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HALOGEN ABSTRACTION BY TRIPHENYLPHOSPHINE OF PERFLUORODIAZA-DICHLOROALKANES CONTAINING N-CCl_2-N GROUPS. X-RAY STRUCTURE ANALYSIS OF PERFLUORO-2,3,5,6-TETRAKIS(DIMETHYLAMINO)-PYRAZINE

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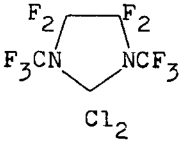
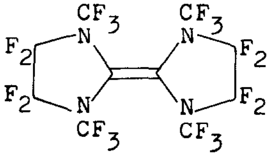
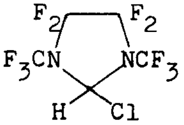
SUMMARY

The reaction of perfluoro-2,2-dichloroimidazolidine (I) with triphenylphosphine (III) yields the bicyclic olefin (IV) while (V) is obtained in the presence of H_2O. From the reaction of $(CF_3)_2NCCl_2NCClN(CF_3)_2$ with (III), only the cyclic dimer (VI) was isolated in a yield of 6 %, predominantly polymeric material being formed. The reaction pathways agree with a carbene as intermediate. (IV), (V) and (VI) were characterized by analyses, NMR, vibrational and mass spectra. A single crystal X-ray examination of (VI), space group $P2_1/n$, a 9.367(2), b 10.909(3), c 10.929(3) Å, β = 103.27(2)°, Z = 2, R = 0.109, revealed a planar, regular pyrazine ring but nonplanar N atoms in the substituent, steric interactions being relieved by rotating the amino groups out of the pyrazine plane.


(I)


(IV)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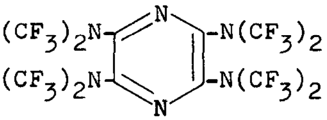
(VI)

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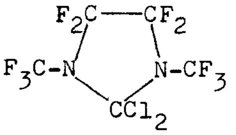
INTRODUCTION

Recently the reaction of perhalomethanes with tertiary phosphines [1] and thiolates [2] has been described, and evidence for the formation of dihalocarbenes as intermediates has been obtained. In preceding contributions we have reported that CF_2 entities linked to two nitrogen atoms are selectively chlorinated by BCl_3 to form the corresponding $N\text{-}CCl_2\text{-}N$ compounds under conditions at which all other CF bonds of the respective molecules are not attacked [3, 4]. In the following we report on investigations directed towards the formation and reactions of perfluoroalkyl-substituted diazacarbenes according to eqn. (1a) and (1b).

$$(R_f)_2N\text{-}CCl_2\text{-}N(R_f)_2 \xrightarrow[-[R_3PCl]^+Cl^-]{R_3P} (R_f)_2N\text{-}\ddot{C}\text{-}N(R_f)_2 \tag{1a}$$

$$(R_f)_2N\text{-}CCl_2\text{-}N< \xrightarrow[-[R_3PCl]^+Cl^-]{R_3P} (R_f)_2N\text{-}\ddot{C}\text{-}N< \tag{1b}$$

Reactions (1a) and (1b) were explored making use of (I) [3] and (II) [4] as starting materials, respectively.



(I)

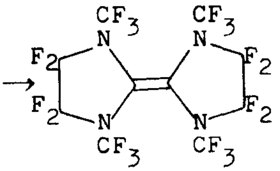
$$(CF_3)_2N\text{-}CCl_2\text{-}N{=}CCl\text{-}N(CF_3)_2 \qquad \text{(II)}$$

In this communication we will report on the results of this investigation.

RESULTS

Reaction of (I) with an excess of triphenylphosphine (III) takes place upon heating as soon as (III) melts (79 °C). The hitherto unknown bicyclic olefin (IV) is formed according to (2) in nearly quantitative yield.

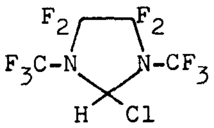
2 (I) + 2 (III) $\longrightarrow$



(IV) + $2[Ph_3PCl]Cl$ (2)

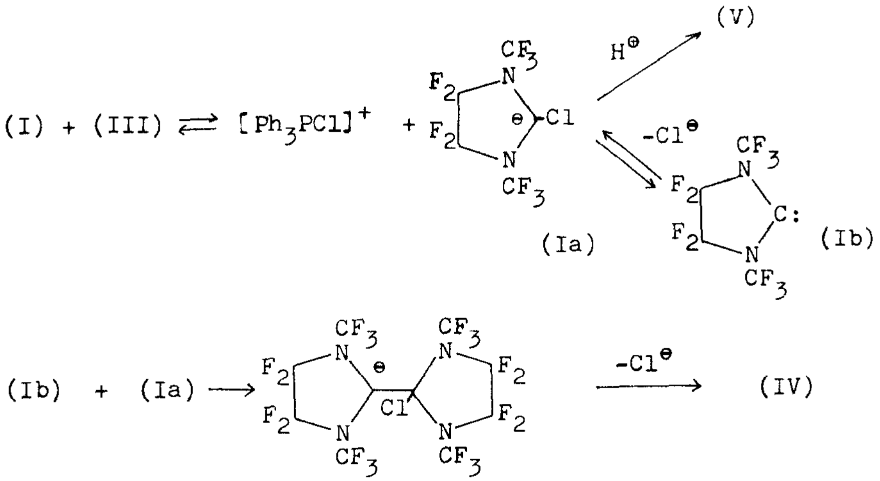
In order to learn more concerning the mechanism of this dimerization reaction, we have carried out the same reaction in the presence of stoichiometric quantities of water. Instead of (IV), the imidazolidine derivative (V) was obtained according to (3) with a yield of ~80 %.

2 (I) + 2 (III) + H_2O $\longrightarrow$

2  (V) + $[Ph_3PCl]Cl$ + Ph_3PO (3)

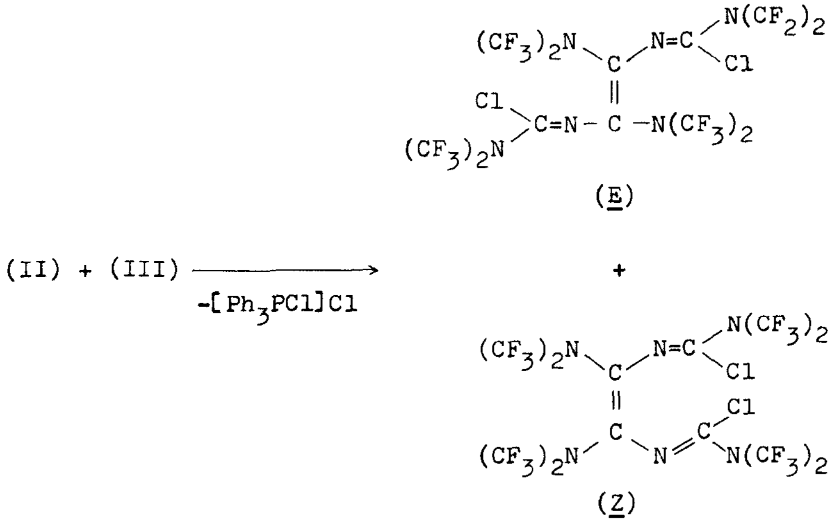
Reactions (2) and (3) are in agreement with a reaction pathway which is initiated by a nucleophilic attack of Ph_3P at the CCl_2 group of (I). The anion (Ia) is formed which, in the presence of $H^{\oplus}$, yields (V). Otherwise, $Cl^{\ominus}$ is abstracted and the carbene (Ib) formed, which is attacked by (Ia) and subsequently forms the dimer (IV), further $Cl^{\ominus}$ being eliminated, Scheme 1. We note however that attempts to trap the carbene (Ib) with cyclohexene or perfluoropropene were not successful, only (IV) being formed even in the presence of these carbene scavengers.

In contrast to (I), the imine (II) possesses two different CCl bonds which might be attacked by (III). With the same conditions as chosen for the synthesis of (IV), only one volatile reaction product was obtained with a 6 % yield. The major product was a brown, non-volatile residue which was not further investigated. The volatile product was identified spectroscopically as perfluoro-2,3,5,6-tetrakis(dimethylamino)-pyrazine (VI). Its constitution was independently confirmed by a single crystal X-ray structure analysis which is reported below.



Scheme 1

The formation of (VI) can be rationalized by assuming a carbene dimerization as set out in Scheme 1 to form the (E) and (Z) dichloro intermediates, eqn. (4).



(4)

Only the (Z) isomer which is supposedly less stable than (E) can undergo cyclization to form (VI), eqn. (5):

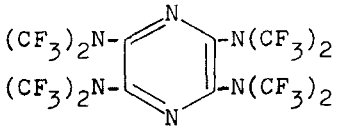
TABLE 1

NMR, IR and Raman spectra

	(IV)	(V)	(VI)
^{19}F NMR[a]			
δ(CF_3) [ppm]	-55.8	-57.5	-56.0
δ(CF_2) [ppm]	-100.6	-91.4(a), -91.9(b)	
^1H NMR[b]			
δ(CH) [ppm]		6.94	
^4J(HF) [Hz]		6.15(a), 1.28(b)	
^{13}C NMR[c]			
δ($\underline{C}F_3$) [ppm]	118.8	118.5	
δ($\underline{C}F_2$) [ppm]	115.6	114.1	
δ(N-$\underline{C}$-N) [ppm]	122.5	77.1	
$^1J(CF_3)$ [Hz]	268.0	264.8	
$^1J(CF_2)$ [Hz]	275.3	268.1	
$^2J(CF_2)$ [Hz]	32.5	30.8	
IR/Raman [cm^{-1}]			
ν(CH)		-/3029m	
ν(C=C, C=N)	-/1710m		1442vs/1554s
ν(CF)	1373vs/- 1338vs/- 1312vs/- 1253vs/- 1235vs/- 1195vs/-	1358 vs/- 1338vs/- 1293vs/- 1253vs/- 1214vs/-	1332vs/- 1280vs/- 1212vs/- 1183vs/-

[a] At 84.67 MHz from $CFCl_3$, positive sign = high frequency, CF_3COOCH_3 = -76.2 [ppm] as internal standard. [b] From TMS. [c] From TMS as external standard.

$(Z) + (III) \longrightarrow [Ph_3PCl]Cl +$



(VI)

(5)

Reactions of the (E) conformer are likely to account for the formation of oligo- and polymeric material.

SPECTRA

The compounds (IV) and (V) were characterized by elemental analyses (see Experimental). NMR, IR and Raman spectra set out in Table 1 and mass spectra listed in Table 2 were recorded on (IV), (V) and (VI). The single CH group of (V) is only indicated in the Raman spectrum. In (VI), effective inversion symmetry is suggested by the generally small number of Raman lines and IR absorptions with mutual exclusion for the ring vibrations. Only some diagnostic vibrations are mentioned and assigned in Table 1.

TABLE 2

EI mass spectra, m/e arranged in the order of decreasing intensity[a]

(IV)	69 $(CF_3)^+$, 100 $(C_2F_4)^+$, 487 $(M-CF_3)^+$, 114 $(CF_3NCF)^+$ 164 $(CF_3NCCF_3)^+$, 209 $(CF_3NCCFNCF_3)^+$, 304 $((CF_2NCF_3)_2CCN)^+$, 556 $(M)^+$, 537 $(M-F)^+$
(V)	69 $(CF_3)^+$, 279 $(M-Cl)^+$, 164 $(CF_3NCCF_3)^+$, 114 $(CF_3CNF)^+$, 80/82 $(FClCN)^+$, 100 $(C_2F_4)^+$, 96 $(CF_3NCH)^+$, 77 $(CF_2NCH)^+$, 295/297 $(M-F)^+$
(VI)	69 $(CF_3)^+$, 328 $((CF_3)_2NCCN(CF_3)_2)^+$, 684 $(M)^+$, 240 $(CF_2NCCN(CF_3)_2)^+$, 665 $(M-F)^+$, 259 $(CF_3NCCN(CF_3)_2)^+$, 596 $(M-CF_4)^+$, 121 $(C_4N_2NCF)^+$, 304 $((CF_2NCF_3)_2CCN)^+$, 204 $(C_4N_2(NCF_2)_2)^+$, 508 $(M-2\,CF_4)^+$, 76 $(C_4N_2)^+$

[a] Varian MAT 311 A, 70 eV.

The ^{19}F-NMR spectra of (IV) and (V) are of higher order. The spin systems have not been analyzed, and therefore coupling constants are not quoted.

EXPERIMENTAL

Perfluoro-bis(1,3-dimethyl-1,3-diazacyclopentan-2-ylidene) (IV)

7 g (20 mmole) (I) and 16 g (61 mmole) (III) are heated in a glass ampoule for 7 hours at 120 °C. (IV), mp. 27 °C, is collected in vacuo in a -35 °C trap. Yield 5.1 g (92 %). Calc/found: % C, 21.58/20.9; % N, 10.08/10.1; % F, 68.34/68.5.

1,3-Bis(trifluoromethyl)-2-chloro-4,4,5,5-tetrafluoro-imidazolidine (V)

(V) is prepared, as described above, in the presence of a stochiometric amount of H_2O. (V), bp. 93 °C, is collected in a -60 °C trap. Yield 80 %. Calc/found: % C, 19.08/19.3; % N 8.91/8.9; % F, 60.42/60.0.

Perfluoro-2,3,5,6-tetrakis(dimethylamino)pyrazine (VI)

5 g (10 mmole) (II) and 10 g (38 mmole) (III) are heated for 6 hours at 120 °C. Volatile material is collected and (VI), mp. 89 °C, obtained in a 0 °C trap. Yield 0.2 g (6 %).

X-RAY STRUCTURAL ANALYSIS

Method

The thin, wedge-shaped crystal used in the X-ray study was obtained by slow sublimation of (VI) at room temperature under vacuum and sealed in a glass capillary. The cell constants (Table 3) were derived from the Bragg angles of 40 reflections which were centered on a Siemens AED1

TABLE 3

Crystal data for (IV)

Formula	$C_{12}F_{24}N_6$	λ(MoK$\bar{\alpha}$)	0.71073 Å
Crystal system	monoclinic	Filter	Zr
Space group	$P2_1/n$	Octants	hkl, $\bar{h}kl$
a	9.367(2)Å	Range (2θ)	4-50°
b	10.909(3)Å	Scan speed (2θ)	3.93°/min
c	10.929(3)Å	Unique reflections	1892
β	103.27(2)°	with $\lvert F_o\rvert \geq 4\sigma(\lvert F_o\rvert)$	1016
Z	2	μ(MoKα)	2.6 cm^{-1}
d(calc.)	2.163 g/cm^3	Transmission	0.874-0.979
t	22°		
	Crystal size	0.16 X 0.32 X 0.38 mm^3	

diffractometer. Intensity data were collected by the 2θ-ω step-scan technique, two passes being made if the initial scan revealed a peak which was between 2 and 25 times its estimated standard deviation. The intensity of three periodically-monitored standard reflections varied less than ±1 % during the measurement. The data were corrected for absorption and converted to $|F_o|$'s. Only those reflections with $|F_o| \geq 4\sigma(|F_o|)$ were deemed observed and used in the refinement.

The structure was solved by direct methods and refined by full-matrix least-squares techniques. Dispersion corrected neutral atom scattering factors [5] were employed. A conventional full anisotropic refinement with unit weights converged with $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.108$. A disturbing structural feature was the large and unreasonable spread in the F-C-F bond angles, 97(2) - 115(2)°. Presumably the large torsional motions of the CF_3 groups, which cannot be accounted for by our anisotropic model, limited the accuracy of the determination of the F positional parameters and prevented a better fit. Therefore the CF_3 groups were constrained to C_3 symmetry, the C-F and F-F distances being included as separate parameters in the refinement. Convergence was reached with R = 0.109. The final difference Fourier synthesis is featureless, densities ranging from 0.54 to -0.55 e/Å^3. Positional parameters are listed in Table 4, and the numbering scheme is shown in Fig. 1 [6]. Computer programs were SHELX-76 [7], ORTEP-2 [8] and locally written routines.

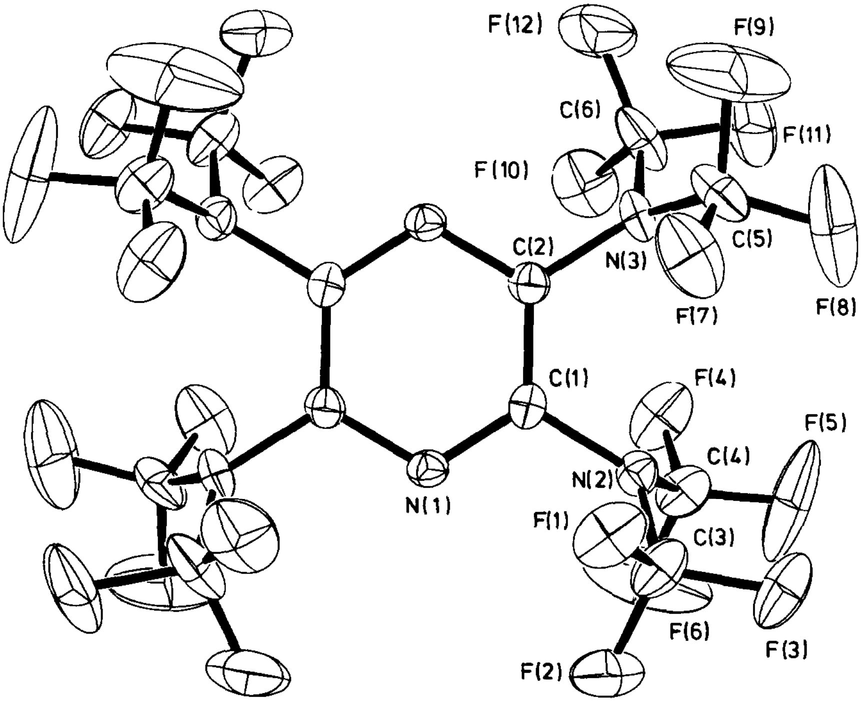


Fig. 1. Perspective drawing of (VI).

Descripton and discussion of the structure

Molecules of (VI) are centered on sites of crystallographic inversion symmetry. Intermolecular contacts are not unusual, the shortest being F(1)-F(5) (0.5-x, y-0.5, 1.5-z) 2.82 (1) Å. Bond distances and angles in the pyrazine ring (Table 5) agree with those reported in pyrazine itself [9]. The ring is planar within experimental error, and the substituent N atoms deviate no more than ±0.02(1)Å from this plane.

TABLE 4

Positional and equivalent isotropic thermal parameters

Atom	x	y	z	U [a]
F(1)	0.1886(8)	0.1087(6)	0.7865(6)	0.104(4)
F(2)	0.1597(9)	0.2529(7)	0.9097(7)	0.118(4)
F(3)	0.2033(9)	0.2945(6)	0.7316(6)	0.118(4)
F(4)	0.596(1)	0.3106(7)	0.9698(8)	0.122(4)
F(5)	0.453(1)	0.401(1)	0.840(1)	0.245(8)
F(6)	0.412(1)	0.370(1)	1.007(1)	0.29(1)
F(7)	0.437(1)	0.0355(9)	0.6745(7)	0.129(5)
F(8)	0.562(1)	0.178(1)	0.635(1)	0.232(9)
F(9)	0.637(1)	0.001(1)	0.634(1)	0.25(1)
F(10)	0.8324(8)	0.1305(8)	0.9710(8)	0.135(5)
F(11)	0.834(1)	0.1812(9)	0.7837(8)	0.170(6)
F(12)	0.862(1)	-0.005(1)	0.8397(9)	0.175(7)
N(1)	0.3832(9)	0.0612(8)	1.0283(8)	0.049(3)
N(2)	0.392(1)	0.2125(8)	0.8804(8)	0.058(4)
N(3)	0.637(1)	0.0864(9)	0.8199(8)	0.067(4)
C(1)	0.449(1)	0.1012(9)	0.9428(9)	0.048(4)
C(2)	0.564(1)	0.042(1)	0.912(1)	0.054(4)
C(3)	0.236(2)	0.2184(5)	0.8281(7)	0.084(6)
C(4)	0.463(1)	0.322(1)	0.9239(9)	0.086(7)
C(5)	0.569(1)	0.0750(8)	0.693(1)	0.094(7)
C(6)	0.788(2)	0.0958(7)	0.8520(7)	0.109(9)

[a] $U = \frac{1}{3}\Sigma_i \Sigma_j a_i^* a_j^* \bar{a}_i \bar{a}_j U_{ij}$.

TABLE 5

Selected distances (Å) and angles (°) in (VI)

C(1)-N(1)	1.31(1)	C(3)-N(2)	1.44(2)	C(3)-F(1)	1.322(6)[b]
C(2)'-N(1)	1.33(1)[a]	C(4)-N(2)	1.40(2)	C(4)-F(4)	1.239(7)[b]
C(1)-C(2)	1.37(1)	C(5)-N(3)	1.40(2)	C(5)-F(7)	1.284(7)[b]
C(1)-N(2)	1.43(1)	C(6)-N(3)	1.38(2)	C(6)-F(10)	1.326(7)[b]
C(2)-N(3)	1.42(1)				

C(1)-N(1)-C(2)'	116.8(9)	F(4)-C(4)-F(5)	105.7(8)[b]
N(1)-C(1)-C(2)	123.1(9)	F(7)-C(5)-F(8)	106.2(8)[b]
C(1)-C(2)-N(1)'	120(1)	F(10)-C(6)-F(11)	106.3(8)[b]
N(1)-C(1)-N(2)	116(1)	N(2)-C(3)-F(1)	109.2(8)
N(1)'-C(2)-N(3)	117(1)	N(2)-C(3)-F(2)	113.8(8)
C(2)-C(1)-N(2)	121(1)	N(2)-C(3)-F(3)	112.1(9)
C(1)-C(2)-N(3)	123(1)	N(2)-C(4)-F(4)	113.9(9)
C(1)-N(2)-C(3)	117.2(7)	N(2)-C(4)-F(5)	113(1)
C(1)-N(2)-C(4)	117.9(8)	N(2)-C(4)-F(6)	112(1)
C(2)-N(3)-C(5)	119.5(9)	N(3)-C(5)-F(7)	112.7(9)
C(2)-N(3)-C(6)	118.2(8)	N(3)-C(5)-F(8)	112(1)
C(3)-N(2)-C(4)	117.1(7)	N(3)-C(5)-F(9)	113(1)
C(5)-N(3)-C(6)	117.6(7)	N(3)-C(6)-F(10)	110.2(9)
F(1)-C(3)-F(2)	107.6(7)	N(3)-C(6)-F(11)	111(1)
		N(3)-C(6)-F(12)	116(1)

[a] Coordinates of primed atoms are related to those in Table 4 by x', y', z' = 1-x, -y, 2-z. [b] Analogous geometrical parameters of this carbon atom are identical.

When an amino group is an aryl substituent, the preferred stereochemistry is characterized by a planar N atom, coplanarity of amine and arene and an N-C(sp^2) bond length (~1.37Å) which has been shortened by conjugation [10]. If, as in (VI), the latter coplanarity is prohibited by steric interactions between the amine and other arene substituents, the molecular distortions required to relieve these repulsions may be difficult to predict [11]. As seen in Fig. 1, steric interactions between adjacent $N(CF_3)_2$ groups are mainly relieved by rotating the amino groups out of the pyrazine plane. Thus the dihedral angles formed by the normal to the pyrazine ring and the plane normals defined by C(1), C(3), C(4) or C(2), C(5), C(6) are 67(1) or 62(1)° respectively. This nonplanarity restricts conjugation, and the mean amine-pyrazine linkage is relatively long, 1.43(1)Å. The valencies of the amino N atoms are nonplanar, the respective deviations of N(2) and N(3) from the planes through their carbon-atom substituents being 0.23(1) and 0.17(1)Å. This slight pyramidality corresponds to that of $N(CF_3)_3$ [12]. As close inspection of Fig. 1 reveals, the N pyramids are oriented head to head. The above-mentioned distortions relax the contacts between $N(CF_3)_2$ groups quite effectively as seen by even the shortest such F-F contact, F(1)-F(7) (2.96(1)Å), not being less than the van der Waals radii sum, 2.94Å [13].

The $N-C(CF_3)$ distances compare well with those in $N(CF_3)_3$ [12]. The spread in the C-F distances, 1.239(7) - 1.326(7)Å, is undoubtedly an artifact of the large torsional amplitudes of the CF_3 groups - especially at C(4) and C(5).

ACKNOWLEDGEMENT

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