2-AZIRIDINO- AND 2-DIAZIRIDINO-3,3-BIS(TRIFLUOROMETHYL)AZIRIDINES*

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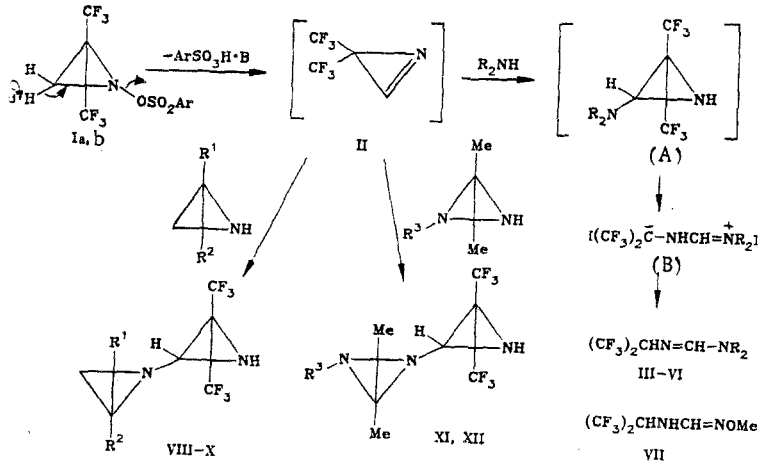
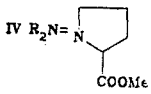
3,3-Bis(trifluoromethyl)-1-azirine, formed by the reaction of 1-arenesulfonyloxy-2,2-bis(trifluoromethyl)aziridines with nucleophilic reagents, reacts with aliphatic amines with ring-opening and formation of formamidines. With aziridines and diaziridines having a lower electron-donor capability of the nitrogen atom, it forms the adducts -2-aziridino- and -2-diaziridino-3,3-bis(trifluoromethyl)aziridines. All the isomers theoretically possible were recorded for these derivitives by the dynamic NMR method.

The reactions of 1-arenesulfonyloxy-2,2-bis(trifluoromethyl)-aziridines (Ia, b) with nucleophiles occur via the intermediately produced 3,3-bis(trifluoromethyl)-1-azirine [2, 3].† Depending on the nature of the nucleophile, the reaction is terminated by its addition at the C=N bond of azirine with the formation of a new aziridine system or is accompanied by a rearrangement with ring opening (preliminary communications, see [3, 9]).



I a Ar=Ph; b Ar=*p*-C_6H_4Me; III $R_2N=Me_2$; V NR_2=MeNOMe; VI $R_2N=HNCMe_3$; VIII $R^1=R^2=H$; IX $R^1=H$, $R^2=Me$; X $R^1=R^2=Me$; XI $R^3=H$; XII $R^3=Me$;



In the reaction of aziridines Ia, b with the usual primary and secondary amines, the expected 2-amino-3,3-bis(trifluoromethyl) aziridines were not obtained for any of them. This is explainable by the fact that the high +M effect of the amino group, on the one hand, and the presence of the CF_3 electron acceptor groups, stabilizing the adjacent carbanion center, on the other hand, cause an opening of the aziridine ring (A) at the C-C bond. The zwitter-

*Article 58 of the series "Asymmetric nitrogen." For Article 57, see [1].

†Only a few examples are known of the extraordinarily reactive 1-azirines unsubstituted at C(2), obtained by the decomposition of vinyl azides [4-8].

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ion (B) thus formed becomes stabilized by converting into formamidine.*

Formamidines III-VI were identified from NMR spectra and the structure of compounds VII was confirmed by deutero exchange with NH (see experimental part).

Through reactions of compounds Ia, b with aziridines in the presence of Et_3N, only adducts were obtained,† the 2-aziridino-3,3-bis(trifluoromethyl)aziridines (VIII-X). This is explainable by the decrease in the +M-ability of the nitrogen atom when contained in a trimembered ring (for example, the ionization potentials are 8.36 for Me NH [14], 9.85 for aziridine, 9.29 eV for 2,2-dimethylaziridine [15]), which also ensured the stability of the compounds formed.

The aziridinoaziridines VIII-X obtained are readily preparatively isolated. At a temperature of 20°C or more, they decompose gradually in order of stability decreasing from compound VIII to compound X.‡ At the temperatures of 0-10°C in an inert gas atmosphere, without access of moisture, they remain unchanged for a prolonged period.

In the PMR spectrum of compound VIII, the signals of the NH and CH group protons of the fluorine-containing ring are observed in the 2-3 ppm region ($^3J_{HH}$ = 7.5 Hz) and are strongly broadened because of the SSC with CF_3. They are shifted by the action of a shifting reagent $Eu(dpm)_3$ to the weak field to the same extent, and the complex multiplet of the second ring protons thus remains unchanged. A D-analog of VIIIa was obtained by the reaction of aziridine I with N-deuteroaziridine, lacking the NH signal in its PMR spectrum. Thus, the signals of the CH and NH group protons were assigned in compound VIII (and in analogy, also in compounds IX and X). When a sample of VIIIa was heated in CCl_4 (100°C, in a sealed ampule),‡‡ the complex multiplet of the ring protons was transformed, but did not merge into a singlet because of the asymmetric induction of the nonequivalency due to the N-substituent [16].

In the electron-donor ability of the nitrogen atom, the diaziridines are comparable with aziridines, which is borne out by their ionization potentials (for example, for 3,3-dimethyldiaziridine and 2,3,3-trimethyldiaziridine, they are equal to 9.90 and 9.29 eV, respectively [17]). It is also known that substituted monocyclic diaziridines exist in the form of thermodynamically favorable trans-isomers [17] and the inversion barrier for their nitrogen atoms is 27-28 kcal/mole [18]. Therefore in the reactions of compounds Ia, b with diaziridines, the formation of mixtures of diastereomers was to be expected. They could be observed from the NMR spectra and separated under normal conditions.

In fact, in the reaction of aziridines Ia, b with diaziridines under mild conditions, adducts XI and XII are formed (see scheme 1). According to the ^{19}F NMR spectra of the reaction mixtures, two diastereomers are observed in each case, in a ratio of ∿2:3. Crystallization of the mixture of the isomers of XI gave an individual predominating diastereomer XIa, mp 108-112°C. A practically predominating individual diastereomer, bp 53-54°C (9 mm Hg), was isolated from the reaction of aziridine Ia with 2,3,3-trimethyldiaziridine by distillation of the mixture of isomers of XII. When pure diastereomers XIa and XIIa are epimerized in toluene-D_8, after 2 h, at 60°C their equilibrium ratio of ∿2:3 is attained, as in the initial reaction mixture. On cooling of the samples of diastereomers XIa and XIIa, signals are recorded in the ^{19}F NMR spectra of invertomers XIa and XIIa at the aziridine nitrogen atom.

A similar pattern is observed in the case of adducts VIII-X. In the ^{19}F NMR spectrum of compound VIII at 20°C, two broadened signals are observed as a result of averaging due to

*The stability of aziridine (A) is determined by the nature of the substituents. This is indicated, for example, by the synthesis of the 1-phenyl-2,2-dimethyl-3-dimethylaminoaziridine by photolysis of the corresponding triazoline [10], and also by the successful addition of 3,4,5-triphenylpyrazole [11] and piperidine [12] to 2-methyl-3-phenyl-1-azirine. No other examples of the synthesis of 2-aminoaziridines are known.

†The synthesis of an aziridinoaziridine system has been reported [13], but its structure has not been absolutely confirmed. In the NMR data, for example, no information is given on the CH_2 protons of the ethoxyl groups and the CH, NH protons of the aziridine rings.

‡The decomposition products were not identified, but in the NMR spectra, the signals of the 2,2-bis(trifluoromethyl)aziridine ring disappear, and signals characteristic of the $(CF_3)_2CH$ fragment appear.

‡‡At this temperature, part of the compound decomposes during the time when the spectrum is taken (40-50 min).

TABLE 1. ^{19}F NMR Spectra of Compounds VIII-XII in Toluene-D_8

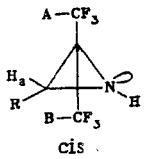
Compound	T, °C	Content of isomer, %	δ, ppm		$\Delta\nu_{CF_3}$, ppm	J, Hz		
			A-CF_3	B-CF_3		CF_3CF_3	B-CF_3H_a	A-CF_3H_b
VIII	25		7,61	14,47		7,0		
cis- VIII	−45	50	7,42	16,06	8,64	6,4	2,2	
trans- VIII	−45	50	8,29	13,49	5,20	7,2		0,5
IX	25		7,68	14,77		7,2		
cis- IXa	−30	20	7,49	16,33	8,84	6,4	2,4	
trans- IXa	−30	40	8,44	13,56	5,12	7,2		1,5
cis- IXb	−30	14	7,49	16,33	8,84	6,4	2,4	
trans- IXb	−30	26	8,30	13,23	4,93	7,2		1,5
X	25		7,73	15,54		7,0		
cis-Xa	−40	28	7,43	16,55	7,81	6,4	2,6	
trans- Xa	−40	57	8,38	13,19	4,81	7,2		0,5
cis- Xb	−40	10	7,73	16,55	9,12	6,4	2,6	
trans-Xb	−40	5	8,85	14,29	5,44	7,2		0,5
XIa	25	60	7,22	15,28		7,0		
XIb	25	40	7,76	14,77		7,0		
cis- XIa	−35	30	7,02	15,73	8,71	6,6	2,6	
trans-XIa	−35	30	8,67	14,01	5,34	6,7		
cis-XIb	−35	27	7,37	16,61	9,24	6,3	2,6	
trans-XIb	−35	13	8,44	14,01	5,57	6,9		
XIIa	25	60	7,17	15,12		6,8		
XIIb	25	40	7,70	15,12		6,7		
cis-XIIa	−40	41	6,96	15,57	8,61	6,6	1,8	
trans-XIIa	−40	19	8,53	14,05	5,52	7,0		
cis-XIIb	−40	13	7,32	16,70	9,38	6,4	1,8	
trans-XIIb	−40	27	8,55	14,04	5,49	6,8		

*PMR spectra of compounds VIII-X, see [9].

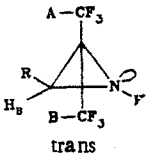
the inversion of the nitrogen atom. On cooling, each of these signals transforms into two quartets (1:1) corresponding to cis- and trans-invertomers (R with respect to NH).

We have already found the configurational NMR criteria for the cis- and trans-1H-3-substituted 2,2-bis(trifluoromethyl)-aziridines:

1. $^4J_{B\text{-}CF_3H_a} > {}^4J_{A\text{-}CF_3H_b}$;
2. $\Delta\nu_{CF_3(cis)} \gg \Delta\nu_{CF_3(trans)}$;
3. $^4J_{FF}^{trans} > {}^4J_{FF}^{cis}$,



cis



trans

from which the signals of the stereoisomers in the NMR spectra of compounds VIII-XII were assigned.

Thus, in the low-temperature spectrum of aziridine VIII, the high-field and low-field signals with $\Delta\nu_{CF_3}$ = 8.64 ppm have a common $^4J_{FF}$ = 6.2 Hz, whereby the low-field signal has an additional splitting $^4J_{FH}$ = 2.4 Hz. In the second pair of signals with $\Delta\nu_{CF_3}$ = 5.2 ppm, $^4J_{FF}$ = 7.2 Hz, a SSCC $^4J_{FH}$ = 0.5 Hz is observed for the low-field signal. In accordance with the above criteria, the first pair of quartets was assigned to cis-VIII, and the second to trans-VIII (Table 1, Fig. 1).

In the ^{19}F NMR spectra of aziridinoaziridines IX, X, two broadened signals are also observed at 20°C. In these compounds, the nitrogen atom of the nonfluorinated ring is asymmetric, and therefore under the conditions of restrained inversion, in the low-temperature spectra, signals are observed of the four diastereomers as compared with two in the case of aziridine VIII.

According to the spectrum of aziridinoaziridine IX, the isomer with $\Delta\nu_{CF_3}$ = 5.12 ppm, larger $^4J_{FF}$ = 7.2 and $^4J_{FH}$ = 1.5 Hz predominates at −40°C. For the corresponding invertomer $\Delta\nu_{CF_3}$ = 8.84 ppm $^4J_{FF}$ = 6.4 and $^4J_{FH}$ = 2.4 Hz. Hence it follows that the trans-isomer predominates.

In 1,2-disubstituted aziridines, the N-substituent has preferentially a trans-orientation with respect to the substituent [19], and therefore, it is logical to assume that in the predominating isomer IX a trans-configuration of the nonfluorinated aziridine ring is

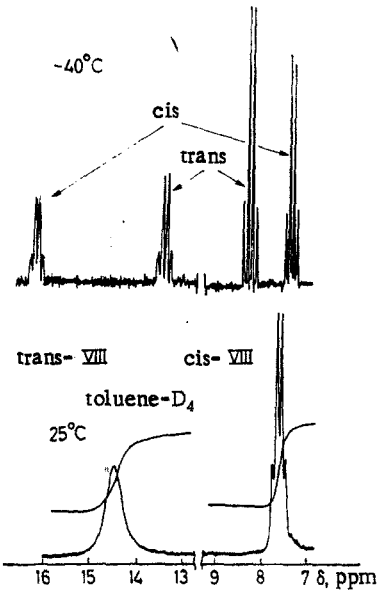
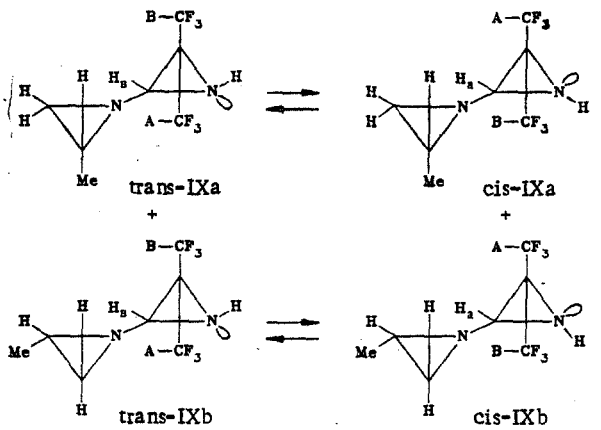


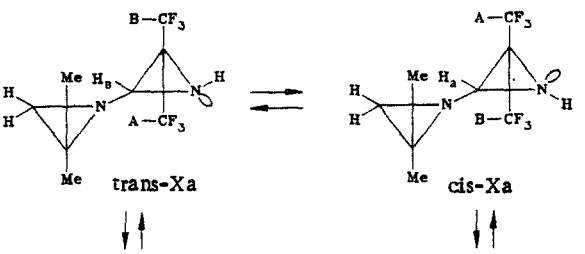
Fig. 1. ^{19}F NMR spectrum of aziridinoaziridine VIII.

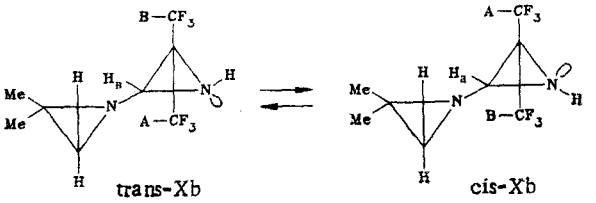
realized. From this and from the relationship of $\Delta\nu_{CF_3}$ and SSCC, and also on the basis of the supposition of the maximal steric distance between the CF_3 and CH_3 groups in the moleeular Dreiding models, a trans-IXa structure was accepted for the predominating isomer of aziridinoaziridine IX, and a cis-IXa for its invertomer. Then, the second pair of isomers can be represented by structures trans-IXb and cis-IXb (see Table 1):



The cis- and trans-isomers of aziridinoaziridine X and diazidinoaziridines XI and XII were assigned on the basis of the relationship of $\Delta\nu$ of the CF_3 groups and SSCC $^4J_{FF}$ and $^4J_{FH}$.

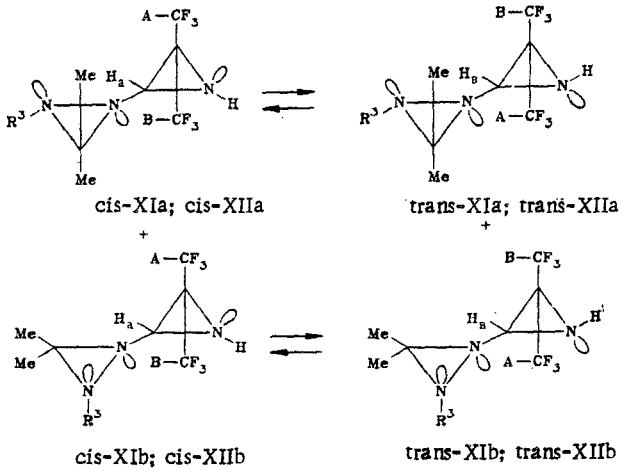
The ^{19}F NMR spectra of compound X show that at -40°C the trans-orientation of the fluorine-containing ring is realized in the preferred invertomer (as in the case of compound IX). Taking into account the assumptions stipulated in the selection of the structure of aziridine IX, the structure trans-X-a was accepted for the predominating invertomer of X, and cis-Xa for the minor invertomer; the second pair of invertomers is trans-Xb and cis-Xb, respectively.





trans-Xb cis-Xb

On cooling, signals of the invertomers of the two diastereomers are observed in the spectra of the diastereomeric mixtures of XI and XII. For the diaziridinoaziridines XIa and XIIa, the structures of cis- and trans-XIa and XIIa and for the epimeric pairs, cis- and trans-XIb and XIIb were accepted, on the basis of the trans-orientation of the substituents in the diaziridine part of the molecule [17] and the assumption of a maximum distance between the CF_3 and CH_3 groups and the unshared electron pairs of all the nitrogen atoms in the most favorable structure during the examination of the Dreiding models (Table 1):



cis-XIa; cis-XIIa + trans-XIa; trans-XIIa +

cis-XIb; cis-XIIb trans-XIb; trans-XIIb

Table 1 shows that in the case of diastereomer XIa at −40°C, the ratio of the cis-XIa/trans-XIa = 1, while for diastereomer XIb, the cis-isomer predominates. This is explainable as due to the stabilization resulting from the formation of a hydrogen bond between the NH of the aziridine ring and the unshared electron pair of the unsubstituted nitrogen atom of the diaziridine ring. The favorable steric possibilities for this interaction are very evident during the examination of the Dreiding models.

Thus, in the 2-aziridino- and 2-diaziridino-3,3-bis(trifluoromethyl)aziridines, all the theoretically possible isomers have been recorded by the dynamic NMR method.

For compounds VIII, X-XII, the energetic parameters were found for the inversion of 2,2-bis(trifluoromethyl)aziridine nitrogen atom (Table 2) from the merging of the CF_3 group signals, which agree with those for the previously obtained 3-substituted NH-2,2-bis(trifluoromethyl)aziridines.

EXPERIMENTAL

The NMR spectra were run on JOEL JNM-C-60 HL (^1H, 60 MHz, relative to MHDS; ^{19}F, 56.45 MHz, relative to CF_3COOH as external standard), Bruker WM-400 (internal standard TMS) spec-

TABLE 2. Energetic Parameters of the Inversion of the N Atom in Compounds VIII, X-XII in Freon-21 (^{19}F NMR 56.45 MHz)

Compound	$\Delta\nu_{CF_3}$, Hz	T_c, °C	$\Delta G^{\neq}_{25}$, kcal/mole
VIII	48	−13	12,8
X	48	−6	13,1
XI	60	8	13,6
XII	54	5	13,5

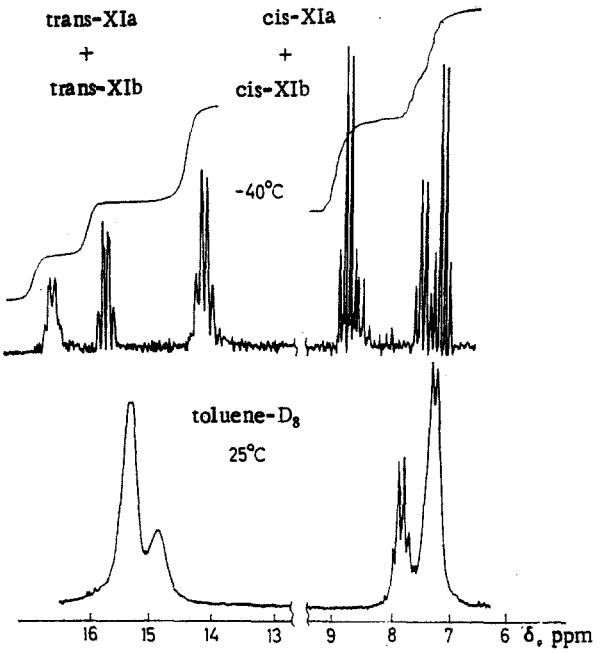


Fig. 2. ^{19}F NMR spectrum of a mixture of diastereomers XIa and XIb obtained by heating the separate diastereomer XIa at various temperatures.

trometers. The melting points were determined on a Boetius RNMK-05 stage.

Chromatographically pure aziridines Ia and Ib [2], dry solvents and dry ET_3N were used for the synthesis.

N-α-Hydrohexafluoroisopropyldimethylformamidine (III).* A mixture of 4.0 g (12 mmoles) of aziridine Ia and 22.5 g (0.5 mole) of dry Me_2NH is held for 24 h in a sealed ampule at 20°C. The excess dimethylamine is removed, and the solid residue is treated by a 1:1 mixture of ether and hexane. The extract was evaporated, and the residue is sublimed at 50°C (1 mm Hg). Yield 1.61 g (62%) of amidine III, mp 52-53°C. NMR spectra (60 MHz, CCl_4): ^1H: 2.9 (Me_2N); 3.7 (CH, $^3J_{HCCF}$ = 6.8 Hz); 7.2 ppm (CH-, $^5J_{HCNCCF}$ = 0.7 Hz); ^{19}F; 6.4 ppm (CF_3). Found: C 32.5; H 3.8; N 12.6%. $C_6H_8F_6N_2$. Calculated: C 32.4; H 3.6; N 12.6%.

Methyl Ester of N-Hexafluoroisopropylforaminoproline (IV). A mixture of 2.1 g (16 mmoles) of the methyl ester of l-proline and 1.5 ml (10 mmoles) of Et_3N in 40 ml of ether is added dropwise, at 0°C with stirring, to a solution of 3.5 g (10 mmoles) of aziridine in 30 ml of ether. The mixture is stirred for 1 h and held for 12 h at 20°C. After filtration the mixture is evaporated, and the residue distilled. Yield, 1.9 g (63%) of ester IV, bp 112-112.5°C (3.5 mm Hg), n_D^{20} 1.4123. IR spectrum (molecular layer): 1540 (C=N), 1745 cm^{-1} (OCO). NMR spectra (60 MHz, CCl_4): ^1H: 3.65 (MeO); 3.92 (CH, $^3J_{HCCF}$ = 6.8 Hz); 7.7 ppm (CH=); ^{19}F: 6.3 ppm (CF_3). Found: C 39.2; H 4.1; N 9.2%. $C_{10}H_{12}F_6N_2O_2$. Calculated: C 39.2; H 3.9; N 9.1%.

General Procedure for the Synthesis of Compounds V-XII. A mixture of 10 mmoles of the corresponding amine and 10 mmoles of Et_3N in 30 ml of ether is added at 20°C, with stirring, to 10 mmoles of aziridine Ib in 30 ml of ether. After 24 h, the precipitate is filtered, the solvent is distilled on a water bath, the liquid residue is distilled, and the solid residue is recrystallized from hexane.

N-α-Hydrohexafluoroisopropyl-N^1-methyl-N^1-methoxyformamidine (V). Yield 34%, bp 39.5-40°C (9 mm Hg), n_D^{18} 1.3672. NMR spectra ($CDCl_3$) ^1H: 3.14 (MeN); 3.07 (MeO); 3.94 (CH, $^3J_{HCCF}$ = 6.7 Hz); 7.73 ppm (CH=); ^{19}F: 4.55 ppm (CF_3, $^3J_{HCCF}$ = 6.7 Hz). Found: C 30.4; H 3.2; N 11.7%. $C_6H_8F_6N_2O$. Calculated: C 30.3; H 3.4; N 11.8%.

N-α-Hydrohexafluoroisopropyl-N^1-tert-butylformamidine (VI). Yield 68%, bp 63-64°C (5 mm Hg), n_D^{15} 1.3674. NMR spectra ($CDCl_3$—CCl_4, 1:1) ^1H: 1.33 (Me_3C); 3.81 ($CHCF_3$, $^3J_{HCCF}$ = 7.5 Hz); 5.10 (NH); 7.41 ppm (CH=); ^{19}F: 4.50 ppm (CF_3, $^3J_{HCCF}$ = 7.5 Hz). Found: C 38.6; H 4.4; N 11.4%. $C_8H_{12}F_6N_2$. Calculated: C 38.4; H 4.8; N 11.2%.

N-α-Hydrohexafluoroisopropyl-N^1-methoxyformamidine (VII). Yield 30%, bp 43.5°C (13 mm Hg), n_D^{22} 1.3538. NMR spectra (CCl_4) ^1H: 3.71 (MeO); 4.18 ($CHCF_3$, $^3J_{HCCF}$ = 6.75, Hz);

*Compounds III, IV were described in [20] without specifying the methods of their synthesis.

$^3J_{HNCH}$ = 11.2 Hz); 5.48 (NH, $^3J_{HNCH}$ = 10.5, $^3J_{HNCH}$ = 11.2 Hz); 6.43 ppm (CH, $^3J_{HNCH}$ = 10.5 Hz); (CD_3OD) ^1H: 3.68 (MeO); 4.98 ($CHCF_3$, $^3J_{HCCF}$ = 7.00, Hz); 6.7 ppm (CH=) ^{19}F: 5.05 ppm (CF_3), $^3J_{HCCF}$ = 7.0 Hz). Found: C 27.0; H 3.0; N 12.7%. $C_5H_6F_6N_2O$. Calculated. C 26.8; H 2.7; N 12.5%.

2-Aziridino-3,3-bis(trifluoromethyl)aziridine (VIII). Yield 76%, bp 39°C (7 mm Hg), mp 32-33.5°C. sublimes at 20°C (1 mm Hg). In the IR spectrum, the C-N band is absent. Found: C 32.7; H 3.0; N 13.0%. $C_6H_6F_6N_2$. Calculated: C 32.7; H 2.7; N 12.7%.

1-Deutero-2-aziridino-3,3-bis(trifluoromethyl)aziridine (VIIIa) is obtained in the same way as VIII from 1-deuteroaziridine. The last compound is obtained as follows: a 3-ml portion of aziridine is stirred for 10 h with 5 ml of D_2O, aziridine is distilled with steam to bp 92°C, and dried, and small pieces of metallic sodium are cautiously added. The thus-deuterated aziridine is mixed with 7 ml of D_2O and treated as in the preceding experiment to yield 1 ml of 1-deuteroaziridine. In the PMR spectrum in CCl_4, only a singlet of ring protons is observed. Aziridine VIIIa, yield50%, bp 43-44°C (10 mm Hg). In the mass spectrum, during a preliminary admission and evacuation of D_2O, a peak with m/z 222 (M^+) is observed. ^1H NMR spectrum (CCl_4) at 25°C: 2.91 (a-H, s); 1.63 ppm (CH_2); at 100°C: 2.98 (a-H, s), 1.69 ppm (CH_2, J_{HH} = 7.0 Hz).

2-(2-Methylaziridino)-3,3-bis(trifluoromethyl)aziridine (IX). Yield 68%, bp 47°C (11.5 mm Hg). Found: C 36.3; H 3.7; N 11.9%. $C_6H_8F_6N_2$. Calculated: C 35.9; H 3.4; N 12.0%.

2-(2,2-Dimethylaziridino)-3,3-bis(trifluoromethyl)aziridine (X). Yield 74%, bp 53-54°C (10 mm Hg), after sublimination at 20°C (1 mm Hg) mp 54.56°C. Found: C 38.6; H 4.2; N 11.1%. $C_8H_{10}F_6N_2$. Calculated: C 38.7; H 4.0; N 11.3%.

2-(3,3-Dimethyldiaziridino)-3,3-bis(trifluoromethyl)aziridine (XI). Yield 56%, mp 112-114 (with sublimation) sublimes at 20°C (1 mm Hg). PMR spectrum ^1H (80 MHz, toluene-D_8): 1.02 and 1.15 (ME_2C); 216 (NH, br.), 3.38 (CH, m $^3J_{HCNH}$ = 7.9, $^3J_{HCCF}$ = 2.15 Hz): XIa ($CDCl_3$): 1.40 and 1.44 (Me_2C); 2.18 (NH), 3.42 (CH); XIb: 1.41 and 1.48 (Me_2C); 2.18 (NH); 3.42 ppm (CH). Found: C 33.6; H 3.5; N 16.8%. $C_7H_9F_6N_3$. Calculated: C 33.6; H 3.6; N 16.9%.

2-(2,3,3-Trimethyldiaziridino)-3,3-bis(trifluoromethyl)aziridine (XII). Yield 80%, bp 53-54°C (9 mm Hg). PMR spectrum ^1H (400 MHz, C_6D_6): XIIa: 0.72 and 0.83 (Me_2C); 1.98 (NH); 1.99 (MeN); 3.11 (CH, q $J_{HN,CH}$ - 8.1, J_{CH,CF_3} = 2.2 Hz); XIIb: 0.72 and 0.83 (Me_2C); 1.98 (NH); 2.07 (MeN); 3.17 ppm (CH, q $J_{NH,CH}$ = 8.5, J_{CH,CF_3} = 2.0 Hz), Found: C 36.5; H 4.3; N 16.3%. $C_6H_{11}F_6N_3$. Calculated: C 36.5; H 4.2; N 16.0%.

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THERMAL CONDENSATION OF PHTHALIMIDE WITH MALONIC ACID

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When phthalimide is reacted with malonic acid in the presence of zinc acetate, 1-hydroxy-1-methyl-1H-3-(1-oxoisoindolin-3-ylidenemethyl)isoindole, the zinc complex of 1-hydroxy-8,13:22,27-diimino-1,6:15,20-dinitrilotetrabenzo[b,d,l,q]eicosin, and zinc tetrabenzoporphin are formed depending on the temperature. The compounds have been characterized by their electronic absorption spectra, IR and mass spectra, and also by their x-ray photoelectron spectra. A possible scheme for the synthesis of zinc tetrabenzoporphin has been proposed.

In contrast to the anhydride condensation of phthalic anhydride [1, 2] the condensation of phthalimide with various active methylene components such as malonic acid or sodium acetate has not been fully studied. Meanwhile, this reaction is of interest from the point of view of research into convenient methods for synthesizing tetrabenzoporphins (TBP), which are being used in various branches of industry to an increasing extent.

There are reports in the literature about attempts to achieve this pathway for the synthesis of TBP. Thus, Helberger and coworkers [3] by reacting phthalimide with zinc acetate at 300°C obtained a 5:1 mixture of zinc TBP and zinc tetrabenzomonoazaporphin in negligible yield, while with ferrous acetate, ferrous TBP was formed with a yield of 0.2%. Reagents such as malonic acid or sodium acetate used by us in this reaction made it possible to reach a yield of 12% for TBP, and in the case of its tert-butyl-substituted analog, the yield reached 25% [4, 5]. As phthalimide sublimes when the temperature is increased, which has an effect on the yield of the final compound, it is more convenient to use potassium phthalimide. The optimum reaction conditions are: molar ratio of potassium phthalimide to malonic acid to zinc acetate 1:1.4:0.75; reaction temperature 340-360°C; reaction time 30 min to 1 h. The method developed has also successfully been used to obtain previously inaccessible polycyclic and unfamiliar meso-substituted analogs of TBP. Thus, starting from the imides of naphthalene-1,2- and naphthalene-2,3-dicarboxylic acids and also 1-phenylnaphthalene-2,3-dicarboxylic acids, tetra-1,2- and tetra-2,3-naphthoporphins [6] were obtained. When instead of malonic acid arylacetic acids are used in the reaction with phthalimide, meso-tetraaryl TBP products are formed [7, 8].

The subject of the present work is a study of the possible reaction scheme of phthalimide with malonic acid in the presence of zinc acetate and also the isolation and identification of some intermediate products. As it was impossible to determine the intermediates under the reaction conditions, it seemed to us desirable to investigate its stepwise pathway at lower temperatures, which in our opinion was also suitable for representing the process taking place under optimum conditions. Thus, when the reaction was carried out at 260°C, apart from unreacted phthalimide and a small quantity of 3-methylenephthalimidine (I) 1-hydroxy-1-methyl-1H-3-(1-oxoisoindolin-3-ylidenemethyl)isoindole (II) was isolated as the main product, and its structure was confirmed from the data of elemental analysis and its IR and mass spectra. In the mass spectrum of compound II* a low-intensity peak from the

*Mass spectra of compounds II and III were recorded by V. K. Shevtsov (P. Lumumba Peoples' University).

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