loading, determined from indexed X-ray powder patterns, are shown on the right-hand axis of Figure 1. There is a steady increase in unit cell volume up to the loading level where maximum SHG is observed followed by a flattening off thereafter. This shows that the NA is within the pores and that the maximum SHG signal occurs when the pores are full.

In contrast, MNA in ALPO-5 shows nearly complete loss of SHG on inclusion. A 13 wt % MNA sample shows SHG of 0.66. Only at higher loadings, when MNA is outside the pores of the zeolite as shown by X-ray powder diffraction, does the SHG increase. In all other respects (color, stability, unit cell volume increase with loading) the NA and MNA samples are very similar.

ALPO-5 thus switches NA on and MNA off. This is a dramatic demonstration of how inclusion can influence nonlinear optical properties. It is clear that subtle size, shape, and symmetry effects are at play. The extra size of the methyl group in MNA must restrict its orientation in the ALPO-5 channels in ways which prohibit the required bulk dipolar alignment. These restrictions must be missing for NA. The acentric structure of ALPO-5 is an important factor in switching on the SHG of NA since the centrosymmetric hosts did not have the same effect.

A more thorough look at loading levels, other sorbate–host combinations including other acentric hosts, and further structural characterization is underway.

Acknowledgment. This work was supported by the Office of Naval Research under contract Grant N00014-87-K0457.

Direct α-Phosphoryloxylation of Ketones and Phosphoryloxylactonization of Pentenoic Acids with [Hydroxy((bis(phenyloxy)phosphoryl)oxy)iodo]benzene

Gerald F. Koser,* Jayant S. Lodaya, Dale G. Ray, III, and Pandurang B. Kokil

Department of Chemistry, The University of Akron Akron, Ohio 44325

Received January 11, 1988

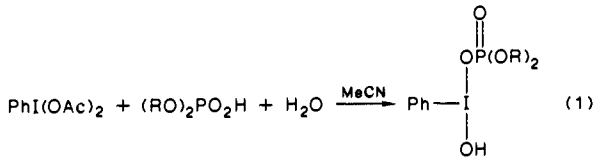
The ability of [hydroxy(tosyloxy)iodo]benzene (**1**) to introduce the tosylate ligand into ketones, alkenes, and alkenoic acids to give α-tosyloxy ketones,[1] *vic*-ditosyloxyalkanes,[2] and tosyloxy lactones[3] prompted us to investigate the synthesis of reagents analogous to **1** with iodine(III)-bound phosphate ligands[4] and to

PhI(OH)OTs (**1**) RC≡COP(O)(OEt)$_2$ (**2**)

RC≡C–I$^+$–Ph, $^-$O$_2$P(OEt)$_2$ (**3**)

explore their efficacy for the preparation of phosphate esters. Precedent for the phosphoryloxylation of carbon via hypervalent iodine species has recently been provided by Stang and his coworkers who described the synthesis of the first alkynyl phosphates **2** from alkynyl(phenyl)iodonium phosphates **3**.[5] We now report the preparation of [hydroxy((bis(phenyloxy)phosphoryl)oxy)-iodo]benzene (**4a**) and a preliminary study of its reactions with ketones and alkenoic acids.

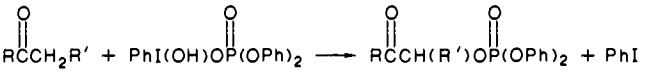
[Hydroxy((bis(phenyloxy)phosphoryl)oxy)iodo]benzene was made from (diacetoxyiodo)benzene and diphenyl phosphate in acetonitrile spiked with water (eq 1) and appropriately characterized.[6] In one preparation, a mixture of PhI(OAc)$_2$ (60 mmol), (PhO)$_2$PO$_2$H (61 mmol), and H$_2$O (120 mmol) in MeCN (150 mL), after ca. 4 h at room temperature and refrigeration, gave a 90% yield of **4a**.



(1)

4a: R = Ph
b: R = PhCH$_2$

Various ketones were converted directly by **4a** into ketol phosphates **5**, compounds of interest as sugar analogues[7] (eq 2).

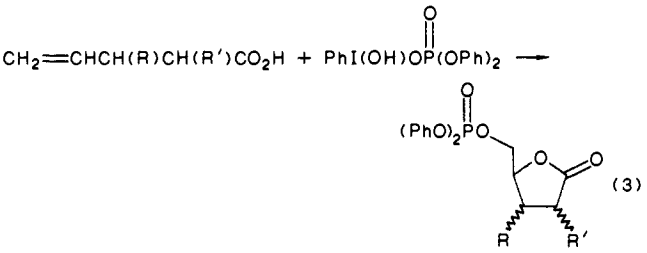


5a: R = Ph, R′ = H
b: R = Me, R′ = H
c: R = cyclopropyl, R′ = H
d: R, R′ = -(CH$_2$)$_4$-
e: R = Ph, R′ = PhCO (2)

For example, a mixture of **4a** and acetophenone in MeCN was heated and concentrated. Treatment of the residual oil (in CH_2Cl_2) with H_2O and 5% $NaHCO_3$ and removal of volatile impurities (e.g., PhI, PhCOMe) gave α-((bis(phenyloxy)-phosphoryl)oxy)acetophenone (**5a**) in 59% yield. Similar reactions of acetone, cyclopropyl methyl ketone, cyclohexanone, and dibenzoylmethane with **4a** gave the ketol phosphates **5b–e**; conditions and yields are summarized in Table I.

In addition to characteristic C=O and P=O absorptions in the infrared, the α-carbon–phosphate linkage produces NMR resonances which are particularly diagnostic of the ketol phosphate structures; i.e., the α-hydrogens are deshielded, and both the α-hydrogens and α-carbon are coupled with phosphorus. Selected spectral data for **5a–e** are given in Table II.

4-Pentenoic acids react with **4a** to give 5-(bis(phenyloxy)-phosphoryl)oxy-4-pentanolactones **6** (eq 3.) For example, a



(3)

6a: R = R′ = H
b: R = H, R′ = Me
c: R = OH, R′ = H

solution of 4-pentenoic acid and **4a** in CH_2Cl_2 was stirred at room temperature (2 h, 40 min), diluted with CH_2Cl_2, washed (H_2O, 5% $NaHCO_3$), dried, and concentrated. Crystallization of the residual oil gave crude **6a** in 55% yield. Similar treatment of 2-methyl-4-pentenoic acid with **4a** gave **6b** as a mixture (ca. 1.2 to 1.4:1) of diastereomers (NMR analysis).

The structural relationship of **6a** and **6b** to the pentofuranose-5-phosphates suggested a study of the action of **4a** on 3-hydroxy-4-pentenoic acid.[8] 3-Hydroxy-4-pentanolactone **6c**

(1) Koser, G. F.; Relenyi, A. G.; Kalos, A. N.; Rebrovic, L.; Wettach, R. H. *J. Org. Chem.* **1982**, *47*, 2487.
(2) Rebrovic, L.; Koser, G. F. *J. Org. Chem.* **1984**, *49*, 2462.
(3) Shah, M.; Taschner, M. J.; Koser, G. F.; Rach, N. L. *Tetrahedron Lett.* **1986**, *27*, 4557.
(4) "*o*-Iodosophenylphosphoric acid" and its methyl ester, heterocyclic iodine(III) phosphates, have been reported, but their chemistry has been little explored, see: Leffler, J. E.; Jaffe, H. *J. Org. Chem.* **1973**, *38*, 2719.
(5) Stang, P. J.; Boeshar, M.; Lin, J. *J. Am. Chem. Soc.* **1986**, *108*, 7832.

(6) White solid; needles from MeCN [mp (uncorrected) 102–105 °C]; IR (CH_2Cl_2) 3399 cm^{-1} br, OH); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.95–7.14 (m, 6 H), 7.14–7.34 (m, 6 H), 7.35–7.43 (apparent t with fine structure, 1 H), 7.75–7.95 (d, 2 H), OH not observed; ^{13}C NMR ($CDCl_3$) δ 120.2 (d, J_{CP} = 5.1 Hz), 124.0 (s), 124.1 (s), 129.4 (s), 130.8 (s), 131.3 (d, J_{CP} = 6.5 Hz), 132.3 (s), 151.8 (d, J_{CP} = 7.3 Hz); ^{31}P NMR ($CDCl_3$) δ −12.4 (s); Anal. Calcd for $C_{18}H_{16}O_5IP$: C, 45.98; H, 3.43; P, 6.59. Found: C, 45.84; H, 3.52; P, 7.08; 6.53 (second sample); molecular weight, calcd 470.2, found (iodometric titration) 473.6.

0002-7863/88/1510-2987$01.50/0

Table I. Conditions and Yields for the Preparation of Ketol Phosphates and Phosphoryloxy Lactones with **4a**[a]

reactant (mmol)	solvent (mL)	time (temp)	product (% yield)[c-e]
PhCOMe (10.4)	MeCN (45)	3 h, 20 min (reflux)	**5a** (59)
MeCOMe (ca 135; 10 mL)	MeCN (40)	30 min (reflux)	**5b** (81)
cyclopropyl methyl ketone (12.1)	MeCN (40)	2 h, 56 min (reflux)	**5c** (59)
cyclohexanone (10.5)	CH_2Cl_2 (35)	7 h, 35 min (room)	**5d** (62)
$CH_2(COPh)_2$ (5.0)	CH_2Cl_2 (40)	15 min (room)	**5e** (90)
$CH_2=CH(CH_2)_2CO_2H$ (7.8)	CH_2Cl_2 (40)	2 h, 40 min (room)	**6a** (55)
$CH_2=CHCH_2CH(Me)CO_2H$ (6.7)	CH_2Cl_2 (40)	8 h, 43 min (room)	**6b** (64)
$CH_2=CHCH(OH)CH_2CO_2H$ (15.0)[b]	CH_2Cl_2 (45)	24 h (room)	**6c** (12.5)

[a] **4a** (5.04 mmol). [b] **4a** (15.0 mmol). [c] Yields rounded off to nearest percent. [d] The phosphates gave satisfactory (±0.4%) elemental (C, H) analyses, sometimes after a second attempt, except **5e** which was a bit off on carbon (calcd. 68.64, found 69.17, 69.00, same sample). [e] **5a**, **5b**, and **6h** were oils with some coloration; **5c**, **5d**, **5e**, **6a**, and **6c** were solids.

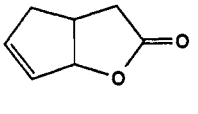
Table II. Selected Spectral Data for Ketol Phosphates and Phosphoryloxy Lactones

	IR[a] (cm^{-1}) P=O, C=O, OH	NMR[b]		
		300 MHz ^1H[c] (mult, J_{HP})	^{13}C[e,f] (mult, J_{CP})	^{31}P[g] (mult, J_{PH})
5a	1292, 1709	5.45 (d, 10.1)	69.8 (d, 5.7), 191.1 (d, 5.7)	−11.6 (t, 10.2)
5b	1292, 1740	4.70 (d, 9.5)	71.6 (d, 6.2), 201.5 (d, 6.6)	−12.2 (t, 9.4)
5c	1296, 1724	4.87 (d, 9.5)	71.7 (d, 6.5), 203.4 (d, 6.8)	−12.2 (t, ca. 9.3)
5d	1285, (1304, sh), 1732	4.91–5.05 (m)	81.3 (d, 6.2), 203.5 (d, 4.1)	−12.7 (d, 8.3)
5e	1296, 1682, 3453	6.79 (d, 8.8)	84.0 (d, 6.3), 190.3 (d, 5.2)	−13.0 (d, 8.5)
6a	1292, 1775	4.22–4.36 (m, 1 H) 4.36–4.51 (m, 1 H)	77.3 (d, 8.0), 176.2 (s)	−12.0 (s)[h]
6b	1292, 1775	4.26–4.34 (m, 1 H) 4.38–4.51 (m, 1 H)[d]	74.8 (d, 8.0), 75.3 (d, 7.8) 178.3 (s), 179.1 (s)	−11.98 (s), −12.04 (s)[h]
6c	1290, 1783, 3540	4.2–4.7 (m's, 5 H)	81.3 (d, 6.3), 174.8 (s)	−10.4 (s)[h]

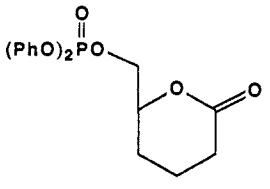
[a] Neat oils (**5a**, **5b**, **6b**); solid films (**5c**, **5d**, **6a**); CH_2Cl_2 (**5e**); Nujol (**6c**). [b] Solvent was $CDCl_3$ for all NMR spectra; chemical shifts given in ppm and coupling constants given in Hz. [c] α-Hydrogens of **5a–e**; C-5 hydrogens of **6a** and **6b**; C-3, C-4, C-5, and O–H hydrogens of **6c**. [d] D_2O added. [e] Chemical shifts relative to $CDCl_3$ at 77.0 ppm. [f] α-Carbon and carbonyl carbon. [g] Referenced to a sample of 85% H_3PO_4 (sealed capillary) in $CDCl_3$. [h] Proton-decoupled spectra (coupled spectra exhibit poorly resolved multiplets).

was obtained, apparently as a single diastereomer (^1H, ^{13}C, ^{31}P NMR), but even the best yield was low (12.5%). Unfortunately, the C-3, C-4, and C-5 hydrogens give rise to a set of complex multiplets, and the stereochemistry of **6c** has not yet been assigned. We note, in this context, that the bromolactonization of 3-hydroxy-4-pentenoic acid has been reported to give *threo*-5-bromo-3-hydroxy-4-pentanolactone (57% yield) free of the erythro diastereomer.[9] Clarification of the stereochemistry of **6c** and efforts to improve the yield with -OH protected 3-hydroxy-4-pentenoic acid will be reported later.

When 2-cyclopentene-1-acetic acid was treated with **4a**, the unsaturated lactone **7** was isolated in ca. 50% yield[10] consistent with the behavior of **1** with the same acid.[3] Efforts to prepare the six-membered lactonol phosphate **8** from 5-hexenoic acid and **4a** have been only partially successful; the spectra (IR, PMR) of the crude product are indicative of **8**, but purification has not been achieved, and the material appears to be somewhat unstable.



7



8

Finally, we have also prepared [hydroxy((bis(benzoyloxy)-phosphoryl)oxy)iodo]benzene (**4b**) (88% yield) and note it reacts similarly to **4a** with ketones and pentenoic acids.[11]

Acknowledgment. We thank the Dow Chemical Company for partial financial support.

(7) Ramirez and his co-workers have prepared a variety of α-phosphoryloxycarbonyl compounds, ketol phosphates among them, from 1,3,2-dioxaphospholenes and 1,3,2-dioxaphosphole-2-oxides, see: (a) Ramirez, F.; Desai, N. B. *J. Am. Chem. Soc.* **1960**, *82*, 2652. (b) Swank, D.; Caughlan, C. N.; Ramirez, F.; Madan, O. P.; Smith, C. P. *J. Am. Chem. Soc.* **1967**, *89*, 6503. (c) Ramirez, F.; Kugler, H. J.; Patwardhan, A. V.; Smith, C. P. *J. Org. Chem.* **1968**, *33*, 1185. (d) Ramirez, F.; Bhatia, S. B.; Bigler, A. J.; Smith, C. P. *J. Org. Chem.* **1968**, *33*, 1192. (e) Ramirez, F.; Glaser, S. L.; Bigler, A. J.; Pilot, J. F. *J. Am. Chem. Soc.* **1969**, *91*, 496. (f) Ramirez, F.; Bauer, J.; Telefus, C. D. *J. Am. Chem. Soc.* **1970**, *92*, 6935. (g) Ramirez, F.; Maracek, J. F.; Ugi, I. *J. Am. Chem. Soc.* **1975**, *97*, 3809. (h) Ramirez, F.; Maracek, J. F. *Synthesis* **1985**, 449.

(8) This experiment was proposed by Professor Stephen D. Darling.

(9) Nakaminami, G.; Shioi, S.; Sugiyama, Y.; Isemura, S.; Shibuya, M.; Nakagawa, M. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 2624.

(10) Minor impurities were present (NMR analysis).

(11) Preliminary studies with acetone, cyclohexanone, 4-pentenoic acid, and 2-methyl-4-pentenoic acid have been conducted. Thus far, only the dibenzyl phosphate of acetone has been obtained "analytically pure" (i.e., ±0.4% C, H).

Corner Attack on Cyclopropane by Deuteron and Mercuric Ions: An Example of Stereospecific Formation and Capture of Unsymmetrical Corner-Deuteriated/Mercurated Cyclopropane Intermediates

James M. Coxon,* Peter J. Steel,* and Barry I. Whittington

Department of Chemistry, The University of Canterbury Christchurch, New Zealand

Merle A. Battiste*

Department of Chemistry, University of Florida Gainesville, Florida 32611

Received May 18, 1987

The regiospecificity and stereochemistry of electrophilic carbon–carbon bond cleavage in cyclopropanes has been the subject of considerable investigation and speculation.[1] In general two possible reaction trajectories for electrophilic attack on cyclo-

(1) (a) Coxon, J. M.; Battiste, M. A. In *The Chemistry of the Cyclopropyl Group*; Rappoport, Z., Ed.; J. Wiley and Sons: London, 1987; Chapter 6. (b) Lambert, J. B.; Schulz, W. J.; Mueller, P. H.; Kobayashi, K. *J. Am. Chem. Soc.* **1984**, *106*, 792. (c) Battiste, M. A.; Coxon, J. M. *Tetrahedron Lett.* **1986**, *27*, 517. (d) Wiberg, K. B.; Kass, S. R. *J. Am. Chem. Soc.* **1985**, *107*, 988.

0002-7863/88/1510-2988$01.50/0