Tetrahedron Letters No.23, pp. 2131-2136, 1967. Pergamon Press Ltd. Printed in Great Britain.

PREPARATION OF 5-NITRO-2-SILATETRAHYDRO-1,3-OXAZINE DERIVATIVES AND THEIR CONFORMATION[x]

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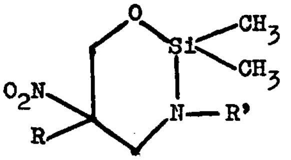
(Received 30 March 1967)

Continuing our research on synthesis and conformation of heterocyclic systems deriving from primary nitroparaffins we succeded now obtaining derivatives of 5-nitro-2-silatetrahydro-1,3-oxazine /I/



I

$R = CH_3, C_2H_5$

$R' = CH_3, C_2H_5, n\text{-}C_4H_9, i\text{-}C_4H_9$

The starting compounds were : 2-alkyl-2-nitro-3-alkylaminopropane-1-ol /II/ obtained by way of acid hydrolysis of derivatives of 5-nitro-tetrahydro-1,3-oxazine[2] and dimethyldielkylaminesilane /III/ which was prepared by acting with primary amines on dimethyldichlorosilane[3].

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[x] Paper LXXI on "Chemistry of Nitroparaffins"

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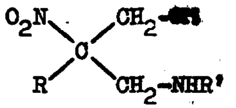
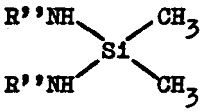


II



III R'' = CH_3, C_2H_5

The reaction between II and III was carried out in anhydrous benzene in the presence of ammonium chloride. Methyl - or ethylamine was evolved and removed by a current of dry nitrogen. 2-Sila-1,3-oxazine derivatives are light yellow oils, readily hydrolising und action of atmospheric moisture. They were purified by distillation under reduced pressure.

Their analytical data agree with the formulae.

Compounds /I/ were subjected to degradation in twofold way :

/1/ when warmed with alcoholic HCl they furnished hydrochlorides of II,

/2/ when warmed with acetic anhydride they yielded dimethyldiacetoxysilane.

IR absorption spectra of compounds /I/ showed maxima : 1100-1000 cm^{-1} /Si - O/, 940-930 cm^{-1} /Si - N/, 1260 and 830-800 cm^{-1} $Si/CH_3/_2$ and 1550 cm^{-1} /asymm, NO_2/.

Dipole moments

In order to determine the conformation of compounds /I/, dipole moments of two typical representatives of I /R=R'=C_2H_5 and R=C_2H_5, R'= n-C_4H_9/ were measured and compared with calculated velues.

The measurements were carried out in anh. benzene at 20° using Dipolmeter DM01 /WTW Weilheim, West Germany/ - Table 1

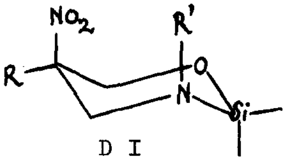
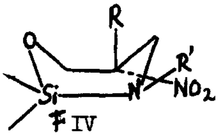
TABLE 1

R	R'	μ/D/
C_2H_5	C_2H_5	4.19
C_2H_5	n-C_4H_9	4.43

Theoretically four ring forms of 2-silatetrahydro-1,3-oxazine are possible : one chair /D/ and three boat forms. Each of them can exist in four conformations depending on the position of substituents at 3 and 5. To calculate dipole moments we used the data existing in the literature on the length of the bonds and the bond angles[4,5]. The dipole moment of NO_2 group was taken as μ = 3.5 D [6].

From the geometry of the rings we calculated the bond angles : ∢C Si C = 106°, ∢ CSiC = 115°, ∢ SiOC = 110°42', ∢ CSiN = 115°. The calculated values of dipole moments of some conformations are collected in Table 2.

TABLE 2

Conformation		NO_2	R'	μ /D/
 D I	D I	a	a	4.59
	D II	a	e	5.11
	D III	e	e	3.22
	D IV	e	a	3.39
 F IV	F III	be	be	4.25
	F IV	be	ba	4.48

The other boat forms gave μ values which appreciably differ from the calculated ones.

The values calculated for conformations D I, F III and F IV fit best to the experimental figures. Considering that chair forms are /generally speaking/ preferred, conformation D I perhaps with a small amount of D III seemed to be most probable.

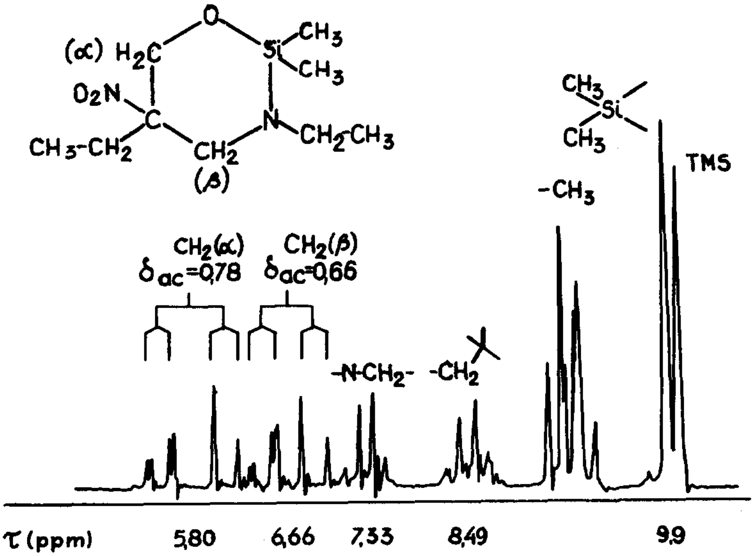
In order to obtain the final answer, n.m.r. spectra of compounds /I, R=R'=C_2H_5 and R=C_2H_5, R'=n-C_4H_9, see Table 2/were examined in Varian HR-60 spectrometer, at 60 megacycles, in deuterochloroform at 20°.

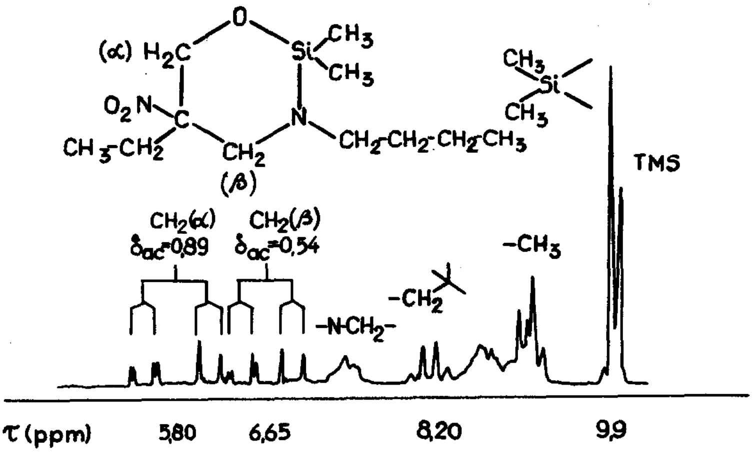
The n.m.r. spectrum of the ring is composed of two quartets. Each of them corresponds to one methylene group. The quartets indicate the presence of two AB systems with two unequal protons ineach. The bands are split off through the long distance coupling /J = 1.5 cps/ of the protons giving lower field doublets. The methylene groups are isolated in our ring system and if an inversion of the ring should occur, both doublets of each quartet would be split. This is not the case and indicates a fixed chair conformation of the ring and a long distance coupling of equatorial protons forming a flat letter W.

This kind of the system is impossible in the boat forms, thus excluding conformations F III and F IV.

The most probable conformation D I, i.e. the chair with the nitro group at 5 and the alkyl group at 3 in the axial positions, agrees with the former findings for simpler cases of 5-nitrotetrahydro-1,3-oxazine derivatives where R' = CH_3 or C_2H_5[6].

The authors are much indebted to Dr. M. Witanowski for his helpful discussion on interpretation of n.m.r. spectra.


(α) H2C
O
Si
CH3
CH3
O2N
C
N
CH2-CH3
CH3-CH2
CH2
(β)
CH3
Si
CH3
TMS
-CH3
CH2(α)
δac=0,78
CH2(β)
δac=0,66
-N-CH2-
-CH2
τ (ppm)
5,80
6,66
7,33
8,49
9,9


(α) H2C
O
Si
CH3
CH3
O2N
C
N
CH2-CH2-CH2-CH3
CH3-CH2
CH2
(β)
CH3
Si
CH3
TMS
CH2(α)
δac=0,89
CH2(β)
δac=0,54
-CH3
-CH2
-N-CH2-
τ (ppm)
5,80
6,65
8,20
9,9

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