Table III. ESR Data for Spin-Coupled Dimeric Vanadyl Complexes

compd	$g_{\parallel}$	$A_{\parallel}$, cm^{-1}	$g_{\perp}$	$A_{\perp}$, cm^{-1}	D, cm^{-1}	ref
$(Bu_4N)_2[(VO)_2(Dcp)_2]$	1.95	0.007 4	1.98	0.003 8	0.0343	this work
$Na_4[VO(d,l\text{-tartrate})]_2\cdot 12H_2O$	1.953	0.007 23	1.982	0.002 13	0.0334	3a
$Na_4[VO(d\text{-tartrate})]_2\cdot 6H_2O$	1.950	0.007 32	1.984	0.002 46	0.0335	3a
$[VO(TCP)]_2(K^+)_4$	1.967	0.007 71 5	1.987	0.002 59 8	0.02685 0.02610	3e

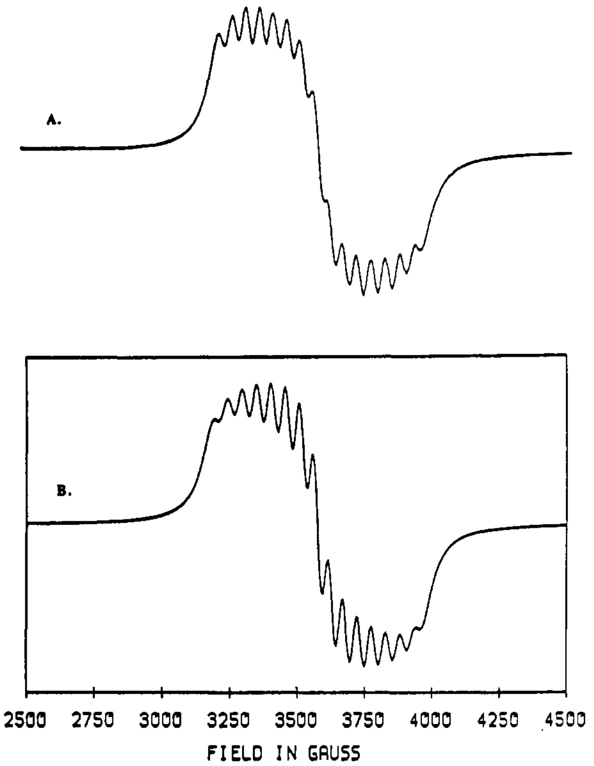


Figure 2. (A) Room-temperature ESR spectrum of $(Bu_4N)_2[(VO)_2(Dcp)_2]$ in acetone. (B) Simulated ESR spectrum for $(Bu_4N)_2[(VO)_2(Dcp)_2]$ using $g = 1.97$ and $A = 50.44 \times 10^{-4}$ cm^{-1} (line width = 53 G).

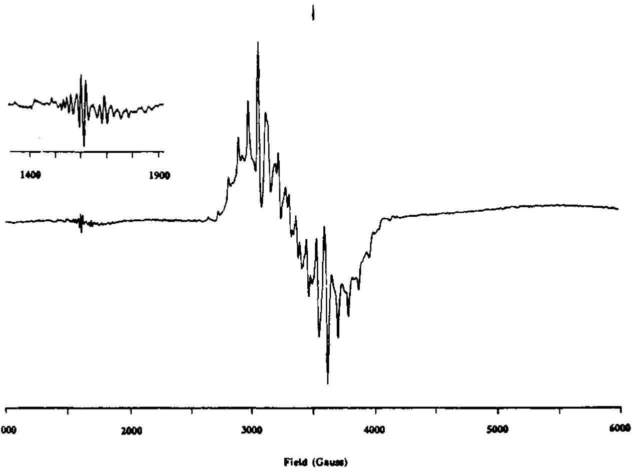


Figure 3. ESR spectrum of the $(Bu_4N)_2[(VO)_2Dcp_2]$ complex at 93 K in acetone/2-propanol/methanol (15:4:1) glass. Inset shows expanded $\Delta M_s \pm 2$ transition.

The isotropic g and A values are from the isotropic room-temperature spectrum. The resulting parameters are compared with those of related vanadium dimers in Table III.

The point-dipole approximation for an axially symmetric system may be used to confirm the value of the zero-field-splitting parameter.[3a] Using the crystallographically determined V–V distance (4.206 Å) and the g values gives calculated zero-field values of $D = 0.0332$ cm^{-1} and $D = 0.0342$ cm^{-1} for $g_{\parallel}$ and $g_{\perp}$, respectively. These values are in very good agreement with the value of $D = 0.0343$ cm^{-1} extracted from the spectrum.

The electronic spectrum for $(Bu_4N)_2[(VO)_2(Dcp)_2]$ shows the three optical bands expected for a vanadyl complex. The assignments of the bands for the complex follow the Ballhausen and Gray model for the one-electron transitions $d_{xy} \rightarrow d_{xz},d_{yz}$, $d \rightarrow d_{x^2-y^2}$, and $d \rightarrow d_{z^2}$, respectively.[10] The bands occur at 609 nm ($\epsilon = 8.21$ cm^{-1}), 530 nm ($\epsilon = 10.01$ cm^{-1}), and 431 nm ($\epsilon = 7.21$ cm^{-1}), respectively. The energy of the third band shows that the vanadyl remains five-coordinate in solution, as axial coordination of a sixth ligand would cause it to occur at <333 nm.[11] The lower symmetry in the vanadyl *d,d*-tartrate spin-triplet dimer lifts the d_{xz},d_{yz} degeneracy, giving rise to four optical bands.[3b]

Cyclic voltammetry of $(Bu_4N)_2[(VO)_2(Dcp)_2]$ showed two irreversible reduction waves at −2.3 and −2.5 V (vs $Ag/AgNO_3$). There is also a broad irreversible oxidation wave at +0.85V with a shoulder at +0.90 V, suggesting two very closely spaced, irreversible one-electron oxidations.

The treatment of the vanadyl complex with *tert*-butyl hydroperoxide (2:1 metal to peroxide) in dichloromethane resulted in protonation of the ligand, which precipitated from solution. A similar result was noted for hydrogen peroxide. The complex appears to lose its integrity upon oxidation and does not facilitate the formation of a peroxo adduct.

Acknowledgment. P.G.R. acknowledges support from the donors of the Petroleum Research Fund, administered by the American Chemical Society. J.C.B. acknowledges support from the Spanish DGICYT Project PB88-0252. C.W.H. acknowledges support from undergraduate research funds of the College of Literature, Science and the Arts. The assistance of Dr. Jeffrey Kampf, X-ray crystallographer of the Department of Chemistry for data collection, is gratefully acknowledged.

Supplementary Material Available: Tables of thermal parameters, bond lengths, bond angles, and crystallographic data (8 pages); a listing of structure factors (24 pages). Ordering information is given on any current masthead page.

---

(10) Ballhausen, C. J.; Gray, H. B. *Inorg. Chem.* **1962**, *1*, 111.

(11) Deeth, R. J. *J. Chem. Soc., Dalton Trans.* **1991**, 1467.

Contribution from the Department of Chemistry,
Tulane University, New Orleans, Louisiana 70118

Conversion of Chlorofluorocarbons into Chlorofluorohydrocarbons Using the Atherton–Todd Reaction with Dimethyl Phosphonate

Emil Georgiev, D. Max Roundhill,* and Koljo Troev[1]

Received September 27, 1991

Introduction

Chlorofluorocarbons in the stratosphere are environmentally harmful because the photolytic cleavage of their carbon–chlorine bonds results in depletion of the ozone layer.[2] Chlorofluoro-

---

[1] Permanent address: Central Laboratory for Polymers, Bulgarian Academy of Sciences, Sofia, Bulgaria.

[2] Molina, M. J.; Rowland, F. S *Nature* **1974**, *249*, 810–2. Rowland, F. S. *Am. Sci.* **1989**, *77*, 36–45.

0020-1669/92/1331-1965$03.00/0 © 1992 American Chemical Society

hydrocarbons have been proposed as refrigerant substitutes for chlorofluorocarbons.[3] These latter molecules are considered to be environmentally less harmful because they contain a carbon–hydrogen bond that can be cleaved by chemical reactions at lower altitudes, thereby preventing the compounds from reaching the stratosphere. Since it is expected that the use of chlorofluorocarbons for industrial purposes will soon be terminated and that chlorofluorohydrocarbons may be used as replacements, reactions that convert carbon–halogen bonds in chlorofluorocarbons into carbon–hydrogen bonds are becoming of increasing interest.

A reaction that has been used to convert aliphatic carbon–chlorine bonds into carbon–hydrogen bonds is the Atherton–Todd reaction.[4] This reaction employs a dialkyl phosphonate as the hydrogen source, and the chlorine is transferred from carbon to phosphorus to give a dialkyl chlorophosphate. This reaction is closely similar to the interchange reaction that occurs between halocarbons and transition-metal hydrides.[5] This latter reaction, which commonly uses the conversion of carbon tetrachloride into chloroform as a test for transition-metal hydrides, is not, however, well understood from a mechanistic viewpoint. Our interest in the Atherton–Todd reaction results from its being a halogen–hydrogen reaction interchange that is amenable to being studied by experimental methods, and one for which mechanistic information can be obtained.

Two important chlorofluorocarbons commonly used as refrigerants are trichlorofluoromethane and dichlorodifluoromethane. In this paper we describe the results of the reactions of these two compounds with dimethyl phosphonate and base. We find that these reactions lead to the formation of chlorofluorohydrocarbons and dimethyl chlorophosphates, and a mechanism is proposed involving initiation by the monomethyl phosphonate anion, followed by cross-reactions between dimethyl phosphonate and the haloalkyl anion.

Experimental Section

Dimethyl phosphonate and diethyl phosphonate were purchased from Aldrich Chemical Corp. and distilled prior to use. The purified compounds were then stored under a nitrogen atmosphere. Cyclohexylamine and triethylamine were purified by distillation and stored over 4-Å molecular sieves. The solvents used in reactions B and D with CCl$_3$F (see below) were dried over sodium (toluene) or 4-Å molecular sieves (dichloromethane). Trichlorofluoromethane, dichlorodifluoromethane, and chlorodifluoromethane were commercial high-grade materials which were used as supplied. The polyphosphonate was synthesized according to the literature procedure using dimethyl phosphonate (20 mL, 269 mmol) and trimethylene glycol (30.8 g, 205 mmol).[6] The NMR spectra were measured on a Bruker AC 200 spectrometer with chemical shifts referenced to CCl$_3$F (^{19}F) and 85% H$_3$PO$_4$ (^{31}P). Unless otherwise stated, the NMR spectra were measured with the samples dissolved in CDCl$_3$. Yields were based on NMR integrations using long delay times (60 s between the pulses) to obtain reliable relative values. The yields of the fluoro compounds were estimated to be the same as those of the phosphates or phosphoramides obtained in the reactions. The correspondence of yields was justified on the basis that these phosphorus compounds resulted entirely from the conversion of P–H bonds into P–Cl bonds and that only a single chlorofluorohydrocarbon product was formed in each case. The yield data are collected in Table I. The ^{19}F NMR spectrum of CCl$_2$FH (δ -8.07, d, ^2J(HF) = 52 Hz) was identified by comparison with the literature value,[7] and that of CClF$_2$H (δ -71.8, d, ^2J(HF) = 64 Hz) by measurement of an authentic sample supplied by PCR, Inc.

Reactions with CCl$_3$F. Reaction A. Cyclohexylamine (4.63 mL, 40 mmol) was added dropwise to a vigorously stirred solution of CCl$_3$F (5 g, 36.3 mmol) in dimethyl phosphonate (1.42 mL, 15.5 mmol) at 0 °C. An immediate precipitate of cyclohexylamine hydrochloride formed. The flask was fitted with a dry ice condenser, and the reaction was stirred at 0 °C. A sample of the liquid was transferred by pipet into a 5-mm NMR tube containing CDCl$_3$, and the tube was sealed with a cap. After 1 h, the reaction mixture was allowed to warm to ambient temperature and then stirred for a further 18 h. The ^{31}P NMR spectrum of the reaction mixture showed the presence of dimethyl-*N*-cyclohexylphosphoramide (δ 10.7, septet, ^3J(PH) = 10.2 Hz, integrated yield = 95%).

Reaction B. Triethylamine (2.2 mL, 15.5 mmol) was added dropwise to a vigorously stirred solution of dimethyl phosphonate (1.42 mL, 15.5 mmol) and CCl$_3$F (5 g, 36.3 mmol) at 0 °C. A sample of the liquid was transferred by pipet into a 5-mm NMR tube containing CDCl$_3$, and the tube was sealed with a cap. The solution was stirred at 0 °C for a further 20 min, during which time the solution turned slightly cloudy due to the formation of a precipitate of methyltriethylammonium chloride. Methanol (1 mL) was added to convert the dimethyl chlorophosphate formed into trimethyl phosphate. The mixture was allowed to warm to ambient temperature and stirred for a further 18 h. The ^{31}P NMR spectrum showed the presence of a mixture of trimethyl phosphate (δ 1.79, decet, ^3J(PH) = 7.8 Hz, integrated yield = 82%), dimethyl phosphonate (δ 10.0 doublet of septets, ^1J(PH) = 702.3 Hz, ^3J(PH) = 120.0 Hz, integrated yield = 7%), and unidentified oligomers with phosphorus NMR resonances at δ -10.0, -10.3, -11.1, and -11.3 (total integrated yield = 11%).

Reaction C. Triethylamine (2.2 mL, 15.5 mmol) was added to a solution containing diethyl phosphonate (2 mL, 15.5 mmol) and CCl$_3$F (6 mL, 65.2 mmol) in toluene (5 mL) at 0 °C. The reaction mixture was stirred at this temperature for 18 h, after which time the temperature was allowed to warm to ambient temperature. A sample of the liquid was transferred by pipet into a 5-mm NMR tube containing CDCl$_3$, and the tube was sealed with a cap. The remaining mixture was then treated with methanol (1 mL) to convert the diethyl chlorophosphate formed into diethyl methyl phosphate. The ^{31}P NMR spectrum of the mixture showed the presence of diethyl methyl phosphate (δ -1.05 m, integrated yield = 19%), diethyl phosphonate (δ 7.0, doublet of quintets, ^1J(PH) = 692.0 Hz, ^3J(PH) = 8.87 Hz, integrated yield = 66%), tetraethylammonium monoethyl phosphonate (δ 4.1, doublet of triplets, ^1J(PH) = 625 Hz, ^3J(PH) = 9.90 Hz, integrated yield = 6%), and tetraethyl pyrophosphate (δ -13.9, multiplet, integrated yield = 9%). The formation of tetraethyl pyrophosphate results from the hydrolysis of the initial product, diethyl chlorophosphate.

Reaction D. A 100-mL stainless steel autoclave was cooled to 0 °C and charged with a mixture of triethylamine (2.5 mL, 27 mmol), polyphosphonate (2.2 mL, 13.6 mmol), CCl$_3$F (2.5 mL, 27 mmol), and dichloromethane (3 mL). The vessel was sealed, and the mixture was magnetically stirred at ambient temperature for 28 h. The gaseous products were vented into CDCl$_3$, and the solution was transferred into a 5-mm NMR tube which was sealed with a cap. The remaining gases were vented into the atmosphere, and the vessel was opened at ambient pressure. The solid product of the reaction was dissolved in D$_2$O to convert any P–Cl bonds formed into P–OD bonds. The ^{31}P NMR spectrum of the solution showed a broad single peak at δ 1.25, verifying that all the P–H groups in the polymer had been converted into P–OD bonds.

Reactions with CCl$_2$F$_2$. All reactions with CCl$_2$F$_2$ were performed in a 100-mL stainless steel autoclave. The filling procedure involved charging the autoclave with the liquid components at -78 °C, evacuating the vessel, and then transferring the CCl$_2$F$_2$ into the solution in the autoclave. The transfer was carried out via a transfer tube with the autoclave at -78 °C and the CCl$_2$F$_2$ bottle at ambient temperature.

Reaction A. The autoclave was charged with dimethyl phosphonate (2 mL, 22 mmol), triethylamine (3.2 mL, 22 mmol), and excess CCl$_2$F$_2$. The reaction mixture was stirred at ambient temperature for 24 h. The volatile products of the reaction were analyzed by venting them through CDCl$_3$ contained in a NMR tube. The nonvolatile materials were treated with methanol (10 mL) in order to convert the dimethyl chlorophosphate formed into trimethyl phosphate. The ^{31}P NMR spectrum showed the presence of trimethyl phosphate with an integrated intensity which corresponded with a yield of 5%.

Reaction B. Cyclohexylamine (1.26 mL, 10.9 mmol) was introduced into a stainless steel autoclave at -78 °C. Onto this solidified cyclohexylamine was condensed triethylamine (1.53 mL, 10.9 mmol), dimethyl phosphonate (1 mL, 10.9 mmol), and excess CCl$_2$F$_2$. The reaction mixture was magnetically stirred at ambient temperature for 24 h. The volatile products were analyzed as in reaction A. The ^{31}P{^{1}H} NMR spectrum of the residue showed the presence of dimethyl-*N*-cyclohexylphosphoramide with an integrated intensity which corresponded with a yield of 10%. The majority of product (90%) was methylcyclohexylammonium monomethyl phosphonate (δ 5.54, dq, ^1J(PH) = 611 Hz, ^3J(PH) = 12.2 Hz).

Results and Discussion

The Atherton–Todd reaction involves the interaction between alkyl phosphonates and chlorocarbons in the presence of a base. For the case of carbon tetrachloride the reaction is exothermic,

---

(3) McFarland, M. *Environ. Sci. Technol.* **1989**, *23*, 1203–8.

(4) Atherton, F.; Openshaw, A.; Todd, A. *J. Chem. Soc.* **1945**, 660–3.

(5) Schunn, R. A. In *Transition Metal Hydrides*; Muetterties, E. L., Ed.; Dekker: New York, 1971; Chapter 5, p 246.

(6) Troev, K.; Borisov, G. *Phosphorus Sulfur* **1987**, *29*, 129–45.

(7) Pendlebury, M. H.; Philips, L.; Wary, V. *J. Chem. Soc., Perkin Trans 2* **1974**, 787–90. Ueji, S.; Nakamura, M.; Kitadani, M.; Sera, A. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 1665–6.

Table I. Yields of Chlorofluorohydrocarbons and Phosphorus-Containing Products[a]

reactions with CCl_3F[b]	yield of CCl_2HF, %	yield of $(RO)_2PR'(O)$,[c] %
A	95	95
B	93	82
C	28	19
D	100	100
reactions with CCl_2F_2[b]	**yield of $CClF_2H$, % %**	**yield of $(RO)_2PR'(O)$, %**
A	5	5
B	10	10

[a] Yields are based on the percentage of products that result from the cleavage of P–H bonds. [b] Present in large excess. [c] R' = OMe or CyNH.

and the products are the dialkyl chlorophosphate and chloroform (eq 1). The reaction does not proceed further because compounds having a carbon–hydrogen bond at the reaction center are unreactive under Atherton–Todd conditions. The initial steps of the reaction path have been considered to involve deprotonation of the dialkyl phosphonate to give the anion, which further reacts with the chlorocarbon to generate a dialkyl chlorophosphate and a carbanion (eq 2).[8] More recently we have found that the Atherton–Todd reaction is catalyzed by the monoalkyl phosphonate anion, $(RO)P(O)H(O)^-$.[9]

$$(RO)_2P(O)H + CCl_4 \xrightarrow{\text{base}} (RO)_2P(O)Cl + CHCl_3 \quad (1)$$

$$(RO)_2P(O)^- + CCl_4 \rightarrow (RO)_2P(O)Cl + CCl_3^- \quad (2)$$

The Atherton–Todd reaction is usually carried out in the presence of primary or secondary amines, although in some cases the addition of a tertiary amine to the primary amine in the reaction results in increased product yields.[4] When cyclohexylamine is used as the primary amine, it reacts further with the dialkyl chlorophosphate formed to give *N*-cyclohexyldialkylphosphoramide as the final product (eq 3). When CCl_3F is treated with dimethyl phosphonate and cyclohexylamine, an immediate precipitate of cyclohexylamine hydrochloride is formed. The other products are $(MeO)_2P(O)NHCy$ (^{31}P NMR: δ 10.7, septet, $^3J(PH)$ = 10.2 Hz) and CCl_2FH (^{19}F NMR: δ −80.8, d, $^2J(HF)$ = 53.4 Hz) (eq 4). This observation verifies that the Atherton–Todd reaction can be used to convert carbon–chlorine bonds in C_1 chlorofluorocarbons into carbon–hydrogen bonds. The yield of dimethyl-*N*-cyclohexylphosphoramide is 95%.

$$(RO)_2P(O)Cl + 2CyNH_2 \rightarrow (RO)_2P(O)NHCy + [CyNH_3]Cl \quad (3)$$

$$(MeO)_2P(O)H + CCl_3F + CyNH_2 \rightarrow (MeO)_2P(O)NHCy + CCl_2FH + [CyNH_3]Cl \quad (4)$$

The Atherton–Todd reaction with dimethyl phosphonate and CCl_3F can be carried out with triethylamine as base instead of cyclohexylamine. In this case the first product of the reaction is the dimethyl chlorophosphate. As the reaction proceeds, a precipitate of methyltriethylammonium chloride is formed in small quantities. This formation of methyltriethylammonium chloride results from a slow elimination reaction between the product, dimethyl chlorophosphate, and the base, triethylamine. This Arbuzov-type reaction yields $(MeO)_2P(O)OP(O)(OMe)Cl$ as the first product (Scheme I) and subsequent elimination reactions yield higher oligomers.[10] These different pyrophosphate oligomers are identified by single $^{31}P\{^1H\}$ NMR resonances at δ −10.0, −10.3, −11.1, and −11.3. Hydrolysis of the dimethyl chlorophosphate formed in the first step can also yield pyrophosphates. The product of the reaction between dimethyl phosphonate and triethylamine is analyzed by the addition of methanol, which converts any dimethyl chlorophosphate into trimethyl phosphate. The yield of trimethyl phosphate is 82%, along with 7% of unreacted dimethyl phosphonate and 11% of methoxylated pyrophosphate oligomers. In a separate experiment is has been shown that the monomethyl compound $MeEt_3N[(MeO)P(O)H(O)]$ is formed from a mixture of dimethyl phosphonate and triethylamine,[9] therefore there is no evidence to indicate that the mechanism with triethylamine is different from that with cyclohexylamine.

Scheme I

$$(MeO)_2P(O)H + CCl_3F \rightarrow (MeO)_2P(O)Cl + CCl_2FH$$

$$2(MeO)_2P(O)Cl + Et_3N \rightarrow (MeO)_2P(O)OP(O)(OMe)Cl + [MeEt_3N]Cl$$

When diethyl phosphonate is used in place of dimethyl phosphate with triethylamine as base, the yield of diethyl methyl phosphate is only 19%, with 66% diethyl phosphonate still remaining. A byproduct is tetraethyl pyrophosphate ($^{31}P\{^1H\}$ NMR: δ −13.9),[11] which is formed from the hydrolysis of diethyl chlorophosphate by traces of water. It is clear that triethylamine in place of cyclohexylamine or changing from dimethyl phosphonate to diethyl phosphonate reduces the yield of the chlorodialkyl phosphonate formed.

Simple thermodynamic considerations of the Atherton–Todd reaction (eq 1) lead to the conclusion that it is exothermic by 20 kcal mol^{-1}. This enthalpy change corresponds to the enthalpic difference between the C–H (~95 kcal mol^{-1}) and the C–Cl (~75 kcal mol^{-1}) bonds. The conversion of a P–H into a P–Cl bond contributes no significant enthalpy change to the overall reaction because each bond has an enthalpy of approximately 78 kcal mol^{-1}. No significant enthalpic difference is found between the chlorocarbons since the C–Cl bond enthalpies in CCl_3F (73 ± 2 kcal mol^{-1}) and CCl_2F_2 (76 ± 2 kcal mol^{-1}) are the same as those in CCl_4 (73 ± 2 kcal mol^{-1}). The respective C–H bond enthalpies in $CHCl_3$, CCl_2FH, and $CClF_2H$ are 96 ± 1, 100.1, and 102 ± 1 kcal mol^{-1}, again closely similar.[12]

The sequence of the addition of the reagents in eq 4 is important. In carrying out the reaction it is important to ensure that dimethyl phosphonate and cyclohexylamine do not remain in contact with each other in the liquid state before the CCl_3F is added to the reaction mixture. Otherwise, the reaction yield is low. This lowered yield is due to the formation of large amounts of the monomethyl phosphonate anion, $(MeO)P(O)H(O)^-$ (eq 5). The formation of this monomethyl anion rather than the dimethyl phosphonate anion, $(MeO)_2P(O)^-$, in the presence of cyclohexylamine, has been verified in a separate experiment. The compound $CyNH_2Me^+[(MeO)P(O)H(O)]^-$ is characterized by $^{31}P\{^1H\}$ NMR spectroscopy (δ 5.54) and by infrared spectroscopy (ν(P—H) = 2338 cm^{-1}, ν(P=O) = 1217 cm^{-1}). Although the monomethyl anion itself can act as a hydrogen donor, it appears that the lowered reactivity of $(MeO)P(O)H(O)^-$ in the Atherton–Todd reaction as compared to $(MeO)_2P(O)H$ is due to the lower acidity of the P—H bond in the anion. The pathway of the Atherton–Todd reaction is believed to involve the formation of an alkyl anion such as CCl_3^-, which then abstracts a proton from a P—H bond to give $CHCl_3$.[9] The higher the acidity of the

$$(MeO)_2P(O)H + CyNH_2 \rightarrow CyNH_2Me^+[(MeO)P(O)H(O)]^- \quad (5)$$

---

(8) Kong, A.; Engel, R. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 3671–2. Nifantiev, E. E.; Blagowestenskij, V. S.; Skljarskij, L. S. *Zh. Obshch. Khim.* **1973**, *44*, 108–10.

(9) Troev, K.; Kirilov, E. M. G.; Roundhill, D. M. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 1284–5.

(10) Steinberg, G. M. *J. Org. Chem.* **1950**, *15*, 637–47.

(11) Crutchfield, M. M.; Dungan, C. H.; Letcher, J. H.; Mark, V.; Van Wazer, J. R. *^{31}P Nuclear Magnetic Resonance, Tropics in Phosphorus Chemistry*; Wiley: New York, 1967; Vol. 5, p 331.

(12) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493–532. The value for CCl_2FH is a calculated one; see: Luke, B. T.; Loew, G. H.; McLean, A. D. *J. Am. Chem. Soc.* **1987**, *109*, 1307–17.

P—H bond, therefore, the more reactive will be the phosphonate to the haloalkyl anion.

The catalysis of the Atherton–Todd reaction by the monomethyl phosphonate anion can be explained by the series of reactions shown in Scheme I, whereby the sequence is initiated by the monomethyl phosphonate anion $(MeO)P(O)H(O)^-$ (Scheme II). Tautomerization of this anion to $(MeO)(HO)P(O)^-$, followed by chlorine abstraction from CCl_3F, completes the initiation stages of the reaction (i–iii). We are proposing, therefore, that the reaction is initiated by steps i through iii but that the major steps leading to product formation are those shown in steps iv and v. The deprotonation of $(MeO)_2P(O)H$ occurs in step iv, but not in step i, because the dichlorofluoromethane anion is a much stronger base than is cyclohexylamine. This proposed pathway only differs slightly from those proposed earlier.[8,9] The major difference, however, is in the involvement of $(MeO)P(O)H(O)^-$ rather than $(MeO)_2P(O)^-$ in the earlier steps of the reaction. The tautomerism of this four-coordinate anion to the three-coordinate anion $(MeO)(HO)P(O)^-$ is proposed in step ii of this scheme in order to generate a nucleophilic center at phosphorus rather than at oxygen. Although we have no *direct* evidence for this pathway, it explains the catalysis of the Atherton–Todd reaction by $(MeO)P(O)H(O)^-$, along with the inhibition of the reaction by this ion when it is present in large quantities. Thus the $(MeO)P(O)H(O)^-$ anion acts as an initiator of the reaction in steps i–iv where the dimethyl phosphonate anion $(MeO)_2P(O)^-$ is then formed as the reactive species for step v. The inhibition by the $(MeO)P(O)H(O)^-$ anion results from its being a poorer proton donor than $(MeO)_2P(O)H$, which is the chain carrier in reaction iv.

Dichlorodifluoromethane reacts with dimethyl phosphonate in the presence of triethylamine to give, after treatment with methanol, trimethyl phosphonate in only 5% yield. We find that dichlorodifluoromethane reacts with dimethyl phosphonate in the presence of a mixture of triethylamine and cyclohexylamine, a tertiary and primary amine mixture,[4] to give dimethyl-*N*-cyclohexylphosphoramide and $CClF_2H$ (^{19}F NMR: δ −71.9, d, $^2J(HF) = 64.6$ Hz) in 10% yield (eq 6). This yield of $CClF_2H$ is slightly

$$(MeO)_2P(O)H + CCl_2F_2 + 2CyNH_2 \rightarrow (MeO)_2P(O)NHCy + CClF_2H + [CyNH_3]Cl \quad (6)$$

higher than that obtained with triethylamine alone, but it is lower (10%) than that of CCl_2FH formed in eq 4 (95%). These observations of the lowered reactivity of CCl_2F_2 as compared to CCl_3F agree with earlier findings that the reactivity of chlorocarbons in the Atherton–Todd reaction decrease as fluoro substituents are introduced onto carbon.[13] From our results we find a relative reactivity that follows the sequence

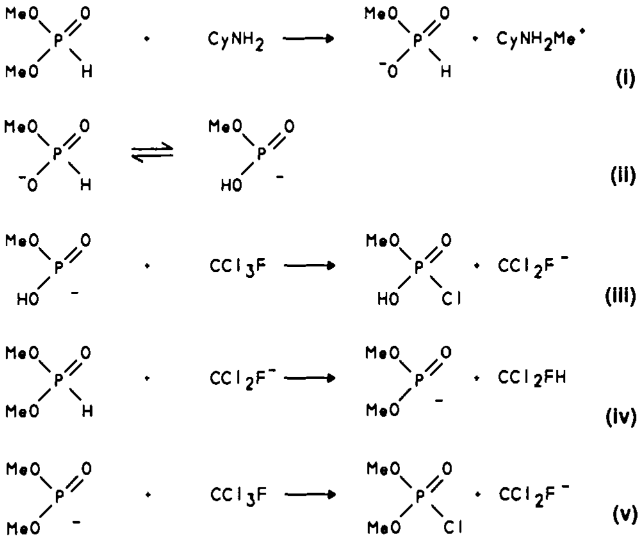
$$CCl_4 > CFCl_3 > CCl_2F_2 \gg CCl_3H$$

The reactivity of chlorocarbons with dialkyl phosphonates is therefore reduced if fluoro substituents are introduced onto the carbon and suppressed if hydrogen substituents are present. Further work is in progress to try to provide an explanation for this reactivity sequence.

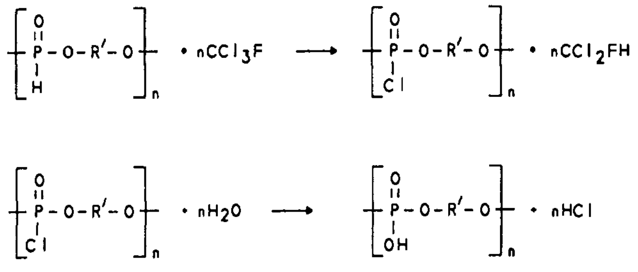
If the Atherton–Todd reaction is to become a useful method for converting carbon–chlorine bonds into carbon–hydrogen bonds, it is necessary for the reaction to be made catalytic or for the phosphorus compound produced in the reaction to be converted into a useful coproduct. At this time our efforts to convert either $(MeO)_2P(O)Cl$ or $(MeO)_2P(O)NHCy$ into $(MeO)_2P(O)H$ by reduction with hydrogen have not been successful. This reaction can, however, be achieved by using sodium borohydride as the reducing agent (eq 7).[14] Lithium aluminum hydride cannot be used because it will reduce the phosphoryl (P═O) group as well as the P—Cl bond.[15]

$$(MeO)_2P(O)Cl + H^- \rightarrow (MeO)_2P(O)H + Cl^- \quad (7)$$

Scheme II



Scheme III



(R′ = $CH_2CH_2CH_2$)

Polyphosphate chains are basic parts of two important groups of biopolymers, namely nucleic acids and teichoic acids.[16] One synthetic route to these compounds is to oxidize a polyphosphonate, which can be readily synthesized by the polycondensation of dialkyl phosphonates and polyols.[6,17] We now find that we can use the Atherton–Todd reaction with dimethyl phosphonate and CCl_3F in the presence of triethylamine to convert the P-H bonds in the polyphosphonate into P–Cl bonds and to then subsequently hydrolyze those functional groups to the desired P–OH bonds of the polyphosphate (Scheme III).

Acknowledgment. We thank the Center for Bioenvironmental Research for financial support. We thank R. Hoff for assistance with the ^{19}F NMR spectra.

Registry No. CCl_3F, 75-69-4; CCl_2F_2, 75-71-8; CCl_2FH, 75-43-4; $CClF_2H$, 75-45-6; dimethyl-*N*-cyclohexylphosphoramide, 32405-87-1; cyclohexylamine, 108-91-8; triethylamine, 121-44-8; dimethyl phosphonate, 868-85-9; trimethyl phosphonate, 512-56-1; diethyl phosphonate, 762-04-9; diethyl methyl phosphonate, 867-17-4; tetraethylammonium monoethyl phosphonate, 139914-78-6; tetraethyl pyrophosphate, 107-49-3; polyphosphonate, 59199-86-9; methylcyclohexylammonium monomethyl phosphonate, 139914-79-7.

---

(13) Atherton, F.; Todd, A. *J. Chem. Soc.* **1947**, 674–8. A recent paper has reported that the reaction between the diethyl phosphite anion and dichlorodifluoromethane gives a phosphonate containing a phosphorus–carbon bond (Blackburn, G. M.; Taylor, G. E. *J. Organomet. Chem.* **1988**, *348*, 55–61). We find no evidence for the formation of such compounds in our reactions.

(14) Engel, R.; Chakraborty, S. *Synth. Commun.* **1988**, *18*, 665–70.

(15) Sasse, K. In *Methoden der Organische Chemie*; Müller, E., Ed.; Georg Thieme Verlag: Stuttgart, Germany, 1963; Vol. XII/1, pp 60–3.

(16) Pretula, J.; Penczek, S. *Makromol. Chem.* **1990**, *191*, 671–80. Brosse, J. C.; Derouet, D.; Fontaine, L.; Chairatanathavorn, S. *Makromol. Chem.* **1989**, *190*, 2339–45.

(17) Kaluzynski, K.; Libiszowski, J.; Penczek, S. *Macromolecules* **1976**, *9*, 365–7.