Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Reaction of Cyclic Sulfates with Phosphines

Kwan Soo Kim [a], Yung Hyup Joo [a], In Wook Kim [a], Kyoung Rim Lee [a], Duk Young Cho [a], Minjeong Kim [a] & In Haeng Cho [a]
[a] Department of Chemistry, Yonsei University, Seoul, 120-749, Korea
Published online: 23 Sep 2006.

To cite this article: Kwan Soo Kim, Yung Hyup Joo, In Wook Kim, Kyoung Rim Lee, Duk Young Cho, Minjeong Kim & In Haeng Cho (1994) Reaction of Cyclic Sulfates with Phosphines, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 24:8, 1157-1163, DOI: 10.1080/00397919408011712

To link to this article: http://dx.doi.org/10.1080/00397919408011712

SYNTHETIC COMMUNICATIONS, 24(8), 1157-1163 (1994)

REACTION OF CYCLIC SULFATES WITH PHOSPHINES

Kwan Soo Kim,* Yung Hyup Joo, In Wook Kim, Kyoung Rim Lee,

Duk Young Cho, Minjeong Kim, and In Haeng Cho

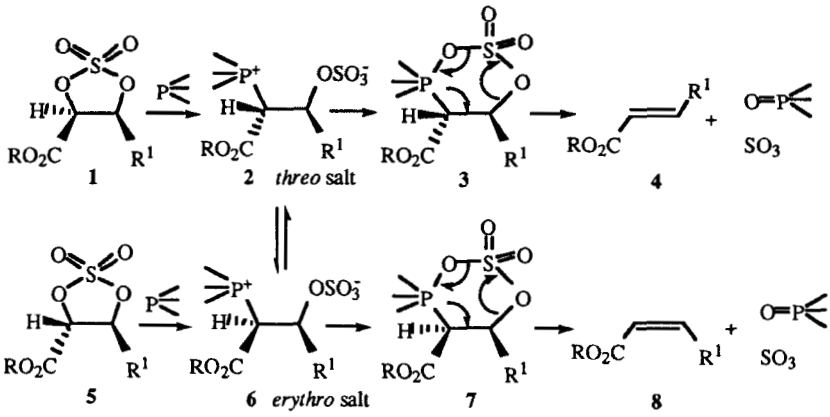
Department of Chemistry, Yonsei University, Seoul 120-749, Korea

ABSTRACT : In their reactions with phosphines, cyclic sulfates **9**, **10**, **11**, and **12** afforded corresponding olefins by way of phosphonium sulfate salts whereas sugar cyclic sulfates **21** and **22** gave anhydrosugar **23**.

Preparation of the cyclic sulfate and its reaction with nucleophiles have been known for a long time,[1] especially in the field of carbohydrate chemistry.[2] Recent works by Sharpless *et. al.* have provided an easier access to cyclic sulfates and have shown their usefulness in organic synthesis.[3] Our initial purpose of the present work was the conversion of the vicinal diol to the olefin employing the cyclic sulfate of the diol. Olefin synthesis by deoxygenation of diols is an important transformation in organic synthesis. A variety of approaches have been developed for the regio- and stereospecific deoxygenation of vicinal diols[4] since the

* To whom correspondence should be addressed.

discovery of Corey-Winter reaction.[5] In our working hypothesis, we anticipated as depicted in the Scheme1. Thus, the first step is the nucleophilic displacement of the cyclic sulfate **1** by a phosphine. Then, the resulting internal salt **2** might cyclize to an unprecedented six-membered heterocycle **3** which might further decompose to an olefin **4**, sulfur trioxide, and a phosphine oxide.



Scheme 1

Reaction of dimethyl *meso*-tartrate cyclic sulfate (**9**) with PPh_3 at 110°C in xylene gave indeed the expected *trans*-olefin **14** in 45% yield. Reaction of cyclic sulfate **10** with PPh_3 at 110°C in xylene also afforded expected *cis*-ethyl cinnamate(**17**) in 30% yield. On the other hand, treatment of dimethyl L-tartrate 2,3-cyclic sulfate (**11**) with PPh_3 in xylene, acetonitrile, or methylene chloride did not provide the expected *cis*-olefin **18** but afforded the *trans*-olefin **14**. Cyclic sulfate **12** under the similar condition also gave *trans*-olefin **15** as shown in Table 1.

The unexpected *trans* double bond in the products obtained from dialkyl L-tartrate 2,3-cyclic sulfates is probably formed by way of *threo* salt **2** which might be produced by the epimerization of the initially formed *erythro* salt **6** as shown in

Table 1. Reactions of Cyclic Sulfates with Phosphines

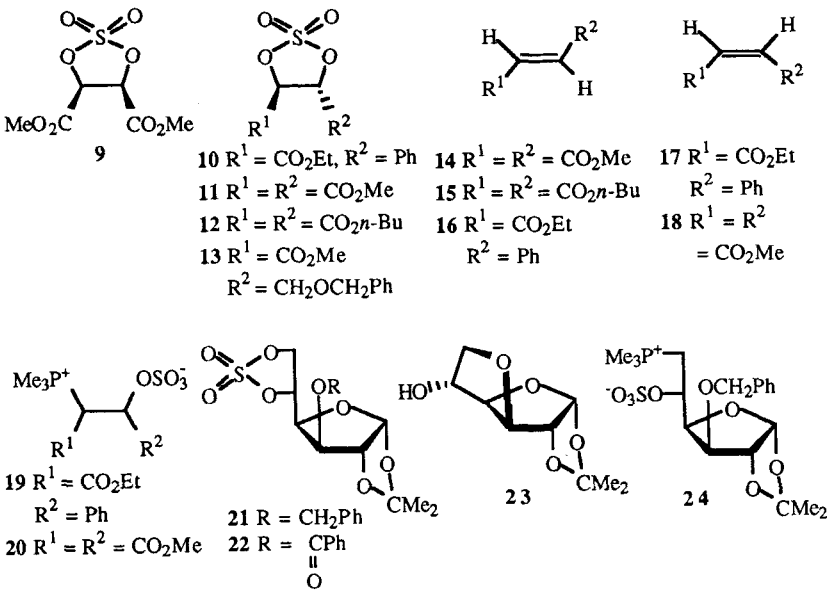
Cyclic Sulfate	Phosphine	Product	Reaction Condition		Yield,%[b]
			Solvent[a]	Temp.,°C	
9	PPh_3	**14**	xylene	110	45
10	PPh_3	**17**	xylene	110	30
11	PPh_3	**14**	xylene	110	36
11	PPh_3	**14**	CH_3CN	reflux	46
12	PPh_3	**15**	xylene	110	46
10	PMe_3	**19**	THF	0 or r.t.	87
11	PMe_3	**20**	THF	0 → r.t.	94
21	PPh_3	**23**	xylene	70	24
21	PMe_3	**24**	THF	30	89
22	PPh_3	**23**	xylene	70	43

[a]Water or methanol in parentheses indicates its presence in a small amount in the solvent.

[b]The yields are isolated ones.

Scheme 1. Salts **2** and **6** would be in rapid equilibrium through enolization since they have very acidic protons. The pathway to fumarate **4** (R^1=CO_2R) from *threo* salt **2** by way of a cyclic intermediate **3** containing *trans*-1,2-substituents would be energetically more favorable than the pathway to maleate **8**(R^1=CO_2R) from *erythro* salt **6** by way of **7** containing *cis*-1,2-substituents. The low yields of olefins are partly attributed to the formation of insoluble phosphonium sulfate salts during reaction. Prolonged reaction time, higher reaction temperature, or reaction in different solvents did not improve the yield of olefins.

Although there is no direct evidence for the existence of the heterocyclic intermediates **3** and **7**, the salts **2** and **6** were isolated and characterized by NMR.



Thus, the reaction of cyclic sulfate **10** with PMe_3 at 0°C or room temperature in THF afforded salt **19** as a white solid in 87% yield.[6] ^1H NMR spectrum of **19** clearly showed a doublet($^2J_{P,H}$=14.5Hz) at 1.90ppm for $^+PMe_3$, a doublet of doublets($J_{2,3}$=3.7Hz, $^2J_{P,H}$=19.5Hz) at 4.61ppm for H-2, and a doublet of doublets($J_{2,3}$=3.7Hz, $^3J_{P,H}$=3.1Hz) at 5.18ppm for H-3. ^{13}C NMR spectrum of **19** also showed characteristic signals for the phosphonium salt ; a doublet ($^1J_{P,C}$=53Hz) at 6.7ppm for $^+PMe_3$, a doublet($^1J_{P,C}$=51Hz) at 42.9ppm for C-2, a doublet ($^2J_{P,C}$=4Hz) at 72.6ppm for C-3, and a doublet($^2J_{P,C}$=15Hz) at 168.0ppm for C-1. The reaction of cyclic sulfate **11** with PMe_3 also afforded salt **20** in 94% yield.[7] When salt **19** was heated to 110°C in DMSO, an equal amount of *trans*- and *cis*-cinnamates **16** and **17** was produced in 40% yield. The fact that the mixture of *trans*- and *cis*-cinnamates was obtained in this reaction further confirmed the epimerization of the phosphonium salts as proposed in the reactions of cyclic

sulfates **11** and **12** with PPh_3. Salt **20** could be converted to olefin **14** as shown in Table 2. The present reaction, however, was not applicable to the cyclic sulfates of simple aliphatic diols. Thus, cyclic sulfates of cyclohexanediol and 4,5-octanediol did not react with phosphines whereas the reaction of 1,2-dodecanediol cyclic sulfate with PMe_3 afforded the phosphonium sulfate salt but the salt could not be converted to the olefin.

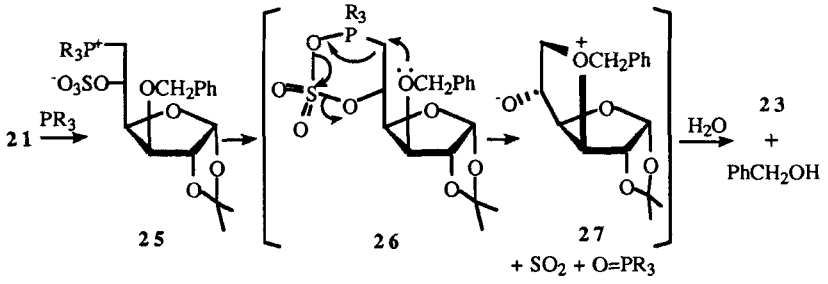
Table 2. Pyrolysis of Phosphonium Sulfate Salts

Phosphonium Sulfate	Product	Reaction Condition		Yield, %[b]
		Solvent[a]	Temp.,°C	
19	**16** + **17**(1:1)	DMSO	110	40
20	**14**	DMSO	110	20
24	**23**	xylene	65	38

[a]Water in parentheses indicates its presence in a small amount in the solvent.
[b]The yields are isolated ones.

On the other hand, the reaction of sugar cyclic sulfate **21** with PPh_3 or PBu_3 in xylene at 70°C gave unexpected anhydro sugar **23**[8] in 24% yield. Treatment of **21** with PMe_3 in THF at 30°C afforded salt **24**[9] in 89% yield. Upon warming, the salt **24** was converted to anhydrosugar **23** in 38% yield. In the reaction of sugar cyclic sulfate **22** with PMe_3 in THF, the intermediate salt could not be isolated but anhydrosugar **23** was also obtained. A plausible mechanism for the formation of **23** can be suggested as depicted in Scheme 2. Thus, the first two steps of the reaction would be same as those of other cyclic sulfates to afforded cyclic intermediate **26** by way of phosphonium sulfate **25**. In the third step, the

benzyloxy group at C-3 of **26** might participate in extrusion of SO_2 and phosphine oxide to give oxonium alkoxide **27** which might be readily converted to **23** and benzyl alcohol by hydrolysis. Although detection of SO_2 was not attempted, phosphine oxide and benzyl alcohol were isolated from the reaction mixture. The indirect evidence for the generation of SO_2 came from the fact that the reaction



Scheme 2

mixtures of cyclic sulfates **9-12** with phosphines were very acidic due to SO_3 whereas those of cyclic sulfates **21** and **22** with phosphines were almost neutral probably because volatile and insoluble SO_2 readily escaped from the reaction mixture.

REFERENCES AND NOTES

1. Fischer, G. W. ; Zimmermann, T., " Five-membered Rings containing Three Oxygen or Sulfur Atoms. In Comprehensive Heterocyclic Chemistry," Potts, K. T. Ed., Pergamon Press, Oxford, 1984; Vol. 5, pp.851-895.
2. Turvey, J. R., Advan. Carbohydr. Chem., 1965, 20, 209 ; Hough, L. ; Richardson, A. C., "Rodds Chemistry of Carbon Compounds," 2nd ed. Coffey, S. Ed., Elsevier, Amsterdam, 1967; Vol 1F, pp. 419-422.

3. Gao, Y.; Sharpless, K. B., J. Am. Chem. Soc., 1988, 110, 7538 ; Kim, B. M.; Sharpless, K. B.,Tetrahedron Lett., 1989, 30, 655 ; Lohray, B. B.; Gao, Y.; Sharpless, K. B., Tetrahedron Lett., 1989, 30, 2623 ; Oi, R.; Sharpless, K. B., Tetrahedron Lett., 1991, 32, 999.

4. Block, E., Organic Reactions, 1984, 30, 457.

5. Corey, E. J.;Winter, R. A. E., J. Am. Chem. Soc., 1963, 85, 2677.

6. Compound **19**: ^{1}H NMR(300MHz, $CDCl_3$) δ 0.81(t, J=7.5Hz, 3H), 1.90(d, $^{2}J_{P,H}$=14.5Hz, 9H), 3.78-4.02(m, 2H), 4.61(dd, J=3.7Hz, $^{2}J_{P,H}$=19.5Hz, 1H), 5.18(dd, J=3.7Hz, $^{3}J_{P,H}$=3.1Hz, 1H), 7.4(brs, 5H); ^{13}C NMR($CDCl_3$) δ 6.7(d, $^{1}J_{P,C}$=53Hz), 13.5, 42.9(d, $^{1}J_{P,C}$=51Hz), 60.5, 72.6(d, $^{2}J_{P,C}$=4Hz), 129.1, 129.3, 129.5, 129.6, 130.9, 131.0, 168.0(d, $^{2}J_{P,C}$=15Hz).

7. ^{1}H and ^{13}C NMR spectra of **20** indicated that a mixture of diastereomeric salts was produced.

8. Compound **23**: $[\alpha]_D^{24}$ +27.4°(c 0.05, H_2O), lit.[10] $[\alpha]_D^{20}$ +29°(c, 3.2, H_2O); ^{1}H NMR(300MHz, $CDCl_3$) δ 1.33(s, 3H), 1.51(s, 3H), 2.45(brs, 1H), 3.47(dd, 1H), 3.93(dd, 1H), 4.24-4.31(m, 1H), 4.50(d, J=3.9Hz, 1H), 4.62(d, J=3.6Hz, 1H), 4.77(t, 1H), 5.93(d, J=3.6Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 26.7, 27.4, 72.4, 72.5, 82.4, 85.1, 85.5, 107.0, 113.1.

9. Compound **24**: ^{1}H NMR(300MHz, $CDCl_3$) δ 1.31(s, 3H), 1.47(s, 3H), 1.55(d, $^{2}J_{P,H}$=12.8Hz, 3H), 1.84(d, $^{2}J_{P,H}$=14.3Hz, 6H), 2.55(m,1H), 2.85 (m, 1H), 4.24(d, J=3.6Hz,1H), 4.59(ABq, 2H), 4.61(d, J=3.6Hz, 1H), 4.73(t, 1H), 4.95(m, 1H), 5.92(d, J=3.6Hz, 1H), 7.31-7.35(m, 5H).

10. Lewis, B. A. ; Smith, F. ; Stephen, A. M., " Methods in Carbohydrate Chemistry," Whistler, R. L., Wolfrom, M. L.; BeMiller, J. N., Eds., Academic Press, New York, 1963; Vol II, pp. 182-183.

11. Financial support from the Korea Science and Engineering Foundation and the Organic Chemistry Research Center is gratefully acknowledged.

(Received in Japan 14 June 1993)