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Synthesis of Aliphatic Isoselenocyanates by the Reaction of Aliphatic Isocyanides with Selenium in the Presence of Triethylamine

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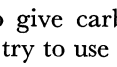
Bulka and co-workers[1] have reported that the reaction of selenium with aryl isocyanide produces aryl-isoselenocyanate. However, the reaction of selenium with aliphatic isocyanide has not been reported yet. We tried the reaction of aliphatic isocyanide under the same conditions to those employed in the reaction of aryl isocyanide.[1] However, the corresponding isoselenocyanate was not obtained. Recently we confirmed that amine catalyzed the reaction between carbon monoxide and selenium to give carbonyl selenide[2] and this fact prompted us to try to use of strongly basic tertiary amine as catalyst in the present reaction, because of similarity of electronical structure between isocyanide and carbon monoxide. Now, we found that the addition of triethylamine promoted the reaction effectively, and aliphatic isoselenocyanate was obtained in a high yield. The results obtained from representative isocyanides were shown in Table 1. The aliphatic isoselenocyanates isolated were identified by IR, NMR, mass spectroscopy, and elemental analyses. These isoselenocyanates were somewhat unstable and gradually decomposed at room temperature.

$$\text{R–NC} + \text{Se} \xrightarrow{\text{Et}_3\text{N}} \text{R–N=C=Se}$$

R:  , *n*-C_4H_9–, *tert*-C_4H_9–

Some characteristic reactions of the isoselenocyanates were carried out. The reaction of aliphatic isoselenocyanates with *n*-butylamine produced corresponding selenoureas in excellent yields, which were fairly stable

TABLE 1. THE REACTION OF ALIPHATIC ISOCYANIDE WITH SELENIUM IN THE PRESENCE OF TRIETHYLAMINE

Isocyanide (R–NC) R	(mmol)	Se (mmol)	Et_3N (mmol)	React. time (hr)	React. temp. (°C)	Product	Yield[a] (%)
Cyclohexyl	59	38	38	4	66	Cyclohexyl isoselenocyanate	96
n-Butyl	21	15	15	1.5	66	*n*-Butyl isoselenocyanate	83
tert-Butyl	21	15	15	6	66	*tert*-Butyl isoselenocyanate	97

a) Based on selenium used.

1) E. Bulka, K. D. Ahlers, and E. Tucek, *Chem. Ber.*, **100**, 1376 (1967).

2) N. Sonoda, T. Yasuhara, T. Ikeda, K. Kondo, and S. Tsutsumi, *J. Amer. Chem. Soc.*, **93**, 6344 (1971).

Table 2. The reaction of aliphatic isoselenocyanate with *n*-butylamine or ethanol

Isoselenocyanate (R–N=C=Se) R	(mmol)	*n*-BuNH$_2$ (mmol)	EtOH (mmol)	React. time (hr)	React. temp. (°C)	Product	Yield[a] (%)
Cyclohexyl	3	3	—	48	r.t.	*N*-*n*-Butyl-*N'*-cyclohexylselenourea	90
n-Butyl	5	5	—	0.5	66	*N*,*N'*-Di-*n*-butylse enourea	98
tert-Butyl	5.5	5.5	—	0.5	66	*N*-*n*-Butyl-*N'*-*tert*-butylselenourea	89
Cyclohexyl	22	—	740	24	78	*N*-Cyclohexylselenocarbamate	49

a) Based on selenium used.

at room temperature. Selenocarbamate was easily obtained by the reaction of isoselenocyanate with ethanol. These results were summarized in Table 2.

$$R\text{–}N{=}C{=}Se + R'\text{–}NH_2 \longrightarrow R\text{–}NH\text{–}\underset{\underset{Se}{\|}}{C}\text{–}NH\text{–}R'$$

$$R\text{–}N{=}C{=}Se + R'\text{–}OH \longrightarrow R\text{–}NH\text{–}\underset{\underset{Se}{\|}}{C}\text{–}OR'$$

Furthermore, it was confirmed that the reaction of isocyanide with selenium and *n*-butylamine yielded the corresponding selenourea directly. In this case *n*-butylamine might catalyze the reaction of isocyanide with selenium to give isoselenocyanate as an intermediate.

Experimental

Cyclohexyl Isoselenocyanate. To a solution of 5.79 g (53 mmol) of cyclohexyl isocyanide in 45 m*l* of THF were added 3.00 g (38 mg atom) of selenium and 3.85 g (38 mmol) of triethylamine. The mixture was stirred under reflux for 4 hr, and at this stage selenium was completely dissolved. The mixture was concentrated, and distillation of the residual liquid gave 6.90 g (96%) of colorless product: bp 90—92°C (3.0 mm); IR 2130 cm^{-1} (N=C=Se); NMR (CCl_4) τ 7.7—8.9 (10H), 6.2 (1H); Mass *m/e* 189 (parent ion containing ^{80}Se), 83 ($C_6H_{11}^+$).

Found: N, 7.32%. Calcd for $C_7H_{11}NSe$: N, 7.45%.

n-*Butyl Isoselenocyanate.* To a solution of 1.74 g (21 mmol) of *n*-butyl isocyanide were added 1.18 g (15 mg atom) of selenium and 1.52 g (15 mmol) of triethylamine. The mixture was stirred under reflux for 1.5 hr. Selenium was dissolved completely and the solution became dark brown. The mixture was concentrated and distillation of the residue gave 2.02 g (83%) of colorless liquid: bp 56—58°C (3 mm); IR 2160 (N=C=Se); NMR (CCl_4) τ 8.8—9.2 (3H), 7.9—8.8 (4H), 6.2—6.4 (2H); Mass *m/e* 163 (parent ion containing ^{80}Se), 57 ($C_4H_9^+$).

Found: N, 8.52%. Calcd for C_5H_9NSe: N, 8.60%.

tert-*Butyl Isoselenocyanate.* To a solution of 1.74 g (21 mmol) of *tert*-butyl isocyanide were added 1.18 g (15 mg atom) of selenium and 1.52 g (15 mmol) of triethylamine. The mixture was concentrated *in vacuo* to give 2.37 g (97%) of colorless solid. This solid was fairly unstable and decomposed on recrystallization or on standing overnight: mp 51—52°C; IR 2050 cm^{-1} (N=C=Se); NMR (CCl_4) τ 8.5 (s); Mass *m/e* 163 (parent ion containing ^{80}Se), 57 ($C_4H_9^+$).

Found: N, 8.43%. Calcd for C_5H_9NSe: N, 8.60%.

N-n-*Butyl*-N'-*cyclohexylselenourea.* *A*: To a solution of 0.55 g (3 mmol) of cyclohexyl isoselenocyanate in 5 m*l* of THF was added 0.24 g (3 mmol) of *n*-butylamine. The solution was allowed to stand for 48 hr at room temperature, then was concentrated *in vacuo* to dryness, and the yellow solid deposited was filtered and recrystallized from ethanol to yield 0.67 g (90%) of colorless crystal: mp 107.5—108.5°C; IR 3210 cm^{-1} (NH); NMR (CCl_4) τ 7.8—9.1 (17H), 6.6 (2H), 5.9 (1H), 3.0 (2H); Mass *m/e* 262 (parent ion containing ^{80}Se), 83 ($C_6H_{11}^+$), 99 ($C_6H_{11}NH_2^+$), 57 ($C_4H_9^+$).

Found: N, 10.68%. Calcd for $C_{11}H_{22}N_2Se$: N, 10.72%.

B: To a solution of 3.85 g (35 mmol) of cyclohexyl isocyanide in 20 m*l* of THF were added 2.37 g (30 mmol) of selenium and 2.20 g (30 mmol) of *n*-butylamine. The mixture was stirred under reflux for 4 hr, and at this stage selenium was dissolved. The mixture was concentrated and the yellow solid deposited was filtered and recrystallized from ethanol to yield 7.60 g (97%) of colorless crystal which was identical with *N*-*n*-butyl-*N'*-cyclohexylselenourea obtained by the procedure *A*.

N,N'-*Di*-n-*butylselenourea.* To a solution of 0.73 g (5 mmol) of *n*-butyl isoselenocyanate in 9 m*l* of THF was added dropwise 0.37 g (5 mmol) of *n*-butylamine. After complete addition of *n*-butylamine, the reaction mixture was stirred under reflux for 0.5 hr to complete the reaction. The solution was concentrated *in vacuo* and the residual solid was recrystallized from benzene–petroleum ether mixture to give 1.05 g (98%) of colorless plates: mp 72—73°C; IR 3220 cm^{-1} (NH); NMR τ 8.8—9.2 (6H), 8.0—8.8 (8H), 6.2—6.8 (4H), 2.5—3.0 (2H); Mass *m/e* 236 (parent ion containing ^{80}Se), 57 ($C_4H_9^+$).

Found: N, 12.13%. Calcd for $C_9H_{10}N_2Se$: N, 11.91%.

N-n-*Butyl*-N'-tert-*butylselenourea.* To a solution of 0.89 g (5.5 mmol) of *tert*-butyl isoselenocyanate in 15 m*l* of THF was added dropwise 0.46 g (5.5 mmol) of *n*-butylamine. After addition of *n*-butylamine, the reaction mixture was stirred under reflux for 0.5 hr to complete the reaction. The reaction mixture was concentrated and the yellow solid deposited was recrystallized from benzene to yield 1.15 g (89%) of colorless plates: mp 76—77°C; IR 3220 cm^{-1} (NH); NMR τ 8.2—9.2 (16H), 6.2—6.7 (2H), 3.1—3.4 (2H); Mass *m/e* 236 (parent ion containing ^{80}Se), 57 ($C_4H_9^+$).

Found: N, 11.68%. Calcd for $C_9H_{10}N_2Se$: N, 11.91%.

N-*Cyclohexylselenocarbamate.* Cyclohexyl isoselenocyanate, 4.19 g (22.3 mmol), was added to 43 m*l* of ethanol. The mixture was refluxed for 24 hr. The resulting solution was concentrated to give yellow solid, which was recrystallized from ethanol to yield 2.57 g (49%) of colorless plates: mp 77—78°C; IR 3210 cm^{-1} (NH); NMR τ 7.7—9.1 (13H), 6.3 (1H), 5.4 (2H), 1.8 (1H); Mass *m/e* 235 (parent ion containing ^{80}Se), 83 ($C_6H_{11}^+$).

Found: N, 5.82%. Calcd for $C_9H_{17}NOSe$: N, 5.98%.