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Interaction of *N*,*N*-dimethylperfluoroarylamines with nitric and nitrous acids

Vyacheslav E. Platonov[a,*], Alois Haas[b,1], Meinolf Schelvis[b], Max Lieb[b], Kira V. Dvornikova[a], Ol'ga I. Osina[a]

[a]*N.N. Vorozhtsov Novosibirsk Institute of Organic Chemistry, 9 Lavrentieva ave., 630090 Novosibirsk, Russia*
[b]*Fakultät für Chemie, Ruhr-Universität Bochum, FNO 034/036, D-44780 Bochum, Germany*

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Abstract

N,*N*-Dimethylpentafluoroaniline enters easily into reactions with a mixture of nitric and sulphuric acids or nitric acid with conversion of the side chain. In the reactions with mixtures of HNO_3 and H_2SO_4, the formation of *N*-nitroso-*N*-methyl and *N*-nitro-*N*-methylpentafluoroanilines is observed. The ratio of these products was found to depend on the ratio of the acids: the formation of *N*-nitro-*N*-methylpentafluoroaniline increases with the quantity of sulphuric acid; *N*-nitroso-*N*-methylpentafluoroaniline is obtained when only nitric acid is employed. *N*,*N*-Dimethylperfluoro-*p*-toluidine, *N*,*N*-dimethylperfluoro-2,4-xylidine, *N*,*N*-dimethylperfluoro-5-aminoindane undergo similar transformations. *N*-Nitroso derivatives were converted by a mixture of HNO_3 and H_2SO_4, HNO_3 or NO_2BF_4 into the corresponding *N*-nitro derivatives. Formation of the corresponding *N*-nitroso-*N*-methyl derivatives occurs when *N*,*N*-dimethylpentafluoroaniline, *N*,*N*-dimethylperfluoro-*p*-toluidine are treated with HNO_2.

Keywords: Polyfluoroaromatic chemistry; *N*,*N*-Dimethylperfluoroarylamines; Nitric and sulphuric acids; Nitrous acid; Nitronium tetrafluoroborate; *N*-Nitroso-*N*-methylperfluoroarylamines; *N*-Nitro-*N*-methylperfluoroarylamines

1. Introduction

We have shown previously that treatment of *N*-alkylperfluoroarylamines with nitric acid readily gives *N*-nitro-*N*-alkylperfluoroarylamines; in the case of *N*-alkylperfluoroanilines, the formation of small amounts of *N*-nitroso-*N*-alkylpentafluoroanilines was also detected. Replacement of amino hydrogen by nitro via electrophilic attack by nitronium cation was proposed to explain the formation of *N*-nitro derivatives (Scheme 1) [1].

We have now investigated the behaviour of *N*,*N*-dialkylperfluoroarylamines with HNO_3. Interaction of the *N*,*N*-dialkylamino group with nitronium cations with formation initially of *N*-nitroammonium cations $Ar_FN^+(Alk)_2NO_2$ was expected, and since it is well known that nitration of *N*,*N*-dimethylaniline with HNO_3–H_2SO_4 gives *N*-nitro-*N*-methyl-2,4,6-trinitroaniline [2], it seemed reasonable to think that the corresponding *N*-nitro-*N*-methyl derivative should be the final product from treating *N*,*N*-dimethylpentafluoroaniline with a mixture of HNO_3 and H_2SO_4. To check this, we have investigated the reactions of *N*,*N*-dimethylperfluoroarylamines with mixtures of HNO_3 and H_2SO_4 and with HNO_3 alone.

2. Results and discussion

We have found that treatment of *N*,*N*-dimethylpentafluoroaniline (**1**) with mixtures of HNO_3 and H_2SO_4 gives *N*-nitroso-*N*-methylpentafluoroaniline (**2**) and/or *N*-nitro-*N*-methylpentafluoroaniline (**3**) depending on the conditions (Scheme 2, Tables 1 and 2). Thus when compound **1**, HNO_3 and H_2SO_4 were used in the ratio 1:5:3, respectively *N*-nitro derivative **3** was obtained. The formation of the *N*-nitroso derivative **2** along with **3** occurred when the relative quantity of sulphuric acid was diminished; *N*-nitroso derivative **2** was obtained as main reaction product when neat nitric acid was employed.

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[*] Corresponding author. Tel.: +7-3832-34-4437; fax: +7-3832-34-4752. *E-mail addresses:* platonov@nioch.nsc.ru (V.E. Platonov), alois.haas@ruhr.uni.bochum.de (A. Haas).

[1] Co-corresponding author. Tel.: +49-234-32-23004; fax: +49-234-32-14541.

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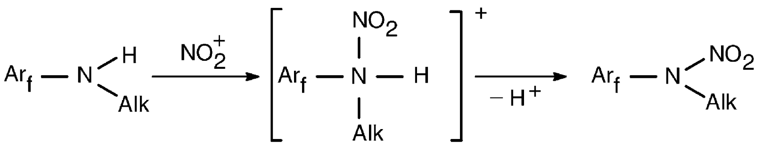
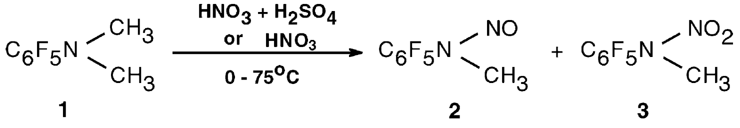


Scheme 1.



Scheme 2.

A negligible quantity of tetrafluoro-*p*-benzoquinone was formed in the reaction of compound **1** with HNO_3, and the order of mixing compound **1** and HNO_3 did not change the main reaction course.

The conversion of compound **1** with HNO_3 to *N*-nitroso derivative **2** prompted us to study the reactions of other *N*,*N*-dimethylperfluoroarylamines with HNO_3, namely *N*,*N*-dimethylperfluoro-*p*-toluidine (**4**), *N*,*N*-dimethylperfluoro-2,4-xylidine (**5**) and *N*,*N*-dimethylperfluoro-5-aminoindane (**6**). The generality of the nitrosation was thereby demonstrated, since the corresponding *N*-nitroso derivatives (**7**–**9**) were obtained. Reactions of amino derivatives **1** and **4** with

Table 1

Interaction of *N*,*N*-dimethylperfluoroarylamines **1**, **4**–**6** and *N*-nitroso-*N*-methylperfluoroarylamines **2**, **7**, and **8** with HNO_3

Compounds		HNO_3 (*d* 1.51) g (mmol)	Molar ratio	Temperature (°C)	Time (h)	Yield of reaction product mixture (g)	Ratio of reaction products (by ^1H and ^{19}F NMR)	
Number	g (mmol)						Compound numbers	Ratio
1	1.0 (4.7)	1.2 (19.0)	1:4	0	0.5	0.90	**2**:**3**	80:1
1	1.0 (4.7)	1.5 (23.8)	1:5	20	0.5	0.92	**2**:**3**	9:1
1	1.0 (4.7)	0.44 (7.0)	1:1.5	20	0.5	0.89	**2**:**3**	14:1
1[a]	1.0 (4.7)	0.44 (7.0)	1:1.5	20	0.5	0.90	**2**:**3**	9:1
1	0.5 (2.4)	1.15[b] (11.9)	1:5	20	0.5	0.40	**2**	
1	0.5 (2.4)	0.75 (11.9)	1:5	75	0.5	0.42	**2**:**3**	3:1
2[c]	0.5 (2.2)	0.42 (6.7)	1:3	20	1.0	0.40	**3**	
4	1.0 (3.8)	1.2 (19.0)	1:5	20	0.5	0.85	**7**	
4	0.5 (1.9)	0.9[b] (9.3)	1:5	60	1.0	0.40	**7**	
4	0.5 (1.9)	0.75 (11.9)	1:6	80	1.0	0.37	**7**:**10**	3.6:1
5	0.5 (1.6)	0.55 (8.7)	1:5	20	0.5	0.47	**8**	
6	1.0 (3.1)	1.0 (15.9)	1:5	20	3.0	0.90	**9**	
7[c]	0.1 (0.4)	0.07 (1.1)	1:3	20	0.5	–[d]	**10**	
8[c]	0.08 (0.3)	0.06 (1.0)	1:3	20	0.5	–[d]	**16**	

[a] To HNO_3 was added **1**.

[b] HNO_3 (*d* 1.39) was used.

[c] Reaction was carried out by analogy with procedure 3.1.

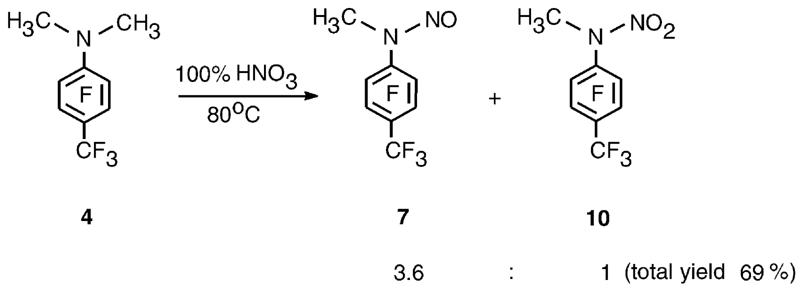
[d] Extract with chloroform (~0.5 ml).

Table 2

Reaction of *N*,*N*-dimethylpentafluoroaniline (**1**) and *N*-nitroso-*N*-methylpentafluoroaniline (**2**) with mixtures of HNO_3 and H_2SO_4

Compounds		Molar ratio compound:HNO_3:H_2SO_4	Temperature (°C)	Yield of reaction product mixture (g)	Ratio of 2:3[a] (by H and ^{19}F NMR)
Number	g (mmol)				
1	0.50 (2.4)	1:5:1	16	0.35	~1.1:1
1	0.50 (2.4)	1:5:2	18	0.35	~1:1.8
1	0.50 (2.4)	1:5:3	20	0.40 (70%)	**3**
2	0.50 (2.2)	1:5:3	20	0.41 (77%)	**3**

[a] Traces of tetrafluoro-*p*-benzoquinone were present.



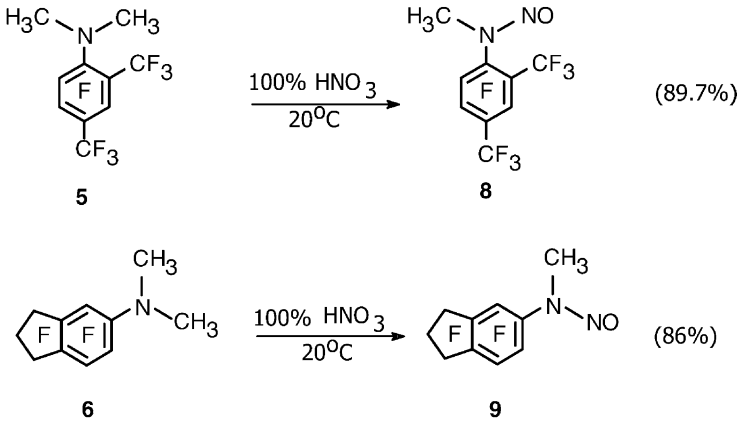
Scheme 3.

concentrated HNO_3 are influenced by the reaction temperature; an elevated temperature favouring formation of *N*-nitro derivatives **3** (**2**: **3** = 3:1 at 75 °C) and **10** (Scheme 3 and Table 1) as minor products. When diluted HNO_3 (65%) was employed, the compounds **1** and **4** afforded only the corresponding *N*-nitroso derivatives **2** at 20 °C and **7** at 60 °C, respectively (Table 1). In the reactions of compounds **4**, **5**, and **6** with concentrated HNO_3 at 20 °C, formation of the corresponding *N*-nitro derivatives were not detected (Scheme 4). *N*-Nitroso derivatives **2**, and **7–9** consist of *E* and *Z* isomers with the former prevailing (*E*:*Z* ~2.2–3.0:1). The structures of *E* and *Z* isomers of *N*-nitroso derivatives **2**, **7–9** are considered in detail in [3].

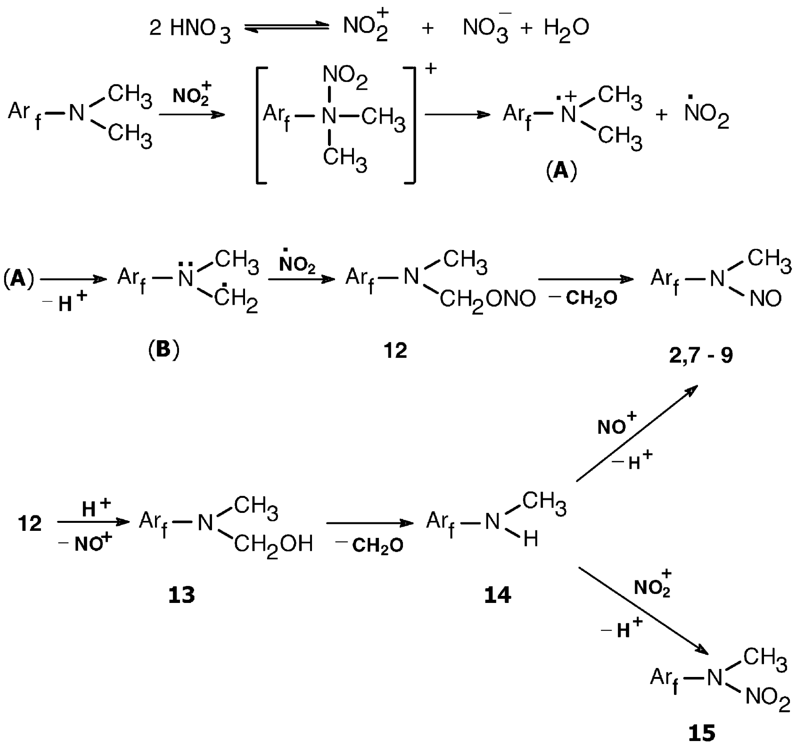
The formation of *N*-nitroso derivatives in the reactions of compounds **1**, **4–6** with HNO_3 can be rationalised by a mechanism involving the decay of intermediate nitroammonium cations to aminium radical cations (**A**) and nitrogen dioxide, as shown in Scheme 5 (cf. [1]). Proton elimination from **A**, giving aminomethyl radicals (**B**), as outlined in the literature [4,5], followed by combination of radicals **B** with nitrogen dioxide can give nitrites (**12**), which, on loss of formaldehyde, will provide *N*-nitroso derivatives **2**, and **7–9**. Earlier, similar conversion of a nitrite was postulated to occur during nitrosation of diethylamine by sodium nitrite in the presence of formaldehyde in the pH range 6.4–11.0 at room temperature [6]. The transformation of carbinolamines into amines and carbonyl compounds is well known [7], of course, but if *N*-methyl derivatives **14** were formed as intermediate products from **13** the corresponding *N*-nitro derivatives **15** would be expected as the main products in the reactions between compounds **1**, and **4–6** and nitric acid [1]. Since the reactions of *N*,*N*-dimethylperfluoroaryl amines with HNO_3 gave *N*-nitro derivatives as minor products, or seemingly not at all, formation of *N*-nitroso derivatives **2**, and **7–9** directly from nitrites **12** seems to be the preferred process.

Although formation of the *N*-nitro-*N*-methyl derivative **3** from compound **1**, and a mixture of HNO_3 and H_2SO_4 (see Scheme 2) could be assumed to involve conversion of nitrite **12** ($Ar_F = C_6F_5$) by H_2SO_4 into the corresponding alcohol **13** ($Ar_F = C_6F_5$) followed by loss of formaldehyde and electrophilic nitration of *N*-methylpentafluoroaniline thus generated, formation of **3** could occur as a result of conversion of *N*-nitroso derivative **2** (produced directly from **12**, as in Scheme 5) by HNO_3–H_2SO_4. Note that, we have shown that treatment of *N*-nitroso derivative **2** with a mixture HNO_3 and H_2SO_4 (ratio 1:5:3, respectively) or with $NO_2{}^+BF_4{}^-$ in sulfolane–dichloromethane at 16–25 °C produced *N*-nitro derivative **3** plus traces of tetrafluoro-*p*-benzoquinone in the former reaction (see Table 2). *N*-*N*itroso derivatives **2**, **7**, and **8** are smoothly converted by 100% HNO_3 to the corresponding *N*-nitro derivatives **3**, **10**, and **16** (Scheme 6).

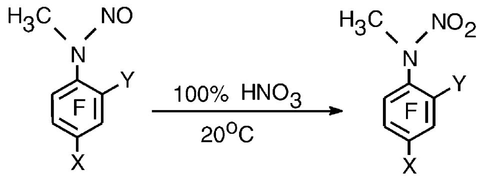
In the hydrocarbon field, the conversion of certain aliphatic *tert*-amines on nitrosation into *sec*-nitrosamines and carbonyl compounds has been described [8], and nitrosation of *N*,*N*-dialkylanilines at the *para* position discussed [9]. We



Scheme 4.



Scheme 5.

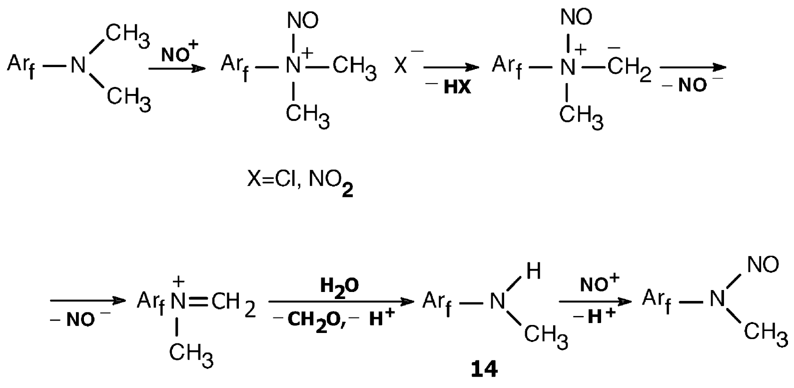


2	X=Y=F	**3**	(75%)
7	X=CF_3, Y=F	**10**	
8	X=Y=CF_3	**16**	

Scheme 6.

found that formation of *N*-nitroso derivatives **2**, **7**, and **8**, respectively from the compounds **1**, **4**, and **5** and HNO_2 ($NaNO_2 + HCl$) took place less readily than that from their monomethyl analogues [3]. This transformation is viewed as occurring via *N*-methyl derivative **14** as shown in Scheme 7, which is similar to that offered previously for nitrosation of *tert*-amines [8].

The lower reactivity of compounds **5** and **6** than compounds **1** and **4** (see Table 3) towards HNO_2 could be accounted for by the greater hydrophobicity of the first two polyfluoroarenes [10]. The steric effect of the *ortho* CF_3 group in compound **5** also could retard transformation of the $N(CH_3)_2$ group by HNO_2.



Scheme 7.

Table 3
Interaction of *N*,*N*-dimethylperfluoroarylamines **1**, and **4–6** with HNO_2

Amine		$NaNO_2$ g (mmol)	Molar ratio	HCl (ml)	Temperature (°C)	Yield of reaction product mixture (g)	Ratio of reaction products (by ^1H and ^{19}F NMR)	
Number	g (mmol)						Compound numbers	Ratio
1	0.5 (2.4)	0.33 (4.8)	1:2	5	20	0.41	**1**:**2**	1:4
4	0.3 (1.1)	0.16 (2.3)	1:2	4	20	0.25	**4**:**7**	1:2
4	0.5 (1.9)	0.39 (5.7)	1:3	5	60	0.41	**4**:**7**	1:5
5	0.3 (1.0)	0.13 (1.9)	1:2	4	20	0.24	**5** and **8**[a]	
5	0.5 (1.6)	0.22 (3.2)	1:2	5	60	0.45	**5**:**8**	2:1
6	0.5 (1.5)	0.22 (3.2)	1:2	5	20	0.41	**6** and **9**[a]	

[a] Traces.

3. Experimental

^{19}F and ^1H NMR spectra were recorded on a Bruker AC-200 instrument at 188.3 and 200 MHz in $CHCl_3$ solution; the standards were hexafluorobenzene and hexamethyldisiloxane. IR spectra were measured in CCl_4 on a UR-20 spectrometer. UV spectra were recorded on a Specord UV–VIS instrument using solutions in EtOH. The molecular weight of **6** was determined by vapor-phase osmometry in acetone on a Knauer instrument. The presence of *N*-nitroso-*N*-methyl, *N*-nitro-*N*-methylperfluoroarylamines and tetrafluoro-*p*-benzoquinone in the reaction product mixtures was determined by a comparison of their ^{19}F and ^1H NMR spectra with the spectra of authentic samples [1,3].

3.1. Interaction of N,N-dimethylperfluoroarylamines with HNO_3: general procedure

HNO_3 (*d* 1.51) was added dropwise, with stirring to the *N*,*N*-dimethylperfluoroarylamine. When the reactions were carried out at 20 °C, the temperature rose to 30–45 °C at the beginning of all the experiments as a result of the exothermic reactions which ensued; this period was short and completed in 3 min (cooling by water containing ice). The reaction mixture was poured into cold water, and the organic material was extracted with chloroform (0.3–0.5 ml twice), washed with water (3 ml) three times, dried over $MgSO_4$, filtered and the solvent was removed by using a Rotavapor at room temperature. The residue was analysed by NMR. Traces of tetrafluoro-*p*-benzoquione were present in reaction product mixture of compound **1**. Results, reaction conditions and experimental data are presented in Table 1.

3.2. Interaction of N,N-dimethylpentafluoroaniline (1) and N-nitroso-N-methylpentafluoroaniline (2) with a mixture of HNO_3 and H_2SO_4: general procedure

A mixture of HNO_3 (*d* 1.51) and concentrated H_2SO_4 was added dropwise, with stirring, to compound **1** or **2**. The temperature of reaction mixture rose from 16 to 28 °C during short period similar to 3.1. Stirring was continued for 2 h at 16–20 °C and then the reaction mixture was poured into cold water. The organic material was extracted with chloroform (0.6 ml twice), washed with water (3 ml) three times. The organic phase was dried over $MgSO_4$, filtered and the solvent was removed by using a Rotavapor at room temperature. Experimental data and analytical results are provided in Table 2.

3.3. Reaction of N-nitroso-N-methylpentafluoroaniline (2) with $NO_2^+BF_4^-$

A stirred solution of compound **2** (0.3 g, 1.3 mmol) in dry sulfolane (2 ml) and dry dichloromethane (~5 ml) was treated with NO_2BF_4 (0.18 g, 1.4 mmol) for 2 h at 20–25 °C. The reaction mixture was quenched with ice and water and the organic material was extracted with chloroform (0.25 ml twice), dried over $MgSO_4$, filtered and analysed by ^{19}F NMR spectroscopy. Compounds **3** and **2** were present in this mixture in the ratio 4:1, respectively.

3.4. Interaction N,N-dimethylperfluoroarylamines with HNO_2: general procedure

An aqueous solution of $NaNO_2$ was added dropwise, with stirring, to a mixture of *N*,*N*-dimethylperfluoroarylamines and concentrated HCl over 1 h; reaction temperatures are given in Table 3. The product was poured into water (10 ml) and the aqueous mixture extracted with chloroform (0.5 ml twice). The organic layer was washed three times with water (5 ml), dried over $MgSO_4$ and filtered. The solvent was removed in vacuum, and the residue analysed by NMR. Experimental data and analytical results are given in Table 3.

3.5. Synthesis of N,N-dimethylperfluoroarylamines 1, and 4–6: general procedure

N,*N*-dimethylperfluoroarylamines **1**, and **4–6** were obtained by treatment of the corresponding perfluoroarenes with a 30% aqueous solution of dimethylamine in isopropanol. Physical data of amines **1**, **4**, and **5** were in agreement with literature data [11–13]. *N*,*N*-Dimethylnonafluoro-5-aminoindane (**6**) was identified as follows: ^{19}F NMR, δ_F ppm: 57.0 and 55.3 (broadened peaks; 1-CF_2 and 3-CF_2), 33.7 (br; 4-F), 32.8 (tt, $J = 5$ Hz, 2-CF_2), 27.3 (t, $J = 17$ Hz, 6-F), 20.3 (m, 7-F); ^1H NMR, δ_H ppm: 3.06 (t, $J = 2.7$ Hz, $N(CH_3)_2$). IR 1500, 1510, 1640, 2945, 2900 cm^{-1}. UV, λ max., nm (log ε): 227.8 (3.92), 287.5 (4.53). Anal., Calcd. for $C_{11}H_6N_1F_9$: C, 40.87; H, 1.85; N, 4.33; F, 52.94%. *MW* 323. Found: C, 40.55; H, 1.76; N, 4.15; F, 52.94%. *MW* 324, 325.

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