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Rhodium-catalyzed α-fluoroalkylation reaction of ketones using silyl enol ethers

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Abstract

The treatment of silyl enol ethers with fluoroalkyl halides (R_f–X) in the presence of $RhCl(PPh_3)_3$ gave α-fluoroalkylated ketones. It seems that a rhodium complex derived from the silyl enol ether and $RhCl(PPh_3)_3$ played an important role for the oxidative addition of fluoroalkyl halides and the reductive elimination of the product.

Keywords: Fluorine; Rhodium; Silyl enol ethers; α-Fluoroalkylation

1. Introduction

Fluorinated compounds have significantly interesting features in the field of bioactive materials as medicine or agricultural chemicals and functional materials as polymers or liquid crystals [1]. However, it is difficult to synthesize the fluorinated compounds for the reason that they have unusual features compared with typical organic compounds. Although many reports have been published on the syntheses of fluorinated compounds, the development of a more efficient methodology is still desired to satisfy the increasing demands [2].

On the other hand, transition metal catalyzed transformations are playing an important role in organic synthesis. Among them, there are a lot of reactions using a rhodium catalyst, such as catalytic reduction, carbonylation and metathesis [3]. Furthermore, recently, rhodium-catalyzed 1,4-addition reaction of organoboronic acids, organostannanes or organosilanes to α, β-unsaturated carbonyl compounds has also been reported [4]. The mechanism of these reactions was illustrated that the transmetalation with rhodium catalyst and organometallics is followed by 1,4-addition of the rhodium compounds to enones to form rhodium enolates.

We recently tried to apply this methodology to fluoroalkylzinc reagents and found a novel α-trifluoromethylation [5] or α-fluoroalkylation [6] of α, β-unsaturated ketones (**1**) by using Et_2Zn and $RhCl(PPh_3)_3$ (Wilkinson's catalyst) (Scheme 1). In general, the treatment of ketones and alkylhalides (R–X) with a base lead to the corresponding α-alkylated ketones. However, it is difficult to synthesize α-fluoroalkylated ketones by treating ketones with fluoroalkyl halides (R_f–X: **2**) in the presence of a base because the halogen of **2** has a partial positive charge due to the strong electron negativity of fluorine, and it cannot work as a leaving group [7] So, our α-fluoroalkylation reactions are valuable reactions.

As an expansion of our α-fluoroalkylation reaction, we attempted to use silyl enol ethers (**4**) instead of α, β-unsaturated ketones expecting the formation of similar α-fluoroalkylated ketones (**5**) (Scheme 2). Herein, we would like to report the reaction of silyl enol ethers (**4**) with **2** in the presence of a Rh catalyst.

2. Discussion

Recently, we have reported that the reaction of various α, β-unsaturated ketones (**1**) with R_f–X (**2**) in the presence of Et_2Zn and Wilkinson's catalyst gives α-fluoroalkylated ketones (**3**) [5,6]. In this reaction, it seems that a rhodium enolate (**6**) derived from **1** and Rh hydride complex played an important

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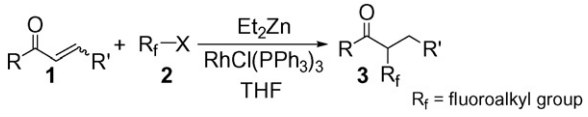
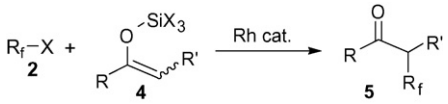


Scheme 1.



Scheme 2.

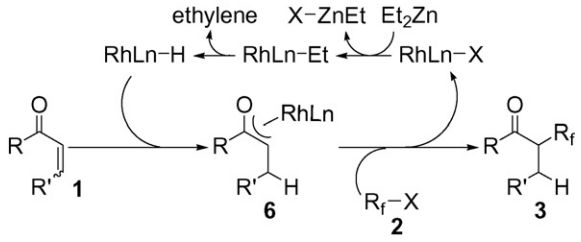


Fig. 1. Reaction mechanism of Rh-catalyzed α-fluoroalkylation of α,β-unsaturated ketones.

role for the oxidative addition and the reductive elimination of **2** (Fig. 1).

So, we expected that α-fluoroalkylated ketones (**5**) could be obtained via a similar rhodium enolate (**7**), if silyl enol ethers (**4**) were used for the reaction instead of **1**. In other words, we expected the generation of **7** by using transmetalation of **4** with a Rh catalyst (Fig. 2).

First, we examined the reaction condition by using the trimethylsilyl enol ether (**4a**) derived from cyclohexanone with $C_{10}F_{21}$–I (**2a**). From the examination of various conditions, we found that the best yield of a product was obtained under the reflux with 10 mol% of $RhCl(PPh_3)_3$ in the 1,4-dioxane.(Table 1) However, further investigations showed that the product was not the objective product (**5a**) but a dehydrofluorinated product (**8a**).

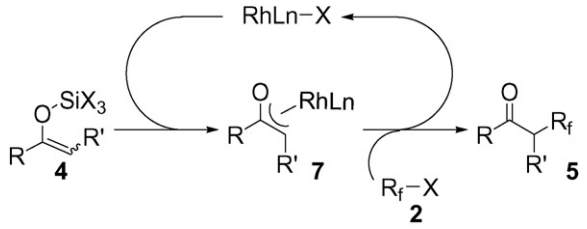
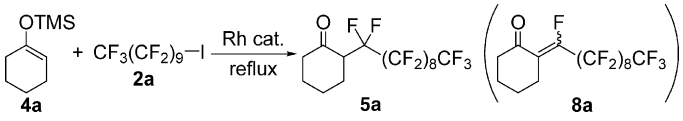


Fig. 2. Expected mechanism of Rh-catalyzed α-fluoroalkylation of ketone silyl enol ethers.

Next, we examined the reaction with various silyl enol ethers as shown in Table 2. The reaction proceeded with aliphatic, aromatic, cyclic or acyclic substrates, although the yield was decreased with crowded substrates (entries 1–7). In this reaction, most substrates gave the dehydrofluorinated product (**8**). We thought that the acidity of the hydrogen atom was increased by the electronic effects of the neibouring carbonyl and R_f groups, and that HF was easily eliminated from **5**. Furthermore, it was found that the dehydrofluorination occurred during the purification with silica gel column chromatography. Namely the ^{1}H NMR of the crude mixture didn't show the peak of the olefinic proton before purification in entry 7. In order to prove this speculation, the crude **5g** was stirred with the silica gel in the same elution solvent (Et_2O:hexane = 5:95), then formation of the dehydrofluorinated product (**8g**) was soon confirmed on GLC and ^{1}H NMR measurement.

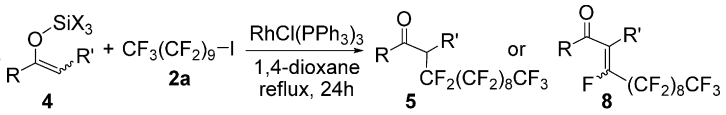
Table 1
Examination of reaction conditions

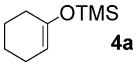
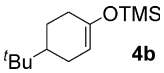
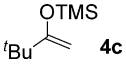
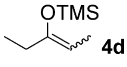
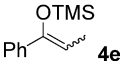
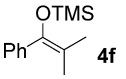
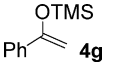
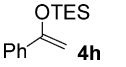
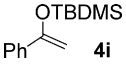
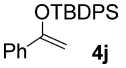
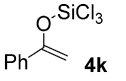


Entry	Rh Catalyst	Ammount of Rh (mol%)	Time (h)	Solvent	Yield[a] of **8a** (%)
1	$RhCl(PPh_3)_3$	2	15	THF	10
2	$Rh(acac)(CO)_2$	2	17	THF	12
3	$Rh_4(CO)_{12}$	2	24	THF	12
4	$[RhCl(cod)]_2$	2	23	THF	No reaction
5	$[RhCl(nbd)]_2$	2	23	THF	No reaction
6	None	None	15	THF	No reaction
7	$RhCl(PPh_3)_3$	2	24	CH_3CN	13
8	$RhCl(PPh_3)_3$	2	24	CH_2Cl_2	10
9	$RhCl(PPh_3)_3$	2	18	Toluene	16
10	$RhCl(PPh_3)_3$	2	21	Et_2O	6
11	$RhCl(PPh_3)_3$	2	22	DME	Trace
12	$RhCl(PPh_3)_3$	2	20	1,4-Dioxane	25
13	$RhCl(PPh_3)_3$	10	21	1,4-Dioxane	39
14	$RhCl(PPh_3)_3$	20	24	1,4-Dioxane	42

[a] Isolated yield.

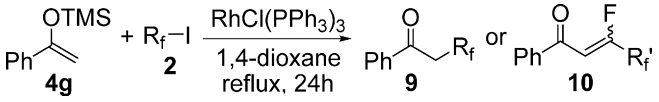
Table 2
Application to the various silyl enol ethers

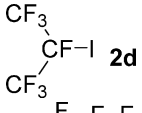
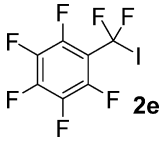


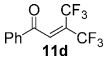
Entry	4	Product	Yield (%)[a]
1	 **4a**	**8a**	39
2	 **4b**	**8b**	28[b]
3	 **4c**	**8c**	37[c]
4	 **4d**	**5d**	32
5	 **4e**	**5e**	46
6	 **4f**	**5f**	13
7	 **4g**	**8g**	53[c]
8	 **4h**	**8g**	44[c]
9	 **4i**	**8g**	43[c]
10	 **4j**	**8g**	14[c]
11	 **4k**	**8g**	20[c]

[a] Isolated yield.
[b] 2:1 mixture of *E*/*Z* products.
[c] *Z*-form was only obtained.

Table 3
Application to the several perfluoroalkyl iodides



Entry	R_f–I	Product	Yield (%)[a]
1	$CF_3(CF_2)_9$–I **2a**	**8g**	53
2[b]	$CF_3(CF_2)_3$–I **2b**	**10b**	37[c]
3[b]	CF_3–I **2c**	**9c**	32
4[b]	 **2d**	**11d**[d]	70
5	 **2e**	**10e**	65[c]

[a] Isolated yield.
[b] In sealed tube.
[c] *Z*-form was only obtained.
[d]  was obtained.

On the other hand, the dehydrofluorination was not found in entries 4–6. This might mean that the methyl group on the α-carbon decreased the acidity of α-hydrogen by the electronic effect or the steric effect. Next, we examined the effect of silyl group as shown in entries 7–11. Also in these cases, the steric hindrance affected the yields.

Finally, we examined the reaction with several fluoroalkyl halides (**2**) (Table 3). The reaction proceeded with all fluoroalkyl halides examined. Interestingly, perfluoroisopropyl iodide (**2d**) and perfluorobenzyl iodide (**2e**) gave the corresponding products in good yields as shown in entries 4 and 5. These results might suggest that the oxidative addition onto rhodium enolate (**7**) and/or the reductive elimination from rhodium complex occurs more easily by the longer carbon–iodine bond owing to the strong electron negativity of the large fluoroalkyl chains. On the other hand, the reaction of perfluorobutyl iodide (**2b**) and trifluoroiodomethane (**2c**) resulted in poor yields (entries 2 and 3). We thought that **2b** or **2c** might be gradually lost from the reaction system ahead of the oxidative addition to the rhodium enolate (**7**) under the reflux condition of 1,4-dioxane, even if a sealed tube was used.

3. Conclusion

We could obtain α-perfluoroalkylated ketones or their dehydrofluorination products by the reaction of silyl enol ethers with perfluoroalkyl halides in moderate yields. We unfortunately have not clarified the mechanism yet, because the possible mechanisms were remained. However, it is no wonder that the rhodium catalyst played an important role, the reason why this reaction did not proceed without the Rh catalyst at all.

4. Experimental

4.1. General

^{1} NMR and ^{13}C NMR spectra were recorded on JNM-GX400 spectrometers. Tetramethylsilane (TMS) was used as an internal standard. ^{19}F NMR spectra were recorded on Hitachi FT-NMR R-1500 and JEOL-ECA-600SN spectrometers. Benzotrifluoride (BTF) was used as an internal standard. Mass spectra were obtained on JEOL JMS-700T spectrometers. IR spectra were recorded on Hitachi 270–30 Infrared spectrophotometer. Gas–liquid chromatography (GLC) was carried out on a Hitachi 263-50 gas chromatograph (column; 5% SE-30 3 mm × 2 m, carrier; N_2 at 30 ml/min). Peak areas were calculated on a Shimadzu C-R5A Chromatopac. Melting points were measured on Yanagimoto micro-melting point apparatus MP-S3. All the solvents were purified by standard procedure under Ar atmosphere, and other commercially available reagents were used without further purification.

4.2. Typical procedure

Under an Ar atmosphere, to a solution of $RhCl(PPh_3)_3$ (92.5 mg, 0.1 mmol) and 1-iodoperfluorodecane (**2a**, 969.0 mg, 1.5 mmol) in 1,4-dioxane (4 mL) was added 1-phenyl-1-trimethylsiloxyethene (**4g**, 0.02 mL, 1.0 mmol), then the mixture was refluxed for 24 h. The solution was quenched with 10% HCl, and extracted with Et_2O. The Et_2O layer was washed with sat. NaCl and dried with $MgSO_4$. The solvent was removed *in vacuo* and purified by column chromatography (SiO_2, Et_2O:hexane = 5:95) to give 3-fluoro-3-perfluorononyl-1-phenylprop-2-en-1-one (**8g**, 330.3 mg, 53%).

4.3. Spectral data

4.3.1. Examination of various silyl enol ethers

*4.3.1.1. 2-(Perfluorodecylidene)cyclohexan-1-one (**8a**).* Colorless crystals; M.p. 69.5–70.5 °C; ^{1}H NMR ($CDCl_3$) δ: 1.83–1.92 (2H, m), 1.92–2.03 (2H, m), 2.54–2.61 (2H, m), 2.62–2.70 (2H, m); ^{19}F NMR (600 MHz, $CDCl_3$) δ: −63.35 to −63.24 (2F, m), −60.61 (2F, m), −59.88 (2F, m), −59.15 to −58.80 (8F, m), −57.77 (1F, m), −51.13 to −51.03 (2F, m), −17.97 (3F, t, *J* = 9.9 Hz); MS *m/z*: 596 (M^+); HRMS Calcd. for $C_{16}H_8F_{20}O$: 596.026 (M^+), Found: 596.026; IR (KBr) cm^{-1}: 1712, 1216, 1154.

*4.3.1.2. 4-tert-Butyl-2-(perfluorodecylidene)cyclohexan-1-one (**8b**) (minor).* Colorless crystals; M.p. 45.0–46.0 °C; ^{1}H NMR ($CDCl_3$) δ: 0.97 (9H, s), 1.56–1.70 (2H m), 2.00–2.10 (1H, m), 2.12–2.21 (1H, m), 2.45–2.56 (1H, m), 2.60–2.67 (1H, m), 3.13–3.20 (1H, m); ^{19}F NMR (600 MHz, $CDCl_3$) δ: −64.17 (1F, m), −63.30 (2F, t, *J* = 12.9 Hz), −59.89 (2F, m), −59.70 to −58.25 (10F, m), −51.75 to −51.10 (1F, m), −50.60 to −49.95 (1F, m), −17.99 (3F, t, *J* = 10.3 Hz); MS *m/z*: 652 (M^+); HRMS Calcd. for $C_{20}H_{16}F_{20}O$: 652.088 (M^+), Found: 652.089; IR (KBr) cm^{-1}: 2980, 1724, 1678, 1216, 1156.

*4.3.1.3. 4-tert-Butyl-2-(perfluorodecylidene)cyclohexan-1-one (**8b**) (major).* Colorless crystals; M.p. 43.0–44.0 °C; ^{1}H NMR ($CDCl_3$) δ: 0.940 (9H, s), 1.52–1.65 (2H, m), 2.00–2.20 (2H, m), 2.41–2.54 (1H, m), 2,64–2.71 (1H, m), 2.98–3.06 (1H, m); ^{19}F NMR (600 MHz, $CDCl_3$) δ: −63.35 to −63.20 (2F, m), −60.49 (2F, m), −59.88 (2F, m), −59.15 to −58.75 (8F, m), −57.74 (1F, m), −51.75 to −51.15 (1F, m), −50.85 to −50.25 (1F, m), −17.97 (3F, m); MS *m/z*: 652 (M^+); HRMS Calcd. for $C_{20}H_{16}F_{20}O$: 652.088 (M^+); Found: 652.087; IR (KBr) cm^{-1}: 2972, 1722, 1218, 1152.

*4.3.1.4. (Z)-5-Fluoro-5-perfluorononyl-2,2-dimethylpent-4-en-3-one (**8c**).* Colorless crystals; M.p. 61.5–62.5 °C; ^{1}H NMR ($CDCl_3$) δ: 1.19 (9H, s), 6.46 (1H, d, *J* = 30.4 Hz); ^{19}F NMR (600 MHz, $CDCl_3$) δ: −63.34 to −63.24 (2F, m), −59.88 (4F, m), −59.15 to −58.85 (8F, m), −55.63 (2F, m), −50.45 to −50.29 (1F, m), −17.97 (3F, t, *J* = 10.2 Hz); MS *m/z*: 598 (M^+); HRMS Calcd. for $C_{16}H_{10}F_{20}O$: 598.041 (M^+), Found: 598.040; IR (KBr) cm^{-1}: 1714, 1654, 1212, 1154.

*4.3.1.5. 2-Perfluorodecylpentan-3-one (**5d**).* Colorless crystals; M.p. 60.5–61.5 °C; ^{1}H NMR ($CDCl_3$) δ: 1.09 (3H, t, *J* = 7.3 Hz), 1.36 (3H, d, *J* = 7.2 Hz), 2.55 (1H, dq, *J* = 18.8, 7.3 Hz), 2.63 (1H, dq, *J* = 18.8, 7.3 Hz), 3.32–3.47 (1H, m); ^{19}F NMR (600 MHz, $CDCl_3$) δ: −63.35 to −63.25 (2F, m), −59.89 (2F, m), −59.20 to −58.70 (10F, m), −57.77 (2F, m), −51.96 to −51.82 (2F, m), −18.01 to −17.95 (3F, m); MS *m/z*: 604 (M^+); HRMS Calcd. for $C_{15}H_9F_{21}O$: 604.032 (M^+), Found: 604.032; IR (KBr) cm^{-1}: 1684, 1208, 1152.

*4.3.1.6. 2-Perfluorodecyl-1-phenylpropan-1-one (**5e**).* Colorless crystals; M.p. 78.0–79.0 °C; ^{1}H NMR ($CDCl_3$) δ: 1.49 (3H, d, *J* = 6.8 Hz), 4.31–4.46 (1H, m), 7.49–7.98 (5H, m); ^{19}F NMR (600 MHz, $CDCl_3$) δ: −63.32 (2F, t, *J* = 14.1 Hz), −59.90 (2F, m), −59.18 to −58.68 (10F, m), −57.83 (1F, d, *J* = 295.3 Hz), −56.92 (1F, d, *J* = 295.3 Hz), −18.04 to −17.97 (3F, m); MS *m/z*: 652 (M^+); HRMS Calcd. for $C_{19}H_9F_{21}O$: 652.032 (M^+), Found: 652.033; IR (KBr) cm^{-1}: 1694, 1228, 1154.

*4.3.1.7. 2-Methyl-2-perfluorodecyl-1-phenylpropan-1-one (**5f**).* Colorless crystals; M.p. 78.5–79.5 °C; ^{1}H NMR ($CDCl_3$) δ: 1.59 (6H, s), 7.39–7.63 (5H, m); ^{19}F NMR (600 MHz, $CDCl_3$) δ: −63.38 to −63.24 (2F, m), −59.90 (2F, m), −59.20 to −58.72 (10F, m), −53.76 (2F, m), −17.98 (3F, m); MS *m/z*: 666 (M^+); HRMS Calcd. for $C_{20}H_{11}F_{21}O$: 666.047 (M^+), Found: 666.047; IR (KBr) cm^{-1}: 1684, 1216, 1154.

*4.3.1.8. (Z)-3-Fluoro-3-perfluorononyl-1-phenylprop-2-en-1-one (**8g**).* Colorless crystals; M.p. 68.0–69.0 °C; ^{1}H NMR ($CDCl_3$) δ: 6.76 (1H, d, J = 32.0 Hz), 7.50–7.96 (5H, m); ^{19}F NMR (600 MHz, $CDCl_3$) δ: −63.29 (2F, m), −59.88 (2F, m), −59.65 (2F, m), −59.20 to −58.7 (9F, m), −55.48 to −55.36 (2F, m), −17.97 (3F, m); MS *m/z*: 618 (M^+); HRMS Calcd. for $C_{18}H_6F_{20}O$: 618.010 (M^+), Found: 618.009; IR (KBr) cm^{-1}: 1702, 1654, 1210, 1152.

4.3.2. Examination of some perfluoroalkyl iodides

*4.3.2.1. (Z)-3-Fluoro-3-perfluoropropyl-1-phenylprop-2-en-1-one (**10b**).* Colorless oil; ^{1}H NMR ($CDCl_3$) δ: 6.75 (1H, d, J = 31.6 Hz), 7.50–7.94 (5H, m); ^{19}F NMR (90 MHz, $CDCl_3$) δ: −64.20 to −63.85 (2F, m), −56.62 to −56.10 (2F, m), −50.00 to −49.05 (1F, m), −17.80 (3F, td, J = 9.1, 2.4 Hz); MS *m/z*: 318 (M^+); HRMS Calcd. for $C_{12}H_6F_8O$: 318.029 (M^+), Found: 318.030; IR (neat) cm^{-1}: 1706, 1674, 1274, 1240, 1192, 1126.

*4.3.2.2. 3,3,3-Trifluoro-1-phenylpropan-1-one (**9c**).* Colorless crystals; M.p. 37.0–38.0 °C; ^{1}H NMR ($CDCl_3$) δ: 3.81 (2H, q, J = 10.0 Hz), 7.48–7.97 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 42.04 (q, J = 28.3 Hz), 123.96 (q, J = 276.8 Hz), 128.26, 128.87, 134.15, 135.67 (q, J = 1.7 Hz), 189.63 (q, J = 2.5 Hz); ^{19}F NMR (60 MHz, $CDCl_3$) δ: 0.78 (3F, t, J = 9.6 Hz); MS *m/z*: 188 (M^+); HRMS Calcd. for $C_9H_7F_3O$: 188.045 (M^+), Found: 188.045; IR (KBr) cm^{-1}: 1690, 1422, 1378, 1286, 1230, 1132, 1104, 758, 688, 624.

*4.3.2.3. 4,4,4-Trifluoro-3-trifluoromethyl-1-phenylbut-2-en-1-one (**11d**).* Colorless oil; ^{1}H NMR ($CDCl_3$) δ: 7.41–7.43 (1H, m), 7.53–7.90 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 119.94 (qq, J = 275.1, 0.9 Hz), 120.22 (qq, J = 273.9, 2.1 Hz), 124.85–126.25 (m), 128.99, 129.12, 134.11 (q, J = 9.0 Hz), 135.07, 139.88–140.12 (m), 189.18; ^{19}F NMR (90 MHz, $CDCl_3$) δ: −1.79 (3F, qd, J = 6.7, 1.3 Hz), 2.73 (3F, q, J = 6.7 Hz); MS *m/z*: 268 (M^+); HRMS Calcd. for $C_{11}H_6F_6O$: 268.032 (M^+), Found: 268.033; IR (neat) cm^{-1}: 1688, 1386, 1286, 1222, 1172.

*4.3.2.4. (Z)-3-Fluoro-3-(pentafluorophenyl)-1-phenylprop-2-en-1-one (**10e**).* Pale yellow crystals; M.p. 98.5–99.5 °C; ^{1}H NMR ($CDCl_3$) δ: 6.60 (1H, d, J = 32.8 Hz), 7.49–7.99 (5H, m); ^{19}F NMR (90 MHz, $CDCl_3$) δ: −97.43 to −96.66 (2F, m), −85.67 (1F, tt, J = 20.7, 4.1 Hz), −75.21 to −74.44 (2F, m), −25.18 (1F, dt, J = 32.8, 19.4 Hz); MS *m/z*: 316 (M^+); HRMS Calcd. for $C_{15}H_6F_6O$: 316.032 (M^+), Found: 316.033; IR (KBr) cm^{-1}: 1688, 1646, 1522, 1502, 1234, 1018, 994.

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