LITERATURE CITED

1. M. S. Malinovskii, A. G. Yudasina, T. S. Skrodskaya, and V. G. Larionova, Zh. Org. Khim., 2, 2142 (1966).
2. R. G. Shin, V. V. Tatarchuk, and G. F. Skiba, Dep. at VINITI, No. 1953-75 Dep.
3. J. Font, An. Real. Soc. Esp. Fiz. Quim., B62, 477 (1966).

^{15}N CHEMICAL SHIFTS IN AZIRIDINES

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UDC 547.717+543.422.25

For a number of 1-substituted aziridines and also some 1,2-disubstituted aziridines it has been shown that electron-donating substituents on the nitrogen atom produce a downfield shift of the ^{15}N resonance. The ^{15}N chemical shifts of aziridines correlate with the ^{15}N shifts in N,N-dimethylamines and primary amines as well as with the ^{17}O shifts in oxiranes. A correlation is also observed between the ^{15}N chemical shifts and the electronegativity of the substituents on the nitrogen atom.

The ^{15}N NMR spectra of 1-substituted aziridines have received very little study. The chemical shifts of 1-alkyl-substituted aziridines [1], 1-arylaziridines [2], and certain aziridinephosphamides [3] have been reported. However, there has been no data up to now on aziridines that contain alkyl radicals with acceptor substituents on the nitrogen atom. In this connection we have obtained the ^{15}N NMR spectra of a number of 1-substituted aziridines synthesized at the Institute of Organic Synthesis, Academy of Sciences of the Latvian SSR, as well as those of some previously unstudied 1,2-disubstituted aziridines (Table 1).

The ^{15}N chemical shifts of 1-substituted aziridines, as in the case of the 2-substituted aziridines that we previously studied [4], give a satisfactory correlation with the E_S steric and σ^* induction constants of Taft.* Based on the data of [1]:

$$\delta_N = -378.9 - 14.0\sigma^* - 9.4E_s \quad (r=0.942;\ s=3;\ n=15). \tag{1}$$

For 2-substituted aziridines (including the data of [4]):

$$\delta_N = -379.7 + 1.9\sigma^* - 5.5E_s \quad (r=0.926;\ s=4.5;\ n=13). \tag{2}$$

The larger steric effect on the shielding of nitrogen atoms in 1-substituted aziridines in comparison with 2-substituted derivatives is evidently due to the fact that in the latter the substituent is remote from the center in question. The difference in sign of the angular coefficient for the inductive effect in the two correlations is worthy of note. Substituents that are joined directly to a nitrogen atom shift the ^{15}N resonance signal upfield as their electron-acceptor properties increase [equation (1)], while substituents separated by one bond, on the other hand, cause deshielding [equation (2)]. This is due to the alternation in substituent effect on the electron density in the vicinity of the nitrogen atom in relation to the number of bonds. In order to compare the inductive effects at both positions of the heterocycle we took a number of 1-methyleneaziridines $(CH_2)_2NCH_2R$ in which the substituent acts through the methylene bridge. In this case

$$\delta_N = -370.4 + 2.0\sigma^* - 1.0E_s \quad (r=0.965;\ s=6.1;\ n=14). \tag{3}$$

*Here and subsequently the data of [1-4] are also used in the correlations. The value of σ^* and E_S are taken from [5, 6].

Institute of Organic Synthesis, Academy of Sciences of the Latvian SSR, Riga 226006.
Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, 1336-1339, October, 1988. Original article submitted June 19, 1986; revision submitted February 29, 1988.

 0009-3122/88/2410-1106$12.50

TABLE 1. ^{15}N Chemical Shifts of Substituted Aziridines I-XX

Compound	1-R¹	2-R²	δ_N, ppm	Compound	1-R¹	2-R²	δ_N, pmm
I	H	H	−390.4	XI	$CH_2C_6H_5$	H	−365.6
II	CH_3	H	−380.0	XII	Cl	H	−330.9
III	CH_2OH	H	−356.0	XIII	NH_2	H	−338.1*²
IV	CH_2OCH_3	H	−363.5	XIV	$Si(CH_3)_3$	H	−384.3
V	CH_2COOCH_3	H	−374.9	XV	CH_3	CH_3	−364.8
VI	$CH_2C{\equiv}CH$	H	−373.0	XVI	$CH_2N(CH_2)_4$	CH_3	−350.7*³
VII	$CH_2CH{=}CH_2$	H	−368.8	XVII	$CH_2N(CH_2CH_2)_2O$	CH_3	−352.3*⁴
VIII	CH_2CH_2CN	H	−367.4	XVIII	NH_2	CH_3	−323.7*²
IX	$CH_2N(CH_2)_2$	H	−365.3	XIX	CH_2OH	$COOCH_3$	−335.8
X	$CH_2N(CH_2)_4$	H	−365.7*¹	XX	Cl	$COOCH_3$	−318.8

*¹For pyrrolidine nitrogen δ_N is −328.7 ppm.
*²For amino group δ_N is −282.6 ppm.
*³For pyrrolidine nitrogen δ_N is −321.6 ppm.
*⁴For morpholine nitrogen δ_N is −328.3 ppm.

It is evident that here an increase in acceptor properties of the substituent also leads to a downfield shift and the contribution of the inductive effect is approximately the same as in the 2-substituted aziridines. The difference in the steric effect is evidently due to the different spatial position of the substituent relative to the nitrogen atom in the two series of compounds.

According to equation (1) the signals from the ^{15}N nuclei in 1-substituted aziridines, just as for ^{13}C nuclei in alkanes and ^{17}O nuclei in alcohols [7], are shifted downfield with an increase of negative σ-charge on the nucleus. In the case of the ^{17}O nuclei this fact is accounted for [8] by the change in average excitation energy ΔE in the expression for the paramagnetic component of shielding. In this case there is a parallelism between the chemical shift and ionization potential, which can be taken as a gage for ΔE.

For mono-, di-, and tri-alkylamines there is also an antibatic relationship between the ^{15}N chemical shifts and the ionization potential of the nitrogen atom [9], in other words, changes in ΔE in the expression for the paramagnetic shielding correctly account for the trends in ^{15}N resonance shifts in alkylamines. Unfortunately, at the present time there is no information on ionization potentials of 1-substituted aziridines that can be used to verify this hypothesis in the case of aziridines.

There are correlations between the ^{15}N chemical shifts in aziridines and the corresponding amines [10] as well as the ^{17}O chemical shifts in oxiranes [11].

$$\delta_N^{\text{1-alkylaziridine}} = 0.64\delta_N^{RNH_2} + 135.7 \quad (r = 0.987;\ n = 6); \tag{4}$$

$$\delta_N^{\text{1-alkylaziridine}} = 1.736\delta_N^{RN(CH_3)_2} + 246.4 \quad (r = 0.953;\ n = 5); \tag{5}$$

$$\delta_N^{\text{aziridine}} = 0.626\delta_O^{\text{oxirane}} - 360.0 \quad (r = 0.982;\ n = 8). \tag{6}$$

Similar correlations between the ^{15}N chemical shifts in amino compounds and the corresponding ^{13}C chemical shifts in alkanes were recorded previously [10, 12]. By comparing the angular coefficients in correlations (4) and (5) it can be observed that the sensitivity of the ^{15}N chemical shift to electronic effects increases in the series: $(CH_3)_2N- < (CH_2)_2N- < H_2N-$.

Quite a different pattern emerges for aziridines in which there is a variation of substituent in the first coordination sphere. For such 1-substituted aziridines the ^{15}N chemical shifts correlate with the electronegativity of the substituent [13] on the nitrogen atom (E_X), the resonance signal being displaced downfield as the electronegativity increases:

$$\delta_N^{(CH_2)NX} = 47.3E_X - 482.2 \quad (r = 0.92); \tag{7}$$
$$X = H,\ CH_3,\ C_6H_5,\ Si(CH_3)_3,\ Cl,\ NH_2,\ P(O)(OCH_3)_2.$$

Similar correlations were previously also observed for chemical shifts of other nuclei [8, 14] and are accounted for by the change in total charge on the given atom. It is usual to assume that with an increase in electronegativity of the substituent, compression of the 2p-orbitals of the nitrogen atom occurs, which leads to an increase in the paramagnetic contribution to the shielding of the nitrogen atom.

It follows from a comparison of the ^{15}N chemical shifts in mono- and di-substituted aziridines (Table 1) that the effect of substituents at the 2-position on δ_N in this case is similar to that in 2-substituted aziridines [4], while the effects of substituents on the nitrogen atom in these molecules is approximately equal to the effects for 1-substituted aziridines. This means that the substituents at the 1- and 2-positions affect the shielding of ^{15}N nuclei virtually independently of each other.

EXPERIMENTAL

^{15}N chemical shifts were measured at 30°C for 50% solutions in $CDCl_3$ on a WH90/DS spectrometer (9.12 MHz) relative to nitromethane-^{15}N as external standard. The recordings were made to an accuracy of ±0.2 ppm. The identity and purity of the samples were monitored by readings from GLC and ^1H NMR spectra.

1-Aminoaziridine (XIII). To a solution of 7.6 g (0.1 mole) of hydrazinoethanol in 100 ml of dry chloroform that contained no ethanol was added 26.1 g (0.1 mole) of triphenylphosphine. Dimethyl azodicarboxylate (14.6 g; 0.1 mole) was added dropwise in an atmosphere of nitrogen over 40 min at a temperature of 15-20°C. The reaction mixture was agitated for 1 h at room temperature and the reaction product was distilled off together with chloroform. After repeated distillation on a fractionating column, 4.4 g (75%) of 1-aminoaziridine (XIII) was obtained, with bp 80-82°C (according to the method in [15], yield 35%, bp 82°C).

1-Methylaziridine (II), 1,2-dimethylaziridine (XV), and 1-amino-2-methylaziridine (XVIII) were obtained in a similar manner.

Compounds III and IX were prepared from aziridine according to the method in [16]; X, XVI, and XVII were synthesized according to [17], V and VIII were prepared according to the method of Bestian [18], and XI by the method of [19]. Chlorination [20] and silylation [21] of aziridine gave compounds XII and XIV respectively. Compounds IV, VI, and VII were synthesized by reaction of aziridine with alkylating agents [22]. Carbinol XIX was obtained by us previously [23].

2-Methoxycarbonyl-1-chloroaziridine (XX). A solution of 9.24 g (0.22 mole) of sodium hydroxide in 38.5 ml of water was cooled to −10°C and saturated with 8.0 g (0.11 mole) of chlorine (from the increase in weight) at such a rate that the temperature of the mixture did not exceed 0°C. To the mixture with agitation at −10°C was added dropwise 10.1 g (0.1 mole) of 2-methoxycarbonylaziridine [24]. Agitation was continued for 30 min at 0°C, then the mixture was extracted with 25 ml of chloroform. The organic layer was separated, washed with 2 × 50 ml of water, and dried. PMR spectrum ($CDCl_3$): 2.48 (1H, d. d, J = 1.3 and 8.0 Hz, trans-3-H relative to the 2-methoxycarbonyl group); 2.60 (1H, d. d, J = 1.3 and 4.9 Hz, cis-3-H); 2.94 (1H, d. d, J = 4.9 and 8.0 Hz, 2-H); 3.73 m. d. (3H, s, OCH_3).

LITERATURE CITED

1. K. Crimaldi and R. L. Lichter, J. Org. Chem., 45, 1277 (1980).
2. K. Crimaldi, R. L. Lichter, and A. Backer, J. Org. Chem., 47, 3528 (1982).
3. G. A. Gray, G. W. Buchanan, and F. G. Moring, J. Org. Chem., 44, 1768 (1979).
4. É. É. Liepin'sh, I. Ya. Kalvin'sh, and P. T. Trapentsier, Khim. Geterotsikl. Soedin., No. 9, 1231 (1981).
5. C. Hansch and A. Leo, Substituent Constants for Correlation Analysis in Chemistry and Biology, Wiley, New York—London (1979), p. 67.
6. S. H. Unger and C. Hansch, in: Progress in Physical Organic Chemistry, R. W. Taft (editor), Vol. 12, Interscience, New York—London (1976), p. 91.
7. S. Fliszar, Charge Distributions and Chemical Effects, Springer Verlag, Berlin—Heidelberg—New York (1983), p. 61.
8. T. Sugawara, Y. Kawada, M. Katon, and H. Iwamura, Bull. Chem. Soc. Japan, 52, 3391 (1979).
9. M. Takasuka and Y. Terui, J. Chem. Soc. Perkin 2, No. 9, 1545 (1984).
10. R. O. Duthaler and J. D. Roberts, J. Am. Chem. Soc., 100, 3889 (1978).
11. A. Sauleau, J. Sauleau, R. Faure, and J. P. Monti, Org. Magn. Res. 21, 403 (1983).
12. R. O. Duthaler, K. L. Williamson, D. D. Giannini, W. H. Bearden, and J. D. Roberts, J. Am. Chem. Soc., 99, 8406 (1977).

13. P. R. Wells in: Progress in Physical Organic Chemistry, R. W. Taft (editor), Vol. 6, Interscience, New York—London (1968), p. 111.
14. J. B. Lambert, D. A. Netzel, H. Sun, and K. K. Lilianstrom, J. Am. Chem. Soc., 98, 3778 (1976).
15. A. F. Graefe, US Patent No. 3,173,910; Chem. Abs., 63, 580 (1965).
16. R. G. Kostyanovskii, Dokl. Akad. Nauk SSSR, 135, 853 (1960).
17. R. G. Kostyanovskii, O. A. Panshin, and V. F. Bystrov, Izv. Akad. Nauk SSSR, Ser. Khim., No. 5, 931 (1962).
18. H. Bestian, Annalen, 566, 210 (1950).
19. A. T. Bottini and J. D. Roberts, J. Am. Chem. Soc., 80, 5203 (1958).
20. A. F. Graefe and R. E. Meyer, J. Am. Chem. Soc., 80, 3939 (1958).
21. O. Scherer and H. Schmidt, Chem. Ber., 98, 2243 (1965).
22. R. G. Kostyanovskii and O. A. Panshin, Izv. Akad. Nauk SSSR, Ser. Khim., No. 4, 740 (1965).
23. P. T. Trapentsier, I. Ya. Kalvin'sh, É. É. Liepin'sh, and É. Ya. Lukevits, Khim. Geterotsikl. Soedin., No. 9, 1227 (1983).
24. S. A. Giller, A. V. Eremeev, I. Ya. Kalvin'sh, É. É. Liepin'sh, and V. G. Semenikhina, Khim. Geterotsikl. Soedin., No. 12, 1625 (1975).

SYNTHESIS AND LACTONIZATION OF 1-(2-HYDROXY-1,1-DIMETHYLETHYL)-AZIRIDINE-2-CARBOXYLIC ACID ESTERS

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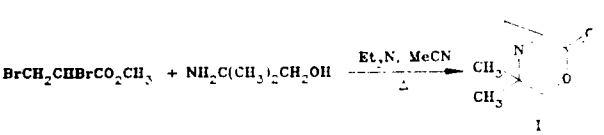
UDC 547.717'464.3:542.97

The reaction of 2,3-dibromopropanoates with 2-amino-2-methyl-1-propanol in the presence of triethylamine gave a number of 1-(2-hydroxy-1,1-dimethylethyl)aziridine-2-carboxylic acid esters, which, under the influence of basic catalysts, were converted to a bicyclic lactone — 2,2-dimethyl-4-oxa-1-azabicyclo[4.1.0]heptan-5-one. The effect of the structure of the substrate and the nature of the lactonizing agent on the rate of cyclization was studied. Two new catalysts for the cyclization of hydroxy esters to lactones, viz., CsF/Al_2O_3 and Cs_2CO_3/18-crown-6, are proposed.

One of the most important methods for the synthesis of lactones is the cyclization of hydroxy esters. In the overwhelming majority of cases it is carried out under the influence of either strong mineral or organic acids or Lewis acids [1-4]. The lactonization of hydroxy esters under the influence of bases is rarely used (see [5-7] for the most typical methods), and the literature contains a limited amount of data on the use of basic reagents with no comparison of the effect of basic catalysts on the effectiveness of lactonization.

In a previous paper [8] it was reported that a bicyclic lactone — 2,2-dimethyl-4-oxa-1-azabicyclo[4.1.0]heptan-5-one — was obtained in the reaction of methyl 2,3-dibromopropanoate with 2-amino-2-methyl-1-propanol.



We have now isolated the intermediate in this reaction, viz., methyl 1-(2-hydroxy-1,1-dimethylethyl)aziridine-2-carboxylate (X), which gives lactone I under the influence of bases.

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Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1340-1343, October, 1988. Original article submitted February 16, 1987; revision submitted March 28, 1988.

0009-3122/88/2410-1109$12.50