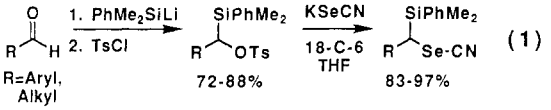
Synthesis of Selenocyanates via Cyanoselenation of Organocopper Reagents

Peter T. Meinke, Grant A. Krafft,* and Anil Guram

Department of Chemistry, Syracuse University, Syracuse, New York 13244

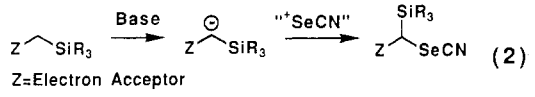
Received November 10, 1987

Recently, we described the synthesis of aryl and alkyl selenoaldehydes by fluoride-induced elimination of α-silyl selenocyanates and their cycloaddition reactions with cyclopentadiene.[1,2] The α-silyl selenocyanates had been prepared via the silyl anion/selenocyanate displacement route shown in eq 1. In order to extend our studies of



(1)

selenoaldehydes to more highly functionalized selenocarbonyl compounds, it was necessary to develop an alternative synthesis of α-silyl selenocyanates compatible with most electron-withdrawing functional groups. A reasonable approach involved incorporation of an electrophilic selenocyanate source into carbanions stabilized by electron-withdrawing substituents, as illustrated in eq 2. Successful development of this strategy was central to

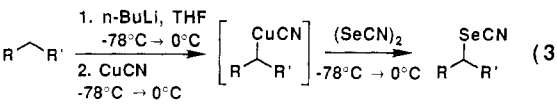


(2)

studies in our laboratory involving other unusual species containing the carbon–selenium double bond such as selenoketones,[3] selenoketenes,[4] and selenocumulenes, the syntheses of which required precursors available most efficiently by incorporation of electrophilic, rather than nucleophiliic, selenocyanate.

Initial experiments involving treatment of lithium enolates or lithium carbanions with selenocyanogen [$(SeCN)_2$] failed to provide desired selenocyanates in synthetically useful yields. The major identifiable product of the multicomponent reactions involving lithium carbanions was the corresponding nitrile, resulting from nucleophilic attack at the cyanide carbon, rather than the selenium atom. Similar results also were obtained from corresponding Grignard reagents.

In order to attenuate the carbanion reactivity, lower order cyanocuprates[5] were prepared by treatment of the corresponding lithium anions with copper(I) cyanide in THF. Addition of these cyanocuprates to 2.0 equiv of selenocyanogen[6,7] at −78 °C resulted in efficient generation of the desired selenocyanates, as illustrated in eq 3. A

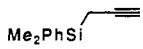
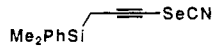
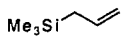
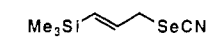
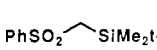
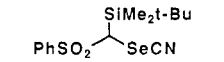
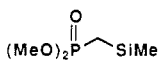
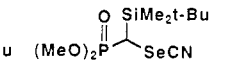
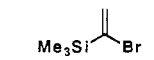
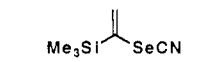
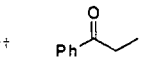
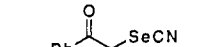
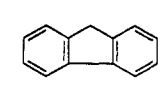
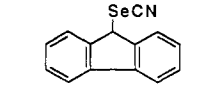
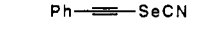
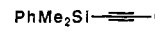
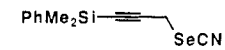


(3)

variety of selenocyanates, including aryl and aliphatic derivatives (Table I), were prepared by this route in good to excellent yields. The vinylic α-silyl selenocyanate **2e** and the alkynyl selenocyanates **2a** also were prepared, in anticipation of their conversion to selenoketenes and selenocumulenes, respectively.

The α-selenocyanate derived from allyltrimethylsilane (**1b**) was sought as a precursor to the unknown seleno-

Table I

Entry	Precursor (1)	Selenocyanate (2)	Yield (%)
a			65
b			70
c			81
d			73
e†			64
f††			68
g			79
h			71
i	PhLi	PhSeCN	77
j	n-BuLi	n-BuSeCN	61
k			75

†The lithium carbanion was prepared by halogen–metal exchange with *n*-BuLi. ††The lithium enolate was prepared with lithium diisopropylamide under standard conditions.

acrolein; however, reaction of the allyltrimethylsilane cyanocuprate with selenocyanogen resulted in selenocyanate incorporation exclusively at the γ-position. This result was not entirely unexpected; however, the resulting selenocyanate **2b** was useless as a selenoacrolein precursor. The lithium and Grignard reagents derived from allyltrimethylsilane also were prepared and treated with selenocyanogen. Neither reagent provided any of the desired α-silyl selenocyanate product, although the Grignard reagent did provide small quantities (<30%) of α-(trimethylsilyl)allyl cyanide, the result of attack by the α-carbon on the nitrile carbon of selenocyanogen. Treatment of the propargylic cuprate derived from 1-(dimethylphenylsilyl)propyne (**1k**) with selenocyanogen led to the formation of **2k** in 75% yield, and a 17% yield of the allene 1-(dimethylphenylsilyl)-1-selenocyanato-1,2-propadiene, which resulted from cyanoselenation at the α-position.

In several instances, this methodology did not produce isolable selenocyanates, though these failed cases involved generation of products that may have been unstable. For instance, repeated attempts to incorporate "+SeCN" into

* Author to whom correspondence should be addressed at Department AP9A, 9MN, Abbott Laboratories, Abbott Park, IL 60064.

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(4) Unpublished results.
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(7) Two equivalents of $(SeCN)_2$ was used to ensure effective trapping of the carbanions.

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the cuprate derived from Me_3SiCH_2CN were unsuccessful, and substitution of the trimethylsilyl group by the more sterically demanding dimethylphenylsilyl or *tert*-butyldimethylsilyl group also failed to produce the desired α-silyl selenocyanate. Cyanoselenation of $MePh_2SiCH_2CO_2Et$[8,9] was unsuccessful, resulting in rapid formation of $MePh_2SiOH$, the sole characterizable product from the complex reaction mixture. The α-cyanocuprate of phenyl ethyl sulfoxide reacted rapidly with selenocyanogen at −78 °C but generated a complex multicomponent product mixture that did not contain identifiable selenocyanate.

Several other electrophilic sources of selonocyanate also were examined, including *N*-selenocyanatosuccinimide, *N*-selenocyanatotetrachlorophthalimide, *N*-selenocyanatophthalimide, and $Cu^{II}Br_2$·KSeCN.[10] Each of these species reacted with organocuprates to generate the desired selenocyanates; however, yields from reactions involving these selenocyanate sources were poor, and purification from byproducts was difficult. The marked insolubility of these other electrophilic selenocyanate sources undoubtedly contributed to inefficient reaction and complex reaction mixtures. Consequently, selenocyanogen was selected as the optimal cyanoselenation reagent. Contrary to a number of published reports,[6] selenocyanogen was easily prepared, simple to handle in solution with anhydrous solvents such as ether or THF, and did not decompose significantly even after 12 h at −32 °C. Furthermore, solutions of electrophilic selenocyanogen reacted rapidly and efficiently at −78 °C with all types of cyanocuprates evaluated in this study.

The identity of the product selenocyanates was verified by NMR, mass spectral data, and the characteristic selenocyanate C≡N infrared stretch (2149–2170 cm^{-1}). Further structural confirmation for **2a–g** was obtained by their successful conversion to selenocarbonyl compounds.[2-4]

Conclusions. The methodology described in this paper facilitates the efficient preparation of a variety of functionalized selenocyanates, which have become important precursors to highly reactive and elusive species containing the carbon–selenium double bond. Application of this chemistry will lead to further investigations into the synthesis and reactivity of new and interesting selenocarbonyl compounds, which will be the subject of subsequent reports from our laboratory.

Experimental Section

General. ^1H and ^{13}C NMR spectra were recorded on a General Electric QE-300 (300 MHz) spectrometer in deuteriochloroform with chloroform (δ = 7.26) or tetramethylsilane (δ = 0.00) as the internal standard. Chemical shifts are given in ppm (δ); multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quadruplet), m (multiplet), or br (broadened). Infrared spectra were obtained on an IBM IR/32 Fourier transform spectrophotometer. Peaks are reported in cm^{-1} with the following relative intensities: s (strong, 67–100%), m (medium, 33–66%), w (weak, 0–35%). Mass spectra were obtained on a Finnigan 4000 quadrupole spectrometer in the Department of Chemistry, State University of New York, School of Environmental Science and Forestry, Syracuse, NY. Ionization was achieved by electron impact (10–70 eV) after sample introduction by direct inlet or GC (Finnigan GLC 950) on a 30 m × 0.2 mm i.d. DB-1 capillary column. Data are reported in the form *m/e* (intensity relative to base peak = 100). TLC was performed on Merck silica gel plates with QF-254 indicator. Visualization was accomplished with iodine, phosphomolybdic acid, anisaldehyde stain, or UV light. Silica gel chromatography was performed on Baker flash silica gel (32–60 μm) by the method of Still.[11] Solvents for extraction and chromatography were reagent grade or better. Anhydrous tetrahydrofuran and diethyl ether were distilled from sodium. Dichloromethane was refluxed and distilled from calcium hydride. All other reagents were ACS reagent grade or better and used as purchased. All reactions were performed in oven- or flame-dried glassware under an atmosphere of dry N_2.

Selenocyanogen. To a solution containing 3.40 g (16 mmol) of anhydrous AgSeCN (dried at 1 Torr/60 °C/24 h) in 20 mL of THF at 0 °C was added directly 2.02 g (8 mmol) of I_2. The mixture was stirred at 0 °C for 30 min until a clear, bright yellow solution was obtained. The reaction was then cooled to −78 °C, filtered through a glass frit in vacuo, and collected in a flask maintained at −78 °C.

General Procedure for Organocopper-Mediated Cyanoselenations. (Dimethyl-*tert*-butylsilyl)selenocyanatomethyl Phenyl Sulfone (2c). To a solution containing 1.00 g (3.70 mmol) of (*tert*-butyldimethylsilyl)methyl phenyl sulfone (**1c**) in 15 mL of THF at −78 °C was added dropwise 1.55 mL (3.90 mmol) of 2.5 M *n*-BuLi. After 30 min at −78 °C followed by 15 min at 0 °C, the reaction was again cooled to −78 °C and transferred via cannula to a solution containing 358 mg (4.00 mmol) of anhydrous CuCN (dried at 120 °C/1 Torr/24 h) in 20 mL of THF. The reaction mixture was warmed to 0 °C, solubilizing virtually all of the CuCN after 45 min. This solution was added via cannula at 0 °C to the selenocyanogen solution, which was maintained at −78 °C over a period of 15 min. The solution was warmed to room temperature and stirred for 1 h, diluted with pentane (50 mL), and filtered through a 3-in. silica gel plug. The solvent was evaporated, and the product was obtained in 81% yield (1.12 g) after purification to homogeneity on silica gel (25:1:1 hexanes–CH_2Cl_2–Et_2O as eluent).

^1H NMR (300 MHz, $CDCl_3$, δ): 7.55–7.96 (m, 5 H, ArH), 3.99 (s, 1 H, –CHSeCN), 1.06 (s, 9 H, $-C(CH_3)_3$), 0.53 (s, 3 H, $-SiCH_3$), 0.34 (s, 3 H, $-SiCH_3$). ^{13}C APT NMR (75 MHz, $CDCl_3$, δ): 137.76 (neg, 1 C), 134.37 (pos), 129.33 (pos), 99.75 (neg, 1 C, –SeCN), 51.82 (pos, 1 C, –CHSeCN), 26.69 (pos, 3 C, $-C(CH_3)_3$), 18.02 (neg, 1 C, $-C(CH_3)_3$), −3.83 (pos, 1 C, $-SiCH_3$), −5.27 (pos, 1 C, $-SiCH_3$). FTIR (film, KBr, cm^{-1}): 2934 vs, 2158 m, 1468 m, 1306 vs, 1140 vs, 760 s. MS (chemical ionization, methane): calcd for $C_{14}H_{21}NO_2SSeSi$ 375, found 376. Exact mass: 375.02262 (calculated), 375.02231 (found).

3-(Dimethylphenylsilyl)-1-selenocyanato-1-propyne (2a). This compound was isolated as a pale yellow oil in 65% yield from the reaction of the cyanocuprate of **1a** with selenocyanogen.

^1H NMR (300 MHz, $CDCl_3$, δ): 7.63–7.41 (m, 5 H), 2.02 (s, 2 H), 0.045 (s, 6 H, $-SiMe_2-$). ^{13}C APT NMR (75 MHz, $CDCl_3$, δ): 138.28 (pos, 1 C), 137.87 (pos, 1 C), 101.55 (neg, 1 C, –SeCN), 33.58 (neg, 1 C), −1.53 (pos, 3 C, $-SiMe_3$). FTIR (film, KBr, cm^{-1}): 2957 w, 2187 s (C≡C), 2149 s (C≡N), 1427 m, 1252 s, 1115 s, 816 m. MS: 279, 241, 173, 137, 136, 135 (base peak), 115, 57. Exact mass: 278.99817 (calculated), 278.9997 (found).

1-Selenocyanato-3-(trimethylsilyl)prop-3-ene (2b). This compound was isolated as a pale yellow oil in 70% yield (152 mg) from the reaction of the cyanocuprate of **1b** with selenocyanogen.

^1H NMR (300 MHz, $CDCl_3$, δ): 5.95–6.18 (m, 2 H), 3.68 (d, J = 7.0 Hz, 2 H), 0.09 (s, 9 H, $-SiMe_3$). ^{13}C APT NMR (75 MHz, $CDCl_3$, δ): 138.28 (pos, 1 C), 137.87 (pos, 1 C), 101.55 (neg, 1 C, –SeCN), 33.58 (neg, 1 C), −1.53 (pos, 3 C, $-SiMe_3$). FTIR (NaCl, film, cm^{-1}): 2957 m, 2168 s, 1591 m, 1427 s, 1252 s, 1115 s, 999 m, 816 s. MS: 219 (molecular ion), 204, 193, 176, 164, 150, 139, 120, 113, 97, 85, 73 (base peak), 59. Exact mass: 218.99817 (calculated), 218.9966 (found).

Dimethyl (Selenocyanato(dimethyl-*tert*-butylsilyl)methyl)phosphonate (2d). This compound was isolated as a viscous yellow oil in 73% yield (1.23 g) from the reaction of the α-cyanocuprate of **1d** with selenocyanogen.

^1H NMR (300 MHz, $CDCl_3$, δ): 3.83 (d, J = 11.4 Hz, 3 H, $-OCH_3$), 4.78 (d, J = 10.7 Hz, 3 H, $-OCH_3$), 2.80 (d, J = 15.9 Hz, 1 H, –CHSeCN), 0.97 (s, 9 H, $-C(CH_3)_3$), 0.26 (s, 3 H, $-SiCH_3$),

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0.15 (s, 3 H, $-SiCH_3$). ^{13}C APT NMR (75 MHz, $CDCl_3$, δ): 101.81 (neg, 1 C, -SeCN), 53.52 (pos, d, 1 C, $-OCH_3$), 53.42 (pos, d, 1 C, $-OCH_3$), 26.51 (pos, 3 C, $-C(CH_3)_3$), 20.32 (pos, d, 1 C, -CHSeCN), 17.80 (neg, 1 C, $-C(CH_3)_3$), -4.76 (pos, 1 C, $-SiCH_3$), -6.37 (pos, 1 C, $-SiCH_3$). FTIR (film, KBr, cm^{-1}): 2860 vs, 2152 m, 1471 s, 1250 vs, 1034 vs, 841 vs. MS (chemical ionization, methane): calcd for $C_{10}H_{22}NO_3PSeSi$ 343, found 344. Exact mass: 343.02704 (calculated), 343.0278 (found).

1-Selenocyanato-1-(trimethylsilyl)ethene (2e). The lithium anion was prepared by addition of 1.1 equiv of *n*-BuLi to a solution of 1-(trimethylsilyl)-1-bromoethene in THF at -78 °C. After stirring for 1 h, the vinyllithium reagent was added to CuCN in THF at -78 °C, and the remainder of the reaction was carried out as described above. Compound **2e** was isolated in 64% yield (109 mg) as a foul-smelling, light yellow oil. ^1H NMR (300 MHz, $CDCl_3$, δ): 4.20 (d, J = 4.4 Hz, 1 H), 3.91 (d, J = 4.4 Hz, 1 H), 0.21 (s, 9 H). FTIR (KBr, film, cm^{-1}): 2960 m, 2163 s, 1585 m, 1432 s, 1245 s, 1001 m. MS: 205 (molecular ion), 190, 179, 162, 150, 125, 113, 97, 85, 73 (base peak). Exact mass: 204.98253 (calculated), 343.0278 (found).

α-Selenocyanatopropiophenone (2f). A THF solution of propiophenone (**1f**) was added to a THF solution of lithium diisopropylamide at -78 °C and stirred for 30 min. The resulting lithium enolate solution was transferred via cannula to CuCN at -78 °C, and the remainder of the reaction was carried out as described above. Compound **2f** was isolated as a pale yellow oil in 68% yield (2.27 g).

^1H NMR (300 MHz, $CDCl_3$, δ): 4.25 (q, J = 7.0 Hz, 2 H), 4.22 (q, J = 7.2 Hz, 1 H), 1.87 (d, J = 7.2 Hz, 3 H), 1.31 (t, J = 7.0 Hz, 3 H). ^{13}C APT NMR (75 MHz, $CDCl_3$, δ): 169.98 (neg), 100.54 (neg), 62.32 (neg), 40.05 (pos), 18.89 (pos). FTIR (film, KBr, cm^{-1}): 2986 s, 2154 s, 1734 vs, 1450 s, 1381 s, 1323 vs, 1219 vs, 1159 vs, 1074 s, 1018 s, 858 m. MS: 239 (molecular ion), 180, 162, 134, 108 (base peak), 73, 55. Exact mass: 238.98488 (calculated), 238.9851 (found).

9-Selenocyanatofluorene (2g). This compound was isolated as a pale yellow powder in 79% yield (210 mg).

Mp: 109-111 °C. ^1H NMR (300 MHz, $CDCl_3$, δ): 7.31-7.82 (m, 8 H, ArH), 5.66 (s, 1 H, C-9). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 141.76, 140.09, 129.39, 128.01, 120.58, 120.50, 101.90 (1 C, -SeCN), 45.36. IR (KBr, film, cm^{-1}): (SeCN) 2160 s, 1610 s, 1450 s, 1300 m, 1190 m, 915 s, 780 m, 735 vs. MS: 271 (molecular ion), 244, 180, 165 (base peak), 139, 126, 115, 106, 89, 82, 76, 63, 51. Exact mass: 270.98997 (calculated), 270.9877 (found).

2-Phenyl-1-selenocyanatoacetylene (2h): This compound was isolated as a pale yellow oil in 77% yield (1.18 g).

^1H NMR (300 MHz, $CDCl_3$, δ): 7.46-7.57 (m, 2 H), 7.28-7.43 (m, 3 H). ^{13}C APT NMR (75 MHz, $CDCl_3$, δ): 132.23 (pos, 2 C), 130.09 (pos, 1 C), 128.51 (pos, 2 C), 121.00 (neg, 1 C), 104.91 (neg, 1 C, SeCN), 96.57 (neg, 1 C), 68.12 (neg, 1 C). FTIR (NaCl, film, cm^{-1}): 3061 w, 2959 m, 2930 m, 2864 w, 2172 s (C≡C), 2170 m (C≡N), 1717 s, 1487 s, 1443 m, 1281 m, 756 s, 689 s. MS: 207 (molecular ion), 205, 181, 141, 127 (base peak), 117, 100, 89, 74, 63, 51. Exact mass: 206.95869 (calculated), 206.9551 (found).

1-(Dimethylphenylsilyl)-3-selenocyanato-1-propyne (2k). This compound was isolated as a pale yellow oil in 75% yield from the reaction of the cyanocuprate of **1a** with selenocyanogen.

^1H NMR (300 MHz, $CDCl_3$, δ): 7.61-7.66 (m, 2 H, ArH), 7.37-7.42 (m, 3 H, ArH), 4.32 (s, 2 H, CH_2Se), 0.45 (s, 6 H, $-SiMe_2-$). ^{13}C APT NMR (75 MHz, $CDCl_3$, δ): 136.5 (pos, 1 C), 133.0 (neg, 1 C), 129.6 (neg, 1 C), 128.0 (neg, 1 C), 105.7 (pos, 1 C, -SeCN), 89.4 (pos, 1 C), 52.2 (pos, 1 C), -1.1 (pos, 2 C, $-SiMe_2$). FTIR (NaCl, film, cm^{-1}): 3071 w, 2961 m, 2178 s (br), 1591 m, 1429 s, 1250 s, 1117 vs, 984 s, 839 s, 818 vs, 781 s, 733 s, 700 s, 665 s. MS: 279, 241, 173, 137, 136, 135 (base peak), 115, 57. Exact mass: 278.99817 (calculated), 278.9973 (found).

Acknowledgment. We thank the National Science Foundation for financial support of this work and the American Cancer Society for a Junior Faculty Research Fellowship to G.A.K. We also acknowledge the NIH Biotechnology Research Resource Center for Multi-Nuclear NMR and Data Processing (Grant RR-01317).

Registry No. **1a**, 75405-39-9; **1b**, 762-72-1; **1c**, 114083-20-4; **1d**, 114083-21-5; **1e**, 13683-41-5; **1f**, 93-55-0; **1g**, 86-73-7; **1h**, 536-74-3; **1i**, 591-51-5; **1j**, 109-72-8; **1k**, 101150-39-4; **2a**, 114908-22-4; **2b**, 114908-23-5; **2c**, 114083-22-6; **2d**, 114083-23-7; **2e**, 114908-24-6; **2f**, 114908-25-7; **2g**, 114263-69-3; **2h**, 114908-26-8; **2i**, 2179-79-5; **2j**, 4700-45-2; **2k**, 114908-27-9; AgSeCN, 5169-33-5; selenocyanogen, 27151-67-3.

Selenium Dioxide Catalyzed Conversion of Alcohols to Alkyl Chlorides by Chlorotrimethylsilane

Jong Gun Lee* and Kap Ku Kang

Department of Chemistry, Pusan National University, Pusan 609, South Korea

Received November 4, 1987

Conversion of alcohols to alkyl chlorides is one of the most frequently used functional group transformation reactions. Thionyl chloride[1] and phosphorus trichloride[2] are the two most popular classical reagents. Triphenylphosphine has been used in combination with carbon tetrachloride,[3] *N*-halo imides,[4] and other chlorine compounds as a mild reagent for the preparation of alkyl chlorides.

More recently, halotrimethylsilanes were found to be useful for halogenation of alcohols. Iodotrimethylsilane converts alcohols to alkyl iodides under mild reaction conditions.[5] Less reactive bromotrimethylsilane needs a higher temperature to react with alcohols to produce alkyl bromides.[6] Chlorotrimethylsilane, on the other hand, generally fails to produce alkyl chlorides. There is only one literature report[7] on the use of chlorotrimethylsilane for the preparation of alkyl chlorides. However, the reaction seems to be limited to some allylic alcohols but not applicable to alcohols in general.

We now report a simple, inexpensive, and high-yield conversion of alcohols to the corresponding alkyl chlorides. Having a similar property to thionyl chloride, selenium oxychloride is belived to be able to serve as a mild chlorinating agent for alcohols. Unlike gaseous sulfur dioxide, selenium dioxide cannot escape out of the reaction mixture. This suggested that only a catalytic amount of selenium dioxide is needed for the effective chlorination of alcohols to alkyl halides, provided that enough chlorine source is present to convert it back to selenium oxychloride. This was, indeed, found to be true. When benzyl alcohol was mixed with slightly more than 2 equiv of chlorotrimethylsilane and 2-3 mol % of selenium dioxide, hydrogen chloride soon started to evolve. The reaction was complete within an hour at reflux. It took slightly longer at room temperature. The conversion was almost quantitative, and no product other than benzyl chloride was present in the reaction mixture.

$$ROH + 2TMSCl \xrightarrow{SeO_2} RCl + HCl + TMSOTMS$$

The in situ generated selenium oxychloride was found to be very effective for converting a wide variety of alcohols to the corresponding alkyl chlorides. The conversion can

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