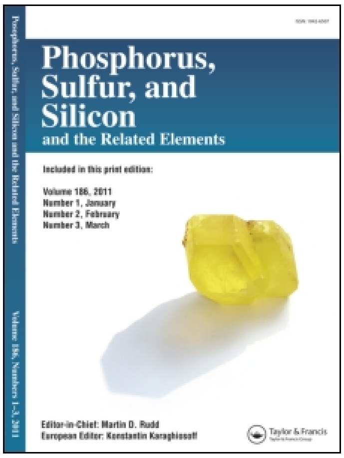

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1,4-CYCLOADDITION REACTION OF SULFUR DIOXIDE TO DIALKYL(3-METHYL-1,2,4-PENTATRIENYL)PHOSPHONATES

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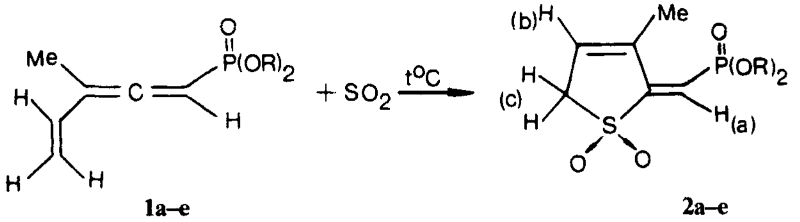
Phosphorylated 2,5-dihydrothiophene-1,1-dioxides are obtained by 1,4-cycloaddition reaction of sulfur dioxide to dialkyl(3-methyl-1,2,4-pentatrienyl)phosphonates. The structure of the products was established by analyses of the ir and ^{1}H-nmr spectra.

INTRODUCTION

Although the 1,4-cycloaddition of sulfur dioxide to conjugated dienes is a well known reaction in organic chemistry,[1-4] until now it has not been used with 1,3-alkadienylphosphonic derivatives. Recently it was shown that dialkyl(3-methyl-1,2,4-pentatrienyl)phosphonates when interacting with electrophilic reagents undergo a five-membered heterocyclization. When this electrophilic agent is halogen the reaction involves the 1,2-alkadienylphosphonic system of double bonds (O═P—C═C═C) thus leading to the formation of 5-vinyl-1,2-oxaphosphol-3-ene-2-oxides.[5] In the case of sulfenyl chlorides, the 1,3-dienic part of double bonds (C═C—C═C) is involved yielding dialkyl(3-methyl-2-thenyl)phosphonates.[6] In the present communication we describe the results of our investigation on the reactivity of the above alkatrienylphosphonates with sulfur dioxide.

RESULTS AND DISCUSSION

Several dialkyl(3-methyl-1,2,4-pentatrienyl)phosphonates (**1a–e**) are treated with sulfur dioxide (gas) in chloroform at 50–60°C. The completion of the reaction is established by the disappearance of the absorption band of the allenic bond (1945 cm^{-1}) in ir spectra of the reacting mixtures. The crude product is a dark oil which crystalizes rapidly. After recrystalization in heptane, colourless crystals are isolated. The ^{1}H-nmr and ir spectroscopic data and elemental analysis of sulfur confirmed our hypothesis that a 1,4-cycloaddition of sulfur dioxide to the 1,3-dienic part of trienylphosphonic system of double bonds takes place. Thus the reaction leads to the formation of a cyclic sulfonphosphonate:



1,2	a	b	c	d	e
R	Me	Et	Pr^n	Pr^i	Bu^n

SCHEME 1

The ir spectra are very useful for the establishment of the structure of 2,5-dihydrothiophene-1,1-dioxides **2a–e**. Along with the absorption bands for phosphorylic (1225–1240 cm^{-1}) and ester (1000–1018 cm^{-1}) groups, two bands corresponding to the conjugated double bonds are observed (see Table I) along with two strong bands at 1120 cm^{-1} and 1310–1312 cm^{-1} which are typical of the sulfogroup.[7] The ^{1}H-nmr spectra of **2a–e** in weak field (6.08–6.24 ppm) show a signals corresponding to two olephinic protons; one of the signals (Ha) consists of two doublets (δ 6.08–6.16, $^2J_{HP}$ 6.8–7.4 Hz, $^5J_{HH}$ 1.7–1.8 Hz) and the other one (Hb) is a complex multiplet (δ 6.14–6.24, $^2J_{HH}$ 5.0–5.5 Hz, $^5J_{HP}$ 3.0–3.4 Hz, $^5J_{HH}$ 1.7–1.8 Hz). At 3.76 ppm one observes two quartets corresponding to the ring methylene group protons (Hc), and at 2.28–2.30 ppm there is a triplet from the protons of the methyl group at the C^3 atom. Along with the signals characterizing the 2,5-dihydrothiophene ring protons, one finds also peaks due to the protons of the alkoxy groups of the phosphonic

TABLE I

^{1}H-nmr and ir data of 2-dialkoxyphosphonylmethylidene-3-methyl-2,5-dihydrothiophene-1,1-dioxides

		Chem. Shift, δ		Coupl. Const., J Hz		ir Spectra, cm^{-1}		
No.	R	Ha[a] (Hb[a])	Hc[a] (Me)	Ha—P (Hb—P)	Ha—Hb (Hc—Hb)	P=O (P—O—R)	>SO$_2$	C=C—C=C
2a	Me	6.08dd	3.76dq	7.0	1.7	1230	1120	1582
		(6.24m)	(2.28t)	(3.4)	(5.0)	(1018)	1310	1640
b	Et	6.08dd	3.76dq	6.8	1.7	1230	1120	1585
		(6.14m)	(2.28t)	(3.0)	(5.5)	(1010)	1310	1645
c	Pr^n	6.16dd	3.76dq	7.0	1.7	1240	1125	1585
		(6.20m)	(2.28t)	(3.2)	(5.0)	(1005)	1312	1640
d	Pr^i	6.11dd	3.76dq	7.2	1.8	1225	1120	1540
		(6.24m)	(2.30t)	(3.0)	(5.0)	(995)	1310	1610
e	Bu^n	6.14dd	3.76dq	7.4	1.8	1225	1120	1588
		(6.22m)	(2.30t)	(3.2)	(5.2)	(1000)	1310	1635

[a] Ha, Hb and Hc see Scheme 1 above.

TABLE II

Physical constants, yields and elemental analyses of 2-dialkoxyphosphonylmethylidene-3-methyl-2,5-dihydrothiophene-1,1-dioxides

No.	Yield %	mp °C	Found S %	Formula	Calculated S %
2a	56	65–66	12.35	$C_8H_{13}O_5PS$	12.71
b	60	58–60	10.85	$C_{10}H_{17}O_5PS$	11.43
c	50	40–41	9.98	$C_{12}H_{21}O_5PS$	10.39
d	58	95–96	9.90	$C_{12}H_{21}O_5PS$	10.39
e	52	39–40	9.17	$C_{14}H_{25}O_5PS$	9.53

substituent. The signal intensity of each group is in agreement with the number of protons in the respective group. In Table II physical constants, yields and elemental analyses of the compounds **2a–e** are given.

The 1,4-cycloaddition of sulfur dioxide to dialkyl (3-methyl-1,2,4-pentatrienyl)phosphonates **1a–e** allowed us to synthesise the so far unknown phosphorylated 2,5-dihydrothiophene-1,1-dioxides **2a–e**. We are now investigating the possibility of applying the above reaction to other 1,3-alkadienylphosphonates. The chemical properties of the obtained 2,5-dihydrothiophene-1,1-dioxides **2a–e** are being studied as well.

EXPERIMENTAL

Methods of Analysis. The ^{1}H-nmr spectra are obtained on "Jeol" JNM-PS-10 (100 MHz) spectrometer as solutions in $CDCl_3$ with internal standard TMS. The ir spectra are determined on a IR-72 spectrophotometer (Karl Zeiss Jena, GDR).

Starting Materials. Dialkyl(3-methyl-1,2,4-pentatrienyl)phosphonates were synthesized according to the literature.[8]

General Method for Preparation of 2-Dialkoxyphosphonylmethylidene-3-methyl-2,5-dihydrothiophene-1,1-dioxides **2a–e**. Through a stirred solution of 3-methyl-1,2,4-pentatrienylphosphonic dialkyl ester in chloroform at 50–60°C sulfur dioxide (gas) was bubbled for one hour. The solvent was removed in vacuo and the crude reaction product was recrystalised in heptane.

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REFERENCES

1. O. Grummitt and J. Splitta, *J. Amer. Chem. Soc.*, **74**, 3924 (1952).
2. W. L. Mock, *J. Amer. Chem. Soc.*, **97**, 3666 (1975).
3. W. L. Mock, *J. Amer. Chem. Soc.*, **97**, 3673 (1975).
4. N. S. Isaacs and A. A. R. Laila, *Tetrahedron Letters*, 715 (1976).
5. Chr. M. Angelov, M. Kirilov, B. I. Ionin and A. A. Petrov, *Zh. Obshch. Khim.*, **49**, 2225 (1979).
6. Chr. M. Angelov, M. Kirilov, K. V. Vachkov and S. L. Spassov, *Tetrahedron Letters*, 3507 (1980).
7. R. M. Silverstein, G. C. Bassler and T. C. Morrill, "Spectrometric Identification of Organic Compounds," John Wiley & Sons (Russian Translation) Moscow (1977), p. 209.
8. Chr. M. Angelov, M. Kirilov and B. I. Ionin, *Zh. Obshch. Khim.*, **49**, 1960 (1979).