

The First Separation of an Optically Active 1,3-Diphospha-allene of Axial Dissymmetry

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Separation of enantiomers of axially dissymmetric 1,3-bis(2,4,6-tri-*t*-butylphenyl)-1,3-diphospha-allene was successful for the first time by h.p.l.c. with a chiral (+)-poly(triphenylmethyl methacrylate) column and the c.d. spectrum of the optically pure (–)-phospha-allene was recorded; racemization occurred on exposure to light but the rate was very slow in the dark.

Certain optically active allenes have provided examples of axially dissymmetric molecules.^{1,2} However, there have been no reports on optically active carbodiimides probably because the activation energies for racemization are too low to allow isolation of enantiomers. We now report the first separation of an optically active phosphorus analogue of carbodiimides, 1,3-diphospha-allene.

We have been interested in chemical reactivities and physicochemical properties of unusual compounds containing phosphorus atom(s) in a low co-ordination state.^{3,4} By introducing an extremely bulky 2,4,6-tri-*t*-butylphenyl moiety as a protective group, we have been successful in isolation and characterization of certain diphosphenes,⁵ phosphaethylenes,⁶ 1-phospha-allene,^{7,8} 1,3-diphospha-allene,⁹ and so on. We have found the first evidence for the optical activity of axially dissymmetric 1,3-bis(2,4,6-tri-*t*-butylphenyl)-1,3-diphospha-allene (**1**), the structure of which was postulated to have *C*₂ symmetry⁹ and very shortly after confirmed by *X*-ray crystallography.¹⁰ Attempts to differentiate the enantiomers in a chiral environment by n.m.r. have failed so far.[†]

As for distinguishing diastereoisomers, (+)-poly-(triphenylmethyl methacrylate), (+)-PTrMA, coated on macroporous silica gel has turned out to be an efficient chiral h.p.l.c. column for resolving racemic compounds,¹¹ particularly in recognizing chirality of planar and axially dissymmetric molecules with aromatic groups. Since the compound (**1**) with its aromatic rings is axially dissymmetric,⁹ attempts were made to separate enantiomeric 1,3-diphospha-allene (**1**) on a (+)-PTrMA-coated column by means of h.p.l.c.

Figure 1 shows a chromatogram of racemic (**1**) on this chiral column, 50 × 0.46 (i.d.) cm using acetonitrile as an eluant being monitored by both optical density (263 nm) and optical activity (Hg lamp without filter). Although the resolution was not base-line separated, fractions marked in Figure 1 were optically pure by h.p.l.c. analysis. The isomer is predicted to have the (*R*)-configuration from the chromatographic data of an analogous racemic compound on (+)-PTrMA.¹² Figure 2 shows the c.d. spectrum of the isolated (–)-diphospha-allene. The estimated [α]_D for the optically pure isomer was –470° (25 °C, heptane, 6.1 g dm^{–3}) from the [α]_D and c.d. intensity of the partially resolved (–)-(**1**) which was isolated with a preparative column. The optical activity did not decrease at

room temperature in the dark,[‡] but was completely lost upon 3 min irradiation with light (370 nm) from a medium pressure mercury lamp. The results on *E/Z* isomerization are similar to those obtained for (*E*)-1-(2,4,6-tri-*t*-butylphenyl)-2-phenylphosphaethylene.⁹ This is the first example of recognition and

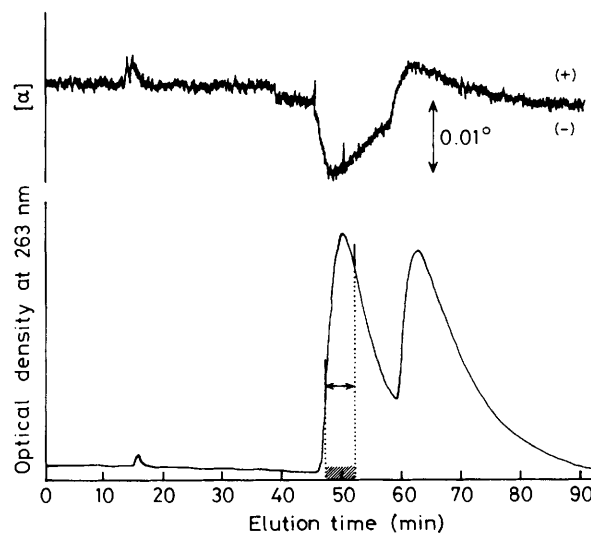


Figure 1. Resolution of 1,3-bis(2,4,6-tri-*t*-butylphenyl)-1,3-diphospha-allene (**1**). Column, (+)-PTrMA, 50 × 0.46 cm (i.d.); eluant, acetonitrile; flow rate, 0.5 ml/min; temperature, 15 °C; detectors, u.v. (263 nm) and polarimeter (Hg lamp).

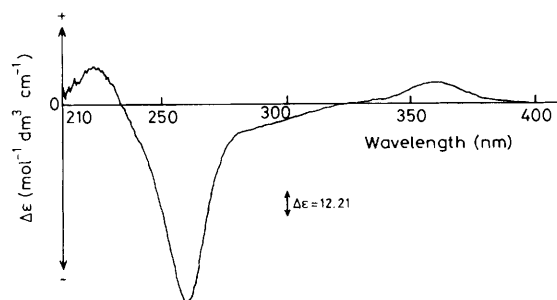
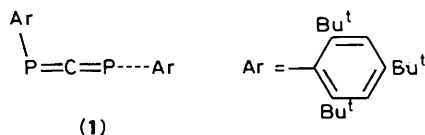


Figure 2. C.d. spectrum of (–)-1,3-bis(2,4,6-tri-*t*-butylphenyl)-1,3-diphospha-allene (**1**). Solvent, heptane; concentration, 0.70 g dm^{–3} (1.24 × 10^{–3} mol dm^{–3}); cell path length, 0.1 mm; JASCO J40.



[†] The ³¹P and ¹H n.m.r. measurements of racemates (**1**) using *D*-(+)-α-phenylethylamine as a solvent or tris-[3-(trifluoromethylhydroxymethylene)-(+)-camphorato]europium(III) as a chiral n.m.r. shift reagent have failed so far to differentiate enantiomers.

[‡] A heptane solution of (–)-(**1**) [58% enantiomeric excess (e.e.)] in a u.v. cell (0.1 mm) was stored at room temperature in the dark. No change was observed in the c.d. spectrum after 48 h. On the other hand, another sample of (–)-(**1**) (58% e.e.) was irradiated in a u.v. cell with a 300 W-mercury lamp through Toshiba filters (UV-35 and UV-D36C; 350–400 nm; max. 370 nm). After 3 min irradiation no c.d. curve was observed and the chromatogram on a (+)-PTrMA column showed that the sample had become completely racemic on exposure to light.

separation of an axially dissymmetric 1,3-diphospha-allene which is of current interest because of its unusual bonding nature as a phosphorus analogue of carbodiimide. The findings may provide a good probe for studying isomerism of phosphorus compounds in a low co-ordination state.

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