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ASYMMETRIC NONBRIDGE NITROGEN

21.* 1-ALKOXY-2,2-BIS(TRIFLUOROMETHYL)AZIRIDINES

R. G. Kostyanovskii, A. V. Prosyanik,
A. I. Mishchenko, N. L. Zaichenko,
I. I. Chervin, and V. I. Markov

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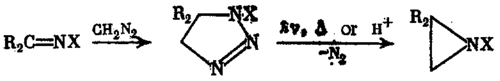
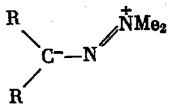
Certain general rules and limitations exist in the syntheses of aziridines by the reactions of N-substituted imines of hexafluoroacetone and mesoxalic ester with diazoalkanes [Scheme (1)]. For example, the cycloaddition of CH_2N_2 is facilitated, while the stability of the intermediate triazoline increases, with increase in the electronegativity of X [2, 3].



(1)

R = CF_3, CO_2R'

The high +M effect of X ($X = Me_2N$) prevents reaction with CH_2N_2 in the case of hexafluoroacetone dimethylhydrazone. This is explained by hindrance to nucleophilic attack by the CH_2N_2 due to the contribution of form A, which is fixed due to a decrease in the barrier of rotation around the C = N bond when compared with hexafluoroacetone O-tosyloxime, with which CH_2N_2 easily reacts [2].



(A)

In the dimethylhydrazone [4], when compared with the O-tosyloxime of mesoxalic ester [5], the barrier of rotation around the C = N bond is also considerably lower. And, as it proved, like the first it remains unchanged even when treated with a large excess of ethereal CH_2N_2 for a month at ~20°C. The easy addition of CH_2N_2 is known for the second compound [3]. With decrease in the +M effect of X (X = RO) the addition of CH_2N_2 is hindered and is not observed when the O-alkyloximes of hexafluoroacetone [2] and mesoxalic ester [3] are treated for a short time. However, the long treatment of the latter (2 weeks) with excess CH_2N_2 leads to reaction by Scheme (1) [3].

In the present paper it was shown that, under analogous conditions, the hexafluoroacetone O-alkyloximes (Ia)-(Ie) (Tables 1 and 2) also react normally with CH_2N_2. (See Scheme 2, next page.)

Here stable triazolines (IIa)-(IIe) (Tables 1 and 3) were obtained, the photolysis and thermolysis of which give in good yields the 1-alkoxy-2,2-bis(trifluoromethyl)aziridines (IIIa)-(IIIe) as nearly equivalent mixtures of the diastereomers (based on the PMR spectra before distillation) (Tables 1 and 4). In contrast to the mesoxalic ester O-alkyloximes [3], the formation of the products of inserting CH_2 at the $C-CF_3$ bond was not

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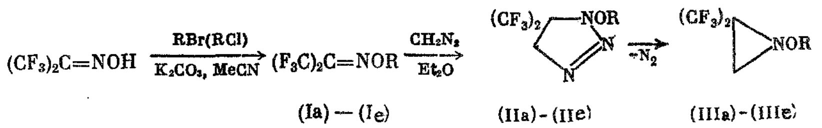
[*] See [1] for Communication 20.

Institute of Chemical Physics, Academy of Sciences of the USSR, Moscow. Chemical-Technological Institute, Dnepropetrovsk. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 4, pp. 882-888, April, 1980. Original article submitted March 1, 1979.



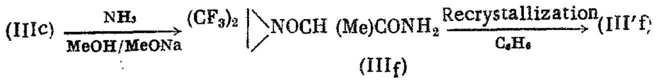
(Ia) — (Ie) (IIa) - (IIe) (IIIa) - (IIIe) (2)

R=$PhCH_2$ (a), EtO_2CCH_2 (b), MeO_2CCHMe (c), *i*-PrO_2CCHMe (d), *t*-BuO_2CCHMe (e)

observed in all of the investigated cases. The same as hexafluoroacetone O-methyloxime [2], when (Ia) is treated for a short time with diazomethane it is recovered unchanged almost quantitatively. Amide (If), obtained by the ammonolysis of (Ic) (Scheme 3), does not react with CH_2N_2, since it is practically insoluble in ether:

$$\text{(Ic)} \xrightarrow[\text{MeOH/MeONa}]{\text{HN}_3\quad f} (CF_3)_2C{=}NOCH(Me)CONH_2\ \text{(If)} \tag{3}$$

The corresponding aziridine (IIIf) was obtained by the ammonolysis of (IIIc):



(4)

A single recrystallization of (IIIf) from benzene gives the diastereomerically pure racemate (III'f).

The structure of all of the synthesized compounds was confirmed by elemental analysis, and by the IR and NMR spectra. It should be mentioned that in the O ethers of hexafluoroacetone oxime, the same as in the O ethers of isonitrosomalonic acid [7] and other oximes [8], the alkoxy group, when compared with the unshared electron pair of N, has a slight shielding effect [$\delta_{B\text{-}CF_3} - \delta_{A\text{-}CF_3} \simeq 2$ ppm (see Table 2)], whereas in the corresponding alkoxyaziridines it strongly deshields the cis substituent of the ring ($\delta_{B\text{-}CF_3} - \delta_{A\text{-}CF_3} \simeq 8$ ppm, $\delta_{H_B} - \delta_{H_A} \simeq 0.4$ ppm (see Table 4), $\delta_{H_B} - \delta_{H_A} \simeq 0.35$ ppm [3, 6]). The degree of hybridization of the N atom is probably the determining value for the shielding effect.

In examining the ASIS effects [8] of the C substituents it was unexpectedly found that the condition of predominant solvation by benzene from the side of the lowest electron density, the deshielding substituent on N, is fulfilled only for the O ethers of unfluorinated oximes [3, 7, 8]. High values of the ASIS effect are observed from the side of the shielding substituent (respectively alkoxy group or unshared electron pair) in the case of the O ethers of hexafluoroacetone oxime (see Table 2) and alkoxyaziridines (see Table 4, [3, 6]).

The activation parameters of N inversion were determined for the diastereomeric alkoxyaziridines (IIIc)-(IIIf) (Table 5). In the case of (IIIc) a low $\Delta\nu$ of the signals of the MeO group of the diastereomers made it possible to find the inversion barrier from the merging of the signals. In the other cases the rate of transition to the equilibrium amount of the diastereomers was studied. The configurational stability of the 1-alkoxy-2,2-

TABLE 1. Characteristics of Synthesized Compounds

Compound	Yield, %	bp, °C (p, mm Hg)	n_D^{20}	ν, cm⁻¹ (mol. layer)		Found (calculated), %		
				C=N	C=O	C	H	N
(Ia)	88,0	77–78(25)	1,4195	1622		44,31(44,29)	2,87(2,60)	5,35(5,17)
(Ib)	72,0	72–74(44)	1,3419	1628	1750	30,98(31,48)	2,65(2,64)[a]	5,21(5,24)
(Ic)	53,0	63–65(38)	1,3485	1629	1746	31,31(31,48)	2,64(2,64)	5,42(5,24)
(Id)	62,5	73(33)	1,3537	1625	1732	36,49(36,62)	3,70(3,76)	4,41(4,74)
(Ie)	36,7	69–70(26)	1,3540	1629	1735	38,96(38,84)	4,15(4,23)	4,65(4,53)
(If)	92,5	mp 132–133	–	1616	1657, 1680	22,66(22,58)	2,24(2,39)	11,30(11,11)
(IIb)	60,0	–	1,3933	1567[b]	1748	31,12(31,08)	2,86(2,93)	13,57(13,59)
(IIc)	64,4	–	1,3881	1561[b]	1742	31,08(31,08)	2,98(2,93)	13,55(13,59)
(IId)	73,3	–	1,3888	1565[b]	1745	35,81(35,62)	3,79(3,88)	12,64(12,46)
(IIe)	75,0	–	1,3910	1564[b]	1742	37,52(37,61)	4,51(4,34)	12,11(11,96)
(IIIa)	71,3	95–96(30)	1,4293	3096[c]	–	46,19(46,33)	3,05(3,18)	5,01(4,91)
(IIIb)	62,5	87–88(20)	1,3653	3115[c]	1746	34,02(34,18)	3,19(3,23)	5,01(4,98)
(IIIc)	70,9	73(30)	1,3671	3116[c]	1750	34,34(34,18)	3,34(3,23)	4,99(4,98)
(IIId)	83,3	96–98(28)	1,3700	3119[c]	1745	38,82(38,84)	4,30(4,23)	4,60(4,53)
(IIIe)	50,0	90(20)	1,3760	3121[c]	1742	41,03(40,87)	4,57(4,68)	4,41(4,33)
(IIIf)	86,7	mp 68–70	–	3120[c]	1665	31,72(31,59)	3,46(3,61)	10,63(10,52)
(IIIf′)	43,3	mp 101	–	3120[c]	1665	–	–	–

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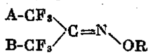
a) F, %: 42.65(42.68). b) ν N=N. c) ν CH-ring.

TABLE 2. NMR Spectra of Hexafluoroacetone O-Alkyloximes [a]



$$(\text{A-CF}_3)(\text{B-CF}_3)\text{C=N-OR}$$

Compound	PMR spectrum				^{19}F NMR spectrum		
	CO_2CHMe	CO_2CH	NOCHMe	NOCH	$B-CF_3$	$A-CF_3$	J_{AB}
(Ia)	–	–	7,30b	5,30 (0,29)	−11,64 (−0,54)	−13,01 (−0,38)	7,25 (7,25)
(Ib)	1,28 (0,54)	4,18 (0,48)	–	4,76 (0,68)	−11,27 (−0,33)	−13,9 (−0,33)	6,53 (6,53)
(Ic)	–	3,74 (0,58)	1,55 (0,45)	4,91 (0,41)	−11,55 (−0,45)	−13,42 (−0,51)	6,0 (6,0)
(Id)	1,19; 1,20 (0,35); (0,36)	4,99 (0,25)	1,53 (0,48)	4,81 (0,40)	−11,61 (−0,49)	−13,45 (−0,49)	6,12 (6,12)
(Ie)	1,39 (0,26)	–	1,50 (0,42)	4,73 (0,37)	−11,56 (−0,60)	−13,39 (−0,54)	6,50 (6,50)
(If)	–	–	1,27		−2,0	−0,70	9,18

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a) 5 mole % solutions in CCl_4, and CD_3OD for (If); δ, ppm from HMDS (^1H) and from CF_3CO_2H (^{19}F); J, Hz; $J_{MeCH_2} = J_{MeCH} = 7.0$ Hz; the values of the ASIS effect in ppm [6] are given in parentheses.
b) Ph.

TABLE 3. NMR Spectra of 1-Alkoxy-5,5-bis(trifluoromethyl)-Δ^2-1,2,3-triazolines [a]

Compound	PMR spectrum					^{19}F NMR spectrum
	CO_2CHMe	CO_2CH	NOCHMe	NOCH	$CH_2N=$	CF_3
(IIa)	–	–	7,38 b	5,18 (0,15)	4,68 (0,60)	−8,25 (−0,78)
(IIb)	1,24 (0,43)	4,16 (0,31)	–	4,69 (0,33)	4,59 (0,55)	−8,25 (−0,38)
(IIc)	–	3,82 (0,44)	1,50 (0,28)	4,80 (0,05)	4,85 (0,72)	−8,18 (−0,39)
(IId)	1,21 (0,28)	4,44 (−0,44)	1,46 (0,23)	4,94 (0,38)	4,68 (0,81)	−8,20 (−0,28)
(IIe)	1,40 (0,15)	–	1,41 (0,17)	4,45 (−0,03)	4,62 (0,63)	−8,42 (−0,48)

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a, b) See Table 2.

bis(trifluoromethyl)aziridines is approximately the same as that of the diaziridines [12], and consequently is sufficient for separation into the antipodes under conventional conditions.

EXPERIMENTAL

The spectra were measured on Jeol JNM-C60-HL (60 MHz) and Tesla BS-487c (80 MHz) spectrometers, and on a UR-20 spectrophotometer.

Hexafluoroacetone O-Benzyloxime (Ia). With cooling and stirring, to a solution of 9.1 g of hexafluoroacetone oxime in 30 ml of MeCN were slowly added in sequence 6.9 g of finely ground K_2CO_3 and 6.3 g of benzyl chloride, and the mixture was stirred for 5 h and then let to stand overnigh. The precipitate was separated, washed well with MeCN, the solvent was removed, and the residue was vacuum-distilled to give 11.9 g (88%) of (Ia). Compounds (Ib)-(Ie) were obtained in a similar manner (see Table 1).

Hexafluoroacetone O-(α-Carbamoylethyl)oxime (If). A solution of 1.0 g (4 mmole) of (Ic), 0.3 g (17 mmole) of NH_3, and a catalytic amount of MeONa in 2 ml of abs. MeOH was kept for 2 weeks at 20°C. After removal of the solvent we obtained 0.93 g (92.5%) of (If) (see Table 1).

1-Benzyloxy-5,5-bis(trifluoromethyl)-Δ^2-1,2,3-triazoline (IIa). A mixture of 5.4 g of (Ia) and excess CH_2N_2 in ether solution was kept for 2 weeks at 20°. The solvent was removed in vacuo, and the residue was chromatographed on a column (silica gel L 100/160μ, $CHCl_3$), to give 3.6 g (60%) of (IIa). Compounds (IIb)-(IIe) were obtained in a similar manner (see Table 1).

TABLE 4. NMR Spectra of 1-Alkoxy-2,2-bis(trifluoromethyl)aziridines[a]

Compound	PMR spectrum							^{19}F NMR spectrum				
	$\text{CO}_2\text{CH}\underline{\text{Me}}$	CO_2CH	$\text{NOCH}\underline{\text{Me}}$	NOCH	H_A	H_B	J_{AB}	A-CF_3	B-CF_3	J_{AB}	$J_{H_A-B-CF_3}$	$J_{H_B-A-CF_3}$
(IIIa)	–	–	7,8 b	4,87	2,42	2,76	–4,0	–8,64	–16,67	7,63	3,0	1,0
				(0,31)	(0,80)	(0,67)	(–4,3)	(–0,37)	(–0,30)	(7,88)	(2,8)	(1,0)
(IIIb)	1,24	4,17 c	–	4,31	2,54	2,96	–4,4	–8,49	–16,44	7,73	2,6	0,85
	(0,32)	(0,16)		(0,36)	(0,67)	(0,49)	(–4,8)	(–0,49)	(–0,57)	(7,73)	(2,6)	(0,90)
(IIIc)	–	3,73	1,38	4,46	2,53	2,83	–4,0	–8,36	–16,13	8,25	3,0	1,0
		(0,35)	(0,24)	(0,12)	(0,62)	(0,56)	(–4,0)	(–0,55)	(–0,40)	–	–	–
		3,73	1,26	4,46	2,53	2,98	–4,5	–8,36	–16,26	7,5	3,0	1,0
		(0,40)	(0,24)	(0,12)	(0,59)	(0,48)	(–4,5)	(–0,55)	(–0,37)	–	–	–
(IIId)	1,20	4,99	1,36	4,35	2,44	2,79	–4,0	–8,40	–16,31	8,25	3,0	1,1
	(0,26; 0,23)	(0,08)	(0,19)	(0,15)	(0,62)	(0,53)	(–4,0)	(–0,38)	(–0,29)	(8,0)	(3,0)	(0,8)
	1,20; 1,22	5,02	1,24	4,35	2,49	2,95	–4,0	–8,50	–16,50	8,25	2,6	1,0
	(0,29); (0,29)	(0,11)	(0,21)	(0,06)	(0,56)	(0,45)	(–4,5)	(–0,37)	(–0,28)	(8,25)	(2,6)	(0,75)
(IIIe)	1,41	–	1,31	4,24	2,43	2,77	–4,0	–8,45	–16,45	8,0	3,0	1,0
	(0,15)		(0,19)	(0,14)	(0,70)	(0,60)	(–4,0)	(–1,06)	(–1,09)	(8,0)	(2,8)	(0,75)
	1,39	–	1,21	4,24	2,48	2,93	–4,0	–16,61	–16,61	8,0	3,0	1,0
	(0,17)		(0,21)	(0,04)	(0,62)	(0,49)	(–4,5)	(–1,09)	(–1,04)	(8,0)	(2,6)	(0,75)
(IIIf)[d]	–	–	1,22	4,28	2,69	3,15	–5,0	–	–	–	2,8	1,0
			1,24	4,17	2,73	3,15	–5,0				2,7	1,0
(IIIf')[d]	–	–	1,23	4,26	2,66	3,11	–5,0	–	–	–	2,8	1,0

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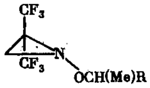
a, b) See Table 2.

c) $\Delta\nu_{AB} = 0.12(0.28)$. $J_{AB} = 17.7(17.4)$.

d) In CD_3OD, concentration < 5%.

TABLE 5. Activation Parameters of Nitrogen Inversion in Alkoxyaziridines [a]



Compound	R	Solvent	Observed group	T, °C	Amount of diastereomers		$\Delta\Delta G$, kcal/mole	$\overrightarrow{k}_{inv}\cdot 10^4$ ($\overleftarrow{k}_{inv}\cdot 10^4$), sec^{-1} at T	$\overrightarrow{\Delta G}^{\neq}_{25^\circ}$ ($\overleftarrow{\Delta G}^{\neq}_{25^\circ}$), kcal/mole	$\overrightarrow{\tau}_{1/2}$, flight at 25°
					initial	equilibrium				
(IIIC)	CO_2Me	Ph_2O	MeO	192 (T_m) $\Delta\nu = 0,8$ Hz	43/57	37/63	0,40	1,78	27,3	0,2
(IIId)	CO_2Pr-*i*	C_6H_6	MeC	100	49/51	66/34	—0,49	2,9 ±0,5 (1,5±0,3)	28,1±0,1 (28,7±0,1)	0,8
(IIIe)	CO_2Bu-*t*	C_6H_6	Me_3C	100	50/50	66/34	—0,49	2,8 ±0,4 (1,45±0,2)	28,2±0,1 (28,7±0,1)	0,9
(IIIf)	$CONH_2$	CD_3OD	MeC	90	100/0	68/32	—0,56	0,30±0,04 (0.60±0,08)	29,0±0,1 (28,5±0,1)	3,5

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a) Based on the temperature of merging for (IIIc) and for the other compounds – from the epimerization rate when 5 mole % solutions are heated (accuracy ± 0.1°) in evacuated sealed ampuls by measuring the integral intensity of the signals of the indicated groups. The epimerization rate constants (k_{ep}) were calculated by the method of least squares [9]. The inversion rate constants (k_{inv}) were determined from the k_{ep} of the reverse equilibrium process. The change in the free activation energy of the inversion ($\Delta G^{\neq}_{T}$) was found from the Eyring equation [10], $\Delta G^{\neq}_{25}$ (from the equation $\Delta G^{\neq}_{25} = \Delta G^{\neq}_{T} + R\,(T-298)$ [11], while the half-reaction time ($\tau_{1/2}$) was found from the equation for first-order reactions.

1-Benzyloxy-2,2-bis(trifluoromethyl)aziridine (IIIa). A solution of 3.1 g of (IIa) in 50 ml of CCl_4 was photolyzed for 6 h (PRK lamp, 250 W). The residue from removal of the solvent was vacuum-distilled to give 2.0 g (71.3%) of (IIIa). Compounds (IIIb)-(IIIe) were obtained in a similar manner (see Table 1). When triazolines (IIa)-(IIe) are kept in the dark at ~20° for a month they are quantitatively converted to the corresponding alkoxyaziridines (IIIa)-(IIIe).

O-(α-Carbamoylethyl)oxy-2,2-bis(trifluoromethyl)aziridine (IIIf). A solution of 0.8 g (3 mmoles) of (IIIc), 0.3 g (17 mmoles) of NH_3, and a catalytic amount of MeONa in 2 ml of abs. MeOH was kept for 2 weeks at 20°. After removal of the solvent we obtained 0.7 g (36.7%) of (IIIf) (see Table 1).

Diastereomerically Pure Racemate of O-(α-Carbamoylethyl)oxy-2,2-bis(trifluoromethyl)aziridine (IIIf'). A solution of 0.6 g of (IIIf) in 30 ml of C_6H_6 was evaporated at ~20° for 1 day to a volume of 15 ml. The obtained crystals were filtered to give 0.26 g (43.3%) of (IIIf') (see Table 1).

CONCLUSIONS

1. When treated with excess diazomethane for a long time the O-alkyloximes of hexafluoroacetone form stable triazolines, which on photolysis or thermolysis give the corresponding 1-alkoxy-2,2-bis(trifluoromethyl)-aziridines.

2. The configurational stability of the 1-alkoxy-2,2-bis(trifluoromethyl)aziridines is sufficient to permit their separation into the antipodes. The derivatives with an asymmetric center in the substituent on oxygen were separated into the diasteromers by recrystallization.

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REACTION OF TRICHLOROACETYL ISOCYANATE WITH SOME β-DIKETONES

B. A. Arbuzov, N. N. Zobova,
and S. K. Yakupova

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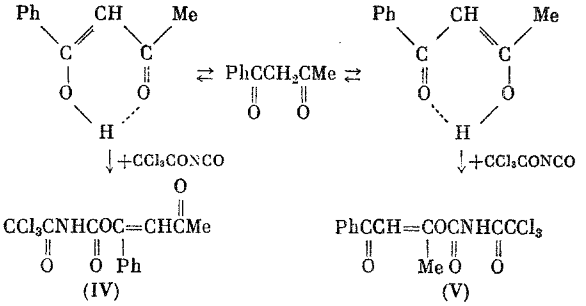
The reaction of trichloroacetyl isocyanate (I) with benzoylacetone (II) and 2-acetyl-1-cyclopentanone (III) was studied. Taking into consideration the keto–enol tautomerism of β-diketones and the results of our previously studied reactions [1], it may be expected that the reaction of (I) with (II) will proceed by the following scheme:



Actually a mixture of isomers (IV) and (V) was isolated from the reaction mixture, as was evidenced by the data of the IR and PMR spectra and thin-layer chromatography (TLC). The IR spectrum of the (IV)–(V) mixture has the bands (ν, cm^{-1}): 3260, with a shoulder at 3175 (NH), 1630 (CH=CCO), 1690 (CCONH), 1760 (OCONH), and 853, 850 (CCl). In the PMR spectrum of the mixture of isomers is observed from the protons of the Me groups a singlet with δ 2.20 ppm for (IV), and a doublet with 2.05 and 2.12 ppm, $^4J = 2.5$ Hz for (V), two multiplets with δ 7.54 and 7.96 ppm from the protons of the Ph groups, from the protons of the =CH groups a singlet with δ 6.21 ppm for (IV) and a quartet with δ 5.90 ppm, $^4J = 2.5$ Hz for (V), and a singlet with δ 9.11 ppm from the protons of the NH groups of one isomer, while the signal of the other isomer is apparently masked by the signals of the protons of the Ph groups. The spin–spin coupling of the protons of the MeC=CH fragment in (V) is in agreement with the data given in [2, 3]. A comparison of the integral intensities of the signals of the protons of the Me groups reveals that the ratio of the (V):(IV) is 1:3.5, which is in agreement with the data on the somewhat greater thermodynamic stability of the tautomer with an enolized PhC=O group in the case of benzoylacetone [4]. We were able to obtain the pure (IV) by fractional recrystallization. Infrared spectrum (ν, cm^{-1}): 3385, 3210 (NH), 1760 (OCONH), 1705 (CCONH), 1620 (CH=CC=O). PMR spectrum (δ, ppm): 2.13 s (Me), 5.46 s (=CH), 7.16 m (Ph), 8.42 br. s (NH).

V. I. Ul'yanov-Lenin Kazan State University. Translated from Izvesitya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 4, pp. 888-892, April, 1980. Original article submitted January 24, 1979.

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