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LETTERS TO THE EDITOR

An Unexpected Redox Reaction between Tris(*Z*-phenylethenyl)phosphine and 4-Hydroxy-4-methyl-2-pentynonitrile

B. A. Trofimov, B. G. Sukhov, N. K. Gusarova, S. F. Malysheva, and A. G. Mal'kina

Favorskii Irkutsk Institute of Chemistry, Siberian Division, Russian Academy of Sciences, Irkutsk, Russia

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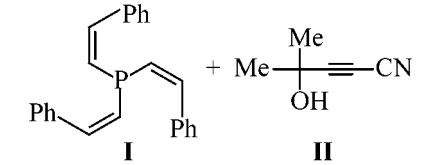
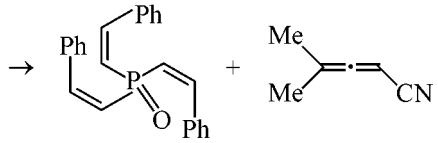
Tris(*Z*-phenylethenyl)phosphine **I** [1] is readily oxidized with 4-hydroxy-4-methyl-2-pentynonitrile **II** into tris(*Z*-phenylethenyl)phosphine oxide **III** (yield 98%). In the process, hydroxyalkyne **II** is reduced to 4-methylpenta-2,3-dienonitrile **IV** (yield 74%).

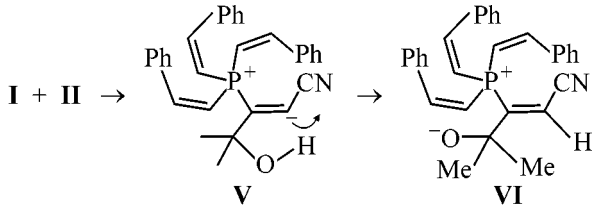


I **II**

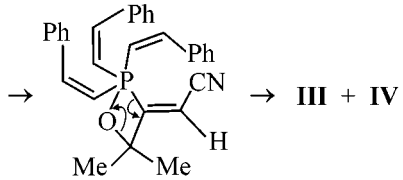


III **IV**

Apparently, the reaction starts with nucleophilic addition of **I** across the triple bond in **II** to form zwitterion **V**, which transforms into zwitterion **VI** by intramolecular proton transfer. Cyclization of **VII** into phosphetane **VII** and its subsequent decomposition yield phosphine oxide **III** and allene **IV**.



V **VI**



VII

Allene **IV** was also prepared in 75% yield from **II** and triphenylphosphine. Thus, the reaction is apparently common for tertiary phosphines and can be used for mild reduction of cyanoacetylenic alcohols into allenes.

Reaction of tris(*Z*-phenylethenyl)phosphine with 4-hydroxy-4-methyl-2-pentynonitrile. A solution of 0.510 g of **I** and 0.147 g of **II** in 2 ml of diethyl ether was kept at room temperature for 3 h. The crystalline precipitate was filtered off and washed with pentane; 0.5 g (94%) of **III** was obtained. The product was identified using an authentic sample [1]. From the ether and pentane filtrates, the solvents were removed, and the residue was vacuum-fractionated; allene **IV** was collected in a cooled trap. Yield 0.18 g (78%). IR spectrum, ν, cm^{-1}: 2222, 1969, 781. ^1H NMR spectrum, δ, ppm: 1.06 d (6H, Me), 4.39 septet (1H, =CHCN). These characteristics are in agreement with published data [2].

In the reaction with triphenylphosphine under similar conditions, the yields of triphenylphosphine oxide and allene **IV** were 95 and 75%, respectively.

The IR spectra were taken on a Specord IR-75 spectrometer (KBr pellets or thin films). The ^1H and ^{31}P NMR spectra were recorded on a Bruker DPX-400 spectrometer (400 MHz) in $CDCl_3$, internal reference HMDS.

REFERENCES

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