Table II. Sonochemical Tin Hydride Reduction[a]

entry	halide	tin hydride (equiv)	solv	time, h	sonochemical		control	
					temp, °C	% yield[b]	temp, °C	% yield[b]
1	1-iodododecane	Bu_3SnH (1.2)	toluene	1	6	90	0	5
2	1-iodododecane	Ph_3SnH (1.1)	toluene	2	4	65	0	15
3	1-iodododecane	Ph_3SnH (2)	THF	2	−64	88		
4	5-bromodecane	Bu_3SnH (1.2)	toluene	11	14	73	0	8
5	1-bromodecane	Bu_3SnH (1.2)	toluene	16	14	66		
6	*p*-iodoanisole	Bu_3SnH (1.2)	toluene	12	40	14	40	1

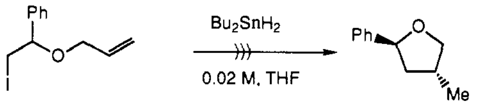
[a] The reaction was carried out in a 0.2 M solution for the halide except in entry 3 (0.5 M). In low-yield runs, high levels of material balance were observed. [b] Determined by GLC yield.

conversion occurred under otherwise identical conditions. Large rate accelerations were also observed in toluene and THF solutions (entries 2 and 3). The sonochemical hydrostannation of phenylacetylene (entries 4 and 5) and (trimethylsilyl)acetylene[10] (entry 6 and 7) also proceeded very smoothly at low temperatures. *The reactions carried out using irradiation proceed 100–600 times faster than those without.* It is particularly noteworthy that these reactions take place even at −50 °C (entries 5 and 7).[11]

The stereochemistry of the hydrostannation reactions (1-hexyne, 0 °C, THF) serves to illustrate the difference between the sonochemical methods and photochemical initiation. Thus, while the former showed very high kinetic cis selectivity (entry 3), the latter (400-W high-pressure Hg lamp, Pyrex filter) produced a ~1:1 mixture of cis and trans isomers (95%) owing to very rapid photochemical equilibration of the product.

Sonochemical hydrostannation of electron-deficient olefins also proceeded smoothly.[7,12] Thus, addition of Ph_3SnH to unsaturated esters proceeded in good yield at 7–8 °C (Table I, entries 8 and 9). Hydrostannation of a thermally unstable cyclopropenone ketal[13] (entry 10) was also accomplished very cleanly.[14]

Ultrasound initiates tin hydride reduction of organic halide[15] at low ambient temperature. For instance, ultrasound irradiation of a mixture of Bu_3SnH and 1-iodododecane in toluene at 0–6 °C (internal) for 1 h resulted in rapid and quantitative formation of decane (Table II, entry 1). Various halides could be reduced similarly at temperatures as low as −60 °C (entry 3). A variety of tin hydrides—Bu_3SnH, Ph_3SnH, and Bu_2SnH_2—can serve as a hydride source, and 10- to 50-fold rate acceleration was generally observed. The low-temperature sonolysis is particularly useful for enhancing the stereoselectivity of radical cyclizations—an important issue in these versatile synthetic reactions.[16] For instance, the sonochemical cyclizations of **1** (eq 1) at 6 °C and at −55 °C gave the tetrahydrofuran **2** in 60–70% yield with trans/cis ratios of 87:13 and 94:6, respectively, while the cyclization under thermal conditions (AIBN, 70 °C, 1 h) gave a 79:21 mixture (77% yield).



(1)

1 **2**

trans:cis = 87:13 (6 °C, 2 h)
94:6 (-55 °C, 13 h)

The high levels of the observed product selectivities indicate that the dominant fraction of the reaction product has been formed in the cold bulk liquid phase and not in the hot cavities (cf. Scheme I). In contrast to the normal thermal conditions, wherein both the initiation and the propagation steps necessarily take place under an identical thermal environment, the sonochemical conditions permit these steps to be carried out under very different thermal environments.[17]

Acknowledgment. We thank Professor Yoshihiko Hatano for helpful discussions on the physicochemical aspects of sonochemistry.

---

(10) (Trimethylsilyl)acetylene is particularly liable to the formation of a trans adduct (cf. ref 6).

(11) The presence of AIBN, which is not essential in any of the reactions reported herein, was found sometimes beneficial in reactions at low temperatures.

(12) van der Kerk, G. J. M.; Noltes, J. G.; Luijten, J. G. A. *J. Appl. Chem.* **1957**, *7*, 356.

(13) Baucom, K. B.; Butler, G. B. *J. Org. Chem.* **1972**, *37*, 1730.

(14) Cyclopropenone ketals are good radical acceptors: unpublished results by S. Yamago and S. Ejiri.

(15) Pereyre, M.; Quintard, J. P.; Rahm, A. *Tin in Organic Synthesis*; Butterworth & Co. Ltd.: London, 1987. Neumann, W. P. *Synthesis* **1987**, 665.

(16) Interest in this field has been renewed in the past several years: Stork, G. In *Current Trends in Organic Synthesis*; Nozaki, H., Ed.; Pergamon Press: Oxford, England, 1983. Ueno, Y.; Chino, K.; Watanabe, M.; Moriya, O.; Okawara, M. *J. Am. Chem. Soc.* **1982**, *104*, 5564. For pertinent recent references, see: RajanBabu, T. V.; Fukunaga, T.; Reddy, G. S. *J. Am. Chem. Soc.* **1989**, *111*, 1759. Reviews: Curran, D. P. *Synthesis* **1988**, 417, 489. Ramaiah, M. *Tetrahedron* **1987**, *43*, 3541.

(17) The cavity temperature can be controlled by the vapor pressure of the solvent: Suslick, K. S.; Gawienowski, J. J.; Schubert, P. F.; Wang, H. H. *Ultrasonics* **1984**, *22*, 33.

Synthesis and Metal-Dependent Condensation Reactions of $M(CO)_4(\eta^2\text{-}HC{\equiv}CH)$ (M = Ru, Os): Formation of Diosmacyclobutene and Heterodimetallacyclopentenones

Melinda J. Burn,[†] Gong-Yu Kiel,* Frank Seils,[‡]
Josef Takats,* and John Washington[†]

Department of Chemistry, University of Alberta
Edmonton, Alberta, Canada T6G 2G2

Received April 12, 1989

It is well documented that the reaction of iron group carbonyls with alkynes gives a myriad of organometallic complexes and a large variety of carbonyl-containing cyclic organic compounds.[1] Yet the isolation of the simple ternary acetylene–tetracarbonyl species $M(CO)_4(\eta^2\text{-}HC{\equiv}CH)$ (**1**), a most plausible intermediate in the reaction with acetylene, has so far remained elusive.[2,3] Here we report the successful synthesis of such molecules for M = Ru (**1a**) and Os (**1b**) and communicate some early results that reveal unexpected reactivity of these coordinatively saturated species.

Photolysis of the respective pentacarbonyls in hydrocarbon solution at low temperature, while purging with acetylene, gives the corresponding acetylene–tetracarbonyl compounds (eq 1).

$$M(CO)_5 \xrightarrow[\text{pentane, }-60\,°\text{C}]{h\nu,\ \lambda > 370\text{ nm}} M(CO)_4(\eta^2\text{-}HC{\equiv}CH) \qquad (1)$$

M = Ru, **1a**; M = Os, **1b**

[†] NSERC Undergraduate Research Awardee.

[‡] Feodor-Lynen Fellow.

(1) (a) Hübel, W. In *Organic Synthesis via Metal Carbonyls*; Wender, I., Pino, P., Eds.; Wiley-Interscience: New York, 1968; Vol. 1. (b) Fehlhammer, W. R.; Stolzenberg, H. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1983; Vol. 4, p 545.

(2) A limited number of ternary alkyne–tetracarbonyl species are known. (a) Pannell, K. M.; Crawford, G. M. *J. Coord. Chem.* **1973**, *2*, 251 ($M(CO)_4(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3$, M = Fe). (b) Ball, R.; Burke, M. R.; Takats, J. *Organometallics* **1987**, 6, 1918 ($M(CO)_4(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)$, M = Ru, Os). (c) Gagné, M. R.; Takats, J. *Organometallics* **1988**, *7*, 561 ($M(CO)_4(\eta^2\text{-}CF_3C{\equiv}CCF_3)$, M = Ru, Os).

(3) Recently, $Fe(CO)_2(PR_3)_2(\eta^2\text{-}HC{\equiv}CH)$ (R = Et, OMe) type compounds have been reported by Berke et al. (a) Birk, R.; Berke, H.; Huttner, G.; Zsolnai, L. *Chem. Ber.* **1988**, *121*, 471. (b) Birk, R.; Grössmann, U.; Hund, H.-U.; Berke, H. *J. Organomet. Chem.* **1988**, *345*, 321.

0002-7863/89/1511-6850$01.50/0

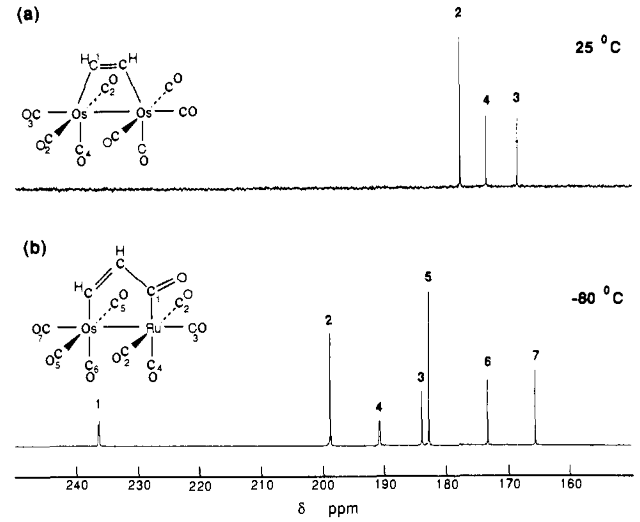


Figure 1. ^{13}C NMR spectra of **2** (a) and **3** (b) in the carbonyl region.

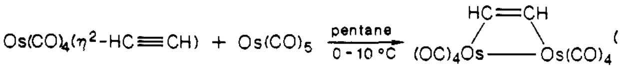
Although the thermal instability of the complexes[4] has prevented a reliable isolated yield to be determined, IR monitoring of the reaction and further conversion of in situ generated compounds (vide infra) indicate exclusive and virtually quantitative formation of **1a** and **1b**. The spectroscopic data[5] on the molecules are in accord with a trigonal-bipyramidal structure where the π-acceptor acetylene ligand occupies an in-plane equatorial position, as is the norm for the related $M(CO)_4(\eta^2\text{-olefin})$ complexes.[6] In particular, the appearance of two carbonyl signals of equal intensity in the low-temperature ^{13}C NMR spectra of **1a** and **1b** supports this conclusion. Predictably, the molecules are fluxional in solution. Reflecting the better π-acceptor ability of acetylene,[7] the activation energies for axial–equatorial carbonyl group exchange in **1a** (9.5 kcal/mol) and **1b** (12.3 kcal/mol) are higher than in the related $M(CO)_4(\eta^2\text{-}H_2C{=}CH_2)$ compounds (Ru = 8.0 kcal/mol, Os = 9.9 kcal/mol).

A surprising discovery was the enhanced solution stability of the compounds under a protective atmosphere of carbon monoxide. The implied CO dissociation initiating decomposition was verified by the ready ^{13}CO enrichment of **1b** (eq 2).

$$Os(CO)_4(\eta^2\text{-}HC{\equiv}CH) \xrightarrow[0\text{-}10\ °C,\ 1\ h]{^{13}CO,\ 1\ atm} Os(^{13}CO)_4(\eta^2\text{-}HC{\equiv}CH) \quad (2)$$

Encouraged by this result and our previous success with directed synthesis of dimetallacycles from $M(CO)_4(\eta^2\text{-HFB})$[2c] (HFB = $CF_3C{\equiv}CCF_3$), we attempted the reaction of **1b** with other 18-electron species.

Reaction of **1b** with $Os(CO)_5$ occurs under conditions similar to the ^{13}CO-exchange reaction and gives the heretofore elusive[8] diosmacyclobutene, $Os_2(CO)_8(\mu\text{-}\eta^1,\eta^1\text{-HCCH})$ (**2**) (eq 3). The



$$\underset{\mathbf{1b}}{Os(CO)_4(\eta^2\text{-}HC{\equiv}CH)} + Os(CO)_5 \xrightarrow[0\text{-}10\ °C]{pentane} \underset{\mathbf{2}}{(OC)_4Os(\mu\text{-}HC{=}CH)Os(CO)_4} \quad (3)$$

structural formulation, verified by X-ray crystallography,[9] follows from the spectroscopic data.[10] In particular, the APT ^{13}C NMR spectrum clearly shows that the bridging unit contains carbon atoms attached to a single hydrogen atom only, thus ruling out the alternate μ-vinylidene, $Os_2(CO)_8(\mu_2\text{-}C{=}CH_2)$, formulation.[11]

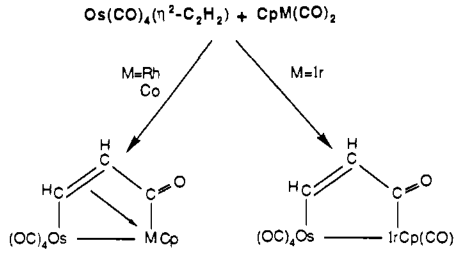
More remarkable than the reaction with $Os(CO)_5$ is the interaction of **1b** with $Ru(CO)_5$. As shown in eq 4, this reaction

$$\underset{\mathbf{1b}}{Os(CO)_4(\eta^2\text{-}HC{\equiv}CH)} + Ru(CO)_5 \xrightarrow[-20°C]{pentane} \underset{\mathbf{3}}{OsRu(CO)_9(C_2H_2)} \quad (4)$$

occurs already at −20 °C and involves the condensation of two 18-electron species *without any ligand loss*. The ^{13}C NMR spectrum of the compound, Figure 1b, uniquely defines the molecular formulation,[12] which has been corroborated in the solid state by X-ray crystallography.[9] Although the central dimetallacyclopentenone core is not novel,[13] the method of formation of compound **3** is, to our knowledge, unprecedented.

With a view to probe the reactivity of **1b** and with an established precedent provided by $Ru(CO)_4(\eta^2\text{-HFB})$,[2c] the reaction with $CpM(CO)_2$ (M = Co, Rh, Ir; Cp = $\eta^5\text{-}C_5H_5$) was carried out. Gratifyingly, these reactions proceed readily as well and, as shown in Scheme I, provide another metal-dependent facet of the condensation reaction.[14] The observed loss of carbon monoxide with cobalt and rhodium is not contrary to the well-known decrease in metal–ligand bond strength as a transition-metal triad is ascended.

Scheme I



Co, **4** ; Rh, **5**

6

The structural diversity exhibited by the simple acetylene derivative **1b** is in sharp contrast to the related HFB complex, which gave only alkyne-bridged dimetallic species.[2c] The opportunities offered by this richness of chemistry as well as further reactivity of compounds **2**–**6** are actively pursued. The relevance of these species to surface-bound acetylene and its subsequent transformation[15] will also be elaborated in future publications.

---

[4] Compound **1a** starts to decompose in hydrocarbon solution above −30 °C; **1b** shows significant deterioration above 0 °C.

[5] IR (pentane, −60 °C, cm^{-1}) ν_{CO}: **1a**, 2115 (w), 2037 (s), 2028 (m), 2002 (s); **1b**, 2122 (w), 2036 (s), 2027 (m), 1994 (s); $\nu_{C\equiv C}$: **1a**, 1670 (m); **1b**, 1642 (m). ^{1}H NMR (CD_2Cl_2, −83 °C, δ): **1a**, 5.70 (s); **1b**, 6.16 (s). ^{13}C NMR (CD_2Cl_2, δ): **1a** (−108 °C), 200.5 (*C*O), 193.4 (*C*O), 70.1 (C_2H_2); **1b** (−86 °C), 179.9 (*C*O), 173.3 (*C*O), 73.5 (C_2H_2).

[6] Kiel, G.-Y.; Takats, J.; Grevels, F.-W. *J. Am. Chem. Soc.* **1987**, *109*, 2227 and references therein.

[7] Mingos, D. M. P. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1983; Vol. 3.

[8] (a) Burke, M. R.; Takats, J. *J. Organomet. Chem.* **1986**, *302*, C25. (b) Burke, M. R.; Seils, F.; Takats, J. *Organometallics*, submitted for publication.

[9] Day, V. W.; Kiel, G.-Y.; Takats, J., to be published.

[10] **2**: moderately air stable, colorless to pale yellow solid, mp 76 °C (dec), yield 92%; IR (pentane, cm^{-1}) ν_{CO} 2129 (w), 2082 (s), 2042 (vs), 2024 (s), 2013 (s), 1997 (s), 1970 (w); ^{1}H NMR (CD_2Cl_2, 25 °C, δ) 6.96 (s); ^{13}C NMR (CD_2Cl_2, 25 °C, δ) 178.4 (2 *C*O), 173.9 (1 *C*O), 169.2 (1 *C*O), 98.4 (C_2H_2). Anal. Calcd for $C_{10}H_2O_8Os_2$: C, 19.05; H, 0.32. Found: C, 19.57; H, 0.47.

[11] The rearrangement of acetylene to vinylidene in the coordination sphere of a metal is a well-known phenomenon. (a) Bruce, M. I.; Swincer, A. G. *Adv. Organomet. Chem.* **1983**, *22*, 59. (b) Silvestre, J.; Hoffman, R. *Helv. Chim. Acta.* **1985**, *68*, 1461.

[12] **3**: moderately air stable, yellow solid, mp 82 °C, yield 95%; IR (pentane, cm^{-1}) ν_{CO} 2129 (w), 2126 (w), 2088 (s), 2066 (m), 2055 (m), 2047 (vs), 2040 (s), 2019 (m), 2011 (s), 2000 (w); $\nu_{C=O}$ 1635 (m); ^{1}H NMR (CD_2Cl_2, 25 °C, δ) 8.17 (d, $J_{H\text{-}H}$ = 9 Hz), 7.46 (d, $J_{H\text{-}H}$ = 9 Hz); ^{13}C NMR of fully ^{13}CO-enriched material (CD_2Cl_2, −80 °C, δ) 236.3 (d, *C*=O), CO_{Ru} {198.9 (2), 190.9 (d, 1), 184.0 (1)}, CO_{Os} {182.9 (2), 173.2 (1), 165.5 (1)}, 166.5 (Os–*C*H), 131.4 (Ru–CO*C*H). Anal. Calcd for $C_{11}H_2O_9OsRu$: C, 23.20; H, 0.35; O, 25.29 Found: C, 23.13; H, 0.41; O, 25.07.

[13] (a) Dixon, R. S.; Gatehouse, B. M.; Nesbit, M. C.; Pain, G. N. *J. Organomet. Chem.* **1981**, *215*, 97. (b) Dyke, A. F.; Knox, S. A. R.; Naish, P. J.; Taylor, G. E. *J. Chem. Soc., Dalton Trans.* **1983**, 1297.

[14] Characterization data on compounds **4**–**6** are available as Supplementary Material. The solid-state structure of **6** is at hand: Washington, J.; Rogers, R. D.; Takats, J., to be published.

[15] (a) Silvestre, J.; Hoffmann, R. *Langmuir* **1985**, *1*, 621 and references therein. (b) Inter alia: Somorjai, G. A. *Chem. Soc. Rev.* **1984**, *13*, 321. Shustokovich, E.; Bell, A. T. *Surf. Sci.* **1988**, *205*, 492. Parameter, J. E.; Hills, M. M.; Weinberg, W. H. *J. Am. Chem. Soc.* **1988**, *110*, 7952. (c) Ozin, G. A.; McIntosh, D. F.; Power, W. J.; Messmer, R. P. *Inorg. Chem.* **1981**, *20*, 1782.

Acknowledgment. We thank the Natural Science and Engineering Research Council of Canada and the University of Alberta for generous financial support. Grateful acknowledgments are also made to the Alexander von Humboldt-Stiftung, Bonn, FRG, for the award of a Feodor-Lynen-Stipendium to F.S. and to NSERC (Canada) for Undergraduate Summer Research Awards to M.J.B. and J.W.

Supplementary Material Available: Characteristic data (IR, NMR, MS, and elemental analysis) on compounds **4**–**6** (1 page). Ordering information is given on any current masthead page.

Generation and Trapping of *O*-Alkyl Metathiophosphates

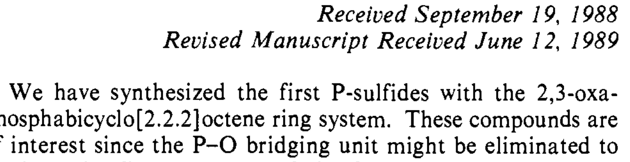
Louis D. Quin,* Narayan D. Sadanani, and Xiao-Ping Wu

Department of Chemistry
University of Massachusetts
Amherst, Massachusetts 01003

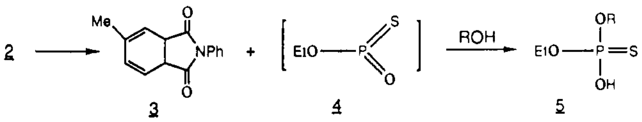
Received September 19, 1988
Revised Manuscript Received June 12, 1989

We have synthesized the first P-sulfides with the 2,3-oxaphosphabicyclo[2.2.2]octene ring system. These compounds are of interest since the P–O bridging unit might be eliminated to produce the first examples of the family of alkyl metathiophosphates, RO–P(S)O. This possibility is suggested from previously reported results with P-oxides in this series, whose fragmentation by both thermal[1] and photochemical[2] means to form alkyl metaphosphates has been studied. No previous attempts to generate alkyl metathiophosphates have been reported, although the anion (PSO_2^-) of the corresponding acid has been detected as a transient species in solution.[3,4] This anion appears to be more stable than PO_3^-, and a salt of the anion PS_3^- has actually been isolated and characterized.[5]

A precursor for O-ethyl metathiophosphate has structure **2**; it was prepared as a crystalline solid, mp 138–139 °C, isolated in 35–40% yield, by thionation of ester **1** (with retention of configuration[6]) with phosphorus pentasulfide or Lawesson's reagent, (p-$CH_3OC_6H_4PS_2)_2$. These reactions are best conducted at room temperature in CH_2Cl_2 to prevent loss of the P–O bridging unit; 5–6 days are required for complete reaction. Compound **2** has been characterized by elemental analysis (C, H, N) and by NMR spectral measurements.[7]



On being heated in dry toluene for 2 h at 110 °C, **2** was completely consumed in a fragmentation process that produced the known[1] dienic compound **3**, and hence is presumed to release the bridging unit as *O*-ethyl metathiophosphate (**4**). The complexity of the ^{31}P NMR spectrum of the reaction mixture suggested that **4** reacted immediately to form other products. However, when ethyl or isopropyl alcohols (about 1 equiv) were included in the reaction mixture as trapping agents, the ^{31}P NMR spectrum was totally different and possessed only one significant signal, in the region expected for an *O*,*O*-dialkyl thionophosphate (**5**), as would arise from a reaction of the alcohol with an initially generated metathiophosphate. Compound **5a** (lit.[8] δ ^{31}P 64) was isolated by chromatography on silica gel, with elution by methanol, and its structure confirmed through spectral studies.[9] Similarly, the new ester **5b** was synthesized and characterized.[10]



5a, R=Et, δ ^{31}P ($CDCl_3$) 63.9
5b, R=i-Pr, δ ^{31}P ($CDCl_3$) 61.2
5c, R=t-Bu, δ ^{31}P ($CDCl_3$) 56.5

Compound **2** (in dioxane or acetonitrile) was also fragmented efficiently on irradiation at 254 nm in the quartz apparatus described elsewhere.[2] The reaction was complete in a few hours at ambient temperatures (around 35 °C). When 1 equiv of ethanol or 2-propanol was present, the released phosphorus fragment was cleanly trapped, as in the thermal fragmentation, as **5a** and **5b**, respectively. From *tert*-butyl alcohol, thionophosphate **5c** was most efficiently formed when triethylamine[2] was also present.

The mechanism of these thermal and photochemical fragmentations (concerted or stepwise) has not yet been studied, but from the alcohol-trapping reactions the structure of the P-containing fragment at the time of its release from the carbon framework seems reasonably represented as that of a metathiophosphate. To provide confirmation of this proposal, we have prepared a metathiophosphate precursor with an optically active O-substituent. Our postulate was that a metathiophosphate with such a substituent would give two diastereomeric thionophosphates on attack of an alcohol, since a new chiral center is being created at phosphorus. The diastereomers should form in equal or nearly equal amounts, since the metathiophosphate is presumably planar and attack of the alcohol could occur at both faces with equal probability, except possibly for a small asymmetric induction effect. This postulate follows from the observation that the metaphosphate ion $^{16}O^{17}O^{18}OP^-$, when generated by the action of base on an aryl phosphate, gives a racemic mixture on reaction with an alcohol.[11] This is taken as proof of the existence of the planar metaphosphate ion as a free species. We therefore synthesized the (*S*)-*sec*-butyl ester **6** by the same procedure used for **2**, giving a mixture of diastereomers having δ ^{31}P NMR ($CDCl_3$) 86.50 and 87.05, and having the expected ^{1}H and ^{13}C NMR spectra and elemental analysis. When ester **6** was heated in toluene with ethanol present, the expected thionophosphate **8** was formed, as determined by ^{31}P, ^{13}C, and ^{1}H NMR analysis. However, the product was seen to be a 1:1 mixture of isomers; this was especially evident from

---

(1) Quin, L. D.; Marsi, B. G. *J. Am. Chem. Soc.* **1985**, *107*, 3389.

(2) Quin, L. D.; Pete, B.; Szewczyk, J.; Hughes, A. N. *Tetrahedron Lett.* **1988**, *29*, 2627.

(3) Harnett, S. P.; Lowe, G. *J. Chem. Soc., Chem. Commun.* **1987**, 1416.

(4) Cullis, P. M.; Misra, R.; Wilkins, D. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1594.

(5) Roesky, H. W.; Ahlrichs, R.; Brode, S. *Angew Chem., Int. Ed. Engl.* **1986**, *25*, 82.

(6) Quin, L. D.; Osman, F. H.; Day, R. O.; Hughes, A. N.; Wu, X.-P.; Wang, L.-Q. *New J. Chem.* In press.

(7) Calcd for $C_{17}H_{18}NO_4PS$: C, 56.1; H, 4.99; N, 3.85. Found: C, 56.0; H, 5.08; N, 3.78. ^{31}P NMR ($CDCl_3$, 121.4 MHz) δ +86.1 (downfield from H_3PO_4); ^{1}H NMR ($CDCl_3$, 200 MHz, couplings confirmed by 2D COSY) δ 1.31 (t, 3 H, $^3J_{HH}$ = 7.0 Hz, H-11), 1.96 (d of d, 3H, J = 1.8 and 4.7 Hz, H-9), 3.62–3.72 (m, 1 H, H-4), 3.89–3.94 (m, 2 H, H-7,8), 4.13–4.30 (m, 2 H, H-10), 5.21 (d of m, 1 H, $^3J_{PH}$ = 21.4 Hz, H-1), 6.12 (m, 1 H, H-5), 7.1–7.5 (m, 5 H, ArH); ^{13}C NMR ($CDCl_3$, 50.31 MHz), δ 16.3 (J_{PC} = 5.7 Hz, C-11), 19.9 (J_{PC} = 2.6 Hz, C-9), 38.4 (s, C-8), 39.8 (J_{PC} = 93.9 Hz, C-4), 45.8 (J_{PC} = 8.8 Hz, C-7), 64.4 (J_{PC} = 6.2 Hz, C-10), 77.7 (J_{PC} = 5.7 Hz, C-1), 122.8 (J_{PC} = 12.9 Hz, C-5), 140.2 (J_{PC} = 13.3 Hz, C-6), 172.9 (s, C-13), 175.3 (J_{PC} = 22.8 Hz, C-12), C_6H_5 at 126.2, 129.1, 129.3, 131.3.

(8) Mlotkowska, B.; Zwierzak, A. P. *J. Prakt. Chem.* **1978**, *320*, 777.

(9) Mass spectrum: calcd for M^+, 170; found m/z 170. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.29 (t, J_{HH} = 6.9 Hz, CH_3), 4.0 (m, CH_2); ^{13}C NMR ($CDCl_3$, 50.31 MHz) δ 16.2 (J_{PC} = 3.0 Hz, CH_3), 62.7 (J_{PC} = 4.0 Hz, CH_2).

(10) ^{1}H NMR (D_2O, 80 MHz) δ 1.17 (d, J = 6.4 Hz, Me_2C), 1.25 (t, J_{PH} = 7 Hz, CH_3CH_2), 3.7–4.2 (m, 2 H, OCH_2), 4.3–4.6 (m, 1 H, OCH); ^{13}C NMR ($CDCl_3$, 50.31 MHz), δ 16.2 (J_{PC} = 8.4 Hz, CH_3CH_2), 23.7 (J_{PC} = 4.0 Hz, CH_3CH), 24.0 (J_{PC} = 4.7 Hz, CH_3CH), 63.0 (J_{PC} = 5.3 Hz, CH_2), 71.7 (J_{PC} = 3.5 Hz, CH).

(11) Friedman, J. M.; Knowles, J. R. *J. Am. Chem. Soc.* **1985**, *107*, 6126. Freeman, S.; Friedman, J. M.; Knowles, J. R. *J. Am. Chem. Soc.* **1987**, *109*, 3166.

0002-7863/89/1511-6852$01.50/0