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Organic Fluoronitrogens. III. Preparation and Reactions of Halogenated Fluorimines¹

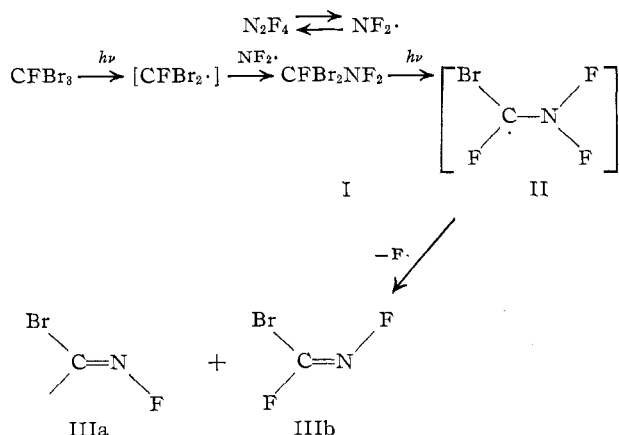
BY DOUGLAS H. DYBVIG

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Irradiation of polyhalogenated methanes in the presence of tetrafluorohydrazine has yielded fluorimines. Thus, tribromofluoromethane has been used to prepare C-bromodifluoromethylenimine in both the *syn* and *anti* forms. Chlorination of the latter has yielded both isomers of C-chlorodifluoromethylenimine; fluorination yielded trifluoromethylenimine. Nmr spectroscopy has been used to assign relative configurations of the *syn* and *anti* isomers.

Relatively few synthetic approaches to fluorimino compounds are to be found in the literature. Fluorimino compounds reported previously have been prepared by fluorination of nitrogen compounds,²⁻⁴ by the reaction of nitrogen trifluoride with fluoroolefins,⁵ and by reductive defluorination of difluoramino compounds.⁶ We wish to report the preparation of fluorimino compounds by the reaction of tetrafluorohydrazine with polyhalogenated compounds, such as tribromofluoromethane, and to describe some reactions of this class of compounds. The use of tetrafluorohydrazine in the preparation of difluoramino compounds under free-radical conditions has been reported previously.^{7,8}

Reaction of tribromofluoromethane with tetrafluorohydrazine initiated by ultraviolet irradiation produced both the *syn* and *anti* isomers of C-bromodifluoromethylenimine, IIIa and IIIb. The initial product of the reaction is believed to be dibromodifluoramino-fluoromethane (I), which may react further to form an intermediate radical bearing the difluoramino group (II); elimination of fluorine from nitrogen then leads to the mixture of isomeric fluorimines, IIIa and IIIb.



Varying amounts of dibromodifluoramino-fluoromethane have been found among the products of this reaction,

(1) Presented in part before the Division of Fluorine Chemistry at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Aug 30-Sept 4, 1964.

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(3) J. A. Cuculo and L. A. Bigelow, *J. Am. Chem. Soc.*, **74**, 710 (1952).

(4) J. A. Attaway, R. N. Groth, and L. A. Bigelow, *ibid.*, **81**, 3599 (1959).

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(6) R. A. Mitsch, *ibid.*, **87**, 328 (1965).

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(8) R. C. Petry and J. P. Freeman, *J. Am. Chem. Soc.*, **83**, 2912 (1961).

particularly in those cases in which the irradiation was performed in Pyrex glass.

Increased yields of the isomers of C-bromodifluoromethylenimine were achieved by photolysis of a mixture of tribromofluoromethane and tetrafluorohydrazine in quartz bulbs coated on the inside with an inert material transparent to ultraviolet light (a thin coating of low molecular weight polychlorotrifluoroethylene grease has proven effective). In the absence of this coating, there resulted a much larger proportion of the usual decomposition products found when fluoronitrogens react with glass, such as silicon tetrafluoride and oxides of nitrogen.

A purified sample of dibromodifluoramino-fluoromethane was irradiated in a coated quartz reactor in an attempt to verify that the isomeric fluorimines are among its photolytic decomposition products. As indicated in Table I both isomers of the fluorimine

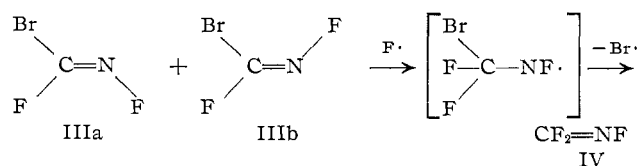
TABLE I

CFBr₂NF₂ IRRADIATION^a

Time, hr	Composition of mixture ^b (pressure in mm)			
	I	IIIa	IIIb	IV
0.0	56
0.25	26	5	2	7
1.0	5	9	3	11
2.0	2	7	2	13

^a A chromatographically pure sample was irradiated at 25° in a coated quartz bulb. ^b Pressures were estimated by means of infrared analysis.

were produced. Trifluoromethylenimine (IV) also formed in the reaction. Presumably, fluorine, formed *in situ* during the decomposition of dibromodifluoramino-methane, attacks the fluorimines to yield a free-radical intermediate which eliminates bromine to yield trifluoromethylenimine. The preparation of tri-



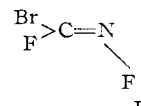
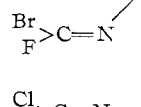
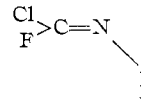
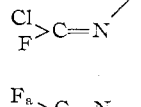
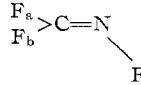
fluoromethylenimine by direct fluorination of acetonitrile or trifluoroacetonitrile was reported several years ago,^{2,3} although no spectral data have been re-

ported for this compound. Because it is the simplest member of the family of fluorimines, the infrared, nuclear magnetic resonance, and mass spectra have been included. The ultraviolet spectrum of trifluoromethylenimine displays end absorption below 2300 Å.

The *syn* and *anti* isomers were readily separated in pure form by gas chromatography. There was no evidence for isomerization of either compound on the chromatographic column, and each isomer was found to be stable for several months when stored in glass bulbs. The *anti* isomer (fluorines on opposite sides of the carbon–nitrogen double bond) formed in consistently higher yield, the ratio being about 2 or 3 to 1.

Configuration of the isomers has been assigned on the basis of their fluorine magnetic resonance spectra by comparison with known compounds. Examination of the spectra, Table II, shows that isomer IIIb displays a larger spin–spin coupling constant between fluorine atoms on carbon and nitrogen than does IIIa, which may be taken as an indication that IIIb possesses the two fluorine atoms in the *anti* configuration. This assignment is made by analogy with carbon–carbon double bonded structures where fluorine atoms known to be *trans* display coupling constants of consistently greater magnitude.^{9,10} For example, the coupling constant for *trans* fluorines in 1,2-dibromo-1,2-difluoroethylene is 124 cps compared to a value of 57 cps for *cis* fluorines.

TABLE II
F¹⁹ NUCLEAR MAGNETIC RESONANCE SPECTRA OF FLUORIMINES

Compound	No.	Chemical shift, ^a φ*	Assign- ment	Coupling constant, J, cps
	IIIa	-7.6 27.9	NF CF	17.6
	IIIb	3.5 62.9	NF CF	218
	VIa	6.8 36.1	NF CF	10.6
	VIb	15.3 71.2	NF CF	209
	IV	60.2 67.0 96.4	CF _b NF CF _a	22.1 (J _{bc}) 52.6 (J _{ab}) 184 (J _{ac})

^a For definition of φ* see G. Filipovich and G. V. D. Tiers, *J. Phys. Chem.*, **63**, 761 (1959).

An attempt was made to isomerize samples of each of the pure isomers to the usual mixture found under the conditions of synthesis. Irradiation of the *syn* isomer was found to produce measurable amounts

of the *anti* isomer (see Table III). However, the tendency of either isomer to undergo conversion to trifluoromethylenimine made accurate measurements of a final equilibrium ratio difficult. No evidence was obtained for the generation of the *syn* isomer from the *anti* although the analytical method was capable of detecting less than 0.1%. Again, the formation of trifluoromethylenimine tended to be the predominant reaction.

TABLE III
IRRADIATION OF ISOMERS OF C-BROMODIFLUOROMETHYLENIMINE^a

Time, hr	Composition of mixture ^{b,c} (pressure in mm)		
	IIIa	IIIb	IV
	(A) Irradiation of IIIa		
0.0	14
0.33	10	1.1	0.9
1.0	3.5	0.7	1.2
	(B) Irradiation of IIIb		
0.0	...	12	...
0.25	...	4.5	1.2
0.50	... ^d	2.1	1.2

^a Coated quartz bulb irradiated at 25°. ^b Pressures estimated by infrared analysis. ^c Not including SiF₄ formed as reaction proceeds. ^d Isomer IIIa was not detectable by gas chromatography or infrared analysis.

In a few instances CFBr=O was found among the products of the photodecomposition of dibromodifluoraminofluoromethane. This product is assumed to have arisen through hydrolysis of C-bromodifluoromethylenimine by small quantities of water present in the glass of the reactor. It was identified on the basis of its mass spectrum and by a comparison of its infrared spectrum with that given by Patty and Lagemann.¹¹

Support for the proposed route to trifluoromethylenimine is found in results obtained by fluorination of a pure sample of the *anti* isomer of C-bromodifluoromethylenimine. Ultraviolet irradiation was eliminated so as to diminish the possibility of photodecomposition of the fluorimine. Fluorination in this case was initiated by the method described by Rodgers¹² in which fluorine radicals are generated in the reaction mixture by the presence of perfluorobutene-2. Thus a mixture of fluorine, perfluorobutene-2, and the *anti* isomer (3:1:3) was found to react in a matter of minutes to produce trifluoromethylenimine in 70% yield.

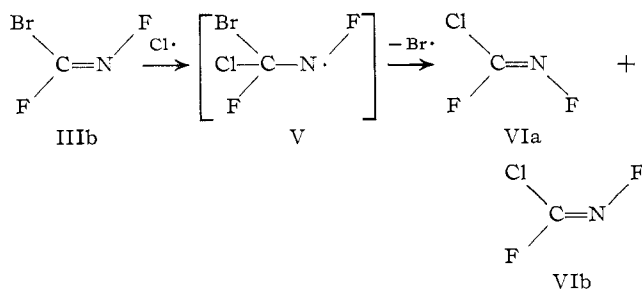
Parallel results were obtained when a pure sample of the *anti* isomer was chlorinated. Irradiation in excess chlorine produced two isomeric compounds which have been identified on the basis of their nuclear magnetic resonance, infrared, and mass spectra as the *syn* and *anti* isomers of C-chlorodifluoromethylenimine, VIa and VIb. As in the case of the bromine compounds, the isomer displaying the larger coupling constant was assigned the *anti* configuration (Table II). Again the *anti* isomer was found to predominate, the ratio being 3.5:1.

(11) R. R. Patty and R. T. Lagemann, *Spectrochim. Acta*, **15**, 60 (1959).

(12) A. S. Rodgers, *J. Phys. Chem.*, **69**, 254 (1965).

(9) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y. 1959, p 335.

(10) G. V. D. Tiers and P. C. Lauterbur, *J. Chem. Phys.*, **36**, 1110 (1962).



The fact that a single isomer, IIIb, upon chlorination yields both isomers of C-chlorodifluoromethylenimine may be taken as additional evidence for the existence of a free-radical intermediate such as V which may undergo rotation at the carbon-nitrogen bond before it eliminates chlorine to give the final product. It is apparent from work with both the chloro and bromo compounds that the configuration involving fluorine on nitrogen *syn* to bromine or chlorine on carbon is more favorable.

Because of the explosive nature of the compounds bearing fluorine or nitrogen, quantities were kept below the 1-g level and protective equipment was used.

Experimental Section

Photolyses were performed in quartz or Pyrex brand glass bulbs. Unless otherwise noted, these bulbs were coated on the inside with a thin film of Kel-F No. 90 grease (Minnesota Mining and Manufacturing Co.) which was applied by rinsing the bulb with a solution of the grease in acetone, followed by evaporation of the solvent. The light source used was a 100-w Hanovia high-pressure quartz mercury-vapor arc lamp (Model SH 616A) placed approximately 3 in. from the bulb, operated at 110 v. The major ultraviolet emissions lines (A) and their intensities (w) are: 3660 (1.82), 3130 (1.30), 3025 (0.57), 2967 (0.30), 2652 (0.47), 2537 (0.37), 2482 (0.19).

Separations were accomplished using a Perkin-Elmer Model 154 vapor fractometer. The stationary phase (unless otherwise noted) consisted of 33% by weight Kel-F Oil 8126 (Minnesota Mining and Manufacturing Co.) on 30/60 mesh acid-washed Chromosorb-P (Johns-Manville). Infrared spectra were recorded on a Perkin-Elmer Model 21 spectrophotometer using a 2.5-cm gas cell with NaCl windows. F^{19} nmr spectra were recorded on a Varian V-4300-2 40.00 Mc/sec spectrometer using $CFCl_3$ as an internal standard for the determination of chemical shifts, negative values indicating low field. Trifluoroacetic acid absorbs at ϕ^* 76.5 on this scale. A Consolidated Electro-dynamics Corp. Model 21-103C mass spectrometer was used to obtain the mass spectra. An ionization potential of 70 v and an ionization chamber temperature of 250° were employed.

The tetrafluorohydrazine used in this work was supplied by E. I. du Pont de Nemours and Co. and was rated as better than 99% pure. Both the fluorine and chlorine were obtained from The Matheson Co. The $CFBr_3$ was prepared by the method of Rathsburg¹³ and was chromatographically pure.

Elemental analyses for carbon and fluorine were performed using the procedure developed in these laboratories for highly fluorinated compounds.¹⁴ Better results were obtained on the bromo compounds by burning the sample in moist oxygen at 1200° instead of the usual 1100°.

Dibromodifluoraminofluoromethane (I).—A coated Pyrex glass bulb was charged with N_2F_4 (0.20 g, 2.0 mmoles) and $CFBr_3$ (0.54 g, 2.0 mmoles). The bulb was placed on a steam bath and irradiated for 52 hr. Chromatographic separation of the resulting mixture yielded pure I (0.22 g, 0.9 mmole, 45%).

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An alternate, less satisfactory method involved the thermally initiated reaction of N_2F_4 (2.0 g, 20.4 mmoles) and $CFBr_3$ (1.1 g, 3.0 mmoles) in a 43-ml stainless steel pressure reactor at 150° for 18 hr. Chromatographic separation gave pure I in approximately 10% yield.

The infrared spectrum of I contained an absorption of medium intensity at 10.66 μ which has been assigned to the N-F bond, as well as absorptions at 8.58 (w), 8.82 (s), 9.54 (m), 11.09 (m), 11.72 (s), and 12.94 μ (w). The mass spectrum exhibited important peaks corresponding to $CNFB_2$, $CFBr_2$ (100%), $CN-F_3Br$, CNF_2Br , $CFBr$, CF_3 , CNF_2 , and CF . The F^{19} nmr spectrum is recorded in Table II.

Anal. Calcd for CBr_2F_3N : C, 4.9; F, 23.5; mol wt, 242.8. Found: C, 4.8; F, 23.9; mol wt, 240.5.

C-Bromodifluoromethylenimine (IIIa and IIIb).—A coated quartz bulb was charged with N_2F_4 (0.13 g, 1.3 mmoles) and $CFBr_3$ (0.35 g, 1.3 mmoles), placed on a steam bath and irradiated for 48 hr. Chromatographic separation of the resulting mixture yielded pure *syn* isomer (T_R ,¹⁵ 68) IIIa (26 mg, 0.18 mmole, 14%), and pure *anti* isomer (T_R , 50) IIIb (60 mg, 0.42 mmole, 32%). There was evidence in the infrared spectrum of the crude reaction mixture that $FC\equiv N$ may have formed in low yield.

The *syn* isomer (IIIa) exhibited an absorption in its infrared spectrum at 6.10 μ (m) assigned to the carbon-nitrogen double bond. Other absorptions were found at 8.15 (w), 8.47 (s), 8.68 (sh), 10.83 (s), and 11.83 μ (m). Unsaturation in the *anti* isomer (IIIb) appeared at 6.12 μ (m). Other absorptions were found at 8.05 (s), 8.35 (w), 9.69 (w), and 10.22 μ (s). Mass spectral data for the *syn* isomer showed major peaks corresponding to CNF_2Br (parent peak, 90.2%), CNF_2 (100%), CNF , and CF . The *anti* isomer displayed a similar spectrum. In this case CNF_2Br was the 100% peak. F^{19} nmr results are given in Table II.

Anal. Calcd for $CBrF_2N$: C, 8.3; F, 26.4; mol wt, 143.9. Found for IIIb: C, 8.5; F, 25.9; mol wt, 143.8. Found for IIIa: mol wt, 144.0.

Trifluoromethylenimine (IV).—Low yields of IV were usually observed in the $CFBr_3-N_2F_4$ reaction mixtures irradiated through quartz. During chromatographic separation of these mixtures all components with retention times less than that of IIIb were collected in a single trap at liquid nitrogen temperature. Several such fractions were combined and from them IV was obtained in small amounts by chromatographic separation using as the stationary phase FC-43 (perfluorotributylamine, produced by Minnesota Mining and Manufacturing Co.) on Chromosorb-P (33% by weight) at -25°. Under these conditions IV possessed a T_R of 48 (relative to CF_2Cl_2 as 100).

Infrared analysis revealed the expected carbon-nitrogen double-bond absorption at 5.77 μ (s), as well as absorptions at 7.27 (s, C-F), 9.83 (s, N-F), and 10.75 μ (w). Important peaks in the mass spectrum were attributable to CNF_3 (parent peak, 98.3%), CNF_2 (100.0%), CF_2 , CNF , and CF . The F^{19} nmr spectrum is given in Table II.

Anal. Calcd for CF_3N : C, 14.5; F, 68.7; mol wt, 83.0. Found: C, 14.4; F, 66.7; mol wt, 83.4.

C-Chlorodifluoromethylenimine (VIa and VIb).—A coated Pyrex bulb was charged with IIIb (50 mg, 0.35 mmole) and chlorine (105 mg, 1.5 mmoles) and the mixture was irradiated for 22 hr. The reaction mixture was examined at intervals by infrared spectroscopy, which showed the gradual formation of C-chlorodifluoromethylenimine (VIa and VIb). At the end of the reaction period, the mixture was chromatographed to yield pure VIa (6 mg, 0.06 mmole, 17%) and VIb (20 mg, 0.20 mmole, 57%). T_R values (relative to $CFCl_3$ as 100) were found to be 30 (VIa) and 23 (VIb) on Kel-F Oil 8126 as the stationary phase.

The *syn* isomer (VIa) exhibited absorptions in its infrared spectrum at 6.08 (s, double bond), 8.29 (s), 10.60 (s), and 11.48 μ (m). The *anti* isomer (VIb) absorbed at 6.10 (s, double bond), 7.99 (s), and 10.14 μ (s).

(15) $T_R = (T_{compd} - T_{air}) / (T_{CFCl_3} - T_{air}) \times 100$; $T_{CFCl_3} = 100.0$.

Important peaks in the mass spectrum of VIa were assigned to CNF_2Cl (parent peak, 96%), CNFCl , CFCl , CNF_2 (100%), CNF , and CF . Isomer VIb displayed important peaks attributable to CNF_3Cl (parent peak, 100%), CNFCl , CFCl , CNF_2 , CNF , and CF .

Fluorination of C-Bromodifluoromethylenimine.—A 12-ml infrared gas cell equipped with NaCl windows was charged with IIIb (2.2 mg, 0.015 mmole) and $\text{C}_4\text{F}_8\text{-2}$ (1.1 mg, 0.005 mmole). After freezing these reactants into the side arm of the cell, it was pressurized with fluorine (20 mm, 0.013 mmole). Immediately upon warming to room temperature (5 min) the infrared spectrum of the mixture was examined. On the basis of this spectrum, the conversion of IIIb was estimated at 23% and the yield of IV was

estimated at 70%. Other products of the reaction were COF_2 , CF_4 , C_4F_{10} , and CF_3COF . No $\text{C}_4\text{F}_8\text{-2}$ remained in the mixture.

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Some Reactions of the Octahalodirhenate(III) Ions.

II. Preparation and Properties of Tetracarboxylato Compounds¹

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The conditions under which tetracarboxylatodirhenate(III) species, $\text{Re}_2(\text{O}_2\text{CR})_4\text{X}_2$, may be prepared, directly or indirectly, from the $\text{Re}_2\text{X}_8^{2-}$ species have been explored and effective methods of preparation developed. A number of new compounds have been prepared and characterized. Certain features of the infrared and visible spectra of these molecules are discussed in relation to the structure and bonding. It is proposed that the terminal X groups may exert a weakening effect on the Re-Re bond comparable to the *trans* effect known in other, more classical complexes.

Introduction

Since the discovery and formulation²⁻⁴ of species containing a quadruply bonded pair of Re(III) atoms, namely the $\text{Re}_2\text{X}_8^{2-}$ ions in which X = Cl or Br, several years ago, investigations of their chemistry have been carried out. One objective has been to determine the range of chemical behavior possible for the unique diatomic species, Re_2 , including ligand substitution reactions, oxidation-reduction behavior, and stability. Another purpose has been to obtain compounds with which experiments shedding more light on the metal-metal bonding and electronic structure could be carried out. A previous paper has reported some reactions of the $\text{Re}_2\text{X}_8^{2-}$ species with phosphines.⁵

In this paper we describe in more detail the chemical relationship of the $\text{Re}_2\text{X}_8^{2-}$ species to the $\text{Re}_2(\text{O}_2\text{CR})_4\text{X}_2$ species which were originally prepared by others⁶⁻⁸ in various ways. It has previously been shown² that

the $\text{Re}_2\text{X}_8^{2-}$ and $\text{Re}_2(\text{O}_2\text{CR})_4\text{X}_2$ species can be interconverted. It should also be noted that the Russian workers^{7,8} have incorrectly formulated their compounds, which were the acetates only, as $\text{Re}_2(\text{CH}_3\text{COOH})_4\text{X}_2$; the implication of this formula, for which there has never been any evidence given, is that Re(I) is present. This is undoubtedly an error unless, despite all appearances, the Russian workers were dealing with different materials than ours.

Experimental Section

$[(n\text{-C}_4\text{H}_9)_4\text{N}]_2\text{Re}_2\text{Cl}_8$ was prepared in 40% yield and converted to $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2\text{Re}_2\text{Br}_8$ in 98% yield as previously described.⁹

Preparation of the Alkanoates.—A mixture of tetra-*n*-butylammonium octachlorodirhenate(III) (1.0 g), acetic acid (40 ml), and acetic anhydride (10 ml) was refluxed gently under nitrogen with a slow stream of nitrogen passing through the solution to prevent bumping and to sweep out the HCl formed. After 1 hr the supernatant liquid was essentially colorless and orange crystals of $\text{Re}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$ had been deposited. The crystals were separated by filtration in air, washed with three 20-ml portions of alcohol, then with 20 ml of diethyl ether, and dried under vacuum. The yield was 95%.

The bromo dimer, $\text{Re}_2(\text{O}_2\text{CCH}_3)_4\text{Br}_2$, was prepared in an analogous way using $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2\text{Re}_2\text{Br}_8$.

Higher alkyl carboxylate chloride and bromide dimers were prepared similarly using the corresponding carboxylic acid and, when available, the anhydride. Due to the solubility of these higher homologs and their sensitivity in solution to traces of oxygen, it was necessary to use carefully deoxygenated solvents and extended reflux periods (up to 48 hr). In each case the orange product was isolated by cooling the dark final solution to about -5° and filtering the product under nitrogen. Yields

(1) This work was supported by the U. S. Atomic Energy Commission under Contract No. AT(30-1)-1965 and the National Science Foundation under Grant No. GP-4329.

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