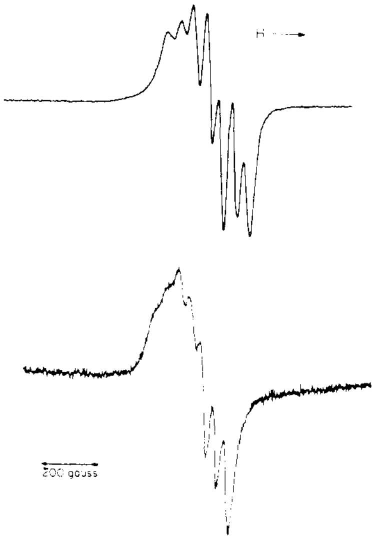

Figure 2. Solution X-band EPR spectra (25 °C) of $Cu^{II}Cu^{I}L(ClO_4)$, **2**, in CH_2Cl_2 (top) and CH_3CN (bottom).

to distorted square planar for copper(II)) become more difficult in frozen solutions resulting in a "locked-in" configuration on the EPR time scale.[16] The latter explanation is especially attractive for CH_2Cl_2 solutions of **2** in which, presumably, only ClO_4^- and CH_2Cl_2 are available for axial ligation.

These EPR results are in contrast to those recently reported by Addison on a similar macrocyclic copper(II)-copper(I) complex, **4** (R = CH_3), which exhibits four-line EPR spectra even at room temperature in CH_3CN.[17] In this case methyl substitution probably alters the conformational properties of the macrocycle sufficiently to inhibit thermal electron transfer on the EPR time scale at temperatures where it occurs with **2**.

It should be noted that several cobalt(III)-cobalt(II) complexes of this macrocycle (R = H) have been prepared and characterized crystallographically, although their mixed-valence spectral properties were not discussed.[18]

Five coordination for copper(I) is most unusual. That **2** exhibited an IT band is good evidence for the presence of copper(I), as opposed to a copper(II) radical anion. Since the $Cu^{II}Cu^{II}L$ complex, **1**, does not react with CO, then the CO adduct, $Cu^{II}Cu^{I}L(CO)$, **3**, if five-coordinate as is expected, must also be regarded as containing copper(I) with a most unusual coordination number.

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(8) Platinum indicating electrodes; 0.1 M in tetrabutylammonium perchlorate; $E^f = (E_{p_a} + E_{p_c})/2$, given vs. the SHE as explained in ref 9. Full details of the electrochemical properties of these complexes will be forthcoming.

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Stereochemistry of the S_N2' Reaction of an Acyclic Allylic Chloride with a Secondary Amine

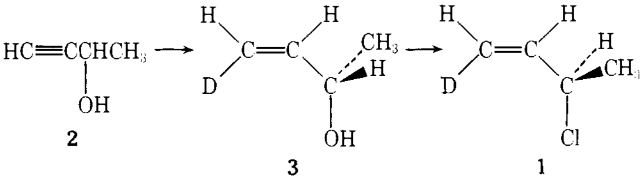
Sir:

The S_N2' reaction (bimolecular nucleophilic substitution with allylic rearrangement) has been of synthetic and mechanistic interest for years.[1] Since the first reported example,[2] numerous instances of the process have been documented. Bordwell[1a,3] has argued that the concerted mechanism is incorrect; rather, all of these reactions proceed via an ion-pair intermediate of the type postulated by Sneen[4] for S_N reactions in general.

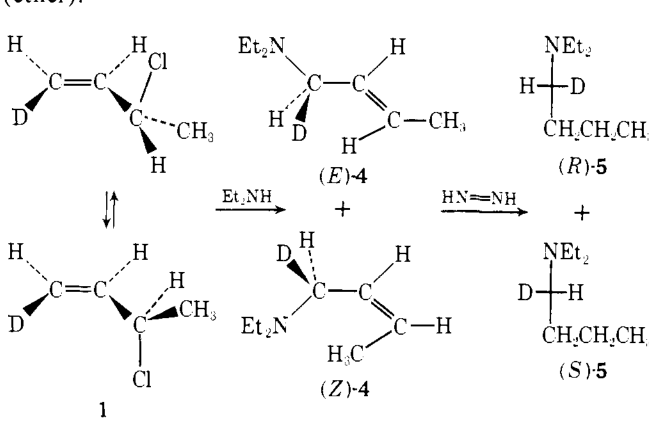
Regardless of the precise timing of the bond-making and bond-breaking steps, one can still inquire into the stereochemistry of the reaction. Most theoretical analyses have led to a predicted preference for syn attack[5,7] (in which the nucleophile and leaving group are on the same face of the allylic system), while allowing the possibility of anti stereochemistry for certain combinations of entering and leaving groups.[7c,e]

Until this year, the definitive experimental investigation of the stereochemistry was that of Stork and White[8] who showed that *trans*-6-alkyl-2-cyclohexen-1-yl 2,6-dichlorobenzoates underwent exclusive syn attack by piperidine and malonate. More recently, Stork and Kreft[9] reinvestigated this system (and the related mesitoate esters of the cis and trans isomers) and demonstrated that the stereochemistry could vary from predominantly syn to largely anti as the nucleophile was changed. One can argue, however, that a cyclohexenyl system has certain built-in conformational biases which force syn attack, independent of any stereoelectronic requirements of the S_N2' reaction.[10] An acyclic case, free of such complications, has been reported by Stork and Kreft[13a] who found that internal nucleophilic attack by a thiolate anion occurred primarily anti, although a closely related intramolecular process involving carbanionic attack proceeded syn.[13b] The only other stereochemical studies are those involving metal hydrides or organometallic reagents with allylic systems;[14] the outcome (a nearly random blend of syn and anti) and the doubtful relevance of such reactions to a truly nucleophilic process render these experiments of little value in the present context. We now report that the intermolecular S_N2' reaction in an unbiased acyclic case proceeds with syn stereospecificity.

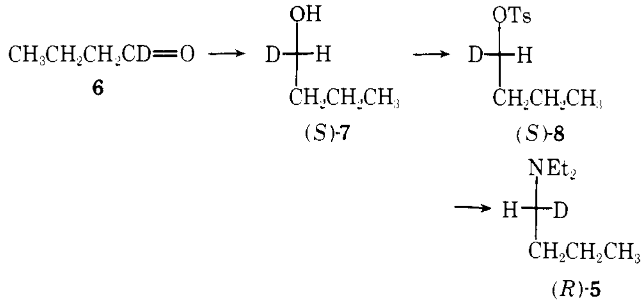
The substrate selected for this study, (*R*)-(−)-3-chloro-(*Z*)-1-butene-*1-d* (**1**), is merely an isotopic variant of α-methylallyl chloride. the compound used by Young and coworkers[2,6,15] to establish the scope of the S_N2' reaction. *dl*-1-Butyn-3-ol (**2**) was reduced to *dl*-1-buten-3-ol-(*Z*)-*1-d* by $LiAlH_4$/THF followed by D_2O.[16] Resolution with brucine via the phthalate half-ester[17] followed by hydrolysis gave (*S*)-(+)-alcohol **3**, α^{30}D +21.04 ± 0.01° (neat, *l* = 1), 76.2 ± 0.3% optically pure.[17,18] Reaction of **3** with triphenylphosphine/hexachloroacetone[19] proceeded with very high regioselectivity and nearly complete inversion of configuration to chloride **1**, α^{24}D −46.13 ± 0.01° (neat, *l* = 1), 75.5 ± 0.1% optically pure.[20]



The reaction of optically active (*R*)-(−)-chloride **1** with diethylamine afforded a 99:1 mixture of S_N2' and S_N2 products from which the latter could be removed by preparative gas chromatography. The major fraction, itself a 95:5 mixture (by GLC) of (*E*)-**4** and (*Z*)-**4**,[21] α^{24}D +1.5 ± 0.1° (neat, *l* = 1), was reduced by diimide[22] to *N,N*-diethyl-1-aminobutane-*1-d* (**5**), $[\alpha]^{25}$D +3.5 ± 0.2° (ether) and $[\alpha]^{25}{}_{365}$ +12.2 ± 0.2° (ether).



Because the absolute configurations and maximum rotations of amines **4** and **5** had not been reported, we prepared (*R*)-(+)-**5** by an unambiguous route. Yeast-catalyzed reduction[23] of butanal-*1-d* (**6**)[24,25] afforded (*S*)-(+)-1-butanol-*1-d* (**7**), $[\alpha]^{25}$D +0.39 ± 0.01° (neat),[26] which was converted into (*S*)-(−)-tosylate **8**, α^{25}D −0.07 ± 0.01° (neat, *l* = 1). Reaction of **8** with diethylamine gave optically pure (*R*)-(+)-**5**, $[\alpha]^{24}$D +5.66 ± 0.03° (ether) and $[\alpha]^{24}{}_{365}$ +19.14 ± 0.03° (ether).[28]



The measured specific rotation of amine **5** from the S_N2' reaction must be adjusted before it can be compared with that of optically pure material. Given that (*Z*)-**4** is present to the extent of 5% and that its chirality should be the reverse of the major isomer (assuming that they are produced by the same mechanism), the reduction product is at best 90% optically pure; furthermore, starting chloride **1** was, itself, but 75.5% optically pure. Correction by these two factors and assuming reasonable error limits gives adjusted values for saturated amine **5** of +5.2 ± 0.3° and +18.0 ± 0.5° at 589 and 365 nm, respectively. With these numbers, one can calculate that the S_N2' reaction has occurred with 96 ± 2% or 97 ± 1%, respectively, syn stereochemistry. Given the uncertainty in the reported maximum rotation of chloride **1** and the error in determining the *E*/*Z* ratio of allylic amine **4**, it is not unreasonable to conclude that the reaction is, in fact, stereospecific.

Ingold[30] argued that the cyclic hydrogen-bonded transition state proposed[6] for secondary amines with allylic halides warrants the designation S_Ni' rather that S_N2'. Regardless of one's preference of terminology, the results reported here demonstrate that in this instance, at least, nucleophile attacks the allylic system syn to the leaving group. Whether this is due to hydrogen bonding or to an inherent stereoelectronic preference in S_N2' reactions will, we hope, be settled by future experiments with different entering and leaving groups.

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(26) Yeast reduction is a stereospecific process, but this value is only 83% of that cited for optically pure material.[23] Within the limits of detection by the camphanate ester method,[27] the compound is optically pure. The diminished $[\alpha]$ is due to the presence of a small amount of a high-rotating levorotatory impurity which we have succeeded in separating (but not identifying) by preparative GLC.
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(28) The unusually large specific rotation of tertiary amine **5** is unprecedented

among saturated chiral deuterium compounds.[29] We have observed a similarly large [α] for the corresponding dimethylamino compound, synthesized either by direct displacement on tosylate **8** or by reaction of **8** with NaN_3 followed by $LiAlH_4$ reduction and Eschweiler-Clarke methylation; because the two routes gave amine with the same [α], it is reasonable to conclude that the reaction of the tosylate with a secondary amine, like the reaction with azide ion,[29c,d] occurs with complete inversion of configuration.

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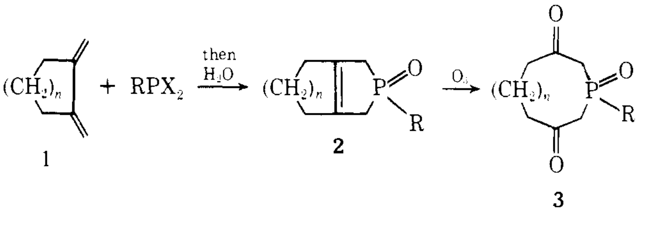
A New Approach to the Synthesis of Large-Ring Phosphorus Compounds[1]

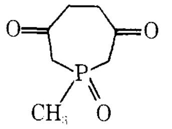
Sir:

Very few monocyclic phosphorus compounds with ring size greater than six have been prepared, and virtually nothing is known about the stereochemical properties of the especially interesting systems where the ring contains about seven-nine members.[2] On the other hand, a great deal of work has been done on five- and six-membered rings, and research continues at a fast rate on these relatively accessible systems. In addition, studies focused on possible aromaticity in the five- and six-membered rings are numerous, but, save for one case, where cyclic delocalization was considered for 1-phenylphosphepin 1-oxide,[3] no attention has been given to delocalization phenomena among phosphorus compounds with larger rings. We have devised a simple synthetic approach for phosphorus compounds containing seven or more ring members that should lead to many new compounds permitting the exploration of stereochemical and delocalization phenomena. Our approach provides diketo derivatives of the ring systems, an extremely desirable feature since the keto functionality permits synthetic maneuverability at important ring positions.

Our method basically comprises two steps from a non-phosphorus-containing starting material. We first employ the family of 1,2-dimethylenecycloalkanes (**1**) as dienes in the McCormack cycloaddition[4] with phosphorus(III) halides, obtaining in good yield under conventional conditions (standing for several days at room temperature) a series of bicyclic phospholene derivatives (**2**). These compounds have been fully characterized by analysis and by ^1H, ^{13}C, and ^{31}P NMR spectroscopy, details of which will be published elsewhere. The phospholene products are then subjected to ring-opening ozonolysis at −78 °C in methanol. Following removal of any excess ozone by nitrogen bubbling, trimethyl phosphite is added to the mixture to reduce the ozonide and the temperature allowed to reach that of the room. Evaporation of the solution leaves a crystalline residue of the diketones **3**, which is broken up in ether for washing and collection on a filter.



We have so far used the dienes[5] based on the cyclobutane, cyclopentane, and cyclohexane systems in this new synthesis, and from methylphosphonous dichloride have obtained derivatives of the phosphepane (**4**), phosphocane (**5**), and phosphonane (**6**) systems, respectively. These products are easily recrystallized (**6**, benzene; **4** and **5**, acetonitrile) stable solids. They are mildly hygroscopic. Some important physical properties are given in Table I; all of the compounds gave correct C, H, and P analyses. The spectra do not reveal the presence of any enol form, in contrast to the behavior of a β-keto derivative of the five-membered phospholane system.[6] However, the four α protons of **6** were found to be rapidly and completely exchanged when D_2O was added to a Me_2SO solution.



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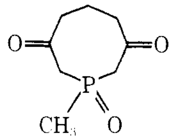

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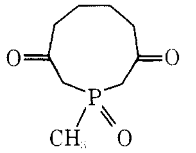

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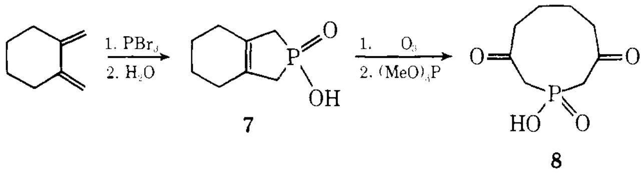
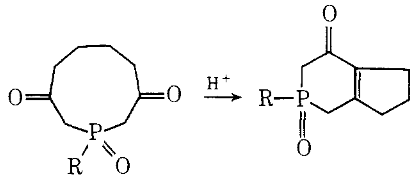
Phosphorus trihalides also have been used in our two-step process, giving diketophosphinic acids. Thus, starting with 1,2-dimethylenecyclohexane and PBr_3 we have formed phosphinic acids **7** and **8**. Compound **8** had the intriguing property of undergoing internal aldol condensation on storage as the solid at room temperature for several weeks. The same reaction occurred within 2.5 h simply on refluxing in benzene with water removal (Dean-Stark). The product is a new bicyclic compound **9**, mp 150–152 °C, whose structure became evident





9, R = OH (93%)
10, R = CH₃ (87%)

Table I. Properties of the 1-Substituted β,β'-Diketophosphacycloalkane 1-Oxides.

Compd	Yield, %	Mp, °C	$\nu_{C=O}$, cm^{-1}	^{31}P NMR, δ[a]	^{13}C NMR, δ[b] C_α	C=O	C_γ	C_δ	*P*-CH_3
4	90	182–184	1690[c]	+29.8	49.2 (50.1)	202.8 (4.9)	38.5[d]		16.2 (70.8)
5	83	204–207	1690[c]	+29.0	45.3 (48.8)	204.5 (4.9)	45.6[d]	19.0[d]	14.7 (70.8)
6	94	130–132	1700[e]	+32.0	46.1 (54.7)	206.0 (4.9)	44.5[d]	23.4[d]	19.2 (72.3)
8	84	102–104	1690[f]	+26.5	47.4 (77.2)	205.8 (2.9)	42.5[d]	23.0[d]	

[a] In Me_2SO-d_6; downfield from 85% H_3PO_4 as reference. Taken on a Bruker HFX-10 spectrometer with proton decoupling. [b] Compounds **4**, **5**, and **8** in Me_2SO-d_6; **6** in $CDCl_3$. Values in parentheses are ^{13}C–^{31}P coupling constants, in hertz. Taken on a JEOL FX-60 spectrometer with proton decoupling. [c] Nujol mull. [d] No ^{13}C–^{31}P coupling observed. [e] $CHCl_3$ solution. [f] KBr disk.