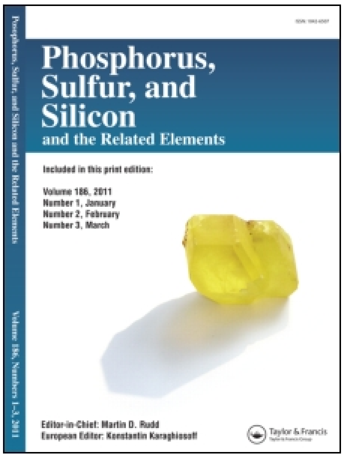

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PHOSPHORYLATED 2,5-DIHYDROTHIOPHENE-1,1-DIOXIDE BY 1,4-CYCLOADDITION OF SULFUR DIOXIDE TO 1,3-ALKADIENEPHOSPHONIC DIALKYL ESTERS

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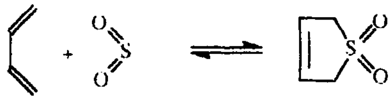
The cycloaddition reaction of sulfur dioxide to conjugated dienic compounds have been discussed and the synthesis of cyclic sulphonephosphonates by the cycloaddition of sulfur dioxide to 2-chloro-1,3-alkadienephosphonates have been reported.

Keywords: Sulfur dioxide; cycloaddition; 1,3 -alkadienephosphonates

CYCLOADDITION OF SULFUR DIOXIDE TO CONJUGATED UNSATURATED COMPOUNDS

The first report concerning the interaction of 1,3-alkadienes and sulfur dioxide was in 1910.[1] The further investigations show that crystalline unsaturated monosulphones[2] and amorphic polymeric unsaturated sulphones[3–7] were isolated as products of these reactions for which a 1,4-cycloaddition mechanism was established:



The cycloaddition reaction is reversible – the obtained sulphones smoothly decompose to starting components of the reaction[8–11]. The formation of cyclic sulphones take place also in the reactions of sulfur dioxide with polyenic hydrocarbons[12].

The interaction of sulfur dioxide with 1,3-alkadienes practically is the only reasonable preparative way for the synthesis of thiophene-1,1-dioxides. This reaction is studied in details for 1,3-butadiene[13–20], isoprene[21–26] and 2,3-dimethyl-1,3-butadiene[9,11,15,27–31].

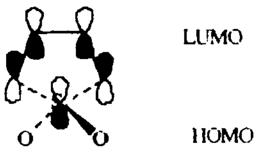
The optimal reaction conditions(temperature, solvents, ratio of the reactants, ets.) vary in wide ranges depending on the structure of the diene hydrocarbons. The best results were obtained when catalysts were used[32].

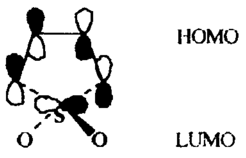
The discussed reactions follow the stereochemical rules of the Dils-Alder reaction. In the reaction only the dienic hydrocarbons with s-*cis*- conformation or those which react in s-*cis*-reaction conformation takes place[33–35].

The substituents at C2 atom of the diene have a significant influence on the reaction velocity[35].

On the other hand the dienic compound retends its configuration in the product of cyclisation[36,37].

The high stereoelectronic specification of the reaction[38], the small secondary isotopic effect(7.5%)[35], the low activation energy of the reaction(10–15kcal /mol)[35,39–42] confirm the synchronous mechanism of the interaction with cyclic intermediate involved the reconstruction of the system of orbitals without formations of ionic or free radical species. From the point of view of the orbital symmetry the attack of the sulfur dioxide on to diene results in the overleaping of the HOMO and LUMO MO of the reagents:





The reaction take place because of suprafacial-suprafacial interaction between the reagents and have to be taken as a linear heletropic process. According to the Fucui data[45] the velocity of the synchronous cycloaddition reactions depend on the energy difference between HOMO of the diene and LUMO of the dienophile.

There are some data for the two step reaction mechanism of the cycloaddition reaction of sulfur dioxide to dienic hydrocarbons[46].

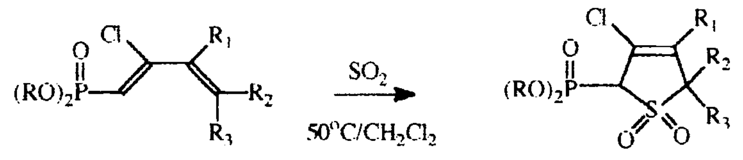
Sulfur dioxide is known as a weak dienophile that is why the introduction of electrondonating groups in the diene promote the reaction, while the electronwithdrawing groups suppress the reaction[35].

Nevertheless the number of investigation of this reaction were dedicated to conjugated dienes bearing electronwithdrawing groups at C2 atom of the dienic system[47–53].

SYNTHESIS OF PHOSPHORYLATED 2,5-DIHYDROTHIOPHENE-1,1-DIOXIDES

We have recently found however that the esters of 3-methyl-1,2,4 -pentatrienylphosphonic acid and the esters of 5-methyl-1,3,4-hexatrienylphosphonic acid react smoothly with sulfur dioxide to yield phosphorylated 2,5-dihydrothiophene-1,1-dioxides[54,55].

Now we report that dialkyl esters of 2-chloro-1,3 -alkadienephosphonic acids *1a-c* add sulfur dioxide in the 1,4-position of the dienic system of double bonds affording 3-chioro –2-dialkoxyphosphonyl.-2.5-dihvdrothiophene- 1,1-dioxides **2a-c**:



1a-c **2a-c**

The reaction was carried out in methylenechloride at 50°C and stirring. Dry sulfur dioxide was passed trough a solution of the appropriate 2-chloro-1,3-alkadienephosphonate for an hour (see experimental). In the ^1H -nmr spectra of the purified products **2a-c** the signal for the olephinic proton at C1 atom of the dienephosphonate system disappears and the signal for the proton at sp^3-hybridized C atom at 4.45–4.47 ppm with characteristic coupling constant with phosphorus (see experimental) appear. At the same time the signals for the protons at C4 atom at 3.77ppm with coupling constant for the protons at sp^3-hybridized atom appear while the signal for the protons of the olephinic methylene group disappear.

These results in addition to our previous ones[54,55] confirm the assumption that the thiophene and selenophene cyclization of the esters and dichlorides of alkatrienephosphonic acids observed in the reactions with suiphenyl- and selenenylchlorides[56–59] takes place via 1,4-cycloaddition of the reagent to 1,3-dienic fragment of the trienephosphonate system of double bonds followed by 1,5-sigmatropic rearrangement and aromatization of the five-membered heterocycles which is the main force of the process. It is important to underlined that the reaction of the alkatrienephosphonates described by us earlier and the present results reported, takes place in the same mode but the lack of free electronic pair at sulfur atom, which would be able to take part in the formation of six π-electronic system, preserve the above mentioned 1,5-sigmatropic rearrangement and the aromatization as well.

The obtained results confirm once again the s-cis-reaction conformation of 2-chloro-1,3-alkadienephosphonates as well as the same reaction conformation of the 1,3-dienic fragment of the alkatrienephosphonate system of double bonds in the trienephosphonate derivatives.

EXPERIMENTAL

1. Starting materials

Dichloromethane (Merck, GR Grade) was distilled from P_4O_{10} and stored over molecular sieves (4A).

Benzene and heptane(Merck GR Grade) was stored and distilled over sodium wire and stored over molecular sieves (5A). Washed and dried sulfur dioxide, prepared from sodium sulfite and hydrochloric acid was used.

2-Chloro-1,3 -alkadienephosphonates were prepared by the procedure described earlier.

2. Analytical methods

The IR-spectra were recorded on IR 72 Carl Zeiss Jena

The 1H- and 31P-nmr spectra were recorded on Jeol JNM-PS-10 spectrometer at 100MHz using TMS as internal standard

3. Synthesis of 2-dialkoxyphosphonyl –3-chloro-5,5 -dimethyl-2,5-dihydrothiophene-1,1-dioxides 2a-c

General procedure

Dry sulfur dioxide was passed for 1h through a solution of 0.05mol of the appropriate 2-chloro-1,3-alkadienephosphonate in dichloromethane. The reaction mixture was heated to 50–60°C. After evaporization of the solvent the residue was washed with heptane/benzene.

2a Yield % 72, oil, Found% P 13.52, S 14.00, Cl 15.49 $C_6H_{10}O_5ClPS$ Calcd.% P 13.55, S 14.02, Cl 15.51; ^1H nmr 6.24(1H J_{HP} 3.4Hz), 3.77(2H J_{HH}1.7Hz), 4.47(1H J_{HP}16.6Hz), IR $cm^{-1}$$1250_{vP=O,}$ 1120, $1300_{vSO2,}$ $1540_{vC=C}$

2b Yield % 70, oil, Found% P 12.02. S 12.45, Cl 13.79 $C_8H_{14}O_5ClPS$ Calcd.% P 12.06, S 12.49, CI 13.81; ^1H nmr 6.22(1H J_{HP} 3.4Hz), 3.77(2H J_{HH}1.7Hz), 4.46(1H J_{HP}16.6Hz), IR $cm^{-1}$$1255_{vP=O,}$ 1120, $1300_{vSO2,}$ $1546_{vC=C}$

2c Yield % 75, oil, Found% P 10.82, S 11.20, CI 12.40 $C_{10}H_{18}O_5ClPS$ Calcd.% P 10.88, S 11.26, Cl 12.45; ^1H nmr 6.24(1H J_{HP} 3.4Hz), 3.77(2H J_{HH}1.7Hz), 4.45(1H J_{HP}16.6Hz), IR $cm^{-1}$$1258_{vP=O,}$ 1120, $1300_{vSO2,}$ $1551_{vC=C}$

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