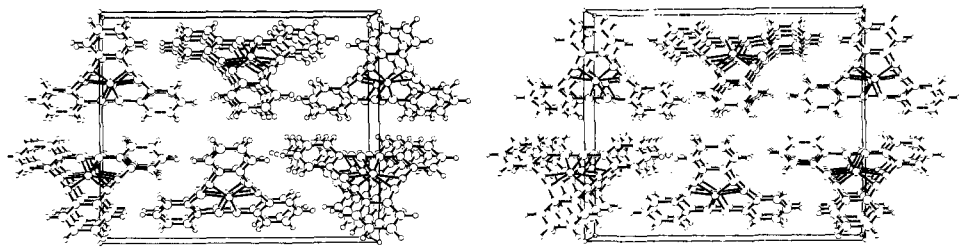

Figure 2. ORTEP stereoview of $Ni(C_{24}H_{12})$ along the *c* axis with the *b* axis to the right. The ellipsoids are drawn at the 50% probability level except for the hydrogen atoms which are drawn arbitrarily small for clarity.

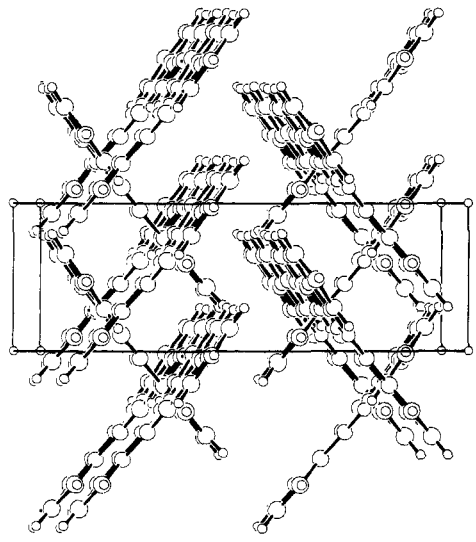

Figure 3. ORTEP packing diagram along the *b* axis with the *a* axis to the right.

Crystals suitable for X-ray diffraction studies were obtained on recrystallization from benzene.[21] Intensity data were collected in air on a Syntex $P2_1$ single-crystal diffractometer. The structure was solved and refined to a final $R_w = 0.044$ ($I \geq 3\sigma(I)$).[22] The molecule is nearly planar with Ni-acetylenic-carbon distances averaging 1.958 (5) Å as compared to 1.899 (19) Å in Ni(*t*-BuN≡C)$_2$(PhC≡CPh).[23] The acetylene linkages are distorted from linearity with C—C≡C angles averaging 173.8 (9)° compared to 178.3 (9)° for the free cyclyne[24] and 148.6 (14)° for Ni(*t*-BuN≡C)$_2$(PhC≡CPh). The distortion from linearity is the least that has been reported for any π-bound acetylene complex and may be imposed by the benzo rings. The acetylenic carbon–carbon bond length in the complex is 1.240 (10) Å compared with 1.192 (2) Å in the free cyclyne and 1.284 (16) Å for Ni(*t*-BuN≡C)$_2$(PhC≡CPh). The ORTEP packing diagram along the *c* axis (Figure 2) shows a slipped-stack arrangement with the benzo groups eclipsed. A view along the *b* axis (Figure 3) shows a herringbone pattern with an interplanar distance of 3.37 (1) Å. The free cyclyne is also slipped stacked[24] with an interplanar spacing of 3.29 Å and the benzo groups staggered.

Further synthetic work will center upon using modified ligands and different metal centers as well as controlled oxidation and reduction. Preliminary reactions with I_2 with TCNQ as oxidizing agents have given several solid phases that are presently under study. Electrochemical, conductometric, spectral, and theoretical studies are in progress.

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Supplementary Material Available: Tables of data collection and structure solution details, atomic positional and thermal parameters, and structure factors (12 pages). Ordering information is given on any current masthead page.

(21) Crystallographic data: Space group, $Pna2_1$, $a = 15.518$ (3) Å, $b = 18.761$ (4) Å, $c = 5.375$ (1) Å; $\rho_{calcd} = 1.528$; $\rho_{obsd} = 1.54$; $Z = 4$; FW = 359.07. The intensity data were collected from $3.0 \leq 2\theta \leq 55.0$. Refinement to convergence on the 848 independent reflections, $I \geq 3\sigma(I)$, resulted in final isotropic $R = 0.046$ and $R_w = 0.044$.

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Stereochemical Course of Phosphoryl Transfer Reactions of P^1,P^1-Disubstituted Pyrophosphate in Aprotic Solvent. A Model for the Enzyme-Catalyzed "Dissociative" Phosphoryl Transfer

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The evidence in favor of a monomeric metaphosphate intermediate in the reactions of monosubstituted phosphates appears to be persuasive.[1] However, recent stereochemical studies[1,2] on nucleophilic displacement reactions of phosphate monoesters have demonstrated that they occur with inversion of configuration in *protic* solvents, which argues against a "free" metaphosphate in these instances. A considerable amount of the direct evidence for the intermediacy of monomeric metaphosphate has been obtained in organic solvents (the three-phase test,[3] Conant and Swan fragmentation,[4] phosphorylation of hindered alcohols[5]). It remains a significant possibility that a metaphosphate-like intermediate may have a longer lifetime in organic solvents. We report here one of the first determinations of the stereochemical course of a phosphoryl transfer reaction in an organic solvent. A chiral [$^{16}O,^{17}O,^{18}O$]pyrophosphate derivative has been used to determine the stereochemical course of the phosphoryl transfer reaction of a P^1,P^1-disubstituted pyrophosphate. This reaction may represent a good model for the hypothetical enzyme-catalyzed "dissociative" phosphoryl transfer, particularly since such enzyme-catalyzed reactions often involve a pyrophosphate phosphoryl donor.

The dianions of P^1,P^1-disubstituted pyrophosphates have been shown to be extremely reactive[6] as compared to the corresponding mono-, P^1,P^2-di-, and trisubstituted pyrophosphates. This reactivity has been explained in terms of a facile dissociative decomposition to give a metaphosphate intermediate, Scheme Ia. The study

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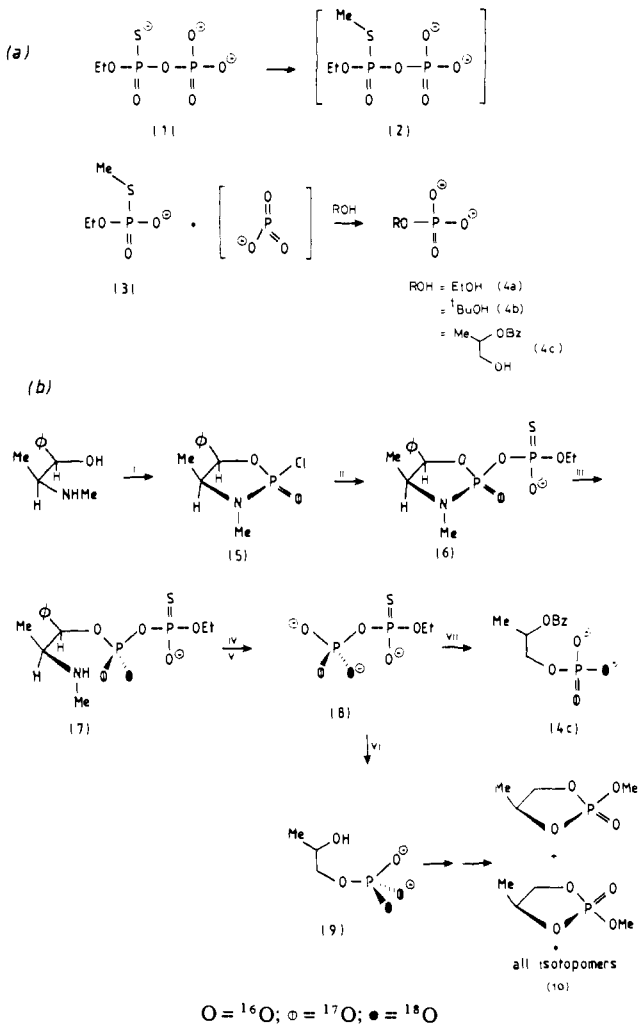
Scheme I



$O = {}^{16}O$; $\oplus = {}^{17}O$; $\bullet = {}^{18}O$

[a] Reagents: (i) $P^{17}OCl_3/Et_3N$; (ii) $EtOPSO_2^{2-}2Bu_3NH^+$; (iii) $H_2{}^{18}O/CF_3CO_2H$; (iv) Me_3SiI; (v) *i*PrOH/Et_3N; (vi) alkaline phosphatase/propane-1,2-diol; (vii) MeI/2-*O*-benzylpropane-1,2-diol.

of such systems has been limited by their extreme lability, and to date few methods for in situ generation of these species have been reported.

P^1-*O*-Alkyl-P^1-thiopyrophosphates can be synthesized by a variety of routes. Treatment of the tris(trialkylammonium) salt of P^1-*O*-ethyl-P^1-thiopyrophosphate (**1**) with methyl iodide in ethanol generates P^1-*O*-ethyl-*S*-methyl-P^1-thiopyrophosphate in situ which decomposes spontaneously to give *O*-ethyl-*S*-methyl thiophosphate (**3**) and ethyl phosphate (**4a**) as the only products. The dianion **2** will phosphorylate hindered alcohols such as *tert*-butyl alcohol and in competitive experiments with *tert*-butyl alcohol and ethanol (1:1) *tert*-butyl phosphate (**4b**) is produced in good yield, consistent with a dissociative reaction involving a metaphosphate-like intermediate.[5] Furthermore, of relevance to the stereochemical studies, the phosphorylating species can be trapped by 2-*O*-benzyl-(*S*)-propane-1,2-diol to give **4c**, Scheme I.[7]

To study the stereochemical course of the phosphoryl transfer reaction requires a route to P^1-*O*-ethyl-P^1-thio[P^2-^{16}O,^{17}O,^{18}O]-pyrophosphate (**8**). The synthesis of **8** is shown in Scheme Ib and is an adaptation of the published route.[8] The presence of sulfur

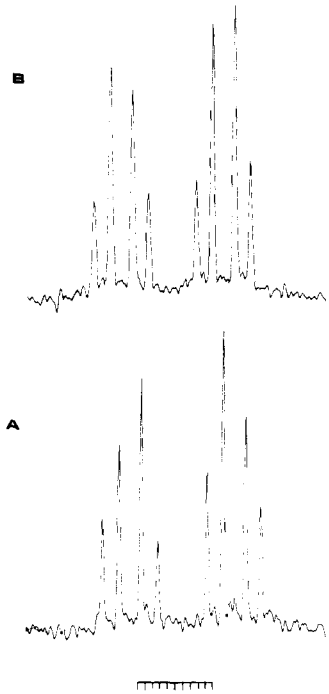


Figure 1. ^{31}P NMR spectra (1 Hz per division) of (A) the product from in-line ring closure and methylation of 1-[^{16}O,^{17}O,^{18}O]phospho-(*S*)-propane-1,2-diol obtained by phosphoryl transfer reaction from P^1-*O*-ethyl-P^1-thio-P^2-(R_p)-[^{16}O,^{17}O,^{18}O]pyrophosphate (**8**) to (*S*)-propane-1,2-diol catalyzed by alkaline phosphatase and (B) the product from in-line ring closure and methylation of 1-[^{16}O,^{17}O,^{18}O]phospho-(*S*)-propane-1,2-diol obtained by phosphoryl transfer reaction from P^1-*O*-ethyl-P^1-*S*-methyl-P^2-(R_p)-[^{16}O,^{17}O,^{18}O]thiopyrophosphate to 2-*O*-benzyl-(*S*)-propane-1,2-diol in dichloromethane. The upfield resonances are the anti isotopomers of **10** and the downfield resonances the syn. The spectra were obtained on a Bruker AM-300 instrument at 121.5 MHz with a deuterium lock and broad-band decoupling: spectral width 1300 Hz; acquisition time 6.21 s; pulse width 10 μs; number of transients 8000; Gaussian multiplication (Gaussian broadening 0.1 Hz, line broadening −0.3 Hz); Fourier transformed in 32 K.

in the thiophosphoryl moiety of **7** prevents hydrogenolysis; however, this can be overcome by the use of trimethylsilyl iodide which can selectively remove the benzylic group without removal of the ethyl ester on the thiophosphoryl portion of **8**. This is achieved without attendant stereochemical implications at phosphorus.

Although the absolute configuration of the isotopically chiral phosphorus in **8** follows from the synthesis, there is no secure precedent for isotopic synthesis via intermediates such as **6**. The absolute configuration and the enantiomeric excess of the P^1-*O*-ethyl-P^1-thio[P^2-^{16}O,^{17}O,^{18}O]pyrophosphate (**8**) was independently established by transfer of the isotopically labeled phosphoryl portion of (*S*)-propane-1,2-diol stereospecifically with retention of configuration by using alkaline phosphatase.[9] Chiral analysis of the [^{16}O,^{17}O,^{18}O]phospho-(*S*)-propane-1,2-diol was achieved by cyclization and methylation followed by analysis of the isotopomers of **10** by high-field ^{31}P NMR spectroscopy as previously described by Knowles et al.[10] (Figure 1A). The isotopic chirality of the thiopyrophosphate **8** was thus established to be ≥80% R_p at phosphorus.[11]

(7) The characterization of the reactivity of this system will be published elsewhere.

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(11) The predicted spectra were calculated on the basis of the known isotopic compositions of the water used in the synthesis together with the isotopic content of the thiopyrophosphate and phosphopropane-1,2-diol. Allowances were made for the following: (i) the 2-*O*-benzyl-(*S*)-propanediol was only 74% optically pure; (ii) the cis isomer of **6** contained ca. 12% of the trans isomer, which could not be separated. It is apparent that the latter does *not* arise from a corresponding amount of trans isomer in **5** but arises through epimerization at phosphorus during the reaction. (iii) In the alkaline phosphatase reaction the ratio of 1- to 2-phosphopropane-1,2-diol was 10:1.

Treatment of the tris(diisopropylammonium) salt of **8** (0.4 mmol) in dichloromethane (10 mL) with methyl iodide (1 mmol) at room temperature in the presence of 2-*O*-benzyl-(*S*)-propane-1,2-diol (8-fold excess) gave [^{16}O,^{17}O,^{18}O] isotopically labeled 2-*O*-benzyl-1-phospho-(*S*)-propanediol (**4c**) in ca. 50% yield. The stereochemical analysis of the resulting 1-[^{16}O,^{17}O,^{18}O]phospho-(*S*)-propane-1,2-diol following removal of the benzyl group by hydrogenolysis is shown in Figure 1B. The pattern expected for total inversion of configuration at phosphorus can be predicted on the basis of the usual assumptions.[11] Comparison of the two spectra in Figure 1 clearly shows that the phosphoryl transfer from P^1,P^1-disubstituted pyrophosphates to alcohols in *aprotic* solvents must proceed with considerable *racemization* of configuration at phosphorus. The amount of phosphoryl transfer proceeding with *retention* of configuration required to account for the observed ratios appears to be ca. 35% which would correspond to ca. 70% proceeding through a pathway involving *racemization*. The excess of the S_p configuration (ca. 30%) at phosphorus would arise from phosphoryl transfer occurring with inversion of configuration.

The observation that the phosphoryl-transfer reaction for which there is good evidence in favor of a metaphosphate-like intermediate occurs with significant racemization of configuration at phosphorus may indicate a relatively "free" metaphosphate but could also accord with a preassociation mechanism[1,2,12] if the nucleophile is not constrained to approach in line with the leaving group in a preassociation reaction. The contrast of this result with the previous studies in aqueous methanol may indicate a significant difference in reactivity in protic and aprotic solvents. Furthermore, it should be stressed that these studies have been conducted in comparatively dilute solution of both metaphosphate precursor and trap.

Acknowledgment. This work was supported by a grant from the S.E.R.C.

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Direct Observation of a Photochemically Produced Dienol: Evidence for a Noncatalyzed Reketonization Pathway Unavailable to Simple Enols[1,2]

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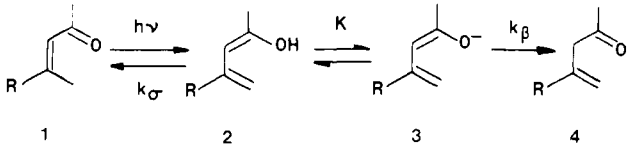
Chemical trapping studies have shown[3] that ultraviolet light irradiation of α,β-unsaturated ketones such as **1a** yields a *Z* dienol (e.g., **2a**). In the absence of a trap **2a** reverts to **1a** so that the ketone appears to be photochemically inert, as do aromatic ketones such as **5** which produce[4] transient photoenols **6a** and **6b**. Generation of **2a** in the presence of a base[5] produces the dienolate **3a** which can be reprotonated at carbon to yield the β,γ-unsaturated isomer **4a**. It has been proposed[5,6] by analogy[4] with the aromatic systems such as **6** that the noncatalyzed reketonization pathway of **2a** leading exclusively to **1a** is a 1,5-sigmatropic hydrogen shift occurring from the syn conformer of **2a**. This paper reports the results of a study in which the *Z* dienols were generated

Scheme I



a R = Me
b R = t-Bu

from **1a** and **1b** and the decays of the corresponding dienolates were monitored by using the technique of flash photolysis, thus enabling an estimate to be made of the rates of the noncatalyzed and base-catalyzed processes for reketonization and also of the p*K*'s of the dienols.

Flash photolysis[7] of **1a** and **1b** in basic aqueous solution produced transient species with absorption maxima at 290 nm, assigned by analogy with the spectra of enolates[8] to the dienolate chromophore. First-order decay of the transients was observed; the rate constants increased with increasing pH and were too small for the transients to be assigned to the triplet excited states of the ketones. The initial intensities of the transients' absorptions declined as the pH was lowered and no absorption was seen below pH 9.5. These results are consistent with the generation of a dienol which rapidly equilibrates during the lamp flash with a dienolate; the observed initial intensities of the transients reflect the proportion of dienol and dienolate present at equilibrium, and the variation of the decay rate constant reflects competition between the processes designated k_σ (noncatalyzed reketonization of the dienol) and k_β (protonation of the dienolate by water) in Scheme I.

It can be shown[9] for the system in Scheme I that the dienolate **3** should decay according to eq 1, where $[\mathbf{2}]^0$ is the initial concentration of the dienol prior to equilibration with the dienolate, and *K* is the dienol–dienolate equilibrium constant. The parameter λ is defined by eq 2. If equilibration of the dienol with the dienolate is rapid relative to K_β and k_σ, λ corresponds to decay of the dienolate and dienol with a common lifetime whose magnitude is governed by the proportions of the dienol and dienolate present. This is determined by the pH of the medium. At higher pH eq 2 reduces to eq 3; thus measurement of λ as a function of $[H^+]$ at high pH allows an estimate of the values of *K* and k_β. Once *K* is known, k_σ can be determined by using eq 4, which is obtained from eq 2 by the substitution $d = K/(K + [H^+])$.

$$[\mathbf{3}] = \frac{K[\mathbf{2}]^0}{K + [H^+]} e^{-\lambda t} \quad (1)$$

$$\lambda = k_\beta \frac{K}{K + [H^+]} + k_\sigma \frac{[H^+]}{K + [H^+]} \quad (2)$$

at low $[H^+]$

$$\lambda = \frac{k_\beta K}{K + [H^+]} \quad (3)$$

at any $[H^+]$

$$\lambda = (k_\beta - k_\sigma)d + k_\sigma \quad (4)$$

(1) Contribution number 349 from The Photochemistry Unit, the University of Western Ontario.

(2) Financial support was provided by Imperial Oil Limited, the Academic Development Fund of the University of Western Ontario, and the Natural Sciences and Engineering Research Council of Canada.

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(7) Solutions were 0.5×10^{-4} M in ketones **1a** or **1b** and contained potassium hydroxide as the base and sufficient KCl to maintain an ionic strength of 0.10. The water used was triply distilled and boiled under N_2 to remove dissolved CO_2. Fresh solutions were used for each flash; purging with N_2 or use of oxygen-saturated solutions gave identical results. The photoflash was of 20-μs duration and 50-J energy. Values of λ are the averages of at least three determinations in all cases. All determinations were made at 23 °C.

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