Amidoselenation of Olefins Using *p*-Toluenesulfonamide as a Nitrogen Nucleophile

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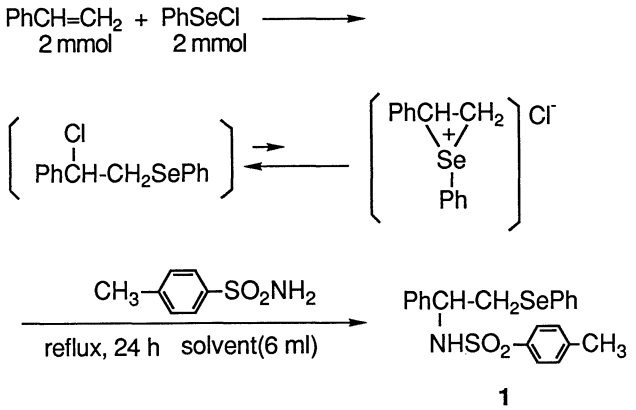
The reaction of olefins, benzeneselenenyl chloride, and *p*-toluenesulfonamide in the presence of zinc(II) chloride affords *N*-[2-(phenylseleno)alkyl]-*p*-toluenesulfonamides in good to excellent yields. When combined with alkylation on the carbon atom bearing the phenylseleno group thus introduced and subsequent oxidative or reductive removal of the selenium moiety, this reaction can be utilized in the preparation of a wide range of allylic or saturated amides.

We have already reported the organoselenium-induced Ritter-type amide syntheses which resulted in the introduction of arylseleno and acylamino groups into the olefins.[1] These reactions were utilized in the preparation of allylic and saturated amides by oxidative and reductive removal of the arylseleno group thus introduced.[1b,2] For the application of selenium chemistry to organic syntheses, introduction of various nitrogen functional groups would be desirable. We now found that *p*-toluenesulfonamide, usually considered as poor nucleophile, reacts cleanly with episelenonium ion to afford *N*-[2-(phenylseleno)alkyl]-*p*-toluenesulfonamides in good to excellent yields. We also tried and succeeded in the lithiation and subsequent alkylation of the carbon atom bearing the phenylseleninyl group generated by the in situ oxidation of the phenylseleno group. In the combination of these procedures, suitable choice of an olefin and an alkylating reagent would allow the preparation of any kind of β-tosylamino-substituted selenide which is a good precursor of allylic or saturated amide by oxidative or reductive removal of phenylseleno group.



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Scheme 1.

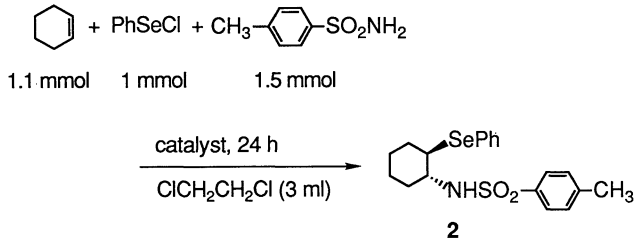
p-Toluenesulfonamide mmol	Solvent	**1** Yield[a] %
2	CH_3CN	45
2	1,4-Dioxane	64
2	$ClCH_2CH_2Cl$	79
3	$ClCH_2CH_2Cl$	96

a) Isolated yield by colomn chromatography.

Results and Discussion

p-Toluenesulfonamide (1 equiv) was added to the adduct of benzeneselenenyl chloride to styrene (prepared in situ) and the resulting mixture was heated under reflux to afford *N*-[1-phenyl-2-(phenylseleno)ethyl]-*p*-toluenesulfonamide (**1**). The effect of solvent was examined briefly and summarized in Scheme 1 which showed that 1,2-dichloroethane was the suitable solvent for this reaction. By the increase of the amount of sulfonamide to 1.5 equivalent, the yield of **1** was improved up to 96%.

When applied to cyclohexene, the yield of β-tosylamino-substituted selenide (**2**) was 66% under the analogous conditions (Scheme 2). We tried to improve the yield by the addition of a catalyst. Typical results are summarized in Scheme 2. Among various acids ex-



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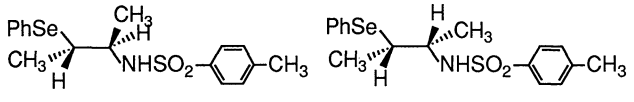
Scheme 2.

Catalyst	(equiv)	Temp	**2**, Yield[a]/%
—	—	Reflux	66
SiO_2	(0.8)	Reflux	60
50% CF_3SO_3H aq	(0.5)	R.T.	53
Dow X	(0.01)	Reflux	89
$ZnCl_2/Et_2O$	(0.2)	R.T.	85

a) Isolated yield by column chromatography.



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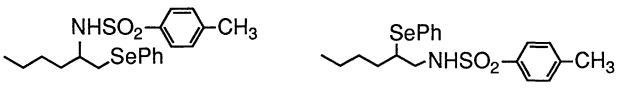

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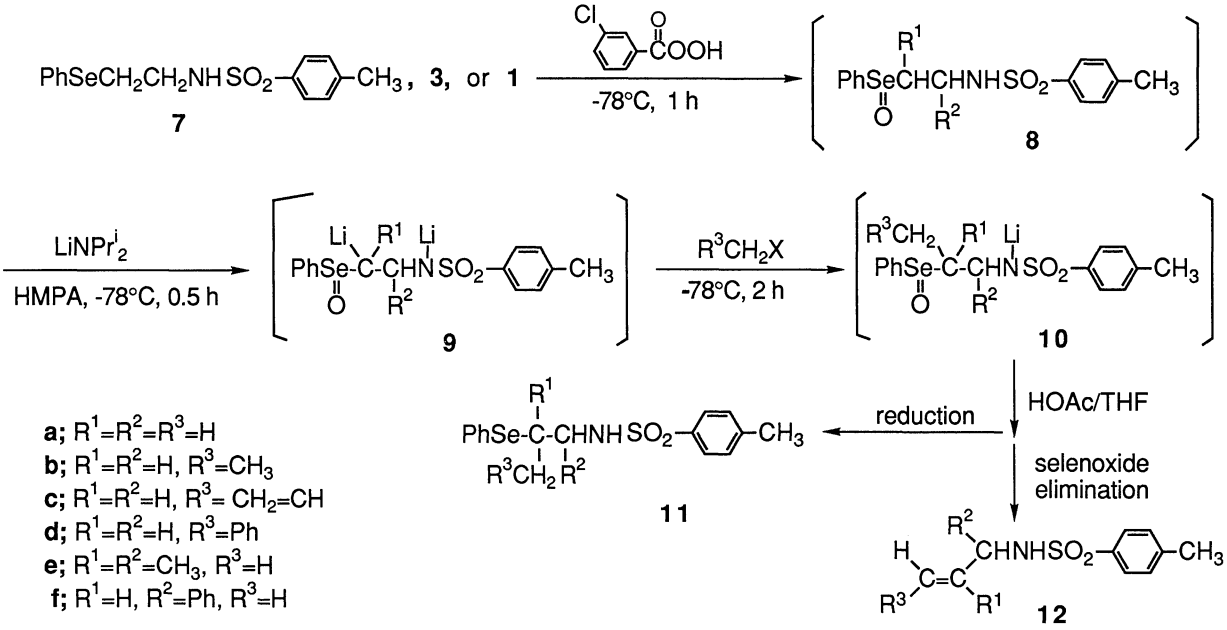
amined, zinc(II) chloride and cation-exchange resin Dow X showed the remarkable effect to produce **2** in satisfactory yields. It is interesting that trifluoromethanesulfonic acid, which was a good catalyst in the amidoselenation using nitriles as the nitrogen source (Ritter-type reaction),[1] did not facilitate the present reaction. The role of the catalyst may be ascribed to the interaction with chlorine atom in 2-chlorocyclohexyl phenyl selenide to form an episelenonium ion intermediate, but the detail is not yet clear.

To confirm the stereospecificity of this reaction, *cis*- and *trans*-2-butene were employed as substrates. In the case of *trans*-2-butene, the yield of **3** (18%) was much worse than that of **2** in the absence of catalyst. The addition of Dow X improved the yield of **3** to moderate (53%), and a satisfactory result was obtained by the use of zinc(II) chloride as catalyst (92%). In all cases, the *erythro*-isomer was found to be the sole product. On the other hand, the *threo*-isomer (**4**) was produced selectively from *cis*-2-butene in quantitative yield ($ZnCl_2$ as catalyst). This stereospecificity can be explained by trans addition of benzeneselenenyl chloride to olefins[3] and subsequent substitution of chlorine atom by *p*-toluenesulfonamide with an anchimeric assistance of phenylseleno group.

When applied to 1-hexene under the same conditions, a mixture of regioisomers (**5** and **6**) was produced in 76% total yield. The Markovnikov-type adduct (**5**) was the major product and the ratio (78:22) was similar to those in the previously reported selenium-induced Ritter-type reactions.[1] This result suggests that the nature of episelenonium ion is similar in both reactions despite the difference of the catalysts and solvents.

It is interesting that **1** was produced in an excellent yield without catalyst while the addition of catalyst was required for the formation of **2**, **3**, **4**, and **5** and **6** in good yields. This difference seems to reflect the activation energy for the formation of episelenonium ion from β-chloroalkyl phenyl selenide. It is reasonable to assume that the episelenonium ion stabilized by phenyl group can be generated more easily than those stabilized by one or two alkyl group(s).

As we succeeded in the introduction of tosylamino and phenylseleno groups into various types of olefins, our interest was focused on the lithiation and subsequent alkylation of the carbon atom bearing the phenylseleno group thus introduced. We adopted the one-pot procedure reported by Reich.[4] As summarized in Scheme 3, this procedure consists of four steps; 1) the oxidation of selenide to selenoxide (**8**) at −78 °C; 2) hydrogen abstraction by lithium diisopropyl amide (LDA) on the carbon atom bearing the seleninyl group in **8**; 3) replacement of the lithium by carbon electrophile (**9**→**10**); 4) reduction of the alkylated selenoxide to selenide (**11**) or to allow the selenoxide to eliminate to afford olefinic compounds (**12**) by raising the reaction temperature. Reaction conditions were examined using unsubstituted selenide **7**. Typical results are summarized in Table 1 using various carbon electrophiles. When the lithiation (**8**→**9**) was carried out in the absence of hexamethylphosphoric triamide (HMPA)(Run 1), the yield of **11a** was a little lower than that in Run 2. Although sodium iodide reduced the selenoxides to selenides effectively in the cases of R^3=H and CH_3 (Runs 2 and 3), it could not reduce the selenoxides **10c** and **10d** efficiently and considerable amounts of elimination products (**12c** and **12d**) were obtained in the cases of R = CH_2=CH and Ph (Runs 4 and 7). This difference seems to be due to the



Scheme 3.

Table 1. Yields of **11** and/or **12** Using Various Electrophiles and Reducers[a)]

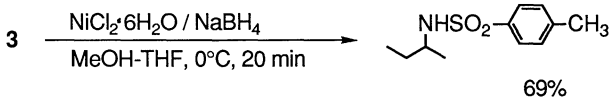
Run	Selenide	R^3	X	mmol	Reducer	mmol	Time/h	Product(s) and yield(s) (%)[b)]
1	**7**	H	I	2	NaI aq	2	0.25	**11a** (61)[c)]
2	**7**	H	I	2	NaI aq	2	0.25	**11a** (75)
3	**7**	CH_3	I	2	NaI aq	2	0.25	**11b** (80)
4	**7**	CH_2=CH	Br	2	NaI aq	2	0.25	**12c** (88)
5	**7**	CH_2=CH	Br	2	$(MeO)_3P$	1.1	12	**11c** (63)+**12c** (13)
6	**7**	CH_2=CH	Br	4	$(MeO)_3P$	2.2	12	**11c** (72)+**12c** (16)[d)]
7	**7**	Ph	Br	2	NaI aq	2	0.25	**11d** (13)+**12d** (58)
8	**7**	Ph	Br	4	$(MeO)_3P$	2.2	12	**11d** (65)+**12d** (35)
9	**3**	H	I	2	—	—	0.5	**12e** (62)[d)]
10	**3**	H	I	4	$(MeO)_3P$	4.4	12	**12e** (55)[d)]
11	**1**	H	I	2	NaI aq	2	2	**12f** (45)[d)]
12	**1**	H	I	4	$(MeO)_3P$	4.4	12	**11f** (50)+**12f** (21)[d)]

a) Carried out using selenide (1 mmol), *m*-CPBA (1.1 mmol), LDA (3.6 mmol), HMPA (5 mmol) in THF (5 ml) and AcOH/THF (1/10; 3.5 ml). b) Isolated yield by column chromatography. c) Carried out without HMPA. d) LDA (4.8 mmol) was used.

conjugation of the forming double bond with the vinyl or phenyl group, which would facilitate the selenoxide elimination reaction. We searched for more powerful reducers and found that selenides **11c** and **11d** were obtained as the major products by the use of trimethyl phosphite (Runs 5,6, and 8). We also studied the methylation of substituted selenides (**3** and **1**) under the analogous conditions. To our surprise, reduced selenide (**11e**) was not obtained even by the use of trimethyl phosphite as reducer in the dimethyl-substituted case (**3**) (Run 10). This seems to reflect the rate enhancement of the elimination reaction by the presence of methyl group (R^1) on the carbon atom bearing the seleninyl group.[7)] The yield of **12e** was a little better when the reaction mixture was allowed to warm up to room temperature without the addition of any reducer (Run 9). The structure of the elimination product was allylic amide (**12e**) and we could not detect the regioisomer (vinylic amide) which would result from the selenoxide elimination with the hydrogen atom attached to the carbon bearing the nitrogen functional group. Similar to the acetamide case,[1b,2)] selenoxide elimination "away from" the nitrogen functional group was confirmed in this sulfonamide case. Even in the phenyl-substituted case (**1**), allylic amide (**12f**) was the product of the selenoxide elimination reaction and vinylic amide, double bond in which would conjugate with phenyl ring, was not detected in the producuts.[5)] In good agreement with the fact that R^1=H in **10f**, selenide (**11f**) was the major product accompanied with the elimination product (**12f**) when trimethyl phosphite was employed as reducer (Run 12).

Finally, we confirmed that reductive removal of phenylseleno group by nickel boride[6)] to afford saturated compounds is applicable to our β-tosylamino-substituted selenides. Thus, the reaction of **3** with nickel chloride and sodium borohydride afforded *N*-(1-methylpropyl)-*p*-toluenesulfonamide in a satisfactory yield (Scheme 4).

As a conclusion, our methodology would allow the introduction of phenylseleno and tosylamino groups into various types of olefins with predicted regioselectivity and also allow the further introduction of various carbon electrophiles into the carbon atom bearing the phenylseleno group. Subsequent reductive or oxidative removal of the phenylseleno group will afford saturated or allylic amide selectively. Thus, the preparation of a wide range of saturated or allylic amides is now possible by the present methodology by a suitable choice of olefins and carbon electrophiles.



Scheme 4.

Experimental

The IR spectra were taken with a JASCO IR-810 spectrometer. ^1H and ^{13}C NMR spectra were recorded with JEOLCO JNM-FX-100 (100 MHz), JNM-GX-400 (400 MHz), and Varian VXR-200 (200 MHz) instruments in $CDCl_3$ using TMS as internal standard. Melting points were determined with a Shimadzu MM-2 micro melting point determination apparatus and were uncorrected. Liquid chromatographic analyses were carried out with a Waters HPLC system equipped with a 6000A solvent delivery system, a Model 440 absorbance detector (at 254 nm), and a Cosmosil packed column (4.6 mm×10 mm). GLC analyses were carried out on a Shimadzu 4CMPF apparatus using EGSS-X (15%)-Chromosorb W (3 m) column. Mass spectra were measured on a JEOL JMS-DX-300 mass spectrometer.

Materials. Tetrahydrofuran (THF) and diethyl ether were dried over benzophenone ketyl and were distilled just before use. All other organic solvents were purified before use by distillation. Zinc(II) chloride was purified by sublimation and was stored and used as saturated solution in diethyl ether (0.69 mol dm^{-3}). LDA was prepared by the addition of a solution of butyllithium in hexane (1.5 mol dm^{-3}) to a solution of diisopropylamine in THF at −78 °C and subsequent stirring at 0 °C for 30 min. Dow X (50 w×8, Na type, 20—50 mesh, Dow

Chemical Company) were treated with aqueous HCl before use. All other organic and inorganic materials were commercial products and were used without further purification.

Preparation of *N*-[2-(Phenylseleno)cyclohexyl]-*p*-toluenesulfonamide (2). Typical Procedure. Cyclohexene (0.12 ml; 1.1 mmol) was added to a solution of benzeneselenenyl chloride (97%, 0.20 g; 1.0 mmol) in 1,2-dichloroethane (3.0 ml) and the resulting colorless solution was stirred at ambient temperature for 15 min. After the addition of *p*-toluenesulfonamide (0.26 g, 1.5 mmol) and stirring for 0.5 h, a saturated solution of zinc(II) chloride in diethyl ether (0.29 ml; 0.20 mmol) was added and the resulting mixture was stirred at ambient temperature for 24 h. The reaction mixture was added to saturated aqueous $NaHCO_3$ (60 ml) and the products were extracted with dichloromethane (20 ml×3). The organic layer was washed with brine (30 ml), dried over $MgSO_4$, and evaporated in vacuo to leave a pale yellow oil. Column chromatography [silica gel (200 mesh), hexane–ethyl acetate (2:1) as eluant] of this oil afforded **2** (0.35 g, 0.85 mmol; 85%) as white crystals; mp 133—134 °C [from hexane–ethyl acetate (5:1)]. IR (KBr disc) 3270 cm^{-1}. ^1H NMR (400 MHz) δ=1.2—1.7 (m. 8H), 2.44 (s. 3H), 2.9—3.1 (m. 2H), 5.10 (br. d. 1H, J=3.4 Hz), 7.2—7.4 (m. 7H), and 7.75 (d. 2H, J=8.3 Hz). ^{13}C NMR (25 MHz) δ=21.5 (q), 23.3 (t), 25.2 (t), 32.2 (t), 32.5 (t), 47.6 (d), 55.8 (d), and phenyl signals. Found: C, 56.07; H, 5.65; N, 3.40%. Calcd for $C_{19}H_{23}NO_2SSe$: C, 55.87; H, 5.69; N, 3.43%.

Spectral and analytical data other β-tosylamino-substituted selenides are as follows.

***N*-[1-Phenyl-2-(phenylseleno)ethyl]-*p*-toluenesulfonamide (1):** White crystals, mp 92—93 °C [from hexane–ethyl acetate (5:1)]. IR (KBr disc) 3270 cm^{-1}. ^1H NMR (100 MHz) δ=2.34 (s. 3H), 3.09 (dd. 1H, J=12.7 and 6.8 Hz), 3.27 (dd, 1H, J=12.7 and 6.8 Hz), 4.36 (q. 1H, J=6.7 Hz), 5.65 (d. 1H, J=6.3 Hz), and 6.8—7.7(m. 14 H). ^{13}C NMR (25 MHz) δ=21.5 (q), 35.1 (t), 57.3 (d), and phenyl signals. Found: C, 58.64; H, 4.73; N, 3.18%. Calcd for $C_{21}H_{21}NO_2SSe$: C, 58.60; H, 4.93; N, 3.26%.

***N*-[*erythro*-1-Methyl-2-(phenylseleno)propyl]-*p*-toluenesulfonamide (3):** White crystals, mp 117—118 °C (from hexane). IR(KBr disc) 3275 cm^{-1}. ^1H NMR (400 MHz) δ=1.08 (d. 3H, J=6.8 Hz), 1.37 (d. 3H, J=7.3 Hz), 2.36 (s. 3H), 3.20 (dq. 1H, J=3.6 and 7.3 Hz), 3.4—3.5 (m. 1H), 5.33 (d. 1H, J=8.8 Hz), 7.2—7.4 (m. 7H), and 7.72 (d. 2H, J=8.3 Hz). ^{13}C NMR (25 MHz) δ=18.3 (q), 19.5 (q), 21.4 (q), 47.7 (d), 53.8 (d), and phenyl signals. Found: C, 53.16; H, 5.43; N, 3.57%. Calcd for $C_{17}H_{21}NO_2SSe$: C, 53.39; H, 5.55; N, 3.66%.

***N*-[*threo*-1-Methyl-2-(phenylseleno)propyl]-*p*-toluenesulfonamide (4):** White crystals, mp 123—124 °C (from hexane). IR (KBr disc) 3260 cm^{-1}. ^1H NMR (400 MHz) δ=1.04 (d. 3H, J=6.8 Hz), 1.30 (d. 3H, J=6.8 Hz). 2.39 (s. 3H), 3.3—3.5 (m. 2H), 5.26 (d. 1H, J=7.3 Hz), 7.2—7.5 (m. 7H), and 7.64 (d. 2H, J=8.3 Hz). ^{13}C NMR (25 MHz) δ=15.9 (q), 16.8 (q), 21.4 (q), 44.0 (d), 53.2 (d), and phenyl signals. Found: C. 53.35; H, 5.56; N, 3.68%. Calcd for $C_{17}H_{21}NO_2SSe$: C, 53.39; N, 5.55; N, 3.66%.

***N*-[1-[(Phenylseleno)methyl]pentyl]-*p*-toluenesulfonamide (5) and *N*-[2-(phenylseleno)hexyl]-*p*-toluenesulfonamide (6)** (identified as a mixture, 78:22 by ^{13}C NMR): IR (liq. film) 3280 cm^{-1}. ^1H NMR (400 MHz) δ=0.75 (t. 3H, J=7.1 Hz; **5**), 0.86 (t. 3H, J=7.1 Hz; **6**), 1.0—1.6 (m. 6H), 2.40 (s. 3H; **5**), 2.44 (s. 3H; **6**), 2.77 (dd. 1H, J=12.7 and 6.4 Hz; **5**), 2.91 (ddd. 1H, J=13.9, 8.7, and 5.8 Hz; **6**), 3.0—3.1 (m. 2H; **6**), 3.10 (dd. 1H, J=12.7 and 3.9 Hz; **5**), 3.3—3.4 (m. 1H; **5**), 4.74 (d. 1H, J=8.3 Hz; **5**), 5.03 (br. t. 1H, J=5.8 Hz; **6**), 7.1—7.5 (m. 7H), 7.62 (d. 2H, J=8.3 Hz; **5**), and 7.69 (d. 2H, J=8.3 Hz; **6**). ^{13}C NMR (25 MHz) δ (**5**)=13.7 (q), 21.4 (q), 22.1 (t), 27.3 (t), 29.6 (t), 33.8 (t), 53.5 (d), and phenyl signals: δ (**6**)=13.7 (q), 21.4 (q), 22.1 (t), 22.2 (t), 32.0 (t), 45.2 (d), 46.5 (t), and phenyl signals. Found: C, 55.57; H, 6.23; N, 3.30%. Calcd for $C_{19}H_{25}NO_2SSe$: C, 55.59; H, 6.15; N, 3.41%.

***N*-[2-(Phenylseleno)ethyl]-*p*-toluenesulfonamide (7):** White crystals, mp 59—60 °C (from hexane). IR (KBr disc) 3270 cm^{-1}. ^1H NMR (200 MHz) δ=2.42 (s. 3H), 2.90 (t. 2H, J=6.8 Hz), 3.14 (q. 2H, J=6.3 Hz), 4.98 (t, 1H, J=5.9 Hz), 7.1—7.4 (m. 7H), and 7.69 (d. 2H, J=8.2 Hz). ^{13}C NMR (25 MHz) δ=21.4 (q), 27.0 (t), 42.5 (t), and phenyl signals. Found: C, 50.77; H, 4.88; N, 3.89%. Calcd for $C_{15}H_{17}NO_2SSe$: C, 50.84; H, 4.85; N, 3.95%.

Methylation of β-Position on *N*-Ethyl Group of 7. General Procedure. To a solution of **7** (0.35 g, 1.0 mmol) in THF (2.0 ml) was added a solution of *m*-chloroperbenzoic acid (*m*-CPBA) (80%; 0.24 g, 1.1 mmol) in THF (1.0 ml) under nitrogen atmosphere at −78 °C and the resulting mixture was stirred at the same temperature for 1 h. A solution of LDA (3.6 mmol) in THF (2.0 ml) and then HMPA (0.87 ml, 5.0 mmol) were added slowly to the mixture and the resulting mixture was stirred at −78 °C for 0.5 h. Methyl iodide (98%; 0.13 ml, 2.0 mmol) was added and the reaction mixture was further stirred at −78 °C for 2 h. Afterward it was not necessary to keep the reaction under nitrogen atmosphere. A mixture of acetic acid and THF (1:10, 3.5 ml) and then sodium iodide (0.30 g, 2.0 mmol) in water (1.0 ml) were added and the resulting mixture was stirred vigorously at ambient temperature for 0.25 h. Saturated aqueous $Na_2S_2O_3$ was added in small portions until pale yellow and the reaction mixture was further stirred at the same temperature for 0.25 h. The reaction mixture was added to saturated aqueous $Na_2S_2O_3$ (10 ml) and the products were extracted with chloroform (15 ml×3). The organic layer was washed with saturated aqueous $NaHCO_3$ and brine, dried ($MgSO_4$), and evaporated in vacuo to leave a brown oil. Column chromatography [silica gel (200 mesh), hexane–ethyl acetate (3:1) as eluant] afforded *N*-[2-(phenylseleno)propyl]-*p*-toluenesulfonamide (**11a**)(0.275 g, 0.75 mmol; 75%) as a brown oil. IR (liq. film) 3280 cm^{-1}. ^1H NMR (400 MHz) δ=1.33 (d. 3H, J=6.8 Hz), 2.40 (s. 3H), 2.96 (dt. 1H, J=19.0 and 6.3 Hz), 2.99 (dt. 1H, J=19.0 and 6.3 Hz), 3.23 (sextet, 1H, J=6.7 Hz), 5.37 (t. 1H, J=6.4 Hz), 7.1—7.4(m. 7H), and 7.69(d. 2H, J=8.3 Hz). ^{13}C NMR(25 MHz) δ=19.1 (q), 21.5 (q), 38.3 (d), 48.2 (t), and phenyl signals. Found: C, 52.13; H, 5.24; N, 4.10%. Calcd for $C_{16}H_{19}NO_2SSe$: C, 52.16; H, 5.21; N, 3.80%.

Spectral and analytical data of other alkylated products are as follows.

***N*-[2-(Phenylseleno)butyl]-*p*-toluenesulfonamide (11b):** Brown oil. IR (liq. film) 3280 cm^{-1}. ^1H NMR(400 MHz) δ=0.98 (t. 3H, J=7.3 Hz), 1.53 (d.quint. 1H, J=13.7 and 7.3 Hz), 1.66 (d.quint. 1H, J=13.7 and 7.3 Hz), 2.40 (s. 3H), 2.9—3.1 (m. 3H), 5.53 (br. t. 1H, J=5.9 Hz), 7.1—7.4 (m. 7H), and 7.69 (d. 2H, J=8.3 Hz). ^{13}C NMR (25 MHz) δ=12.2 (q), 21.5 (q), 25.6 (t), 46.2 (d), 46.2 (t), and phenyl signals. Found: C, 53.57; H, 5.58; N, 3.79%. Calcd for $C_{17}H_{21}NO_2SSe$: C, 53.39; H, 5.55; N, 3.66%.

***N*-[2-(Phenylseleno)-4-pentenyl]-*p*-toluenesulfonamide (11c):** Pale yellow oil. IR(liq. film) 3290 cm^{-1}. ^1H NMR (400 MHz) δ=2.37 (t. 2H, J=6.8 Hz), 2.42 (s. 3H), 2.95 (quint.

1H, J=6.8 Hz), 3.07 (dt. 1H, J=19.3 and 6.8 Hz), 3.14 (dt. 1H, J=19.3 and 6.8 Hz), 5.0—5.1 (m, 2H), 5.15 (t. 1H, J=6.1 Hz), 5.76 (ddt. 1H, J=17.1, 10.3, and 6.8 Hz), 7.1—7.4 (m. 7H), and 7.68 (d. 2H, J=8.3 Hz). ^{13}C NMR (25 MHz), δ=21.4 (q), 36.5 (t), 43.7 (d), 46.0 (t), 117.7 (t), 134.7 (d), and phenyl signals. Found: C, 54.39; H, 5.37; N, 3.45%. Calcd for $C_{18}H_{21}NO_2SSe$: C, 54.81; H, 5.38; N, 3.55%.

***N*-[2-(phenylseleno)-3-phenylpropyl]-*p*-toluenesulfonamide (11d):** Pale yellow oil. IR (liq. film) 3280 cm^{-1}. ^{1}H NMR (400 MHz) δ=2.40 (s. 3H), 2.88 (dd. 1H, J=14.2 and 7.8 Hz), 2.93 (dd. 1H, J=14.2 and 7.3 Hz), 2.97 (dt. 1H, J=19.4 and 6.4 Hz), 3.01 (dt. 1H, J=19.4 and 6.4 Hz), 3.31 (quint. 1H, J=6.6 Hz), 5.17 (t. 1H, J=6.1 Hz), 7.0—7.4 (m. 12H), and 7.60 (d. 2H, J=8.3 Hz). ^{13}C NMR (25 MHz) δ=21.3 (q), 38.7 (t), 45.7 (d), 45.7 (t), and phenyl signals. High-resolution mass spectrum, M$^+$. Found: m/z 445.06217. Calcd for $C_{22}H_{23}NO_2SSe$: M, 445.06210.

***N*-[1-Phenyl-2-(phenylseleno)propyl]-*p*-toluenesulfonamide (11f)** (identified as a mixture of *threo* and *erythro*[8] isomers, *threo*:*erythro*=80:20 by ^{13}C NMR): White solid. IR (KBr disc) 3270 cm^{-1}. ^{1}H NMR (200 MHz) δ=1.20 (d. 3H, J=7.2 Hz; *threo*), 1.32 (d. 3H, J=7.0 Hz; *erythro*), 2.34 (s. 3H), 3.39 (quint. 1H, J=7.2 Hz), 4.21 (dd. 1H, J=7.5 and 5.1 Hz; *threo*), 4.44 (dd. 1H, J=7.2 and 4.3 Hz; *erythro*), 5.50 (d. 1H, J=4.3 Hz; *erythro*), 5.74 (d. 1H, J=5.1 Hz; *threo*), and 7.0—7.5 (m. 14H). ^{13}C NMR (25 MHz) (*threo*) δ=19.0 (q), 21.3 (q), 44.8 (d), 62.2 (d), and phenyl signals. (*erythro*) δ=18.1 (q), 21.3 (q), 46.2 (d), 61.7 (d), and phenyl signnals. Found: C, 59.73; H, 5.24; N, 3.18%. Calcd for $C_{22}H_{23}NO_2SSe$: C, 59.44; H, 5.23; N, 3.15%.

***N*-(trans-2,4-pentadienyl)-*p*-toluenesulfonamide (12c):** White crystals, mp 89—90 °C [from hexane–ethyl acetate (5:1)]. IR (KBr disc) 3270 cm^{-1}. ^{1}H NMR (400 MHz) δ=2.42 (s. 3H), 3.60 (t. 2H, J=6.1 Hz), 4.93 (t. 1H, J=6.1 Hz), 5.06 (d. 1H, J=10.3 Hz), 5.13 (d. 1H, J=16.6 Hz), 5.53 (dt. 1H, J=15.0 and 6.5 Hz), 6.09 (dd. 1H, J=15.0 and 11.0 Hz), 6.21 (dt. 1H, J=16.6 and 10.3 Hz), 7.30 (d. 2H, J=8.3 Hz), and 7.76 (d. 2H, J=8.3 Hz). ^{13}C NMR (25 MHz) δ=21.5 (q), 44.8 (t), 117.9 (t), 128.1 (d), 133.4 (d), 135.8 (d), and phenyl signals. Found: C, 60.71; H, 6.43; N, 5.82%. Calcd for $C_{12}H_{15}NO_2SSe$: C, 60.72; H, 6.38; N, 5.90%.

***N*-(trans-3-Phenyl-2-propenyl)-*p*-toluenesulfonamide (12d):** White crystals, mp 106—107 °C [from hexane–ethyl acetate (5:1)] (lit,[9] mp 110 °C). IR (KBr disc) 3290 cm^{-1}. ^{1}H NMR (100 MHz) δ=2.34 (s. 3H), 3.70 (t. 2H, J=6.1 Hz), 5.28 (t. 1H, J=6.1 Hz), 5.94 (dt. 1H, J=15.9 and 6.1 Hz), 6.39 (d. 1H, J=15.9 Hz), 6.8—7.4 (m. 7H), and 7.77 (d. 2H, J=8.3 Hz). ^{13}C NMR (25 MHz) δ=21.4 (q), 45.4 (t), 124.3 (d), 132.8 (d), and phenyl signals.

***N*-(1,2-Dimethyl-2-propenyl)-*p*-toluenesulfonamide (12e):** Pale yellow oil. IR(liq. film) 3280 cm^{-1}. ^{1}H NMR (400 MHz) δ=1.15 (d. 3H, J=7.3 Hz), 1.57 (s. 3H), 2.41 (s. 3H), 3.83 (quint. 1H, J=7.3 Hz), 4.68 (s. 1H), 4.80 (s. 1H), 5.40 (d. 1H, J=7.3 Hz), 7.27 (d. 2H, J=8.3 Hz), and 7.78 (d. 2H, J=8.3 Hz). ^{13}C NMR (25 MHz) δ=18.1 (q), 20.5 (q), 21.5 (q), 54.8 (d), 111.9 (t), 145.1 (s), and phenyl signals. High-resolution mass spectrum, M$^+$. Found: m/z 239.09506. Calcd for $C_{12}H_{17}NO_2S$: M, 239.09535.

***N*-(1-Phenyl-2-propenyl)-*p*-toluenesulfonamide (12f):** Pale yellow oil (lit,[9] mp 103 °C). IR (liq. film) 3290 cm^{-1}. ^{1}H NMR (200 MHz) δ=2.43 (s. 3H), 4.93 (t. 1H, J=6.7 Hz), 5.0—5.2 (m. 3H), 5.86 (ddd. 1H, J=16.6, 10.8, and 6.7 Hz), 7.0—7.4 (m. 7H), and 7.66 (d. 2H, J=8.2 Hz). ^{13}C NMR (25 MHz) δ=21.4 (q), 59.8 (d), 116.6 (t), 137.1 (d), and phenyl signals.

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