Reaction of *N*,*N*-Dimethylselenocarbamoyl Chloride with Nucleophiles. Preparation of Diselenocarbamates, Selenothiocarbamates, and Selenoureas

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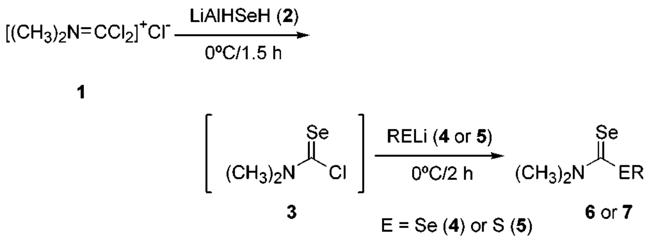
Abstract: Reactions of *N*,*N*-dimethylselenocarbamoyl chloride prepared by using LiAlHSeH with nucleophiles such as lithium alkylselenolate, lithium alkylthiolate, and amines afford the corresponding diselenocarbamates, selenothiocarbamates, and selenoureas. The crystal structure of the *Se*-phenyl *N*,*N*-dimethyldiselenocarbamate was also determined by X-ray diffraction.

The synthesis of compounds bearing a carbon−selenium double bond and their activities have received increasing attention in recent years. The syntheses of many selenocarbonyl compounds have been reported, and the recent reviews detail these studies.[1] Among compounds having a selenocarbonyl group bonded to nitrogen, the syntheses of selenoamides, selenoureas, selenocarbamates, and selenothiocarbamates have often been reported, while the synthesis of diselenocarbamates have rarely been reported. Recently, we confirmed that the reaction of lithium aluminum hydride (1 equiv) with elemental selenium (1 equiv) in THF gave LiAlHSeH and hydrogen gas quantitatively. The use of the obtained LiAlHSeH can afford a wide range of selenium-containing compounds, including diselenocarbamates.[2] Herein, we report the reaction of *N*,*N*-dimethylselenocarbamoyl chloride prepared by using LiAlHSeH with nucleophiles such as lithium alkylselenolate, lithium alkylthiolate, and amines to afford the corresponding diselenocarbamates, selenothiocarbamates, and selenoureas. The crystal structure of the *Se*-phenyl *N*,*N*-dimethyldiselenocarbamate was also determined by X-ray diffraction. Although the synthesis of *S*-alkyl selenothiocarbamates has been described,[1b] to our knowledge, this is the first reported crystal structure and characterization of an *Se*-alkyl diselenocarbamate.

Scheme 1



Dichloromethylenedimethyliminium chloride $[Cl_2C{=}N(CH_3)_2]^+Cl^-$ **1** was added to an anhydrous THF solution of LiAlHSeH **2**.[2] *N*,*N*-Dimethylselenocarbamoyl chloride $(CH_3)_2NC({=}Se)Cl$ **3** was readily prepared in situ. The reaction mixture was stirred at 0 °C for 1.5 h. This solution was added to the solution of $PhSe^-Li^+$ **4a** (1.0 equiv), which was prepared by the reaction of lithium aluminum hydride (1.2 equiv) with diphenyl diselenide (0.5 equiv) in dry THF at 0 °C under an argon atmosphere. The reaction mixture was stirred at 0 °C for 2 h. After workup, *Se*-phenyl *N*,*N*-dimethyldiselenocarbamate **6a** was obtained as yellow crystals in a 95% yield (Scheme 1). Reactions of **3** with other lithium alkylselenolates **4** also gave the corresponding *N*,*N*-dimethyldiselenocarbamates **6** in 51−83% yields. Similarly, the reactions with lithium alkylthiolates **5** afforded the corresponding *S*-alkyl *N*,*N*-dimethylselenothiocarbamates **7a** and **7b** in 74 and 66% yields, respectively (Table 1). Though there is one example of the synthesis of *S*-alkyl *N*,*N*-dimethylselenothiocarbamate **7**,[1b] the syntheses of *Se*-diselenocarbamates have never been reported.

The ^{77}Se NMR spectra of **6** and **7** afforded the chemical shifts shown in Table 1. The chemical shifts of two selenium atoms of **6** and that of **7** are at higher fields than those of selenoketones (δ > 1600 ppm) and selenothioic acids (δ 1420−1640 ppm),[3] but at lower fields than those of selenoureas (δ 180−360 ppm).[1k] The selenoamides, telluroamides, and benzanilides show a partial double-bond character in the C−N bond, owing to delocalization of the lone pair electrons on nitrogen to the C═Se, C═Te, or C═O bond.[4] The chemical shifts of

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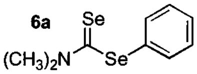
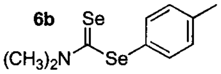
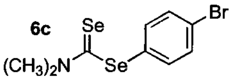
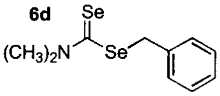
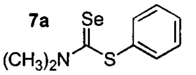
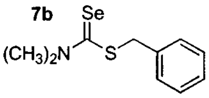
Table 1. Synthesis of Diselenocarbamates and Selenothiocarbamates

entry	carbamate	yield (%)[a]	^{77}Se NMR[b] δ (ppm)
1	**6a** 	95	670.5, 727.5
2	**6b** 	83	663.5, 716.9
3	**6c** 	56	660.0, 720.5
4	**6d** 	51	606.6, 644.5
5	**7a** 	74	607.5
6	**7b** 	66	547.8

[a] Isolated yield. [b] In $CDCl_3$.

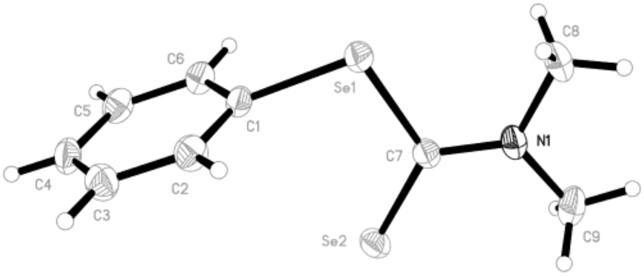
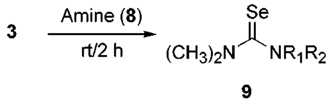


Figure 1. ORTEP diagram (50% thermal ellipsoids) of compound **6a**.

Table 2. Selected Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) for Compound 6a

C1−Se1	1.919(4)
Se1−C7	1.939(4)
C7−N1	1.326(5)
C7−Se2	1.816(4)
C1−Se1−C7	100.32(16)
N1−C7−Se2	124.1(3)
N1−C7−Se1	113.0(3)
Se2−C7−Se1	122.8(2)
C7−N1−C9	120.9(3)
C7−N1−C8	123.0(3)
C9−N1−C8	116.0(3)
C1−Se1−C7−N1	−176.85(0.27)
C1−Se1−C7−Se2	3.12(0.24)
Se1−C7−N1−C9	179.15(0.30)
Se2−C7−N1−C9	−0.81(0.50)

Scheme 2



selenium atoms of **6** and **7** are explained by this notion. The X-ray crystal structure of **6a** was carried out to characterize the structure of diselenocarbamate. An ORTEP drawing, depicted in Figure 1, shows the molecular structure of the *Se*-phenyl *N*,*N*-dimethyldiselenocarbamate **6a**. The selected bond lengths, bond angles, and torsion angles for **6a** are listed in Table 2. The two bond lengths, 1.816(4) (Se2−C7) and 1.939(4) (Se1−C7) Å, between selenium and carbon in **6a** are intermediate of those for the Se−C single (1.98 Å) and double bonds (1.67 Å).[5] The bond length of C7−N1 (1.326(5) Å) in **6a** is shorter than that of the normal carbon−nitrogen single bond and is similar to selenoamides, selenoformamides, and selenoureas.[1,4e,f] The bond lengths of Se2−C7 and C7−N1 are consistent with the delocalization of the lone pair electrons on N1 to the Se2−C7. The downfield of the chemical shift of Se2 in **6** in the ^{77}Se NMR spectra could be similarly explained. The sum of the three angles around the C7 is 359.9°. It is consistent with Se2, C7, N1, Se1, and C1 atoms nearly lying almost in the same plane owing to the the double-bond character of the C7−N1 bond. The bond length and the double-bond character of the selenocarbonyl group adjacent to nitrogen are most affected by the nitrogen, but are hardly influenced by the oxygen, sulfur, and selenium atoms adjacent to the selenocarbonyl group.[1n] This notion also applies to the case of the *Se*-phenyl *N*,*N*-dimethyldiselenocarbamate **6a**. Although the normal bond angle of noncyclic C−Se−C is reported to be 98°,[6] in **6a**, this bond angle is 100.32(16)°. The increased bond angle in **6a** might be due to the steric repulsion between the bulky selenium atom and hydrogen of the aromatic ring (see Supporting Information).

The trapping of **3** with various amines **8** also afforded the corresponding selenoureas **9** (Scheme 2). The results of reactions of **3** with various primary and secondary amines **8** are summarized in Table 3. The yields of the reactions using secondary amines **8a**−**d** were relatively higher than those using primary amines **8e**−**g**. Differences in the chemical shifts of C═Se in **9a**−**d** (δ 336.2 ± 20.3) and **9e**−**g** (δ 177.7 ± 7.7) were observed in the ^{77}Se NMR spectra. In conclusion, *Se*-phenyl *N*,*N*-dimethyldiselenocarbamates **6** were synthesized by reacting *N*,*N*-dimethyl selenocarbamoyl chloride $(CH_3)_2NC({=}Se)Cl$ **3** with lithium alkylselenolates **4** and the crystal structure of **6a** was determined.

Experimental Section

General. Tetrahydrofuran was distilled from sodium-benzophenone immediately prior to use. The ^{77}Se chemical shifts were expressed in parts per million deshielded with respect to neat Me_2Se, added as an external standard, in $CDCl_3$.

***N*,*N*-Dimethylselenocarbamoyl Chloride $(CH_3)_2NC({=}Se)Cl$ (3).** *N*,*N*-Dimethylselenocarbamoyl chloride $(CH_3)_2NC({=}Se)Cl$ **3** could not be purified by flash chromatography on silica gel and recrystallization because it easily decomposed. However, the reaction proceeded quantitatively; the concentrate of the reaction mixture gave reasonable spectral data. ^{1}H NMR ($CDCl_3$): δ 3.48 (3H, s), 3.62 (3H, s). ^{13}C NMR ($CDCl_3$): δ 45.6, 48.8, 174.4. ^{77}Se NMR ($CDCl_3$): δ 715.5. MS (CI) *m*/*z*: 172 [M$^+$ + 1].

***Se*-Phenyl *N*,*N*-Dimethyldiselenocarbamate (6a).** To anhydrous THF solution (10 mL) of LiAlHSeH **2** (2.0 mmol) was added dichloromethylenedimethyliminium chloride **1** (0.32 g, 2.0 mmol) at 0 °C under an argon atmosphere. The reaction mixture was stirred at 0 °C for 1.5 h. This solution was added to the

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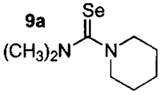
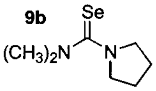
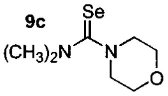
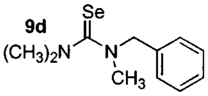
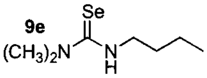
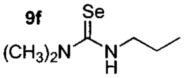
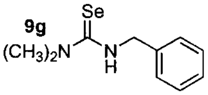
Table 3. Synthesis of Selenoureas

selenourea	yield (%)[a]	^{77}Se NMR[b] δ (ppm)
9a 	95	333.0
9b 	93	310.7
9c 	80	359.7
9d 	75	341.5
9e 	55	170.8
9f 	34	176.2
9g 	27	186.0

[a] Isolated yield. [b] In $CDCl_3$.

solution of $PhSe^-Li^+$ **4a** (1.0 mmol), which was prepared by the reaction of lithium aluminum hydride (0.046 g, 1.2 mmol) with diphenyl diselenide (0.16 g, 0.5 mmol) in dry THF (10 mL) at 0 °C under an argon atmosphere. The reaction mixture was stirred at 0 °C for 2 h. The mixture was extracted with dichloromethane (100 mL) and washed with water (30 mL). The organic layer was dried over sodium sulfate and evaporated to dryness. The residue was purified by flash chromatography on silica gel with dichloromethane to yield 0.28 g of **6a** (95%) by flash chromatography on silica gel as yellow crystals. Mp: 126.4−127.3 °C. ^{1}H NMR ($CDCl_3$): δ 3.43 (3H, s), 3.65 (3H, s), 7.43 (2H, t, J = 7.2 Hz), 7.49 (1H, t, J = 7.2 Hz), 7.58 (2H, d, J = 8.4 Hz). ^{13}C NMR ($CDCl_3$): δ 44.9, 49.6, 129.3, 129.8, 132.2, 137.7 196.8. ^{77}Se NMR ($CDCl_3$): δ 670.5, 725.5. MS (CI) m/z: 294 [M^+ + 1]. HRMS m/z: 292.9221 calcd for $C_9H_{11}NSe_2$, found 292.9236. Anal. Calcd for $C_9H_{11}NSe_2$: C, 37.13; H, 3.81; N, 4.81. Found: C, 37.02; H, 3.66; N, 4.82.

***Se*-(4-Methylphenyl) *N,N*-Dimethyldiselenocarbamate (6b).** Compound **6b** was prepared following the same procedure as **6a** except using 4-$MePhSe^-Li^+$ **4b** (1.0 mmol). Compound **6b** (0.25 g, 83%) was obtained by flash chromatography on silica gel as yellow crystals. Mp: 92.6−93.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.40 (3H, s), 3.42 (3H, s), 3.65 (3H, s), 7.24 (2H, d, J = 8.0 Hz), 7.46 (2H, d, J = 8.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.4, 44.8, 49.6, 128.8, 130.2, 137.5, 140.0, 197.4. ^{77}Se NMR (76 MHz, $CDCl_3$): δ 663.5, 716.9. MS (CI) m/z: 308 [M^+ + 1]. HRMS m/z: 306.9378 calcd for $C_{10}H_{13}NSe_2$, found 306.9358. Anal. Calcd for $C_{10}H_{13}NSe_2$: C, 39.36; H, 4.19; N, 4.59. Found: C, 39.16; H, 4.16; N, 4.61.

***Se*-(4-Bromophenyl) *N,N*-Dimethyldiselenocarbamate (6c).** Yield: 56% (0.21 g). Mp: 116.2−117.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.43 (3H, s), 3.65 (3H, s), 7.42 (2H, d, J = 8.0 Hz), 7.55 (2H, d, J = 8.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 44.8, 49.7, 124.9, 131.0, 132.6, 139.3, 195.9. ^{77}Se NMR (76 MHz, $CDCl_3$): δ 680.0, 720.5. MS (CI) m/z: 372 [M^+ + 1]. Anal. Calcd for $C_9H_{10}NSe_2Br$: C, 29.22; H, 2.72; N, 3.79. Found: C, 29.21; H, 2.70; N, 3.77.

***Se*-Benzyl *N,N*-Dimethyldiselenocarbamate (6d).** Yield: 51% (0.16 g). Mp: 62.4−62.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.33 (3H, s), 3.68 (3H, s), 4.66 (2H, s), 7.23−7.43 (5H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 43.7, 44.3, 49.3, 127.4, 128.6, 129.3, 136.4, 196.2. ^{77}Se NMR (76 MHz, $CDCl_3$): δ 606.6, 644.6. MS (CI) m/z: 308 [M^+ + 1]. Anal. Calcd for $C_{10}H_{13}NSe_2$: C, 39.36; H, 4.29; N, 4.59. Found: C, 39.30; H, 4.18; N, 4.62.

***S*-Phenyl *N,N*-Dimethylselenothiocarbamate (7a).** Yield: 74% (0.19 g). Mp: 84.5−85.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.45 (3H, s), 3.66 (3H, s), 7.43−7.52 (5H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 43.0, 49.6, 128.9, 130.1, 132.9, 136.8, 199.5. ^{77}Se NMR (76 MHz, $CDCl_3$): δ 607.5. MS (CI) m/z: 246 [M^+ + 1]. Anal. Calcd for $C_9H_{11}NSSe$: C, 44.26; H, 4.54; N, 5.74. Found: C, 44.20; H, 4.41; N, 5.77.

***S*-Benzyl *N,N*-Dimethylselenothiocarbamate (7b).** Yield: 65% (0.17 g). Mp: 47.2−47.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.31 (3H, s), 3.67 (3H, s), 4.62 (2H, s), 7.24−7.41 (5H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 42.5, 46.4, 49.1, 127.5, 128.5, 129.2, 135.2, 198.3. ^{77}Se NMR (76 MHz, $CDCl_3$): δ 547.9. MS (CI) m/z: 260 [M^+ + 1]. Anal. Calcd for $C_{10}H_{13}NSSe$: C, 46.51; H, 5.07; N, 5.42. Found: C, 46.35; H, 4.91; N, 5.55.

1-(*N,N*-Dimethylselenocarbamoyl)piperidine (9a). Dichloromethylenedimethyliminium chloride **1** (0.16 g, 1.0 mmol) was added to an anhydrous THF solution (10 mL) of LiAlHSeH **2** (1.0 mmol) at 0 °C under an argon atmosphere. The reaction mixture was stirred at 0 °C for 1.5 h. To the solution was added piperidine **8a** (0.40 mL, 4.0 mmol), and was the mixture was stirred at room temperature for 2 h. The mixture was extracted with dichloromethane (100 mL) and washed with water (30 mL). The organic layer was dried over sodium sulfate and evaporated to dryness. The residue was purified by flash chromatography on silica gel with dichloromethane to give **9a** 0.20 g (95%) as a yellow oil. IR (KBr): 1506 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.66 (6H, m), 3.18 (6H, s), 3.52 (4H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.2, 25.7, 44.7, 54.0, 194.7. ^{77}Se NMR (76 MHz, $CDCl_3$): δ 333.0. MS (CI) m/z: 221 [M^+ + 1]. Anal. Calcd for $C_8H_{16}N_2Se$: C, 43.84; H, 7.36; N, 12.78. Found: C, 43.88; H, 7.41; N, 12.54.

1-(*N,N*-Dimethylselenocarbamoyl)pyrrolidine (9b). Yield: 93% (0.19 g). Mp: 46.2−46.4 °C. IR (Neat): 1508 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.94 (4H, m), 3.156 (3H, s), 3.162 (3H, s), 3.65 (4H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.4, 44.4, 54.8, 188.8. ^{77}Se NMR (76 MHz, $CDCl_3$): δ 310.8. MS (CI) m/z: 207 [M^+ + 1]. Anal. Calcd for $C_7H_{14}N_2Se$: C, 40.98; H, 6.88; N, 13.65. Found: C, 41.12; H, 6.94; N, 13.61.

4-(*N,N*-Dimethylselenocarbamoyl)morpholine (9c). Yield: 80% (0.18 g). Mp: 44.2−45.4 °C. IR (KBr): 1522 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.22 (6H, s), 3.59 (4H, t, J = 4.8 Hz), 3.76 (4H, t, J = 4.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 44.6, 53.1, 66.2, 195.3. ^{77}Se NMR (76 MHz, $CDCl_3$): δ 359.7. MS (CI) m/z: 223 [M^+ + 1]. Anal. Calcd for $C_7H_{14}N_2OSe$: C, 38.02; H, 6.38; N, 12.67. Found: C, 38.18; H, 6.44; N, 12.51.

***N*-Benzyl-*N,N′,N′*-trimethylselenourea (9d).** Yield: 75% (0.19 g). IR (Neat): 1508 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.93 (3H, s), 3.19 (6H, s), 4.93 (2H, s), 7.26−7.36 (5H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 41.9, 44.8, 60.9, 127.4, 127.7, 128.5, 136.4, 195.3. ^{77}Se NMR (76 MHz, $CDCl_3$): δ 341.6. MS (CI) m/z: 257 [M^+ + 1]. Anal. Calcd for $C_{11}H_{16}N_2Se$: C, 51.77; H, 6.32; N, 10.98. Found: C, 51.75; H, 6.33; N, 10.95.

***N*-Butyl-*N′,N′*-dimethylselenourea (9e).** Yield: 55% (0.11 g). IR (Neat): 1546 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.95 (3H, t, J = 7.2 Hz), 1.37 (2H, m), 1.64 (2H, quinted, J = 7.6 Hz), 3.34 (6H, s), 3.71 (2H, q, J = 6.8 Hz), 5.99 (1H, br s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.3, 19.5, 31.0, 41.5, 48.1, 179.5. ^{77}Se NMR (76 MHz, $CDCl_3$): δ 170.8. MS (CI) m/z: 209 [M^+ + 1]. Anal. Calcd for $C_7H_{16}N_2Se$: C, 40.58; H, 7.78; N, 13.52. Found: C, 40.44; H, 7.55; N, 13.55.

***N,N*-Dimethy-*N′*-propylselenourea (9f).** Yield: 26% (0.05 g). IR (Neat): 1547 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.97 (3H, t, J = 7.2 Hz), 1.68 (2H, m), 3.34 (6H, s), 3.69 (2H, m), 5.72 (1H, br s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.3, 22.6, 41.9, 50.6, 180.4. ^{77}Se NMR (76 MHz, $CDCl_3$): δ 176.2. MS (CI) m/z: 195 [M^+ + 1]; Anal. Calcd for $C_6H_{14}N_2Se$: C, 37.31; H, 7.31; N, 14.50. Found: C, 37.28; H, 7.24; N, 14.44.

***N*-Benzyl-*N′,N′*-dimethylselenourea (9g).** Yield: 35% (0.09 g). Mp: 98.3−98.8C. IR (KBr): 1553 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.23 (6H, s), 4.86 (2H, d, J = 4.8 Hz), 5.85 (1H, br s), 7.21−7.27 (5H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 41.9, 52.8, 127.5, 127.7, 128.6, 137.5, 180.7. ^{77}Se NMR (76 MHz, $CDCl_3$): δ186.0. MS (CI) m/z: 243 [M^+ + 1]. Anal. Calcd for $C_{10}H_{14}N_2Se$: C, 49.80; H, 5.85; N, 11.61. Found: C, 49.75; H, 5.77; N, 11.84.

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Supporting Information Available: Complete tables of crystallographic data, structure-refinement parameters, final atomic coordinates and equivalent isotropic thermal parameters, bond distances, bond angles, torsion angles, and an ORTEP figure of **6a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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