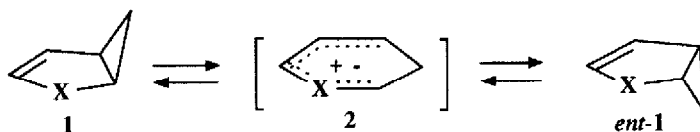


## REACTIVITY OF CYCLOPENTENYL-ANION ANALOGOUS HETEROCYCLES: SYNTHESIS AND 1,5-ELECTROCYCLIZATION OF HOMOPHOSPHOLE

Dirk Oebels and Frank-Gerrit Klämer\*  
 Fakultät für Chemie der Ruhr-Universität  
 Postfach 10 21 48, D-4630 Bochum 1, FRG

**Summary:** The key step of a novel homophosphole synthesis is the reaction of the phospholes 3 with diazomethane in the presence of water leading surprisingly to the oxidized 1,3-dipolar cycloadducts 7. The 1,5-electrocyclization of homophosphole was observed by the racemization of optically active 10c at 120°C to be 641 times slower than that of homofuran 1a. The activation barrier seems to be largely determined by the barrier of inversion at the phosphorus which has to proceed concomitantly.

Carbonyl ylides, thiocarbonyl ylides and azomethine ylides - formally the products of the oxirane, thiirane and aziridine ring-opening - have attracted great attention (e.g. as reaction partners in 1,3-dipolar cycloadditions).<sup>1</sup> The corresponding ylides of type 2 were recently shown to be involved in the 1,5-electrocyclization of the heterocycles homofuran 1a, homothiophene 1b, and homopyrrole 1c.<sup>2</sup> The rate of reaction was found to be strongly dependent on the nature of the heteroatom. At 120°C the ring-opening of homothiophene 1b, and homopyrrole 1c proceeds 63100 times and 72 times faster, respectively, than that of homofuran 1a. Evidently the heteroatoms (O, N and S) stabilize the carbonyl ylide-like intermediate very differently. The extraordinarily strong effect of sulfur may be explained by its ability to form a  $d\pi-p\pi$  interaction in 2b.<sup>3</sup> As a second row element, phosphorus should also be able to stabilize the corresponding, hitherto unknown phosphomethine ylide 2d by a similar electronic interaction. In this communication a novel synthesis of the homophosphole system and its electrocyclization are reported.



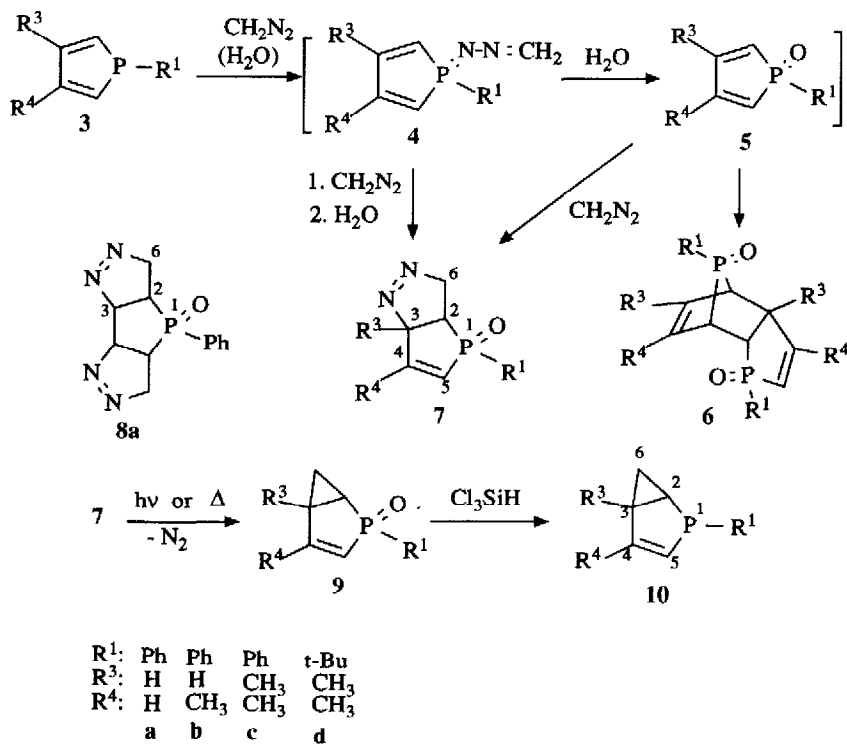
X: O, S, N-CO<sub>2</sub>CH<sub>3</sub>, P-R

a    b            c            d

Scheme 1

The preparation of 1,2,5-triphenylhomophosphole, the only known homophosphole, was started by a 1,3-dipolar cycloaddition of diazomethane to 1,2,5-triphenylphosphole-1-oxide.<sup>4</sup> Since the oxides of the parent and the methyl-substituted phospholes 3a-d are unstable and rapidly dimerize in a Diels-Alder fashion,<sup>5</sup> we investigated the addition of diazomethane to the phospholes 3a-d.

The reaction of the phospholes 3 with diazomethane led only in the presence of a small amount of water (10% relative to 3) to identifiable products, which were characterized by their spectral properties (<sup>1</sup>H NMR, IR, MS) to be not the expected 1,3-dipolar cycloadducts of 3, but the corresponding oxides 7 (Table 1).<sup>6</sup> In order to account for the surprising formation of the oxidized cycloadducts 7, we suggest the following mechanism depicted in scheme 2: The first step consists of the addition of diazomethane to the phosphorus of 3,<sup>7</sup> followed by the hydrolysis of the phosphazines 4. The intermediate phosphole oxides 5 react spontaneously with excess of diazomethane to give the observed cycloadducts 7. As an alternative route first cycloaddition of diazomethane to 4 and subsequently hydrolysis leading again to 7 cannot be excluded. The observation, however, that in the reaction of 3a and 3b the Diels-Alder dimers 6a and 6b are formed as by-products when more than 10% water are used supports the hydrolysis-cycloaddition mechanism. Using a tenfold excess of diazomethane, 3a can also be converted into the bisadduct 8a (80% besides 20% 7a).



Scheme 2

Starting from **7** the desired homophospholes **10** can be obtained by photochemically or thermally induced N<sub>2</sub> extrusion (high pressure mercury lamp, HPK 125 (Philips), pyrex (7c,d) or quartz (7a,b), toluene, yield 50-91%, or 120°C, yield ca. 50%), followed by reduction of **9** using trichlorosilane (tenfold excess in refluxing benzene, 1.5h, yield 35-75%).

Table 1: Selected spectral properties (<sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>)) and yields of the new compounds:

compound (m.p.)	yield [%]		δ [ppm] (J( <sup>31</sup> P- <sup>1</sup> H) [Hz])					
			2-H	3-H	4-H	5-H	6endo-H	6exo-H
<b>7a</b> <b>8a</b>	80	80 20	2.40 2.68	6.0 5.98	7.40 (>26) -	6.20 (24.0) -	5.12 (19.0) 4.80 (18.0)	4.88 (14.5) 4.53 (16.0)
<b>7b</b> 137°C	60		2.45	5.85	2.47 <sup>b)</sup>	5.82	5.25 (19.0)	4.90 (14.5)
<b>7c</b> 156°C	86		2.05	1.67 <sup>b)</sup>	2.37 <sup>b)</sup>	5.76 (22.8)	5.28 (19.0)	4.93 (14.2)
<b>7d</b> 87°C	91		1.34	1.08 <sup>b)</sup>	1.85 <sup>b)</sup>	5.23 (22.0)	5.44 (17.5)	4.47 (13.8)
<b>10b</b>	13 <sup>a)</sup>		1.60	2.22	1.08 <sup>b)</sup>	5.40	0.08	1.20
<b>10c</b>	54 <sup>a)</sup>		1.37 (11.5)	1.38 <sup>b)</sup>	2.02 <sup>b)</sup>	5.35 (41.5)	0.22 (6.5)	1.05 (7.5)
<b>10d</b>	40 <sup>a)</sup>		1.12 (11.5)	1.27 <sup>b)</sup>	1.90 <sup>b)</sup>	5.15 (39.5)	0.05 (5.8)	0.94 (6.0)

a) over all yield starting from **7**

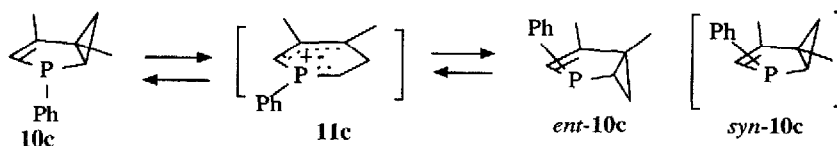
b) δ (CH<sub>3</sub>) instead of δ (H)

Racemic **10c** was separated into its enantiomers by HPLC on triacetylcellulose (Macherey and Nagel) with 95% ethanol as eluant, first fraction: (+)-**8c**, second fraction: (-)-**8c**. The enantiomeric excess (*ee*) of (-)-**8c** ([α]<sub>D</sub><sup>20</sup>=756° (463nm), c=0.00571g/ml in ethanol) was determined by HPLC to be 88%. Optically active **10c** racemizes at temperatures above 100°C. The temperature dependence of the rate constants determined by the decrease of [α]<sub>D</sub><sup>436</sup> with time between 110 and 150°C (in decalin) fits the Arrhenius' equation:

$$k = 6.8 \times 10^{12} \exp [(-32.01 \pm 0.17) \text{ kcal / RT}] \text{ [s}^{-1}\text{]}$$

$$129^\circ\text{C: } \Delta H^* = (31.21 \pm 0.17) \text{ kcal / mol; } \Delta S^* = (-2.41 \pm 0.43) \text{ cal K}^{-1} \text{ mol}^{-1}$$

A comparison of the activation parameters of the racemization in the related heterocycles **1** and **10c** shows that the electrocyclic ring- opening in homophosphole **10c** at 120°C is even 641 times slower than that in homofuran **1a** (ΔΔH<sup>\*</sup>=3.55kcal/mol).



Scheme 3

Accordingly a  $d\pi\text{-}p\pi$  interaction stabilizing the intermediate phosphomethine ylide 11c seems to be negligible. The racemization of homophosphole, however, requires an inversion of configuration at the phosphorus to proceed concomitantly with the epimerization of the cyclopropane ring.<sup>8</sup> The barrier of inversion at the phosphorus known for tetrahydrophosphole and benzodihydrophosphole derivatives<sup>9</sup> is in the same order of magnitude as the barrier of racemization of 10c and seems to make a significant contribution to the rate of the electrocyclic ring-opening.<sup>10</sup> Thus, both reactions may be considered as cooperative processes. The question for the  $d\pi\text{-}p\pi$  interaction in the phosphomethine ylide, however, has to remain still open.

**Acknowledgement:** Financial support from the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie is gratefully acknowledged.

## References and Notes

- 1) a) Review: Huisgen, R. *Angew. Chem.* 1977, 89, 589; *Angew. Chem. Int. Ed. Engl.* 1977, 16, 572; b) theoretical studies: Volatron, F.; Trong Anh, N.; Jean, Y. *J. Am. Chem. Soc.* 1983, 105, 2359; Feller, D.; Davidson, E.R.; Borden, W.T. *ibid* 1984, 106, 2513, and references cited therein.
- 2) Klämer, F.-G.; Schröer, D. *Angew. Chem.* 1987, 99, 1295; *Angew. Chem. Int. Ed. Engl.* 1987, 26, 1294.
- 3) An alternative interpretation of the stabilizing effects on ylides formed by second row elements can be found by Kutzelnigg, W. *Angew. Chem.* 1984, 96, 262; *Angew. Chem. Int. Ed. Engl.* 1984, 23, 272.
- 4) a) Campbell, I.G.M.; Cookson, R.C.; Hocking, M.B.; Hughes, A.N. *J. Chem. Soc.* 1965, 2184; b) Hughes, A.N.; Srivanavit, C. *Can. J. Chem.* 1971, 49, 874.
- 5) a) Hughes, A.N.; Srivanavit, C. *J. Heterocycl. Chem.* 1970, 7, 1; b) Märkl, G.; Potthast, R. *Tetrahedron Letters* 1968, 1755
- 6) The reaction of diazomethane with 3c catalyzed by CuCl led exclusively to unsaturated open-chained phosphine-oxides.
- 7) The reaction of diazomethane with  $\text{Ph}_3\text{P}$  gives the according phosphazine, which hydrolyzes in  $\text{EtOH}/\text{H}_2\text{O}$  to  $\text{Ph}_3\text{PO}$ . Wittig, G.; Haag, W. *Chem. Ber.* 1955, 88, 1655
- 8) An alternative mechanism of racemization consisting of two consecutive sigmatropic [1,3]- or [1,4]-shifts of C-6 could be ruled out by the observation that 10b is thermally stable at the conditions of racemization.
- 9) The  $\Delta G^\ddagger$  for the inversion of the phosphorus of 3-methyl-1-phenylphosphindoline is 35.2 kcal/mol. Egan, W.; Tang, R.; Zon, G.; Mislou, K. *J. Am. Chem. Soc.* 1971, 93, 6205; Egan, W.; Tang, R.; Zon, G.; Mislou, K. *J. Am. Chem. Soc.* 1970, 92, 1442
- 10) Every synthesis of homophosphole introduced here gave only one configurational isomer which was tentatively assigned to the sterically less hindered anti-isomer (e.g. 10c). In order to gain further information on the barrier of inversion at the phosphorus we are now trying to prepare syn-10c.

(Received in Germany 27 April 1989)