

REACTION OF ALLYLIC ARSENITES WITH LOW VALENT TRANSITION METAL COMPLEXES

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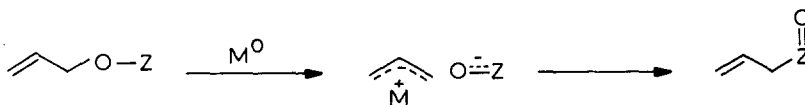
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Summary

Three reactions were carried out to study the reactions of triallyl arsenite with zero-valent palladium and platinum complexes: (i) the reaction of triallyl arsenite with nucleophiles using $\text{Pd}(\text{PPh}_3)_4$ as catalyst; (ii) the preparation of the π -allylplatinum complex from triallyl arsenite and (iii) the reaction of deuterium-labelled triallyl arsenite with $\text{Pd}(\text{PPh}_3)_4$. The mechanisms of the above reactions are briefly discussed.

Introduction

The oxidative addition of a C–O–C bond to a low valent transition metal complex has been widely studied [1], but very few reports have been made dealing with the compounds containing C–O–Z (Z = heteroatom) bonds. It has been reported that when the leaving group is an ambident nucleophile [2], the following rearrangements occur by the catalysis of zero-valent transition metal complexes under much milder conditions than that of the corresponding thermal rearrangements [3,4].



(Z = S, P ; M = Pd, Ni)

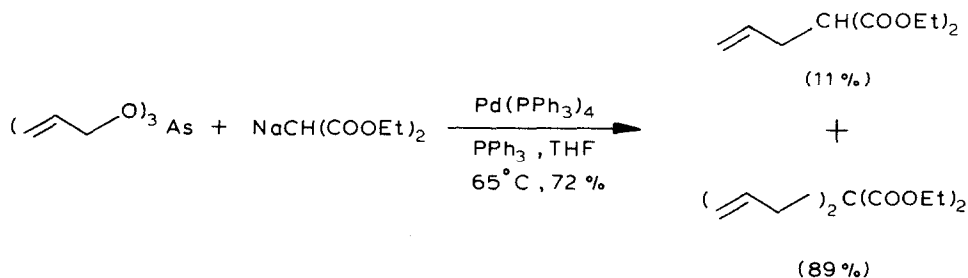
When Z = P, the thermal reaction is well known as the Arbuzov rearrangement. Although arsenic is in the same group as phosphorus, no similar thermal rearrangement, so far as we know, has been reported in the arsenic analogs [5,6]. In a systematic study of the reaction of allylic esters of inorganic acids with low valent transition metals [3,4], it is interesting to investigate whether allylic arsenite will rearrange under the catalysis of transition metal complexes or not. We report our results here.

Results and discussion

When triallyl arsenite or allyl diphenyl arsinite was treated with a catalytic amount of $\text{Pd}(\text{PPh}_3)_4$ or $\text{Ni}(\text{cod})_2$ ($\text{cod} = 1,5\text{-cyclooctadiene}$), no rearranged product was found and only the starting materials were recovered. Certain questions arise from these results. Could the C-O-As bond oxidatively add to Pd^0 ? If so, which bond would break, the C-O bond or the O-As bond? Thus, three reactions were carried out to make it clear.

Reaction with nucleophiles using $\text{Pd}(\text{PPh}_3)_4$ as catalyst

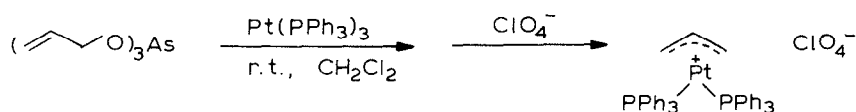
The reaction of triallyl arsenite with sodium diethyl malonate using $\text{Pd}(\text{PPh}_3)_4$ as catalyst gave 2-allylated malonic ester in a 72% yield. The ratio of mono- to di-allylated product was 11/89. It demonstrates that the C-O bond of allyl



arsenite is cleaved by the catalysis of Pd^0 in the presence of a nucleophile.

Preparation of π -allyl platinum complex from triallyl arsenite

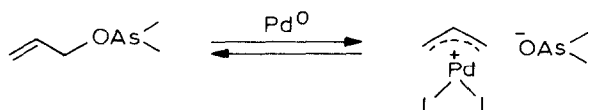
Treatment of triallyl arsenite with $\text{Pt}(\text{PPh}_3)_3$ in CH_2Cl_2 at room temperature, after anion exchange with perchlorate, gave a complex whose m.p. and spectra were identical with those of the known complex synthesized from allyl acetate [7].

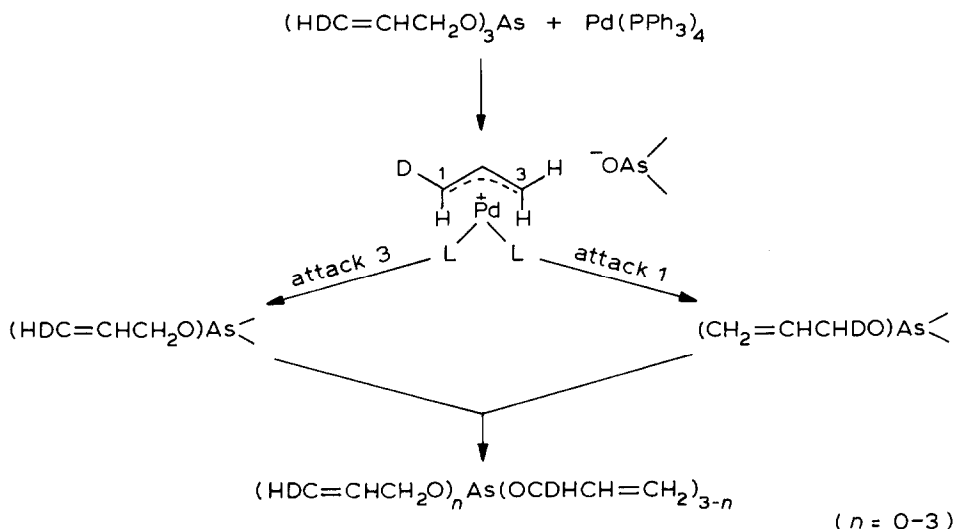


It also indicates that the C-O bond of allyl arsenite could oxidatively add to the transition metal.

Study with deuterium-labelled triallyl arsenite

It has been proved that the C-O bond is cleaved by the low valent transition metals, the question then is why the rearrangement does not take place. A possible explanation may be that the arsenite ion, which is produced by oxidative addition, couples with the π -allyl group by its oxygen atom again instead of the arsenic atom, regenerating the starting material as shown in the following equation:

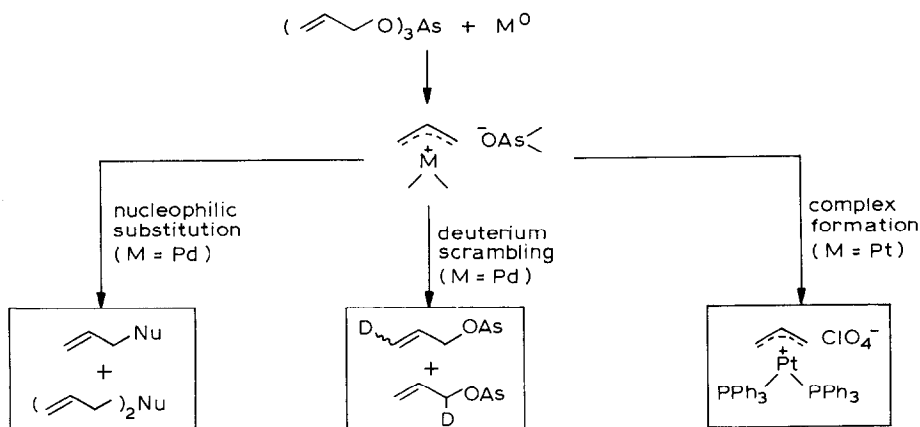




SCHEME 1

3-Deuteriated triallyl arsenite was stirred with $\text{Pd}(\text{PPh}_3)_4$ in THF at room temperature and the products were separated. The ^1H NMR data showed that half of the deuterium atoms changed their position from (1) to (3), which indicated that after forming the π -allyl palladium complex, the arsenite ion $^-\text{OAs}<$ might attack either position 1 or position 3 with the same opportunity and give the deuterium-scrambled recoupling product (see Scheme 1).

According to the three reactions mentioned above, it is likely that the oxidative addition of the C–O bond of triallyl arsenite to a low valent transition metal occurs. The π -allyl metal complex generated will react with nucleophiles, if present, to form a new C–C bond. Because the arsenite ion $^-\text{OAs}(\text{OR})_2$ is not a good ambident nucleophile, it attacks the π -allyl metal complex again with its oxygen atom regenerating the starting material. The results are given in Scheme 2.



SCHEME 2

Experimental

All reactions were carried out under prepurified nitrogen using Schlenk techniques. All solvents and starting materials were distilled under nitrogen before use. ^1H NMR spectra were recorded on an EM-360 or Varian XL-200 spectrometer. Infrared spectra were taken using a Perkin-Elmer 683 IR spectrometer. Mass spectra were obtained on a Finnigan 4021 GC/MS/DC instruments. 3-Deuteriated triallyl arsenite was prepared from arsenic oxide and 3-deutero-allyl alcohol [8].

Reaction of triallyl arsenite with sodium diethyl malonate using $\text{Pd}(\text{PPh}_3)_4$ as catalyst

Diethyl malonate (136 mg, 0.85 mmol) was added dropwise to a suspension of NaH 30 mg (72% in mineral oil, 0.9 mmol) in dry THF (8 ml). The resulting mixture was then added to a solution of triallyl arsenite (200 mg, 0.8 mmol), $\text{Pd}(\text{PPh}_3)_4$ (50 mg, 0.04 mmol) and PPh_3 (50 mg, 0.2 mmol) in dry THF. The reaction mixture was refluxed with stirring for 5.5 h and TLC (silica gel/ethyl acetate/petroleum ether (1/9)) showed the disappearance of diethyl malonate. On removal of THF, a small amount of water was added and ether was then used to extract the organic layer. After evaporation of ether, a mixture of diethyl mono- and di-allylated malonate with a ratio of 11/89 (determined by ^1H NMR) was obtained by distillation, b.p. 90°C (bath temperature)/0.3 Torr; yield 72%. This mixture was further separated by column chromatography on silica gel.

$\text{CH}_2=\text{CH}-\text{CH}(\text{COOEt})_2$: ^1H NMR (δ , CCl_4 , 60 MHz, TMS): 1.22 (t, J 7 Hz, 6H), 2.55 (m, 2H), 3.23 (t, J 7 Hz, 1H), 4.13 (q, J 7 Hz, 4H), 4.86–6.09 (m, 3H). IR (neat, cm^{-1}): 1750s, 1730s, 1640m. MS: 201 ($M^+ + 1$), 127, 81, 43.

$(\text{CH}_2=\text{CH})_2\text{C}(\text{COOEt})_2$: ^1H NMR (δ , CCl_4 , 60 MHz, TMS): 1.25 (t, J 7 Hz, 6H), 2.60 (d, J 6 Hz, 4H), 4.17 (q, J 7 Hz, 4H), 4.90–6.08 (m, 6H). IR (neat, cm^{-1}): 1750s, 1730s, 1640m. MS: 241 ($M^+ + 1$), 181, 123, 43.

Preparation of a π -allylplatinum complex from triallyl arsenite

To a solution of $\text{Pt}(\text{PPh}_3)_3$ (80 mg, 0.08 mmol) in dichloromethane (4 ml), a solution of triallyl arsenite (160 mg, 0.65 mmol) in dichloromethane (2.5 ml) was dropped with stirring. Then excess sodium perchlorate was added and the mixture was stirred at room temperature for 5.5 h. After the reaction mixture was filtered and the solvent was removed, the residue was washed with a few drops of ethyl acetate and recrystallized from dichloromethane/*n*-hexane. Yield 58%; m.p. $255\text{--}260^\circ\text{C}$ (lit. m.p. $255\text{--}260^\circ\text{C}$). ^1H NMR (δ , CDCl_3 , 200 MHz, TMS): 3.04 (m, 2H), 3.77 (d, J 7 Hz, 2H), 5.56 (m, 1H). IR (cm^{-1}): 1470m, 1420m, 1080s.

Reaction of deuterium-labelled triallyl arsenite with $\text{Pd}(\text{PPh}_3)_4$

A solution of 3-deuteriated triallyl arsenite (350 mg, 1.4 mmol), $\text{Pd}(\text{PPh}_3)_4$ (50 mg, 0.04 mmol) and PPh_3 (30 mg, 0.1 mmol) in THF (8 ml) was stirred at room temperature for 11 h. After removal of THF, the residue was distilled at 80°C (bath temperature)/0.3 Torr, nearly all the products were recovered. ^1H NMR (δ , CCl_4 , 60 MHz, TMS): before reaction; 4.16 (d, J 6 Hz, 6H), 4.98 (d, J 10.4 Hz, 3H), 5.74 (m, 3H), after reaction: 4.20 (d, J 6 Hz, 4.5H), 4.97, 5.38 (d, J 10.4 Hz; d, J 18 Hz, 4.5H), 5.55–6.11 (m, 3H).

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