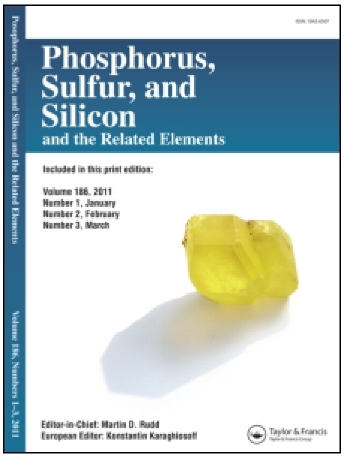

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STUDY ON SYNTHESES AND REACTIONS OF CAGED BICYCLOPHOSPHATES (VIII)

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Communication

STUDY ON SYNTHESES AND REACTIONS OF CAGED BICYCLOPHOSPHATES (VIII)†

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We report in this communication our findings on the reactivity and regioselectivity of thionation between the formacyl derivatives of 1-oxo-1-phospha-2,6,7-trioxacyclo[2.2.2]octane and Lawesson's Reagent (LR) in detail.

Key words: Caged bicyclophosphate, Lawesson's Reagent, reactivity, regioselectivity.

The chemistry of caged bicyclophosphate containing molecules has been of growing interest over the past few years due to its highly symmetric structure and unique mechanism of biological-activity.[1–3]

In continuation of our studies in this field,[3–6] we have tried to prepare the acid **3** and its derivatives through the following reactions. Unfortunately, we only found its oxygen analogue **2**, rather than the acid **3** itself.

In order to obtain the corresponding sulfur-containing derivatives, we performed the route to prepare a series of compounds **4** and then thionate them using Lawesson's Reagent (LR).[7]

We have presumed that there should be at least three products **5**, **6** and **7** after treatment of compounds **4** with excess LR for a long time, compounds **6** and **7** being the main products. But, surprisingly, when X = O, S, compounds **5** are the only products and the yields are 75–90%, no compounds **6** and **7** were detected, furthermore, no reaction occurred at all when X = NR^2, no matter how to improve the

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†Part (VII) will be published.

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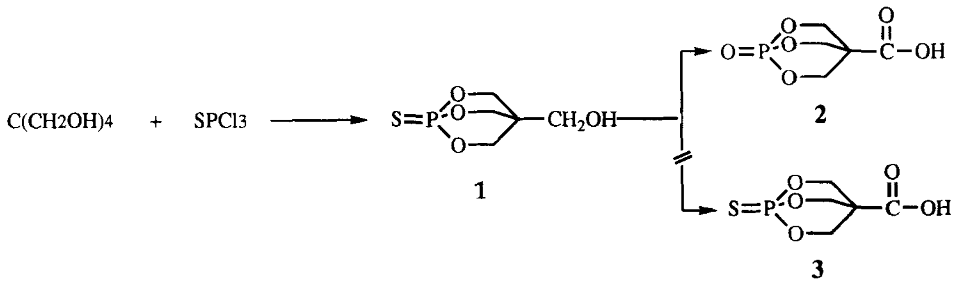
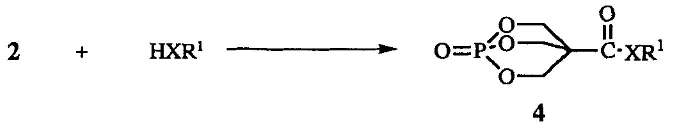
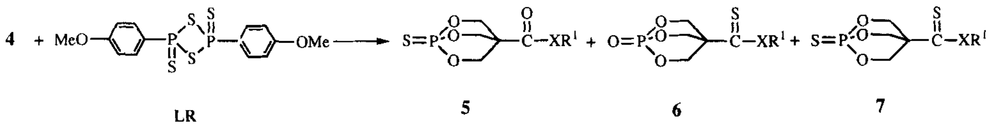




No	X	R^1	No.	X	R^1
4a	O	Me	4k	NH	Me
4b	S	t-Bu	4l	NH	n-Bu
4c	S	i-Pr	4m	NEt	Et
4d	S	$(CH_2)_4CH_3$	4n	NH	Et
4e	S	Ph	4o	NBu-n	n-Bu
4f	S	Et	4p	NMe	Me
4g	S	i-Bu	4q	NH	H
4h	S	$(CH_2)_7CH_3$	4r	NH	i-Pr
4i	S	CH_2Ph	4s	NH	i-Bu
4j	S	n-Pr	4t	NPr-i	i-Pr
			4u	NH	n-Pr



conditions including changing solvent, reaction temperature and molar ratios between materials. There is no reaction between either phosphorus pentasulfide or sulfur and compounds **4** yet.

In view of thermodynamics factors, the carbonyl functions should be more easy to be thionated than the P═O bond, and the thionation is smoother after treatment of amides than esters or thioesters with LR.[8,9] Prompted by the unexpected results, we supposed that there is an unique kind of electronic-effect rather than a normal inductive-effect, due to the special structure of caged bicyclophosphates; furthermore,

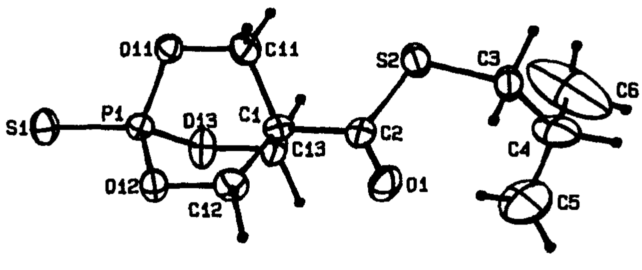


FIGURE 1 X-Ray crystal structure of 5g[11]

TABLE I

Bond angles (°) of crystal 5g[#]

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
S1	P1	O11	116.1(3)	C11	C1	C12	110.(1)
S1	P1	C12	114.7(3)	C11	C1	C13	105.9(9)
S1	P1	O13	115.7(3)	C11	C1	C2	114(1)
O11	P1	O12	104.5 (4)	C12	C1	C13	108(1)
O11	P1	O13	101.8(4)	C12	C1	C2	109.6(9)
O12	P1	O13	102.2(4)	C13	C1	C2	108.7(9)
C2	S2	C3	101.6(6)	S2	C2	O1	124.3(9)
P1	O11	C11	114.9(7)	S2	C2	C1	113.8(8)
P1	O12	C12	114.6(7)	O1	C2	C1	122.(1)
P1	O13	C13	116.1(7)	S2	C3	C4	119.(1)
O11	C11	C1	112.(1)	C3	C4	C5	112.(2)
O12	C12	C1	111.8(9)	C3	C4	C6	108.(2)
O13	C13	C1	109.7(9)	C5	C4	C6	114.(2)

[#] Numbers in parentheses are estimated standard deviations in the least signifcant digits.

TABLE II

Bond distances in angstroms of crystal 5g*

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
P1	S1	1.881(4)	O13	C13	1.43(1)
P1	O11	1.566(7)	C11	C1	1.49(2)
P1	O12	1.577(7)	C12	C1	1.51(2)
P1	O13	1.595(8)	C13	C1	1.55(1)
S2	C2	1.75(1)	C1	C2	1.52(1)
S2	C3	1.79(1)	C3	C4	1.52(2)
O1	C2	1.17(1)	C4	C5	1.43(3)
O11	C11	1.44(2)	C4	C6	1.42(5)
O12	C12	1.44(2)			

* Numbers in parenheses are estimated standard deviations in the least significant digits.

does such an effect determine mainly the reactivity and regioselectivity of compounds **4** with LR. This hypothesis is complementary to the fact that the bond distance of P=O is slightly shorter, when R^1 are electron-donating groups than electron-withdrawing groups, discovered by the analysis of the X-Ray diffraction of crystals.[10] Further studies are in progress in order to obtain the quantitative results.

EXPERIMENTAL

Experimental procedure: To a 50 ml four-necked flask equipped with a condensor (CaCl$_2$ dry tube) were successively added 2.66 g (10 mmol) **4g** (X = S, R^1 = i-Bu), 4.4 g (11 mmol) LR and 40 ml of anhydrous xylene. The mixture was heated, with stirring, to 135°C and became homogenous. It was kept 15 hours until **4g** almost disappeared, monitored by means of TLC. After removing xylene, the residue was chromatographed using a solvent mixture, petrolether/ethyl acetate (from 1/8 to 1/3), as eluant, 2.12 g **5g** was isolated, yield 75%. Recrystallization from petrolether/ethyl acetate (2/1) gave colorless crystals of m.p. 88.0–90.0°C. ^{1}H NMR δ (CDCl$_3$. TMS), ppm: 0.95–1.01 (d, CH$_3$, 6H), 1.60–1.90 (m, CH, 1H), 2.86–2.94 (d, CH$_2$, 2H), 4.78–4.85 (d, OCH$_2$, 6H), IR, γ (KBr), cm^{-1}: 1653.01 (C=O), 1174.8 –992.3 (P—O—C), 871.5, 812.3 (bicyclo), 684.6 (P=S). Elemto. Anal. [Found (Calcd.)], %: C, 35.25 (35.27), H, 5.28 (5.37). In similar procedures other compounds **5** were obtained.

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