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SEPARATION OF AN OPTICALLY ACTIVE PHOSPHAALLENE OF PSEUDO AXIAL DISSYMMETRY

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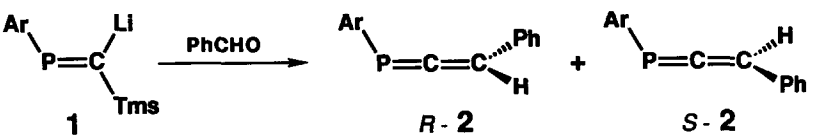
Abstract: Separation of enantiomers of a 1-phosphaallene was successful by a chiral HPLC column and the CD spectrum was recorded; racemization occurred on exposure to light but it was reluctant in the dark.

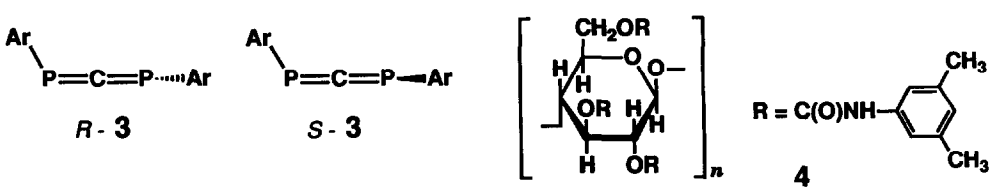
We have reported that 2-(2,4,6-tri-t-butylphenyl)-1-trimethylsilyl-2-phospha-ethenyl-lithium (**1**) reacts with benzaldehyde to give 1-(2,4,6-tri-t-butylphenyl)-3-phenyl-1-phosphaallene (**2**),[1] as a stable multiple bonded compound containing phosphorus in low coordination state (coordination number 2). Mp 109.0 - 114.2 °C. ^{31}P NMR ($CDCl_3$) δ_P 75.2 ppm (d, $^3J_{PH}$ = 24.4 Hz). UV (hexane) λ_{max} (ε) 259 nm (26700). From the structural point of view, 1-phosphaallene (**2**) is isoelectronic to 1,3-diphosphaallene (**3**), which was recently shown to be isolated in enantiomerically pure form with a chiral HPLC column coated with (+)-poly(trityl methacrylate).[2]

We now report our preliminary results on resolution of optically active phosphaallene **2** and its photo-isomerization.



1 *R*-**2** *S*-**2**

(Ar = 2,4,6-$Bu^t_3C_6H_2$; Tms = Me_3Si)



R-**3** *S*-**3** **4**

Recently, liquid chromatographic separation of enantiomers has attracted great attention and several useful chiral stationary phases have been reported including phenylcarbamates of various polysaccharides which exhibit unique resolution ability for HPLC.[3] In this study, an HPLC chromatograph equipped with UV and polarimetric detectors was used to recognize enantiomers of the phosphaallene **2**. Optical rotation was followed in a flow cell (50 x 2 i.d. cm) at full lamp (mercury) intensity without filters. Resolution was carried out with hexane as an eluent at a flow-rate of 0.5 ml/min at 25 °C, using a chiral column of cellulose tris(3,5-dimethylphenylcarbamate) (**4**)[4] (25 x 0.46 i.d. cm) as a stationary phase coated on macroporous silica gel. The enantiomers of (-)-**2** and (+)-**2** were eluted at t_1 = 8 min 40 sec and t_2 = 13 min, respectively, and completely separated as shown in Fig. 1. The chromatographic separation factor and the resolution factor R_S for the phosphaallene **2** were 2.60 and 4.44, respectively. High chiral recognition was attained. The chiral column may be useful for the separation of not only polar compounds but also non-polar compounds.

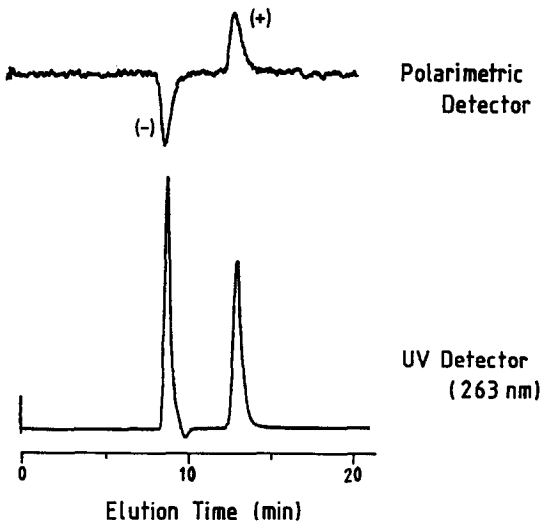


Fig. 1. Resolution of racemic **2** using chiral HPLC column **4**.

Table 1. Decay of Optical Activity on Irradiation of **2**

	Activity of **2**					
Time / min	0	5	15	25	35	90
% e.e.	99.4	67.5	19.7	3.8	0	0

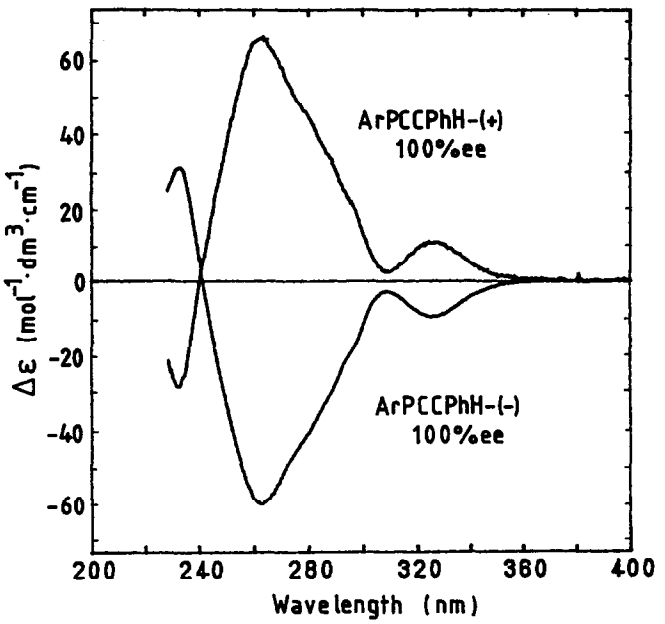


Fig. 2. CD spectra of (-)- and (+)-phosphaallene (**2**). Solvent, hexane. (-)-**2**: c = 0.42 x 10^{-2} M (86.7 e.e. %). (+)-**2**: c = 1.57 x 10^{-3} M (73.2 e.e. %). Cell path length, 0.1 mm. These curves were corrected as 100% e.e. pure.

It should be noted that attempted resolution of the enatiomeric **2** using amylose tris(3,5-dimethylphenylcarbamate)[5] as a stationary phase failed under similar conditions employed for the (**4**)-column, indicating that chiral recognition requires quite delicate conditions.

Furthermore, CD (circular dichroism) spectra of both enantiomers, which were fractionally collected through this column, were recorded. During the process of collection, however, some degree of racemization might have occurred by room light resulting in the loss of activity to some extent: 86.7 e.e. % for the first fraction of the (-)-enantiomer and 73.2% e.e. for the second fraction of the (+)-antipode. Figure 2 depicts the CD spectra of **2** after correction to 100% e.e.

When an optically active sample of 99.4% e.e. thus obtained was irradiated in a 1-mm path length cell with a mercury lamp (125 W) at 31.0 °C through filters (Toshiba UV-35 and UV-36C) to cut off light of shorter wavelength than 370 nm, the activity gradually diminished, where the chiral separation was performed by HPLC with the column of **4** (Table 1). The decay plot of -ln(% e.e.) vs. time gave a straight line exhibiting the half-life time of an enantiomer $t_{1/2}$ as 5.27 min and k = 2.2 x 10^{-3} sec^{-1} for the first order rate constant. In contrast, thermal isomerization or racemization seemed

very slow, since an optically active sample of 80.0% e.e. did not lose its activity in the dark at either 0 °C or 50 °C for 15 h.

These results indicate that the system P=C=C is racemized on irradiation, whereas in the dark the system is stable even at 50 °C for a certain period of time. These phenomena are very similar to those observed for the systems of double bonded phosphorus compounds in low coordination state such as diphosphaallene 3[2] of similar axial dissymmetry which resulted in racemization on photolysis as well as diphosphenes[6-8] and phosphaethylenes[9-11] of D_h symmetry which resulted in E/Z isomerization on photolysis. The racemization of the 1-phosphaallene might presumably involve either the rotation around the P=C (or C=C) bond or the inversion at the phosphorus atom. Theoretical studies on the mechanism of photo-racemization are in progress.

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