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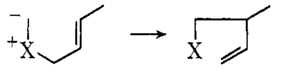
[2,3]-Sigmatropic Rearrangements of Acetylenic and Allenic Sulfonium Ylides. Synthesis of Allenes and Conjugated Dienes

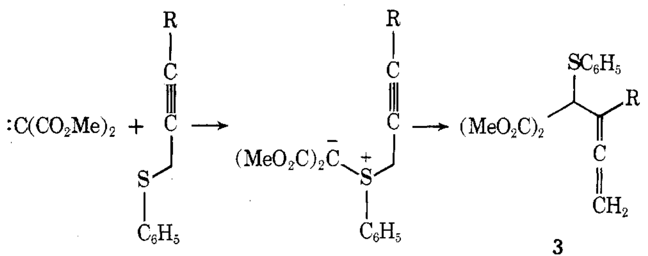
Summary: The [2,3]-sigmatropic rearrangement of acetylenic and allenic sulfonium ylides results in the formation of allenes and conjugated dienes, respectively, in good yield.

Sir: The synthetic utility of the [2,3]-sigmatropic rearrangement of allylic sulfonium ylides and related species (*e.g.*, i → ii) for the construction of β,γ-unsaturated carbonyl compounds,[1] trisubstituted olefinic linkages,[2] and formation of asymmetry at quaternary carbon[3] has been demonstrated in several recent publications. As part of a continuing program aimed at development of the synthetic potential of [2,3]-sigmatropic rearrangements in organic synthesis,[4] we wish to report that acetylenic sulfonium ylides (*e.g.*, **2** and **4**) undergo such a rearrangement providing a route to terminal and internal allenes.[5] The first observation that sp-hybridized bonds participate in the electrocyclic rearrangement of sulfonium ylides with formation of allenes was reported by Baldwin some years ago.[6] In addition, we further report that allenic sulfonium ylides undergo the [2,3]-sigmatropic process providing a new route to conjugated dienes.



i ii

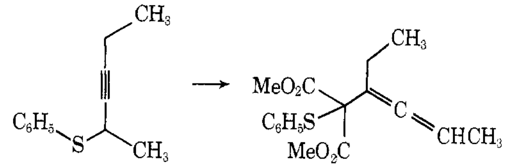
Allylic sulfonium ylides have previously been generated by the addition of the appropriate carbenes to allylic sulfides[7] or by the action of base on allylic sulfonium salts.[8] Employing the former procedure, acetylenic sulfonium ylides (*e.g.*, **2**) can be conveniently prepared *via* the copper salt catalyzed thermal decomposition of diazo compounds in acetylenic sulfides. The rearrangements are conveniently carried out in the absence of solvent at elevated temperatures. Heating a mixture of methyl diazomalonate (1.8 equiv)[9] and the acetylenic sulfide **1** (R = C_2H_5) [prepared by successive treatment of the corresponding acetylenic alcohol in ether–hexamethylphosphoramide (HMPA) (4:1) with methyllithium (1.0 equiv), tosyl chloride (1.05 equiv), and lithium thiophenoxide (1.05 equiv)[10]] in the presence of a catalytic amount of anhydrous cupric sulfate at 95–100° for ~15 hr (no solvent) results in a 71% isolated yield of pure allene **3** (R = C_2H_5) after preparative thin layer chromatography. The assigned structure **3** is in accord with the observed spectral data: ir 1950, 1735, 850 (terminal allene) cm^{-1}; nmr δ 0.85 (t, 3 H), 2.05 (m, 2 H), 3.62 (s, 6 H), 4.70 (t, 2 H, J = 3.5 Hz, $=CH_2$); *m/e* 306.



1 2 3

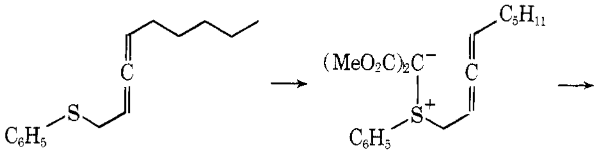
Similarly, reaction of bis(carbomethoxy)carbene with acetylenic sulfide (R = n-Bu) results in an 80% isolated yield of pure terminal allene **3** (R = n-Bu).

The utility of the procedure is indicated by the construction of internal allenes as well. For example, treatment of the acetylenic sulfide **4** (prepared by treatment of thiophenoxy-2-pentyne at −78° in anhydrous THF with n-BuLi, followed by addition of methyl iodide and warming to room temperature) with methyl diazomalonate as described above provides a 60% yield of pure internal allene **5** after preparative thin layer chromatography.

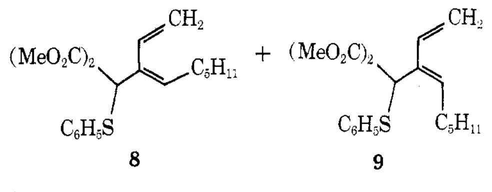


4 5

Finally, the [2,3]-sigmatropic rearrangement is also applicable to allenic sulfonium ylides (*e.g.*, **7**) as was demonstrated by the smooth conversion of allenic sulfide **6** [prepared by successive treatment of nona-2,3-dien-1-ol[11] in ether–HMPA (4:1) with methyllithium, tosyl chloride, and lithium thiophenoxide[10]] into a 4:1 mixture of dienes **8** and **9** (indicated by 250-MHz nmr) employing the procedure described above in 66% isolated yield after purification.



6 7



8 9

The conversion of acetylenic and allenic sulfonium ylides into allenes and conjugated dienes, respectively, further demonstrates the potential of [2,3]-sigmatropic rearrangements in organic synthesis. The extension of our work to the synthesis of naturally occurring allenes is now in progress.

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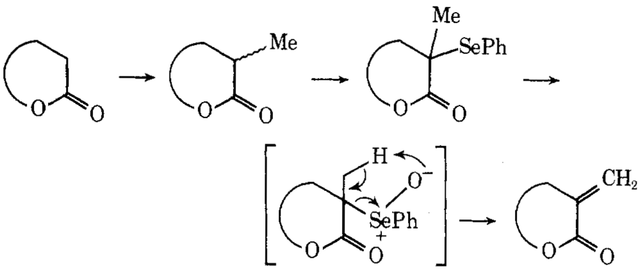
Organoselenium Chemistry. α-Phenylseleno Lactones. A New General Route to the Synthesis of Fused α-Methylene Lactones

Summary: A general high yield "α-methylenation sequence" has been developed for cis- and trans-fused lactone rings employing the reported capabilities of alkylphenyl selenoxides to undergo facile syn elimination at low temperatures.

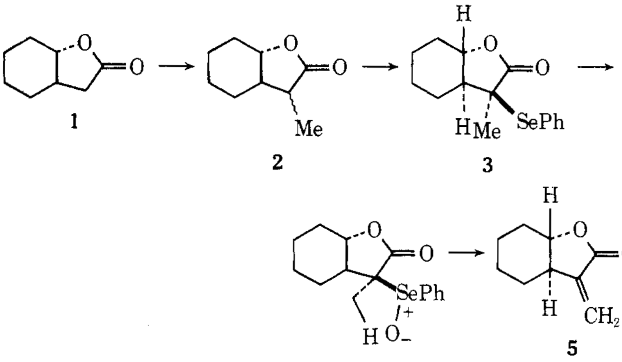
Sir: We report here a general method for the conversion of cis- and trans-fused γ- and δ-lactones into their corresponding α-methylene-γ-butyrolactones and α-methylene-δ-valerolactones which represent structural units found in many naturally occurring cytotoxic sesquiterpenes[1] (*e.g.*, vernolepin[2]). Although the α-methylene lactone structural moiety has been a synthetic objective in several laboratories,[3,4] the number of general approaches[4] remains small.

Our approach requires (a) a method for specific high yield methylation of preformed lactone enolates, (b) a method for stereospecific introduction of an α-phenylseleno substituent (*vide infra*), and (c) a method for specific elimination of the corresponding selenoxide to the exocyclic methylene group (Scheme I). The method is based on the observations by Sharpless[5] and Reich[6] that lithium enolates of ketones, aldehydes, and esters react rapidly and cleanly with phenylselenenyl halides to give α-phenylseleno carbonyl compounds[7] and on the report that alkylphenyl selenoxides readily undergo syn[8] elimination to form olefins.[9]

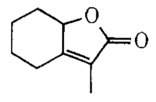
Scheme I



In the case of the trans-fused γ-butyrolactone **1**, the overall method is illustrated for the conversion of 1 into the *trans*-α-methylene-γ-butyrolactone (**5**), with complete exclusion of the endocyclic isomer **6**. The specific formation of **5** comes about as a result of a stereospecific alkylation of the lactone enolate derived from 2 with diphenyl diselenide[10] which establishes the required anti relationship between the α-phenylseleno substituent and the adjacent methine proton; hence, syn elimination of selenoxide **4** can only lead to **5**.



1 2 3 4 5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In the conversion of lactones to α-methylene lactones employing the above scheme, the yields of monoalkylated α-methyl lactones are in the range of 90–98%.[12] Similarly, yields for the introduction of the α-phenylseleno group are very high.[11] Formation of the selenoxides is carried out with 30% hydrogen peroxide and results in 90–99% yields of α-methylene lactones. A typical procedure for the conversion of the trans-fused γ-butyrolactone 1 into the trans-fused α-methylene-γ-butyrolactone 5 is as follows. To a solution of 2.4 mmol of lithium diisopropylamide (LDA, prepared from 0.35 ml of diisopropylamine and 1.6 ml of 1.65 *M* butyllithium in hexane under nitrogen at −78°) in 3 ml of anhydrous tetrahydrofuran (THF) was added dropwise over a period of 1 hr, 280 mg (2.0 mmol) of trans-fused lactone 1[13] in 3 ml of THF. The solution was stirred at −78° for 20 min, 0.15 ml of methyl iodide in 1 ml of THF containing 1 equiv (430 mg) of hexamethylphosphoramide (HMPA) was added rapidly dropwise, and then the mixture was warmed to −40°. The reaction mixture was stirred for 3 hr at −40° and was quenched by the addition of 10% hydrochloric acid. The mixture was diluted with ether and washed with water and saturated sodium chloride solution. There was obtained 310 mg (100%) of crude monoalkylated lactone 2 which was >95% pure by glc analysis.