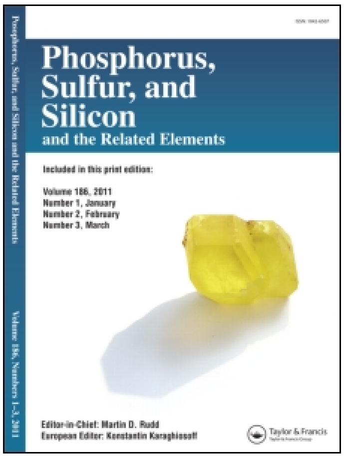


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Formation of Spirophosphonium Salts By Protophilic Heterocyclization of 2-(3-Methyl-1,2-Alkadienyl)1,3,2-Dioxaphospholane 2-oxides

Christo M. Angelov[a]; Christo Zh. Christov[a]; Diana M. Mondeshka[b]
[a] Department of Chemistry, Higher Pedagogical Institute, Shoumen [b] Department of Organic Chemistry, Higher Institute of Chemical Technology, Sofia, Bulgaria

To cite this Article Angelov, Christo M. , Christov, Christo Zh. and Mondeshka, Diana M.(1984) 'Formation of Spirophosphonium Salts By Protophilic Heterocyclization of 2-(3-Methyl-1,2-Alkadienyl)1,3,2-Dioxaphospholane 2-oxides', Phosphorus, Sulfur, and Silicon and the Related Elements, 21: 2, 249 — 251

To link to this Article: DOI: 10.1080/03086648408077664

URL: http://dx.doi.org/10.1080/03086648408077664

Phosphorus and Sulfur, 1984, Vol. 21, pp. 249–251
0308-664X/84/2102-0249/$10.00/0

SHORT COMMUNICATION

Formation of Spirophosphonium Salts By Protophilic Heterocyclization of 2-(3-Methyl-1,2-Alkadienyl)-1,3,2-Dioxaphospholane 2-oxides

CHRISTO M. ANGELOV* and CHRISTO ZH. CHRISTOV

Department of Chemistry, Higher Pedagogical Institute, 9700 Shoumen

DIANA M. MONDESHKA

Department of Organic Chemistry, Higher Institute of Chemical Technology, 1156 Sofia, Bulgaria

(Received March 12, 1984; in final form May 16, 1984)

The reaction of 2-(3-methyl-1,2-alkadienyl)-1,3,2-dioxaphospholane 2-oxides with 96% sulfuric acid leads to the formation of spirophosphonium salts.

INTRODUCTION

It was shown recently[1,2] that the reaction of halogens, sulfenyl and selenenyl chlorides with 2-(1,2-alkadienyl)-1,3,2-dioxaphospholane 2-oxides proceeds via a cycloaddition of the reagent and formation of 1,2-oxaphosphol-3-ene derivatives. In that case we proposed that the reaction probably passed through a spirophosphonium structure, but it was not sufficiently stable to be isolated, because of the fast second stage of the reaction—opening of the dioxaphospholane ring. Continuing our investigations in this field, now we reported evidence for the generation of such spirophosphonium compounds from the same dioxaphospholanes.

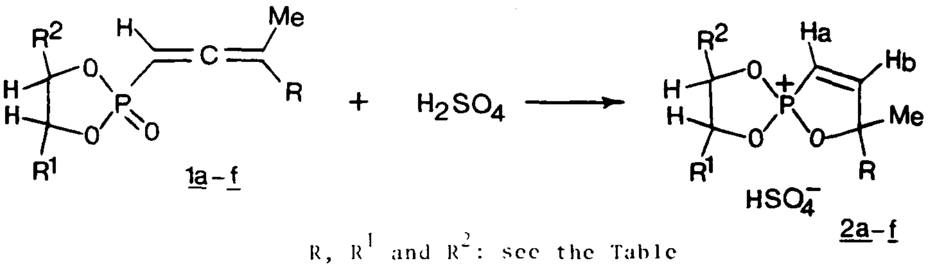
RESULTS AND DISCUSSION

It was found that the reaction of the allene-substituted dioxaphospholanes **1a–f** with 96% sulfuric acid proceeds with heterocyclization of the 1,2-alkadienylphosphonic system of double bonds (O=P—C=C=C) and, at the same time, the dioxaphospholane ring remains intact. After treatment with H_2SO_4 for a few hours, a full conversion of **1a–f** to the spirophosphonium salts **2a–f** was observed (see Scheme 1).

In sulfuric acid solution, the compounds **2a–f** are stable at room temperature for a period of several days. However, it was impossible to isolate them in a pure state. The formation of phosphonium structures can be verified from the ^1H- and ^{31}P-nmr spectra of **2a–f** (see Table I). It should be noted that the spectra of spiranes **2a–f**

---

*Author to whom all correspondence should be addressed.



SCHEME 1

TABLE I

^{1}H-nmr spectral data of the spirophosphonium salts **2a–f**

No.	R	Chemical shifts, δ ppm R^1 (R^2)	 H_a (H_b)	 R^1CH	 R^2CH	 R	 Me	Coupl. Const., J Hz P—H_a	 P—H_b	 H_a—H_b
2a	Me	H (H)	5.84 q (7.21 q)	4.08 s	4.08 s	1.25 s	1.25 s	35.5	53.0	8.8
2b	Me	Me (H)	5.83 q (7.02 q)	Me 1.00 d H 3.20–4.08 m	3.20–4.08 m	1.23 s	1.23 s	35.0	51.0	8.5
2c	Me	Me (Me)	5.83 q (7.10 q)	Me 1.10 d H 4.28 m	Me 1.10 d H 4.28 m	1.21 s	1.21 s	38.0	57.0	8.5
2d	Et	H (H)	5.82 q (7.39 q)	4.30 s	4.42 s	Me 0.42 t CH_2 1.52 m	1.22 s	38.5	57.5	8.5
2e	Et	Me (H)	5.80 q (7.36 q)	Me 1.10 d H 3.90–4.86 m	3.90–4.86 m	Me 0.42 t CH_2 1.50 m	2.10 s	38.0	57.0	8.5
2f		Me (Me)	5.83 q (7.38 q)	Me 1.10 d H 4.30 m	Me 1.10 d H 4.30 m	Me 0.42 t CH_2 1.50 m	1.19 s	38.5	57.5	8.5

s—singlet, d—doublet, t—triplet, q—quartet, m—multiplet.

strongly differ from those of the 2-alkoxy-1,2-oxaphosphol-3-ene 2-oxides. In the latter, the phosphorus atom is chiral, which renders the methyl groups at C-5 in the ring diastereotopic, and in the ^{1}H-nmr spectra two singlets (δ 1.45–1.68) for protons from these groups appear.[1–3] In **2a**, the P-atom is achiral and only one singlet for the protons of the methyl groups at C-5 is observed. When there are two different substituents at C-5, the 1,2-oxaphosphol-3-ene 2-oxides are mixtures of diastereoisomers, which are seen in the ^{1}H-nmr spectra. Although the compounds **2b**, **2c**, **2e** and **2f** have more than one chiral center the stereoisomers cannot be distinguished. The ^{31}P chemical shifts of **2b** (δ 78.9 ppm) and **2c** (δ 76.0 ppm) are quite different from those of the oxaphospholenes with tetracoordinate phosphorus (δ 27.0–36.0 ppm),[4–6] and characteristic of compounds with a phosphonium structure.[7]

The above results confirm our assumption that the reactions of 1,3,2-dioxaphospholane 2-oxides with electropholes probably proceed through spirophosphonium intermediates.[1,2]

EXPERIMENTAL

Methods of Analysis. The ^{1}H- and ^{31}P-nmr spectra of **2a–f** were obtained on "Jeol" JNM-PS-10 (100 MHz) and FX 90 (90 MHz) spectrometers by using 96% H_2SO_4 solutions with TMS and 85% H_3PO_4 respectively, as external standards.

ACKNOWLEDGMENT

The authors are indebted to Dr. Otto Dahl (The H. C. Ørsted Institute, University of Copenhagen, Denmark) for the ^{31}P-nmr spectra.

REFERENCES

1. Ch. M. Angelov and Ch. Zh. Christov, *Heterocycles*, **20**, 219 (1983).
2. Ch. M. Angelov and Ch. Zh. Christov, *Phosphorus and Sulfur*, **15**, 205 (1983).
3. Ch. M. Angelov, *Zh. Obshch. Khim.*, **50**, 2448 (1980).
4. T. S. Mikhailova, Ch. M. Angelov, V. M. Ignat'ev, A. V. Dogadina, V. I. Zakharov, B. I. Ionin and A. A. Petrov, *Zh. Obshch. Khim.*, **47**, 2701 (1977).
5. T. S. Mikhailova, V. M. Ignat'ev, B. I. Ionin and A. A. Petrov, *Zh. Obshch. Khim.*, **48**, 717 (1978).
6. D. van Aken, A. M. C. F. Castelijns and H. M. Buck, *Rec. Trav. Chim. Pays Bas*, **99**, 322 (1980).
7. T. S. Mikhailova, N. K. Skvortsov, V. M. Ignat'ev, B. I. Ionin and A. A. Petrov, *Dokl. Akad. Nauk USSR*, **241**, 1095 (1978).