2,3-BIS(DIPHENYLPHOSPHINYL)-1,3-BUTADIENE VIA A DOUBLE [2,3]-SIGMATROPIC REARRANGEMENT. A REINVESTIGATION OF THE REACTION OF 2-BUTYNE-1,4-DIOL WITH CHLORODIPHENYLPHOSPHINE

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<u>Summary</u>: Contrary to previous reports, the reaction of 2-butyne-1,4-diol with chlorodiphenylphosphine yields 2,3-bis(diphenylphosphinyl)-1,3-butadiene <u>3</u> instead of the 1,4-isomer. The structure of the product has been elucidated from ¹H, ¹³C and ³¹P-NMR spectroscopic data.

In the course of research on phosphino-substituted olefins¹⁻⁶ we were interested in the reaction of 2-butyne-1,4-diol with chlorodiphenylphosphine, which was reported to give 1,4-bis(diphenylphosphinyl)-1,3-butadiene $(\underline{1})^7$. Despite the possibility of E/Z isomers, no comment has been made on the configuration of the product, nor have any conclusive spectroscopic data been given.

A recent report⁸ describes the formation of 2,3-di(phenylsulfinyl)-1,3butadiene ($\underline{2}$) from 2-butyne-1,4-diol and phenylsulfenyl chloride via a double sigmatropic rearrangement of the bis-sulfenate ester formed as the precursor.



It is known that chlorophosphines and sulfenyl chlorides show similar reaction behaviour towards propargylic alcohols: The intermediate phosphinous (or sulfenic) esters undergo [2,3]-sigmatropic rearrangements to allenic phosphine oxides or sulfoxides, respectively⁹⁻¹¹. According to this analogy, the reaction of butynediol with chlorodiphenylphosphine should thus yield 2,3-bis(diphenylphosphinyl)-1,3-butadiene (<u>3</u>) rather than the proposed butadiene <u>1</u>.

This suggestion was verified by the following experiment: A solution of 25 ml chlorodiphenylphosphine (29 g, 131.4 mmol) in 75 ml THF is added dropwise at 0°C to 5.65 g 2-butyne-1,4-diol (65.6 mmol) and 12.5 ml pyridine (155 mmol) in 75 ml THF. The mixture is stirred at room temperature over night. After an hydrolytic workup (water, dil. HCl, K_2CO_3 -solution, water) the solvent is evaporated in vacuo. The residue is recrystallized from ether/THF (1:1) to afford 19.6 g <u>3</u> as a white solid (66% yield, mp. 179-181°C, calcd. for $C_{28}H_{24}O_2P_2$ (454.44): C 74.00, H 5.32; found: C 74.04, H 5.38).

Obviously the product is identical with the material obtained by Miller⁷ (reported mp. 182.5-184°C), but on the basis of its NMR spectroscopic data¹² the structure of the isomer <u>3</u> appears to be valid. The vinylic protons give two signals at δ =5.7 and 6.8 ppm, each split into a dublet by coupling to phosphorus (cis-³J(PH) = 19.4 Hz, trans-³J(PH) = 40.6 Hz). The lines are broadened by the unresolved geminal HH-coupling which is expected to be small. This part of the spectrum closely resembles the corresponding portion of the ¹H NMR spectrum of isopropenyldiphenylphosphine oxide^{13,14}, whereas a vicinal substitution as in <u>1</u> should show a different pattern (for the proton NMR spectra of E- and Z-1-propenyldiphenylphosphine oxides see ^{14,15}).

Unequivocal evidence for structure $\underline{3}$ comes from the proton coupled ${}^{13}C-NMR$ spectrum where the signal of the CH₂-carbon atoms is split into a virtual triplet with ${}^{1}J(CH) = 161.8$ Hz, while the signal of the CP-carbon atoms shows only small long range CH-couplings.

The mechanism for the formation of $\underline{3}$ is probably the same as proposed for the formation of the analogous sulfur compound⁸: The primary product, bisphosphinous ester $\underline{4}$, undergoes a [2,3]-sigmatropic rearrangement to the allenic intermediate $\underline{5}$, which subsequently is subject to a second [2,3]-sigmatropic shift to afford $\underline{3}$.

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The diene <u>3</u> is a promising educt for further syntheses. Through Diels-Alder reactions it should give access to 1,2-diphosphino cyclohexenes, but preliminary experiments showed that it is rather unreactive in [2+4]-cycloadditions. This may be due to the electron deficiency caused by the two electronegative phosphinyl groups. Moreover, the transoid conformation possibly prevailing in solution as a consequence of the steric bulk of the diphenylphosphinyl substituents is an additional handicap. Cycloadditions are known to require a cisoid conformation, less readily available for <u>3</u>.

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- 12. ¹H-NMR (CDCl₃): 5.7 ppm, d, ³J(PH)=19.4 Hz, 2 H, cis-CH; 6.8 ppm, d, ³J(PH)=40.6 Hz, 2 H, trans-CH; 7.3-8.0 ppm, m, 20 H, C₆H₅. {¹H}-¹³C-NMR (CDCl₃): 128.3 ppm, "t" (AXX'), N=12.7 Hz, C3; 131.0 ppm, centered dd (AXX'), N=110.1 Hz, C1; 131.7 ppm, "t" (AXX'), N=9.9 Hz, C2; 131.8 ppm, s, C4; 135.6 ppm, "t" (AXX'), N=13.8 Hz, =CH₂; 137.9 ppm, centered dd (AXX'), N=98.0 Hz, =CP-. ¹H-coupled ¹³C-NMR (CDCl₃): 135.6 ppm, "tt", ¹J(CH)=161.8 Hz, =CH₂. ³¹P-NMR (CDCl₃): 32.2 ppm, s.
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