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EFFICIENT PHOSPHOROUS-SULFUR BOND REDUCTION IN BICYCLIC THIAPHOSPHORANES WITH TRI-n-BUTYLTIN HYDRIDE

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Abstract

High yield photolytic reduction of a series of thiaphosphoranes Z_4PSR to give Z_4PH with UV-light-induced tri-n-butyltin hydride through phosphoranyl radical $Z_4\dot{P}$ is described. This reaction is inhibited by α-methylstyrene and initiated by a radical initiator such as azobisisobutyronitrile.

Introduction

Phosphoranyl radicals are well known for their scission reactions [1]. Spiro or bicyclic ones can be trapped by a non-scission process [2-3]. Due to their relative stability, they have been used for the preparation of certain pentacovalent phosphorous compounds [4].

Abstraction of hydrogen atom from tin hydride by phosphoranyl radical or in other words the reduction of thiaphosphoranes to the corresponding hydrido-phosphoranes has not been reported. In this communication we wish to report the preliminary results on photolytic reduction of thiaphosphoranes 1-4 with tri-n-butyltin hydride to the corresponding hydridophosphoranes 5 and 6 respectively.

The photo-initiated reactions of 1-4 with tri-n-butyltin hydride were monitored quantitatively by ^{31}P NMR. High NMR yields were found (Table 1). Preparative reactions were run on a 0.8g scale with 1 and 4 to give isolated hydridophosphoranes 5 and 6 (80-92% yields respectively).

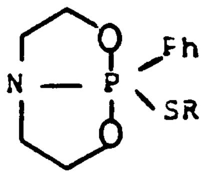
a Samples in C_6D_6 (0.5 ml). Starting amounts of thiophosphorane 0.2-0.3 mmol and tin hydride 0.4-0.9 mmol.

b In perdeuteriobenzene at 32.2 MHz chemical shift of 5 and 6 is -45.06 and -46.00 respectively.

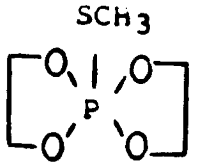
Keywords: Phosphorous-sulfur; Reduction; Butyltin

Table 1. ^{31}P NMR^{a} yields of hydridophosphorane^{b} from reactions of thiaphosphoranes with tri-n-butyltin hydride.

Thiaphosphoranes	^{31}P^{c}	% Yield^{d}	Reaction time in h
1	-29.80	92	6
2	-29.58	94	6
3	-29.37	85	5
4	-27.52	90	5



1:R=CH_3 ; 2: R=n-but
3: R=sec-but



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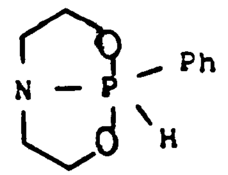

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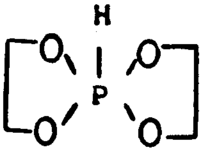

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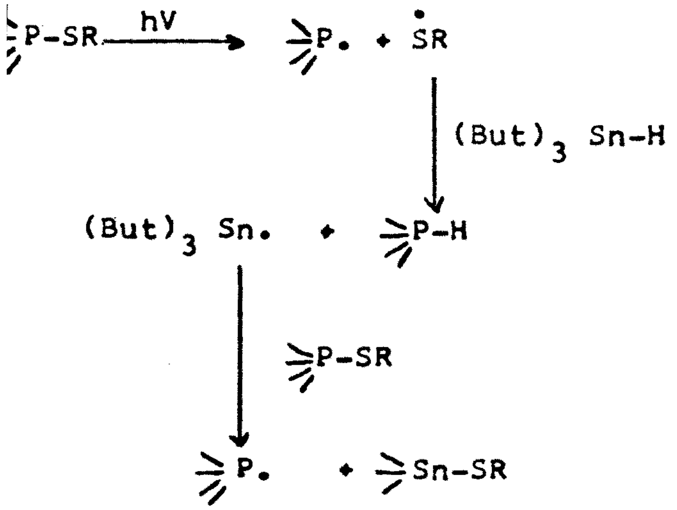
c In ppm upfield (negative of external H_3PO_4 at 32.2 MHz and in C_6D_6.

d Calculated relative to external $(CH_3O)_3 P=0$ standard (experimental section) and number of experiments averaged is 2 for each reaction.

The proposed mechanism for this free radical chain process is based on the fact that the reaction is initiated photochemically or with a radical initiator such as azobisisobutyronitrile and a proposed mechanism for the reduction of carbon-halogen bonds [5, 6], or the reductive cleavage of cyclopropyl ketone with tri-n-butyltin hydride by UV-light [7], and the trapping of phosphoranyl radicals by addition to alkenes [8]. The failure of the light-initiated reaction with inhibited reagent such as α-methylstyrene is also an indication of the generation of phosphoranyl radicals in the free-radical chain process. This proposed mechanism is shown by Scheme 1.



Experimental Section

Compounds 1-4 were prepared according to Bentrude's method [4]. The following is a representative procedure for thiaphosphoranes. Reduction by UV-light induced tin hydride and an inhibition reaction by α-methylstyrene.

The thiaphosphorane 1 (0.0565 g, 0.250 mmol) was dissolved in perdeuteriobenzene (0.50 ml) in a screw-top 5-mm NMR tube containing a sealed capillary tube of trimethyl phosphate (0.425 molar in perdeuteriobenzene).

The NMR tube was sealed with a screw cap fitted with a Teflon/Buta-rubber seal. Dry deoxygenated nitrogen was bubbled through the solution for 5 minutes by means of an inlet needle and a shorter exhaust needle. The needles were removed. The cap was covered with parafilm to ensure a good seal. ^{31}P NMR spectra were run to determine the ratio of thiaphosphoranes to trimethyl phosphate. Tri-n-butyltin hydride (202 ml, 0.750 mmol) was added. The tube was sealed and deaerated as above. The solution was irradiated for 6 hours and ^{31}P NMR spectra was taken immediately. The ratios of hydridophosphorane 5 to trimethylphosphate were determined from duplicate proton-deupled spectra and yields of 90% were determined. All photolytic reductions of thiaphosphoranes to the corresponding hydridophosphorane were run in this manner and were completed within 7 to 8 hours. The products were compared chromatographically and spectroscopically with authentic materials [9].

Inhibition Reaction of Thiaphosphorane with Tri-n-Butyl Hydride by α-Methylstyrene

To the reaction sample, which was prepared as above, before the addition of thin-hydride 3% relation to thiaphosphorane α-methylstyrene was added. The sample was irradiated for 2 hours. A ^{31}P NMR spectrum of the sample showed that no reaction of thiaphosphorane with tri-n-butyltin hydride had occurred. A control sample containing similar amounts of reagents (except α-methyl styrene) run at the same time went to 30% completion for thiaphosphorane 1.

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