ALKATRIENYL SULFOXIDES AND SULFONES. PART III.[1] 5-METHYL-3-(METHYLSULFONYL)HEXA-1,3,4-TRIENE - SYNTHESIS AND ELECTROPHILE-INDUCED CYCLIZATION REACTIONS

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Abstract: A method for synthesis of the 5-methyl-3-(methylsulfonyl)hexa-1,3,4-triene **3** by [2,3]-sigmatropic rearrangement of the 5-methyl-1-hexene-3-yn-5-yl methanesulfinate **2**, formed in the reaction of the 5-methyl-1-hexene-3-yn-5-ol **1** with methylsulfinyl chloride has been found. Electrophile-induced reactions of **3** occur in different pathways depending on the kind of the electrophile. The halogenation leads to formation of the 3-halo-2-methyl-4-(methylsulfonyl)hexa-1,3,5-trienes **4** and **5** while reactions with phenylsulfenyl and selenenyl chlorides afford only heterocyclic products - the 2-isopropyl-3-thienyl sulfone **6** in the case of sulfenyl chloride and a mixture of the 2,5-dihydroselenophene **7** and the selenophene **8** in the case of selenenyl chloride.

INTRODUCTION

One of the characteristic reactions of the allenes are the electrophilic addition reactions in which the addition products of the reagent to the one and/or other double bond of the allenic system are usually obtained.[2] Functionalized allenes are very interesting substrates as a material of choice to study the addition reactions on the carbon-carbon double bonds.[2d,2e] Unlike the allenic hydrocarbons, the presence of a functional group linked to the allenic system, considerably changes the course of the reactions with electrophilic reagents. It has been shown[2d,2e] that the reactions proceeded with cyclization of the allenic system bearing a functional group to give heterocyclic compounds in most cases. It makes the investigations on the functionalized allenes, more specifically in studying their reactions with electrophilic reagents, quite an interesting and topical task.

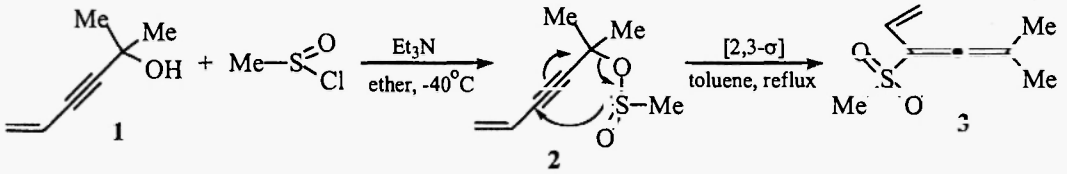
Literature data on the electrophilic addition reactions to sulfur-containing allenes (sulfoxides, sulfinates and sulfones) show that various five-membered heterocyclizations proceed in most cases.[3b,3d,4] On the other hand, the reactions of the phosphorylated 1,2,4- and 1,3,4-alkatrienes with electrophiles lead to the synthesis of various heterocyclic compounds depending on the kind of the electrophilic reagent as well as on the position of the vinylic group. For example, the halogenation reactions afford the 3- or 5-vinyl-substituted 2,5-dihydro-1,2-oxaphospholes,[5] while the interaction with sulfenyl[5d,6] and selenenyl[5c,5d,7] chlorides gives the thiophene- or selenophene-2- or 3-phosphonates.

There are methods[3] for the synthesis of sulfur-containing allenes (sulfoxides,[3a-3c] sulfinates,[3d] sulfinamides[3e,3f] and sulfones[3g,3h]) including reactions of α-alkynols with sulfenyl or sulfinyl chlorides followed by [2,3]-sigmatropic rearrangement. The synthetic utility of the remarkable and efficient [2,3]-sigmatropic rearrangement of propargylic sulfenates has been further demonstrated, by Okamura and coworkers, in a variety of preparations and interesting reactions of allenyl sulfoxides,[8a-8d] including the preparation of vinylallenes[8] which are useful intermediates in organic synthesis in general[8e] and natural polyenes, such as Vitamins A and D, in particular.[8f]

As part of our program[1] on the synthesis and cyclization reactions of alkatrienyl sulfoxides and sulfones, we now report the results on the synthesis and the reactions with some electrophilic reagents (sulfuryl chloride, bromide, phenylsulfenyl and selenenyl chlorides) of 5-methyl-3-(methylsulfonyl)hexa-1,3,4-triene as a substrate for study of the electrophile-promoted cyclization reactions.

RESULTS AND DISCUSSION

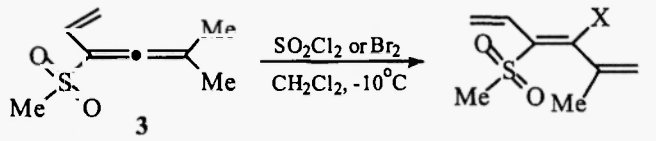
Since its discovery three decades ago,[3g,3h] the reversible interconversion of propargylic sulfinates to allenyl sulfones has become one of the most studied and synthetically useful [2,3]-sigmatropic rearrangement known. Numerous synthetic applications of the rearrangement have been reported, including its use in the total synthesis of a variety of natural products such as steroids, prostaglandins and leukotrienes.[4a] Our strategy for the synthesis of 5-methyl-3-(methylsulfonyl)hexa-1,3,4-triene **3**, using our experience on the preparation of the 3-methyl-1,2,4-pentatrienyl[1a] and 5-methyl-1,3,4-hexatriene-3-yl phenyl sulfoxides[1b], relies on the well-precedented [2,3]-sigmatropic shift of propargylic sulfinates to α-allenic sulfones.[3g,3h] This compound was prepared in 55 % yield by reaction of freshly distilled methylsulfinyl chloride with 5-methyl-1-hexene-3-yn-5-ol **1** in the presence of triethylamine and following [2,3]-sigmatropic rearrangement of the formed 5-methyl-1-hexene-3-yn-5-yl methanesulfinate **2** in toluene at reflux according to Scheme 1. After a conventional work-up, the resulting compound **3** was isolated by column chromatography as a light yellow oil and identified by ^1H and ^{13}C NMR and IR spectra as well as elemental analysis.



Scheme 1

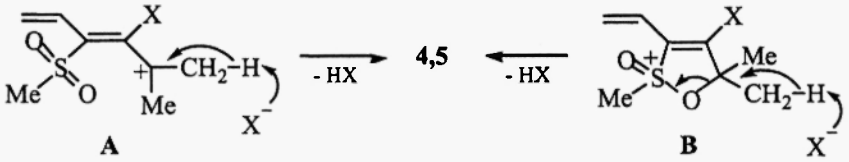
The alkatrienyl sulfone **3** isolated in preparative amounts allowed us to study its chemical behavior in the reactions with electrophilic reagents. From general considerations as well as from the literature data on the electrophilic addition reactions to sulfur-containing allenes,[3b,3d,4] to phosphorylated alkatrienes,[5-7] to 3-methyl-1,2,4-pentatrienyl[1a] and to 5-methyl-1,3,4-hexatriene-3-yl phenyl sulfoxides,[1b] the following pathways of the reactions could be assumed: (i) attack of the reagent on the C^4-C^5 double bond with formation of 4,5-adduct; (ii) attack of the reagent on the C^3-C^4 double bond with formation of 4,3- and/or 4,1-adduct; (iii) attack of the reagent on the C^4-C^5 double bond of the trienic system and following neighboring group participation of the internal nucleophile (sulfone group) and ring closure to five-membered cyclic compound; (iv) attack of the reagent on the C^3-C^4 double bond of the trienic system and following neighboring group participation of the C^1-C^2 double bond and ring closure to cyclic compound; and (v) elimination reactions after realization of some of above mentioned pathways (i-iv).

We established that reactions of the trienyl sulfone **3** with sulfuryl chloride or bromide in dichloromethane proceeded with formation of the 3-halo-2-methyl-4-(methylsulfonyl)hexa-1,3,5-trienes **4** and **5** in 87 and 88 % yield respectively, according to the reaction sequence outlined in Scheme 2. Resulting compounds **4** and **5** were isolated by column chromatography as white (**4**) or yellow crystals (**5**) and identified by ^1H and ^{13}C NMR and IR spectra as well as elemental analysis. Mechanistic rationale for the formation of the 1,3,5-trienyl sulfones **4** and **5** in elimination reaction of hydrogen chloride would appear not to be straightforward. The result reported above can be considered in terms of the following



Scheme 2

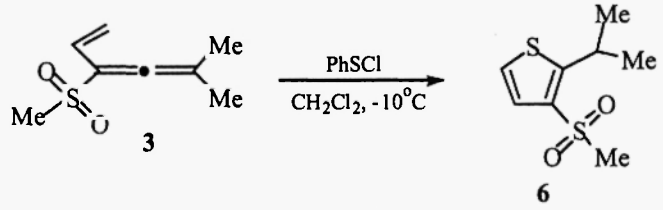
two assumptions (Scheme 3): (i) intermediate formation of the carbenium ion **A** and the following attack of halide anion on the one of the methyl groups and elimination of hydrogen halide as it has been shown by Braverman and Reisman[9] in the case of halogenation of allenyl sulfones; and (ii) deprotonation in the stage of the *in situ* generated cyclic sulfonium halide **B** as shown by Horner and Binder[7] in the reaction of allenyl sulfoxides with electrophilic reagents. The results reported before[1b] confirm our second assumption that the reaction of vinylallenyl sulfone **3** with halogens leading to the



Scheme 3

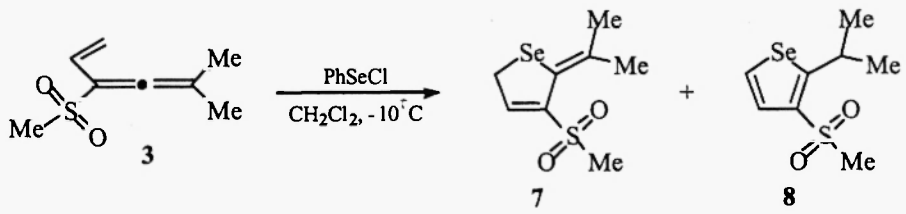
preparation of the 3-halohexatrienes **4** and **5** probably proceed through the cyclic sulfonium halide **B**. Moreover, the configuration of the sulfones **4** and **5**, assigned on the base on the chemical shift value[12] of the olefinic proton at C^5 atom, is most likely to be (*E*). In addition, the intermediate formation of the cyclic sulfonium salts **B** predetermines the (*E*) configuration of the 4-(methylsulfonyl)-1,3,5-trienes **4** and **5**.

Reaction of the vinylallenyl sulfone **3** with phenylsulfenyl chloride was carried out by electrophile-promoted cyclization by neighboring participation of the C^1-C^2 double bond and ring closure to give the 2-isopropyl-3-thienyl methyl sulfone **6** in 65 % yield as shown in Scheme 4:



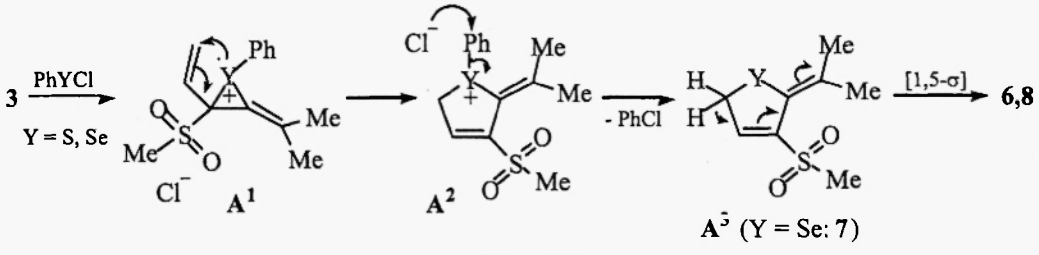
Scheme 4

In a similar way, a *ca.* 1:1 mixture of the methyl 2-(1-methylethylidene)-2,5-dihydro-3-selenophenyl sulfone **7** and the 2-isopropyl-3-selenophenyl methyl sulfone **8** was obtained with 59 % overall yield from the reaction of the vinylallenyl sulfone **3** with phenylselenenyl chloride in dry dichloromethane at -10 °C, according to the reaction sequence outlined in Scheme 5. Resulting dihydroselenophene **7** and selenophene **8** were isolated by column chromatography and identified by ^1H and ^{13}C NMR and IR spectra as well as elemental analysis. The obtained compounds **7** and **8** contain the isotope ^{77}Se which is magnetically active and interacts with other nuclei. This interaction becomes evident with the protons and carbons of the neighboring groups which exhibit symmetric satelite signals of the main signal in the ^1H and ^{13}C NMR spectra.[9]



Scheme 5

The chemical transformations thus observed (Schemes 4 and 5) are in accordance with the following reaction mechanisms (see Scheme 6). The initial act is the attack of electrophilic sulfur or selenium on the most nucleophilic atom of the trienic system of π-bonds (C^4) with the formation of the cyclic onium [thiiranium (episulfonium) or seleniranium (episelenonium)] ions $\mathbf{A^1}$ after an attack on the C^3-C^4 double bond. The ions $\mathbf{A^1}$ are in the plane of the ∃-bond of the vinyl group (*s-cis* conformation), and for this reason, $\mathbf{A^1}$ are easily transformed into the more stable five-membered cyclic ions $\mathbf{A^2}$. Further the ions $\mathbf{A^2}$ are transmuted into the intermediate $\mathbf{A^3}$ by elimination of chlorobenzene which was isolated and identified. In the case of selenenyl chloride, the 2,5-dihydroselenophene **7** was isolated as yellow oil in 29 % yield. A [1,5]-prototropic shift and aromatization of the formed dihydrothiophene $\mathbf{A^3}$ (not isolated) or dihydroselenophene **7** occurred to give the thiophene **6** or the selenophene **8**. The realization of the heterocyclization process is connected with introduction of the 1,3-alkadienic parts of the 1,3,4-alkatrienic system into the reaction course. This fact is obviously due to the ability of the sulfur and selenium atoms to form cyclic ions,[10] which are further transformed into five-membered heterocyclic compounds.



Scheme 6

In conclusion, we noted the following points from this investigation: (i) the 5-methyl-3-(methylsulfonyl)hexa-1,3,4-triene **3** is readily available by reaction of methylsulfinyl chloride with 3-methyl-1-pentene-4-yn-3-ol followed by [2,3]-sigmatropic shift; (ii) electrophile-induced reactions of the 5-methyl-3-(methylsulfonyl)hexa-1,3,4-triene **3** occur in different pathways depending on the kind of electrophile. The halogenation reaction leads to formation of the high unsaturated 3-halo-2-methyl-4-(methylsulfonyl)hexa-1,3,5-trienes **4** and **5** while interaction with phenylsulfenyl and selenenyl chlorides yields only heterocyclic products - the 2-isopropyl-3-thienyl sulfone **6** in the case of sulfenyl chloride and a mixture of the 2,5-dihydroselenophene **7** and the selenophene **8** in the case of selenenyl chloride; and (iii) the 5-methyl-3-(methylsulfonyl)hexa-1,3,4-triene **3** is a versatile synthon for heterocyclic compounds in organic synthesis.

Results of an initial investigation of the physiological activity of the compounds prepared were encouraging and the activity of selected compounds is now under extensive investigation. A continuation of these studies towards the synthesis and electrophile-induced cyclization reactions of other alkatrienyl sulfones is currently in progress.

EXPERIMENTAL

Method of analysis. ^1H and ^{13}C NMR spectra were obtained on a BRUCKER DRX-250 spectrometer for solutions in $CDCl_3$. Chemical shifts are in parts per million downfield from internal TMS. IR spectra were recorded with an IR-72 spectrophotometer (Carl Zeiss, Jena). Elemental analyses were carried out by the University of Shoumen Microanalytical Service Laboratory. The melting points were measured in open capillary tubes and are uncorrected. The solvents were purified by standard methods. All reactions were carried out in oven-dried glassware under an argon atmosphere and exclusion of moisture. All compounds were checked for their purify on TLC plates.

Starting materials. Methylsulfinyl chloride was prepared from dimethyl disulfide and sulfuryl chloride in acetic acid and distilled *in vacuo* (bp 36 / 20 mm Hg) before used.[11] 5-Methyl-1-hexene-3-yn-5-ol and phenylselenenyl chloride were commercially available and were purified by usual methods.

Synthesis of 5-methyl-3-(methylsulfonyl)hexa-1,3,4-triene 3: To a solution of 5-methyl-1-hexene-3-yn-5-ol **1** (30 mmol) and triethylamine (33 mmol) in dry diethyl ether (100 ml) at -40 °C was added dropwise with stirring a solution of freshly distilled methylsulfinyl chloride (30 mmol) in the same solvent (20 ml). The reaction mixture was stirred for an hour at the same temperature and for 3 hours at room temperature. The mixture was then washed with water, 2N HCl, extracted with ether, washed with saturated NaCl, and dried over anhydrous sodium sulfate. After evaporation of the solvent, the residue was dissolved in dried toluene (30 ml) and refluxed for 5 hours. After evaporation of the solvent, the residue was chromatographied on a column (silica gel, Kieselgel Merck 60 F_{254}) with a mixture of ethyl acetate and heptane as a eluent to give the pure product as light yellow oil, which had the following properties:
Yield 55 %. Eluent for TLC: ethyl acetate : heptane 3 : 1. *Anal.* Calcd. for $C_8H_{12}O_2S$ (MW 172.25), S 18.62 %. Found, S 18.51 %. ^1H NMR ($CDCl_3$), δ: 1.62 (s, 6H, 2Me), 2.78 (s, 3H, SO_2Me), 5.74 (dd, J_{cis} 10.4 Hz, J_{gem} 1.3 Hz, 1H, CH_a=CH_aH_b), 6.03 (dd, J_{trans} 16.4 Hz, J_{gem} 1.3 Hz, 1H, CH_a=CH_aH_b), 6.15 (dd, J_{cis} 10.4 Hz, J_{trans} 16.4 Hz, 1H, CH_a=CH_aH_b). ^{13}C NMR ($CDCl_3$), δ: 20.7, 39.3, 102.5, 108.8, 126.2, 124.1, 202.6. IR (neat), cm^{-1}: 1131 (ν^s SO_2), 1292 (ν^{as} SO_2), 1598 (C=C), 1954 (C=C=C).

Electrophile-induced reactions of the 5-methyl-3-(methylsulfonyl)hexa-1,3,4-triene 3 *(General procedure):* To a solution of **3** (10 mmol) in dry dichloromethane (20 ml) at -10 °C was added dropwise with stirring a solution of electrophilic reagent (sulfuryl chloride, bromide, phenylsulfenyl or phenylselenenyl chlorides) (10 mmol) in the same solvent (10 ml). The reaction mixture was stirred for an hour at the same temperature and for 3 hours at room temperature. The solvent was removed using a rotatory evaporator and the residue was chromatographied on a column (silica gel, Kieselgel Merck 60 F_{254}) with a mixture of ethyl acetate and heptane as a eluent to give the pure products, which had the following properties:

3-Chloro-2-methyl-4-(methylsulfonyl)hexa-1,3,5-triene 4: Yield 87 %, white crystals, mp 101-102 °C. Eluent for TLC: ethyl acetate : heptane 5 : 1. *Anal.* Calcd. for $C_8H_{11}ClO_2S$ (MW 206.69), S 15.51 %, Cl 17.15 %. Found, S 15.46 %, Cl 17.32 %. ^1H NMR ($CDCl_3$), δ: 1.98 (m, 3H, Me), 3.09 (s, 3H, SO_2Me), 4.97 (m, J_{gem} 2.1 Hz, 1H, C=CH_aH_b), 5.63 (m, J_{gem} 2.1 Hz, 1H, C=CH_aH_b), 5.88 (dd, J_{cis} 10.2 Hz, J_{gem} 1.3 Hz, 1H, CH_a=CH_aH_b), 5.99 (dd, J_{trans} 16.6 Hz, J_{gem} 1.3 Hz, 1H, CH_a=CH_aH_b), 6.34 (m, J_{cis} 10.2 Hz, J_{trans} 16.6 Hz, 1H, CH_a=CH_aH_b). ^{13}C NMR ($CDCl_3$), δ: 21.8, 41.0, 110.4, 117.8, 122.8, 138.1, 144.2, 146.1. IR (nujol), cm^{-1}: 1138 (ν^s SO_2), 1301 (ν^{as} SO_2), 1594-1621 (C=C).

3-Bromo-3-methyl-4-(methylsulfonyl)hexa-1,3,5-triene **5***:* Yield 88 %, pale yellow crystals, mp 66-67 °C. Eluent for TLC: ethyl acetate : heptane 5 : 1. *Anal.* Calcd. for $C_8H_{11}BrO_2S$ (MW 251.15), S 12.77 %, Cl 31.82 %. Found, S 12.87 %, Cl 31.97 %. ^1H NMR ($CDCl_3$), δ: 2.13 (m, 3H, Me), 3.11 (s, 3H, SO_2Me), 5.17 (m, J_{gem} 2.2 Hz, 1H, C=CH_aH_b), 5.74 (m, J_{gem} 2.2 Hz, 1H, C=CH_aH_b), 5.82 (dd, J_{cis} 10.4 Hz, J_{gem} 1.3 Hz, 1H, CH_a=CH_aH_b), 5.89 (dd, J_{trans} 16.5 Hz, J_{gem} 1.3 Hz, 1H, CH_a=CH_aH_b), 6.27 (m, J_{cis} 10.4 Hz, J_{trans} 16.5 Hz, 1H, CH_a=CH_aH_b). ^{13}C NMR ($CDCl_3$), δ: 21.9, 39.8, 118.4, 118.5, 127.9, 131.8, 143.2, 148.4. IR (nujol), cm^{-1}: 1135 (ν^s SO_2), 1299 (ν^{as} SO_2), 1600-1624 (C=C).

2-Isopropyl-3-thienyl methyl sulfone **6**: Yield 65 %, pale yellow crystals, mp 96-97 °C. Eluent for TLC: ethyl acetate : heptane 4 : 1. *Anal.* Calcd. for $C_8H_{12}O_2S_2$ (MW 204.43), S 31.37 %. Found, S 31.22 %. ^1H NMR ($CDCl_3$), δ: 1.33 (d, *J* 7.0 Hz, 6H, 2Me), 3.12 (s, 3H, SO_2Me), 3.62 (m, *J* 7.0 Hz, *J* 0.6 Hz, 1H, $CHMe_2$), 7.24 (dd, *J* 5.3 Hz, *J* 0.6 Hz, 1H, βH), 7.41 (d, *J* 5.3 Hz, 1H, αH). ^{13}C NMR ($CDCl_3$), δ: 20.1, 36.3, 40.6, 115.7, 134.2, 141.2, 150.5. IR (nujol), cm^{-1}: 1127 (ν^s SO_2), 1300 (ν^{as} SO_2), 1468, 1556 (thiophene).

Methyl 2-(1-methylethylidene)-2,5-dihydro-3-selenophenyl sulfone **7**: Yield 29 %, yellow oil. Eluent for TLC: ethyl acetate : heptane 5 : 1. *Anal.* Calcd. for $C_8H_{12}O_2SeS$ (MW 252.33), S 12.71 %. Found, S 12.50 %. ^1H NMR ($CDCl_3$), δ: 1.73 (s, 6H, 2Me), 3.11 (s, 3H, SO_2Me), 3.34 (m, *J* 1.9 Hz, *J* 19.5 Hz, 2H, CH_2), 7.03 (t, *J* 1.9 Hz, 1H, =C-H). ^{13}C NMR ($CDCl_3$), δ: 23.8, 24.5 *J* 40.8 Hz, 40.4, 111.9 *J* 73.1 Hz, 128.4, 149.7, 155.9. IR (neat), cm^{-1}: 1131 (ν^s SO_2), 1282 (ν^{as} SO_2), 1579, 1600 (C=C).

2-Isopropyl-3-selenophenyl methyl sulfone **8**: Yield 30 %, yellow oil. Eluent for TLC: ethyl acetate : heptane 3 : 1. *Anal.* Calcd. for $C_8H_{12}O_2SeS$ (MW 252.33), S 12.71 %. Found, S 12.84 %. ^{1}H NMR ($CDCl_3$), δ: 1.14 (d, *J* 6.4 Hz, 6H, 2Me), 2.75 (s, 3H, SO_2Me), 3.19 (m, *J* 6.4 Hz, 1H, $CHMe_2$), 7.92 (dd, *J* 5.6 Hz, *J* 9.4 Hz, 1H, βH), 8.03 (dd, *J* 5.6 Hz, *J* 46.7 Hz, 1H, αH). ^{13}C NMR ($CDCl_3$), δ: 17.8, 34.7, 41.6, 116.3, 134.1 *J* 63.0 Hz, 140.6, 153.5 *J* 71.0 Hz. IR (neat), cm^{-1}: 1128 (ν^s SO_2), 1313 (ν^{as} SO_2).

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