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PALLADIUM(II) CATALYZED THIONO-THIOLO REARRANGEMENT OF PROPARGYL THIONOPHOSPHATES

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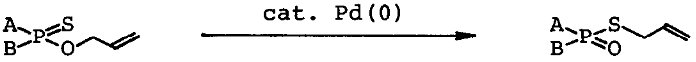
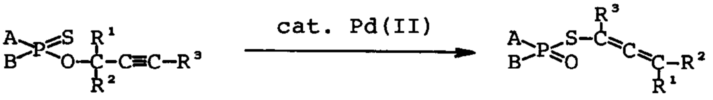
Abstract: Palladium(II) effectively catalyzes the [3,3]-sigmatropic type rearrangement of propargyl thionophosphates to provide allenyl thiolophosphates specifically.

Recently we have reported that Pd(0) nicely catalyzes the rearrangement of allyl thionophosphates to provide allyl thiolophosphates in almost quantitative yields (eq. 1).[1] This superficial [3,3]-sigmatropic rearrangement was denied mainly on the basis of the non-specific inversion of the migrating group and concluded to proceed via a π-allylpalladium intermediate.[1b] Similar non-specificity was observed for the rearrangement of 2-butyn-1-yl diethyl phosphorothionate by the catalysis of 1 mol% of tetrakis(triphenylphosphine)palladium, providing a mixture of S-1,2-butadien-3-yl and S-2-butyn-1-yl diethyl phosphorothiolates in a low conversion.[2]



(1)[1]



(2)

1 2

In this paper we wish to disclose the palladium(II) catalyzed polyhetero-Claisen rearrangement[3] of 1,5-enyne system: the thiono-thiolo rearrangement of propargyl thionophosphates (1) to allenyl thiolophosphates (2). That is, making marked contrast to the palladium(0) catalyzed reactions described above, 1 rearranged specifically to provide the inversion product 2 by the catalysis of palladium(II) (eq 2). The results are summarized in Table 1.

In the cases of entries 1-5 and 7 (Table 1), the rearrangements attained almost completion in the presence of 1 mol% of bis(acetonitrile)palladium(II) chloride in 1,2-dimethoxyethane (DME) at 80°C within 20-40 minutes or even at r.t. within 5 hours. In the absence of the catalyst, no reaction occurred even after the prolonged reaction time (entry 6). Small amount of K_2CO_3 (1 mol%) was applied in order to maintain the reaction system neutral or somewhat basic. By monitoring the reaction with VPC, it was revealed that the rate of reaction is generally fast but changes slightly depending on the substitution pattern of propargyl group: α-substituent tends to accelerate the rearrangement, while γ-substituent tends to decelerate.

Then the reaction was investigated about variations of substituents on phosphorus atom, and the results are summarized in the same table (entries 8-12, Table 1). Somewhat lower reactivity was noted for the rearrangements of ethyl propargyl phenylphosphonothionate and bis(propargyl) phenylphosphonothionate. In these cases, there was required the use of an increased amount of catalyst in order to attain the completion (entries 8 and 9). On the other hand, N-methyl and N,N-dimethyl propargyl phenylphosphonoamidothionates underwent the rearrangement very slowly and reached only 66% (after 1.5 h) and 51% (after 1 h) conversions even in the presence of 10 mol% of the catalyst, respectively (entries 11 and 12). The sluggishness may be due to the precipitation-out of the catalyst.[4] In each reaction allenyl thiolate was the only isolable product despite the dirty-looking reaction mixture.

The representative procedure is as follows: Into an argon purged mixture of bis(acetonitrile)palladium chloride (5.2 mg, 0.02 mmol) and potassium carbonate (2.8 mg, 0.02 mmol) was added a solution of propargyl diethyl phosphorothionate (416 mg, 2.0 mmol) in 2.4 ml of DME. This mixture was stirred and kept at 80°C for 20 minutes. The progression of reaction was monitored by VPC. Then the mixture was evaporated to dryness and subjected to column chromatography (silica gel, n-C_6H_{14}-EtOAc gradient) to give diethyl S-propadien-1-yl phosphorothiolate (387 mg, 93%) as an oil.[5]

Finally it is worth mentioning that, although there have been reported a few examples of [2,3]-sigmatropic type rearrangement of propargyl phosphites,[6] this is the first example of a [3,3]-sigmatropic type rearrangement of 1,5-enyne system[7] in organophosphorus chemistry. The wide flexibility of substituents around both phosphorus atom and propargyl group, mild conditions and high yields of reaction will find useful applications in organic synthesis.

Table 1. Palladium(II) Catalyzed Thiono-Thiolo Rearrangement of Propargyl Thionophosphates[a]

entry	1					cat.	temp.	time	conv.[b]	yield[c] of 2
	A	B	R^1	R^2	R^3	(mol%)	(°C)	(h)	(%)	(%)
1	EtO	EtO	H	H	H	1	80	0.33	100	93
2	"	"	"	"	"	1	r.t.	5	100	81
3	"	"	H	H	Me	1	80	0.67	98	93
4	"	"	Et	H	H	1	80	0.33	100	95
5	"	"	"	"	"	1	r.t.	4	100	91
6	"	"	"	"	"	0	80	3	0	—
7	"	"	Me	Me	H	1	80	0.25	100	75
8	EtO	Ph	H	H	H	4	80	0.25	100	72
9	$HC\equiv CCH_2O$	Ph	"	"	"	4	80	0.5	97	77
10	Ph	Ph	"	"	"	1	80	1	100	95
11	MeNH	Ph	"	"	"	10	80	1.5	66	39
12	Me_2N	Ph	"	"	"	10	80	1	51	62

a) For the structures of 1 and 2, see eq. 2. b) Conversion, based on VPC area intensities. c) Isolated yields, based on the conversion.

References and Notes

1. (a) Y. Yamada, K. Mukai, H. Yoshioka, Y. Tamaru and Z. Yoshida, Tetrahedron Lett., 1979, 5015. (b) Y. Tamaru, Z. Yoshida, Y. Yamada, K. Mukai and H. Yoshioka, J. Org. Chem., 1983, 48, 1293.
2. A mixture of S-1,2-butadien-3-yl and S-2-butyn-1-yl diethyl phosphorothiolates (in a ratio of 23:77) was obtained by the Pd(0) catalyzed reaction of 2-butyn-1-yl diethyl phosphorothionate (1 mol% of $Pd(PPh_3)_4$ / DME / 80 °C / 6h ; conv. 67%): Y. Yamada, K. Mukai, H. Yoshioka, Y. Tamaru and Z. Yoshida, unpublished data.
3. For the palladium catalyzed Claisen and polyhetero-Claisen rearrangements see: (a) L. E. Overman and F. M. Knoll, Tetrahedron Lett., 1979, 321. (b) Idem, J. Am. Chem. Soc., 1980, 102, 865. (c) P. A. Grieco, T. Takigawa, S. L. Bongers and H. Tanaka, ibid., 1980, 102, 7587. (d) P. A. Grieco, P. A. Tuthill and H. L. Sham, J. Org. Chem., 1981, 46, 5005. (e) Y. Tamaru, M. Kagotani and Z. Yoshida, ibid., 1980, 45, 5221. (f) Idem, Tetrahedron Lett., 1981, 22, 4245. (g) M. Mizutani, Y. Sanemitsu, Y. Tamaru and Z. Yoshida, J. Org. Chem., 1983, 48, 4585.
4. Soft acids such as $HgCl_2$, $AuCl_3$, $PtCl_4$, $AgNO_3$ and $AgBF_4$ are known to form solid adducts with triesters of phosphorothioic acid, while hard acids such as $SbCl_5$, $SnCl_4$, $SnBr_4$, $TiCl_4$, $AlCl_3$ and $FeCl_3$ react with such phosphorothionates to form the corresponding phosphorothiolate adducts. (a) H. Teichmann and G. Hilgetag, Angew. Chem. Internat. Ed., 1965, 4, 914. (b) G. Hilgetag and H. Teichmann, ibid., 1967, 6, 1013.
5. Diethyl S-propadien-1-yl phosphorothiolate : bp 150°C (2.5 mmHg); IR (neat film) 1945 (mw), 1255 (s), 1015 (vs), 975 (s), 860 (m); NMR δ ($CDCl_3$) 1.42 (6H, t, J=7.2 Hz), 4.28 (4H, d.q, J=9.2 Hz, 7.2 Hz), 5.08 (2H, d.d, J=7.0 Hz, 7.0 Hz), 5.83 (1H, d.t, J=7.0 Hz, 7.0 Hz); mass spectrum, m/e (relative intensity) 208 (M^+, 9), 180 (23), 152 (100), 83 (27). Anal. Calcd for $C_7H_{13}O_3PS$: C, 40.38; H, 6.29; P, 14.88. Found: C, 40.11; H, 6.48; P, 15.12.

   All other new compounds were also characterized in a similar manner as above.
6. (a) A. P. Boisselle and N. A. Meinhardt, J. Org. Chem., 1962, 27, 1828. (b) R. S. Macomber and E. R. Kennedy, ibid., 1976, 41, 3191. (c) R. S. Macomber, J. Am. Chem. Soc., 1977, 99, 3072.
7. For the rearrangement of 1,5-enyne system, see: (a) A. Viola, J. J. Collins and N. Filip, Tetrahedron, 1981, 37, 3765. (b) P. D. Landor and S. R. Landor, J. Chem. Soc., 1956, 1015. (c) R. C. Cookson, M. C. Cramp and P. J. Parsons, J. Chem. Soc., Chem. Commun., 1980, 197.

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