20-25°C for 4 h. The resulting precipitate was removed by filtration and recrystallized from CCl_4 to give 0.91 g (60%) of 2H,6H-2,6-dimethyl-4-dideuteroamino-1,3,5-dithiazine with mp 105.5-106.5°C. The degree of deuteration (70-75%) was determined from the ratio of the intensities of the absorption bands of the N—H stretching vibrations in the IR spectra of the undeuterated and deuterated samples.

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REACTIONS OF 1-ALKOXYCARBONYLAZIRIDINES WITH NUCLEOPHILIC REAGENTS

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1-Methoxycarbonylaziridines react under mild conditions with a number of nucleophilic reagents such as water, acids, alcohols, and amines with opening of the aziridine ring. In the case of 7-methoxycarbonyl-7-azabicyclo[4.1.0]heptane it was shown by PMR spectroscopy that the ring-opening reaction is realized stereoselectively to give trans-1,2-disubstituted cyclohexanes.

In contrast to epoxides, considerably less study has been devoted to the reactions of aziridines with nucleophilic reagents. This is explained by the substantial differences in the reactivities of epoxides and aziridines that are associated with the presence of a more basic nitrogen atom in the ring and the lower degree of accessibility of the latter. 1-Alkoxycarbonylaziridines are easily obtained compounds [1, 2]; their basicities are close to the basicities of epoxides, and they therefore should have similar reactivities. Individual examples of opening of the rings of 1-alkoxycarbonylaziridines by acids [3, 4], malonic ester [5], and aniline [6] are known.

We have investigated the reaction of 1-methoxycarbonylaziridine (I) and 7-methoxycarbonyl-7-azabicyclo[4.1.0]heptane (III) with various nucleophilic reagents at ∿20°C and have found that aziridines that are activated by a methoxycarbonyl group readily react under mild conditions with the most diverse nucleophiles, viz., water, alcohols, acids, hydrogen sulfide, and amines. The reaction with ring opening is realized both in acidic and alkaline media. This makes it possible to obtain various β-functionally substituted carbamates in high yields from 1-alkoxycarbonylaziridines (Table 1).

In the case of the reaction of III with various nucleophiles we showed that the reaction proceeds stereoselectively to give the trans products. This conclusion was drawn on the basis of an analysis of the PMR spectra of IVa-g (Table 2), for which, with the excep-

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TABLE 1. Substituted Methoxycarbonylaminoethanes (II) and Methoxycarbonylaminocyclohexanes (IV)

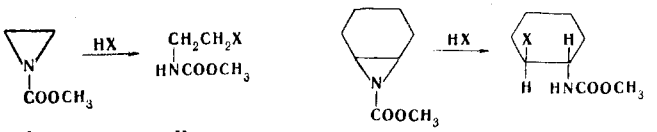
Compound	bp, °C (mm) or mp,* °C	n_D^{20}	IR spectrum, cm^{-1}	Found, %			Empirical formula	Calc., %			Yield, %
				C	H	N		C	H	N	
IIa	145—150 (2,5)	1,4534	1253, 1516, 1708, 3320, 3620	40,2	7,5	11,7	$C_4H_9NO_3$	40,3	7,6	11,8	56
IIb	49—50 (1)	1,4350	1252, 1527, 1700, 3323	45,1	8,2	11,5	$C_5H_{11}NO_3$	45,1	8,3	11,5	88
IIc	92—93 (1)	1,4440	1227, 1527, 1727, 3335	44,8	6,8	8,5	$C_6H_{11}NO_4$	44,7	6,9	8,7	65
IId	52—53 (0,6)	1,4862	560, 1246, 1513, 1702, 3331	26,4	4,2	7,8	$C_4H_9BrNO_2$	26,4	4,4	7,7	90
IIe	59—60	—	1260, 1533, 1689, 2229, 3319	46,8	6,4	22,2	$C_5H_8N_2O_2$	46,9	6,3	21,9	52
IIf	85—87 (1,5)	1,4905	1247, 1541, 1689, 2523, 3309	35,6	6,8	10,4	$C_4H_9NO_2S$	35,5	6,7	10,4	62
IIg	99—101 (12)	1,4563	1240, 1523, 1700, 3324	49,2	9,7	19,1	$C_6H_{14}N_2O_2$	49,3	9,7	19,2	75
IVa	111—112	—	1224, 1516, 1680, 3317	55,4	8,4	8,1	$C_8H_{15}NO_3$	55,5	8,5	8,1	63
IVb	58—59	—	1242, 1520, 1688, 3320	59,6	9,6	6,8	$C_{10}H_{19}NO_3$	59,7	9,5	7,0	70
IVc	75—76	—	1220, 1527, 1660, 1693, 3347	55,7	8,1	6,5	$C_{10}H_{17}NO_4$	55,8	8,0	6,5	73
IVd	127—128 [7]	—	710, 1248, 1570, 1705, 3285	—	—	—	$C_8H_{14}BrNO_2$	—	—	—	85
IVe	109—110	—	1507, 1695, 2207, 3353	59,4	7,6	15,4	$C_9H_{14}N_2O_2$	59,3	7,8	15,4	50
IVf	129—130	—	1510, 1677, 2540, 3302	50,7	8,0	7,3	$C_8H_{15}NO_2S$	50,8	8,0	7,4	82
IVg	68—69	—	1240, 1520, 1685, 3330	60,0	10,1	14,1	$C_{10}H_{20}N_2O_2$	60,0	10,0	14,0	75

*Compounds IIe and IVa, e were recrystallized from ether, while IVb-d, f, g were recrystallized from benzene.

TABLE 2. PMR Spectra of Substituted Methoxycarbonylaminocyclohexanes (IV)

Compound	Chemical shift, δ, ppm*				J_{12} Hz
	H—C—X	CO_2Me	NH	remaining signals	
IVa†	3,07	3,37	5,52	2,59 (OH)	9,5
IVc	4,53	3,54	4,95	1,96 (COMe)	10
IVe	2,52	3,58	5,10	—	10
IVf	2,47	3,58	5,11	—	11
IVg	3,16	3,55	5,41	2,16 (NMe_2)	10

*The signal of the proton attached to the carbamate group is overlapped by the CO_2Me signal, and its chemical shift therefore cannot be determined accurately.
†In C_6H_6; the remaining signals were obtained in $CDCl_3$.



I II a-g III IV a-g

IIa, IVa X=OH; IIb X=OMe; IVb X=OEt; IIc, IVc X=OCOMe; IId, IVd X=Br; IIe, IVe X=CN; IIf, IVf X=SH; IIg, IVg X=NMe_2

tion of 1-methoxycarbonylamino-2-ethoxycyclohexane (IVb), sextets of protons of the H—C—X group with spin—spin coupling constants (SSCC) of 9-11, 9-11, and 2-3 Hz are observed, which constitutes evidence for a trans-diaxial orientation of the vicinal methylidyne protons. The trans configuration of IVb was proved by alkaline hydrolysis of this product to the previously described trans-2-ethoxycyclohexylamine [8]. The structures of the synthesized compounds were also confirmed by IR spectroscopic data.

The stereoselectivity and mild conditions under which the opening of activated (by the methoxycarbonyl group) aziridines is carried out make it possible to obtain various functionally substituted carbamates.

EXPERIMENTAL

The IR spectra of microlayers or mineral oil suspensions of the compounds were recorded with a UR-10 spectrometer. The PMR spectra of solutions of the compounds in $CDCl_3$ or C_6H_6 were recorded with a Varian HA-100 spectrometer with hexamethyldisiloxane as the internal standard.

2-Methoxycarbonylaminoethanol (IIa). A 10-ml sample of a 30% aqueous solution of perchloric acid was added at 0°C to a solution of 3.03 g (0.03 mole) of 1-methoxycarbonylaziridine (I) in 50 ml of ether, and the mixture was stirred at ∿20°C for 1 h. It was then neutralized with solid sodium carbonate, the ether layer was separated, and the aqueous layer was extracted with chloroform (four 20-ml portions). The extracts were combined and dried with magnesium sulfate, the solvent was removed by distillation, and the residue was distilled to give 2 g (56%) of IIa.

trans-2-Methoxycarbonylaminocyclohexanol (IVa). This compound was similarly obtained from 7-methoxycarbonyl-7-azabicyclo[4.1.0]heptane (III).

1-Methoxycarbonylamino-2-methoxyethane (IIb). Three drops of 60% perchloric acid were added to a solution of 3.03 g (0.03 mole) of aziridine I in 50 ml of absolute methanol, and the mixture was allowed to stand at ∿20°C for 1 h. It was then neutralized with solid sodium carbonate and filtered, and the filtrate was evaporated. The residue was distilled to give 3.51 g (88%) of IIb.

trans-1-Methoxycarbonylamino-2-ethoxycyclohexane (IVb). This compound was obtained as in the preceding experiment from azabicycloheptane III in absolute ethanol.

1-Methoxycarbonylamino-2-acetoxyethane (IIc). A solution of 0.2 ml of BF_3 etherate in 30 ml of acetic acid was added at 0°C to a solution of 3.03 g (0.03 mole) of aziridine I in 30 ml of acetic acid, and the mixture was allowed to stand at ∿20°C for 1 h. It was then evaporated *in vacuo* to one fourth of its original volume, and the concentrate was naturalized with a saturated solution of potassium carbonate and extracted with chloroform (six 20-ml portions). The chloroform extracts were dried with magnesium sulfate, and the solvent was removed by distillation. The residue was distilled to give 3.14 g (65%) of IIc.

trans-1-Methoxycarbonylamino-2-acetoxycyclohexane (IVc). This compound was obtianed from azabicycloheptane III by the method used to prepare IIc.

1-Methoxycarbonylamino-2-bromoethane (IId). A) A solution of 3.03 g (0.03 mole) of aziridine I in 40 ml of ether was added at 0°C to 30 ml of 48% hydrobromic acid, and the mixture was stirred at ∿20°C for 1 h. It was then neutralized with solid sodium carbonate, and the ether layer was separated. The aqueous layer was extracted with chloroform (three 20-ml portions), and the combined extracts were dried with magnesium sulfate. The solvent was removed by distillation, and the residue was distilled to give 4.91 g (90%) of IId.

B) A solution of 3.03 g (0.03 mole) of aziridine I, 11.9 g (0.1 mole) of potassium bromide, and 11 g (0.03 mole) of $Mg(ClO_4)_2 \cdot 6H_2O$ in 200 ml of 40% aqueous ethanol was refluxed for 2 h, after which the mixture was evaporated *in vacuo*, and the residue was extracted with hot chloroform (three 20-ml portions). The chloroform extracts were dried with magnesium sulfate, the solvent was removed by distillation *in vacuo*, and the residue was distilled to give 4.82 g (88%) of IId.

trans-1-Methoxycarbonylamino-2-bromocyclohexane (IVd). This compound was obtained in the same way as IId from azabicycloheptane III in 85% yield by method A and in 82% yield by method B.

3-Methoxycarbonylaminopropionitrile (IIe). A solution of 3.03 g (0.03 mole) of aziridine I in 10 ml of ethanol was added to a solution of 8.8 g (0.18 mole) of sodium cyanide and 12.5 ml (0.15 mole) of 36% hydrochloric chloric acid in 60 ml of aqueous ethanol, and the mixture was allowed to stand for 2 days at ∿20°C. It was then evaporated *in vacuo*, and the residue was extracted with hot chloroform (six 20-ml portions). The chloroform extracts were evaporated *in vacuo*, and the residue was dissolved in 100 ml of ether. The solution was filtered through L 40/100 μm silica gel, the ether was removed by distillation, and the residue was recrystallized to give 2 g (52%) of IIe.

trans-2-Methoxycarbonylaminocyclohexanecarbonitrile (IVe). This compound was obtained from azabicycloheptane III by the method used to prepare IIe.

2-Methoxycarbonylaminoethanethiol (IIf). A solution of 3.03 g (0.03 mole) of aziridine I in 10 ml of ethanol was added to a solution of 24 g (0.1 mole) of $Na_2S \cdot 9H_2O$ and 5 ml (0.06 mole) of 36% hydrochloric acid in 100 ml of 40% aqueous ethanol, and the mixture was allowed to stand at ~20°C for 2 days. It was then evaporated *in vacuo*, and the residue was extracted with hot chlroform (three 20-ml portions). The chloroform extracts were dried with magnesium sulfate, the solvent was removed by vacuum distillation, and the residue was distilled to give 2.5 g (62%) of IIf.

trans-2-Methoxycarbonylaminocyclohexanethiol (IVf). This compound was obtained from azabicycloheptane III by the method used to prepare IIf.

1-Methoxycarbonylamino-2-dimethylaminoethane (IIg). A solution of 3.03 g (0.03 mole) of aziridine I in 10 ml of ethanol was added to a solution of 4.5 g (0.1 mole) of diethylamine in 20 ml of ethanol, and the mixture was allowed to stand at ~20°C for 5 h. It was then evaporated *in vacuo*, and the residue was distilled to give 3.28 g (75%) of IIg.

trans-1-Methoxycarbonylamino-2-dimethylaminocyclohexane (IVg). This compound was obtained from azabicycloheptane III by the method used to prepare IIg.

Hydrolysis of trans-1-Methoxycarbonylamino-2-ethoxycyclohexane (IVb). A solution of 2.01 g (0.01 mole) of IVb and 2.8 g (0.05 mole) of KOH in 20 ml of ethanol was refluxed for 30 min, after which the mixture was evaporated *in vacuo*, and the residue was extracted with ether (four 20-ml portions). The ether extracts were dried with KOH and filtered. A saturated ether solution of HCl was added to the filtrate, and the resulting precipitate was removed by filtration and washed with ether to give 1.23 g (69%) of trans-2-ethoxycyclohexylamine hydrochloride with mp 171-172°C (from ethanol) (mp 172-173°C [8]).

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