PYRAMIDAL AMIDE NITROGEN IN N-ACYLDIAZIRIDINES AND N-ACYLOXAZIRANES

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A stable amide nitrogen pyramid is known only for bridge bicyclic systems with the nitrogen in the "head" of the bridge [1]. The data on the slow inversion of amide nitrogen in an open chain proved to be wrong; they correspond to hindered rotation, which is observed in biphenyls [2]. Our previous attempts to build a sterically hindered nonplanar group with the nitrogen in an open chain also proved unsuccessful [3].

The pyramidal amide nitrogen could be recorded in the N-acylethylenimines by the x-ray structure analysis and electron diffraction method [4]. However, on the NMR time scale the nitrogen inversion in the N-acylethylenimines is quite rapid and it can be retarded only by adding mesomerically positive substituents to the carbonyl group, which competitively reduce the amide conjugation with the aziridine nitrogen [5]. On the basis of these data a rule was formulated that the amide conjugation is weakened when the nitrogen is contained in a three-membered ring [6] due to an increase in the inversion barrier of the nitrogen and a decrease in its +M capacity. A substantial increase in the inversion barrier of the nitrogen in diaziridines and oxaziranes [7] when compared with the aziridines [8] should lead to an increase in the pyramidal stability of the amide nitrogen in the corresponding acyl derivatives.

The pyramidal configuration of nitrogen and its slow inversion on the NMR time scale were proved in the present paper for derivatives (II)-(X), which were obtained from 3,3-dimethyldiaziridine (I), and also for N-acyloxazirane (XVI) (Table 1). The indicated rule and the theory expressed in [6] that the amide conjugation with the diaziridine and oxazirane nitrogen is weakened were confirmed in this manner.

A check of the configuration of the N-acyl nitrogen in 1-acyl-2-alkyl-3,3-dimethyldiaziridines based on the NMR spectra is complicated by the fact that if a configurationally more stable N-alkyl nitrogen is present the methyl groups of the ring are nonequivalent outside the dependence on the configuration of the N-acyl nitrogen. For example, for PhNHCONC(Me_2)NMe in Ph_2O the methyl groups of the ring are nonequivalent both at 36 ($\Delta\nu$ 2.4 Hz) and at 100° ($\Delta\nu$ 1.2 Hz) [9]. In N-monoacyldiaziridines (II)-(IV) and vinylog (V) this difficulty could be eliminated. It proved that the acyldiaziridines are so stable in acid that they could even be obtained via the acid chlorides without binding the HCl. Consequently, the configuration of the N-acyl nitrogen could be checked by adding CD_3COOD under the conditions of rapid NH exchange (δ_{NH-OH} ~8-9 ppm), which is equivalent to its effective flattening. The inversion barrier does not change with increase in the acid concentration.

A decrease in the pyramidal stability of the N-acyl nitrogen when going from (II) and (III) to (IV) is due to a decrease in the competitive conjugation of the substituent with the carbonyl group and a corresponding enhancement of the amide conjugation with the nitrogen of the ring. A similar effect is observed in the aziridine analogs $Me_2NCON(CH_2)_2$ (T_m −86°, $\Delta G^{\neq}$ 10.8 kcal/mole), $MeOCON(CH_2)_2$ (T_m −138°, $\Delta G^{\neq}$ 7.6 kcal/mole) [5]. Retarded nitrogen inversion under the conditions of rapid NH exchange can also be observed for the N-acyldiaziridine vinylog (V), in contrast to the aziridine analog, where the inversion rate of the nitrogen is slightly too great [5, 10]. The signals of the protons and methyl groups of the ring are not split and do not broaden at −50° in the spectra of $(CH_2)_2NCH=CHCOOMe$ (cis/trans = 1) and cis-$Me_2CCH_2NCH=CHCN$ (in CH_2Cl_2). The inversion parameters of (IV) and the vinylog (V) differ slightly.

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TABLE 1. $RC\overline{N(Me_2)}NR^1$

Compound	R	R^1	Solvent	T., °C	δ, ppm: Me_2C	Me_2N MeCH	MeO Ph	other signals	Observed group	$\Delta\nu$f, Hz	T_c, °C	$\Delta G^{\neq}$, kcal/mole
(II)	PhNHCO	H	CH_2Cl_2 + CD_3COOD	—50	1,82 1,98				Me_2C	9,8	2	14,3
(III)	Me_2NCO	H	$CDCl_3$	20	1,36	2,91 3,03		NH 3,0				
			$CDCl_3$	—50	1,26	2,89		NH 3,21				
			cis[a]		1,32	3,00						
			trans[a]		1,18 1,47	2,83 2,95		NH 2,41				
			$CDCl_3$ + CD_3COOD[b]	—50	1,30 1,50	2,94 3,02		NH(OH) 8,8	Me_2C	8,8	—6	14,0
(IV)	MeOCO	H	CCl_4 + CD_3COOD	—50	1,27 1,42		3,60	NH(OH) 9,1	Me_2C	10,4	—34	12,4
(V)	MeOCOCH=CH	H[c]	$CDCl_3$ + CD_3COOD	—50	0,98 1,21		3,18	CH(CO) 5,16, CH(N) 7,60, NH(OH) 9,66	Me_2C Me_2C	14,0 16,0	—32 13	11,3 15,3
(VI)	Me_2NCO	PhCO	CD_3OD	—40	1,22 1,52	2,91 3,02	7,70					
(VII)	Me_2NCO	PhNHCO	$CDCl_3$	—40	1,38 1,51	2,90 2,99	7,15	NH 7,49	Me_2C	7,7	—14	13,6
(VIII)	Me_2NCO	MeOCO	$CDCl_3$	—30	1,33 1,51	3,02 3,11	3,77		Me_2C	11,0	—17	13,3
(IX)	S—Ph(Me)CHNHCO	S—Ph(Me)CHNHCO	$CDCl_3$	20[e]	1,14 1,42	1,35 1,43	7,14	NH 6,27 CH 5,86	MeCH	4,2	33	16,6
(X)	S—Ph(Me)CHNHCO	H[d]	$CDCl_3$	20	1,15 1,35 1,45 1,48	1,42 1,44	7,30	NH 2,40, CH 5,00 NH(CO) 6,40				

[a] Ratio of trans/cis isomers = 4/3.

[b] For the rotation around the CO—NMe_2 bond: $\Delta\nu$ 5.5 Hz, T_m 46°, $\Delta G^{\neq}$ 1.71 kcal/mole.

[c] J_{HCCH} = 13.5 Hz.

[d] $J_{HCMe} = J_{HCNH}$ = 7 Hz.

[e] The ratio of the diastereomers is 1:1.05 at 20° and 1:1.25 at —20°.

[f] The values were obtained from the temperature dependence of $\Delta\nu$ and extrapolating to the temperature of merging.

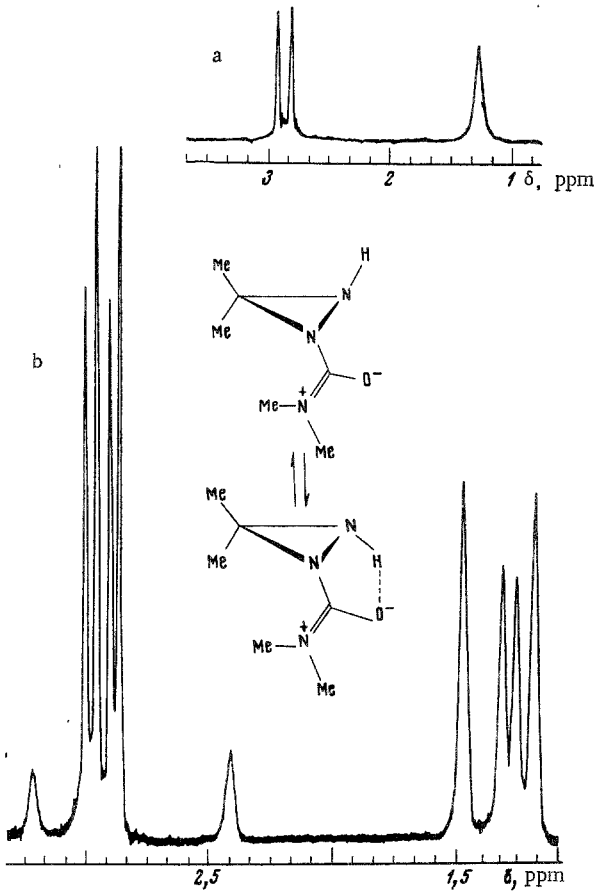

Fig. 1

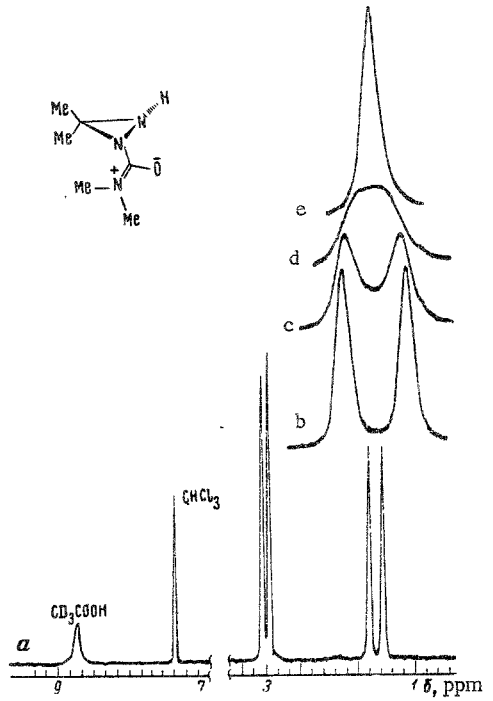

Fig. 2

Fig. 1. NMR spectra (60 MHz) in $CDCl_3$: a) at 20° the methyl protons of the ring are averaged due to the rapid inversion of the ring nitrogen, while the methyl protons of the substituent are nonequivalent due to the hindered rotation around the CO–N bond; b) complete sets of signals exist for the cis- and trans-isomers at −50°, with an intensity ratio of 3/4. Here the methyl protons of the ring are nonequivalent due to the hindered inversion of the ring nitrogens.

Fig. 2. NMR spectrum (60 MHz) in $CDCl_3$ + CD_3COOD: a) at −50° (due to the rapid exchange with the acid the NH nitrogen is effectively flat, and consequently the nonequivalence of the methyl protons of the ring is caused by the pyramidal configuration and slow inversion of the amide nitrogen of the ring). The spectra of these protons at temperature, °C: b) −30; c) −20; d) −6; e) 4.

Similar parameters of phosphorus inversion were found for the acylphosphine MeCOP $(i\text{-Pr})_2$ (T_m 148°, $\Delta G^{\neq}$ 24 kcal/mole [10]) and the vinylog MeOOCCH = CHP $(i\text{-Pr})_2$ [10] (in Ph_2O, $\Delta\nu$ 4.5 Hz, T_m 144°, $\Delta G^{\neq}$ 23 kcal/mole).

The competing amide conjugation with the substituent attached to the carbonyl group is distinctly manifested in compound (III): the rotation around the $CONMe_2$ bond is more hindered than the inversion of the N-acyl nitrogen (see Table 1). Complete sets of signals for the two compounds in a 3/4 ratio are observed in the NMR spectrum at −50° if acid is not added (Fig. 1), which were assigned to the cis- and trans-isomers. The cis-isomer in this case was stabilized due to the NH hydrogen bond with the carbonyl oxygen (five-membered ring). Here the NH proton was deshielded, and consequently the downfield NH signal and all of the other less intense signals were assigned to the cis-isomer. When acid is added the low-temperature spectrum of (III) corresponds to one compound with an effectively flat NH (due to exchange with the acid) and a pyramidal N-acyl nitrogen (Fig. 2).

Two signals of the methyl groups of the ring are observed in the low-temperature NMR spectra of the unsymmetrical 1,2-diacyldiaziridines (VI)-(VIII). The inversion barriers of the most slowly inverted nitrogen were found from their merging (see Table 1).

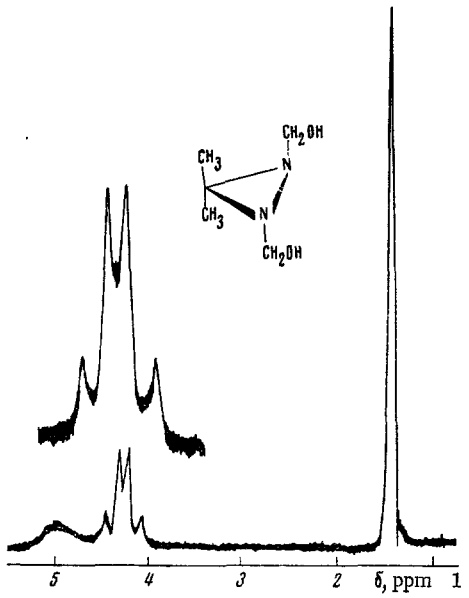

Fig. 3

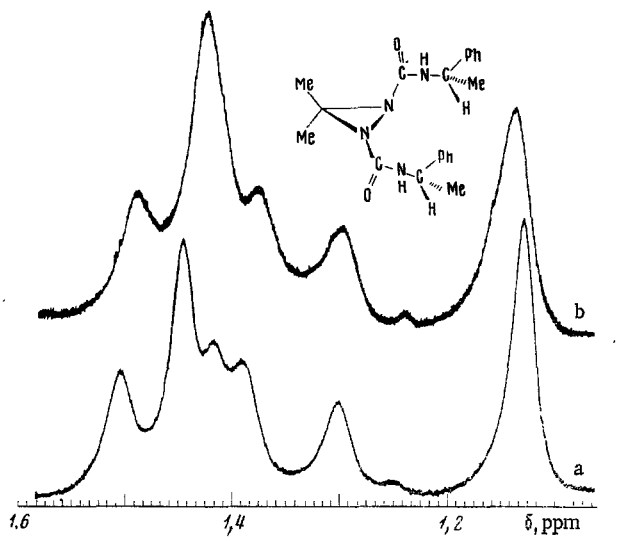

Fig. 4

Fig. 3. NMR spectrum (60 MHz) in $CDCl_3$. The equivalence of the methyl and the germinal nonequivalence of the methylene protons (AB spectrum) testify to the trans-orientation of the substituents on the pyramidal nitrogen atoms.

Fig. 4. NMR spectrum of methyl protons of ring and substituent (60 MHz) in $CDCl_3$: a) at −20°; b) at 20°. Complete sets of the signals of the diastereomers due to the asymmetric amide nitrogens are present in the low-temperature spectrum.

The trans-orientation of the 1,2-substituents in the diaziridines [9] follows, for example, from the equivalence of the methyl groups in 1,2-bis(hydroxymethyl)-3,3-dimethyldiaziridine (XI) (Fig. 3). The criterion of the pyramidality of the nitrogens in this case, the same as in the aziridine analog [10], is the diastereotopicity of the methylene protons (AB spectrum). In the symmetrical 1,2-diacyl-3,3-dimethyldiaziridines the methyl groups of the ring should also be equivalent outside the dependence on the configuration of the nitrogens (either flat or pyramidal when the N-acyl substitutents are trans-oriented). However, the configuration of the nitrogens can also be checked in this case if asymmetric centers with the same absolute configuration are present in the acyl substituents. If the nitrogens are pyramidal, then diastereomers should be observed here. Actually, the NMR spectrum of such a derivative (IX) corresponds to two diastereomers, the ratio of which differs noticeably from 1 (Fig. 4).

The inversion parameters of (IX) were determined from the merging of the **Me**CH signals of the diastereomers. The signals of the methyl groups of the ring broaden when the temperature is raised, but a complete merging could not be achieved, since the compound decomposes at 50°. Diastereomers are also observed in the monocarbamoyl derivative (X) (Fig. 5). However, the inversion parameters could not be determined in this case, since the addition of CD_3COOD leads to decomposition of the compound. When CD_3OD is added the NH exchange rate is slower than the inversion rate of the N-acyl nitrogen. Here the CH signal represents a mixture of a quartet and quintuplet due to a partial substitution of the NH by deuterium. The methyl portion of the spectrum does not change even when heated up to 50°. The possibility of assigning the two sets of signals in the NMR spectrum of (X) to the isomers caused by the rotation of the substituent around the amide linkage [like in (II), (VII), and (IX)] is excluded by the fact that such isomers are not observed for the 2-methyl analog (II) [9] and, in addition, the spectra of the model N-acylaziridines (XII)-(XIV) each have only one set of signals even at −50° (Table 2).

In 1-α,α-difluorodiaziridine (XV) the nitrogen inversion is also substantially retarded when compared with the aziridine analog [10]. In the NMR spectrum at 20° is observed a nonequivalence of the methyl groups of the ring and of the diastereotopic fluorine atoms of the CF_2 group, and a selective spin − spin coupling of one fluorine atom of the CH_2 group with one of the CH_3 groups of the ring (Fig. 6). The spectrum does not change during effective NH exchange [addition of CD_3COOD, $\delta_{NH(OH)}$ 9.5 ppm] and when heated to 73° in nitrobenzene, while on further heating the compound decomposes.

TABLE 2. R'NHCO$\overbrace{NCH_2CR_2}$

Compound	R	R'	Solvent	δ, ppm				
				MeCH	Me_2C	CH_2	CH	NH
(XII)	Me	Ph	$CHCl_3$	—	1,11	1,97	—	—
(XIII)	Me	Ph(Me)CH	$CHCl_3$	1,10	1,37	2,00	4,85	5,60
(XIV)	H	Ph(Me)CH	$CHCl_3$	1,17	—	1,95	4,63	5,77

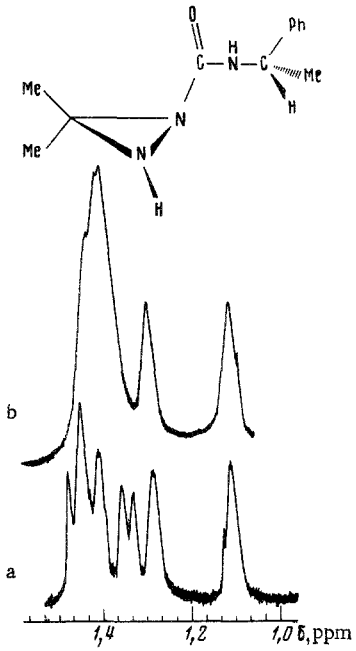

Fig. 5. NMR spectrum (60 MHz) of methyl protons of ring and substituent in $CDCl_3$ + CD_3OD at 50°: a) usual spectrum; b) when the CH proton is suppressed.

The pyramidal stability of the amide nitrogen increases substantially when going from the N-acyldiaziridines to the N-acyloxaziranes. The NMR spectrum of N-acyloxazirane (XVI) has two methyl doublets of the MeCH group of the diastereomers with an asymmetric center on the amide nitrogen (Fig. 7). The inversion parameters of the amide nitrogen were determined from the merging of these signals when heated (Fig. 7b): $\Delta\nu$ 2.4 Hz, T_m 74°, $\Delta G^{\neq}$ 19.3 kcal/mole. A nonequivalence of the phenyl groups of the diastereomers is observed from the NMR spectrum (Fig. 7c), which merge at 70° ($\Delta\nu$ 1.9 Hz, $\Delta G^{\neq}$ 19.3 kcal/mole). Compound (XVI) can be enriched somewhat in one of the isomers by recrystallization from hexane (Fig. 7d), the ratio of which remains practically unchanged after keeping the crystals at ~20° for a month.

The N-acyldiaziridines (II)-(X), N-acylaziridines (XII)-(XIV), and N-acyloxazirane (XVI) were obtained by the acylation of (I), the aziridines, and 3,3-pentamethyleneoxazirane with acid chlorides and isocyanates (see "Experimental Method"). The attempted acylation of (I) with bis(trifluoromethyl)ketene gave the isomeric acylhydrazone (XVII), the structure of which was proved by counter synthesis.

$$\underline{HNC(Me_2)NH} \xrightarrow{(CF_3)_2C=C=O} \underset{(XVII)}{(CF_3)_2CHCONHN=CMe_2} \xleftarrow{(CF_3)_2C=C=O} Me_2C=NNH_2$$

Similar to the aziridines [10], the reaction of (I) with perfluoroisobutylene gives only the saturated product (XV) [11].

EXPERIMENTAL METHOD

The ^1H and ^{19}F NMR spectra, and the temperature dependence of the spectra, were obtained on a JEOL JNM-C-60HL spectrometer (60 MHz), the IR spectra were obtained on UR-10 and UR-20 spectrophotometers, while the mass spectra were obtained on the following instruments: MX-1303 at 30 and 12 eV, LKB-9000 at 70 and 12 eV, and JMS-01-S62 at 75 and 14 eV. The mass spectra are given in the text: the m/e values of the peaks with an intensity above 20% are listed, while the relative intensity (in %) at 30 and 12 eV [or at 70 (75) and 12 (14) eV] is indicated in parentheses.

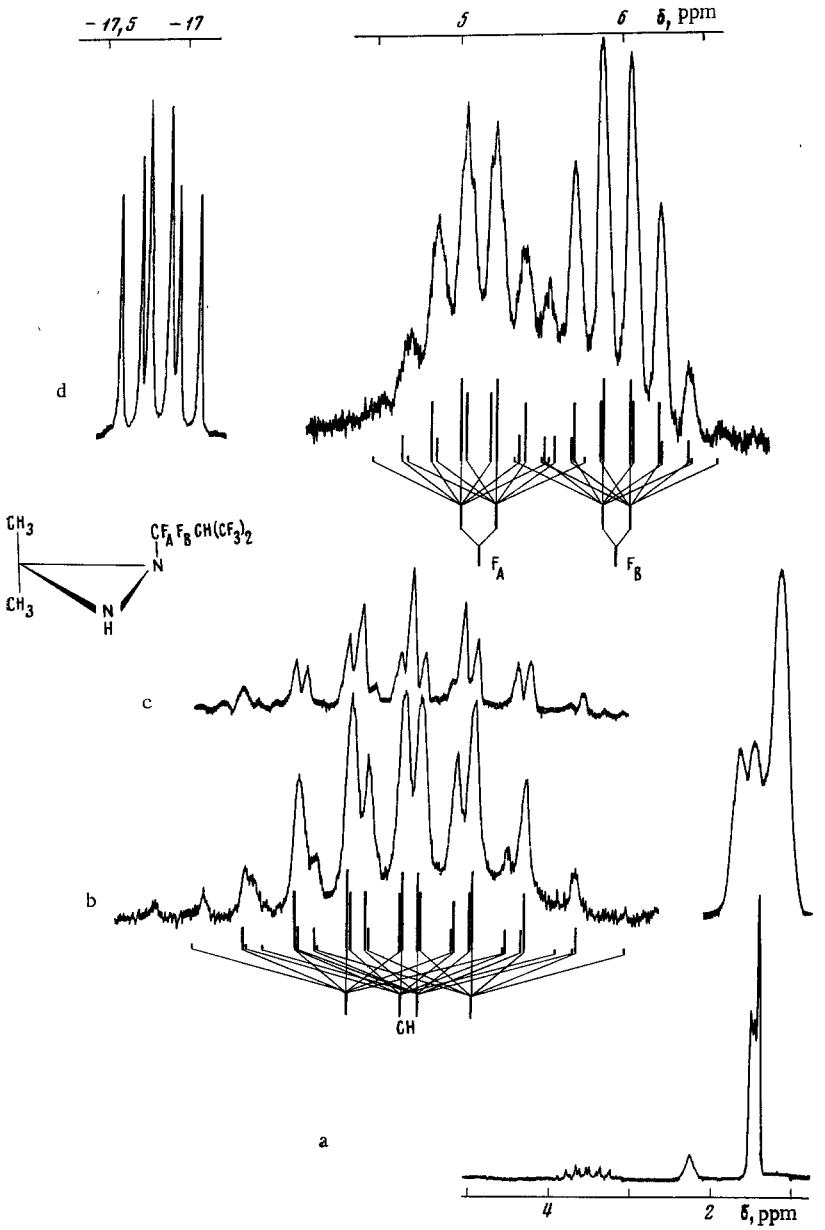

Fig. 6. NMR spectra: a) ^1H (60 MHz) in CCl_4, general spectrum; b) in CCl_4, methyl protons and CH; c) in Ph_2O, CH; d) ^{19}F (56.452 MHz) of CF_3 and CF_AF_B (from CF_3COOH as the internal standard).

3,3-Dimethyldiaziridine (I) and 1-phenylcarbamoyl-2,2-dimethylaziridine (XII) were obtained as, respectively, described in [12, 13].

1-Phenylcarbamoyl-3,3-dimethyldiaziridine (II). From 0.17 g of phenylisocyanate and 0.1 g of (I) in 45 ml of ether was obtained 0.25 g (94.3%) of (II), mp 93-95° (from ether by freezing). Found: C 62.90; H 7.02; N 21.71%. $C_{10}H_{13}N_3O$. Calculated: C 62.81; H 6.85; N 21.97%.

1-Dimethylcarbamoyl-3,3-dimethyldiaziridine (III). The reaction of 1.12 g of (I) and 1.64 g of dimethylcarbamoyl chloride in the presence of 1.72 g of triethylamine in 40 ml of ether (24 h) gave 0.78 g (35%) of (III), bp 63° (1 mm); n_D^{15} 14,738. Mass spectrum: M^+ 143 (4; 8), 72 (100; 100), 45 (28; 60), 44 (31; 28), 43 (28; 10), 42 (45; 13), 28 (45; 5). Found: C 50.36; H 9.24; N 29.34%. $C_6H_{13}N_3O$. Calculated: C 50.33; H 9.15; N 29.35%.

1-Methoxycarbonyl-3,3-dimethyldiaziridine (IV). The reaction of 3 g of (I) and 3.15 g of methyl chloroformate in the presence of 4.2 g of triethylamine in 60 ml of ether (–10°, 24 h) gave 2.8 g (51.6%)

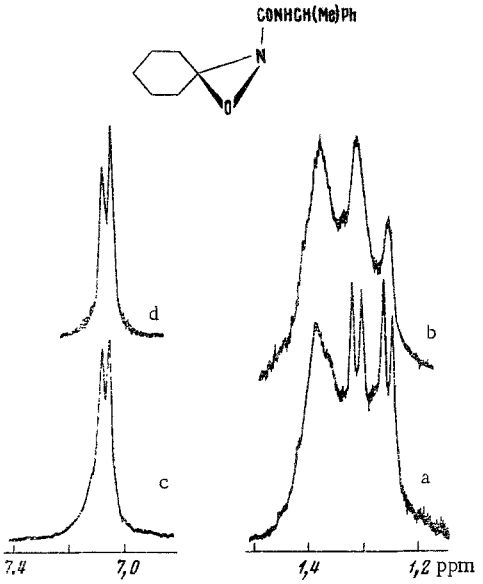

Fig. 7. NMR spectra (60 MHz) in CCl_4 a) region of methyl and methylene protons at 20°; b) the same at 78°; c) signals of phenyl protons of diastereomers at 20°; d) the same after fractional crystallization from hexane.

of (IV), bp 71-74° (4 mm). Infrared spectrum (ν, cm^{-1}, molecular layer): 1750 (CO), 3260 (NH). Mass spectrum: M^+ 130 (7; 20), 115 (25; 60), 99 (42; 60), 98 (61; 96), 83 (37; 32), 72 (10; 62), 71 (16; 50), 59 (60; 45), 56 (45; 34), 42 (100; 100), 30 (66; 42). Found: C 46.16; H 7.78; N 21.43%. $C_2H_{10}N_2O_2$. Calculated: C 46.14; H 7.74; N 21.52%.

Methyl Ester of trans-β-(3,3-Dimethyldiaziridino)acrylic Acid (V). A mixture of 1.73 g of (I) and 2.1 g of (I) and 2.1 g of methyl propiolate in 75 ml of ether was kept for 3 days at 20°. Distillation gave 1.65 g (44%) of (V), bp 62-63° (1 mm); n_D^{21} 1.5020. Mass spectrum: M^+ 156 (43; 100), 125 (20; 6), 124 (47; 32), 112 (48; 42), 97 (72; 42), 84 (26; 3.5), 83 (24; 10), 42 (52; 5.5). Found: C 53.61; H 7.62; N 18.07%. $C_7H_{12}N_2O_2$. Calculated: C 53.84; H 7.75; N 17.93%.

1-Dimethylcarbamoyl-2-benzoyl-3,3-dimethyldiaziridine (VI). From 0.22 g of (III) and 0.29 g of benzoyl chloride in 40 ml of ether, in the presence of 0.2 ml of triethylamine, was obtained 0.35 g (92%) of (VI), mp 86-89°. Infrared spectrum (ν, cm^{-1}, KBr pellets): 1690 and 1718 (CO). Mass spectrum: M^+ 247 (12; 100), 232 (5; 48), 203 (14; 65), 142 (12; 64), 105 (67; 56), 72 (100; 84), 58 (38; 37), 43 (51; 26). Found: C 63.20; H 7.07; N 16.75%. $C_{13}H_{17}N_3O_2$. Calculated: C 63.14; H 6.93; N 16.99%.

1-Dimethylcarbamoyl-2-phenylcarbamoyl-3,3-dimethyldiaziridine (VII). From 0.72 g of (III) and 0.59 g of phenyl isocyanate in 30 ml of ether was obtained 1.16 g (88%) of (VII), mp 149° (from ether by freezing). Mass spectrum (70 and 12 eV): M^+ 262 (2; 16), 164 (15; 20), 143 (23; 100), 119 (38; 41), 72 (100; 5). Found: C 59.57; H 7.03; N 21.40%. $C_{13}H_{18}N_4O_2$. Calculated: C 59.53; H 6.90; N 21.36%.

1-Dimethylcarbamoyl-2-methoxycarbonyl-3,3-dimethyldiaziridine (VIII). From 2 g of (IV) and 1.65 g of dimethylcarbamoyl chloride in the presence of 2.1 ml of triethylamine in 70 ml of ether (12 h) was obtained 1.16 g (37.5%) of (VIII), bp 48° (1 mm). The product was characterized by the NMR spectrum (see Table 1).

1-[S-α-Phenylethylcarbamoyl]-3,3-dimethyldiaziridine (X) and 1,2-Bis-[S-α-phenylethylcarbamoyl]-3,3-dimethyldiaziridine (IX). A mixture of 0.28 g of (I) and 1.2 g of S-(−)-α-phenylethyl isocyanate [7] in 20 ml of ether was kept at 20° for 1 h and the obtained crystals were separated. We obtained 0.3 g (35.2%) of (X), mp 89-92° (from ether). Infrared spectrum (ν, cm^{-1}): 1680 (CO), 3340 and 3320 (NH). Mass spectrum (70 and 12 eV): M^+ 219 (11; 28), 204 (6; 14), 161 (14; 20), 120 (36; 73), 105 (100; 20), 77 (26; 0), 72 (96; 80), 58 (42; 100). Found: C 65.64; H 7.87; N 18.10%. $C_{12}H_{17}N_3O$. Calculated: C 65.73; H 7.81; N 19.16%. From the residual mother liquor after 3 days we isolated 0.38 g (26.7%) of (IX), mp 96-98° (from hexane). Infrared spectrum (ν, cm^{-1}, KBr pellets): 1690 (CO), 3290 (NH). Mass spectrum (70 and 12 eV): M^+ Ph(Me)CHNCO 219 (15; 50), 147 (36; 100), 132 (78; 68), 120 (30; 53), 105 (100; 12), 77 (40; 3), 72 (84; 82), 58 (60; 90). Found: C 68.86; H 7.22; N 15.25%. $C_{21}H_{26}N_4O_2$. Calculated: C 68.82; H 7.22; N 15.29%.

1,2-Bis(hydroxymethyl)-3,3-dimethyldiaziridine (XI). Vacuum-dried α-polyoxymethylene (1.25 g) was depolymerized by heating in 15 ml of absolute methanol under reflux in the presence of catalytic amounts of granulated KOH. Then 1.5 g of (I) in 10 ml of methanol was added and the mixture was kept

at 20° for 2 h. After removal of the solvent the product was recrystallized from chloroform. We obtained 1.64 g (59.2%) of (XI), mp 108-110°; after sublimation at 90° (1 mm), mp 111-112° (from acetone). NMR spectrum (δ, ppm, CCl_4): Me_2C 1.38; CH_2 4.25; OH 4.98 (see Fig. 1). Found: C 45.48; H 9.17; N 21.44%. $C_5H_{12}N_2O_2$. Calculated: C 45.40; H 9.16; N 21.18%.

S-1-α-Phenylethylcarbamoyl-2,2-dimethylaziridine (XIII). The reaction of 0.23 g of 2,2-dimethylaziridine and 0.5 g of S-(−)-α-phenylethyl isocyanate in 15 ml of ether (2 h) gave 0.7 g (quantitative yield) of (XIII), mp 101-102° (from CCl_4). Infrared spectrum (ν, cm^{-1}, KBr pellets): 1660 (CO), 3260 (NH). Mass spectrum (70 eV): M^+ 218 (30), 120 (30), 105 (62), 77 (20), 71 (100), 56 (22). Found: C 71.47; H 8.31; N 11.96%. $C_{13}H_{18}N_2O$. Calculated: C 71.54; H 8.30; N 12.83%. From [13]: mp 100-104.5°.

S-1-α-Phenylethylcarbamoylaziridine (XIV). From 0.05 g of ethylenimine and 0.1 g of S-(−)-α-phenylethyl isocyanate in 15 ml of hexane (1.5 h) was obtained 0.033 g (26%) of (XIV), mp 51-52°. The NMR spectrum is given in Table 2. Found: C 69.53; H 7.58; N 14.97%. $C_{10}H_{14}N_2O$. Calculated: C 69.45; H 7.41; N 14.72%.

1-β-Hydroperfluoroisobutyl-3,3-dimethyldiaziridine (XV). A solution of 1.91 g of (I) in 25 ml of ether was added to a solution of 5.1 g of perfluoroisobutylene in 50 ml of ether at −50°. After 1 h the mixture was brought up to ~20° and the solvent was evaporated. We obtained 4.48 g (62%) of (XV), mp 26° (from ether by freezing), bp 24° (1 mm); n_D^{25} 1.3520. NMR spectrum (δ, ppm, CCl_4): Me_2C 1.41, 1.48; NH 2.27; CH 3.53. J_{MeCNCF} = 2.4, J_{HCCF_3} = 8.4, J_{HCCF_2} = 8.0; 10.4 Hz. ^{19}F NMR spectrum (ppm from CF_3COOH): CF_3 −17.2; CF_2 5.2, 5.9; $J_{CF_3CF_2}$ = 23.2 Hz. Mass spectrum: M^+ HF 252 (70; 100), 237 (92; 7), 212 (32; 27), 173 (31; 5), 101 (21; 82), 69 (46; 0), 61 (87; 0), 60 (65; 0), 56 (57; 0), 55 (70; 34), 54 (40; 0), 43 (37; 0), 42 (27; 8), 41 (100; 0), 40 (100; 0), 39 (60; 0), 28 (84; 0). Found: C 30.84; H 3.07; N 10.40%. $C_7H_8F_8N_2$. Calculated: C 30.90; H 2.98; N 10.29%. The product remains unchanged when its dehydrofluorination is attempted by refluxing for 5 h with ground KOH in ether.

2-α-Phenylethylcarbamoyl-3,3-pentamethyleneoxazirane (XVI). The reaction of 2.26 g of 3,3-pentamethyleneoxazirane [14] with 2.94 g of α-phenylethyl isocyanate in 60 ml of benzene (16 h) gave 2.95 g (56.7%) of (XVI), mp 92-92.5°. The product gives a positive oxidizing test with KI. Infrared spectrum (ν, cm^{-1}, KBr pellets): 1390 (oxazirane ring [15]), 1680 (CO), 3280 (NH). NMR spectrum (δ, ppm, CCl_4): Me 1.42, 1.38; CH 4.76; NH 5.57; CH_2 1.6; Ph 7.05, 7.08. J_{MeCH} = 7.0 Hz. Mass spectrum (75 and 14 eV): M^+ 260 (2.2; 6.6), 217 (3; 13), 120 (14; 20), 113 (9.3; 21.4), 105 (100; 100). Found: C 69.32; H 8.00; N 10.71%. $C_{15}H_{20}N_2O_2$. Calculated: C 69.20; H 7.74; N 10.76.

Acetone N-α-Hydrohexafluoroisobutyroylhydrazone (XVII). A mixture of 2.1 g of (I) and 5.2 g of bis(trifluoromethyl)ketene in 50 ml of ether was kept in a sealed ampul for 7 days. After removal of the solvent we obtained 5.22 g (71.6%) of (XVII), mp 120-122° (from hexane). Infrared spectrum (ν, cm^{-1}, KBr pellets): 1655 (C=N), 1710 (CO), 3200 (NH). NMR spectrum (δ, ppm, CCl_4): Me 2.03, 2.07; CH 5.4. J_{HCCF_3} = 7.8 Hz. Mass spectrum (70 eV): M_3 250 (20), 235 (100), 179 (20), 71 (50), 69 (36), 56 (23), 41 (21), 30 (38). The identical (XVII) product was obtained by reacting 1.72 g of acetone hydrazone with 4.26 g of bis(trifluoromethyl)ketene in 35 ml of ether; yield 3.25 g (54.4%).

CONCLUSIONS

The pyrimidal stability of the amide nitrogen increases in the order: N-acylaziridines, N-acyldiaziridines, and N-acyloxaziranes.

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