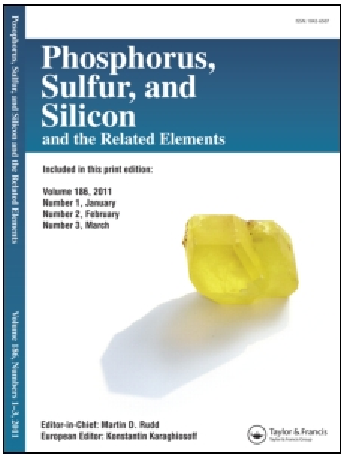


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

CONFORMATIONAL PREFERENCE IN 1,3-DITHIANES CONTAINING PHOSPHONIUM AND PHOSPHINO SUBSTITUENTS AT THE ANOMERIC CARBON ATOM

Piotr Graczyk[a]; Marian Mikołajczyk[a]
[a] Center of Molecular and Macromolecular Studies, Polish Academy of Sciences, Sienkiewicza, Poland

To cite this Article Graczyk, Piotr and Mikołajczyk, Marian(1991) 'CONFORMATIONAL PREFERENCE IN 1,3-DITHIANES CONTAINING PHOSPHONIUM AND PHOSPHINO SUBSTITUENTS AT THE ANOMERIC CARBON ATOM', Phosphorus, Sulfur, and Silicon and the Related Elements, 59: 1, 211 — 214

To link to this Article: DOI: 10.1080/10426509108045726

URL: http://dx.doi.org/10.1080/10426509108045726

Phosphorus, Sulfur, and Silicon, 1991, Vol. 59, pp. 211–214
Reprints available directly from the publisher
Photocopying permitted by license only

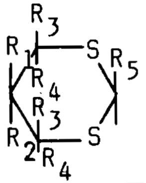
Printed in the United Kingdom

CONFORMATIONAL PREFERENCE IN 1,3-DITHIANES CONTAINING PHOSPHONIUM AND PHOSPHINO SUBSTITUENTS AT THE ANOMERIC CARBON ATOM

PIOTR GRACZYK and MARIAN MIKOŁAJCZYK
Center of Molecular and Macromolecular Studies,
Polish Academy of Sciences, 90-363 Łódź, Sienkiewicza 112, Poland

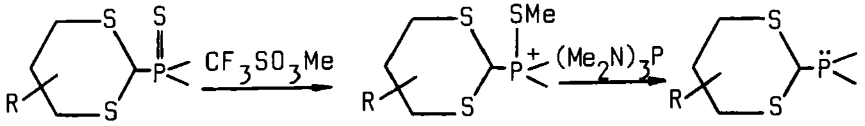
Abstract The synthesis and conformational analysis of 1,3-dithiane, 5,5-dimethyl-1,3-dithiane, 5-tert-butyl-1,3-dithiane and 4,6-dimethyl-1,3-dithiane containing different phosphonium and phosphino groups at the anomeric carbon atom are described.

In the course of our studies[1] on the anomeric effect in 1,3-heteroanes containing organophosphorus substituents we became interested in the conformation of 1,3-dithianes bearing the phosphino and phosphonium groups at the anomeric carbon atom. The conformational behavior of 2-phosphonio-1,3-dithianes was especially interesting in view of the reverse anomeric effect observed for the ammonium substituted heteroanes[2]. In this communication we wish to report the synthesis and conformational analysis of a series of 2-substituted 1,3-dithianes shown below.

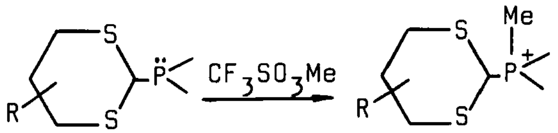


R_1	R_2	R_3	R_4	R_5									
				$\mathrm{MeS\overset{+}{P}Me_2}$	$\mathrm{MeS\overset{+}{P}PhMe}$	$\mathrm{MeS\overset{+}{P}Ph_2}$	$\mathrm{\ddot{P}Me_2}$	$\mathrm{\ddot{P}PhMe}$	$\mathrm{\ddot{P}Ph_2}$	$\mathrm{\overset{+}{P}Me_3}$	$\mathrm{\overset{+}{P}Me_2Ph}$	$\mathrm{\overset{+}{P}MePh_2}$	$\mathrm{\overset{+}{P}Ph_3}$
H	H	H	H	**1a**	**2a**	**3a**	**4a**	**5a**	**6a**	**7a**	**8a**	**9a**	**10a**
Me	Me	H	H	**1b**	**2b**	**3b**	**4b**	**5b**	**6b**	**7b**	**8b**	**9b**	**10b**
Bu^t	H	H	H	**1c**	**2c**	**3c**	**4c**	**5c**	**6c**	**7c**	**8c**	**9c**	**10c**
H	Bu^t	H	H	**1d**	**2d**	**3d**	**4d**	**5d**	**6d**	**7d**	**8d**	**9d**	**10d**
H	H	H	Me	**1e**	**2e**	**3e**	**4e**	**5e**	**6e**	**7e**	**8e**	**9e**	**10e**
H	H	Me	H	**1f**	**2f**	**3f**	**4f**	**5f**	**6f**	**7f**	**8f**	**9f**	**10f**

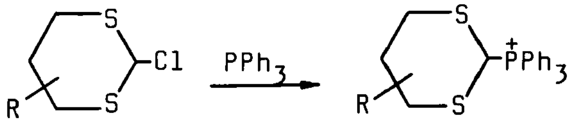
2-Phosphino-1,3-dithianes **4-6** were prepared from the corresponding thiophosphoryl compounds utilizing alkylation-desulfurization procedure (eq.1) worked out in our Laboratory[3]. In the case of diastereomeric cis-trans dithianes it is necessary to control the alkylation time because methylthiomethylphenyl- and methylthiodiphenyl-phosphonium salts undergo epimerization. For the same reason it is advantageous to carry out the desulfurization reaction at -60°C.



1-3 **4-6** (1)



4-6 **7-9** (2)

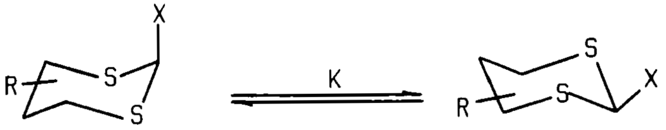


10 (3)

The phosphonium salts **7-9** were obtained by methylation of the phosphines **4-6** with methyl trifluoromethanesulfonate (eq.2) while triphenylphosphonium chlorides **10** were synthesized from the appropriate 2-chloro-1,3-dithianes and triphenylphosphine (eq.3).

The latter rection with 2-chloro-5-tert-butyl- and 2-chloro-4,6-dimethyl-1,3-dithiane afforded a mixture of the diastereomeric triphenylphosphonium salts in a ratio 9:1. The axial position of the $\overset{+}{P}Ph_3$-group in major diastereomers was confirmed by X-ray analysis of the diastereomerically pure **10c** and ^1H-, ^{13}C- and ^{31}-P NMR studies. Among many spectral parameters which may be used to assign the geometry of the dithianes **4-10**, the γ-effect values in ^{13}C NMR spectra are the most conclusive. Thus, these values are negative (-2.8÷-4.8) when the 2-phosphonium or 2-phosphino substituents are axial and positive (+0.7÷+2.4) when they occupy an equatorial position.

In order to determine the equilibrium constants for the process, shown below, the equilibration of the diastereomeric pairs of 2-phosphonio-1,3-dithianes **8c-8f**, **9c-9f** and **10c-10f** was carried out in dichloromethane-d_2 solutions in the presence of catalytic amounts of triethylamine or diisopropylethylamine.



(4)

The equilibrium constants for the conformationally labile 1,3-dithianes were calculated using the γ-effect value as a conformational probe and cis and trans 5-tert-butyl-1,3-dithiane derivatives as reference systems. The correctness of this approach was checked experimentally for **10b** by the low-temperature ^{31}P NMR spectra (-100°C) showing two singlets for both conformers. The calculated and experimentally determined equilibrium constants are collected in Table I.

TABLE I Equilibrium constants for 2-phosphonio-1,3-dithianes (CD_2Cl_2, 293K)

No	a	b	c,d	e,f
7	1.35	1.29	-	-
8	0.69	0.52	0.34	0.58
9	2.38	1.57	0.83	2.12
10	4.84	3.14	1.74	6.10

The data in Table I reveal that the triphenylphosphonium group shows a tendency to occupy an equatorial position. However, a rather bulky dimethylphenylphosphonium group shows a small preference for an axial orientation. Similarly, in 5-tert-butyl-1,3-dithiane the methyldiphenylphosphonium group prefers also an axial position. Based on the above observations one can conclude that the reverse anomeric effect is not observed in the 1,3-dithiane systems investigated here and the conformational preference of the 2-phosphino or 2-phosphonium substituents depends on the normal anomeric effect and steric effect (1,3-syn diaxial interactions) operating in opposite directions.

REFERENCES

1. M.Mikołajczyk, P.Graczyk, M.I.Kabachnik and A.P.Baranov, J.Org.Chem., **54**, 2859 (1989) and references therein.
2. See A.J.Kirby, The Anomeric Effect and Related Stereoelectronic Effects at Oxygen, Springer Verlag, Berlin, 1983, pp 15-17.
3. J.Omelańczuk and M.Mikołajczyk, Tetrahedron Lett., **25**, 2493 (1984).