a given alkylated or protonated species. Examples include ethyl bromide $(C_2H_5)_2Br^+$ and methane $C_2H_5^+$ for ethylation, methyl fluoride $(CH_3)_2F^+$ and methyl chloride $(CH_3)_2Cl^+$ for methylation, and isobutane $C_4H_9^+$, methane CH_5^+, and hydrogen H_3^+ for protonation.

Our conclusions are in broad agreement with those of theoretical calculations, including the similar basicities of ring and substituent sites in aniline. There is less agreement with an earlier study[21] on the ethylation of phenol although we interpret the corresponding aniline results rather differently than these authors. (Our high collision energy aniline data were further confirmed by use of a VG Instruments ZAB reverse-geometry mass spectrometer.) It should also be noted that our results for methylation of phenol and aniline are quite different from those obtained[25,26] under nonequilibrium conditions at much higher pressures. These authors found predominant substituent methylation for phenol and a substantial degree of ring alkylation for aniline. Although the reasons for these differences are not fully understood, the short reaction times, and quenching associated with the higher pressures used, could result in kinetically controlled processes. Key features of the present results, which are representative of chemical-ionization conditions, are the contrasting behavior of aniline and phenol on the one hand and the contrasting results obtained for protonation and alkylation on the other. The data are self-consistent, and agreement between the high- and low-energy MS/MS data is good.

Acknowledgment. This work was supported by National Science Foundation Grant CHE 80 11425. D.J.B. acknowledges the Phillips Petroleum Co. for a graduate fellowship.

Registry No. Aniline, 62-53-3; phenol, 108-95-2; thiophenol, 108-98-5; thioanisole (protonated), 77421-01-3; *p*-methylbenzenethiol (protonated), 87728-89-0; *p*-toluidine (protonated), 17112-11-7; *N*-methylaniline (protonated), 17456-49-4; *N*-ethylaniline (protonated), 23388-60-5; *p*-ethylaniline (protonated), 41265-89-8; *o*-cresol (protonated), 58142-00-0; *m*-cresol (protonated), 37396-35-3; anisole (protonated), 18223-09-1; *p*-ethylphenol (protonated), 87728-90-3; phenetole (protonated), 87728-91-4.

Supplementary Material Available: Figures showing MS/MS spectra for collision-induced dissociation of ethylated aniline, spectra of fragment ions produced on collision-induced dissociation of ethylated phenol and ions formed by protonation of *p*-ethylphenol and phenetole, spectra of fragment ions from protonated and deuterated aniline, and daughter-ion spectra of protonated aniline (6 pages). Ordering information is given on any current masthead page.

Selenium-Stabilized Carbocations. Formation of 2-(Phenylseleno)allyl Cations and Their Reactions with Furan, Pyrrole, and Thiophene

Serge Halazy and Lâszlô Hevesi*

Department of Chemistry, Facultês Universitaires Notre-Dame de la Paix, B-5000 Namur, Belgium

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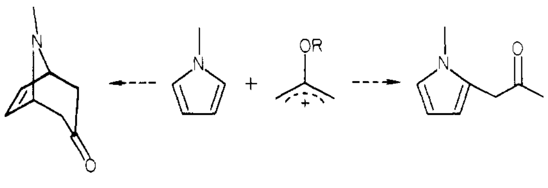
β-Bromovinyl selenides I (R_1 = H, CH_3, C_2H_5; R_2 = H, CH_3; R_3 = H, CH_3) have been prepared in excellent yields from allenes and benzeneselenenyl bromide. On treatment with silver perchlorate in nitromethane at −15 °C and in the presence of a weak base, these β-bromovinyl selenides reacted smoothly with electron-rich aromatic molecules such as furan, *N*-methylpyrrole, thiophene, or 1,3,5-trimethoxybenzene to give electrophilic substitution products exclusively and in good yields (60–70%). From this and from the systematic absence of [4 + 3 → 7] cycloaddition products it is tentatively concluded that the actual reactive species might be III rather than allylic cation II. It has also been shown that the substitution products can be efficiently deselenated by the use of tri-*n*-butyltin hydride at reflux in benzene and in the presence of azobis(isobutyronitrile) (AIBN).

Allyl cations substituted at position 2 are interesting reactive intermediates from both synthetic and theoretical points of view. The synthetic usefulness of these species arises primarily from their ability to undergo [4 + 3 → 7] cycloadditions,[1-3] thus providing a new entry to the class of seven-membered-ring compounds including the bicyclic ones. It is known, however, for the 2-oxyallyl[4-6] and the 2-[(trimethylsilyl)oxy]allyl[3] species that in the case of their reactions with aromatic molecules such as furan or pyrrole, substantial competition exists between the two major pathways, i.e., cycloaddition and electrophilic substitution (eq 1). A number of factors have been shown to affect



(1)

R = metal, alkyl, $Si(CH_3)_3$

this competition, the most important ones being (i) the specific electronic nature of the cationic species,[4b,5a,6,7] (ii) the substitution pattern of the aromatic reagent,[4b,5,6,8] and (iii) the reaction medium.[3]

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(1) First example by: Fort, A. W. *J. Am. Chem. Soc.* **1962**, *84*, 4981. For reviews see: (a) Hoffmann, H. M. R. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 819. (b) Noyori, R. *Acc. Chem. Res.* **1979**, *12*, 61. (c) Chan, T. H. *Ibid.* **1977**, *10*, 442. Chan, T. H.; Ony, B. S. *Tetrahedron* **1980**, *36*, 2269.

(2) Hoffmann, H. M. R.; Matthei, J. *Chem. Ber.* **1980**, *113*, 3837.

(3) Shimizu, N.; Tanaka, M.; Tsuno, Y. *J. Am. Chem. Soc.* **1982**, *104*, 1330 and references cited.

(4) (a) Noyori, R.; Baba, Y.; Makino, S.; Takaya, H. *Tetrahedron Lett.* **1973**, 1741. (b) Noyori, R.; Baba, Y.; Hayakawa, Y. *J. Am. Chem. Soc.* **1974**, *96*, 3336.

(5) (a) Cowling, A. P.; Mann, J. *J. Chem. Soc., Perkin Trans. 1* **1978**, 1564. (b) Cowling, A. P.; Mann, J.; Usmani, A. A. *Ibid.* **1981**, 2116.

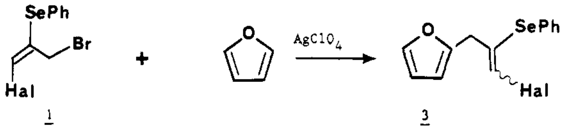
(6) Rowson, D. I.; Carpenter, B. K.; Hoffmann, H. M. R. *J. Am. Chem. Soc.* **1979**, *101*, 1786.

(7) Cookson, R. C.; Nye, M. J.; Subrahmanyam, G. *J. Chem. Soc. C* **1967**, 473.

(8) Hill, A. E.; Hoffmann, H. M. R.; *J. Am. Chem. Soc.* **1974**, *96*, 4597.

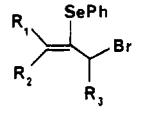
0022-3263/83/1948-5242$01.50/0

Scheme I

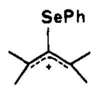


1	Hal	conditions	3	yield, %
a	Cl	CH_3NO_2, $CaCO_3$, 0 °C	a	64
a	Cl	CH_3NO_2, 0 °C	a	25
b	Br	CH_3NO_2, $CaCO_3$, 0 °C	b	61
b	Br	furan as solvent, $CaCO_3$ 0 °C	b	23

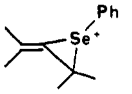
In connection with the influence of the nature of the allyl cationic species, we report here our first results on the reactions of 2-(phenylseleno)allyl cations II and III with the aromatic heterocycles furan, pyrrole, and thiophene.



I



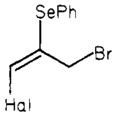
II

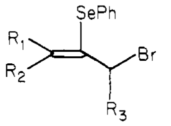


III

Results and Discussion

We have prepared two distinct groups of 2-(phenylseleno)allyl cation precursors 1 and 2. **1a** and **1b** have





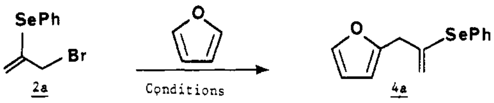
1a, Hal = Cl
b, Hal = Br

2a, $R_1 = R_2 = R_3 = H$
b, $R_1 = H$; $R_2 = R_3 = CH_3$ ($Z + E$)
c, $R_1 = C_2H_5$; $R_2 = R_3 = H$ ($Z + E$)
d, $R_1 = R_2 = CH_3$; $R_3 = H$

been obtained by addition of benzeneselenenyl chloride or bromide to propargyl bromide in dichloromethane solution at room temperature in 91% and 69% yields, respectively.[9] A single isomer was isolated in both cases; therefore, these reactions are regio- and stereospecific, the addition being presumably trans. Benzeneselenenyl chloride reacts rapidly with propargyl bromide (complete color discharge was observed within 1 h), but benzeneselenenyl bromide requires a longer reaction time (incomplete bleaching after 5 h). It is also worth noting that keeping the reaction mixtures at room temperature for 15–20 h did not change the structure of the products **1a** and **1b**.

In an analogous manner **2a–d** have been prepared by the addition of benzeneselenenyl bromide to the corresponding allenes[10] in essentially quantitative yields. These reactions are known to produce adducts in which selenyl moieties are linked exclusively to the central carbon atom of the starting allene. While the addition products of benzeneselenenyl chloride to allenes did not exhibit any subsequent regioisomerization,[11] we found that compounds **2a–d** are subject to three different kinds of isomerization, some of which occur spontaneously, others require acid catalysis. These transformations are discussed elsewhere.[12]

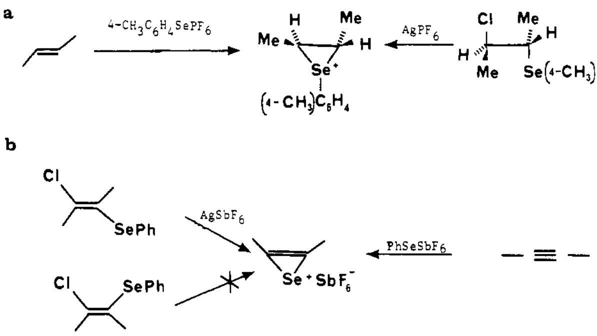
Scheme II



conditions	4a yield, %
$AgClO_4$, CH_3NO_2, $CaCO_3$, 0 °C	45
$AgClO_4$, CH_3NO_2, $CaCO_3$, −15 °C	62
$AgBF_4$, CH_3NO_2, $CaCO_3$, −15 °C	53
$AgOCOCH_3$, CH_3NO_2, 20 °C	0[a]
$AgClO_4$, CH_3CN, $CaCO_3$, −15 to 0 °C	0
$AgClO_4$, hexane, $CaCO_3$, −15 to 0 °C	0
$AgOCOCF_3$, CH_3NO_2, Na_2CO_3, −15 to 0 °C	~0[b]

[a] In this case $CH_2{=}C(SePh)CH_2OCOCH_3$ was isolated in 47% yield. [b] Mostly carbonyl-containing compounds (IR 1720 and 1780 cm^{-1}).

Scheme III



Rapid screening was necessary to define the optimal working conditions for the generation of selenium-substituted allylic cations. The results relative to the reactions of 1 and **2a** with furan are displayed in Schemes I and II, respectively.

First we note that both reaction systems lead exclusively to products 3 and **4a**, resulting from electrophilic substitution of the furan ring. Scheme I also shows a substantial increase in yield due to the buffering effect of added calcium carbonate, and use of furan as a solvent gives a much lower yield in **3b** as compared to nitromethane. On the other hand, it appears from Scheme II that the 2-(phenylseleno)allyl cation is most efficiently generated by the use of silver perchlorate in nitromethane at −15 °C and in the presence of calcium carbonate. However, by no means should it be inferred that other methods would not lead to this type of intermediates with comparable efficiency. Thus, treating allylic acetates or trifluoroacetates corresponding to 1 and 2 with zinc chloride[2] might be a valuable alternative.

Next we investigated mainly the reactivity of 2-(phenylseleno)-1,3-alkyl-substituted allyl cations generated from 2 toward five-membered aromatic heterocycles, furan, *N*-methylpyrrole, and thiophene. A few reactions have also been performed on pyrrole itself, but they always gave intractable mixtures of highly colored products which were not analyzed.

As witnessed by the results gathered in Table I electrophilic substitution products have been obtained usually

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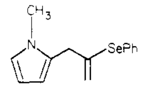
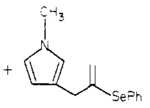
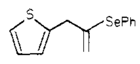
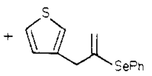
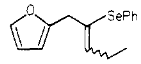
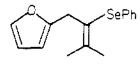
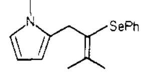
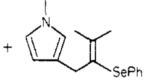
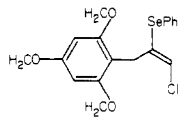
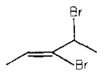
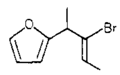
(9) Garratt, D. G.; Beaulieu, P. L.; Morisset, V. M. *Can. J. Chem.* **1981**, *59*, 927.

(10) Allene was prepared according to: Cripps, H. N.; Kiefer, E. F. "Organic Synthesis"; Wiley: New York, 1973; Collect. Vol. V., p 22. Alkyl-substituted allenes were obtained from the corresponding *gem*-dibromocyclopropane derivatives. See: Logan, T. J. *Tetrahedron Lett.* **1961**, 173. Moore, W. R.; Ward, H. R. *J. Org. Chem.* **1962**, *27*, 4179. Skattebol, L. *Acta Chem. Scand.* **1963**, *17*, 1683.

(11) (a) Beaulieu, P. L.; Morisset, V. M.; Garratt, D. G. *Tetrahedron Lett.* **1980**, *21*, 129. (b) Schmid, G. H.; Garratt, D. G.; Beaulieu, P. L. *Chem. Scr.* **1980**, *15*, 128. (c) Garratt, D. G.; Beaulieu, P. L.; Ryan, M. D. *Tetrahedron* **1980**, *36*, 1507.

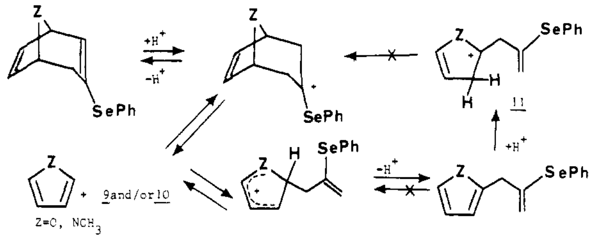
(12) Halazy, S.; Hevesi, L. *Tetrahedron Lett.* **1983**, *24*, 2689.

Table I. Reactions of 2-(Phenylseleno)allyl Cations with Aromatic Compounds

entry	cation precursor	aromatic compd	conditions^a	products	yield, %
1	**2a**	furan	A	**4a**	62
2	**2a**	*N*-methylpyrrole	A^b	 **5a** +  **5a′**	72^c
3	**2a**	thiophene	A	 **6a** +  **6a′**	61^d
4	**2b**	furan	A	**4b** (*Z* + *E*)	65
5	**2c**	furan	A^b	 **4c** (*Z* + *E*)	58
6	**2d**	furan	A^b	 **4d**	59
7	**2d**	furan	A^e	**4d**	44
8	**2d**	*N*-methylpyrrole	A^c	 **5d** +  **5d′**	50^f
9	**1a**	1,3,5-trimethoxybenzene	A, 0 °C	 **7**	65
10	 *Z* + *E*	furan	A^g	 **8** (*Z* + *E*)	63

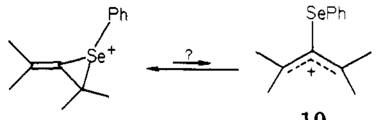
^{a} "A" stands for $AgClO_4/CH_3NO_2/CaCO_3/-15$ °C. ^{b} Na_2CO_3 used instead of $CaCO_3$. ^{c} An isomeric ratio of 85/15 was found by GLC but no structure assignment was made. ^{d} Nonassigned ratio of 60/40 by GLC. ^{e} $AgBF_4$ instead of $AgClO_4$ and Na_2CO_3 instead of $CaCO_3$. ^{f} Isomeric ratio (nonattributed) of 55/45 by GLC. ^{g} $AgOCOCF_3$ instead of $AgClO_4$.

Scheme IV



in good yields, but no trace of cycloaddition product could be isolated from or detected in any of the reaction mixtures. In this regard all the structural variations that have been made in the cation precursor proved to be useless. At present we cannot offer a fully consistent rationalization of these observations. However, the systematic absence of cycloaddition products as well as the fact that cyclopentadiene and **2a** only gave polymeric material suggest that peculiar features of our reactive species are responsible for the observed results. It is indeed described[13] that β-chloro-*p*-tolyl selenides form seleniranium salts when treated with silver hexafluorophosphate or antimonate (Scheme IIIa). The same seleniranium derivative is obtained from the reaction of 4-tolueneselenenyl salts with the corresponding alkenes. Similarly, phenylselenirenium hexafluoroantimonate was isolated both from 2-butyne and from the corresonding (*E*)-β-chlorovinyl selenide (Scheme IIIb). Interestingly, in the latter case (*Z*)-vinyl selenide did not lead to the selenirenium salt.[13] This shows that heterolysis of a vinylic carbon–chlorine bond requires the participation of the neighboring divalent selenium atom.

It seems, therefore, that heterolysis of the carbon–halogen bond in **1** and **2** and possibly also in 3,4-dibromopent-2-ene (Table I, entry 10) leads to bridged cationic species of the type **9**. Alkylideneseleniranium cation **9**



9 **10**

would then preferentially react with aromatic substrates in Friedel–Crafts fashion, or at least it would react in a stepwise rather than concerted manner to give the observed products.

Another explanation of our results is offered[14] in Scheme IV. Let us assume that both **9** and **10** are present in the reaction mixture so that both reaction paths (cycloaddition and substitution) can in principle be followed. It is quite reasonable that the bicyclic vinyl selenide, if formed, can

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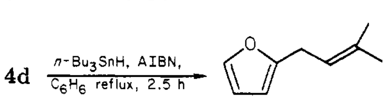
[13] Schmid, G. H.; Garratt, D. G. *Tetrahedron Lett.* **1975**, 3991.

[14] Private discussion with Prof. H. M. R. Hoffmann (University of Hannover).

revert to starting materials or to the Wheland intermediate. On the other hand, protonation of the substitution product could preferentially produce cation **11** and not the Wheland intermediate.[15] Therefore, incomplete neutralization of the acid present in the medium results in driving all the equilibria of Scheme IV irreversibly toward the Friedel–Crafts products. This kind of transformation of bicyclic to aromatic compounds has been reported in the literature.[8,16,17].

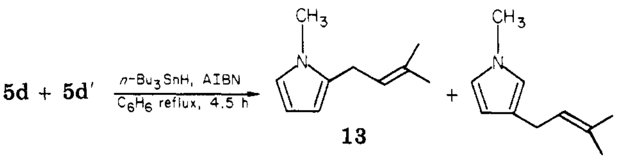
For illustration of the possibilities for further transforming the products **4–6**, two different types of reactions have been explored, hdyrolysis and reduction of the vinyl selenide moieties. It is known[18] that aliphatic vinyl selenides can efficiently be hydrolyzed by using either sulfuric acid or mercuric chloride in aqueous acetonitrile. Yet surprisingly **4d** was recovered unchanged after 20 h of heating at 80 °C with these reagents.

The same compound **4d** reacted smoothly with tri-*n*-butyltin hydride[19,20] in the presence of azobis(isobutyronitrile) (AIBN) to produce 2-isopentenylfuran **12** in good yield (eq 2). Similarly the mixture of **5d** and **5d′** was transformed to the corresponding mixture of 2- and 3-isopentenyl-*N*-methylpyrroles **13** and **14** (eq 3).



(2)

12 (70%)



(3)

13

14

(67%)

Further work is in progress in order to assess more closely the nature of the above selenium-containing cationic species as well as to define structural modifications which would allow preparation of bicyclic vinyl selenides corresponding to the [4 + 3 → 7] cycloaddtion reactions.

Experimental Section

General Methods. Commercial chemicals of 97% purity were used as such without further purification. 1-Butene, 2-butene, and isobutene have been purchased from Merck (Belgolabo) and 1,1-dichloro-2-propene, propargyl bromide, furan, *N*-methylpyrrole, thiophene, and 1,3,5-trimethoxybenzene from Aldrich Europe (Beerse).

Solvents were purified and dried by following standard procedures. Methylene chloride, nitromethane, and acetonitrile were stored on 4-Å molecular sieves.

Infrared spectra were recorded on a Perkin-Elmer Model 377 spectrometer, and nuclear magnetic resonance spectra were recorded on the JNM-MH-100 and JNM-FX90Q instruments of JEOL. Chemical Shifts are reported in parts per million (δ) relative to an internal tetramethylsilane reference. Normal mass spectral and exact mass measurements were carried out on an AEI MS-30 apparatus.

Benzeneselenenyl chloride (PhSeCl) and benzeneselenenyl bromide (PhSeBr) were prepared from diphenyl diselenide and sulfuryl choride and bromine, respectively, according to known methods.[21]

1-Chloro-2-(phenylseleno)-3-bromo-1-propene (1a) was prepared by adding through a syringe a 5.5×10^{-3} M solution of propargyl bromide dissolved in 3 mL of dichloromethane to an ice-cool solution of 5.5×10^{-3} M benzeneselenenyl chloride in 8 mL of CH_2Cl_2 under a nitrogen atmosphere. The initially dark brown solution turned to pale yellow within 1 h. The crude material obtained by evaporation of the solvent was purified by PLC (SiO_2, eluent pentane) and isolated as a pale yellow liquid: 1.56 g (91%); IR ($\bar{\nu}$ liquid film) 3050, 1590, 1575, 1470, 1435, 1205, 890, 780, 735 cm^{-1}; ^{1}H NMR (CCl_4) 7.4–7.2 (m, 5 H), 6.40 (s, 1 H), 4.05 (s, 2 H); ^{13}C NMR ($CDCl_3$) 133.5, 130.5, 129.4, 128.3 (aromatic and quaternary olefinic), 123.6 (d, olefinic), 29.6 (t, allylic); mass spectrum, *m/e* 310, calcd 309.86635, found 309.866 ± 0.006. The dibromo analogue **1b** was prepared in the same way, but purification (PLC, SiO_2, eluent pentane, R_f 0.5) after 14 h reaction gave a 69% yield: ^{1}H NMR (CCl_4) 7.4–7.2 (m, 5 H), 6.54 (s, 1 H), 4.05 (s, 2 H); ^{13}C NMR ($CDCl_3$) 133.8, 132.8, 132.0, 129.5, 128.4 (aromatic and quarternary olefinic), 111.6 (d, olefinic), 32.0 (t, allylic); mass spectrum, *m/e* 354, calcd 353.81589, found 353.816 ± 0.007.

2-(Phenylseleno)-3-bromo-1-propene (2a). Allene (4 g, 0.1 mol) was dissolved in 150 mL of dry dichloromethane at −78 °C. To this a solution of 22.5 g (0.095 mol) of benzeneselenenyl bromide in 50 mL of CH_2Cl_2 was added dropwise at the same temperature. Although an immediate color discharge was observed, the mixture was stirred at room temperature for 0.5 h. Evaporation of the solvent and purification by column chromatography (SiO_2, pentane eluent) yielded 26.2 g of **2a** as pale yellow liquid (95%).

Anal. Calcd: C, 39.16; H, 3.29. Found: C, 39.19; H, 3.27. Alkyl-substituted analogues **2b–d** have been prepared in a similar way, excepted for the following minor modifications. **2b** (*Z/E*, 75:25) is formed after 30 min of reaction of 2,3-pentadiene with benzeneselenenyl bromide in ether at 0 °C.

The same reaction performed on 1,2-pentadiene led after 1 h in ether at 20 °C to a mixture of **2c** (*Z* + *E*) and 2-(phenylseleno)-3-bromo-1-pentene in a 60:40 ratio. The latter regioisomer spontaneously transforms into **2c** (*Z* + *E*, >95%) after 8 days. Since compounds **2b,c** and their regioisomers undergo decomposition on silica gel, they were used without purification.

Finally, **2d** and its regioisomer 2-(phenylseleno)-3-(bromomethyl)-1-butene were formed (in a ratio of 92:8 in favor of the former) in ether at −30 °C. Again the latter isomer completely transformed into **2d** in 5 days. Moreover, **2d** can be purified by chromatography (SiO_2, pentane) without decomposition. ^{1}H and ^{13}C NMR as well as mass spectral data of compounds **2a–d** have been provided elsewhere.[12]

General Procedure for the Reactions of 2-(Phenylseleno)allyl Cations with Aromatic Compounds. Silver perchlorate (1.4 equiv) and 3 equiv of calcium or sodium carbonate were suspended in 3 mL of dry nitromethane under argon and at −15 °C. To the stirred suspensions was added by a syringe a mixture of 1.5–2 equiv of the aromatic compound and of 1 equiv of cation precursor **1** or **2** dissolved in 1 mL of nitromethane. Usually after a few minutes of reaction a dark color appeared (green, brown, or black, depending on the reagents). The reaction progress was monitored by TLC, after 5–6 hours saturated bicarbonate solution was added, and the mixture was extracted with ether. After the ethereal solution was dried over magnesium

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(15) It is known that unsubstituted furan, pyrrole, and thiophene can be protonated at both positions 2 and 3; the former species is formed faster and is also the more stable one. Nevertheless, the presence of an alkyl group in position 2 perturbs this trend and in the case of 2-methylpyrrole protonation at position 3 leads to the more stable species. See, for example: Joule, J. A.; Smithe, G. S. "Heterocyclic Chemistry"; Van Nostrand Reinhold: London, 1978.

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(18) (a) For example, 2-(phenylseleno)-2-undecene produces 2-undecanone (73% yield) when heated to 80 °C for 4 h in 0.5 M H_2SO_4 in H_2O/CH_3CN (20/80 v/v). The same result was obtained by using 1 equiv of $HgCl_2$ instead of sulfuric acid: Burton, A.; Hevesi, L., unpublished results. (b) Hevesi, L.; Piquard, J. L.; Wautier, H. *J. Am. Chem. Soc.* **1981**, *103*, 870.

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sulfate and the solvents were evaporated, the crude product was purified by PLC.

Data for the products 3–8 are as follows.

3a: ^{1}H NMR (CCl_4) 7.4–7.2 (m, 6 H), 6.40 (br s 1 H), 6.2 (m, 1 H), 6.0 (m, 1 H), 3.72 (br s, 2 H). ^{13}NMR ($CDCl_3$) 150.6, 141.5, 133.4, 130.3, 129.3, 128.5, 127.9, 120.5, 110.3, 107.2, 31.8. mass spectrum, *m/e* 298, calcd 297.966 35, found 297.966 ± 0.006.

3b: ^{1}H NMR (CCl_4) 7.4–7.2 (m, 6 H), 6.45 (br s, 1 H), 6.16 (m, 1 H), 5.96 (m, 1 H), 3.74 (br s, 2 H); ^{13}C NMR ($CDCl_3$) 150.3, 141.6, 133.9, 132.0, 129.4, 128.4, 128.1, 110.3, 107.9, 107.3, 34.1; mass spectrum *m/e* 342, calcd 341.915 89, found 341.916 ± 0.007.

4a: IR ($\bar{\nu}$, liquid film) 3105, 3050, 1610, 1580, 1502, 1475, 1440, 735, 690 cm^{-1}; ^{1}H NMR (CCl_4) 7.44–7.2 (m, 6 H), 6.18 (m, 1 H), 5.96 (m, 1 H), 5.40 (br s, 1 H), 5.16 (br s, 1 H), 3.48 (br s, 2 H); ^{13}C NMR ($CDCl_3$) 150.4, 141.6, 134.7, 129.2, 127.9, 118.6, 110.3, 107.3, 37.2; mass spectrum, *m/e* 264, calcd 264.005 32, found 264.005 ± 0.004. Anal. Calcd: C, 59.33; H, 49.60. Found: C, 59.44; H, 4.72.

4b: isolated as a mixture of *E* and *Z* isomers; IR ($\bar{\nu}$, liquid film) 3050, 2985, 1580, 1505, 1478, 735 cm^{-1}; ^{1}H NMR (CCl_4) 7.4–7.0 (m, 6 H), 6.14–5.74 (m, 3 H), 4.08 and 3.61 (quadruplets, J = 7 Hz, 1 H), 1.78 (d, J = 7 Hz, 3 H), 1.40 (d, J = 7 Hz, 3 H); mass spectrum, *m/e* 292, calcd 292.036 62, found 292.036 ± 0.006. Anal. Calcd: C, 61.86; H, 5.54. Found: C, 61.52; H, 5.34.

4c: isolated as a mixture of *E* and *Z* isomers; ^{1}H NMR (CCl_4) 7.4–7.0 (m, 6 H), 6.16–5.70 (m, 3 H), 3.5 and 3.44 (2 br s, 2 H), 2.4–1.9 (2 quintet, J = 7.5 Hz, 2 H), 1.1–0.88 (2 t, J = 7.5 Hz, 3 H); mass spectrum *m/e* 292, calcd 292.036 62, found 292.036 ± 0.006. Anal. Calcd: C, 61.86; H, 5.54. Found: C, 61.54; H, 5.44.

4d: IR ($\bar{\nu}$, liquid film) 3050, 2905, 1578, 1500, 1475, 1438, 732, 690; ^{1}H NMR (CCl_4) 7.3–7.0 (m, 6 H), 6.1 (m, 1 H), 5.80 (m, 1 H), 3.60 (br s, 2 H), 2.0 (s, 3 H), 1.92 (s, 3 H); mass spectrum, *m/e* 292, calcd 292.036 62, found 292.036 ± 0.006. Anal. Calcd: C, 61.86; H, 5.54. Found: C, 61.62; H, 5.53.

5a was isolated together with the corresponding β isomer **5a′**: IR ($\bar{\nu}$, liquid film) 3050, 2890, 1610, 1580, 1490, 1475, 1440, 1300, 740, 710, 690 cm^{-1}; ^{1}H NMR (CCl_4) 7.5–7.2 (m, 6 H), 6.32 (m, 1 H), 5.80 (m, 1 H), 5.4–5.0 (m, 2 H), 3.6–3.2 (m + s, 5 H); mass spectrum, *m/e* 277, calcd 277.036 95, found 277.037 ± 0.005. Anal. Calcd: C, 60.87; H, 5.47. Found: C, 61.08; H, 5.44.

5d + **5d′**: ^{1}H NMR (CCl_4) 7.05 (m, 5 H), 6.2 and 5.7 (m, 3 H), 3.40 and 3.18 (br s, 5 H), 1.99 (s, 3 H), 1.91 (s, 3 H).

6a was isolated together with its β isomer **6a′**: ^{1}H NMR (CCl_4) 7.6–6.6 (m, 8 H), 5.42, 5.34, 5.14, 5.09 (br s, 2 H), 3.66 and 3.48 (br s, 2 H); mass spectrum, *m/e* 280, calcd 279.982 48, found 279.983 ± 0.005. Anal. Calcd: C, 55.91; H, 4.33. Found: C, 55.96; H, 4.49.

7: ^{1}H NMR (CCl_4) 7.2–6.84 (m, 5 H), 6.04 (m, 1 H), 5.72 (m, 2 H), 3.72–3.46 (m, 11 H); mass spectrum, *m/e* 398, calcd 398.018 47, found 398.018 ± 0.008.

8: **1H** NMR (CCl_4) 7.18 (br s, 1 H), 6.15 (m, 1 H), 5.98 (m, 1 H), 5.67 (g, J = 7 Hz, 1 H), 3.68 (g, J = 6 Hz, 1 H), 1.71 (d, J = 6 Hz, 3 H), 1.44 (d, J = 7 Hz, 3 H); ^{13}C NMR ($CDCl_3$) 156.0, 141.3, 131.3, 123.9, 110.1, 105.9, 43.7, 18.1, 16.8. Anal. Calcd: C, 50.25; H, 5.15. Found: C, 50.20; H, 5.12.

Tri-*n*-butyltin Hydride Reduction of 5d + 5d′ to 13 + 14. A 500-mg (1.6 × 10^{-3} mol) sample of a mixture of **5d** and **5d′** was refluxed for 4.5 h in 5 mL of benzene solution containing 1 g (3.4 × 10^{-3} mol) of tri-*n*-butyltin hydride and 100 mg of azobis(isoburyronitrile) (AIBN). The reaction mixture was then cooled to room temperature, and water was added. Extraction with ether, drying over magnesium sulfate and evaporation of the solvents gave 1.6 g of crude product. This was then bulb-to-bulb distilled [bp 120 °C (15 mmHg)] to give 200 mg of product mixture still containing some tin derivatives, which was purified by PLC (SiO_2, eluent pentane/ether, 95:5, v/v). A mixture of **13** and **14** (160 mg, 67%) was thus isolated as a colorless liquid: ^{1}H NMR (CCl_4) 6.4–6.2 (m, 1 H), 6.0–5.7 (m, 2 H), 5.4–5.1 (m, 1 H), 3.52 and 3.44 (s, 3 H), 3.15–3.04 (m, 2 H), 1.72 and 1.69 (s, 6 H); mass spectrum, *m/e* 149, calcd 149.120 44, found 149.120 ± 0.003.

In the same way **12** was obtained from **4d** (70% yield) after 2.5 h of reflux in benzene solution: ^{1}H NMR (CCl_4) 7.24 (br s, 1 H), 6.22 (m, 1 H), 5.92 (m, 1 H), 5.28 (t, J = 6 Hz, 1 H), 3.30 (d, J = 6 Hz, 2 H), 1.72 and 1.66 (2 s, 6 H).

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Registry No. (*E*)-**1a**, 87728-65-2; (*E*)-**1b**, 87728-66-3; **2a**, 8728-67-4; (*Z*)-**2b**, 87405-71-8; (*E*)-**2b**, 87405-70-7; (*Z*)-**2c**, 87728-68-5; (*E*)-**2c**, 87728-69-6; **2d**, 87405-68-3; **3a**, 87728-70-9; **3b**, 87728-71-0; **4a**, 87728-72-1; (*E*)-**4b**, 87728-73-2; (*Z*)-**4b**, 87728-74-3; (*E*)-**4c**, 87728-75-4; (*Z*)-**4c**, 87728-76-5; **4d**, 87728-77-6; **5a**, 87728-78-7; **5a′**, 87728-79-8; **5d**, 87728-80-1; **5d′**, 87728-81-2; **6a**, 87728-82-3; **6a′**, 87728-83-4; (*E*)-**7**, 87728-84-5; (*Z*)-**8**, 87728-85-6; (*E*)-**8**, 87728-86-7; **13**, 87728-87-8; **14**, 87728-88-9; (*Z*)-3,4-dibromo-2-pentene, 87760-77-8; (*E*)-3,4-dibromo-2-pentene, 87760-78-9; furan, 110-00-9; *N*-methylpyrrole, 96-54-8; thiophene, 110-02-1; 1,3,5-trimethoxybenzene, 621-23-8.

Reaction of Olefins with a Mixture of Phenylselenenyl Chloride and Mercury(II) Thiocyanate. Selective Syntheses of β-(Phenylseleno)alkyl Isothiocyanates as Precursors of Vinylic Isothiocyanates

Akio Toshimitsu,* Sakae Uemura, and Masaya Okano

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611, Japan

Nanao Watanabe

Koei Chemical Co., Ltd., Joto-ku, Osaka 536, Japan

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The reaction of olefins with a mixture of phenylselenenyl chloride and mercury(II) thiocyanate in benzene as the solvent affords β-(phenylseleno)alkyl isothiocyanates selectively in good to excellent yields. The mercury salt not only increases the N selectivity in a kinetically controlled reaction but also accelerates the isomerization of β-(phenylseleno)alkyl thiocyanates to the corresponding isothiocyanates. Oxidative elimination of the β-(phenylseleno)alkyl isothiocyanates gives predominantly vinylic isothiocyanates together with a small amount of allylic isothiocyanates. This sequence constitutes a convenient method for conversion of olefins to vinylic isothiocyanates.

It has been reported that the ambident nature of thiocyanate ion is affected by the presence of a mercury salt to increase the N selectivity in nucleophilic substitution reactions.[1] It was deemed valuable to introduce simul-