stance of systems containing hydrogen bonds, the experiments are complementary. The heteronuclear difference NOE experiment should work well in all cases, except where severe spectral crowding in the ^1H NMR makes selective irradiation difficult.

Experimental Section

Compounds 1 and 2 have been previously reported.[7] The synthesis of compounds 3 and 4 have been described elsewhere.[10] All spectra were obtained on a JEOL FX-200 spectrometer in a 5-mm C/H probe. The experiments on 1 and 2 were obtained on CH_3OH (deuterioacetone lock) and CD_3OD samples. 2K scans were collected by using 16K double-precision accumulation. The NOE difference spectrum for 2 was obtained in deuteriochloroform solution. The spectra were transformed with a 2.5-Hz line broadening. The proton-decoupled and heteronuclear NOE experiments on 3 and 4 were obtained with use of deuteriochloroform as solvent and lock. The NOE difference spectra required overnight accumulation and were collected with a pulse delay of 5 s.

Acknowledgment. We thank Dr. J. Nadelson (Sandoz) for the use of his compounds and Dr. C. A. Evans (JEOL) for helpful discussions. T.L.L. acknowledges the Robert A. Welch Foundation Grant E-711 for partial support of this research.

Registry No. 2a, 87829-34-3; 3, 82501-33-5; 4, 82501-28-8.

Convenient Preparation of Sterically Hindered Selones

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Received June 14, 1983

Selenoketones (selones) 2 are very important intermediates in the preparation of a variety of extremely sterically hindered molecules.[1] They have interesting photochemical properties[2] and also have proved to be very efficient spin traps for a large number of common free radicals.[3] Unfortunately, further investigations of the properties and reactivities of selones have been severely limited by difficulties in the preparation of these molecules.

The most widely used method for the preparation of selones involves pyrolysis of a phosphoranylidenehydrazone (phosphazine) 1 in the presence of excess selenium, affording the selone, nitrogen, and triphenylphosphine selenide.[4] While these reactions can be optimized to afford the selones in typical yields of 66–85%, the yields are markedly affected by the age and purity of the selenium powder. The purity of the phosphazine is also important. Crystallization of the moisture-sensitive phosphazines is often difficult, lowering overall yields, and small amounts of hydrazone contaminants lead to significant reduction of the initially formed selones to unstable selenols. Finally, and perhaps most importantly, the temperature and rate of heating seem to be critical in the pyrolysis reaction. The pyrolysis of phosphazines without selenium affords diazo compounds in good to excellent yield;[4,5] if the rate of heating in the selone preparation is too rapid the selone initially formed can react with the in situ generated diazo compound to afford an olefin in a twofold extrusion reaction, significantly lowering selone yields (Scheme I). Recently an alternative method for the preparation of selenofenchone utilizing bis(tricyclohexyltin) selenide (3)–boron trichloride has been reported.[6]

Scheme I

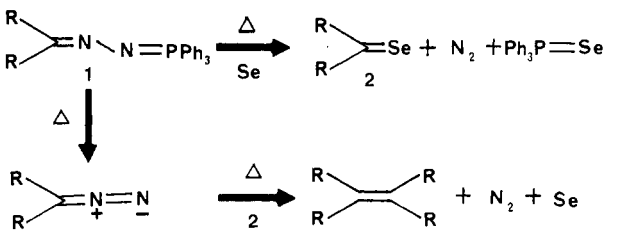
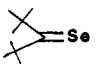
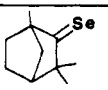
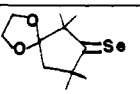
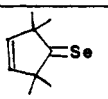
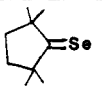
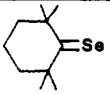
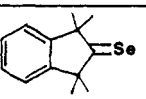
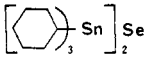


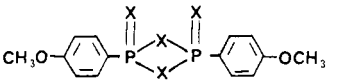
Table I[a]

Product Selone	Se_2Cl_2	Se_2Br_2	c
7 	45%	65%	29% (ref 4)
8 	40%	76% (50%)[b]	25% (ref 4)
9 	66%	80% (61%)[b]	48%
10 	—	70%	53% (ref 1a)
11 	—	68%	54%
12 	37%	73%	40%
13 	53%	80% (74%)[b]	75% (ref 1b)

[a] Isolated yield of pure product. [b] Diisopropylethylamine used in place of triethylamine. [c] Overall yield of selone from hydrazone via triphenylphosphoranylidenehydrazone.



3



4a, X = Se
4b, X = S

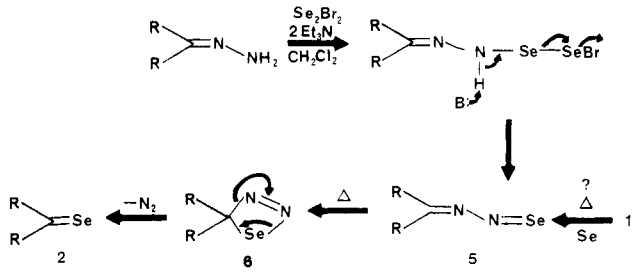
Unfortunately this method uses relatively large amounts of the selenium reagent and appears to be useful only for the preparation of small quantitites of selones.

In our investigations of selone reactivity, we required multigram quantities of these compounds. One potential method for preparing selones in quantity would involve the use of the selenium analogue **4a** of the dimer of (*p*-methoxyphenyl)thioxophosphine sulfide (**4b**), which is widely used as a thionating reagent.[7] Unfortunately the

(1) (a) Cullen, E. R.; Guziec, F. S., Jr.; Murphy, C. J. *J. Org. Chem.* **1982**, *47*, 3563 and references therein. (b) Cullen, E. R.; Guziec, F. S., Jr.; Hollander, M. I.; Murphy. C. J. *Tetrahedron Lett.* **1981**, *22*, 4563.
(2) Fung, N. Y. M.; de Mayo, P.; Ruge, B.; Weedon, A. C.; Wong, S. K. *Can. J. Chem.* **1980**, *58*, 6.
(3) Scaiano, J. C.; Ingold, K. U. *J. Am. Chem. Soc.* **1977**, *99*, 2079 and references therein.
(4) Back, T. G.; Barton, D. H. R.; Britten-Kelly, M. R.; Guziec, F. S., Jr. *J. Chem. Soc., Perkin Trans. 1* **1976**, *19*, 2079.
(5) Guziec, F. S. Jr.; Luzzio, F. A. *J. Org. Chem.* **1983**, *48*, 2434.
(6) Steliou, K.; Mrani, M. *J. Am. Chem. Soc.* **1982**, *104*, 3104.

0022-3263/84/1949-0189$01.50/0

Scheme II



reaction of anisole with commercial phosphorus pentaselenide under a variety of conditions analogous to the preparation of **4b** did not afford the desired selenating reagent.[8] Sulfur(I) chloride has also proved to be an effective reagent for converting hydrazones to thiones.[9] We therefore investigated the use of selenium(I) halides in attempts to carry out the analogous selenations.

Treatment of a hindered ketone hydrazone with selenium(I) chloride or selenium(I) bromide[10] in the presence of excess tertiary amine readily affords selones in good yields (Table I). Yields were significantly better when selenium(I) bromide[12] was used than those with the corresponding chloride; changing the amine had less effect on the selone yield. Direct preparation of the selone from the hydrazone avoids the additional steps of phosphazine formation and purification and also affords the selone in consistently higher yields.

The mechanism for the reaction is intriguing (Scheme II). Presumably nucleophilic attack of the hydrazone on the selenium halide and fragmentation affords an unstable *N*-selenonitrosimine (**5**), which rearranges to the 1,2,3-selenadiazetine **6**, which then extrudes nitrogen to afford the selone. This suggested mechanism differs from that proposed for the sulfur reagent.[9] In the first stage of the selone preparation, 2 equiv of triethylamine hydrobromide and selenium precipitate. At this point the crude mixture typically contains no selone. The pyrolysis of the concentrate, presumably **5** or **6**, affords only traces of selenium as a residue, consistent with the expected pyrolysis of such intermediates. A detailed spectroscopic examination of these intermediates is unfortunately hampered by their thermal sensitivity. Intermediates **5** and **6** could also be potential intermediates in the phosphoranylidenehydrazone route to selones.[14]

As mentioned earlier, one limitation of the phosphoranylidenehydrazone reaction was the inability to prepare unhindered or moderately hindered selones due to competing olefin formation. Attempts to use the selenium(I) reagents to prepare selenobenzophenone, selenofluorenone, or (±)-selenocamphor were similarly unsuccessful. In the case of benzophenone or fluorenone, the corresponding dimeric olefins were obtained in yields of 45% and 61%, respectively, as the only characterizable products; in the case of (±)-camphor apparently no olefin was obtained and no characterizable products could be isolated. In no case were diselenides observed. Despite these limitations, this procedure appears to be the method of choice for preparing very hindered selones in quantity.

Experimental Section

General Methods. Melting points were determined on a Fisher Mel-temp apparatus and are uncorrected. GLC analyses were performed with a GOW-MAC Series 550P TCD gas chromatograph with a 80/100 mesh OV-101 column. Infrared spectra were recorded with a Perkin-Elmer Model 283-B spectrometer. The 100-MHz ^{1}H NMR spectra were recorded with a JEOLCO JNM-PS-100 high-resolution spectrometer. The 200-MHz ^{1}H NMR and ^{13}C NMR spectra were recorded with a Varian XL200 high-resolution spectrometer. The 300-MHz ^{13}C NMR spectra were recorded on a Nicolet NT-300 spectrometer. Tetramethylsilane was used as an internal standard for 100- and 200-MHz spectra; deuteriochloroform was used as an internal standard for 300-MHz spectra. Mass spectra were obtained on a Hewlett-Packard 5995A gas chromatograph–mass spectrometer with an HP 9885M flexible disk drive. Elemental analyses were performed by Galbraith Laboratories.

Triethylamine was distilled from barium oxide. Technical grade dichloromethane was used without further purification. All solvents were removed by rotoevaporation under reduced pressure unless stated otherwise. Detailed ^{13}C and ^{77}Se NMR data on the selones have been reported elsewhere.[15]

Selenium(I) Bromide. A three-necked flask is fitted with a dropping funnel, a gas inlet for nitrogen, and an outlet, which leads through an air trap to a water trap. To a stirred solution of 11.5 g of selenium dioxide (0.10 mol) in 89.5 g of 47–49% aqueous hydrobromic acid (0.52 mol) was added 24 g of powdered selenium metal (0.30 mol). Concentrated sulfuric acid (approximately 40 mL) was added dropwise until hydrogen bromide gas no longer evolved. (Care must be taken when adding the sulfuric acid as the reaction is exothermic. An ice/water bath should be kept nearby in the event that the reaction proceeds too rapidly.) The nitrogen gas continuously flushes the reaction vessel of hydrogen bromide gas as well as providing a dry, inert atmosphere. When gas evolution ceased a slight excess of sulfuric acid was added slowly (10–20 mL): The sulfuric acid acts as a desiccant for the selenium monobromide. The water-sensitive selenium(I) bromide separates from the reaction mixture as a heavy, dark metallic red liquid. The reaction mixture was allowed to cool and was then transferred to a 125-mL separatory funnel. The selenium monobromide was removed and washed with several portions of concentrated sulfuric acid until the acid layer was free of suspended particles. Traces of sulfuric acid remain in the selenium monobromide to stabilize it. The selenium(I) bromide was obtained in quantitative yield, and the reaction scale could be doubled with no lowering of yield. The crude isolated product was used directly in the selenation reaction.

Selone Preparation: General Procedure. A solution of the dry hydrazone[16] (5 mmol) in dichloromethane (15 mL) and a solution of selenium(I) bromide (5 mmol) in dichloromethane (15 mL) were simultaneously added dropwise over 15 min to a cooled 0 °C solution of freshly distilled triethylamine (11 mmol) in dichloromethane (20 mL). The reaction mixture was then allowed to come to room temperature and stirred for 30 min. The resulting

(7) Hofmann, H.; Schumacher, G. *Tetrahedron Lett.* **1967**, 2963. Pedersen, B. S.; Scheibye, S.; Nilsson, N. H.; Lawesson, S. O. *Bull. Soc. Chim. Belg.* **1978**, *87*, 223.

(8) This is perhaps not surprising because of the insolubility of phosphorus pentaselenide and the difficulties in adequately characterizing this compound. (Klayman, D. L.; Gunther, W. H. H. "Organic Selenium Compounds: their Chemistry and Biology"; Wiley-Interscience: New York, 1973; pp 44–46.)

(9) Okazaki, R.; Inoue, K.; Inamoto, N. *Tetrahedron Lett.* **1979**, 3673.

(10) Selenium(I) chloride and selenium(I) bromide are both commercially available (Alfa Products, Danvers, MA). The reagent of choice, selenium(I) bromide, can be readily prepared by a modification of the literature procedure[11] (See Experimental Section).

(11) Lenher, U.; Kao, C. H. *J. Am. Chem. Soc.* **1925**, *47*, 772.

(12) The difference in yield in comparing the selenium(I) bromide with selenium(I) chloride may reflect the apparent difference in stability of these reagents. Both reagents give better yields of selones than the corresponding sulfur halides give of thiones. Selenium halides are known to be more stable than the corresponding sulfur halides.[13]

(13) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 2nd Ed.; Interscience: New York, 1966; p 539.

(14) Pyrolysis of an equimolar amount of diazo compound and triphenylphosphine in the presence of selenium powder affords only traces of selone (F. Guziec and C. J. Murphy, unpublished experiments). This strongly suggests that the diazo compound is not an intermediate in this reaction.

(15) Cullen, E. R.; Guziec, F. S., Jr.; Murphy, C. J.; Wong, T. C.; Andersen, K. K. *J. Am. Chem. Soc.* **1981**, *103*, 705; *J. Chem. Soc., Perkin Trans. 2* **1982**, 473. Wong, T. C.; Guziec, F. S., Jr.; Moustakis, C. A. *J. Chem. Soc. Perkin Trans. 2* **1983**, 1471.

(16) The hydrazones are typically hygroscopic and should be dried before use. Simply drying a dichloromethane solution of the hydrazone with anhydrous sodium sulfate before use is satisfactory.

suspension was filtered under vacuum to remove triethylamine hydrobromide and selenium, and the filtrate was washed with water, quickly filtered through a layer (~4.0 g) of potassium carbonate, and dried over sodium sulfate. The dichloromethane was removed under reduced pressure on a rotary evaporator below room temperature, and the residue was carefully pyrolyzed (~50–75 °C) with a heat gun in a bulb-to-bulb distillation apparatus under reduced pressure, continually collecting the volatile selone in a dry ice/acetone-cooled receiver. Generally, the selone is pure by GLC and no further purification is necessary.

2,2,4,4-Tetramethylpentane-3-selone (7). Deep blue selone 7 was obtained from hydrazone[17] in 65% yield by distillation at 0.1–5 torr. All physical constants and spectra were identical with those reported in the literature.[4]

(-)-Selenofenchone (8). The deep blue selone 8, identical in all respects with that previously reported,[4] was obtained from the hydrazone[17] in 76% yield, by distillation at 0.5–5 torr.

2,2,5,5-Tetramethyl-3-oxocyclopentaneselone 3-Ethylene Ketal (9). Deep blue selone 9 was prepared from the hydrazone[18] by a modification of the general procedure. Three equivalents of triethylamine were used, and the filtrate was washed with water instead of dilute hydrochloric acid. The selone was obtained in 80% yield by distillation at 0.5–5 torr; bp 70 °C (0.1 torr) (Kugelrohr oven temperature); ^{1}H NMR (CCl_4) δ 3.90 (s, 4 H), 2.17 (s, 2 H), 1.32 (s, 6 H), 1.16 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 292.75 (C=Se), 117.48, 65.04, 60.16, 46.22, 31.67, 23.86; MS, *m/e* 262 (^{80}Se) (M^+); IR (neat) 1470, 1450, 1380, 1360, 1300, 1220, 1160, 1140, 1070, 1050, 1020, 980, 950, 785, 760 cm^{-1}. Anal. Calcd for $C_{11}H_{18}O_2Se$: C, 50.58; H, 6.93. Found: C, 50.87; H, 6.82.

Preparation of selone 9 via the phosphazine, mp 140–140.5 °C dec, according to the standard procedure[1a] afforded this compound in 48% overall yield.

2,2,5,5-Tetramethyl-3-cyclopenteneselone (10). Deep blue selone 10 was prepared by a modification the general procedure using 6.3 mmol of hydrazone.[1a] Since this selone is quite volatile, the solvent was removed by a stream of nitrogen at atmospheric pressure. Selone 10, identical with that previously reported,[1a] was obtained in 70% yield by distillation at 16–20 torr. This reaction was also run on a 33-mmol scale, affording 10 in 60% yield.

2,2,5,5-Tetramethylcyclopentaneselone (11). Deep blue selone 11 was prepared from the hydrazone,[19] according to the general procedure. The selone was isolated in 68% yield by distillation at 16–20 torr: mp 74–77 °C; ^{1}H NMR ($CDCl_3$) δ 1.21 (12 H, s), 1.93 (4 H, s); ^{13}C NMR ($CDCl_3$) δ 297.8 (C=Se), 64.2, 37.4, 29.3; MS, *m/e* 204 (M^+) (^{80}Se); IR (film) 1461, 1381, 1361, 1220, 1056 cm^{-1}. Anal. Calcd for $C_9H_{16}Se$: C, 53.20; H, 7.94. Found: C, 53.02; H, 7.86.

2,2,6,6-Tetramethylcyclohexaneselone (12). Deep blue selone 12 was prepared from the hydrazone, mp 46–47 °C, by the general procedure. The selone was obtained in 73% yield, by distillation at 0.1–5 torr: bp 28 °C (0.05 torr) (Kugelrohr oven temperature); 200-MHz ^{1}H NMR ($CDCl_3$) δ 1.39 (12 H, s), 1.78–1.79 (6 H, br s); ^{13}C NMR ($CDCl_3$) δ 294.7 (C=Se), 58.9, 38.4, 33.5, 18.3; MS, *m/e* 262 (M^+) (^{80}Se); IR (neat) 1465, 1450, 1380, 1360, 1220, 1065, 990, 975, 760 cm^{-1}. Anal. Calcd for $C_{10}H_{18}Se$: C, 55.30; H, 8.35. Found: C, 55.42; H, 8.46.

Preparation of selone 12 via the phosphazine, mp 115–123 °C, according to the standard procedure[1a] afforded this compound in 40% overall yield.

1,1,3,3-Tetramethylindan-2-selone (13). Deep blue selone 13 was prepared from the hydrazone, according to the general procedure. Selone 13, identical with that previously reported,[1b,20] was obtained in 80% yield by distillation at 0.5–5 torr; IR (neat) 1590, 1485, 1455, 1375, 1358, 1310, 1050, 1020, 755 cm^{-1}.

Acknowledgment. We thank the New Mexico State University Arts and Sciences Research Center for partial financial support of this research (Grant 1-3-43673) and Dr. E. R. Cullen for providing starting materials for the preparations of selone 9.

Registry No. 7, 56956-23-1; 7 hydrazone, 33420-22-3; 8, 56956-24-2; 8 hydrazone, 87900-48-9; 9, 87842-33-9; 9 hydrazone, 87842-34-0; 9 phosphoranylidenehydrazone, 87842-35-1; 10, 79958-61-5; 10 hydrazone, 81396-37-4; 11, 87842-36-2; 11 hydrazone, 70302-22-6; 11 phosphoramylidenehydrazone, 70302-23-7; 12, 87842-37-3; 12 hydrazone, 87842-38-4; 12 phosphoranylidenehydrazone, 87842-39-5; 13, 74768-64-2; 13 hydrazone, 74768-84-6; SeO_2, 7446-08-4; Se_2Br_2, 7789-52-8.

(17) Barton, D. H. R.; Guziec, F. S., Jr.; Shahak, I. *J. Chem. Soc. Perkin Trans. 1* **1974**, 1794.
(18) Cullen, E. R.; Guziec, F. S., Jr., manuscript in preparation.
(19) de Mayo, P.; Petrasiunas, G. L. R.; Weedon, A. C. *Tetrahedron Lett.* **1978**, 4621.
(20) Klages, C.-P.; Voss, J. *Chem. Ber.* **1980**, *113*, 2255.

Aerosol Direct Fluorination. Indirect Syntheses of Perfluorocyclic Ketones

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The aerosol direct fluorination method provides a continuous process for the production of perfluorocarbons from hydrocarbons with efficient fluorine utilization and minimal fragmentation.[1] The application of this process to alkanes, ethers, cycloalkanes, ketals, and ketones has been demonstrated.[1-3] Whereas the aerosol direct fluorination of alicyclic ketones yields the corresponding perfluoro ketone as the majority product,[2] aerosol fluorination of cyclic ketones has produced none of the perfluorinated analogues. In the case of cyclopentanone, the major product was *F*-pentanoyl fluoride, resulting from the opening of the cyclopentyl ring;[2] aerosol direct fluorination of cyclohexanone produced only nonvolatile products; no evidence for the formation of *F*-cyclohexanone was found.[4] However, on employment of a two-step process, perfluorocyclopentanone and perfluorocyclohexanone have been synthesized. Sulfuric acid hydrolysis of the appropriate perfluorinated ketal or ether, formed via aerosol fluorination of the corresponding ketal or ether, produced the corresponding perfluoro cyclic ketone in high yields.

Previous preparations of *F*-cyclopentanone and *F*-cyclohexanone are relatively few in number; the only synthesis involving direct fluorination is that reported by Holub and Bigelow wherein *F*-cyclopentanone was formed in trace amounts from the direct fluorination of cyclopentanone.[5] *F*-Cyclopentanone and *F*-cyclohexanone have been prepared via the treatment of the corresponding 2,2-dichloroperfluoro cyclic ketones or 1,2-dichloroperfluorocycloalkene epoxides with potassium fluoride in tetramethylene sulfone[6] and by the contact of Lewis acids or bases with the appropriate perfluor olefin epoxides.[7] In addition to the above methods, Tatlow et al.[8] prepared

(1) (a) Adcock, J. L.; Horita, K.; Renk, E. B. *J. Am. Chem. Soc.* **1981**, *103*, 6937. (b) Adcock, J. L.; Renk, E. B. U.S. Patent 4 330 475, May 1982.
(2) Adcock, J. L.; Robin, M. L. *J. Org. Chem.* **1983**, *48*, 3128.
(3) Adcock, J. L.; Robin, M. L. *J. Org. Chem.* **1983**, *48*, 2437.
(4) Robin, M. L.; unpublished results.
(5) Holub, F. F.; Bigelow, L. A. *J. Am. Chem. Soc.* **1950**, *72*, 4879.
(6) (a) Anello, L. G.; Price, A. K.; Sweeney, R. F. *J. Org. Chem.* **1968**, *33*, 2692. (b) Price, A. K.; Sweeney, R. F. (Allied). U.S. Patent 3 350 457, 1967. (c) Anello, L. G.; Sweeney, R. F. (Allied). *Ibid.* 3 379 765, 1968.
(7) (a) Coe, P. L.; Sleigh, J. H.; Tatlow, J. C. *J. Fluorine Chem.* **1980**, *15*, 339. (b) Moore, E. P.; Milan, S., Jr. (E. I. duPont de Nemours & Co.). Brit. Pat. 1 019 788, 1966. (c) E.I. duPont de Nemours & Co. Fr. Pat. 1 416 013, 1965. (d) Moore, E. P.; Milan, A. C. (E.I. duPont de Nemours & Co.). U.S. Patent 3 321 515, 1970.
(8) Clayton, A. B.; Stephens, R.; Tatlow, J. C. *J. Chem. Soc.* **1965**, 7373.

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