This is ruled out, however, because ionic addition to 2,4-dehydroadamantane has been studied and is known to give not **4** but **7**.[9] Alternatively, an unprecedented heterolytic photocleavage could have occurred in the polar solvent methanol giving an adamantyl cation which could have added methanol to form ether **4**. This explanation is satisfactory for ester **2** but not for ester **3**. The latter would give the 2-adamantyl cation which is known not to rearrange[10] but to give ether **7** which was not observed.

The evidence leaves little doubt that adamantene was formed. It is interesting to note that similar but unsuccessful attempts to generate this alkene from ketone precursors have been reported during this study.[4] Possibly the higher singlet excitation energy of esters accounts for this different behavior. Further studies are now in progress to increase the alkene yield[5] and to detail the properties of adamantene.

Acknowledgment. Partial support of this work by the donors of the Petroleum Research Fund (PRF-1511G), administered by the American Chemical Society, and the ardent competitory instigation of Dr. J. L. Fry are thankfully acknowledged.

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Phosphoranes as Nonobligatory Intermediates in Reactions of Alkoxyphosphonium Salts

Sir:

A number of reactions exist in the field of organophosphorus chemistry which involve the formation of an alkoxyphosphonium salt intermediate followed by dealkylation to the corresponding phosphoryl compound.[1] A few well-known examples of these reactions would include the Arbusov reaction,[2] the Perkow reaction,[3] as well as the acid-catalyzed hydrolysis of phosphorus esters.[4] In general, the dealkylation step involves a nucleophilic displacement at carbon of the alkyl group, with C–O bond cleavage.

In other reactions of alkoxyphosphonium salts such as alkaline hydrolysis,[5,6] the nucleophile attacks at phosphorus rather than at carbon resulting in P–O bond cleavage. The possibility exists that many nucleophiles, which ultimately react at carbon with C–O bond cleavage, may prefer attack at phosphorus to form a pentacoordinate intermediate but are prevented energetically from displacing the relatively poor alkoxy leaving group. Instead, return to phosphonium salt with subsequent attack at carbon would be the overall lower energy pathway. Thus, a pentacoordinate phosphorus intermediate may be involved only as a nonobligatory intermediate in the reaction of nucleophiles with alkoxyphosphonium salts.

We decided to test the possibility of a reversible phosphorane formation in competition with nucleophilic attack at carbon by investigating the stereochemistry of the reaction of various nucleophiles with a chiral phosphonium salt. Formation of the stereochemically nonrigid phosphorane[7] could lead to loss of stereospecificity in the overall reaction, rendering the phosphorane operationally detectable. Our results indicate that the reaction of nucleophiles with an acyclic dialkoxyphosphonium salt, menthoxymethoxymethylphenylphosphonium tetrafluoroborate (**1**), resulting in eventual C–O bond cleavage may proceed with either complete retention of configuration at phosphorus or loss of stereospecificity, depending on the nature of the nucleophile.

Pure $(S)_P$-**1**[8,9] (mp 67–69°), prepared by O-methylation[10] of $(S)_P$-menthyl methylphenylphosphinate, $(S)_P$-**2**,[11] was mixed with an equal molar amount (1 mmol) of the various nucleophiles in the solvents (10 ml) listed in Table I. After *ca.* 10 min, work-up by diluting with dichloromethane (100 ml), extracting with water,[12] drying, and reconcentrating under vacuum resulted in the quantitative formation of **2**. Thus cleavage of the O–CH_3 bond is the exclusive mode of reaction. The product stereochemistry was identified by ^1H nmr[11] and the results are indicated in Table I. The product phosphinate, **2**, was stereochemically stable to the reaction conditions, indicating that any loss in stereospecificity at phosphorus must have occurred prior to product formation.[13]

Table I. Stereochemistry of the Products from the Reaction of $(S)_P$-**1** with Various Nucleophiles

Nucleophile	Solvent	Products $(S)_P$-**2**	Products $(R)_P$-**2**	Stereochemistry
I^- (Li^+)	*a*	100	0	Retention
Br^- (Li^+)	*a*	100	0	Retention
Cl^- (Li^+)	*a*	100	0	Retention
F^- (Li^+)	*b*	60	40	Epimerization
$PhNH_2$	*b*	100	0	Retention
i-$PrNH_2$	*b*	60	40	Epimerization
Pyridine	*b*	100	0	Retention
Et_3N	*b*	60	40	Epimerization

[a] Acetone. [b] Dichloromethane.

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(8) The configuration notations $(S)_P$ and $(R)_P$ refer to the stereochemistry at phosphorus.

(9) The ^1H nmr spectrum (CH_2Cl_2) of $(S)_P$-**1** featured PCH_3 (d, δ 2.5, J_{HCP} = 14 Hz) and $POCH_3$ (d, δ 4.2, J_{HCOP} = 12 Hz).

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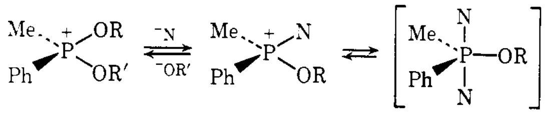
(12) $(S)_P$-**1** in the absence of a nucleophile is stable to these work-up conditions.

A common feature of any reasonable mechanism which can explain epimerization at phosphorus in the presence of a nucleophile involves bond formation between the nucleophile and the phosphorus atom. Two mechanisms can be advanced involving the formation of a pentacoordinate intermediate (phosphorane). This intermediate, by virtue of its stereochemical nonrigidity, can isomerize[14] prior to re-formation of the phosphonium salt, resulting in epimerization. Alternatively, this phosphorane can react with a second mole of nucleophile to form a hexacoordinate species which may be achiral at phosphorus (trans arrangement of the two nucleophiles). This latter mechanism is difficult to rule out; however, it is important to point out that in one case[17] where nucleophilic substitution at pentacoordinate phosphorus has been observed and postulated to proceed through a hexacoordinate intermediate or transition state, displacement of the equatorial ligands was the preferred pathway. Thus, if the assumption is made that the first addition of a nucleophile to the phosphonium salt occurs in the axial position,[18] the second nucleophile would add to form the octahedral intermediate or transition state of the cis configuration. This species is chiral and would not lead to epimerization at phosphorus without further rearrangements.

A third mechanism, which has been postulated in similar reactions,[5,19] involving multiple displacements at phosphorus (eq 1), is less likely from our results. It

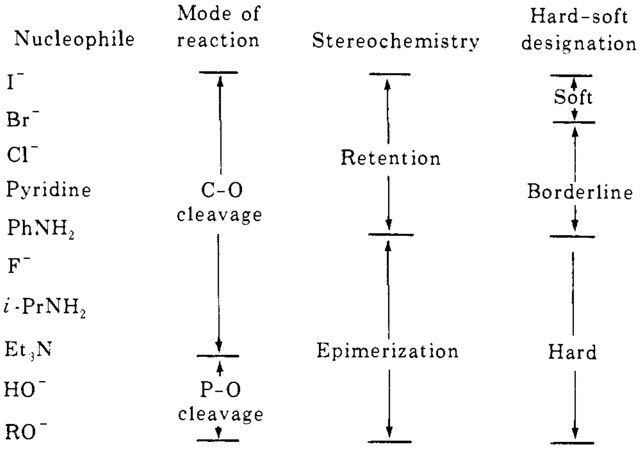


(1)

has been observed in the alkaline hydrolysis of $(S)_P$-**1** (displacement at phosphorus) that appreciable (26%) loss of the menthoxy group occurs. Thus in the above system, one would expect crossover to occur in re-formation of the dialkoxyphosphonium salt, leading to dimethoxymethylphenylphosphonium tetrafluoroborate (**3**). The formation of methyl methylphenylphosphinate (**4**) by eventual C–O cleavage of **3** was not detected.

Our results above have indicated that certain nucleophiles in fact prefer to react at phosphorus rather than at carbon in the dialkoxyphosphonium salt **1** and that this attack is, in certain cases, stereochemically detectable. There appears to be a close analogy between the ability of a nucleophile to induce epimerization at phosphorus and its classification according to the empirical concept of hard and soft acids and bases.[20] Scheme I demonstrates this analogy. Apparently, in

Scheme I



the terminology of the HSAB concept, the phosphorus acts as a "hard" acid while the carbon is "soft" or "borderline" in this system. It should be pointed out that our stereochemical probe is not able to detect phosphorane formation of insufficient lifetime to undergo the further transformation necessary to yield epimerized phosphonium salt. Thus, the change in stereochemistry of the displacement reaction as a function of the nucleophile may not directly reflect the change in mode of addition of a nucleophile to the phosphonium salt. We are presently undertaking studies to test the validity of this doubt.

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(13) We have not been able to purify $(R)_P$-**1** to the degree necessary to establish that the 60:40 ratio of $(S)_P$-**2**:$(R)_P$-**2** reflects complete loss of stereospecificity.

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Evidence for a Steric Effect on Directly Bonded Carbon–Fluorine and Carbon–Proton Nuclear Magnetic Resonance Couplings[1]

Sir:

Systematic investigations of the proton nmr spectra of a number of alkenes, cycloalkenes, and aromatic hydrocarbons have demonstrated that various types of steric distortions affect the magnitudes of proton–proton coupling constants.[2–5] In the case of the cis-vicinal vinylic coupling, $^3J_{\mathrm{HH}}$, both experimental results and approximate theoretical treatments[4,5] of all the reasonable types of strain-induced molecular distortions suggest that in-plane C═C—H bond angle changes

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