(6) Multi-charged anionic derivatives of amino esters have also been reported by A. P. Krapcho and E. A. Dundulis, *Tetrahedron Lett.*, 2205 (1976).
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(9) J. J. Bloomfield, D. C. Omsley, and J. M. Nelke, *Org. React.*, **23**, 259 (1976).
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(13) The yields of these compounds were determined by gas chromatography. The compounds were characterized by NMR and mass spectra and elemental analyses.

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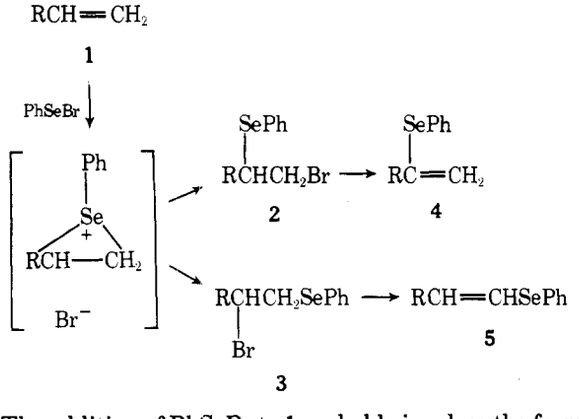
Regioselective Synthesis of Vinyl Phenylselenides[1]

Summary: Reaction of monosubstituted alkenes with phenylselenenyl bromide under either kinetically or thermodynamically controlled conditions followed by dehydrohalogenation of the resulting adducts provides a method for the regioselective synthesis of either 2-phenylselenoalkenes or 1-phenylselenoalkenes, respectively.

Sir: The utility and versatility of organoselenium compounds has become apparent.[2] Recently we undertook the preparation of both 2-phenylselenoalkenes **4** and 1-phenylselenoalkenes **5**, since these compounds are potentially useful for a number of synthetic transformations.[3] An obvious approach to the synthesis of **4** and **5** involves dehydrohalogenation of the appropriate β-bromoalkyl phenylselenides **2** and **3**, respectively. We therefore initiated a study to determine the feasibility of converting alkenes **1** to the desired vinyl phenylselenides **4** or **5** regioselectively via addition of PhSeBr and subsequent dehydrohalogenation.



The addition of PhSeBr to **1** probably involves the formation of a seleniranium ion, which may then be attacked by bromide ion, either at the less hindered but less electropositive primary carbon to give the anti-Markownikoff adduct **2**, or at the more electropositive but more hindered secondary carbon to give the Markownikoff adduct **3**.[4] Preliminary regioselectivity studies indicated that 1-hexene and PhSeBr react under kinetically controlled conditions (CCl_4, −20 °C) to give predominantly the anti-Markownikoff adduct **2b** [^{1}H NMR (CCl_4): δ 3.8–3.2 (m, 3 H)], which isomerizes[5] slowly in CCl_4 (48 h, 25 °C) or very rapidly in CH_3CN (<5 min, 25 °C) to give predominantly the Markownikoff adduct **3b** [^{1}H NMR (CCl_4): $-CH_2SePh$, δ 3.30 (dd, J = 12, 10 Hz) and 3.65 (dd, J = 12, 7 Hz), total 2 H; $-CHBr$, δ 4.3–3.8 (m, 1 H)]; however, due to the proximity and complexity of the ^{1}H NMR signals[6] and the thermal lability of the β-bromoalkyl phenylselenides, the exact determination of regioselectivity was deferred until both the addition and dehydrohalogenation were affected.

Table I. Percentage of 4/5 Formed Under Kinetic and Thermodynamic Conditions[a]

Entry	Alkene	Kinetic conditions[b] 4/5	Thermodynamic conditions[c] 4/5
a	Propene	85:15	9:91
b	1-Hexene	90:10	8:92
c	1-Octene	90:10	9:91
d	1-Hexadecene	90:10	7:93
e	4-Methyl-1-pentene	90:10	8:92
f	3-Phenyl-1-propene	98:2	2:98
g	3-Methyl-1-butene	98:2	3:97
h	3,3-Dimethyl-1-butene	100:0	0:100
i	3,3-Dimethyl-1-heptene	100:0	0:100

[a] Percentages determined by VPC (see ref 8). [b] PhSeBr (THF, −78 °C); *t*-BuOK (THF, −78 to 25 °C). [c] PhSeBr (CH_3CN, 25 °C); *t*-BuOK (THF, 25 °C).

For the kinetically controlled conditions the reaction of **1** with PhSeBr and subsequent dehydrohalogenation with *t*-BuOK was carried out in THF at −78 °C without isolation[7] of the intermediate β-bromoalkyl phenylselenide to give **4** regioselectively in high overall yield (Table I).[8] The regioselectivity of this process increases with increasing steric bulk at C-3 in **1**.

A typical procedure for the kinetically controlled conditions follows: a solution of 1-hexene (2.0 mmol) in dry THF (5 mL) was added dropwise (2 min) to a cooled (−78 °C) stirring solution of PhSeBr (2.0 mmol) in dry THF (20 mL). Stirring was continued until the dark brown color dissappeared (1 min) and *t*-BuOK (4.0 mmol) was added immediately.[9] The mixture was stirred at −78 °C for 5 min, allowed to warm to 25 °C, and stirred for 30 min. The THF was removed in vacuo, and the residue was extracted with ether, washed with brine, dried ($MgSO_4$), and purified by evaporative distillation (85 °C, 0.01 mm) to give a colorless liquid (430 mg, 90%): [^{1}H NMR (CCl_4) δ 2.4–2.1 (m, 2 H), 5.06 (s, 1 H), 5.45 (t, J = 0.5 Hz, 1 H)]. VPC analysis showed a 90:10 ratio of **4b/5b**.[8]

For the thermodynamically controlled conditions the reaction of **1** with PhSeBr was carried out in CH_3CN at 25 °C, the CH_3CN was removed in vacuo, and the resulting β-bromoalkyl phenylselenide was dehydrohalogenated with *t*-BuOK in THF at 25 °C to give **5** regioselectively in high overall yield (Table I). The ^{1}H NMR of **5h** [(CCl_4) δ 0.90 (s, 9H), 6.03 (d, J = 15 Hz, 1 H), 6.40 (d, J = 15 Hz, 1 H)] and **5i** [(CCl_4) δ 6.00 (d, J = 15 Hz, 1 H), 6.38 (d, J = 15 Hz, 1 H)] indicates that only the *E* isomer is formed; however, compounds **5a–g** are mixtures of *E* and *Z* isomers.

A typical procedure for the thermodynamically controlled conditions follows: a solution of 1-hexene (2.0 mmol) in CH_2Cl_2 (2 mL) was added to a solution of PhSeBr (2.0 mmol) in dry CH_3CN (10 mL) at 25 °C. The dark brown color disappeared immediately, and stirring was continued for 30 min. The solvents were removed in vacuo (25 °C), the residue was dissolved in THF (10 mL), and *t*-BuOK (4.0 mmol) was added. The mixture was stirred at 25 °C for 30 min, the THF removed in vacuo, the residue extracted with ether, washed with brine, dried ($MgSO_4$), and purified by evaporative distillation (85 °C, 0.01 mm) to give a colorless liquid (439 mg,

92%) [^{1}H NMR (CCl_4) δ 2.3–2.0 (m, 2 H), 7.6–5.5 (m, 2 H)]. VPC analysis showed an 8:92 ratio of **4b/5b**.[8]

Thus, it is now possible to convert monosubstituted alkenes to either 2-phenylselenoalkenes **4** or 1-phenylselenoalkenes **5** regioselectively. We are currently developing a variety of synthetic transformations for these substances and will report on them in due course.

References and Notes

(1) Organoselenium Chemistry. 1. This research was supported in part by a grant from the Petroleum Research Fund, administered by the American Chemical Society.

(2) (a) D. L. Klayman and W. H. H. Gunther, Ed., "Organic Selenium Compounds: Their Chemistry and Biology", Wiley-Interscience, New York, N.Y., 1973; (b) K. B. Sharpless, R. F. Lauer, D. W. Patrick, S. P. Singer, and M. W. Young, *Chem. Scr.*, **8A**, 9 (1975), and references cited therein; (c) H. J. Reich and S. K. Shah, *J. Am. Chem. Soc.*, **99**, 263 (1977), and references cited therein.

(3) We have successfully utilized vinyl phenylselenides as synthons for the construction of new carbon to carbon bonds. This work will be reported soon.

(4) (a) Stable seleniranium ions have recently been prepared by the reaction of $ArSePF_6$ with alkenes: G. H. Schmid and D. G. Garrett, *Tetrahedron Lett.*, 3991 (1975). (b) PhSeCl reacts with propene in CH_2Cl_2 to give a 1:1 mixture of i and ii (R = CH_3, X = Cl), and in HOAc to give ii (R = CH_3, X = Cl) exclusively: E. G. Kataev, T. G. Mannafov, E. A. Berdnikov, and O. A. Komarovskaya, *Zh. Org. Khim.*, **9**, 1983 (1973); D. G. Garrett and G. H. Schmid, *J. Org. Chem.*, **42**, 1776 (1977). (c) PhSeOAc reacts with 1-dodecene to give a 1:1 mixture of i and ii (R = n-$C_{10}H_{21}$, X = OAc): K. B. Sharpless and R. F. Lauer, *J. Org. Chem.*, **39**, 429 (1974). (d) $PhSeOCOCF_3$ gives mixtures of adducts with 1-methylcyclohexene and 1-hexene: H. J. Reich, *J. Org. Chem.*, **39**, 428 (1974); S. Raucher, unpublished results. (e) For studies of the regioselectivity of PhSCl see W. H. Mueller and P. E. Butler, *J. Am. Chem. Soc.*, **90**, 2075 (1968); D. G. Garrett and G. H. Schmid, *J. Org. Chem.*, **42**, 1776 (1977).

$RCH(SePh)CH_2X$ (i) $RCH(X)CH_2SePh$ (ii)

(5) This isomerization presumably involves the reversible formation of the seleniranium ion and the rate is dependent on the leaving group, X. For example, we have observed that for R = n-C_4H_9, i isomerizes to ii in <5 min when X = Br, but requires 24 h when X = Cl (CH_3CN, 25 °C). Also, for R = n-C_4H_9 a 1:1 mixture of i and ii isomerizes to ii in 48 h when X = $OCOCF_3$, but undergoes no apparent change even after 7 days when X = OAc (CH_3CN, 25 °C).

(6) Considerably simpler ^{1}H NMR spectra were obtained for the adducts of 3,3-dimethyl-1-butene and PhSeBr. Kinetic conditions gave exclusively **2h** [NMR (CCl_4): $(CH_3)_3C$– δ 1.15 (s, 9 H); >CHSePh δ 3.30 (dd, J = 6, 12 Hz, 1 H); $-CH_2Br$ δ 3.9–3.6 (m, 2 H)]. Thermodynamic conditions gave exclusively **3h** [NMR (CCl_4): $(CH_3)_3C$– δ 1.05 (s, 3 H); $-CH_2SePh$ δ 3.6–3.1 (m, 2 H); >CHBr δ 4.0 (dd, J = 4, 10 Hz, 1 H)].

(7) This procedure gave better regioselectivity than one which involved the reaction of **1** with PhSeBr in CCl_4 (−20 °C) or $PhCH_3$ (−78 °C), isolation of the β-bromoalkyl phenylselenide, and subsequent dehydrohalogenation (*t*-BuOK, THF, 25 °C).

(8) (a) All compounds were fully characterized by spectroscopic methods. (b) Isolated overall yields from **1** of the vinyl phenylselenide mixtures indicated in Table I were >85% in all instances. (c) VPC analysis was carried out on a Varian 920 using a 5 ft × ¼ in. 1.5% OV 101 on 100/120 Chromosorb G column at 60 mL He/min. In all cases, the retention time of **4** was less than that of **5**. Ratios were determined by triangulation of peaks. (d) A sample of **5b** was prepared by the reaction of $Ph_3P{=}CHSePh$ with pentanal: N. Petragnani, R. Rodrigues, and J. V. Comasseto, *J. Organomet. Chem.*, **114**, 281 (1976); a sample of **4a** was prepared by an alternate procedure which will be detailed shortly: S. Raucher and G. Koolpe, unpublished results.

(9) The rate of disappearance of the dark brown color (THF, −78 °C) is <1 min for **1a–e**, and ~5 min for **1f–l**.

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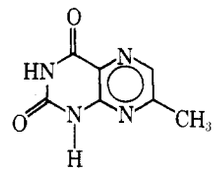
Novel α-Ionization of 7-Methylpteridines. Direct Synthesis of 7-Alkylidenepteridines[1]

Summary: 7-Methylpteridines containing amino or hydroxy groups in the 2,4-positions are converted by aqueous base to carbanions which readily condense with aromatic aldehydes to afford 7-alkylidenepteridines.

Sir: The carbanion chemistry of parent pteridine systems such as **1–3** which contain an aromatic pyrazine ring appears not to have been explored. In fact, such base-catalyzed chemistry of any pteridines seems limited to the conversion of the N-substituted 3,5,7-trimethylxanthopterin (**4**) to methyl ester **5** using dimethyl oxalate in the presence of potassium methoxide,[2] and to the reaction of N^8-lithio salts of various 2,4-diamino-7,8-dihydropteridines with alkyl halides to afford N^8-alkyl derivatives **6**.[3]



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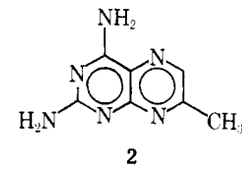

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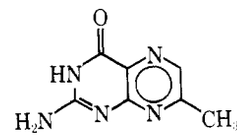

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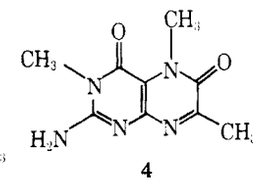

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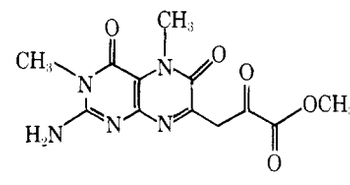

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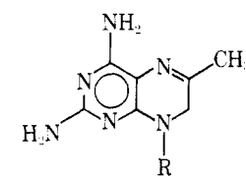
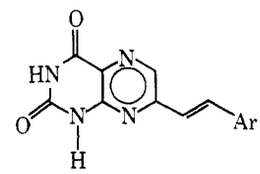


6

We have found that the methyl groups of 7-methyllumazine (**1**), 2,4-diamino-7-methylpteridine (**2**), and 7-methylpterin (**3**) are conveniently ionized by aqueous/ethanolic sodium hydroxide to afford carbanions α to the aromatic pyrazine rings. Such carbanions readily condense with aromatic aldehydes via the Claisen–Schmidt reaction[4] to give alkylidene derivatives **7**, **8**, and **9**, respectively. Thus, 7-alkylidenelumazines **7**[5] have been derived from **1** and benzaldehyde (53%), *p*-anisaldehyde (27%), 3,4-dimethoxybenzaldehyde (50%), and furfural (39%). Similarly, 7-alkylidene-2,4-diaminopteridines **8**[5] have been obtained from **2** and benzaldehyde (80%), piperonal (73%), and furfural (59%). 7-Methylpterin (**3**) also reacts with such aldehydes; however, the alkylidene derivatives **9** have resisted complete purification thus far since it has not been possible to remove all of the unreacted **3** from the products. As a result, the NMR spectra of these latter products derived from benzaldehyde, *p*-anisaldehyde, and piperonal, though consistent with **9**, contain small absorptions due to **3**.



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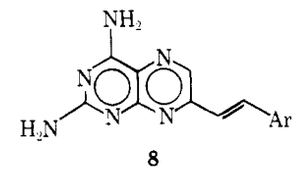

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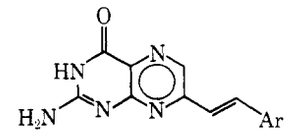

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In a typical experiment, a suspension of 10 mmol of 7-methyllumazine (**1**) and 36 mmol of sodium hydroxide in 20 mL of water is gently warmed until the heterocycle dissolves. The solution is then treated with 15 mmol of benzaldehyde in 10 mL of 95% ethanol and brought to reflux for 2–3 h. Upon