Acknowledgment. The authors gratefully acknowledge the assistance of Messrs. Edward Orton and Michael E. Newman in performing some of the experiments.

Registry No.—**1a,** 100-63-0; **1b,** 555-96-4; **1c,** 51-71-8; **2a,** 17420-03-0; **2b,** 69517-45-9; **2c,** 69517-46-0; thionyl chloride, 7719-09-7; phenyl azide, 622-37-7; *p*-(dimethylamino)azobenzene, 60-11-7; *N,N*-dimethylaniline, 121-69-7; *N*-thionylaniline, 1122-83-4.

References and Notes

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(4) Professor Klamann has informed us that the 82% yield reported[3] was obtained once and that the exact experimental conditions were not determined. We thank him for providing this information to us.
(5) C. Grundmann, *Methoden Org. Chem. (Houben-Weyl), 4th Ed., 1965,* **10,** Part 3, 806 (1965).
(6) No attempt was made to determine the presence of aniline as it would be expected to react with the diazonium ion.
(7) Benzonitrile and benzaldehyde have been identified from the neat pyrolysis of **2b.** Details of these investigations will be reported in a future publication.

New Route to Selenoacetals: Exchange Reaction between Acetals and Tris(phenylseleno)borane

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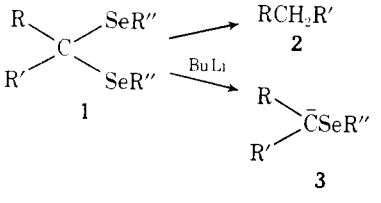
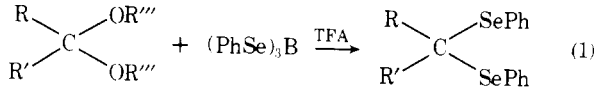
We report a new method for preparing selenoacetals (**1,** R″ = Ph), a class of compounds that promises to be very useful in organic synthesis.[1] These substances are reduced smoothly by triphenyltin hydride (**1** → **2**), and this process, taken together with the conversion of a carbonyl compound into a selenoacetal, constitutes an alternative to the classical Wolf–Kishner reduction.[2] Selenoacetals are converted by the action of butyllithium into selenium-stabilized carbanions[1,3] (**1** → **3**) which can be used, inter alia, for making carbon–carbon bonds[1,3] and for preparing sulfur-stabilized carbanions that are *not* available by deprotonation.[3b,4,5]

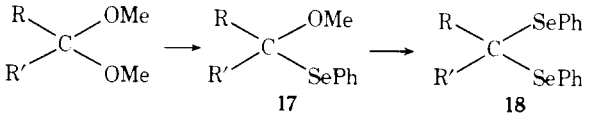


These reactions have established a need for simple methods of preparing selenoacetals from a variety of readily accessible precursors.[6] The crystalline reagent, $(PhSe)_3B$,[7] is convenient in this respect as it is easy to handle,[8] and it reacts[9] with ketones and aldehydes to generate diphenyl diselenoacetals.[10] In the case of acetophenone and 2′-acetylnaphthalene the performance of the boron reagent is unsatisfactory,[11] but we have found that oxygen acetals undergo an exchange reaction (eq 1) which constitutes an efficient alternative route to the phenylseleno analogues. The following procedure gives the results shown in Table I. The acetal is added to a stirred mixture of $(PhSe)_3B$ (1.1 equiv) and an inert solvent, usually $CHCl_3$. Trifluoroacetic acid [ca. 3–20 mol % (based on acetal)] is injected at 0–25 °C, and the product **1** (R″ = Ph) can be isolated by chromatography after an appropriate time at room temperature. Under these standard conditions the dithioacetal **10** is inert.[12]



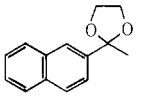
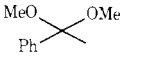
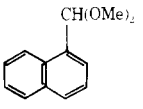
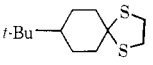
(1)

The presence of trifluoroacetic acid is essential.[13] When the reactions are monitored by NMR, the two stages of the process (eq 2) can be observed. For example, in an experiment with



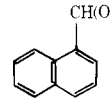
(2)

Table I

starting material	mol % TFA	conditions: time, temp., solvent	diphenyl diselenoacetal compd no.	diphenyl diselenoacetal yield, %
$C_{10}H_{21}CH(OMe)_2$ **4**	19	0.5 h at 0 °C, then 1 h at 25 °C, $CHCl_3$	**11**	85
 **5**	1	0.5 h at 0 °C, then 1.5 h at 25 °C, CH_2Cl_2	**12**	71
 **6**	10	3 h at 25 °C, $CHCl_3$	**13**	80
 **7**	4	3 h at 25 °C, $CHCl_3$	**14**	89
$Bu_2C(OMe)_2$ **8**	17	0.5 h at 0 °C, then 1 h at 25 °C, $CHCl_3$	**15**	83
$HC(OEt)_3$ **9**	3	13 h at 25 °C, $CHCl_3$	$HC(SePh)_3$ **(16)**	76[a]
 **10**	7	24 h at 25 °C, $CHCl_3$		*b*

[a] The corresponding reaction with $CH_3C(OMe)_3$ to give $CH_3C(SePh)_3$ is very sluggish. [b] No reaction (TLC control).

Table II

starting material	conditions:[a] time (h), solvent	mixed acetal compd no.	mixed acetal yield, %
$C_{10}H_{21}CH(OMe)_2$  **7**	6, toluene[b]	**19**	87[c]
	7.5, $CHCl_3$	**20**	78[d]
$Bu_2C(OMe)_2$ **8**	1, toluene[b]	**21**	80[e]

[a] Reactions were conducted at room temperature. For workup the mixture was diluted with MeOH, decolorized with $NaBH_4$, and partitioned between water and pentane. Further purification was not necessary for the first two entries. [b] Reaction in toluene was cleaner than that in chloroform. [c] δ ($CDCl_3$) 4.88 (t, J = 6 Hz). [d] Isolated by crystallization from hexane: mp 60–63 °C; δ ($CDCl_3$) 6.54 (s). [e] A satisfactory oxygen analysis could not be obtained for this compound, the value being 0.33% too high.

0022-3263/79/1944-1883$01.00/0

the dimethyl acetal of undecanal an NMR spectrum within 15 min of beginning the reaction showed no methine signal attributable to the starting acetal [expected signal at δ ($CDCl_3$) 4.3], but a new signal at δ ($CDCl_3$) 4.9 (t, J = 6 Hz) and a weak signal at δ ($CDCl_3$) 4.6 (t, J = 6 Hz). We assign the former to the mixed acetal **17** (R = $C_{10}H_{21}$, R′ = H) and the latter to compound **18** (R = $C_{10}H_{21}$, R′ = H). The signals due to **18** gradually increase in intensity at the expense of the signals representing **17**.[14]

When trifluoroacetic acid is omitted and the amount of $(PhSe)_3B$ is reduced to the appropriate stoichiometric quantity, the process stops at the intermediate stage. The mixed acetal **17** can then be isolated (Table II).[15]

The oxygen acetals required for the reactions described here can be obtained not only from carbonyl compounds by well-established methods,[16] but directly by the process of dialkoxymethylation.[17,18]

Experimental Section

If the bottle containing the tris(phenylseleno)borane is to be opened frequently, it is best manipulated in a small glovebag filled directly with tank nitrogen (99.99% pure). Reactions with the reagent were monitored by TLC or NMR and were conducted under anhydrous conditions in a septum-closed flask whose contents were kept under a slight static pressure of nitrogen. Product isolation by chromatography can be facilitated if excess reagent is first destroyed by addition of a little water. All solvents were distilled before use. Dry CH_2Cl_2 and toluene were distilled from CaH_2. Dry $CHCl_3$ was distilled from P_2O_5 under nitrogen. Solvents were evaporated under water pump vacuum at room temperature during product isolation. Where liquid products were obtained by evaporation of their solutions, the residues were kept under oil pump vacuum and checked for constancy of weight. PLC plates were 20 × 60 × 0.1 cm and were heated at 110 °C for 1 h before use. Alumina for PLC and TLC was Merck type GF-254 (type 60/E), and silica gel was Merck type 60-PF-254. Alumina for column chromatography was Camag neutral aluminum oxide. Except where indicated NMR spectra were measured on a 100-MHz instrument at a probe temperature of 32 °C. Small satellite signals are not reported. IR spectra of all compounds were unexceptional.

1,1-Bis(phenylseleno)undecane (11). A magnetically stirred mixture of tris(phenylseleno)borane (368 mg, 0.77 mmol) in $CHCl_3$ (4 mL) was cooled in an ice bath. 1,1-Dimethoxyundecane[19] (228 mg, 1.05 mmol) was added from a syringe over 4 min, and then TFA (15 μL, 0.20 mmol) was injected in one portion. After 0.5 h the ice bath was removed and stirring was continued for 1 h. The solvent was evaporated, and the residue, in a little $CHCl_3$, was applied to two alumina PLC plates which were developed with hexane. The appropriate bands were extracted with ethyl acetate. Evaporation of the solvent gave 422 mg (85%) of **11**[3b,10] as a homogeneous (TLC, alumina, hexane) colorless oil: NMR ($CDCl_3$) δ 0.7–2.1 (m, 19 H), 4.45 (t, 1 H, J = 6.4 Hz), 7.25 (m, 6 H), 7.55 (m, 4 H); m/e 468.0832 (calcd for $C_{23}H_{32}{}^{80}Se_2$, 468.0834).

1-(2-Naphthyl)-1,1-bis(phenylseleno)ethane (12). A magnetically stirred mixture of tris(phenylseleno)borane (719 mg, 1.50 mmol) in CH_2Cl_2 (2 mL) was cooled in a bath kept at −30 °C. The acetal **5**[20] (482 mg, 2.25 mmol) in CH_2Cl_2 (1 mL) was added over 7 min from a syringe. [More CH_2Cl_2 (2 × 0.5 mL) was used to rinse the remaining contents of the syringe into the reaction vessel.] TFA (15 μL, 0.02 mmol) was added, and after 30 min the cooling bath was removed. Stirring was continued for 1.5 h more, and the reaction mixture was placed onto the top of a column of grade III alumina (1 × 5 cm) made up with CH_2Cl_2. Elution with CH_2Cl_2 (100 mL) and evaporation gave a residue which was dissolved in boiling hexane (17 mL). The solution was allowed to cool to room temperature and was then stored at 5 °C for 1 h. The resulting crystals were washed with a little cold (−10 °C) hexane. A second crop was obtained by cooling the combined filtrate and washings to −10 °C. The total solids were recrystallized in the same way from hexane (7 mL) to give 663 mg of **12** as pale yellow crystals. The filtrates from the crystallizations were evaporated, and a further 90 mg of **12** was obtained by PLC (one alumina plate developed with 1:20 ethyl acetate–hexane) followed by crystallization from hexane (2 mL). The total yield of homogeneous (TLC, alumina, 1:2 ethyl acetate–hexane) product was 753 mg (71%): mp 88–92 °C; NMR ($CDCl_3$) δ 2.14 (s, 3 H), 6.98–8.1 (m, 17 H); m/e 311.0326 [calcd for $C_{18}H_{15}{}^{80}Se$ (M − PhSe), 311.0339]. Anal. Calcd for $C_{24}H_{20}Se_2$: C, 61.81; H, 4.32. Found: C, 61.86; H, 4.56.

[1,1-Bis(phenylseleno)ethyl]benzene (13). The acetal **6**[21] (145 mg, 0.87 mmol) was added from a syringe over ~5 min to a magnetically stirred mixture of tris(phenylseleno)borane (320 mg, 0.67 mmol) and $CHCl_3$ (5 mL). TFA (6 μL, 0.08 mmol) was added, the mixture was stirred for 3 h, and then the solvent was evaporated. The residue was stirred (open to the atmosphere) for 2 h with THF (3 mL) and water (2 drops). The solvent was evaporated, and the residue was chromatographed over grade III alumina (1.5 × 30 cm) with hexane to afford 291 mg (80%) of **13**[10] as a pure (TLC, alumina, hexane) colorless oil: NMR ($CDCl_3$) δ 2.03 (s, 3 H), 6.9–7.63 (m, 15 H); m/e 417.9733 (calcd for $C_{20}H_{18}{}^{80}Se_2$, 417.9739).

1,1-[Bis(phenylseleno)methyl]naphthalene (14). With the differences noted below, this reaction was carried out as described for **13** using tris(phenylseleno)borane (1.038 g, 2.17 mmol), $CHCl_3$ (5 mL), acetal **7**[22] (648 mg, 3.20 mmol), and TFA (8 μL, 0.10 mmol). After a 3-h reaction period, the solvent was evaporated and the product was isolated from the residue by PLC using three silica plates which were developed with 1:40 ethyl acetate–hexane. The appropriate bands were extracted with ethyl acetate, and the solution was evaporated to afford 1.299 g (89%) of **14** as a pure (TLC, alumina, 5:95 ethyl acetate–hexane) pale yellow oil: NMR ($CDCl_3$) δ 6.12 (br, 1 H), 6.85–7.84 (m, 16 H), 8.09 (br, 1 H); m/e 453.9728 (calcd for $C_{23}H_{18}{}^{80}Se_2$, 453.9739). Anal. Calcd for $C_{24}H_{20}Se_2$: C, 61.07; H, 4.01. Found: C, 61.06; H, 4.02. At 60 °C the broad NMR signal originally at δ 6.12 is sharper ($W_{1/2}$ = 4 Hz) and is now at δ 6.21.

5,5-Bis(phenylseleno)nonane (15). The reaction and isolation were carried out as described for **11** using tris(phenylseleno)borane (381 mg, 0.80 mmol), $CHCl_3$ (3 mL), acetal **8**[23] (221 mg, 1.17 mmol), and TFA (15 μL, 0.20 mmol). The product **15**[10] was obtained as a colorless homogeneous (TLC, alumina, hexane) oil which weighed 427 mg (83%): NMR ($CDCl_3$) δ 0.8 (t, J = 6.6 Hz), 1.15 (m), 1.62 (m, signals at 0.8–1.62 correspond to 18 H), 7.25 (m, 6 H), 7.67 (m, 4 H); m/e 440.0530 (calcd for $C_{21}H_{28}{}^{80}Se_2$, 440.0521).

1-Methoxy-1-(phenylseleno)undecane (19). The acetal **4**[19] (515 mg, 2.38 mmol) was added from a syringe over 2 min to a magnetically stirred mixture of tris(phenylseleno)borone (416 mg, 0.87 mmol) and toluene (2 mL). After 6 h the solution was diluted with MeOH (3 mL) and $NaBH_4$ was added in portions to give a colorless solution which was partitioned between pentane (200 mL) and water (100 mL). The pentane layer was washed with water (3 × 100 mL), dried (Na_2SO_4), filtered, and evaporated to leave 714 mg (87%) of **19** as a pale yellow oil: NMR ($CDCl_3$) δ 0.75–2.05 (m, 21 H), 3.41 (s, 3 H), 4.89 (t, 1 H, J = 6.1 Hz), 7.25 and 7.6 (m, 5 H); m/e 342.1458 (calcd for $C_{18}H_{30}O^{80}Se$, 342.1462). Anal. Calcd for $C_{18}H_{30}OSe$: C, 63.33; H, 8.86; O, 4.69. Found: C, 63.11; H, 8.88; O, 4.82.

1-[Methoxy(phenylseleno)methyl]naphthalene (20). A magnetically stirred mixture of tris(phenylseleno)borane (540 mg, 1.13 mmol) in $CHCl_3$ (5 mL) was cooled in a bath kept at −30 °C. The acetal **7**[22] (681 mg, 3.37 mmol) was added from a syringe over 1 min. After 15 min the cooling bath was removed and stirring was continued for 7.5 h. The solvent was evaporated, the residue was stirred with MeOH (6 mL), and $NaBH_4$ was added in small portions until a colorless methanol solution (covering a pale yellow oil) was obtained. The mixture was partitioned between pentane (200 mL) and water (100 mL). The aqueous layer was washed with pentane (100 mL), and the combined pentane layers were washed with water (4 × 100 mL) and dried (Na_2SO_4). Filtration, evaporation of the solvent, and crystallization of the residue from hexane (3 mL) gave 860 mg (78%) of **20** as pale yellow crystals: mp 60–63 °C; NMR ($CDCl_3$) δ 3.6 (3 H), 6.55 (s, 1 H), 7.0–8.25 (m, 12 H); m/e 328.0361 (calcd for $C_{18}H_{16}O^{80}Se$, 328.0367). Anal. Calcd for $C_{18}H_{16}OSe$: C, 66.06; H, 4.93; O, 4.89. Found: C, 66.12; H, 4.97; O, 4.89.

5-Methoxy-5-(phenylseleno)nonane (21). With the differences noted, this reaction was carried out as described for **19** using the acetal **8** (390 mg, 2.07 mmol), tris(phenylseleno)borane (351 mg, 0.73 mmol), and toluene (2 mL). After 1 h the mixture was diluted with MeOH (4 mL) and processed as described for **19** to yield 520 mg (80%) of **21** as a pale yellow liquid: NMR ($CDCl_3$) δ 0.75–1.9 (m, 18 H), 3.42 (s, 3 H), 7.25 and 7.5 (m, 5 H); m/e 157.1589 [calcd for $C_{10}H_{21}O$ (M − PhSe), 157.1592]. Anal. Calcd for $C_{16}H_{26}OSe$: C, 61.33; H, 8.36; O, 5.11. Found: C, 61.45; H, 8.59; O, 5.43.

Acknowledgments. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support and to the National Research Council of Canada and the University of Alberta.

Registry No.—**4,** 52517-67-6; **5,** 69470-12-8; **6,** 4316-35-2; **7,** 33250-32-7; **8,** 69470-13-9; **9,** 122-51-0; **10,** 65851-13-0; **11,** 53198-55-3; **12,** 69470-14-0; **13,** 67808-80-4; **14,** 69470-15-1; **15,** 67808-79-1; **16,** 22859-16-1; **19,** 69470-16-2; **20,** 69493-63-6; **21,** 69470-17-3; tris(phenylseleno)borane, 29680-62-4.

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(2) D. L. J. Clive, G. Chittattu, and C. K. Wong, *J. Chem. Soc., Chem. Commun.*, 41 (1978). Use of triphenyltin deuteride affords labeled hydrocarbons.
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(5) D. Seebach, N. Meyer, and A. Beck, *Justus Liebigs Ann. Chem.*, 846 (1977).
(6) Selenoacetals are available by the action of selenols on carbonyl compounds: W. Dumont and A. Krief, *Angew. Chem., Int. Ed. Engl.*, **16**, 540 (1977). See also D. Seebach and N. Peleties, *Chem. Ber.*, **105**, 511 (1972).
(7) M. Schmidt and H. D. Block, *J. Organomet. Chem.*, **25**, 17 (1970).
(8) See Experimental Section.
(9) The presence of up to about 10 mol % of trifluoroacetic acid is sometimes advantageous.
(10) D. L. J. Clive and S. M. Menchen, *J. Chem. Soc., Chem. Commun.*, 356 (1978).
(11) The yields of diphenyl diselenoacetal are 52 and <26%, respectively.
(12) Recovery of purified dithioacetal is 76%. The dithioacetal **10** (mp 65–66 °C from acetone) was prepared in 39% yield by the reaction of ethanedithiol and 4-*tert*-butylcyclohexanone in the presence of BF_3-Et_2O. Cf. L. F. Fieser, *J. Am. Chem. Soc.*, **76**, 1945 (1954). Anal. Calcd for $C_{12}H_{22}S_2$: C, 62.55; H, 9.62. Found: C, 62.77; H, 9.49.
(13) Other acids have not been examined.
(14) Comparison of the NMR data obtained from the reaction mixture with data for the pure monophenyl monoselenoacetal and diphenyl diselenoacetal shows that the boron species do not cause appreciable shifts of the methine signal.
(15) The mixed acetal from **8** decomposed on attempted chromatography over alumina or silica. Chromatography was not attempted in the other cases.
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(18) With the exception noted in Table II, satisfactory (±0.3%) combustion analytical values were obtained for all new compounds. For the chemistry of tris(phenylthio)borane, see, for example, T. Cohen, D. A. Bennett, and A. J. Mura, Jr., *J. Org. Chem.*, **41**, 2506 (1976). Cf. also F. Bessette, J. Brault, and J. M. Lalancette, *Can. J. Chem.*, **43**, 307 (1965); R. H. Cragg and J. P. N. Husband, *Inorg. Nucl. Chem. Lett.*, **6**, 773 (1970); A. Pelter, T. E. Levitt, K. Smith, and A. Jones, *J. Chem. Soc., Perkin Trans. 1*, 1672 (1977).
(19) The acetal [bp 105–108 °C (3 mm)] was prepared by treating undecanal with trimethyl orthoformate, methanol, and a trace of concentrated sulfuric acid. Cf. M. T. Bogert and P. P. Herreva, *J. Am. Chem. Soc.*, **45**, 238 (1923).
(20) This acetal [bp 110–118 °C (0.5 mm)] was prepared by refluxing (using a Dean-Stark trap) a benzene solution of 2′-acetonaphthalene, ethylene glycol, and a trace of *p*-toluenesulfonic acid. Anal. Calcd for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 78.44; H, 6.55.
(21) Prepared from acetophenone by the method of ref 19.
(22) Prepared by the general method of ref 19. Cf. *Chem. Abstr.*, **75**, 129556p (1971).
(23) This acetal [bp 74–76 °C (4 mm)] was prepared by the general method of ref 19. Anal. Calcd for $C_{11}H_{24}O_2$: C, 70.16; H, 12.85. Found: C, 70.33; H, 12.81.

Regiospecific Synthesis of 2,3-Disubstituted Furans, Pyrroles, and Thiophenes. Claisen Ortho Ester Rearrangement of Heterocyclic Glycolates[1]

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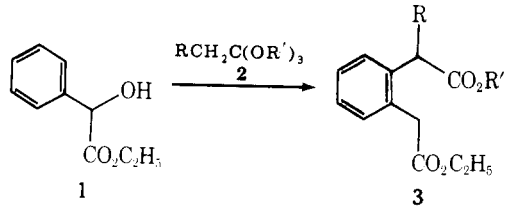
Received October 27, 1978

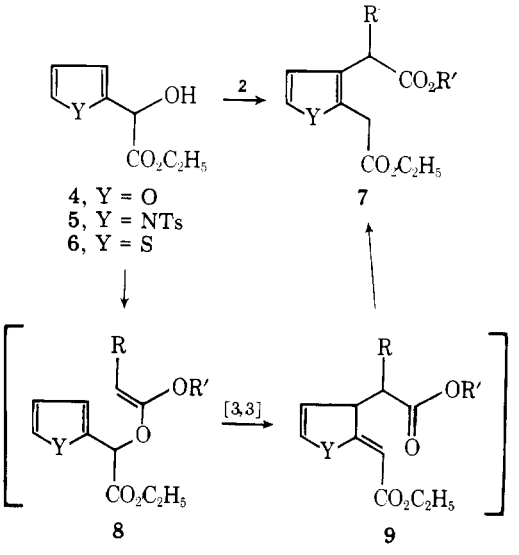
The [3,3] sigmatropic rearrangement of allyl vinyl ethers provides a versatile method for the construction of new carbon to carbon bonds with high regio- and stereospecificity.[2] Although [3,3] sigmatropic rearrangements of systems in which the *vinyl* moiety is formally incorporated in an aromatic ring (allyl *phenyl* ethers) are well known,[3] [3,3] sigmatropic rearrangements of systems in which the *allyl* moiety is formally incorporated in an aromatic ring (*benzyl* vinyl ethers) are not generally possible.[4]

We recently demonstrated that the Claisen ortho ester rearrangement of benzyl alcohols is facilitated by a carbethoxy group at the benzylic position; namely, ethyl mandelate (**1**) readily undergoes a Claisen ortho ester rearrangement with ortho esters **2** to give ortho-disubstituted arenes **3**, whereas benzyl alcohol fails to rearrange under the same conditions.[5]



1 **3**

We now wish to report that the Claisen ortho ester rearrangement of ethyl 2-furanglycolate (**4**), ethyl *N*-tosyl-2-pyrroleglycolate (**5**), or ethyl 2-thiopheneglycolate (**6**) with ortho esters **2** provides an extremely convenient method for the regiospecific synthesis of 2,3-disubstituted furans,[6] pyrroles, or thiophenes. The results of these studies are summarized in Table I.[7]



The above transformation is amenable to the synthesis of 2,3-disubstituted heterocycles for a number of reasons: (1) a variety of heterocyclic glycolates and ortho esters[8] are readily available; (2) the reaction conditions are compatible with a wide array of functionality; (3) the reaction provides a method for the regiospecific synthesis of substituted heterocycles that would be difficultly accessible by alternative methods; (4) the carbethoxy groups provide convenient handles for subsequent synthetic transformations; and (5) no ester exchange occurs under the reaction conditions (entry g of Table I); hence, differentiation of the two ester groups is possible.[9]

The influence of the carbethoxy group in facilitating the reaction is presumably due to the increased stabilization of the putative intermediate **9** formed by [3,3] sigmatropic rearrangement of the benzyl vinyl ether **8**.[5]

Attempts to effect Claisen ortho ester rearrangement of **4** or **6** with trimethyl orthoisobutyrate led to complex mixtures accompanied by extensive decomposition. This outcome is possibly caused by homolytic scission of the benzylic carbon–oxygen bond[4a-e] due to the increased stability of the resulting methyl-α-isobutyryl radical.[10]

The preparation of the 2-heterocyclic glycolates is quite straightforward. Ethyl 2-furanglycolate (**4**) was prepared from furfural cyanohydrin.[11] Ethyl *N*-tosyl-2-pyrroleglycolate (**5**)

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