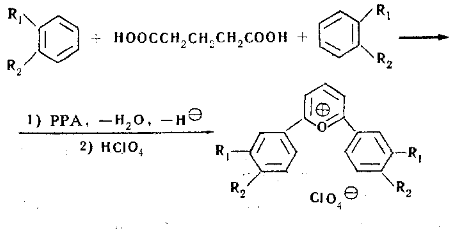
2, 6-Diphenyl-substituted pyrylium salts can be obtained by methods described in the literature [1–3]. We propose a new method for the synthesis of 2, 6-diaryl-substituted pyrylium salts consisting in the reaction of phenol esters with glutaric acid in the presence of PPA, which in this case is not only a condensing agent but also a dehydrogenating agent.



a $R_1 = H$, $R_2 = OCH_3$; b $R_1 = H$, $R_2 = OC_2H_5$; c $R_1 = R_2 = OCH_3$

The reaction takes place when a mixture of a phenol ether and glutaric acid (2 : 1) is heated with a six- to tenfold weight of PPA at 100° C for 60–80 min. The reaction products are isolated by treating the reaction mixture with water in the form of brightly colored pyrylium phosphates, which are converted by the action of aqueous $HClO_4$ into the readily analyzed 2, 6-diaryl-substituted pyrylium perchlorates in good yield (35–55%). By this method using anisole and glutaric acid we obtained 2, 6-di(4'-methoxyphenyl)pyrylium perchlorate in the form of bright red crystals with a yield of 55%. Mp 248° C (nitromethane). IR spectrum: 1624, 1606, 1240 cm^{-1}.

Similarly, by the acylation of phenetole and veratrole with glutaric acid we obtained, respectively, 2, 6-di(4'-ethoxyphenyl)pyrylium perchlorate with a yield of 52%, mp 221° C (nitromethane), and 2, 6-di-(3', 4'-dimethoxyphenyl)pyrylium perchlorate with a yield of 35%, mp 254° C (nitromethane).