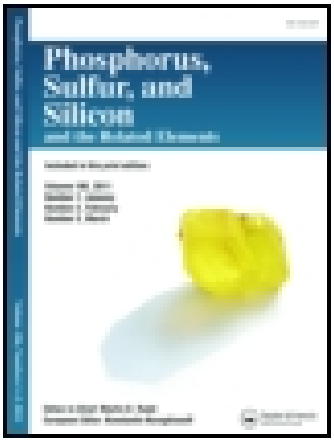

Phosphorus, Sulfur, and Silicon and the Related Elements

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Bifunctionalized Allenes. Part XII. Electrophilic Cyclization and Addition Reactions of 4-Sulfinylated or 4-Sulfonylated Allenecarboxylates

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BIFUNCTIONALIZED ALLENES. PART XII. ELECTROPHILIC CYCLIZATION AND ADDITION REACTIONS OF 4-SULFINYLATED OR 4-SULFONYLATED ALLENECARBOXYLATES

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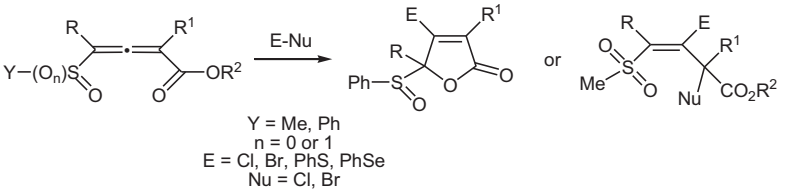
GRAPHICAL ABSTRACT



Abstract *Reaction of 4-sulfinylated or 4-sulfonylated allenecarboxylates with different electrophilic reagents such as sulfuryl chloride, bromine, benzenesulfenyl, and benzeneselenenyl chlorides takes place with 5-endo-trig cyclization or 3,2-addition reaction depending on the kind of the substituent at the sulfur atom. Treatment of 4-(benzenesulfinyl)-allenoates with electrophiles gives 5-(benzenesulfinyl)-2,5-dihydrofuran-2-ones as a result of the neighboring carboxylate group participation in the cyclization. On the other hand, (3E)-4-(methansulfonyl)alk-3-enoates were prepared by chemo-, regio-, and stereoselective electrophilic addition to the C^2—C^3-double bond in the allenoate moiety of 4-(methanesulfonyl)allenecarboxylates. When R^1 = Me, the treatment with electrophiles gives mixtures of (3E)-4-(methanesulfonyl)alk-3-enoates and (3E)-4-(methanesulfonyl)-2-methylenealk-3-enoates with ratios of about 1.6:1 as a result of addition and elimination reactions. A possible mechanism involving cyclization, addition, and elimination reactions of the 4-sulfinylated or 4-sulfonylated allenecarboxylates is proposed.*

Keywords 4-Sulfinylated allenoates; 4-sulfonylated allenoates; 2,5-dihydrofuran-2-ones; neighboring group participation; (3*E*)-3,2-adducts

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This paper is dedicated to Professor Marko Kirilov from Sofia University, Bulgaria on the occasion of his 90th anniversary and to Professor Toru Minami from Kyushu Institute of Technology, Kitakyushu, Japan on the occasion of his 75th anniversary.

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INTRODUCTION

Functionalized allenes have attracted a growing attention because of their versatility as key building blocks for organic synthesis.[1] The synthetic potential of the functionalized allenes has been explored extensively in recent years, and this has led to the development of novel methods for the construction of a variety of functionalized heterocyclic and carbocyclic systems.[2] An impressive number of heterocyclic systems has been prepared from allenic starting materials.

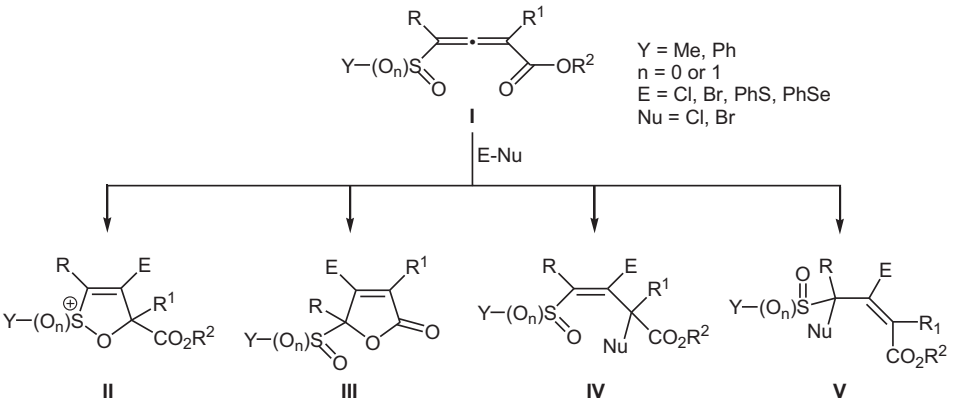
2,5-Dihydrofuran-2-ones (γ-lactones) are important intermediates in organic synthesis due to the presence of the conjugated C=C bond as well as the five-membered lactone ring. Much attention has been paid to the development of efficient and diverse synthetic methods for construction of this five-membered ring system.[3] Among these, cyclization involving allenecarboxylic acids and their derivatives, the so-called lactonization reaction, is one of the most efficient pathways.[4] α-Allenecarboxylic acids and their esters, disubstituted at the γ-carbon atom, underwent electrophilic attack at the central atom and ring closure to 2,5-dihydrofuran-2-ones (γ-lactones) when treated with electrophile.[4]

On the other hand, the reactions of allenyl sulfoxides, allenesulfinates, allenyl, and diallenyl sulfones with electrophilic reagents have been investigated in the 1980s. It has been shown[5] that depending on the structure of the starting allenic compounds, the reactions proceed with ring closure to give 5*H*-1,2-oxathiol-2-ium salts[5a] or 5*H*-1,2-oxathiole 2-oxides (γ-sultines).[5b–d] Recently, it was also observed by Ma and coworkers that the electrophilic chlorohydroxylation,[6] bromohydroxylation,[6] iodohydroxylation,[7] oxidative hydroacetoxylation,[8] and selenohydroxylation[9] reactions of allenyl sulfoxides with corresponding electrophiles afford *E*-2,3-adducts with high regio- and stereoselectivity, which the authors[6,7c] believed to be determined by the intramolecular attack of the sulfoxide oxygen at the allenic C^3-atom gave the five-membered intermediate.

As a part of our long-standing studies directed toward the development of efficient electrophilic cyclization reactions of 1,1-bifunctionalized allenes,[10] we became interested in 1,3-bifunctionalized allenes comprising a sulfoxide or sulfone and an ester groups such as **I** (Scheme 1). Of particular interest are the applications of these groups as temporary transformers of chemical reactivity of the allenic system in the eventual synthesis of heterocyclic compounds. This molecule can be considered as a combination of an allenyl sulfoxide or an allenyl sulfone and allenecarboxylates and might have different reactivity profiles in electrophilic reactions. Recently, we presented a convenient and efficient method for regioselective synthesis of 4-sulfinylated or 4-sulfonylated allenecarboxylates, derived by an atom economical [2,3]-sigmatropic rearrangement of the intermediate alkoxycarbonyl-functionalized propargyl sulfenates or sulfinates formed by reaction of the alkyl 2-hydroxy-alk-3-ynoates with benzenesulfenyl or methanesulfinyl chlorides, respectively, in the presence of a base.[10b]

RESULTS AND DISCUSSION

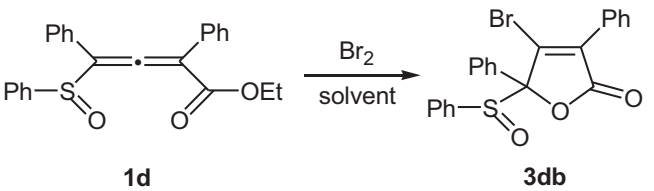
It should be pointed out that conceptually there exist two distinct modes of cyclization of the 4-sulfinylated or 4-sulfonylated 2,3-alkadienoates if the electrophilic atom forms a new bond with the central carbon of the allenic system, which seems likely.[3–9] It is evident that these pathways are closely connected with the intramolecular neighboring group participation of the sulfoxide or sulfone and/or the ester groups as internal nucleophile(s)



Scheme 1 Probable products of the electrophilic reaction of 4-sulfinylated or 4-sulfonylated allenecarboxylates I.

in the final step of the cyclization. Besides the 5-*endo-trig* cyclizations[11] to the 5*H*-1,2-oxathiol-2-ium salts **II** or to the 2,5-dihydrofuran-2-ones (butenolides, γ-lactones) **III**, electrophilic addition might afford the 3,2-adduct **IV** and/or the 3,4-adduct **V** (Scheme 1).

This paper is a part of our general synthetic strategy for the investigation of the scope and limitations of the electrophilic cyclization reactions of 1,3-bifunctionalized allenes. Here, we wish to report our recent results of these investigations.



Scheme 2 Electrophilic cyclization reaction of ethyl 4-(benzenesulfinyl)-2,4-diphenylbuta-2,3-dienoate 1d with bromine.

We initiated this study with the electrophilic cyclization reaction of ethyl 4-(benzenesulfinyl)-2,4-diphenylbuta-2,3-dienoate **1d** with bromine (Scheme 2). We established that the reaction occurs with cyclization by neighboring carboxylate group participation with formation of the 5-(benzenesulfinyl)-4-bromo-3,5-diphenyl-2,5-dihydrofuran-2-one **3db**. We tried to optimize the reaction conditions to get a useful selectivity and the best yield for the product by studying the equivalents of electrophile, reaction temperature, time, and solvent effect. Note that when the reaction was conducted in 1,2-dichloroethane at room temperature, TLC showed that the two reactants still interacted and the reaction was completed within 10 h with the formation of the desired product. It is necessary to carry out this reaction under dry argon since the electrophilic reagents are sensitive to moisture. The desired product **3db** was obtained with 44% yield (see Table 1, entry 1). When the reaction was carried out at reflux, it was complete within 6 h and the yield was considerably lower (31%, entry 2). With 1.5 equiv. of bromine in dichloroethane and trichloromethane, the yield is higher (entries 3, 4, and 5). Polar solvents such as THF, ethanol, acetonitrile, and nitromethane gave low yields, even with longer

Table 1 Screening of the cyclization reaction of **1d** with bromine under different conditions

Entry	Bromine (equiv.)	Solvent[a]	Reaction temp. (°C)	Reaction time (h)	Yield[b] (%)
1	1.0	$ClCH_2CH_2Cl$	r.t.	10	44
2	1.5	$ClCH_2CH_2Cl$	reflux	6	31
3	1.5	$ClCH_2CH_2Cl$	−78	7	51
4	1.5	$ClCH_2CH_2Cl$	−20	7	60
5	1.5	$CHCl_3$	−20	6	52
6	1.5	THF	−20	8	51
7	1.5	EtOH	−30	6	28
8	1.5	MeCN	−20	8	49
9	1.5	$MeNO_2$	−20	7	57
10	1.5	benzene	r.t.	8	35
11	1.0	CH_2Cl_2	r.t.	8	56
12	1.2	CH_2Cl_2	−20	7	66
13	**1.5**	**CH_2Cl_2**	**−20**	**7**	**73[c]**
14	2.0	CH_2Cl_2	−20	9	65

[a]Reaction was carried out in the appropriate solvent (10 mL + 10 mL); [b]Yields determined by ^1H and ^{13}C NMR analysis; [c]Isolated yields after chromatographic purification on silica gel.

reaction times (6–8 h) (entries 6, 7, 8, and 9, respectively). Similar yields were obtained in benzene as a solvent (entries 10). Fortunately, when dichloromethane was used as a solvent at room temperature or lower for 7–9 h, the yield improved to 73% (entries 11–14). A temperature of –20°C turned out to be the best and most convenient: when the temperature is higher or lower, the yield is worse (compare entries 1, 2, 10, and 11 with entries 3, and 7). When 1.5 equiv. of electrophilic reagent was used, the reaction was higher yielding (entry 13). We therefore, conducted the remainder of the reactions in dichloromethane at –20°C using 1.0 equiv. of the 4-sulfinylated or 4-sulfonylated allenoates **1a-d** and 1.5 equiv. of the electrophilic reagent for several hours (see Table 2). The product **3db** was fully characterized by means of NMR (^1H, and ^{13}C) and IR spectroscopy.

Having determined the optimized reaction conditions, we explored the scope of the electrophilic cyclization reaction of the alkyl 4-(benzenesulfinyl)alka-2,3-dienoates **1a-d** (Scheme 3). The obtained results are summarized in Table 2. It should be noted that the reaction under this set of standard reaction conditions in the favored 5-*endo-trig* mode affords the 5-(benzenesulfinyl)-2,5-dihydrofuran-2-ones **3** as a result of the neighboring

Table 2 Synthesis of the 2,5-dihydrofuran-2-ones **3** by electrophilic cyclization of **1a-d**

Entry	Allene	R	R^1	R^2	E	Nu	Time (h)	**3**, Yield[a] (%)
1	**1a**	Pr	Me	Et	Cl	Cl	4	**3aa**,70
2	**1a**	Pr	Me	Et	SePh	Cl	6	**3ad**,68
3	**1b**	Pr	Ph	Me	Br	Br	6.5	**3bb**,72
4	**1c**	Bu	Me	Et	Br	Br	5	**3cb**,71
5	**1c**	Bu	Me	Et	SePh	Cl	6	**3cd**,67
6	**1d**	Ph	Ph	Et	Cl	Cl	6	**3da**,71
7	**1d**	Ph	Ph	Et	Br	Br	7	**3db**,73
8	**1d**	Ph	Ph	Et	SPh	Cl	11	**3dc**,68
9	**1d**	Ph	Ph	Et	SePh	Cl	9	**3dd**,66

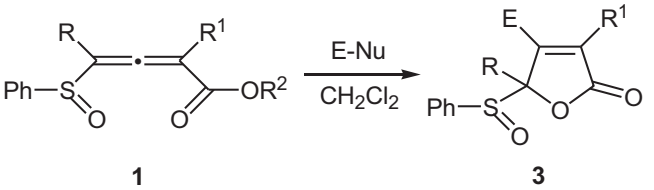
[a]Isolated yields after chromatographic purification on silica gel.

Table 3 Synthesis of the (3*E*)-alk-3-enoates **4** by electrophilic addition of **2b,d**

Entry	Allene	R	R^1	R^2	E	Nu	Time (h)	**4**, Yield[a] (%)
1	**2b**	Bu	Ph	Me	Br	Br	7	**4bb**,68
2	**2b**	Bu	Ph	Me	SePh	Cl	9	**4bd**,64
3	**2d**	Ph	Ph	Et	Cl	Cl	6	**4da**,67
4	**2d**	Ph	Ph	Et	Br	Br	9.5	**4db**,70
5	**2d**	Ph	Ph	Et	SePh	Cl	13	**4dd**,64

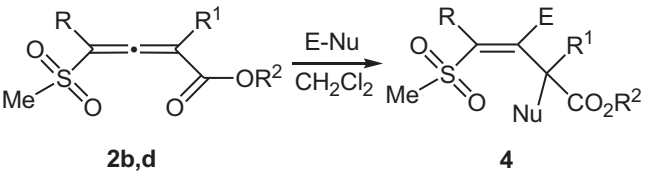
[a]Isolated yields after chromatographic purification on silica gel.

carboxylate group participation in the cyclization with good to excellent yields irrespective of the nature of the substituents at the allenic system and the ester group. The reaction scope is wide: R can be propyl, butyl, or phenyl; R^1 can be methyl, or phenyl; R^2 can be methyl, or ethyl; and E can be Cl, Br, PhS, and PhSe.



Scheme 3 Synthesis of the 2,5-dihydrofuran-2-ones 3 by electrophilic cyclization reaction of 1a-d.

To establish the generality of this methodology, the reaction of the alkyl 4-(methanesulfonyl)allenecarboxylates **2b,d** with different electrophilic reagents such as sulfuryl chloride, bromine, and benzeneselenenyl chloride was examined. To our surprise, when we applied the current standard conditions to the 1,3-bifunctionalized allenes comprising a sulfone and alkoxycarbonyl groups such as **2** (Scheme 4), instead of the 2,5-dihydrofuran-2-ones **3**, the acyclic compounds **4** were isolated with 64%–70% yield after stirring for several hours at –20°C and for another hour at room temperature. The results are summarized in Table 3. Interestingly, this protocol could also be successfully applied to the electrophilic reaction of the alkyl 4-(methanesulfonyl)allenoates **2b,d**, which afforded the alkyl (3*E)*-4-(methanesulfonyl)alk-3-enoates **4** with high regio- and stereoselectivity, indicating a highly chemoselective addition reaction of electrophilic reagents to the C^2-C^3-double bond of the allenoate system.



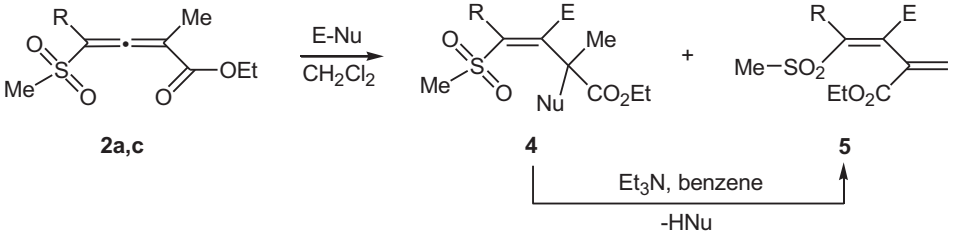
Scheme 4 Synthesis of the (3E)-alk-3-enoates 4 by electrophilic addition reaction of 2b,d.

Table 4 Synthesis of the (3*E*)-alk-3-enoates **4** and the (3*E*)-2-methylenealk-3-enoates **5** by electrophilic addition and elimination reaction of **2a,c**

Entry	Allene	R	E	Nu	Time (h)	**4**, Yield[a] (%)	**5**, Yield[a] (%)	Ratio
1	**2a**	Bu	Br	Br	6	**4ab**,43	**5ab**,27	1.55:1
2	**2a**	Bu	SePh	Cl	8	**4ad**,41	**5ad**,25	1.63:1
3	**2c**	Ph	Br	Br	8	**4cb**,44	**5cb**,27	1.61:1
4	**2c**	Ph	SePh	Cl	10.5	**4cd**,41	**5cd**,24	1.72:1

[a]Isolated yields after chromatographic purification on silica gel.

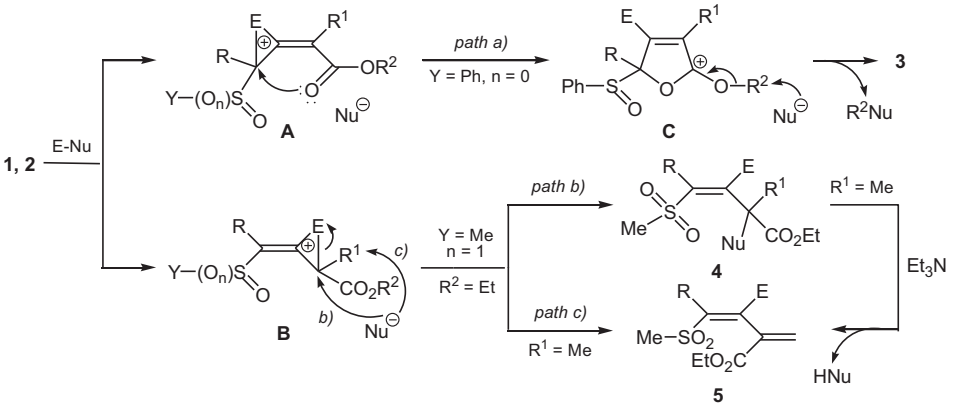
On the other hand, when R^1 = Me, the treatment of the ethyl 4-(methanesulfonyl)-2-methyl-allenecarboxylates **1a,c** with electrophiles gives mixtures of the ethyl (3*E*)-4-(methanesulfonyl)alk-3-enoates **4** and the ethyl (3*E*)-4-(methanesulfonyl)-2-methylenealk-3-enoates **5** in ratios of about 1.6:1 as a result of the highly chemo-, regio-, and stereoselective addition to the C^2-C^3-double bond of the allenoate system and further elimination reaction (Scheme 5, Table 4).



Scheme 5 Synthesis of the (3E)–alk-3-enoates 4 and the (3E)-2-methylenealk-3-enoates 5 by electrophilic addition and elimination reaction of 2a,c.

Thus, on the basis of the literature data on the electrophilic addition on allenes,[1,2] on allenecarboxylates,[4] on allenyl sulfoxides, and on sulfones,[5–9] and our previous results,[10] a rationale for this reaction is depicted in Scheme 6. The initial act is the attack of the electrophile (Cl^+, Br^+, S^+, or Se^+) on the most nucleophilic atom of the allenic system of π-bonds (C^3) with the formation of the cyclic onium (chloronium, bromonium, thiiranium or seleniranium) ions **A** after attack at the C^3-C^4-double bond or the ions **B** after attack on the C^2-C^3-double bond. Subsequently, the ions **A** are easily transformed into the more stable five-membered cyclic ions **C** via the neighboring group participation of the oxygen atom of the carboxylate functionality (*path a*). Furthermore, the intermediates **C** undergo attack of the external nucleophile at the R^2O group and elimination of alkyl halides (R^2Nu) affording the final cyclic product **3**.

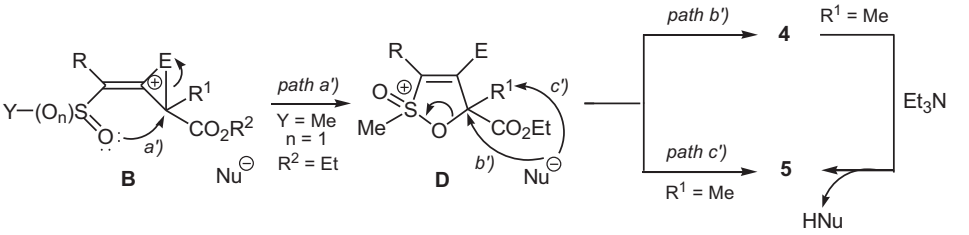
On the other hand, in the case of ethyl 4-(methanesulfonyl)allenoates **2** (Y = Me, n = 1) as starting materials, the formation of the ethyl(3*E*)-4-(methanesulfonyl)alk-3-enoates **4** can be considered in terms of the assumption for nucleophilic attack on the cyclic three-membered onium ions **B** (*path b*) leading to the formation of the (3*E*)-3,2-adduct **4**. The observed stereoselectivity may be explained by the favorable *trans*-arrangement of the electrophile and the sulfone group and anti-attack of the external nucleophile in the onium ions on the allenoate C^2-C^3-double bond **B**. Moreover, when R^1 = Me, together with the nucleophilic attack at the C^2-atom of the onium ions **B** leading to formation of the



Scheme 6 A rationale for electrophilic cyclization and addition reactions of 4-sulfinylated or 4-sulfonylated allenecarboxylates 1,2.

(3*E*)-3,2-adducts **4** (*path b*), an attack of the nucleophile at the C^2-methyl group of the ions **B** affords the elimination products **5** (*path c*) as the ratio between **4** and **5** is about 1.6:1.

A possible explanation of the occurring addition and subsequent elimination reactions consists in the following. This reaction pathway is probably favorable from an energetic point of view. If the sulfonyl group acts as an internal nucleophile in the cyclization, the obtained cyclic compounds should be oxosulfonium salts (like **II**, Scheme 1) with a positive-charged sulfur atom[6,12] **D** (Scheme 7), since in this case, the stabilization by the elimination of methyl halide and formation of stable cyclic products with sulfinate group is impossible. Another rationale for the formation of the (3*E*)-3,2-adducts **4** and the elimination products **5** consists in the intermediate formation of the oxosulfonium salts **D** via neighboring group participation of the oxygen atom of the sulfone functionality (*path a′*). Subsequent nucleophilic attack at the C^5-atom of the oxosulonium ions **D** leads to the formation of the (3*E*)-3,2-adducts **4** (*path b'*), but the attack of the nucleophile at the hydrogen of the C^5-methyl group (R^1) of the ions **D** affords the elimination products **5** (*path c′*). Moreover, the reason for the absence of the adducts (like **V**, Scheme 1) on the C^3-C^4-double bond of the allenoate system probably is the stronger destabilization effect of a sulfonyl group, in comparison with a sulfoxide group, on the corresponding onium ions **A** (not shown in Schemes 6 and 7).



Scheme 7

The above-mentioned explanation should be corroborated or refuted from the results of the study on the reactions of other 4-functionalized allenecarboxylates with electrophilic reagents and especially their stereochemistry. Further work in this area is being focused on exploiting and extending the synthetic utility of the 1,3-bifunctionalized allenes for the preparation of different heterocyclic systems using the electrophilic cyclization methodology.

CONCLUSION

We have developed a simple and convenient protocol for the reaction of the 4-sulfinylated or 4-sulfonylated allenecarboxylates with different electrophilic reagents, which takes place with 5-*endo-trig* cyclization or 3,2-addition reaction depending on the kind of the substituent at the sulfur atom. Treatment of the 4-sulfinylallenoates with electrophiles gives 2,5-dihydrofuran-2-ones as a result of the neighboring carboxylate group participation in the cyclization. On the other hand, (3*E*)-4-sulfonylalk-3-enoates were prepared by chemo-, regio-, and stereoselective electrophilic addition to the C^2-C^3-double bond in the allenoate moiety. Due to the easy availability of starting materials, the convenient operation and the usefulness of the butenolide products, the reaction may show potentials and will be useful in organic synthesis. Further studies on the synthetic applications of this reaction and the physiological activity of selected cyclic and acyclic products are now under investigation in our laboratory. Furthermore, a continuation of these studies toward the synthesis and electrophilic cyclization reactions of other bifunctionalized allenes is currently in progress in our laboratory.

EXPERIMENTAL

General

All new synthesized compounds were purified by column chromatography and characterized on the basis of NMR, IR, and microanalytical data. NMR spectra were recorded on DRX Bruker Avance-250 (Bruker BioSpin GmbH, Karlsruhe, Germany) (^{1}H at 250.1 MHz, ^{13}C at 62.9 MHz) and Bruker Avance II+600 (Bruker BioSpin GmbH, Karlsruhe, Germany) (^{1}H at 600.1 MHz, ^{13}C at 150.9 MHz) spectrometers for solutions in CDCl3. Chemical shifts are in parts ppm downfield from internal TMS (^{1}H and ^{13}C). *J* values are given in Hz. IR spectra (neat, cm^{-1}) were recorded with an FT-IRAfinity-1 Shimadzu spectrophotometer (Shimadzu Corp., Japan). Elemental analyses were carried out by the Microanalytical Service Laboratory of Faculty of Chemistry and Pharmacy, University of Sofia using Vario EL3 (Elementar Analysensysteme GmbH, Hanau, Germany). Column chromatography was performed on Kieselgel F_{254}60 (70–230 mesh ASTM, 0.063–0.200 nm, Merck). The melting points were measured in open capillary tubes and are uncorrected. The solvents were purified by standard methods. Reactions were carried out in oven-dried glassware under an Ar atmosphere and exclusion of moisture. All compounds were checked for purity on TLC plates Kieselgel F_{254}60, Merck.

General Procedure for the Reactions of 4-Sulfinyl- or 4-Sulfonylallenecarboxylates with Electrophilic Reagents

To a solution of 4-sulfinyl- or 4-sulfonyl-2,3-alkadienoates **1** or **2** (3 mmol) in dry CH_2Cl_2 (10 mL) at –20°C was added dropwise with stirring a solution of the electrophilic

reagent (sulfuryl chloride, bromine, benzenesulfenyl chloride, benzeneselenenyl chloride) (4.5 mmol) in the same solvent (10 mL). The reaction mixture was stirred at the same temperature for several hours (see Tables 2 and 3) and 1 h at room temperature. The solvent was removed using a rotatory evaporator and the residue was purified by column chromatography on silica gel (Kieselgel Merck 60 F_{254}) with ethyl acetate/hexane. The pure 5-(benzenesulfinyl)-2,5-dihydrofuran-2-ones **3** exhibit the following properties:

5-(Benzenesulfinyl)-4-chloro-3-methyl-5-propyl-2,5-dihydrofuran-2-one (3aa). Light orange oil, yield: 0.63 g (2.10 mmol, 70%). TLC:EtOAc-hexane = 1:1, R_f = 0.75; IR: 1048 (S=O), 1120 (C−O−C), 1440, 1485 (Ph), 1617 (C=C), 1751 (C=O). ^{1}H NMR (600.1 MHz): 0.97 (t, J = 7.4 Hz, 3H, Me−$(CH_2)_2$), 1.28 (m, 2H, Me−CH_2−CH_2), 1.97 (s, 3H, Me), 2.21 (m, 2H, Me−CH_2−CH_2), 7.42–7.57 (m, 5H, Ph). ^{13}C NMR (150.9 MHz): 13.1 (CH_3), 13.3 (CH_3), 16.9 (CH_2), 34.8 (CH_2), 100.9 (C), 126.2 (C), 154.2 (C), 167.9 (C). $C_{14}H_{15}O_3SCl$ (298.79). Calcd: C 56.28, H 5.06; found: C 56.36, H 4.99.

5-(Benzenesulfinyl)-4-bromo-3,5-diphenyl-2,5-dihydrofuran-2-one (3db). Light yellow oil, yield: 0.96 g (2.19 mmol, 73%). TLC:EtOAc-hexane = 1:4, R_f = 0.77; IR: 1044 (S=O), 1121 (C−O−C), 1439, 1488 (Ph), 1620 (C=C), 1751 (C=O). ^{1}H NMR (250.1 MHz): 7.20–8.06 (m, 15H, 3Ph). ^{13}C NMR (62.9 MHz): 87.4 (C), 127.8–132.4 (3Ph), 140.9 (C), 143.2 (C), 160.8 (C). $C_{22}H_{15}O_3SBr$ (439.32). Calcd: C 60.15, H 3.44; found: C 60.09, H 3.50.

The pure alkyl (3*E*)-4-methanesulfonyl-alk-3-enoates **4** had the following properties:

Ethyl (3E)-2,3-dibromo-4-(methanesulfonyl)-2-methyloct-3-enoate (4ab). Orange oil, yield: 0.54 g (1.29 mmol, 43%). TLC:EtOAc-hexane = 1:4, R_f = 0.78; IR: 1149, 1318 (SO_2), 1594 (C=C), 1724 (C=O). ^{1}H NMR (600.1 MHz): 0.99 (t, J = 7.1 Hz, 3H, Me−$(CH_2)_3$), 1.36 (t, J = 7.3 Hz, 3H, Me−CH_2O), 1.48 (m, 4H, Me−$(CH_2)_2$−CH_2), 1.67 (m, 2H, Me−$(CH_2)_2$−CH_2), 2.00 (s, 3H, Me), 3.03 (s, 3H, $MeSO_2$), 4.28 (m, 2H, Me−CH_2O). ^{13}C NMR (150.9 MHz): 14.0 (CH_3), 14.7 (CH_3), 21.4 (CH_2), 28.2 (CH_2), 32.7 (CH_2), 36.0 (CH_3), 42.4 (CH_3), 61.3 (CH_2), 67.1 (C), 125.7 (C), 148.1 (C), 166.5 (C). $C_{12}H_{20}O_4SBr_2$ (420.16). Calcd: C 34.30, H 4.80; found: C 34.36, H 4.73.

Ethyl (3E)-2,3-dibromo-4-(methanesulfonyl)-2,4-diphenylbut-3-enoate (4db). Yellow oil, yield: 1.05 g (2.10 mmol, 70%). TLC:EtOAc-hexane = 1:3, R_f = 0.79; IR: 1139, 1318 (SO_2), 1444, 1489 (Ph), 1589 (C=C), 1723 (C=O). ^{1}H NMR (250.1 MHz): 0.95 (t, J = 7.2 Hz, 3H, Me−CH_2O), 3.13 (s, 3H, $MeSO_2$), 3.99 (m, 2H, Me−CH_2O), 7.31–7.99 (m, 10H, 2Ph). ^{13}C NMR (62.9 MHz): 14.6 (CH_3), 38.4 (CH_3), 62.6 (C), 74.0 (C), 125.5–137.5 (2Ph), 126.2 (C), 147.8 (C), 156.4 (C). $C_{19}H_{18}O_4SBr_2$ (502.22). Calcd: C 45.44, H 3.61; found: C 45.35, H 3.68.

The pure ethyl (3*E*)-4-methanesulfonyl-2-methylene-alk-3-enoates **5** exhibit the following properties:

Ethyl (3E)-3-bromo-4-(methanesulfonyl)-2-methyleneoct-3-enoate (5ab). Light orange oil, yield: 0.27 g (0.81 mmol, 27%). TLC:EtOAc-hexane = 1:4, R_f = 0.49; IR: 1146, 1326 (SO_2), 1589–1621 (C=C), 1727 (C=O). ^{1}H NMR (600.1 MHz): 0.91 (t, J = 7.0 Hz, 3H, Me−$(CH_2)_3$), 1.30 (t, J = 7.1 Hz, 3H, Me−CH_2O), 1.36–1.51 (m, 4H, Me−$(CH_2)_2$−CH_2), 2.14 (m, 2H, Me−$(CH_2)_2$−CH_2), 3.30 (s, 3H, $MeSO_2$), 4.21 (m, 2H, Me−CH_2O), 6.22 (m, 1H, EtO_2C_aC=C(H_a)(H_b)), 6.31 (m, 1H, EtO_2C_aC=C(H_a)(H_b)). ^{13}C NMR (150.9 MHz): 13.1 (CH_3), 14.0 (CH_3), 23.2 (CH_2), 28.1 (CH_2), 32.3 (CH_2), 41.4 (CH_3), 61.1 (CH_2), 124.6 (C), 127.3 (C), 143.5 (C), 144.8 (C), 165.7 (C). $C_{12}H_{19}O_4SBr$ (339.25). Calcd: C 42.48, H 5.65; found: C 42.56, H 5.71.

Ethyl (3E)-3-(benzeneselenenyl)-4-(methanesulfonyl)-2-methylene-4-phenylbut-3-enoate (5cd). Yellow oil, yield: 0.31 g (0.72 mmol, 24%). TLC:EtOAc-hexane = 1:4, R_f = 0.46; IR: 1145, 1328 (SO_2), 1442, 1492 (Ph), 1583–1616 (C=C), 1721 (C=O). ^{1}H NMR

(600.1 MHz): 1.29 (t, J = 7.1 Hz, 3H, Me−CH_2O), 3.26 (s, 3H, $MeSO_2$), 4.21 (m, 2H, Me−CH_2O), 5.84 (m, 1H, $EtO_2C_aC = C(H_a)(H_b)$), 6.20 (m, 1H, $EtO_2C_aC{=}C(H_a)(H_b)$), 7.22–8.02 (m, 10H, 2Ph). ^{13}C NMR (150.9 MHz): 14.7 (CH_3), 41.4 (CH_3), 60.2 (CH_2), 117.8 (C), 126.7 (C), 127.4–131.1 (2Ph), 132.3 (C), 142.3 (C), 175.1 (C). $C_{20}H_{20}O_4SSe$ (435.40). Calcd: C 55.17, H 4.63; found: C 55.25, H 4.69.

General Procedure for the Preparation of Ethyl (3*E*)-4-(methanesulfonyl)-2-methylenealk-3-enoates 5

To a stirred solution of the ethyl (3*E*)-4-(methanesulfonyl)-2-methylalk-3-enoates **4ad** or **4cb** (1 mmol) in dry benzene (5 mL) at 8–10 °C was added dropwise with stirring, a solution of NEt_3 (1.5 mmol) in the same solvent (5 mL). The reaction mixture was stirred at the same temperature for 20 min, was refluxed for 2 h and after cooling was quenched with 2N HCl, extracted with EtOAc, washed with saturated NaCl, and dried over anhydrous Na_2SO_4. After evaporation of the solvent, the residue was chromatographed on a column (silica gel, Kieselgel Merck 60 F_{254}) using a mixture of EtOAc and hexane as eluent to give the pure ethyl (3*E*)-4-(methanesulfonyl)-2-methylenealk-3-enoates **5ad** (73% yield) and **5cb** (71% yield).

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SUPPLEMENTAL MATERIALS

Supplementary data for this article can be accessed on the publisher's website, www.tandfonline.com/gpss

Method of analysis, starting materials, and full spectroscopic and characterization data including ^{1}H and ^{13}C NMR, IR data, and elemental analyses for all new compounds as well as literature references to these data for known compounds are listed.

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