The authors express their gratitude to M. M. Mestechkin, Yu. B. Vysotskii, and V. R. Blok for a valuable discussion of the work.

CONCLUSIONS

1. A semiempirical method was proposed for calculating the chemical shifts of the ^{13}C carbon nuclei in saturated hydrocarbons on the basis of the correlation dependence of $\delta_{^{13}C}$ on the effective charges Q_i^{eff} of the atoms that surround a given ^{13}C nucleus.

2. A computer program was composed for calculating $\delta_{^{13}C}$ on the basis of the proposed correlation method.

3. The chemical shifts of the ^{13}C nuclei were calculated for a number of n-alkanes ranging from propane to nonane.

4. It was shown that the values of $\delta_{^{13}C}$, calculated within the framework of the self-consistent scheme of perturbation theory, are less accurate than the $\delta_{^{13}C}$ obtained using the correlation method.

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INTRAMOLECULAR REARRANGEMENTS IN 6-ACETYL-2,9-DIOXA-1-AZABICYCLO[4.3.0]NONANE SERIES

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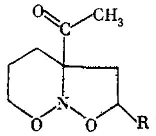
UDC 541.124:547.518

When reacted with boron trifluoride etherate (BTE) the 6,8-disubstituted 2,9-dioxa-1-azabicyclo[4.3.0]-nonanes undergo various rearrangements, in which connection the direction of the reaction depends on the nature and spatial arrangement of the substituents [1,2]. The reactions of BTE with this class of compounds, which have an acetyl group at C^6 (Ia-c), were studied in the present paper.



(Ia-c)

R = $COOCH_3$ (a), mixture of cis and trans isomers;
CH_2Cl (b), mixture of cis and trans isomers;
Ph(c), cis isomer.

The reaction of BTE with (Ia) and (Ib) leads to the formation of isoxazoline derivatives (IIa) and (IIb), respectively.

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 5, pp. 1149–1152, May, 1978. Original article submitted June 8, 1977.

0568-5230/78/2705-0996$07.50

TABLE 1. Data of ^{13}C NMR Spectra of (IIa,b) ($CHCl_3$, δ, ppm from TMS)

Compound	C=O	C=N	$H_2C—O$	$H_2C—Cl$	$H_3C—O$	C^4	$H_2C^{\alpha}—C^{\beta}H_2$	CH_3
(IIa)	170,3 s 170,5 s	157,5 s	63,0 t	–	52,0 q	40,7 t	23,6 t 24,9 t	20,2 q
(IIb)	170,3 s	157,2 s	62,9 t	45,1 t	–	40,2 t	23,8 t 24,8 t	20,3 q

TABLE 2. Data of PMR Spectra of (IIa, b) ($CDCl_3$)

Compound	CH_2O	β-CH_2	α-CH_2	CH_3CO	CHO	CH_2Cl	OCH_3	$CH_2C=$
(IIa)	4,03 t	1,56–2,11 m	2,37 t	1,97 t	4,87 t	–	3,72 s	3,16 d
(IIb)	4,08 t	1,64–2,10 m	2,36 t	1,96 t	4,75 t	3,54 m	–	2,96 m

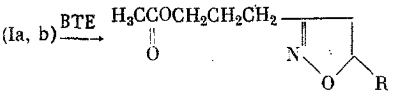
TABLE 3. Data of PMR Spectrum of (IIIa, b) (toluene-d_8, δ, ppm from HMDS, J, Hz)

Compound	CH_3CO	H_A	H_B	H_X	J_{AX}	J_{BX}	J_{AB}	CH_2O	H_2C_4*	H_2C_3*
(III a)	2,03 s	2,29	1,98	5,12 q	5,4	10,4	12,6	3,37—3,85 m(1H)	1,93—2,40 m	1,25—1,80 m
(III b)	2,03 s	2,50	2,22	4,64 q	9,1	7,5	12,8	3,85—4,35 m(1H)		

*The assignment was made by the double resonance method via the CH_2O group.

TABLE 4. Data of ^{13}C NMR Spectrum of (IIIa, b) ($CHCl_3$, δ, ppm from TMS)

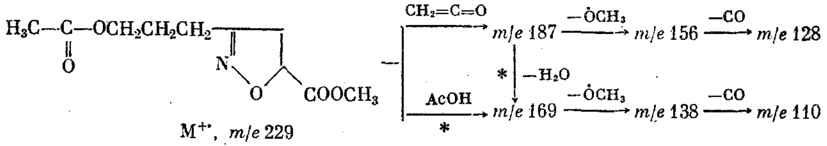
Compound	C=O	CH_3	$C^3(C^{2'})$	C^5	$C^{5'}$	C^4	$C^{3'}$	$C^{4'}$	Ph_s	Ph
(IIIa)	168,2 s	21,9 q	99,1 s	79,3 d	69,8 t	49,9 t	33,2 t	25,4 t	136,5 s	128,2 126,4
(IIIb)	166,5 s	21,9 q	99,5 s	80,3 d	69,2 t	50,5 t	34,0 t	25,4 t	138,1 s	126,1 125,3



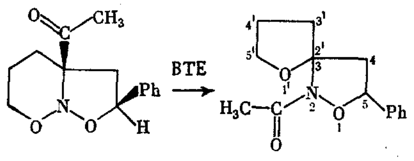
(IIa, b)

The structure of (IIa, b) was proved via the spectral data. The IR spectra of (IIa, b) have the absorption bands of the ester group (ν 1750 cm^{-1}), in which connection in (IIa) this band is quite broad. The data of the ^{13}C NMR spectra (Table 1) confirm the fact that (IIa, b) have a C =N bond and that the acetyl group is attached to the O atom, and not to C like in the starting (Ia, b). In the PMR spectra (Table 2) the signals of the side-chain protons practically coincide for (IIa) and (IIb). In (IIa) the protons of the CH_2CHO grouping appear as the A_2X system (J_{AX} = 9.2 Hz), while in (IIb) they apparently appear as the ABX system (an exact assignment of the signals in the AB portion could not be made due to the high multiplicity of the X portion). The presence of the CH_2CHOCH_2Cl grouping in (IIb) was confirmed by the results of employing double resonance via the CH group. The multiplicity of the protons of the CH_2Cl group is associated with the presence of an asymmetric C^5 center. The high resolution mass spectrum of (IIa) does not contradict the postulated structure (Scheme 1).

Scheme 1



The reaction of BTE with (Ic) gives two steric isomers of the spiro [isoxazolidine-3,2']tetrahydrofuran derivative (IIIa, b), with a predomiance of (IIIa).



(Ib) (IIIa, b)

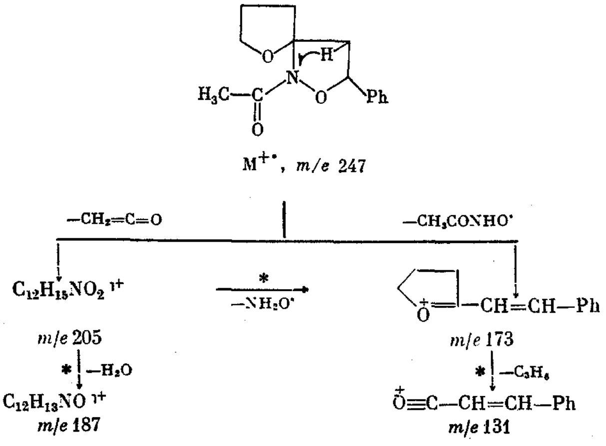
The structure of (IIIa, b) was proved by the elemental analysis, and by the IR, PMR, ^{13}C NMR, and mass spectra. The IR spectrum of (IIIa, b) has an absorption band at 1660 cm^{-1}, which testifies to the presence of the amide function. The PMR spectral data are given in Table 3. The protons of the isoxazolidine ring appear as the ABX system, whose parameters were determined by the INDOR method. The assignment of the protons of the methylene groups $H_2C^{4'}$ and $H_2C^{3'}$ was made on the basis of the double resonance data for the CH_2O group. From the ^{13}C NMR spectral data (Table 4) it follows that (IIIa, b) has a quaternary C atom that is linked to two hetero atoms $(\mathrm{O{-}\overset{|}{\underset{|}{C}}{-}N{<}})$, while the acetyl group is linked to the N atom. The assignment of the signals of the C^4, $C^{4'}$, and $C^{3'}$ atoms was made employing the selective monochromatic decoupling from the protons of the methylene groups H_2C^4 and $H_2C^{4'}$ (~225 Hz from HMDS in the PMR spectrum, in $CHCl_3$ solution), and also on the basis of the ^{13}C NMR speccral data for the product doubly deuterated in the 4 position (IIIa, b) (IIIa, b-d_2).*

The high resolution mass-spectral data for (IIIa, b) does not contradict the proposed structure. The most intense peak in the mass spectrum (Schene 2) is that of the ion $C_{12}H_{13}O_2$ (experimental m/e 173.0927; calculated m/e 173.0967), which is formed by the cleavage of the fragment $[\mathrm{CH_3{-}\underset{\underset{O}{\|}}{C}{-}NH\dot{O}}]^{\bullet}$ from the (IIIa, b) molecular ion. This type of fragmentation is characteristic for isoxazolidines [3] (Scheme 2).

EXPERIMENTAL

The PMR spectra were taken on Perkin—Elmer R-12 and Varian DA-60 instruments. The ^{13}C NMR spectra were obtained on a Varian XL-100 instrument, with an operating frequency of 25.15 MHz for the ^{13}C nuclei. The mass spectra were taken on an MS-30 AEI instrument. For the chromatography we used silica gel LCL 5/40 with a luminescent indicator.

Scheme 2



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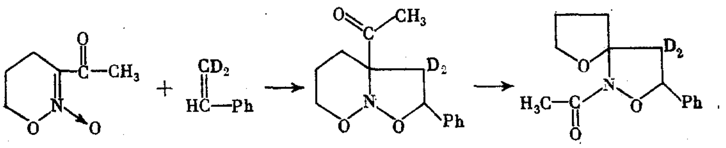
*Compound (IIIa, b)-d_2 was synthesized by the following scheme:



(IIIa, b-d_2)

Preparation of (IIa). To a solution of 0.35 g of (Ia) in 10 ml of abs. benzene at 2-4°C was added in drops 0.22 ml of BTE in 2 ml of abs. benzene, after which the mixture was stirred at ~20° for 1.5 h, neutralized with a solution of 0.33 g of Na_2CO_3 in 30 ml of H_2O, extracted with ether, and dried over $MgSO_4$. After distilling off the solvents the residue was subjected to preparative TLC (eluant = 1 : 1 ethyl acetate : ether) to give 0.24 g (68%) of (IIa), R_f 0.45, bp 145° (0.8 mm). Found: C 52.04; H 6.50; N 6.38%. $C_{10}H_{15}NO_5$. Calculated: C 52.40; H 6.55; N 6.11%.

Preparation of (IIb). To a solution of 0.35 g of (Ib) [4] in 10 ml of abs. benzene at 4-7° was added in drops 0.23 ml of BTE in 2 ml of abs. benzene, after which the mixture was stirred at ~20° for 2 h, neutralized with a solution of 0.36 g of Na_2CO_3 in 30 ml of H_2O, extracted with ether, and dried over $MgSO_4$. After distilling off the solvents the residue was subjected to preparative TLC (eluant = 1 : 1 $CHCl_3$: ether) to give 0.11 g (32%) of (IIb), R_f 0.35. Found: C 49.53; H 6.45; N 6.38; Cl 16.57%. $C_9H_{14}NO_3Cl$. Calculated: C 49,20; H 6.38; N 6.38; Cl 16.37%.

Preparation of (IIIa, b). To a solution of 0.6 g of (Ic) [4] in 10 ml of abs. benzene at 4-7° was added in drops 0.36 ml of BTE in 2 ml of abs. benzene, after which the mixture was stirred at ~20° for 30 min, neutralized with a solution of 0.5 g of Na_2CO_3 in 30 ml of H_2O, extracted with ether, and dried over $MgSO_4$. After distilling off the solvents we obtained 0.56 g (93%) of (IIIa, b), mp 84-86° (hexane). Found: C 67.70; H 7,12; N 5.46%. $C_{14}H_{17}NO_3$. Calculated: C 68.02; H 6.88; N 5.67%.

CONCLUSIONS

1. When reacted with boron trifluoride etherate, the 8-carbomethoxy- and 8-chloromethyl-6-acetyl-2,9-dioxa-1-azabicyclo[4.3.0]nonanes are respectively rearranged to the 5-carbomethoxy- and 5-chloromethyl-3-γ-acetoxypropylisoxazolines.

2. When reacted with BTE, 6-acetyl-8-phenyl-2,9-dioxa-1-azabicyclo[4.3.0]nonane is rearranged to spiro [N-acetyl-5-phenylisoxazolidine-3,2']tetrahydrofuran.

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