among saturated chiral deuterium compounds.[29] We have observed a similarly large $[\alpha]$ 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 $[\alpha]$, 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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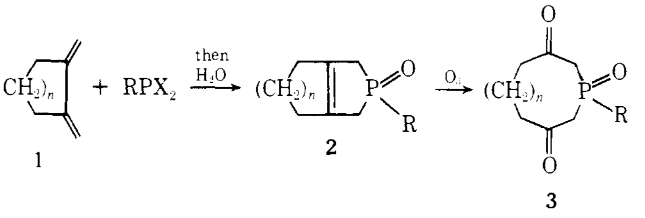
A New Approach to the Synthesis of Large-Ring Phosphorus Compounds[1]

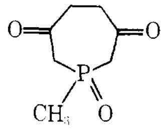
Sir:

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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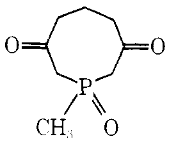

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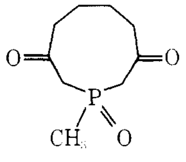

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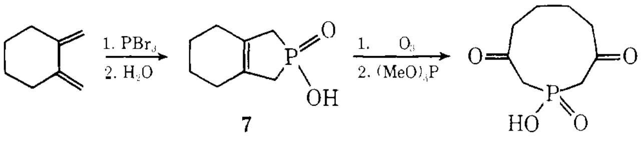
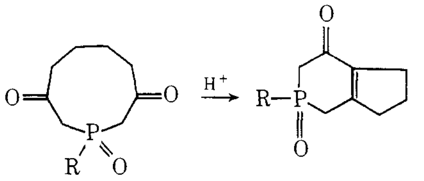
Phosphorus trihalides also have been used in our two-step process, giving diketophosphinic acids. Thus, starting with 1,2-dimethylenecyclohexane and PBr_3 we have formed phosphinic acids **7** and **8**. Compound **8** had the intriguing property of undergoing internal aldol condensation on storage as 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 = CH_3 (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.

from analysis and spectral features for an α,β-unsaturated ketone (^{13}C NMR δ 188.9 (C=O), 140.0 (=C$_\alpha$), 154.7 (=C$_\beta$); IR $\nu_{C=O}$ 1650, $\nu_{C=C}$ 1610 cm^{-1}) in a monomeric system (single ^{31}P signal at δ +46.8). The phosphine oxide counterpart of **8** (**6**) also could be made to undergo the internal aldol condensation, but required the presence of a trace of added acid (*p*-toluenesulfonic) catalyst in the refluxing benzene medium. The product (**10**) had mp 97-98 °C and similar spectral features to those of **9**. These bicyclic compounds are members of a new series and may prove to have value as intermediates for construction of multicyclic phosphorus compounds, another area under intense development.[7]

References and Notes

(1) Supported in part by Public Health Service Grant CA-05507 from the National Cancer Institute.

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A Comparison of Allyl and Nitrosyl Coordination in the 18-Electron Complex Allylnitrosylbis(triphenylphosphine)ruthenium and Its CO Adduct

Sir:

The dual nature of both allyl and nitrosyl ligands as 1e$^-$ and 3e$^-$ donors in transition metal complexes is well established,[1,2] and recent attention has focused on the catalytic potential which this duality provides.[3-6] Sorely lacking, however, are examples of stable, mixed allyl nitrosyl complexes, and the comparative studies of these ligands and their bonding propensities which such species will allow. To date, only two systems of this type have been reported,[7,8] the most extensively studied being Fe(NO)(η^3-C$_3$H$_5$)L$_2$ where L = CO, tertiary phosphine.[8] We wish to report the synthesis and crystal structure of the first platinum group metal complex of this type, and evidence for its reaction with CO to form a five-coordinate species containing a bent nitrosyl.

Reaction of RuCl(NO)(PPh$_3$)$_2$[9] in benzene or THF with tetraallyltin at room temperature gives the red, air-sensitive Ru(NO)(η^3-C$_3$H$_5$)(PPh$_3$)$_2$, **1**, in 70% yield. Recrystallization from THF/Et$_2$O affords analytically pure[10] crystals which are stable in air for several weeks. The complex is soluble in C$_6$H$_6$, THF, and CH$_2$Cl$_2$, but decomposes rapidly in CHCl$_3$ and CCl$_4$ to form RuCl$_3$(NO)(PPh$_3$)$_2$. The IR spectrum of **1** (KBr) shows a nitrosyl stretch at 1620 cm^{-1} (1640 cm^{-1} in CH$_2$Cl$_2$), while the ^{1}H NMR spectrum exhibits a pattern characteristic of essentially symmetric η^3-allyl coordination with phosphorus coupling to the anti protons. The ^{1}H NMR spectrum of **1** is shown in Figure 1A and a computer simulation[11] is given in Figure 1B (central proton, δ 4.70; anti protons, 1.00; syn protons, 2.40 and 2.42 ($^3J_{syn}$ = 4.0 Hz; $^3J_{anti}$ = 10.0 Hz; $J_{PH_{anti}}$ = 6.0 Hz)).

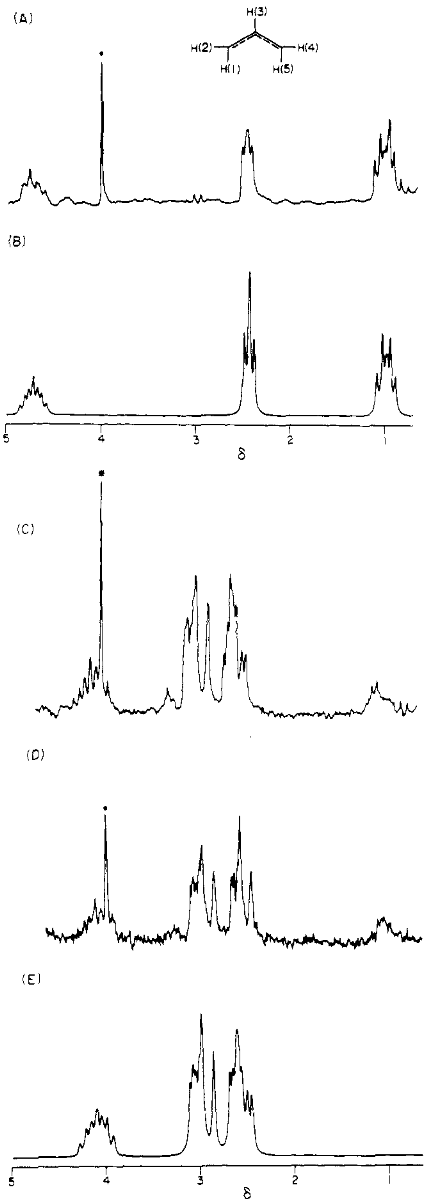

Figure 1. ^{1}H NMR spectra of the allyl-nitrosyl complexes in benzene-d_6: (A) Ru(η^3-C$_3$H$_5$)(NO)(PPh$_3$)$_2$; (B) computer simulation of spectrum A; (C) Ru(η^3-C$_3$H$_5$)(NO)(CO)(PPh$_3$)$_2$; (D) ^{31}P-decoupled spectrum of the carbonyl adduct above; (E) computer simulation of spectrum C. Resonances marked with an asterisk (*) are due to traces of H$_2$O in solvent.

The coordination geometry of **1** and the mode of nitrosyl coordination were unambigously established by a single-crystal x-ray analysis. The complex crystallizes in the monoclinic space group $P2_1$ in a cell of dimensions a = 9.04 (1), b = 17.47 (3), c = 11.51 (1) Å; β = 115.39 (5)° with Z = 2. The structure was solved by standard heavy-atom methods and refined by least-squares procedures to final agreement factors R and R' of 0.0299 and 0.0383 for 2074 reflections having $F_0 \geq 3\sigma(F_0)$ and 159 variables.[12] Tables of final structural parameters and intramolecular distances and angles are available as supplementary material (see paragraph at the end of the paper).

Figure 2 presents a perspective view of the structure of **1**