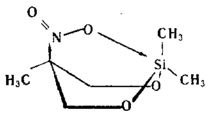
Chemical Shifts in the PMR Spectra of 2,2-Dimethyl-2-sila-1,3-dioxanes

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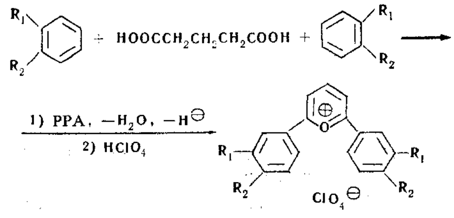
2,6-Diphenyl-substituted pyrylium salts can be obtained by methods described in the literature [1–3]. We propose a new method for the synthesis of 2,6-diaryl-substituted pyrylium salts consisting in the reaction of phenol esters with glutaric acid in the presence of PPA, which in this case is not only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

Mixtures of the salts obtained with samples of 2,6-diaryl-substituted pyrylium perchlorates synthesized previously [3] gave no depression of the melting point. The structure of the compounds obtained is also confirmed by IR spectroscopy.

The study of the given method is continuing.

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STRUCTURE OF THE CONDENSATION PRODUCT OF 3,4-XYLENOL WITH CROTONALDEHYDE

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In our recent paper [1], by an oversight no reference was made to the paper by L. P. Zalukaev and N. I. Poplavskaya [2] in which, using the condensation of crotonaldehyde with β-naphthol, which is similar in structure to 3,4-xylenol, the authors first established the formation of 4-(2-hydroxylnaphthyl)-2-methyl-5,6-benzochromane. Thus, our investigation on the structure of the product of the condensation of 3,4-xylenol with crotonaldehyde [1] is a confirmation of Zalukaev and Poplavskaya's conclusions [2].

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SYNTHESIS OF 1-ALKYL-, 1-ARALKYL-, and 1-ARYL-2-AMINOIMIDAZOLES

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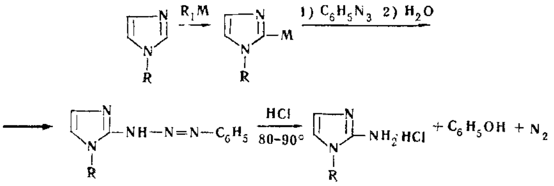
Several methods for the synthesis of 2-aminoimidazoles have been described [1-7].

We have established that the amino group can easily be introduced into position 2 of a N-substituted imidazole by treating the organosodium or organolithium compound of the corresponding imidazole with phenyl azide and subjecting the triazene formed to cleavage with mineral acid at 80-90° C.



$R = CH_3, C_2H_5, CH_2C_6H_5, C_6H_5;\ R_1 = C_6H_5, C_4H_9;\ M = Na, Li$

2-Amino-1-methylimidazole hydrochloride monohydrate. Obtained from 2-lithio-1-methylimidazole. Mp 83-84° C, which corresponds with that given in the literature [6,7]. Yield 70%.

2-Amino-1-methylimidazole. Bp 136-137° C (5 mm), mp 81.5-82.5° C. Found, %: C 49.66; H 7.51; N 43.38. Calculated for $C_4H_7N_3$, %: C 49.47; H 7.26; N 43.27.

2-Amino-1-ethylimidazole. Obtained from 1-ethyl-2-lithioimidazole. Bp 133-135° C (6 mm). Yield 51%. Found, %: C 53.84; H 8.47; N 37.70. Calculated for $C_5H_9N_3$, %: C 54.03; H 8.16; N 37.81.

2-Amino-1-benzylimidazole hydrochloride. Obtained from 1-benzyl-2-sodioimidazole. Mp 185-186° C. Yield 63.5%: Found, %: C 57.48; H 5.95; Cl 17.20; N 20.36. Calculated for $C_{10}H_{11}N_3 \cdot HCl$, %: C 57.28; H 5.77; Cl 16.91; N 20.04.

2-Amino-1-benzylimidazole. Mp 139-140° C (from water). Found, %: C 69.22; H 6.56; N 24.59. Calculated for $C_{10}H_{11}N_3$, %: C 69.34; H 6.40; N 24.26.