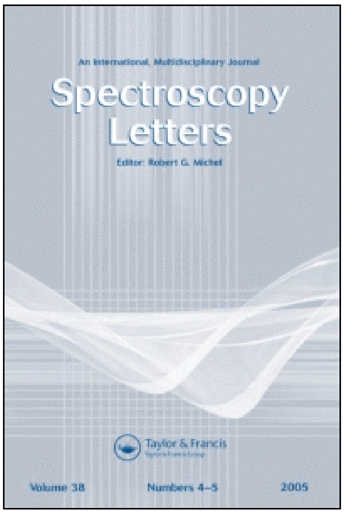

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^{1}H-NMR Elucidation of the Structure of Some 1,3,5-Triazines

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^{1}H-NMR ELUCIDATION OF THE STRUCTURE OF SOME 1,3,5-TRIAZINES

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An attempt has been made to elucidate the structure of products of the reactions of some 1-/4-R-phenyl/-3-/3,5,5-trimethyl-2-pyrazoline-1-carbonimidoyl/guanidines with benzoyl chloride, propionoyl chloride and ethyl orthoformate on the basis of their ^{1}H-NMR and UV spectra.

Biguanides have been known to react with carboxylic acids and their derivatives such as esters, acyl chlorides, anhydrides and amides as well as with ortho esters to afford compounds containing the 1,3,5-triazine ring.

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A literature survey shows that in reactions with ortho esters, 1,3,5-triazines are the sole products/1/,whereas reactions biguanides with esters or acyl chlorides afford either 1,3,5-triazines /2,3/ or 1,2,3,4-tetrahydro-1,3,5-triazines /4,5/. As both types of the compounds have identical molecular formulas, spectral analysis has usually been employed to elucidate their structure.

According to many authors, the IR of the 1,3,5-triazine ring exhibits the following characteristic group frequencies /cm^{-1}/: 673 and 753 /6/, 805-825 /7-9/, 1410 /6-8/, 1500 /7,8/, 1555-1590 /7-9/ and 1617-1635 /7-9/. Somogyi /7/ argues that the 1617, 1556 and 1410 cm^{-1} bands are missing in the spectra of 1,2-dihydro-1,3,5-triazines. Other authors, however, consider the 1410^{-1} band as being characteristic of 1,2-dihydro-1,3,5-triazines /10/ and hexahydro-1,3,5-triazines /11/, while the 1590-1515 cm^{-1} appeares in the spectra of 1,2-dihydro-1,3,5-triazines /12/. These literature data show identification of the triazine structures on the basis of their oscillational spectra is rather doubtful.

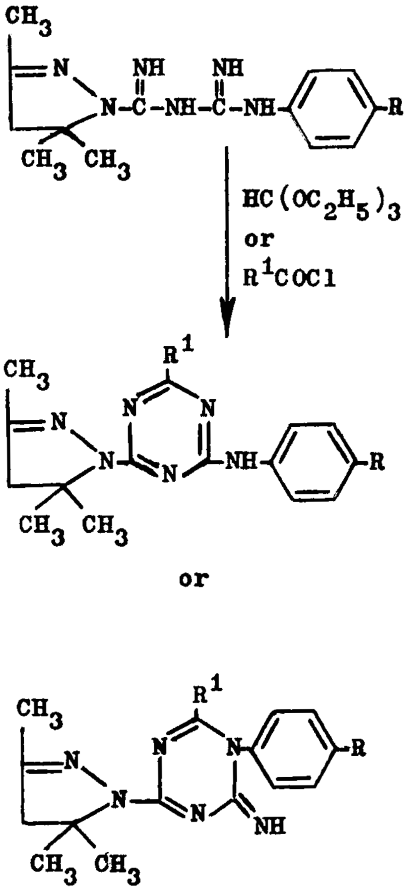
In this paper an attempt has been made to elucidate the structure of five compounds containing presumably 1,3,5-triazine rings in their molecules on the basis of their ^{1}H-NMR and UV spectra.

EXPERIMENTAL

The compounds were obtained /14/ in reactions of 1-/4-R-phenyl/-3-/3,5,5-trimethyl-2-pyrazoline-1-carbonimidoyl/guanidines /13/ with ethyl orthoformate /I/ or acyl chlorides /II-V/,

The ^{1}H-NMR spectra were taken on a BS 487 Tesla spectrometer operated at 80 MHz in DMSO solutions using hexamethyldisiloxane as an internal reference.

Scheme 1



R=Cl	R^1=H	(I)
R=CH_3	R^1=C_2H_5	(II)
R=CH_3	R^1=C_6H_5	(III)
R=Cl	R^1=C_2H_5	(IV)
R=Cl	R^1=C_6H_5	(V)

TABLE 1

Proton chemical shifts / δ , ppm/ of particular groups of protons

Compound	Chemical shift and number of protons. All singlets			
II	1.70/s/ 6H	2.14/s/ 3H	2.39/s/ 3H	2.97/s/ 2H
III	1.84/s/ 6H	2.12/s/ 3H	2.39/s/ 3H	3.01/s/ 2H
IV	1.72/s/ 6H	2.14/s/ 3H	-	3.01/s/ 2H
V	1.77/s/ 6H	2.12/s/ 3H	-	2.97/s/ 2H

TABLE 2

Proton chemical shifts / δ , ppm/ of particular groups of protons

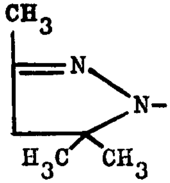
Compound	Chemical shift, multiplicity of signal, spin-spin coupling constant /J, Hz/ and number of protons			
II	7.20/d//8/2H	* 7.85/d//8/2H	$-CH_2-$ 2.65/ q //7/2H	$-CH_2-CH_3-$ 1.37/t//7/3H
III	7.27/d//7/2H	* 7.92/d//7/2H	7.68 /mpl/ 3H	8.47 /mpl/2H
IV	7.45/d//8/2H	* 8.02/d//8/2H	$-CH_2-$ 2.65/ q //7/2H	$-CH_2-CH_3-$ 1.37/t//7/3H
V	7.47/d//8/2H	* 8.08/d//8/2H	7.65 /mpl/ 3H	8.45 /mpl/2H

d - doublet, d* - broadened doublet, q - quadruplet,

m - multiplet, t - triplet

RESULTS

Singlets appearing in the spectra are shown in Table 1 /δ scale throughout/.
They reveal the presence of the 3,5,5-trimethyl-2-pyrazoline fragment



/II-V/

in the spectra of 1-/4-R-phenyl/-3-/3,5,5-trimethyl-2-pyrazoline-1-carbonimidoyl/guanidines arising in reactions of the following R^1COCl /scheme 1/: R = CH_3; R^1 = C_2H_5 /II/; R = CH_3, R^1 = C_6H_5 /III/; R = Cl, R^1 = C_2H_5 /V/; R = Cl, R^1 = C_6H_5 /IV/.

In the spectra of II ans III the p-tolyl group manifests itself in a singlet at 2.39 ppm /CH_3/ and signals of the benzene ring protons /Table 2/. The signals of the p-chlorophenyl group protons confirm its presence in compounds IV and V /Table 2/. In these spectra also the presence of signals due to the phenyl /III and V/ and ethyl /II and IV/ groups was ascertained /Table 2/.
The spectra of II-V display also a broadened signal due to one -NH-proton /Table 3/.
In the spectra of the products of reaction between 1-/4-chlorophenyl/-3-/3,5,5-trimethyl-2-pyrazoline-1-carbonimidoyl/guanidine and ethyl orthoformate, proton signals shown in Table 4 were found.
The data of Table 4 indicate that the charge distribution in I is unlike that in compounds II-V. This difference, particularly in the position of the N$\underline{H}$ proton signals, is indicative of a different structure of I as compared to that of the remaining compounds.

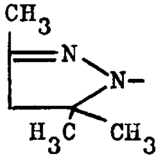
TABLE 3

Chemical shifts /δ, ppm/

Compound	Chemical shift
II	9.62
III	9.90
IV	9.90
V	9.90

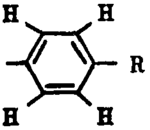
DISCUSSION AND CONCLUSIONS

An inspection of the chemical ahift values of the 3,5,5-trimethyl-2-pyrazoline fragment /Table 1/



shows that the resonance lines of the methyl protons at position 5 in III and V are slightly deshielded /in particular in III/ relative to analogous signals of II and IV.

The data of Table 2 show also that the aromatic protons of the fragment



where R=CH_3 /II/, Cl /IV/

are strongly deshielded and their signals are shifted relative to the "normal" position /15/. The same

TABLE 4

Chemical shifts /δ , ppm/ of particular groups of protons in compound

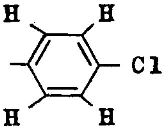
Solvent	Chemical shift, multiplicity of signal, spin-spin coupling constant /J, Hz/, number of protons of particular group						
DMSO	1.69/s/6H	2.12/s/3H	2.92/s/2H	5.37/s/1H*	7.00/d//8/2H	7.40/d//8/2H	-
$CDCl_3$	1.50/s/6H	1.87/s/3H	2.60/s/2H	-	6.70/d//8/2H	7.10/d//8/2H	7.13/s/1H
d_5-Py	1.37/s/6H	1.60/s/3H	2.34/s/2H	4.57/s/*	6.77 2H	7.07 3H	-

d- doublet , s - singlet,

* - signal broadened owing slow proton exchange

phenomenon is observed with III and V /Table 2/ carrying the ethyl and phenyl /R^1 = C_6H_5/ substituents. On the other hand, there is a strikingly strong deshielding of the N$\underline{H}$ protons /Table 3/, this revealing the presence of the Ar-NH-Ar moiety.

If one assumes the compounds under consideration to be 1,3,5-triazines /Scheme 1/, similarity of their structures would not have resulted in so large differences in the positions of the respective signals. This assumption, however, does not explain the abnormal position of the N$\underline{H}$ proton signals. The difference in the spectra of II - V on the one hand, and of I on the other, can be explained under assumption that I is a derivative of 1,2-dihydro-1,3,5-triazine, while II-V are 1,3,5-triazines. The stronger proton deshieldings caused by the 1,3,5-triazine ring as compared to that of the 1,2-dihydro-1,3,5-triazinyl ring can be explained in terms of either the greather electronegativity of the ring or the stronger diamagnetic anisotropy due to higher ring current in 1,3,5-triazine. An interplay of both phenomena is still more probably. The weaker deshielding effect of the 1,2-dihydro-1,3,5-triazinyl ring has been confirmed by analyzing the spectra of I taken in three solvents /Table 4/. An interesting conclusion can be drawn from comparison of the spectra taken in DMSO and pyridine-d_5. The basic nature of the latter causes specific interaction with I resulting in the shielding of the methyl group protons of the 3,5,5-trimethyl-2-pyrazoline fragment /Table 4/. However, one of the most interesting results of this interaction is the shielding of the aromatic protons the fragment



and the appearance of the chemical pseudo-equivalence of these protons in the pyridine-d_5 medium. Structural differences between I on the one hand and II on the other have also been supported by the UV spectra. Instability constant, K, relating to the rate of disappearance of the 273 nm-band at $20 \pm 0,5\ ^{o}C$, in an alkaline solution, is for I /K = 0,052 min^{-1}/ about 4 times less than for II /K = 0.184 min^{-1}/. This may be indicative of the greater stability of the 1,3,5-triazine ring /II/ than that of the 1,2-dihydro-1,3,5-triazine /I/ in this medium.

SUMMARY

An attempt has been made to identify 1,3,5-triazine derivatives on the basis of inspection of their ^{1}H-NMR and UV spectra. It was demonstrated that the product of the reaction of 1-/ -R-phenyl/-3-/3,5,5-trimethyl-2-pyrazoline-1-carboimidoyl/guanidine with ethyl orthoformate is the 1,2-dihydro-1,3,5-triazine derivative, whereas the products of the reactions with some acyl chlorides are the derivatives of 1,3,5-triazine.

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