hexene-1-methanol, 127492-02-8; 3-buten-2-ol, 598-32-3; 1-octen-3-ol, 3391-86-4; 1,5-hexadien-3-ol, 924-41-4; 2-methyl-1-hepten-3-ol, 13019-19-7; (*E*)-3-penten-2-ol, 3899-34-1; 2-cyclohexen-1-ol, 822-67-3; (*E*)-3-methyl-2-octen-4-ol, 136707-95-4; (*E*)-cinnamyl alcohol, 4407-36-7; (*R*)-(−)-myrtenol, 19894-97-4; δ-valerolactone, 542-28-9; methylenetriphenylphosphorane, 3487-44-3; vinylmagnesium bromide, 1826-67-1; ξ-caprolactone, 502-44-3; (*E*)-1-methoxy-1,8-nonadien-7-ol, 136707-96-5; (*Z*)-1-methoxy-1,8-nonadien-7-ol, 136707-97-6; 3,3,7-trimethyl-6-octenal, 17920-90-0; 2,4,6-trimethylbenzoic acid, 480-63-7.

Supplementary Material Available: Characterization of new compounds by NMR (20 pages). Ordering information is given on any current masthead page.

One-Flask, Consecutive [3,3] and [2,3] Sigmatropic Rearrangements for Conversions of Propargylic Alcohols into Two-Carbon-Extended 4-Oxo-2-alkenoate Esters. Use of a New 1-Chloro-1-ethoxy-2-sulfinylethylene

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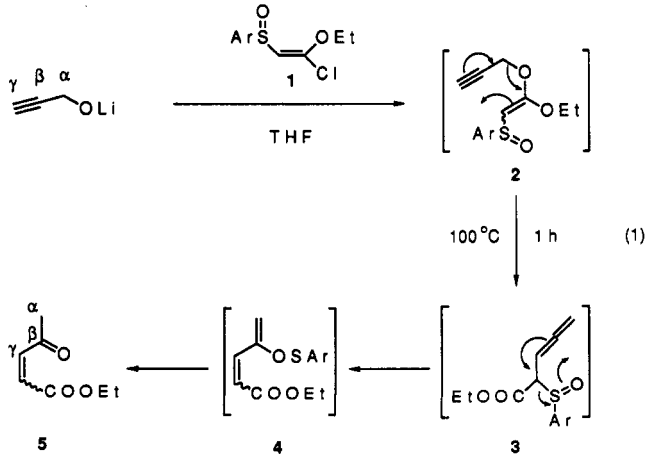
Received May 22, 1991

Seven differently substituted primary and secondary propargylic alcohols are shown to react with (arylsulfinyl)vinylic chloride **1a** at 100 °C for 1 h sequentially via a [3,3] sigmatropic rearrangement and then a [2,3] sigmatropic rearrangement to form 4-oxo-2-alkenoates **8a–8e** and **9a** and **9b** in 52–80% yields. This one-flask, intramolecular carbon–carbon bond-forming process represents a simple and convenient method not only for regiospecific γ-attachment onto a propargylic alcohol of a two-carbon (ethoxycarbonyl)methylene unit but also for α → β transposition of oxygen. The synthetic utility of this procedure is illustrated further by eqs 2 and 3 for preparation of regiospecifically functionalized carbocycles and heterocycles. Also, two different primary allenic allylic alcohols are shown to produce directly two-carbon extended 3-(hydroxyalkyl)-2,4-pentadienoates (*E*)-**18** and the corresponding unsaturated lactones (*Z*)-**18** in 37–41% yields.

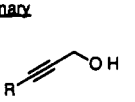
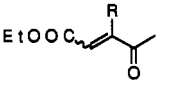
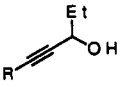
Introduction

In connection with our design, synthesis, and use of a new sulfinyl orthoester for one-flask conversions of allylic alcohols into 2-carbon-extended dienoate esters,[1] we have discovered (1) that 1-chloro-1-ethoxy-2-(arylsulfinyl)-ethylenes **1** are easily prepared[2] and (2) that the sulfinylethylene **1** with Ar = 4-ClPh is a relatively stable compound that, among the aryl derivatives studied, reacts most efficiently with propargylic alcoholates to form 2-carbon-extended 4-oxo-2-alkenoate esters **5** (eq 1). This one-flask



sequence proceeds most likely via [3,3]-sigmatropic rearrangement of intermediate allylic propargylic ethers **2** and subsequent [2,3]-sigmatropic rearrangement of intermediate β-allenic aryl sulfoxides **3**. Herein is reported a full account of this new synthetic method, including some applications and limitations, as well as some similar transformations of allenic allylic alcohols.

Table I. Two-Carbon Chain Extension According to eq 1 with Ar = 4-ClPh

propargylic alcohol	product 4-oxo-2-alkenoate	% yield of purified product
Primary		
		
	8a, R = Me	55
	8b, R = Ph	57
	8c, R = Me_3Si	52
	8d, R = t-$BuMe_2SiOCH_2$	80
	8e, R = $ClCH_2$	77
Secondary		
		
	9a, R = Me	66
	9b, R = Et	77

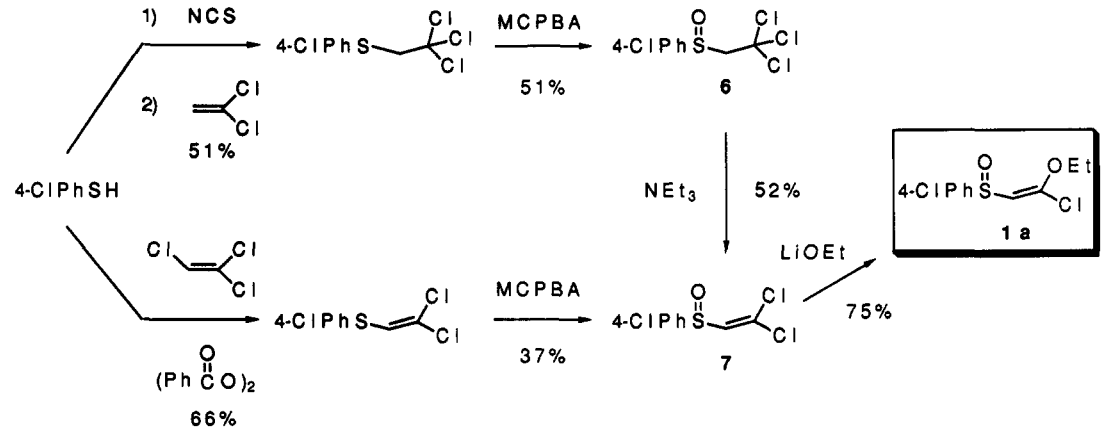
Results and Discussion

Although primary and secondary propargylic alcohols did react with sulfinyl orthoacetate $PhS(O)CH_2C(OEt)_3$ under acidic conditions[1] to produce 4-oxo-2-alkenoates, consistently and considerably better results were obtained under basic conditions using 1-chloro-1-ethoxy-2-(aryl-

(1) Posner, G. H.; Crouch, R. D.; Kinter, C. M.; Carry, J.-C. *J. Org. Chem.*, in press.
(2) For a review of related (organothio)chloroacetylenes, see: Mirskova, A. N.; Seredkina, S. G.; Voronkov, M. G. *Sulfur Reports* **1984**, *9*, 75.

0022-3263/91/1956-6987$02.50/0

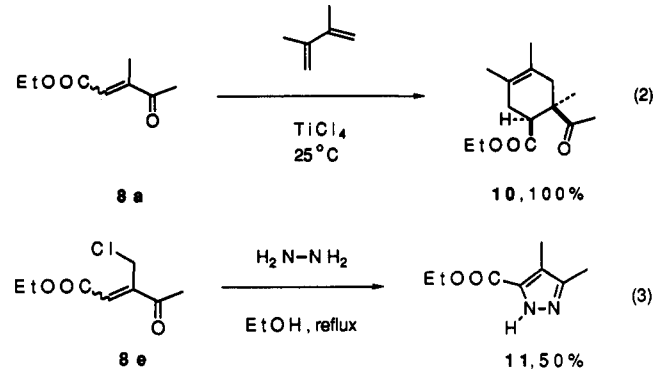
Scheme I



sulfinyl)ethylenes **1**. For example, in the synthesis of product **8a** (see Table I) an improvement of 15–34% of the overall yield was observed on going from sulfinyl orthoacetate $PhS(O)CH_2C(OEt)_3$ to 1-chloro-1-ethoxy-2-(arylsulfinyl)ethylenes **1**.

Such heteroatom-rich trisubstituted ethylenes were prepared on gram scale in a straightforward manner as shown in Scheme I, illustrated with Ar = 4-ClPh. 4-Chlorophenylsulfinyl trichloride **6** is a white solid stable to storage at room temperature for at least 1 year; likewise, solid dichlorovinylic sulfoxide **7** has a good shelf life. The *E* stereochemistry of chloroethoxyvinylic sulfoxide **1a** was assigned by 400-MHz ^1H NMR spectroscopy in comparison with the corresponding diethoxyvinylic sulfoxide; the proximity of the ethyl methylene group to the sulfinyl oxygen atom in *E* isomer **1a** caused that CH_2 group to be shifted to δ 4.3 and to appear as a multiplet rather than as a simple quartet.

Of several different aryl derivatives examined (phenyl, 4-chlorophenyl, 3-chlorophenyl, 4-fluorophenyl, 4-nitrophenyl, and 2,6-dimethylphenyl), [(4-chlorophenyl)-sulfinyl]ethylene **1a** consistently gave the highest yields (52–80%) for rapid conversion (i.e., 1-h reaction time) of both primary and secondary propargylic alcohols into the corresponding 2-carbon-extended and $\alpha \rightarrow \beta$ oxygen-transposed 4-oxo-2-alkenoate esters **8a–8e** and **9a** and **9b** as a mixture of *E* and *Z* geometric isomers (Table I). Of special note is the convenience of this protocol to prepare in good yields highly functionalized keto ester silyl-protected alcohol **8d** and keto ester allylic chloride **8e**. Regiospecific formation of allylic chloride **8e** represents a striking success of this *intra*molecular carbon–carbon bond-forming process in sharp contrast to *inter*molecular nucleophilic substitution that would consume the reactant propargylic chloride functionality and would give mainly allenic substitution products via S_N2' displacement of chloride.[3] These enedicarbonyl products are compact and versatile synthetic building blocks capable of many subsequent, useful chemical manipulations. For example, room-temperature Lewis acid-catalyzed intermolecular 2 + 4 cycloaddition of highly electron-deficient alkene **8a** with 2,3-dimethyl-1,3-butadiene produced pentasubstituted cyclohexene **10** in quantitative yield as a single stereoisomer with a cis relationship between the tertiary hydrogen atom and the adjacent methyl group as shown by an NOE experiment (eq 2).[4] For another example, keto ester allylic chloride **8e** reacted with anhydrous hydrazine in ethanol at reflux to form 3,4,5-trisubstituted pyrazole **11** in 50% yield (eq 3).[5]



A tertiary propargylic alcohol, 1,1-dimethyl-2-butynol, was inert to sufinylethylene **1a** as well as to sulfinyl orthoacetate $PhS(O)CH_2C(OEt)_3$.

These one-flask conversions (eq 1) involve four discrete steps *without isolation of intermediates*: (1) propargylic alcoholate replacement of chloride in sulfinylvinylic chloride **1a**; (2) [3,3] sigmatoropic (orthoester type)[6] rearrangement producing β-allenic sulfoxide **3**; (3) [2,3] sigmatropic rearrangement of the allylic sulfoxide moiety to produce an enol sulfenate ester **4**; and finally (4) collapse of enol sulfenate **4** into the corresponding ketone **5**. Each of these steps deserves comment.

Replacement of chloride in sulfinylvinylic chloride **1a** by propargylic alcoholate can occur in principle via an addition–elimination sequence or conversely via an elimination–addition sequence. Although literature precedent favors an elimination–addition path[2,7,8] and the *E* stereochemistry of chloroethoxyvinylic sulfoxide **1a** is consistent

(3) (a) Gelin, R.; Gelin, S.; Albrand, M. *Bull. Soc. Chim. France* **1971**, 4146. (b) Pasto, D. J.; Chou, S.-K.; Waterhouse, A.; Shults, R. H.; Hennion, G. F. *J. Org. Chem.* **1978**, *43*, 1385. (c) Jeffery-Luong, T.; Linstrumelle, G. *Tetrahedron Lett.* **1980**, *21*, 5019.

(4) For a closely related reaction, see: Kowalski, C. J.; Lal, G. S. *J. Am. Chem. Soc.* **1988**, *110*, 3693.

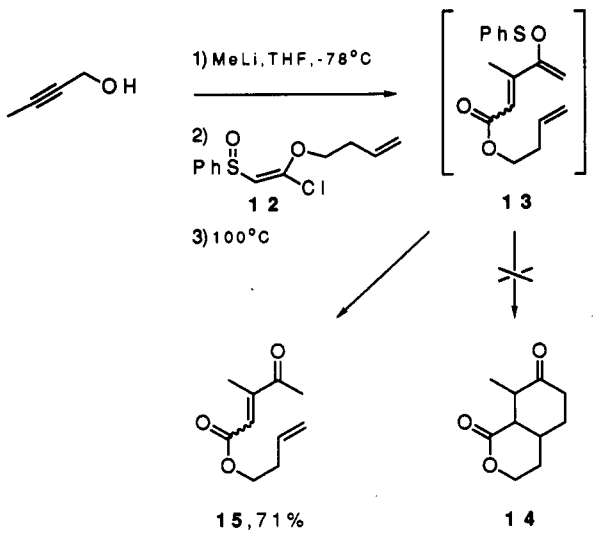
(5) (a) Kitaev, Y. P.; Buzykin, B. I. *Russ. Chem. Rev.* **1972**, *41*, 495 and references cited therein. (b) Elguero, J.; Guiraud, G.; Jacquier, R. *Bull. Soc. Chim. Fr.* **1966**, 3727.

(6) (a) For a review of Claisen rearrangements involving triple bonds, see: Viola, A.; Collins, J. J.; Filipp, N. *Tetrahedron* **1981**, *37*, 3765. See also: (b) Crandall, J. K.; Tindell, G. C. *J. Chem. Soc., Chem. Commun.* **1970**, 1411. (c) Bennett, G. *Chem. Lett.* **1975**, 939. (d) Ficini, J.; Lumbroso-Bader, N.; Pouliquen, J. *Tetrahedron Lett.* **1968**, 4139. (e) Schuijl, P. J. W.; Bos, H. J. T.; Brandsma, L. *Recl. Trav. Chim.* **1969**, 597. (f) Ishino, Y.; Nishiguchi, I.; Kim, M.; Hirashima, T. *Synthesis* **1982**, 740.

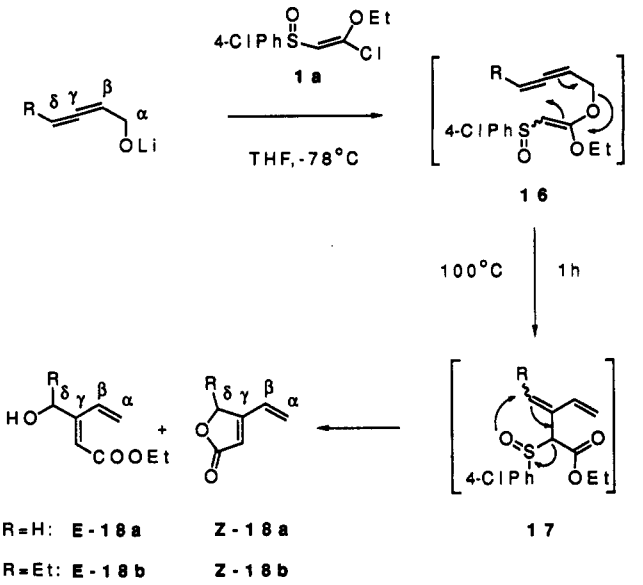
(7) (a) Truce, W. E.; Boudakian, M. M.; Heine, R. F.; McManimie, R. J. *J. Am. Chem. Soc.* **1956**, *78*, 2793. (b) Flynn, J., Jr.; Badiger, V. V.; Truce, W. E. *J. Org. Chem.* **1963**, *28*, 2298.

(8) For an example of an addition reaction to an α,β-unsaturated phenyl sulfoxide being helped by a *p*-chloro substituent on a phenyl ring, see: Mandai, T.; Ueda, M.; Hasegawa, S.; Kawada, M.; Tsuji, J. *Tetrahedron Lett.* **1990**, *31*, 4041.

Scheme II



Scheme III



with antiaddition of ethanol to the corresponding chlorosulfinylacetylene, several experiments were done to provide evidence for this sequence proceeding through such an acetylenic sulfoxide intermediate. [(2,6-Dimethylphenyl)sulfinyl]vinylic chloride **1b** was prepared and was shown to be inert to propargylic alcoholates associated with lithium, sodium, or potassium counterions, suggesting that steric hindrance around the sulfinyl group was preventing abstraction of the neighboring vinylic hydrogen atom and thus thwarting β-elimination of HCl. Furthermore, 1,1-dichloro-2-(phenylsulfinyl)*propylene* was prepared and was found to be inert to lithium, sodium, and potassium ethoxides whereas the corresponding sulfinyl*ethylene* underwent replacement of one chloride by ethoxide instantaneously even at −78 °C. Use of silver tetrafluoroborate to assist loss of chloride ion from the 2-sulfinylpropylene[9] or use of a potassium instead of a lithium counterion for the alcoholate, even in the presence of 18-crown-6 ether[10] to make the alcoholate more nucleophilic, did not effect replacement of chloride. These results support an elimination–addition path.

Ample precedent exists generally for successful [3,3] sigmatropic rearrangements of propargylic vinylic ethers such as **2**.[6] At the start of this project, however, it was not clear what effect(s), if any, the sulfinyl group in propargylic vinylic ether **2** would have on the [3,3] sigmatropic rearrangement. Analogy with successful [3,3] sigmatropic Carroll rearrangements of allylic and especially of propargylic β-keto esters, however, was considered to be encouraging.[11] It was gratifying therefore to find the sulfinyl group to be a noninterfering passenger carried along this structural reorganization path.

Although [2,3] sigmatropic rearrangements of allylic sulfoxides into allylic sulfenate esters and of propargylic sulfenates into α-allenic sulfoxides have ample precedents,[12] to our knowledge no publication has exploited this functional group manipulation in the context of *β-allenic* sulfoxides.[13] This one-flask transformation of intermediate β-allenic aryl sulfoxides **3** into 4-oxo-2-alkenoates **5** is presumed to proceed via intermediate dienol sulfenate **4**. Unsuccessful attempts were made to intercept diene **4** either intermolecularly or intramolecularly. For example, lithium 2-butynoate was treated with sulfinylvinylic *butenyl* ether **12** in the hope that intermediate triene **13** would undergo intramolecular cycloaddition[14] to form bicycle **14**. The only product isolated, however, was 4-oxo-2-alkenoate **15** (Scheme II). It remains unclear exactly how dienol sulfenates[5] like **4** (e.g., dienol sulfenate **13**) are transformed in situ into the corresponding methyl ketones **5** (e.g., **15**) even in the absence of thiophiles[12] or aqueous workup. A control experiment run in an NMR tube with THF-d_8 as solvent showed that a singlet at δ 2.1 characteristic of product methyl ketone appeared even after only 1 h at 100 °C without any workup. The operational simplicity and the good yield in which highly functionalized dienedicarbonyl compound **15** is formed via Scheme II suggest that this protocol could be used to prepare conveniently and directly versatile 4-oxo-2-alkenoates carrying other unsaturated (and otherwise functionalized) groups using appropriately unsaturated analogues of sulfinylvinylic ether **12**.

Primary allenic alcohols[14] also reacted with [(chlorophenyl)sulfinyl]ethylene **1a** at 100 °C to form directly 2-carbon-extended 3-(hydroxyalkyl)-2,4-dienoates (Scheme III). Presumably, intermediate β-allenic vinylic ether **16** underwent [3,3] sigmatropic rearrangement and the resultant allylic sulfoxide **17** then underwent [2,3] sigmatropic rearrangement to form the product dienoates as a roughly 1:1 mixture of *E* and *Z* isomers; spontaneous cy-

(9) Use of silver tetrafluoroborate to convert a vinylic halide into the corresponding vinylic carbonium ion has been achieved by: Hanack, M.; Harder, I.; Bofinger, K.-R., *Tetrahedron Lett.* **1981**, *22*, 553.

(10) (a) Sam, D. J.; Simmons, H. E. *J. Am. Chem. Soc.* **1974**, *96*, 2252. For reviews see: (b) Pedersen, C. J. *Aldrichimica Acta* **1971**, *4*, 1. (c) Gokel, G. W.; Durst, H. D. *Ibid.* **1976**, *9*, 3. (d) Christensen, J. J.; Eatough, D. J.; Izatt, R. M. *Chem. Rev.* **1974**, *74*, 351.

(11) Kimel, W.; Sax, N. W.; Kaiser, S.; Eichmann, G. G.; Chase, G. O.; Ofner, A. *J. Org. Chem.* **1958**, *23*, 153.

(12) For reviews see: (a) Evans, D. A.; Andrews, G. C. *Acc. Chem. Res.* **1974**, *7*, 147. (b) Braverman, S. In *The Chemistry of Sulphones and Sulphoxides*, Patai, S., Rapporport, Z., Stirling, C. J. M., Eds.; John Wiley: New York, 1988; pp 717–757.

(13) For [2,3] sigmatropic rearrangements of related β-allenic sulfonium ylides, see: (a) Grieco, P. A.; Meyers, M.; Finkelhor, R. S. *J. Org. Chem.* **1974**, *39*, 119. (b) Pourcelot, G.; Veniard, L.; Cadiot, P. *Bull. Soc. Chim. Fr.* **1975**, 1281.

(14) For reviews see: (a) Brieger, G.; Bennett, J. N. *Chem. Rev.* **1980**, *80*, 63. (b) Taber, D. F. *Intramolecular Diels–Alder and Alder–Ene Reactions*; Springer-Verlag: New York, 1983. (c) Ciganek, E. *Org. React.* **1984**, *32*, 1. (d) Fallis, A. G. *Can. J. Chem.* **1984**, *62*, 183. (e) Lipshutz, B. H. *Chem. Rev.* **1986**, *86*, 795. (f) Craig, D. *Chem. Soc. Rev.* **1987**, *16*, 123.

(15) (a) Ficini, J.; Pouliquen, J. *Compt. Rend. Acad. Sci. (C)* **1969**, 268. (b) Huché, M.; Cresson, P. *Bull. Soc. Chim. Fr.* **1974**, 2040. (c) Bertrand, M.; Viala, J. *Tetrahedron Lett.* **1978**, 2575. (d) Egert, E.; Beck, H.; Schmidt, D.; Gonschorrek, C.; Hoppe, D. *Tetrahedron Lett.* **1987**, *28*, 789.

clization of the *Z* hydroxy ester gave labile lactones (*Z*)-18. About 15% better yields in this three step, one-flask process were obtained using sulfinyl orthoacetate $PhS(O)CH_2C(OEt)_3$ under acidic conditions;[1] for example, in this way (*E*)-18 and (*Z*)-18 were isolated and purified in 37% and 41% yields for R = H and Et, respectively. No advantage was found using chlorine-substituted sulfinyl orthoester $4\text{-}ClPhS(O)CH_2C(OEt)_3$. Although secondary allenic alcohol 1,2-hexadien-3-ol also reacted with sulfinyl orthoester $PhS(O)CH_2C(OEt)_3$, two-carbon extended products like 18 were isolated in only 20% yield.

Conclusion

In summary, [(chlorophenyl)sulfinyl]vinylic chloride **1a** is an easily prepared, stable reagent able to transform diverse primary and secondary propargylic alcohols rapidly at 100 °C in one flask without isolation of any intermediates into richly functionalized 4-oxo-2-alkenoate esters. This intramolecular carbon–carbon bond-forming process is a new, convenient, and efficient synthetic method accomplishing globally regiospecific γ-attachment of a two-carbon (alkoxycarbonyl)methylene unit and also 1,2-transposition of oxygen from the α- to the β-position of the reactant propargylic alcohol. Diverse synthetic applications of this protocol can be envisioned besides those shown in eqs 2 and 3 for preparation of regiospecifically substituted monocycles.[16-18]

Experimental Section

General Experimental Data.[1] Tetrahydrofuran and diethyl ether were distilled from benzophenone ketyl prior to use. Methylene chloride, triethylamine, benzene, and ethanol were distilled from calcium hydride prior to use. Methanol was distilled from magnesium. Commercially available alcohols were distilled from calcium hydride prior to use. All other alcohols were prepared according to literature procedures and were distilled from calcium hydride prior to use. *n*-BuLi was titrated with 2,5-dimethoxybenzyl alcohol.[19] All other reagents and solvents were used as received.

3-(Trimethylsilyl)-2-propyn-1-ol.[20a,b] Propargyl alcohol (11.6 mL, 11.2 g, 0.20 mol) gave 3-(trimethylsilyl)-2-propyn-1-ol (23.1 g, 90%) as a colorless oil: bp_9 74–76 °C (lit.[20a] bp_{10} 64–67 °C); IR ($CHCl_3$, cm^{-1}) 3331 (br), 2167; ^1H NMR ($CDCl_3$) δ 0.18 (s, 9 H), 1.68 (s, 1 H), 4.27 (s, 2 H).

4-[(*tert*-Butyldimethylsilyl)oxy]-2-butyn-1-ol.[21] 2-Butyne-1,4-diol (392.0 mg, 4.51 mmol) gave 4-[(*tert*-butyldimethylsilyl)oxy]-2-butyn-1-ol (313.8 mg, 35%) as a yellowish oil: IR ($CHCl_3$, cm^{-1}) 3613; ^1H NMR ($CDCl_3$) δ 0.12 (s, 6 H), 0.91 (s, 9 H), 1.56 (s, 1 H), 4.30 (t, *J* = 1.6 Hz, 2 H), 4.35 (t, *J* = 1.6 Hz, 2 H).

4-Chloro-2-butyn-1-ol.[22a,b] Propargyl chloride (5.3 mL, 5.3 g, 71.8 mmol) gave 4-chloro-2-butyn-1-ol (3.8 g, 55%) as a colorless oil: bp_{10} 102–103 °C (lit.[22a] bp_{20} 95 °C); IR ($CHCl_3$, cm^{-1}) 3601, 3460 (br); ^1H NMR ($CDCl_3$) δ 1.66 (m, 1 H), 4.18 (t, *J* = 2.0 Hz, 2 H), 4.33 (dt, *J* = 6.0, 2.0 Hz, 2 H).

2,3-Butadien-1-ol.[22c,d] 4-Chloro-2-butyn-1-ol (3.8 g, 35.9 mmol) gave 2,3-butadien-1-ol (1.6 g, 64%) as a colorless oil: bp_{20} 48 °C (lit.[22c] bp_{12} 38 °C); IR ($CHCl_3$, cm^{-1}) 3601, 3436 (br) 1954; ^1H NMR ($CDCl_3$) δ 1.55 (m, 1 H), 4.15 (m, 2 H), 4.86 (dt, *J* = 6.6, 3.0 Hz, 2 H), 5.35 (m, *J* = 6.6 Hz, 1 H).

Hexa-1,2-dien-4-ol. 3-(Tetrahydropyran-2-yloxy)prop-1-yne.[23a,b] Propargyl alcohol (2.1 mL, 2.0 g, 35.7 mmol) gave 3-(tetrahydropyran-2-yloxy)prop-1-yne (2.9 g, 58%) as a colorless oil: bp_{10} 83–84 °C; ^1H NMR ($CDCl_3$) δ 1.50–1.85 (m, 6 H), 2.41 (t, *J* = 2.4 Hz, 1 H), 3.51–3.56 (m, 1 H), 3.81–3.87 (m, 1 H), 4.23 and 4.28 (AB, dd, *J* = 15.6, 2.4 Hz, 2 H), 4.82 (t, *J* = 3.2 Hz, 1 H).

1-(Tetrahydropyran-2-yloxy)hex-2-yn-4-ol.[23b] 3-(Tetrahydropyran-2-yloxy)prop-1-yne (3.6 g, 26.0 mmol) gave 1-(tetrahydropyran-2-yloxy)hex-2-yn-4-ol (4.9 g, 96%) as a yellow oil: IR ($CHCl_3$, cm^{-1}) 3601, 3425 (br); ^1H NMR ($CDCl_3$) δ 1.00 (t, *J* = 7.4 Hz, 3 H), 1.51–1.81 (m, 9 H), 3.52–3.55 (m, 1 H), 3.81–3.83 (m, 1 H), 4.24–4.35 (m, 3 H), 4.81 (t, *J* = 3.4 Hz, 1 H).

Hexa-1,2-dien-4-ol.[22c,d] 1-(Tetrahydropyran-2-yloxy)hex-2-yn-4-ol (2.6 g, 13.2 mmol) gave hexa-1,2-dien-4-ol as a colorless oil: bp_{10} 57 °C; IR ($CHCl_3$, cm^{-1}) 3601; ^1H NMR ($CDCl_3$) δ 0.95 (t, *J* = 7.4 Hz, 3 H), 1.59 (dq, *J* = 7.6, 6.4 Hz, 2 H), 1.70 (s, 1 H), 4.10 (m, 1 H), 4.85 (ddd, *J* = 6.4, 2.4, 1.2 Hz, 2 H), 5.23 (q, *J* = 6.4 Hz, 1 H).

Hexa-2,3-dien-1-ol. 3-(Tetrahydropyran-2-yloxy)pent-1-yne.[23a,b] 1-Pentyn-3-ol (2.8 mL, 2.7 g, 31.8 mmol) gave 3-(tetrahydropyran-2-yloxy)pent-1-yne (2.9 g, 54%) as a colorless oil, bp_{10} 95–97 °C. Inseparable mixture of two diastereomers: ^1H NMR ($CDCl_3$) δ 1.00 (t, *J* = 7.4 Hz, 3 H), 1.04 (t, *J* = 7.4 Hz, 3 H), 1.50–1.67 (m, 8 H), 1.67–1.87 (m, 8 H), 2.37 (d, *J* = 2.0 Hz, 1 H), 2.43 (d, *J* = 2.0 Hz, 1 H), 3.50–3.56 (m, 2 H), 3.79–3.84 (m, 1 H), 3.99–4.05 (m, 1 H), 4.24 (td, *J* = 6.4, 2.0 Hz, 1 H), 4.36 (td, *J* = 6.4, 2.0 Hz, 1 H), 4.75 (t, *J* = 3.4 Hz, 1 H), 4.98 (t, *J* = 3.4 Hz, 1 H).

4-(Tetrahydropyran-2-yloxy)hex-2-yn-1-ol.[22a,b] 3-(Tetrahydropyran-2-yloxy)pent-1-yne (2.9 g, 17.3 mmol) gave 4-(tetrahydropyran-2-yloxy)hex-2-yn-1-ol (3.4 g, 99%) as an amber oil. Unseparated mixture of two diastereomers: IR ($CHCl_3$, cm^{-1}) 3601, 3413 (br), 3295; ^1H NMR ($CDCl_3$) δ 0.99 (t, *J* = 7.6 Hz, 3 H), 1.03 (t, *J* = 7.6 Hz, 3 H), 1.49–1.65 (m, 8 H), 1.67–1.86 (m, 10 H), 3.50–3.54 (m, 2 H), 3.77–3.80 (m, 1 H), 3.97–4.00 (m, 1 H), 4.27–4.31 (m, 5 H), 4.37–4.39 (m, 1 H), 4.74 (t, *J* = 3.2 Hz, 1 H), 4.96 (t, *J* = 3.2 Hz, 1 H).

Hexa-2,3-dien-1-ol.[22c,d] 4-(Tetrahydropyran-2-yloxy)hex-2-yn-1-ol (2.9 g, 14.8 mmol) gave hexa-2,3-dien-1-ol as a yellowish oil: bp_{10} 72–74 °C; IR ($CHCl_3$, cm^{-1}) 3613, 3472 (br), 3295; ^1H NMR ($CDCl_3$) δ 1.01 (t, *J* = 7.4 Hz, 3 H), 1.51 (s, 1 H), 2.04 (m, 2 H), 4.11 (br s, 2 H), 5.36 (m, 2 H).

2,2,2-Trichloroethyl 4-Chlorophenyl Sulfide.[24a,b] 4-Chlorothiophenol (11.5 g, 79.6 mmol) gave 2,2,2-trichloroethyl 4-chlorophenyl sulfide (11.2 g, 51%) as a yellow oil: $bp_{0.5}$ 120–140 °C; IR ($CHCl_3$, cm^{-1}) 3002, 1472, 1202, 1096, 1008, 908; ^1H NMR ($CDCl_3$) δ 4.05 (s, 2 H), 7.30 and 7.48 (AB, *J* = 8.6 Hz, 4 H).

2,2-Dichlorovinyl 4-Chlorophenyl Sulfide.[25] 4-Chlorothiophenol (13.6 g, 94.2 mmol) gave 2,2-dichlorovinyl 4-chlorophenyl sulfide (14.8 g, 66%) as a yellowish oil: $bp_{0.5}$ 145 °C; IR

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Table II. Characteristic NMR Data

	^{1}H (δ)
$ArSCHRCCl_3$	
Ar = Ph, R = H	4.09 (s, 2 H), 7.30 (m, 3 H), 7.55 (dd, J = 6.8, 1.2 Hz, 2 H)
Ar = 2,6-Me_2Ph, R = H	2.60 (s, 6 H), 3.84 (s, 2 H), 7.11–7.17 (m, 3 H)
Ar = 4-O_2NPh, R = H	4.21 (s, 2 H), 7.59 (d, J = 9.0 Hz, 2 H), 8.18 (d, J = 9.0 Hz, 2 H)
Ar = Ph, R = Me	1.75 (d, J = 6.9 Hz, 3 H), 3.96 (q, J = 6.9 Hz, 1 H), 7.23–7.36 (m, 3 H), 7.49–7.57 (m, 2 H)
$ArS(=O)CHRCCl_3$	
Ar = Ph, R = H	4.05 (d, J = 3.6 Hz, 2 H), 7.58 (m, 3 H), 7.75 (dd, J = 8.0, 2.0 Hz, 2 H)
Ar = 2,6-Me_2Ph, R = H	2.66 (s, 6 H), 4.21 (d, J = 13.9 Hz, 1 H), 4.50 (d, J = 13.9 Hz, 1 H), 7.11 (d, J = 7.6 Hz, 2 H), 7.29 (t, J = 7.6 Hz, 1 H)
Ar = 4-O_2NPh, R = H	4.10 (s, 2 H), 7.89 (d, J = 8.8 Hz, 1 H), 7.95 (d, J = 8.8 Hz, 1 H), 8.44 (dd, J = 13.6, 8.8 Hz, 2 H)
Ar = Ph, R = Me	1.34 (d, J = 6.8 Hz, 3 H), 3.87 (q, J = 6.8 Hz, 1 H), 7.54–7.58 (m, 3 H), 7.75–7.77 (m, 2 H)
$ArS(=O)CR{=}CCl_2$	
Ar = Ph, R = H	6.67 (s, 1 H), 7.57 (m, 3 H), 7.70 (m, 2 H)
Ar = 2,6-Me_2Ph, R = H	2.73 (s, 6 H), 5.39 (s, 1 H), 7.19 (d, J = 7.4 Hz, 2 H), 7.38 (t, J = 7.4 Hz, 1 H)
Ar = 4-O_2NPh, R = H	6.66 (s, 1 H), 7.89 (d, J = 9.0 Hz, 2 H), 8.42 (d, J = 9.0 Hz, 2 H)
Ar = Ph, R = Me	1.87 (s, 3 H), 7.51–7.54 (m, 3 H), 7.65–7.67 (m, 2 H)
$ArS(=O)CH{=}CCl(OR')$	
Ar = Ph, R' = Et	1.44 (t, J = 7.2 Hz, 3 H), 4.29 (m, 2 H), 5.74 (s, 1 H), 7.50 (m, 3 H), 7.65 (m, 2 H)
Ar = 2,6-Me_2Ph, R' = Et (**1b**)	1.35 (t, J = 7.0 Hz, 3 H), 2.61 (s, 6 H), 4.14–4.23 (m, 2 H), 6.16 (s, 1 H), 7.05 (d, J = 7.6 Hz, 2 H), 7.22 (d, J = 7.6 Hz, 1 H)
Ar = Ph, R' = $CH_2CH_2CH{=}CH_2$ (**12**)	2.55 (qm, J = 6.8 Hz, 2 H), 4.20 (td, J = 6.8, 2.4 Hz, 2 H), 5.18 (dd, J = 12.0, 1.6 Hz, 1 H), 5.22 (dm, 17.2 Hz, 1 H), 5.72 (s, 1 H), 5.87 (ddm, J = 17.2, 10.4 Hz, 1 H), 7.47–7.51 (m, 3 H), 7.62–7.64 (m, 2 H)

($CHCl_3$, cm^{-1}) 1567, 1478, 1390, 1091; ^{1}H NMR ($CDCl_3$) δ 6.45 (s, 1 H), 7.30 and 7.49 (AB, J = 8.6 Hz, 4 H).

2,2,2-Trichloroethyl 4-Chlorophenyl Sulfoxide (6a). To 11.23 g (40.69 mmol) of 2,2,2-trichloroethyl 4-chlorophenyl sulfide in 9.0 mL of methylene chloride maintained at −20 °C was added dropwise a solution of *m*-CPBA (12.89 g, 41.10 mmol) in 65.0 mL of methylene chloride. After complete addition, the reaction mixture was warmed to rt and stirred for 1 h, upon which it was poured into 75 mL of saturated aqueous sodium bicarbonate. The aqueous layer was extracted three times with 30 mL of diethyl ether. The organic phases were combined and dried over magnesium sulfate. The solvent was evaporated to afford 11.22 g of a yellow oil which was purified by short-path column chromatography (silica gel, eluting solvent diethyl ether/hexanes (1:4), then CH_2Cl_2) to yield 2,2,2-trichloroethyl 4-chlorophenyl sulfoxide (**6a**) (6.05 g, 51%) as a white solid: mp 102.5–103.5 °C; IR ($CHCl_3$, cm^{-1}) 1091; ^{1}H NMR ($CDCl_3$) δ 4.01 and 4.05 (AB, J = 14.0 Hz, 2 H), 7.57 and 7.69 (AB, J = 8.6 Hz, 4 H). Anal. Calcd for $C_8H_6OSCl_4$: C, 32.91; H, 2.07; S, 10.91; Cl, 48.56. Found: C, 32.92; H, 2.12; S, 10.91; Cl, 48.49.

2,2-Dichlorovinyl 4-Chlorophenyl Sulfoxide (7a). The above procedure, using 14.8 g (62.0 mmol) of 2,2-dichlorovinyl 4-chlorophenyl sulfide in 14 mL of methylene chloride and 12.8 g (63.2 mmol) of *m*-CPBA in 150 mL of methylene chloride yielded 2,2-dichlorovinyl 4-chlorophenyl sulfoxide (**7a**) (5.9 g, 37%) as a white solid along with recovered sulfide (8.2 g, 52%).

Following the procedure described in the literature,[24a] sulfoxide **6a** (5.8 g, 19.8 mmol) gave product **7a** (2.2 g, 52%) as a yellowish solid: mp 81–82 °C; IR ($CHCl_3$, cm^{-1}) 3013, 1584, 1478, 1390, 1219, 914; ^{1}H NMR ($CDCl_3$) δ 6.64 (s, 1 H), 7.54 and 7.63 (AB, t, J = 8.8, 2.0 Hz, 4 H); ^{13}C NMR ($CDCl_3$) δ 125.2, 129.7 (2 C), 132.1, 136.1 (2 C), 137.8, 141.3. Anal. Calcd for $C_8H_5OSCl_3$: C, 37.73; H, 1.96; C, 12.49; Cl, 41.49. Found: C, 37.60; H, 1.97; S, 12.55; Cl, 41.62.

2-Chloro-2-ethoxyvinyl 4-Chlorophenyl Sulfoxide (1a). To 0.172 mL (2.93 mmol) of ethanol in 5.8 mL of THF at −78 °C was added dropwise 2.09 mL (2.93 mmol) of methyllithium, 1.4 M in diethyl ether. The resulting mixture was stirred at −78 °C for 15 min and was then cannulated into a solution of 748.8 mg (2.93 mmol) of 2,2-dichlorovinyl 4-chlorophenyl sulfoxide (**7a**) in 5.8 mL of THF at −78 °C. The reaction mixture was allowed to warm to rt. The solvent was then evaporated to afford a brown oil. Subsequent purification via short-path column chromatography (silica gel, eluting solvent diethyl ether/hexanes (3:2)) yielded 2-chloro-2-ethoxyvinyl 4-chlorophenyl sulfoxide (**1a**) (574.6 mg, 75%) as a yellow oil: IR ($CHCl_3$, cm^{-1}) 1606, 1249, 1089, 1071; ^{1}H NMR ($CDCl_3$) δ 1.43 (t, J = 7.0 Hz, 3 H), 4.26–4.33 (m, 2 H), 5.69 (s, 1 H), 7.48 (dt, J = 8.8, 2.0 Hz, 2 H), 7.58 (dt, J = 8.8, 2.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 14.4, 69.1, 115.1, 125.4 (2 C), 129.5 (2 C), 136.9, 143.6, 152.4; HRMS calcd for M − 48 $C_{10}H_{10}Cl_2SO_2$ 216.0109, found 216.0111.

For characteristic NMR data of related compounds, see Table II.

Ethyl 3-Methyl-4-oxo-2-pentenoate (8a). To 52.9 mg (0.200 mmol) of 2-chloro-2-ethoxyvinyl 4-chlorophenyl sulfoxide (**1a**) in 0.15 mL of THF at −78 °C was added 0.282 mL (0.166 mmol) of a 0.589 M solution of lithium alkoxide of 2-butyn-1-ol in THF at −78 °C. [The latter was generated via addition of 0.119 mL (0.166 mmol) of methyllithium, 1.4 M in diethyl ether, to 12.7 μL (0.166 mmol) of 2-butyn-1-ol in 0.15 mL of THF at −78 °C and subsequent stirring at −78 °C for 15 min.] The reaction mixture was stirred at −78 °C for 1 h, upon which it was allowed to warm to rt. It was then transferred under nitrogen into an hydrolysis tube equipped with a Teflon screw cap, THF (0.4 mL) was added, and the tube was sealed (by screwing its cap tightly) and then maintained at 100 °C for 1 h. The reaction mixture was then cooled to rt and concentrated to afford a brown oil. Subsequent purification via short-path column chromatography (silica gel, eluting solvent diethyl ether/pentane (1:199, 1:49, 1:9, 1:4)) yielded ethyl (*E*)-3-methyl-4-oxo-2-pentenoate (**8a**) (14.3 mg, 55%) as a yellow oil: IR ($CHCl_3$, cm^{-1}) 1719, 1684; ^{1}H NMR ($CDCl_3$) δ 1.33 (t, J = 7.2 Hz, 3 H), 2.21 (d, J = 1.6 Hz, 3 H), 2.39 (s, 3 H), 4.25 (q, J = 7.2 Hz, 2 H), 6.57 (q, J = 1.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 13.0, 14.2, 26.6, 60.8, 126.5, 150.4, 166.2, 199.9; HRMS calcd for $C_8H_{12}O_3$ 156.0786, found 156.0789.

Ethyl 3-Phenyl-4-oxo-2-pentenoate (8b). The above procedure, using 52.2 mg (0.197 mmol) of 2-chloro-2-ethoxyvinyl 4-chlorophenyl sulfoxide (**1a**) in 0.1 mL of THF, 0.117 mL (0.164 mmol) of methyllithium 1.4 M in diethyl ether, 20.1 μL (0.164 mmol) of 3-phenyl-2-propyn-1-ol in 0.1 mL of THF, and 0.4 mL of additional THF, yielded ethyl 3-phenyl-4-oxo-2-pentenoate (**8b**) (20.4 mg, 57%) as an inseparable mixture of stereoisomers (7:1), yellow oil: IR ($CHCl_3$, cm^{-1}) 1755, 1708; ^{1}H NMR ($CDCl_3$) δ, stereoisomer 1, 1.32 (t, J = 7.2 Hz, 3 H), 2.44 (s, 3 H), 4.23 (q, J = 7.2 Hz, 2 H), 6.15 (s, 1 H), 7.42 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 14.1, 30.4, 61.0, 115.4, 126.8, 129.1 (2 C), 130.5 (2 C), 132.8, 158.1, 165.4, 204.4; HRMS calcd for $C_{13}H_{14}O_3$ 218.0943, found 218.0939; ^{1}H NMR ($CDCl_3$) δ, stereoisomer 2, 1.32 (t, J = 7.2 Hz, 3 H), 2.30 (s, 3 H), 4.23 (q, J = 7.2 Hz, 2 H), 6.20 (s, 1 H), 7.31 (m, 5 H).

Ethyl 3-(Trimethylsilyl)-4-oxo-2-pentenoate (8c). The above procedure, using 34.7 mg (0.131 mmol) of 2-chloro-2-ethoxyvinyl 4-chlorophenyl sulfoxide (**1a**) in 0.1 mL of THF, 0.095 mL (0.133 mmol) of methyllithium, 1.4 M in diethyl ether, 12.2 mg (0.095 mmol) of 3-(trimethylsilyl)-2-propyn-1-ol in 0.1 mL of THF, and 0.4 mL of additional THF, yielded ethyl 3-(trimethylsilyl)-4-oxo-2-pentenoate (**8c**) (10.7 mg, 52%) as an inse-

parable mixture of stereoisomers (8:1), yellow oil: IR ($CHCl_3$, cm^{-1}) 1719, 1684; ^1H NMR ($CDCl_3$) δ, stereoisomer 1, 0.24 (s, 9 H), 1.31 (t, J = 7.2 Hz, 3 H), 2.27 (s, 3 H), 4.22 (q, J = 7.2 Hz, 2 H), 6.37 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ −0.7 (3 C), 14.1, 29.8, 61.0, 130.9, 165.7, 166.2, 207.0; HRMS calcd for M − 15 $C_{10}H_{18}O_3Si$ 199.0790, found 199.0787; ^1H NMR ($CDCl_3$) δ, isomer 2, 0.19 (s, 9 H), 1.31 (t, J = 7.2 Hz, 3 H), 2.27 (s, 3 H), 4.22 (q, J = 7.2 Hz, 2 H), 6.33 (s, 1 H).

Ethyl 3-[[(*tert*-Butyldimethylsilyl)oxy]methyl]-4-oxo-2-pentenoate (8d). The above procedure, using 69.5 mg (0.262 mmol) of 2-chloro-2-ethoxyvinyl 4-chlorophenyl sulfoxide (**1a**) in 0.1 mL of THF, 0.150 mL (0.211 mmol) of methyllithium, 1.4 M in diethyl ether, 42.2 mg (0.211 mmol) of 4-[(*tert*-butyldimethylsilyl)oxy]-2-butyn-1-ol in 0.1 mL of THF, and 0.4 mL of additional THF, yielded ester **8d** (48.5 mg, 80%) as a nonseparated mixture of stereoisomers (4:1), yellow oil: IR ($CHCl_3$, cm^{-1}) 1719, 1684. Isomer 1: ^1H NMR ($CDCl_3$) δ 0.06 (s, 6 H), 0.87 (s, 9 H), 1.30 (t, J = 7.2 Hz, 3 H), 2.39 (s, 3 H), 4.22 (q, J = 7.2 Hz, 2 H), 4.90 (d, J = 1.2 Hz, 2 H), 6.29 (d, J = 1.2 Hz, 1 H); HRMS calcd for M − 15 $C_{14}H_{26}O_4Si$ 271.1366, found 271.1362. Isomer 2: ^1H NMR ($CDCl_3$) δ 0.08 (s, 6 H), 0.91 (s, 9 H), 1.28 (t, J = 7.2 Hz, 3 H), 2.38 (s, 3 H), 4.18 (q, J = 7.2 Hz, 2 H), 4.32 (d, J = 2.0 Hz, 2 H), 5.91 (t, J = 2.0 Hz, 1 H). Anal. Calcd for $C_{14}H_{26}O_4Si$: C, 58.70; H, 9.15. Found: C, 58.61; H: 9.14.

Ethyl 3-(Chloromethyl)-4-oxo-2-pentenoate (8e). The above procedure, using 66.2 mg (0.250 mmol) of 2-chloro-2-ethoxyvinyl 4-chlorophenyl sulfoxide (**1a**) in 0.1 mL of THF, 0.146 mL (0.205 mmol) of methyllithium, 1.4 M in diethyl ether, 21.4 mg (0.205 mmol) of 4-chloro-2-butyn-1-ol in 0.1 mL of THF, and 0.5 mL of additional THF, yielded ester **8e** (29.9 mg, 77%) as an inseparable mixture of stereoisomers (5:1), yellow oil, along with recovered 4-chloro-2-butyn-1-ol (2.4 mg, 11%): IR ($CHCl_3$, cm^{-1}) 1719, 1690. Isomer 1: ^1H NMR ($CDCl_3$) δ 1.35 (t, J = 7.2 Hz, 3 H), 2.44 (s, 3 H), 4.30 (q, J = 7.2 Hz, 2 H), 4.78 (s, 2 H), 6.65 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.1, 26.4, 34.6, 61.6, 128.6, 148.4, 164.8, 197.2; HRMS calcd for M − 15 $C_8H_{11}O_3Cl$ 175.0162, found 175.0163. Isomer 2: ^1H NMR ($CDCl_3$) δ 1.29 (t, J = 7.2 Hz, 3 H), 2.46 (s, 3 H), 4.20 (d, J = 1.2 Hz, 2 H), 4.21 (q, J = 7.2 Hz, 2 H), 6.02 (t, J = 1.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.1, 33.7, 43.8, 61.4, 120.1, 148.4, 186.0, 198.0. Anal. Calcd for $C_{18}H_{11}O_3Cl$: C, 50.41; H, 5.82. Found: C, 50.43; H: 5.87.

Ethyl 3-Methyl-4-oxo-2-heptenoate (9a). The above procedure, using 52.7 mg (0.199 mmol) of 2-chloro-2-ethoxyvinyl 4-chlorophenyl sulfoxide (**1a**) in 0.1 mL of THF, 0.118 mL (0.166 mmol) of methyllithium, 1.4 M in diethyl ether, 18.7 μL (0.166 mmol) of 4-hexyn-3-ol in 0.1 mL of THF, and 0.3 mL of additional THF, yielded crude ethyl 3-methyl-4-oxo-2-heptenoate (**9a**) as an amber oil. Subsequent purification via short-path column chromatography (silica gel, eluting solvent diethyl ether/pentane (1:199, 1:49)) followed by purification via PTLC (1 × 500 μm, eluting solvent diethyl ether/hexanes (1:1), extraction solvent methylene chloride) yielded ethyl 3-methyl-4-oxo-2-heptenoate (**9a**) (20.1 mg, 66%) as an inseparable mixture of stereoisomers (1.3:1), yellow oil: IR ($CHCl_3$, cm^{-1}) 1719, 1684; ^1H NMR ($CDCl_3$) δ, isomer 1, 0.94 (t, J = 7.4 Hz, 3 H), 1.33 (t, J = 7.0 Hz, 3 H), 1.66 (m, J = 7.4 Hz, 2 H), 2.23 (d, J = 1.2 Hz, 3 H), 2.68 (t, J = 7.2 Hz, 2 H), 4.24 (q, J = 7.2 Hz, 2 H), 6.54 (d, J = 1.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 11.7, 14.2, 14.3, 23.7, 53.2, 60.8, 129.3, 150.6, 165.9, 197.2; HRMS calcd for $C_{10}H_{16}O_3$ 184.1099, found 184.1098; ^1H NMR ($CDCl_3$) δ, isomer 2, 1.02 (t, J = 7.4 Hz, 3 H), 1.31 (t, J = 7.0 Hz, 3 H), 1.66 (m, J = 7.2 Hz, 2 H), 2.29 (d, J = 1.6 Hz, 3 H), 2.68 (t, J = 7.2 Hz, 2 H), 4.21 (q, J = 7.2 Hz, 2 H), 6.36 (d, J = 1.2 Hz, 1 H). Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 64.64; H, 8.57.

Ethyl 3-Ethyl-4-oxo-2-heptenoate (9b). The above procedure, using 52.9 mg (0.200 mmol) of 2-chloro-2-ethoxyvinyl 4-chlorophenyl sulfoxide (**1a**) in 0.1 mL of THF, 0.119 mL (0.166 mmol) of methyllithium, 1.4 M in diethyl ether, 19.1 mg (0.166 mmol) of 4-heptyn-3-ol in 0.1 mL of THF, and 0.4 mL of additional THF, yielded crude ethyl 3-ethyl-4-oxo-2-heptenoate (**9b**), as an amber oil. Subsequent purification via short-path column chromatography (silica gel, eluting solvent diethyl ether/pentane (1:199, 1:49)) followed by purification via PTLC (1 × 500 μm, eluting solvent diethyl ether/hexanes (1:1), extraction solvent methylene chloride) yielded ethyl 3-ethyl-4-oxo-2-heptenoate (**9b**) (25.2 mg, 77%) as an inseparable mixture of stereoisomers (1:3), light yellow oil: IR ($CHCl_3$, cm^{-1}) 1713, 1684; ^1H NMR ($CDCl_3$) δ, isomer 1, 0.94 (t, J = 7.4 Hz, 3 H), 1.02 (t, J = 7.4 Hz, 3 H), 1.32 (t, J = 7.2 Hz, 3 H), 1.65 (m, J = 7.4 Hz, 2 H), 2.66 (t, J = 7.2 Hz, 2 H), 2.77 (q, J = 7.4 Hz, 2 H), 4.24 (q, J = 7.2 Hz, 2 H), 6.45 (s, 1 H); HRMS calcd for $C_{11}H_{18}O_3$ 198.1256, found 198.1256; ^1H NMR ($CDCl_3$) δ, isomer 2, 1.01 (t, J = 7.2 Hz, 3 H), 1.07 (t, J = 7.4 Hz, 3 H), 1.31 (t, J = 7.2 Hz, 3 H), 1.65 (m, J = 7.4 Hz, 2 H), 2.66 (t, J = 7.2 Hz, 2 H), 2.77 (q, J = 7.4 Hz, 2 H), 4.13 (q, J = 7.2 Hz, 2 H), 6.28 (s, 1 H). Anal. Calcd for $C_{11}H_{18}O_3$: C, 66.62; H, 9.16. Found: C, 66.30; H, 8.79.

Ethyl 2,4,5-Trimethyl-2-(oxoethyl)-4-cyclohexene-1-carboxylate (10). Ethyl 3-methyl-4-oxo-2-pentenoate (**8a**) (46.9 mg, 0.30 mmol), 2,3-dimethyl-1,3-butadiene (348.4 μL, 252.9 mg, 3.0 mmol), and 0.50 mL of methylene chloride were combined under argon. A solution of titanium tetrachloride, 1 M in CH_2Cl_2 (120.1 μL, 0.12 mmol), was then added dropwise at rt. The reaction mixture was then stirred at rt for 18 h, upon which it was diluted with CH_2Cl_2 and washed with water. The aqueous phase was extracted three times with CH_2Cl_2, and the combined organic phases were washed with brine, dried over magnesium sulfate, and filtered. Concentration afforded a yellow oil which was purified via short-path column chromatography (silica gel, eluting solvent diethyl ether/hexanes (1:4)) to yield product **10** (76.4 mg, quant) as a yellow oil: IR ($CHCl_3$, cm^{-1}) 1719, 1696; ^1H NMR ($CDCl_3$) δ 1.21 (s, 3 H), 1.23 (t, J = 7.2 Hz, 3 H), 1.62 (s, 3 H), 1.64 (s, 3 H), 1.77 (d, J = 16.8 Hz, 1 H), 2.10–2.30 (m, 3 H), 2.21 (s, 3 H), 3.04 (dd, J = 10.8, 6.0 Hz, 1 H), 4.10 (qd, J = 7.2, 1.6 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 14.1, 16.5, 18.5, 19.0, 25.6, 31.5, 42.0, 44.4, 48.9, 60.4, 122.7, 123.5, 174.0, 212.9; HRMS calcd for $C_{14}H_{22}O_3$ 238.1569, found 238.1570.

Ethyl 4,5-Dimethylpyrazole-3-carboxylate (11). To alkenoate **8e** (24.4 mg, 0.128 mmol) in 0.5 mL of ethanol at rt was slowly added under argon a solution of anhydrous hydrazine (16.2 μL, 16.4 mg, 0.512 mmol) in 0.5 mL of ethanol. The reaction mixture was then heated at reflux for 4 h, upon which it was cooled to rt and concd to afford a yellow oil which was purified via short-path column chromatography (silica gel, eluting solvent diethyl ether/hexanes (1:2.3, 1:1.5, 1:1)) to yield product **11** (10.8 mg, 50%) as a white solid: mp 81–82 °C; IR ($CHCl_3$, cm^{-1}) 1713; ^1H NMR ($CDCl_3$) δ 1.39 (t, J = 7.2 Hz, 3 H), 2.22 (s, 3 H), 2.24 (s, 3 H), 4.37 (q, J = 7.2 Hz, 2 H), consistent with literature data.[5b]

3-Butenyl 3-Methyl-4-oxo-2-pentenoate (15). The procedure described for alkenoate **8a**, using 204.5 mg (0.796 mmol) of reagent **12** in 0.4 mL of THF, 0.474 mL (0.664 mmol) of methyllithium, 1.4 M in diethyl ether, 50.7 μL (0.664 mmol) of 2-butyn-1-ol in 0.4 mL of THF, and 0.8 mL of additional THF, yielded ester **15** (85.9 mg, 71%) as an inseparable mixture of two stereoisomers (4:1), yellow oil: IR ($CHCl_3$, cm^{-1}) 1719, 1684; ^1H NMR ($CDCl_3$) δ, isomer 1, 2.21 (d, J = 1.6 Hz, 3 H), 2.39 (s, 3 H), 2.45 (qt, J = 6.8, 1.4 Hz, 2 H), 4.25 (t, J = 6.8 Hz, 2 H), 5.10 (dm, J = 10.4 Hz, 1 H), 5.14 (dm, J = 18.0 Hz, 1 H), 5.81 (m, 1 H), 6.57 (q, J = 1.6 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 13.1, 26.2, 32.9, 63.9, 117.4, 126.3, 133.7, 150.6, 166.1, 199.8; HRMS calcd for $C_{10}H_{14}O_3$ M − 15 167.0708, found 167.0710; ^1H NMR ($CDCl_3$) δ, isomer 2, 2.24 (d, J = 1.6 Hz, 3 H), 2.39 (s, 3 H), 2.45 (qt, J = 6.8, 1.4 Hz, 2 H), 4.25 (t, J = 6.8 Hz, 2 H), 5.10 (dm, J = 10.4 Hz, 1 H), 5.14 (dm, J = 18.0 Hz, 1 H), 5.81 (m, 1 H), 6.48 (q, J = 1.6 Hz, 1 H).

Ethyl 3-(Hydroxymethyl)-2,4-pentadienoate ((*E*)-18a) and Corresponding Lactone (*Z*)-18a. 1-(Phenylsulfinyl)-2,2,2-triehoxyethane[1] (176.0 mg, 0.615 mmol), 2,3-butadien-1-ol (20.4 mg, 0.291 mmol), and 2,4,6-trimethylbenzoic acid (0.96 mg, 5.8 μmol) were combined under N_2 in an hydrolysis tube equipped with a Teflon screw cap. Methylene chloride (0.5 mL) was then added and the tube was sealed (by screwing its cap tightly). The reaction mixture was subsequently maintained at 100 °C for 1 h, upon which it was cooled to rt and concd to afford a crude mixture of (*E*)-**18a** and (*Z*)-**18a** (1:1) as a yellow oil. Subsequent purification via short-path column chromatography (silica gel, eluting solvent diethyl ether/pentane (1:199, 1:49, 1:9, 1:4, 1:1.5)) followed by purification via PTLC (1 × 500 μm, eluting solvent diethyl ether/hexanes (1.5:1), extraction solvent methylene chloride) yielded compounds (*E*)-**18a** (14.5 mg, 32%) as a colorless oil and (*Z*)-**18a** (1.7 mg, 5%) as a yellow oil. **Ester (*E*)-18a:** IR ($CHCl_3$, cm^{-1}) 3613, 3483 (br) 1702; ^1H NMR ($CDCl_3$) δ 1.29 (t, J = 7.0 Hz, 3 H), 1.77 (t, J = 5.4 Hz, 1 H), 4.19 (q, J = 7.2 Hz, 2 H), 4.47 (d, J = 4.0 Hz, 2 H), 5.42 (dd, J = 11.4, 1.3 Hz, 1 H),

5.53 (d, J = 18.2 Hz, 1 H), 6.05 (s, 1 H), 7.64 (dd, J = 18.0, 11.3 Hz, 1 H). ^{13}C NMR ($CDCl_3$) δ 14.2, 60.0, 62.5, 116.1, 119.5, 131.5, 151.6, 166.3; HRMS calcd for $C_8H_{12}O_3$ 156.0786, found 156.0783. **Lactone (*Z*)-18a**: ^{1}H NMR ($CDCl_3$) δ 4.99 (dd, J = 1.8, 0.5 Hz, 2 H), 5.61 (d, J = 11.0 Hz, 1 H), 5.62 (d, J = 17.7 Hz, 1 H), 5.98 (m, 1 H), 6.70 (ddd, J = 17.8, 10.9, 0.7 Hz, 1 H), consistent with literature data.[26] IR and HRMS could not be taken, due to the instability of this compound.

Ethyl 3-(1-Hydroxypropyl)-2,4-pentadienoate ((*E*)-18b) and Corresponding Lactone (*Z*)-18b. The above procedure, using 796.0 mg (2.78 mmol) of 1-(phenylsulfinyl)-2,2,2-trieth-oxyethane,[1] 137.5 mg (1.40 mmol) of hexa-2,3-dien-1-ol, a catalytic amount of 2,4,6-trimethylbenzoic acid, and 2.0 mL of methylene chloride, yielded a crude mixture of (*E*)-18b and (*Z*)-18b (3:1) as a brown oil. Subsequent purification via short-path column chromatography (silica gel, eluting solvent diethyl ether/pentane (1:199, 1:49, 1:9, 1:4)) followed by purification via PTLC (2 × 1500 μm, eluting solvent diethyl ether/hexanes (1.5:1), extraction solvent methylene chloride) yielded compounds (*E*)-18b (74.2 mg, 29%) as a yellow oil and (*Z*)-18b (23.7 mg, 12%) as a yellow oil. **Ester (*E*)-18b**: IR ($CHCl_3$, cm^{-1}) 3601, 3519 (br), 1702; ^{1}H NMR ($CDCl_3$) δ 0.98 (t, J = 7.4 Hz, 3 H), 1.29 (t, J = 7.2 Hz, 3 H), 1.59 (m, 2 H), 1.80 (m, 1 H), 4.18 (qd, J = 7.2, 2.3 Hz, 2 H), 4.61 (m, 1 H), 5.43 (ddd, J = 11.6, 1.5, 1.0 Hz, 1 H), 5.55 (d, J = 18.1 Hz, 1 H), 6.06 (s, 1 H), 7.61 (dd, J = 18.6, 11.6 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 10.2, 15.5, 30.4, 60.3, 66.1, 116.1, 119.8, 132.1, 156.2, 166.8; HRMS calcd for $C_{10}H_{16}O_3$ 184.1099, found 184.1103. **Lactone (*Z*)-18b**: IR ($CHCl_3$, cm^{-1}) 1749; ^{1}H NMR ($CDCl_3$) δ 0.93 (t, J = 7.4 Hz, 3 H), 1.67 (m, 1 H), 2.11 (m, 1 H), 5.15 (m, 1 H), 5.64 (d, J = 11.2 Hz, 1 H), 5.67 (d, J = 17.8 Hz, 1 H), 5.98 (s, 1 H), 6.57 (dd, J = 17.8, 11.1 Hz, 1 H).

Acknowledgment. We thank the Petroleum Research Fund, administered by the American Chemical Society, for financial support and Rhône-Poulenc for a graduate fellowship to J.-C.C.

Supplementary Material Available: Characterization of new compounds by NMR (11 pages). Ordering information is given on any current masthead page.

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Photochemical Decomposition of 1-Alkoxy-2-azidophenazines. Addition of Nitrenes to Azides

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Received August 2, 1990 (Revised Manuscript Received August 7, 1991)

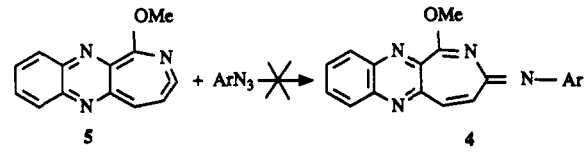
The photolysis of 2-azido-1-methoxyphenazine (**1a**) and its ethoxy homologue (**1b**) takes an unusual course. It involves the addition of a singlet nitrene or one of its cyclic tautomers to the ground-state azide to form the *N*-phenazinyl iminoether **9a** (from **1a**) and a 2-oxazolo[5,4-*a*]phenazinyl derivative of a quinoxalinylpropenenitrile (**10**, from both **1a** and **1b**). Products derived from the triplet nitrene are formed as well. The effects of varying some of the experimental conditions were determined. A mechanism for the photolysis is proposed.

Introduction

For several years we have been interested in the photochemical decomposition of heterocyclic azides, in particular, azidophenazines. Depending on the reaction conditions, such compounds give high yields of either, from the singlet nitrene, products of trapping by nucleophiles or, from the triplet nitrene, dimers and products of trapping by radical scavengers.[1] In contrast, the photolysis of carbocyclic aromatic azides usually gives poor yields of such products.[2]

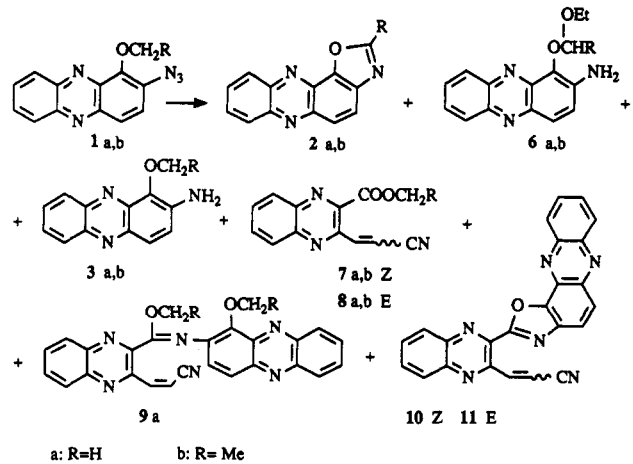
We earlier reported[1a] some results of the photolysis of 2-azido-1-methoxyphenazine (**1a**). Besides the oxazole **2a** and the amine **3a**, which were derived from the triplet nitrene (Scheme I), another major product arose from what appeared to be the coupling of two molecules of the substrate. We assigned an iminoazepine structure (formula **4**) to this compound and postulated that it was formed by the 1,3-dipolar cycloaddition of the ground-state azide to the dehydroazepine **5**, a cyclic isomer of singlet nitrene (Scheme II).

Scheme I



Ar = (1-methoxy-2-phenazinyl)

Scheme II



a: R=H b: R= Me

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