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An Efficient Synthesis of Selenocarbonyl Compounds by the Treatment of Carbonyl Compounds with Bis[1,5-cyclooctanediylboryl] Selenide

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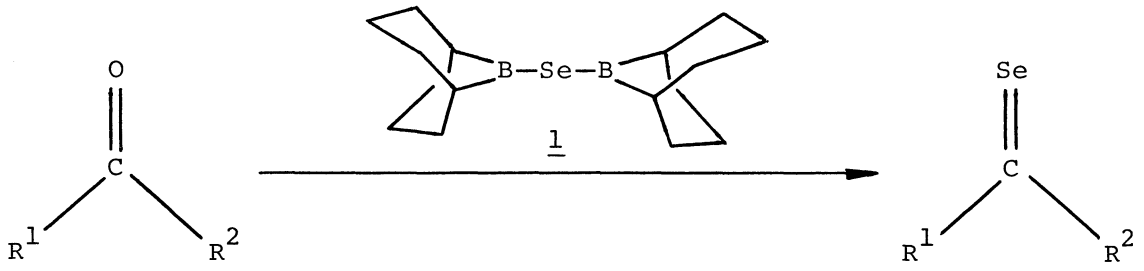
An efficient synthesis of selenoaldehydes, selenoketones, and selenoamides was achieved by the treatment of carbonyl compounds with bis[1,5-cyclooctanediylboryl] selenide.

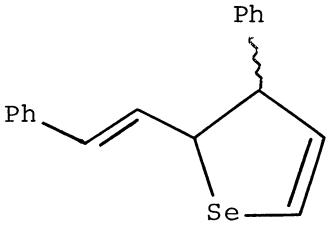
One-step conversion of carbonyl compounds to the corresponding selenocarbonyl compounds by using selenating reagents is one of the most important concerns in organic heteroatom chemistry.[1-5] However, among the reagents possessing reactive metal-Se bonds, boryl selenides and boryl metal selenides have been investigated mainly from structural interests[6] in spite of their selenating potential resulting from the significant affinity of B-Se bonds to oxygen functionalities. Actually, some boryl selenide was thought to play an essential role in the selenation of carbonyl compounds by the treatment of $(Me_3Si)_2Se\text{-}BF_3{\cdot}OEt_2$[5] or $[(c\text{-}C_6H_{11})_3Sn]_2Se\text{-}BCl_3$.[6] It was naturally supposed that structural modification of boryl selenides by so-called steric protection was much effective in reducing their air-lability, as is widely known to be the case with general dialkylborane compounds. Herein, we wish to report a novel and efficient conversion of carbonyl compounds to the corresponding selenocarbonyl compounds by using bis[1,5-cyclooctanediylboryl] selenide 1.



Bis[1,5-cyclooctanediylboryl] selenide 1 was prepared by treating elemental selenium with 9-BBN in mesitylene at refluxing temperature under N_2 atmosphere based on the Köster's method.[7] Subsequently, reagent 1 was treated with aldehydes and ketones under N_2 atmosphere at room or a higher temperature in the presence of 2,3-dimethyl-1,3-butadiene. After usual work-up and chromatographic separation, [4+2] cycloadducts of selones with the diene were isolated in modest to high yields besides the recovery of small amounts of aldehydes and ketones. N,N-Dialkyl carboamides and an ester were similarly treated with reagent 1 in the absence of a diene, and the corresponding selenoamides and a selenoester were isolated in modest yields. All results are shown in Table 1 and Table 2.

In particular, the excellent selenating activity of reagent 1 was exhibited by the reaction with benzaldehyde 2 and sterically crowded ketones, 3 and 4, in the absence of 2,3-dimethyl-1,3-butadiene. By treating with reagent 1, 2 was converted to dibenzyl diselenide 5(44%) derived by the further reduction of transiently-generated selenobenzaldehyde 6.[8] Fenchone 3 and sagetone 4 also afforded selones, 7[9-11] and 8[12], in 35% and 23% yields, respectively, besides inseparable stereoisomeric mixtures of diselenides in 20-40% yields.[8,13,14] Subsequent $NaBH_4$ or $LiAlH_4$ reduction of the resulting selones in MeOH or Et_2O at 0 °C to room temperature followed by an aerobic work-up afforded sole diselenides, 9(quant.) and 10(67%) respectively.[12] Orientation of the C-Se bonds of each product was supposed to be endo and exo, respectively, as were similarly mentioned in the hydride reduction of 3[15] and 4.[16] These results demonstrated that the strong electronic interaction of boron atom with carbonyl oxygen atom behaved as a substantial controlling factor of the reactions and steric factors of substrates and the reagent played a less important role in the reactions. In contrast, selenation of cinnamic aldehyde gave an unexpected compound 11(37%)[12] which may be produced by selenium-extrusion of a dimeric cycloadduct of α, β-unsaturated selenoaldehyde.[17,18]

Conclusively, efficient synthesis of selenocarbonyl compounds was achieved by treating carbonyl compounds with bis[1,5-cyclooctanediylboryl] selenide 1. Further synthetic expansions of reagent 1 to tellurium-transfer reagents as well as the application of diselenides 9 and 10 to novel chiral auxiliaries for asymmetric syntheses are now in progress in our laboratory.



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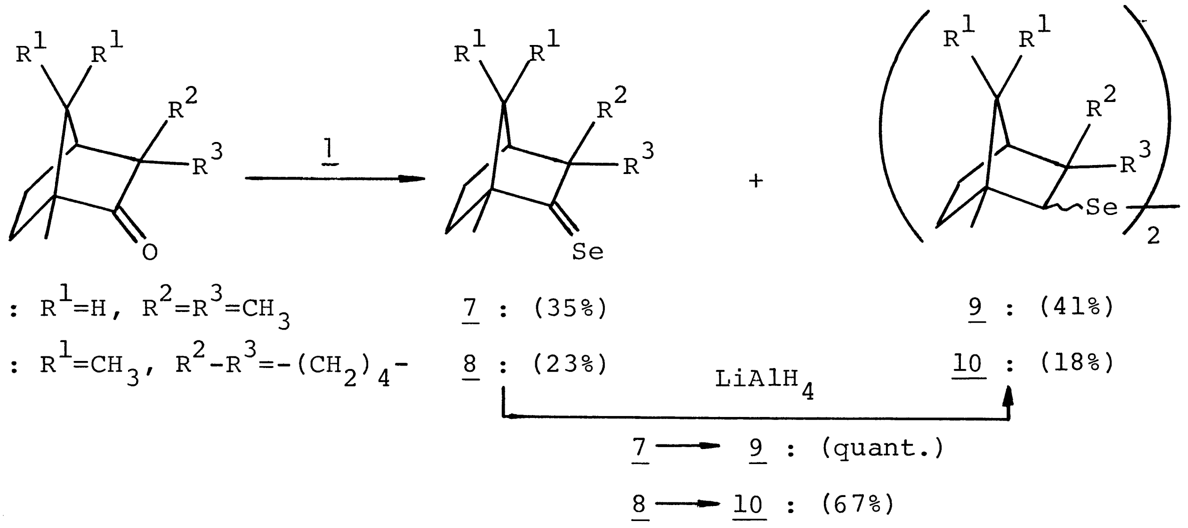


3 : R^1=H, R^2=R^3=CH_3

4 : R^1=CH_3, R^2-R^3=-$(CH_2)_4$-

7 : (35%)

8 : (23%)

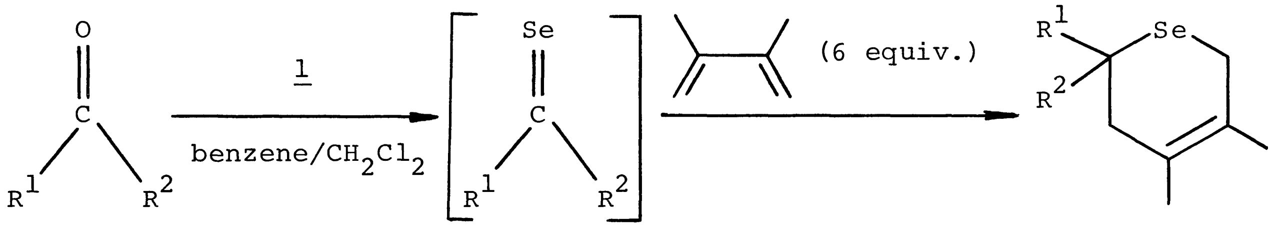
9 : (41%)

10 : (18%)

7 → 9 : (quant.)

8 → 10 : (67%)

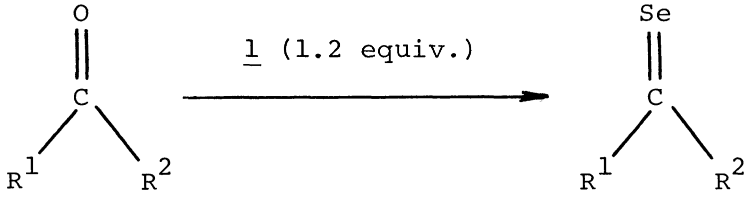
Table 1. Trapping of selenoaldehydes and selenoketones with 2.3-dimethyl-1,3-butadiene[a)]



Substrate R^1	R^2	1 equiv.	Temp °C	Time h	Yield %
C_6H_5	H	1.2	110	18	79
4-CH_3-C_6H_4	H	1.2	110	8	82
CH_3	H	1.2	150	18	32
C_6H_5	CH_3	2.0	80	15	54
C_6H_5	C_2H_5	2.0	80	24	81
C_6H_5	C_6H_5	2.0	110	24	96
C_2H_5	CH_3	2.0	110	48	38
$(CH_3)_2CH$	CH_3	2.0	110	48	53
$-(CH_2)_5-$		2.0	130	48	50
9-fluorenone		2.0	110	24	82

a) All reactions were carried out in a sealed tube.

Table 2. Synthesis of selenocarbonyl compounds by treating carboxylic acid derivatives with reagent 1[a)]



Substrate R^1	R^2	Solvent	Temp °C	Time h	Yield %
H	$N(CH_3)_2$	toluene	r.t.	24	39
H	$N[CH(CH_3)_2]_2$	benzene/CH_2Cl_2	110	1	16
CH_3	$N(CH_3)_2$	mesitylene/$CHCl_3$	63	5	34
C_6H_5	OC_2H_5	benzene/CH_2Cl_2	130	10	14[b)]

a) All reactions were carried out in a sealed tube. b) Starting ester was recovered in 81% in this case.

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12) 8: A deep blue oil; bp 130 °C(7 mmHg); MS(m/e) 270(M^+,15%,^{80}Se); IR(neat) 2990, 1450, 1080, 800 cm^{-1}; ^{1}H NMR($CDCl_3$) δ 0.83(3H,s), 1.04(3H,s), 1.20(3H,s), 1.30-2.30(13H,m); 9: Yellow needles; mp 50.0-51.0 °C; MS(m/e) 434(M^+,2%,^{80}Se), 137(bp); IR(KBr) 2860, 1440, 1360, 720 cm^{-1}; ^{1}H NMR($CDCl_3$) δ 1.02(6H,s), 1.08(6H,s), 1.20(6H,s), 0.95-1.88 (14H,m), 3.10(2H,d,J=3.0 Hz); 10: Yellow oil; MS(m/e) 542(M^+,21%,^{80}Se); IR(neat) 2950, 1390, 1380, 880, 780 cm^{-1}; ^{1}H NMR($CDCl_3$) δ 0.83(6H,s), 0.94(6H,s), 1.04(6H,s), 1.17-2.32(24H,m), 1.18-1.29(2H,m), 3.20-3.53(2H,m); 11: Colorless needles; mp 105.5-106 °C; MS(m/e) 312(M^+,bp,^{80}Se), 310(M^+,42%,^{78}Se), 231(88%,M^+-PhCH=CH); IR(KBr) 1570, 1470, 1440, 1270, 1240, 1140, 1100, 1070, 1010, 960, 730, 670 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.13(1H,ddd,J=7.5,3.0,2.5 Hz), 4.67(1H,dd,J=8.5,7.5 Hz), 6.07(1H,dd,J=6.5, 3.0 Hz), 6.28(1H,d,J=15.5 Hz), 6.57(1H,dd,J=15.5,8.5 Hz), 6.83(1H,dd,J=6.5,2.5 Hz), 7.01-7.49(10H,m). Found: C,68.73; H,5.14%. Calcd for $C_{18}H_{16}Se$: C,69.45; H,5.18%.

13) Trapping of selones with 2,3-dimethyl-1,3-butadiene was not successful in these cases.

14) $NaBH_4$ reduction of diselenides in ethanol followed by the treatment of an excess amount of methyl iodide afforded inseparable stereoisomeric mixtures of methylseleno derivatives in modest yields.

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17) Treatment of cinnamic aldehyde with 1 at 110 °C for 18 h in the presence of an excess amount of 2,3-dimethyl-1,3-butadiene in a sealed tube also afforded 11 in 51% yield.

18) The stereochemistry of 11 was not characterized by ^{1}H NMR data.

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