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Competitive [4 + 2] Cycloadditions in Equimolar Mixtures of 1-Arylphosphole Oxides

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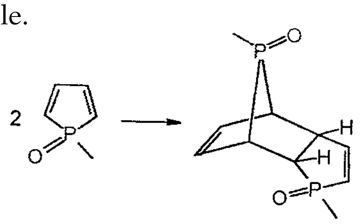
ABSTRACT: *Four different [4 + 2] cycloadditions were observed to take place in the equimolar mixtures of two different arylphosphole oxides* **2a** + **2b** *or* **2b** + **2c**. *In addition to the phosphole oxide dimers* **3a-a** *and* **3b-b**, *or* **3b-b** *and* **3c-c**, *the crossed cycloadducts* **3a-b** *and* **3b-a**, *or* **3b-c** *and* **3c-b** *were also formed in considerable portions.* © 2001 John Wiley & Sons, Inc. Heteroatom Chem 12:633–635, 2001

The [4 + 2] cycloaddition of two molecules of phosphole oxides to afford phosphole oxide dimers has been known for many years [1,2]. The advantage of the cyclodimerization giving an easy access to phosphanorbornenes useful in fragmentation reactions [2–4] is that it takes place in a regio- and stereospecific manner [5]. The prefered isomer is the one in which the phosphole rings are joined in the endo fusion and in which the oxygen atoms of the P=O groups are directed toward the centre of the molecule.



The phosphole oxides can be generated from phospholes by oxidation or from 3,4-dibromotetrahydrophosphole oxides by the elimination of two molecules of hydrogen bromide [2].

In some cases, especially those in which a sterically demanding trialkylphenyl substituent is bonded to the phosphorus atom, it was possible to detect the phosphole oxide intermediates in the reaction medium [6–8]. In the presence of dienophiles such as *N*-phenylmaleimide, the phosphole oxides were efficiently trapped [2].

In this article, we describe our results on the outcome of cycloadditions as applied to equimolar mixtures of two different of arylphosphole oxides.

In the first experiment, an equimolar mixture of 1-phenyl-3,4-dimethylphosphole oxide (**2a**) and 1-(2,4,6-tri-tert-butylphenyl-)3-methylphosphole oxide (**2b**), both generated from the corresponding

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Dedicated to Dr Imre Petneházy on the occasion of his sixtieth birthday.

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phospholes (**1a** and **1b**, respectively) by hydrogen peroxide oxidation, were reacted at 0°C for 1 h. The reaction mixture obtained after removing the excess of the peroxide and after flash column chromatography was analyzed by ^{31}P NMR spectroscopy and FAB-MS (Table 1). It was easy to recognize that the mixture of four cycloadducts **3a-a**, **3b-b**, **3a-b**, and **3b-a** had been formed (Scheme 1). Products **3a-a** (25%) and **3b-b** (22%) were the dimers of phosphole oxides **2a** and **2b**, respectively. The other two components were mixed cycloadducts **3a-b** (25%) and **3b-a** (28%). In **3a-b**, phenylphosphole oxide **2a** functioned as the diene, while in **3b-a**, phosphole oxide **2a** served as the dienophile. It can be seen that the relative proportions of dimers **3a-a** and **3b-b** were comparable with those of the mixed cycloadducts **3a-b** and **3b-a**. Attempts to isolate the mixed cycloadducts **3a-b** and **3b-a** from the reaction mixture by column chromatography were not succesful, only a partial enrichment in both these could be achieved. The dimer with a tri-tert-butylphenyl substituent on the phosphorus atoms (**3b-b**) could, however, be obtained in a pure form.

At 0°C neither the phenylphosphole oxide **2a** nor the tri-tert-butylphenyl derivative **2b** discriminated between the two phosphole oxides **2a** and **2b** present in the reaction mixture. In an attempt to effect a crossed cycloaddition at 15°C, practically no mixed "dimers" could be detected in the reaction mixture. According to this, the selection process seems to be very sensitive to the reaction temperature.

In the second experiment, an equimolar mixture of 2,4,6-tri-tert-butylphosphole oxide (**2b**) and the tri-isopropylphenyl derivative **2c**, both generated in situ by oxidation of the corresponding phospholes **1b** and **1c**, respectively, were reacted at 0°C for 1.5 h. The ^{31}P NMR and FAB-MS analyses of the reaction mixture (Table 1) revealed that the comparable stability of the phosphole oxides **2b** and **2c** had resulted in a less efficient mixed Diels–Alder reaction: 16% of **3b-c** and 11% of **3c-b** were formed in addition to 35% of dimer **3b-b** and 38% of dimer **3c-c** (Scheme 2). It is noteworthy that in this case, the self-dimerization was favored to a major extent.

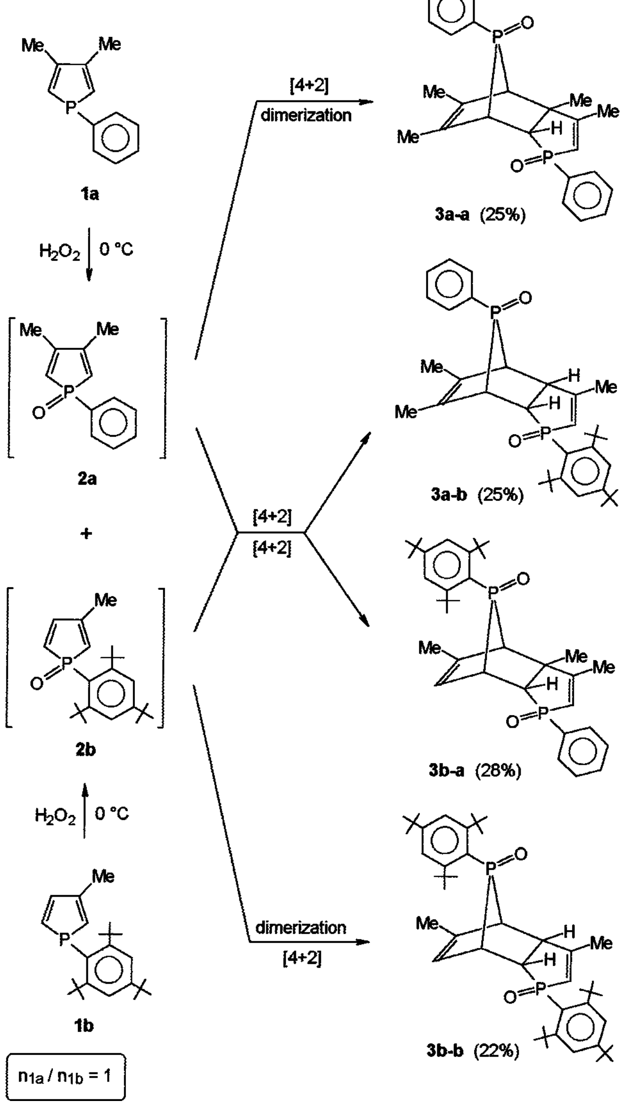
TABLE 1 ^{31}P NMR and FAB-MS Data of Phosphole Oxide Cycloadducts **3**

	^{31}P NMR ($CDCl_3$)			FAB-MS
Comp.	δ_{P_1}	δ_{P_8}	$^3J_{PP}$ (Hz)	[M + H]
3a-a	52.9	74.4	38.7	409
3b-b	56.8 (57.1)[a]	84.2 (84.1)[a]	39.8 (39.6)[a]	717
3c-c	57.0 (56.4)[b]	80.6 (80.1)[b]	38.0 (38.1)[b]	633
3a-b	56.3	74.3	37.6	563[c]
3b-a	54.0	83.8	40.2	563[c]
3b-c	57.0	84.7	37.7	675
3c-b	57.1	79.8	39.7	675

[a] From Ref. [8].

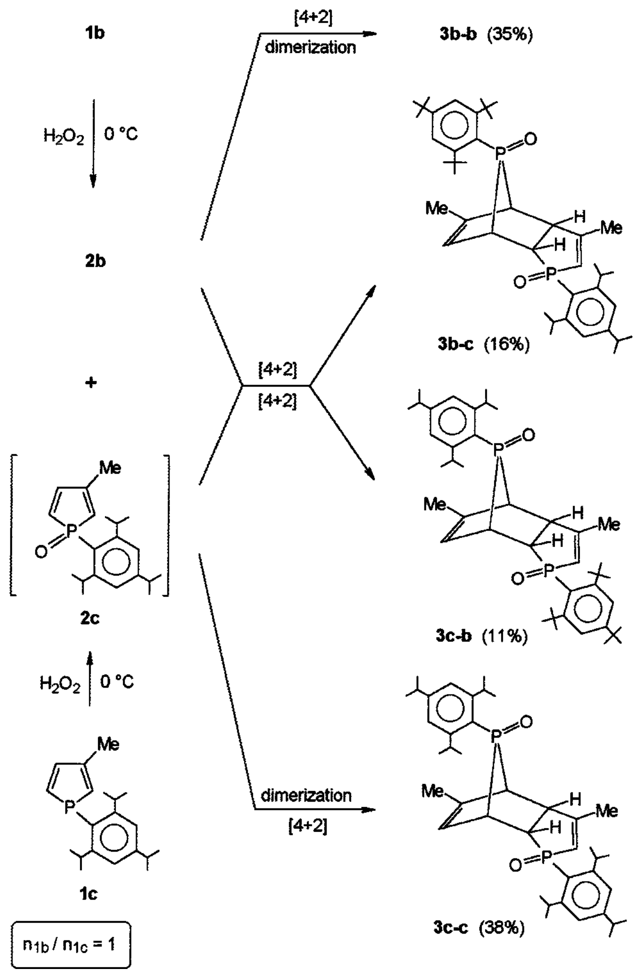
[b] From Ref. [7].

[c] HR-FAB, $[M + H]^+_{found} = 563.3101$; $C_{35}H_{49}O_2P_2$ requires 563.3208.



SCHEME 1 The composition of the reaction mixture was analyzed on the basis of relative ^{31}P NMR intensities (estimated error ± 2.5%).

It can be concluded that all possible Diels–Alder cycloadducts are formed in the equimolar mixtures of two different arylphosphole oxides. This is the first case in which mixed phosphole oxide "dimers" are described. Extension of the above experiments to



SCHEME 2 The composition of the reaction mixture was analyzed on the basis of relative ^{31}P NMR intensities (estimated error ±2.5%).

three or more phosphole oxides may be a real combinatorial technique giving valuable information on the reactivity of the different phosphole oxides.

EXPERIMENTAL

The ^{31}P NMR spectra were obtained on a Bruker DRX-500 instrument at 202.4 MHz. The FAB-MS measurements were performed on a ZAB-2SEQ spectrometer.

The arylphospholes **1b** and **1c** were prepared as described earlier [7,9].

General Procedure for the Preparation of the Mixture of Cycloadducts

To the mixture of 0.53 mmol of phosphole **1a** or **1b** and 0.18 g (0.53 mmol) of phosphole **1c** in 30 ml of chloroform was added 1.5 ml (~13 mmol) of 30% hydrogen peroxide at 0°C. After a 1 h of stirring, 3 ml of water was added and the mixture stirred for an additional 5 min. The extraction was repeated with another 3 ml portion of water, and then the organic phase was separated and dried (Na_2SO_4). The oil obtained after evaporation was purified by flash column chromatography (silica gel, 3% methanol in chloroform) to give the mixtures in practically quantitative yields, as shown in Schemes 1 and 2 and as characterized in Table 1.

Repeated column chromatography (as above) afforded **3b-b** (first experiment) and **3c-c** (second experiment) in an efficiency of 21% and 32%, respectively. The content of the mixed dimers **3a-b** and **3b-a** (first experiment), as well as that of products **3b-c** and **3c-b** (second experiment) could be enriched to an extent of 32–53%.

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