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Cheletropic Reactions of Tricyclo[5.3.1.$0^{4,9}$]undeca-2,5-diene with Dichlorophosphines. Synthesis of Novel Phosphapolycycles

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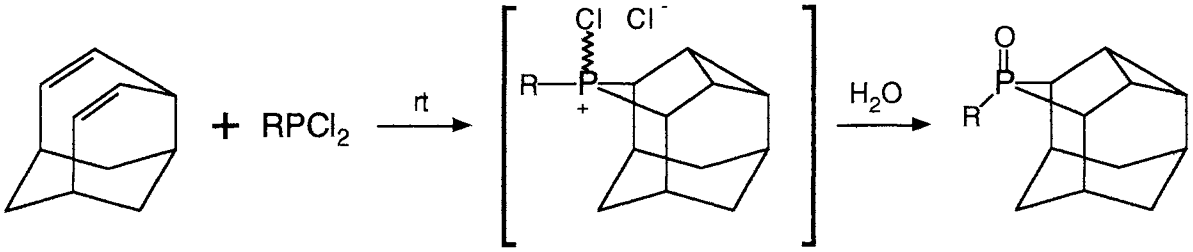
The cheletropic reaction of dichlorophosphines to tricyclo[5.3.1.$0^{4,9}$]undeca-2,5-diene, followed by hydrolysis with water gave 6-substituted-6-oxo-6-phosphapentacyclo[6.3.1.$0^{2,4}$.$0^{3,7}$.$0^{5,10}$]dodecanes whose structures were established by an X-ray crystallography.

Although bridged aza-1) and oxa-polycycles2) have been reported from several research groups, only few examples of bridged phosphapolycycle have been described as far as we know.3) It occurred to us that McCormack reaction4) of tricyclo[5.3.1.$0^{4,9}$]undeca-2,5-diene (**1**)5) with dichlorophosphines would provide an extremely simple entry to a novel type of phosphapolycycle. This is a subject of the present communication. Reaction of **1** with dichlorophenylphosphine (**2a**) at room temperature under nitrogen for 21 h gave 6-oxo-6-phenyl-6-phosphapentacyclo[6.3.1.$0^{2,4}$.$0^{3,7}$.$0^{5,10}$]dodecane (**3a**) as a single product in 85% yield after hydrolysis. Unfortunately, inspection of ^{1}H- and ^{13}C-NMR did not permit determination of stereochemistry around the phosphorous moiety, but the structure of which was unambiguously established by an X-ray analysis (Fig. 1).6) It is interesting to note that C3-C3' (1.528(3) Å) is significantly longer than C2-C3 (1.502(3) Å) and the lengthening of C4-C7(1.568(2) Å) may be due to the eclipsed conformations around C4-C7 and C4'-C7' bonds as well as the close approach (2.38(3) Å) of O9 and an axial H-atom on C6.



1 **2a-c** **3a-c**

A controlled experiment has revealed that the diene **1** was much more reactive toward **2a** than norbornadiene; an equimolar mixture of **1** and norbornadiene with **2a** produced exclusively **3a**. This is in agreement with unusually strong through-space interaction in a 1,4-cyclooctadiene system of **1**.7) Although the mechanism of hydrolysis of the initial adducts is unknown because of their instability and of their rapid equilibrium through the pentacovalent bipyramidal intermediate involved in hydrolysis,[8] the steric hindrance between R and C6-H is presumably responsible to the exclusive formation of the exo adduct **3a**.

Analogous cheletropic reactions of dichloroethylphosphine (**2b**) and dichloroethylphosphite (**2c**) to **1** produced the corresponding phosphapolycycles **3b**[9] and **3c** in moderate yields (Table 1).

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Table 1. 6-Substituted 6-oxo-6-phosphapentacyclo-[6.3.1.0^{2,4}.0^{3,7}.0^{5,10}]dodecanes

	R		Yield	Mp	^{31}P-NMR
	2a-c	3a-c	%	θm/°C	(δ /ppm)
a	Ph	Ph	85	216	67.63
b	Et	Et	40	121	77.99
c	OEt	Cl	19	154	101.01

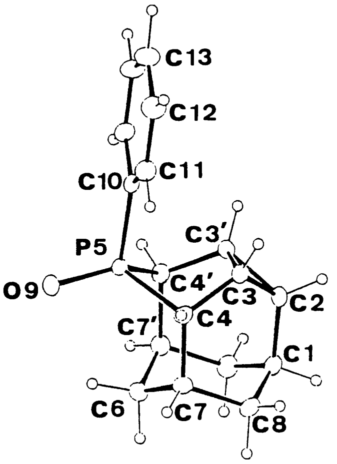

Fig. 1. Perspective drawing of the molecule **3a**. Selected bond length(Å) and angles(°): C2-C3 1.502(3); C3-C3' 1.528(3); C4-P5 1.833(2); C4-C7 1.568(2); C1-C2-C3 119.6(2); C2-C3-C4 120.0(1); C3-C2-C3' 61.1(2); C2-C3-C3' 59.4(1); C3-C4-P5 97.0(1); C4-P5-C4' 89.1(1); C4-P5-O9 121.2(1).

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6) Crystal data: $C_{17}H_{19}OP$, M=270.31, monoclinic, space group C2/m, a=19.456(5), b=8.508(3), c=8.252(3) Å, β=92.32(3)°, V=1364.9(7) Å^3, Z=4, Dc=1.315 gcm^{-3}, μ=1.84 cm^{-1}. 1300 Reflections with <50.0° were recorded on a four circle diffractometer using graphite-monochromated Mo-Kα radiation. The structure was solved using SHELX86 and refined by full-matrix least-squares method to R=0.032(Rw=0.046) for 1108 reflections with I>3σ>(I).

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9) The structure was confirmed by an X-ray analysis.

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