

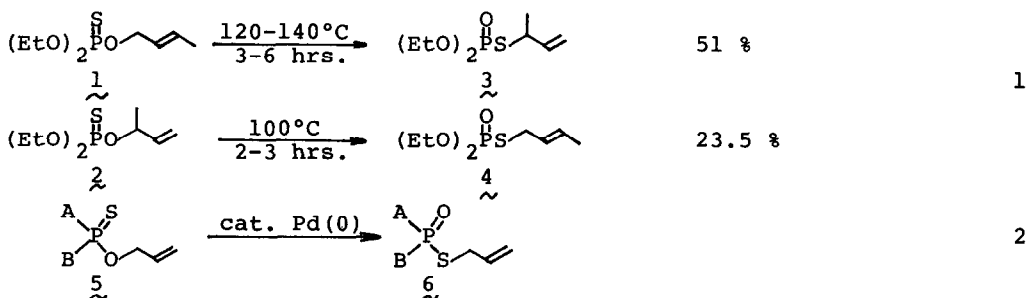
PALLADIUM CATALYZED THIONO-THIOLO ALLYLIC
 REARRANGEMENT OF O-ALLYL PHOSPHORO- AND PHOSPHONOTHIONATES

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Summary: A new thiono-thiolo allylic rearrangement of phosphoro- and phosphonothionates with $\text{Pd}(\text{PPh}_3)_4$ catalyst is described, where a variety of thionates are converted to the corresponding thiolates in excellent yields.

A. N. Pudovik et al.¹ previously reported the thermal Claisen rearrangement of O-allyl phosphorothionates, where O,O-diethyl O- α -(2) or γ -methallyl phosphorothionate (1) had been isomerized to O,O-diethyl S- γ -(4) or α -methallyl phosphorothiolate (3), respectively, with inversion of the methallyl radical (eq. 1). But the thermal rearrangement was not satisfactory both in yield and regioselectivity on our available data²: especially in the rearrangement of 1, both isomers 3 and 4 were produced in a ratio of ca. 7:3.

During the course of our study on the thiono-thiolo allylic rearrangement, we have found that a catalytic amount of palladium(0)³ nicely assists the rearrangement of O-allyl phosphoro-(5; A=B=OR) and phosphonothionates (5; A=Ph, B=OEt, NEt₂, NHet or SET) to S-allyl phosphoro- and phosphonothiolates⁴, respectively (6, eq. 2).



The reaction of 8 kinds of O-allyl thionates has been examined in the presence of 1 mol% of $\text{Pd}(\text{PPh}_3)_4$ and K_2CO_3 using diglyme as a solvent and found to give the corresponding S-allyl thiolates. No alkyl migration was observed. Neither acetonitrile nor xylene gave the satisfactory results as a solvent. Re-

sults are summarized in Table 1, which reveals the wide applicability of the present procedure for the rearrangement of a variety of O-allyl phosphoro- and phosphonothionates. In all cases examined, the reaction proceeds smoothly at 70-80 °C and attains completion within 10-25 minutes, making contrast to the result in entry 2: without palladium catalyst, no rearrangement was observed even after a prolonged reaction time. The reaction in entry 7 proceeds smoothly, but ceases essentially at 80 % conversion regardless of the reaction temperature or the reaction time. This might be a result of deactivation of catalyst by some degradation products. Yields are almost quantitative except for one case (entry 1). This drop in yield is apparently owing to loss of the product in the water layer during an aqueous work-up.

Unlike the results reported by A. J. Burn *et al.*⁵ (ionic conversion of thionates to thiolates), the rate of rearrangement was not affected largely by the kind of substituents on a phosphorous atom or the structure of allylic groups. Both 1 and 2 gave the similar results giving the thermodynamically more stable regio-isomer 4 selectively together with a small amount of 3 in a ratio of 95:5 (eq. 3, entries 8 and 9, cf. eq. 1). These observations are reminiscent of the palladium(II) catalyzed allylic acetate rearrangements reported by L. E. Overman *et al.*⁶. But in our reaction, Pd(II) is not so effective as Pd(0). One possible mechanistic rationale is illustrated in eq. 4, which includes an oxidative addition of Pd(0) to the O-C(allylic) bond and a recombination between softer nucleophile (S⁻ rather than O⁻) and the less hindered allylic terminus. The intermediacy of π -allylpalladium intermediate⁷ was suggested by the reaction of O-allyl O-ethyl phenylphosphonothionate (7) with diethyl malonate (eq. 5); under the usual reaction conditions 7 was converted in the presence of 1.1 eq. of diethyl malonate to give the rearranged thiolate (8, 85 %) and diethyl allylmalonate (15 %) ⁸. No diethyl allylmalonate was detectable under the similar reaction conditions in the absence of Pd(0).

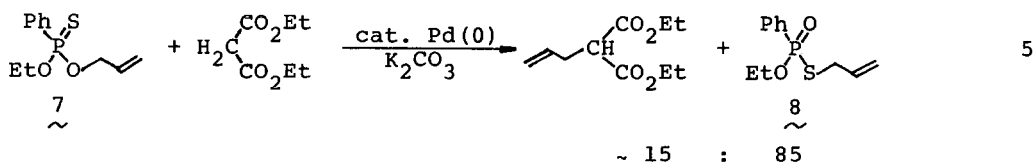
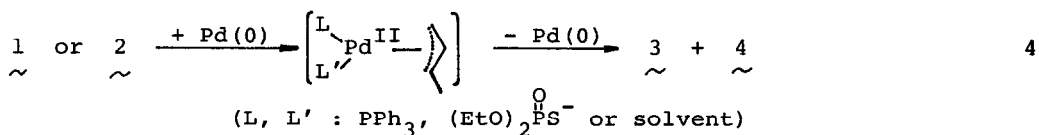
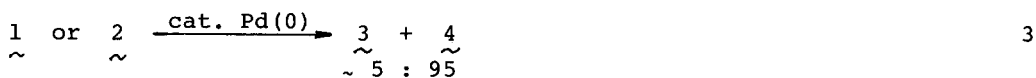


Table 1. Palladium catalyzed thiono-thiolo allylic rearrangement of phosphoro- or phosphonothionates

Entry	Starting Material	Temp. (°C)	Time (min)	Conv. (%)	Products (Yield ^a , %)			
1		70	25	100		(73)		
2 ^b	"	80	120	0	—			
3		80	10	100		(96)		
4		80	20	100		(97)		
5		80	20	99		(95)		
6		80	20	100		(98)		
7 ^c		80	10	80		(95)		
8		80	20	100		[95.2] (93)		[4.8] (2)
9		80	20	100	"	[94.4] (93)	"	[5.6] (2)

- a. The values in the parentheses denote the isolated yields and the values in the brackets denote the vpc yields, which were calculated from the area intensities on vpc (5% SE-30, 1 m, He).
- b. Phosphorothionate (2.5 mmol) and K_2CO_3 (0.025 mmol) in 3 ml of diglyme were heated without palladium catalyst under nitrogen atmosphere.
- c. The reaction essentially stopped at the 80 % conversion regardless of the reaction temperature or the reaction time.

The following example is illustrative of the simplicity and utility of this catalytic reaction: to a mixture of $\text{Pd}(\text{PPh}_3)_4$ (57.8 mg, 0.05 mmol) and K_2CO_3 (6.9 mg, 0.05 mmol) was added a solution of O,O-diethyl O-allyl phosphorothionate (1.05 g, 5 mmol) in 6 ml of diglyme under a nitrogen atmosphere. The reaction mixture was stirred at 80 °C for 10 minutes, and then poured into ether and washed with water. After usual work-up, the residue was chromatographed over silica gel in order to remove palladium catalyst to give 1.01 g (96 %) of O,O-diethyl S-allyl phosphorothiolate (6, A=B=OEt). The product was identical in all respects with the authentic specimen¹.

This is the first report on the application of palladium catalyst to the thiono-thiolo isomerization of phosphoro- or phosphonothionates. And the present reaction provides a new and efficient method to prepare S-allyl phosphoro- or phosphonothiolates starting from the easily accessible thionates under the very mild conditions. Some applications and the full details of the reaction will be reported in due course.

References and notes

1. A. N. Pudovik and I. M. Aladzheva, Zhur. Obshchei Khim., 30, 2617 (1960).
2. Details will be reported in due course.
3. D. R. Coulson, Inorg. Synth., 13, 121 (1972).
4. All new products were characterized by microanalytical and spectral data.
5. A. J. Burn and J. I. G. Cadogan, J. Chem. Soc., 1961, 5532.
6. L. E. Overman and F. M. Knoll, Tetrahedron Lett., 1979, 321.
7. B. M. Trost, Tetrahedron, 33, 2615 (1977), and references therein.
8. To a mixture of $\text{Pd}(\text{PPh}_3)_4$ (11.6 mg, 0.01 mmol) and K_2CO_3 (152 mg, 1.1 mmol) was added a solution of O-allyl O-ethyl phenylphosphonothionate (242 mg, 1 mmol) and diethyl malonate (176 mg, 1.1 mmol) in 1.2 ml of diglyme. The reaction mixture was stirred at 80 °C under a nitrogen atmosphere. After 20 minutes a small portion of the reaction mixture was subjected to vpc in order to confirm the completion of the reaction. The ratio of the products was calculated from the area intensities and not corrected.

Without the palladium catalyst, diethyl malonate also did not react with the rearranged product, S-allyl O-ethyl phenylphosphonothiolate, otherwise under the same conditions.

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