a 90% yield of 4a.

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.

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

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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 lactones³ prompted us to investigate the synthesis of reagents analogous to 1 with iodine(III)-bound phosphate ligands⁴ and to

PhI(OH)OTs
$$RC \equiv COP(O)(OEt)_2$$

 1 2
 $RC \equiv C-I^+-Ph, -O_2P(OEt)_2$
 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)₂PO₂H (61 mmol), and H₂O (120 mmol) in MeCN (150 mL), after ca. 4 h at room temperature and refrigeration, gave

$$PhI(OAc)_{2} + (RO)_{2}PO_{2}H + H_{2}O \xrightarrow{MeCN} Ph - I \qquad (1)$$

$$Ha: R = Ph$$

$$b: R = PhCH_{2}$$

Various ketones were converted directly by 4a into ketol phosphates 5, compounds of interest as sugar analogues⁷ (eq 2).

$$\begin{array}{c} 0 \\ RCCH_2R' + PhI(OH)OP(OPh)_2 & \longrightarrow \\ RCCH(R')OP(OPh)_2 + PhI \\ \hline \textbf{5a:} R = Ph, R' = H \\ \textbf{b:} R = Me, R' = H \\ \textbf{c:} R = cyclopropyl, R' = H \\ \textbf{d:} R, R' = -(CH_2)_4 - \\ \textbf{e:} R = Ph, R' = PhCO \qquad (2) \end{array}$$

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% NaHCO₃ 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



solution of 4-pentenoic acid and 4a in CH_2Cl_2 was stirred at room temperature (2 h, 40 min), diluted with CH₂Cl₂, washed (H₂O, 5% NaHCO₃), 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

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⁽⁶⁾ White solid; needles from MeCN [mp (uncorrected) 102–105 °C]; IR (CH₂Cl₂) 3399 cm⁻¹ br, OH); ¹H NMR (300 MHz, CDCl₃) 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; ¹³C NMR (CDCl₃) 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); ³¹P NMR (CDCl₃) δ –12.4 (s); Anal. Calcd for C₁₈H₁₅O₃IP: C, 45.98; H, 3.43; P, 6.59. Found: C, 45.84; H, 3.52; P, 7.09; 6 for (c, and c, and b) and both product which where the other of 20.2 found (c, and c, and c, and c, and c) an P, 7.08; 6.53 (second sample); molecular weight, calcd 470.2, found (iodometric titration) 473.6.

Table I.	Conditions and	Yields for the	Preparation of Ke	tol Phosphates and	Phosphoryloxy	Lactones with 4a ^a

1			
 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)
$\dot{C}H_{2}(COPh)_{2}(5.0)$	CH ₂ Cl ₂ (40)	15 min (room)	5e (90)
$CH_{2} = CH(CH_{2})_{2}CO_{2}H(7.8)$	$CH_{2}Cl_{2}$ (40)	2 h, 40 min (room)	6a (55)
$CH_2 = CHCH_2CH(Me)CO_2H$ (6.7)	$CH_{2}Cl_{2}$ (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)

^a4a (5.04 mmol). ^b4a (15.0 mmol). ^cYields rounded off to nearest percent. ^dThe 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). *5a, 5b, and 6b were oils with some coloration; 5c, 5d, 5e, 6a, and 6c were solids.

Table II.	Selected	Spectral	Data	for	Ketol	Phosphates	and	Phosphoryloxy	Lactones
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	IR^{a} (cm ⁻¹) P=0.	NMR ^b					
	С=0, ОН	300 MHz ¹ H ^c (mult, J _{HP})	$^{13}C^{ef}$ (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); CH₂Cl₂ (5e); Nujol (6c). ^bSolvent was CDCl₃ for all NMR spectra; chemical shifts given in ppm and coupling constants given in Hz. ϵ_{α} -Hydrogens of **5a**-e; C-5 hydrogens of **6a** and **6b**; C-3, C-4, C-5, and O-H hydrogens of **6c**. ⁴D₂O added. *Chemical shifts relative to CDCl₃ at 77.0 ppm. f_{α} -Carbon and carbonyl carbon. *Referenced to a sample of 85% H₃PO₄ (sealed capillary) in CDCl₃. ^hProton-decoupled spectra (coupled spectra exhibit poorly resolved multiplets).

was obtained, apparently as a single diastereomer (¹H, ¹³C, ³¹P 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 3hydroxy-4-pentenoic acid has been reported to give threo-5bromo-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-4pentenoic acid will be reported later.

When 2-cyclopentene-1-acetic acid was treated with 4a, the unsaturated lactone 7 was isolated in ca. 50% yield¹⁰ 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.



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

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

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(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

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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-

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