Tetrahedron Letters 51 (2010) 4957–4958

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Synthesis of acylphosphine sulfides by rhodium-catalyzed reaction of acid fluorides and diphosphine disulfides

Mieko Arisawa[a], Toru Yamada[a], Masahiko Yamaguchi[a,b,*]

[a] *Department of Organic Chemistry, Graduate School of Pharmaceutical Sciences, Tohoku University, Aoba, Sendai 980-8578, Japan*
[b] *WPI Research Center, Advanced Institute for Materials Research, Tohoku University, Aoba, Sendai 980-8577, Japan*

ARTICLE INFO

Article history:
Received 19 May 2010
Revised 3 July 2010
Accepted 8 July 2010
Available online 11 July 2010

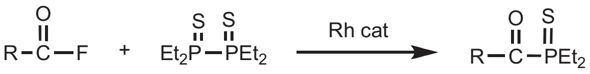
ABSTRACT

A rhodium complex catalyzed the reaction of acid fluorides and tetraethyldiphosphine disulfide giving acylphosphine sulfides. Aromatic acid fluorides with electron donating *p*-groups reacted smoothly giving the products in high yields. Aliphatic acid fluorides with secondary and tertiary α-carbons were also converted to alkanoylphosphine sulfides, whereas the reaction of a substrate with an α-methylene carbon was accompanied by enol ester formation.

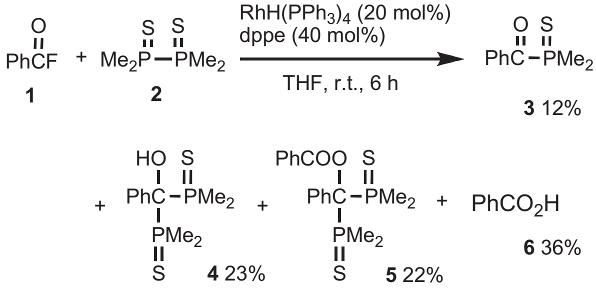
Acylphosphorus compounds are phosphorus analogs of amides and esters, and their synthesis have attracted much interest:[1] The Arbuzov reaction of acid chlorides with trialkyl phosphites was often used to obtain acylphosphonates;[2] acylphosphines were obtained by the reaction of phosphines and phosphine oxides with acid chlorides in the presence of bases;[3] and silylphosphines were employed for this transformation without the base.[4] These syntheses provided acylphosphonates, acylphosphines, or oxides. In contrast, only a scattered synthesis of acylphosphine sulfides appeared, which generally used a sulfuration reaction of acylphosphines.[5] Described in this work is a versatile method for the synthesis of acylphosphine sulfides from acid fluorides and diphosphine disulfides, which was catalyzed by a rhodium complex (Scheme 1). Our previous work showed a high reactivity of the organofluorine compounds under rhodium catalysis,[6] and this method was applied here to the reaction of acid fluorides.[7,8]

When an equimolar mixture of benzoyl fluoride **1** and tetramethyldiphosphine disulfide **2** were reacted at room temperature in THF for 6 h in the presence of $RhH(PPh_3)_4$ (20 mol %) and 1,2-bis(diphethylphosphino)ethane (dppe, 40 mol %), benzoyldimethylphosphine sulfide **3** was obtained in 12% yield by ^1H NMR analysis of the crude products (Scheme 2). Bis(dimethylthiophosphinyl)-phenylmethanol **4** (23%) and its benzoate ester **5** (22%) were isolated along with benzoic acid **6** (36%). The byproducts **4**, **5**, and **6** were formed by hydrolysis of **3** followed by the addition of $HPSMe_2$ to **3**. No reaction occurred in the absence of the rhodium complex or dppe.

In order to suppress the formation of the byproducts, the substrate structure was examined. It turned out that the introduction of an electron-donating *p*-substituent on the benzoyl moiety stabilized the benzoylphosphine sulfides towards hydrolysis, and the *p*-methoxybenzoylphosphine sulfide obtained from *p*-methoxybenzoyl fluoride could be purified by rapid silica gel chromatography without decomposition. In addition, use of tetraethyldiphosphine disulfide **7** in place of **2** further improved the stability of the product. Using these substrates, the catalyst loading could be reduced to 1 mol %. *p*-Methoxybenzoyl fluoride was reacted with **7** (1 equiv) in the presence of $RhH(PPh_3)_4$ (1 mol %) and $(Ph_2PCH_2CH_2)_2PPh$ (2 mol %) in refluxing THF for 3 h, and *p*-methoxybenzoyldiethylphosphine sulfide was obtained in 97% yield (Table 1, entry 1). The formation of Et_2PSF was indicated by ^{19}F NMR δ −96.3 (J = 1017 Hz) and ^{31}P NMR δ 133.4 (J = 1013 Hz). The effect of the phosphine ligand was critical, and no reaction occurred in its absence.



Scheme 1.



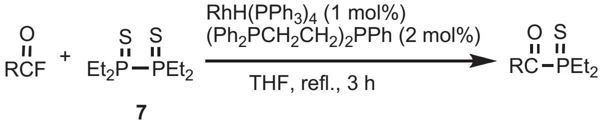
Scheme 2.

---

[*] Corresponding author.
E-mail address: yama@mail.pharm.tohoku.ac.jp (M. Yamaguchi).

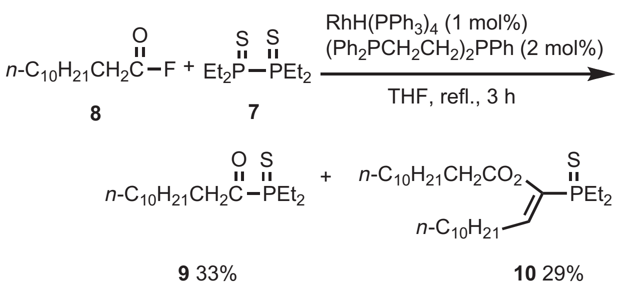
0040-4039/$ - see front matter © 2010 Published by Elsevier Ltd.
doi:10.1016/j.tetlet.2010.07.038

Table 1
Rhodium-catalyzed reaction of acid fluoride and **7**



Entry	R	Yield (%)
1	p-MeOC$_6$H$_4$	97
2	p-MeC$_6$H$_4$	79 (88)[a]
3	3,5-(MeO)$_2$C$_6$H$_5$	76
4	2,4,6-Me$_3$C$_6$H$_2$	53, 73[b]
5	p-Me$_2$NC$_6$H$_4$	77, 99[b]
6	Ph	63 (80)[a]
7	p-ClC$_6$H$_4$	18 (52)[a]
8	n-Pr$_2$CH	93
9	PhMeCH	88
10	1-Methylcyclohexyl	85
11	1-Adamantyl	94

[a] In parentheses are crude yields obtained by ^{1}H NMR.
[b] RhH(PPh$_3$)$_4$ (2 mol %), (Ph$_2$PCH$_2$CH$_2$)$_2$PPh (4 mol %).



Scheme 3.

Bidentate ligands with the phosphino groups separated by two carbon atoms such as 1,2-bis(diethylphosphino)ethane (depe), 41%; 1,2-bis(diphenylphosphino)ethane (dppe), 85%; 1,2-bis(diphenylphosphino)ethylene (dppv), 54%; and 1,2-bis(diphenylphosphino)benzene (dppBz), 78% exhibited catalytic activity. Among these, the tridentate phosphine (Ph$_2$PCH$_2$CH$_2$)$_2$PPh gave a higher yield of the product. Other ligands such as (p-MeOC$_6$H$_4$)$_3$P, (p-ClC$_6$H$_4$)$_3$P, 1,2-bis(diphenylphosphino)methane (dppm), 1,2-bis(diphenylphosphino)propane (dppp), and 1,2-bis(diphenylphosphino)ferrocene (dppf) were not effective at all. It was also noted that essentially no reaction occurred under the same rhodium-catalyzed conditions using p-methoxybenzoyl chloride.

The reaction was applied to several aromatic acid fluorides possessing electron-donating groups, and aroylphosphine sulfides were obtained in high yields (entries 1–5). Benzoyl fluoride and p-chlorobenzyl fluoride also gave the products in good yields as indicated by crude ^{1}H NMR analysis (entries 6 and 7). They, however, decomposed during isolation, which resulted in lower isolated yields. The reaction could be applied to aliphatic acid fluorides with secondary or tertiary α-carbons, and alkanoylphosphine sulfides were obtained in high yields (entries 8–11).

An aliphatic acid fluoride with an α-methylene group exhibited a different reactivity. When undecanoyl fluoride **8** was reacted with **7** in the presence of RhH(PPh$_3$)$_4$ (1 mol %), (Ph$_2$PCH$_2$CH$_2$)$_2$PPh (2 mol %) in refluxing THF for 4 h, undecanoyldiethylphosphine sulfide **9** was obtained in 33% yield, which was accompanied by (E)-(1-undecanoyloxy-1-undecenyl)diethylphosphine sulfide **10** in 29% yield (Scheme 3). The stereochemistry at the olefin moiety was determined by ^{1}H(vinyl)–^{31}P coupling constant 10.4 Hz and NOE experiments. The enol ester **10** should be formed from **9** by the reaction with **8**, which was confirmed by the following experiment. The reaction of **8** and **9** in the presence of RhH(PPh$_3$)$_4$ (2 mol %) and (Ph$_2$PCH$_2$CH$_2$)$_2$PPh (4 mol %) in refluxing THF for 4 h gave **10** in 13% yield. This reaction was also rhodium-catalyzed, which indicated the involvement of ketone α-activation by the rhodium complex.[9] Such a reactivity of the rhodium complex towards α-phenylthio ketones was recently reported.[10]

In summary, a rhodium-catalyzed method for the synthesis of acylphosphine sulfides was developed using acid fluorides and diphosphine disulfide. The method provided a series of aromatic and aliphatic acylphosphine sulfides, and the properties and reactivities of these novel organophosphorus compounds now can be studied in a systematic way.

Typical experimental procedures

In a two-necked flask equipped with a reflux condenser was placed p-methoxybenzoyl fluoride (77.1 mg, 0.5 mmol), **7** (121.2 mg, 0.5 mmol), RhH(PPh$_3$)$_4$ (5.8 mg, 1.0 mol %), and bis(2-diphenylphosphinoethyl)-phenylphosphine (5.3 mg, 2.0 mol %) in tetrahydrofuran (1 mL) under an argon atmosphere, and the solution was stirred under reflux for 4 h. Then, the solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel within 10–15 min giving diethyl(4-methoxybenzoyl)phosphine sulfide (124.6 mg, 97%).

Acknowledgments

This work was supported by the Grant-in-Aid for Scientific Research (No. 21229001), GCOE program, and WPI Initiative from JSPS. M.A. expresses her thanks to the Grant-in-Aid for Scientific Research from MEXT (No. 22689001) and also to the Naito Foundation.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.07.038.

References and notes

1. Whitehead, A.; Sieck, S. R.; Mukherjee, S.; Hanson, P. R. Product Class 14: Acylphosphorus Compounds. In *Science of Synthesis*; Georg Thieme Verlag: Stuttgart, New York, 2005; Vol. 21, p 907.
2. For recent example, Migianu, E.; Guénin, E.; Lecouvey, M. *Synlett* **2005**, 425.
3. Baber, R. A.; Clarke, M. L.; Orpen, A. G.; Ratcliffe, D. A. *J. Organomet. Chem.* **2003**, *667*, 112; Also see, Liotta, C. L.; McLaughlin, M. L.; O'Brien, B. A. *Tetrahedron Lett.* **1984**, *25*, 1249; Kostyanovsky, R. G.; Yakshin, V. V.; Zimont, S. L. *Tetrahedron* **1968**, *24*, 2995.
4. Kunzek, H.; Braun, M.; Nesener, E.; Rühlmann, K. *J. Organomet. Chem.* **1973**, *49*, 149.
5. Osaki, T.; Otera, J.; Kawasaki, Y. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 1803; Al'fonsov, V. A.; Pudovik, D. A.; Batyeva, E. S.; Pudovik, A. N. *J. Gen. Chem., Eng. Trans.* **1985**, *55*, 1956; Barron, A. R.; Hall, S. W.; Cowley, A. H. *J. Chem. Soc., Chem. Commun.* **1987**, 1753; Majima, T.; Schnabel, W. *J. Photochem. Photobiol. A, Chem.* **1989**, *50*, 31; Goerlich, J. R.; Müller, C.; Schmutzler, R. *Phosphorus, Sulfur, Silicon* **1993**, *85*, 193.
6. Arisawa, M.; Suzuki, T.; Ishikawa, T.; Yamaguchi, M. *J. Am. Chem. Soc.* **2008**, *130*, 12214.
7. Review. Arisawa, M.; Yamaguchi, M. *J. Synth. Org. Chem., Jpn.* **2007**, *65*, 1213; Arisawa, M.; Yamaguchi, M. *Pure Appl. Chem.* **2008**, *80*, 993.
8. Our recent work on the rhodium-catalyzed cleavage reactions of diphosphine disulfide. Arisawa, M.; Ono, T.; Yamaguchi, M. *Tetrahedron Lett.* **2005**, *46*, 5669; Arisawa, M.; Onoda, M.; Hori, C.; Yamaguchi, M. *Tetrahedron Lett.* **2006**, *47*, 5211; Arisawa, M.; Yamaguchi, M. *Tetrahedron Lett.* **2009**, *50*, 45; Arisawa, M.; Yamaguchi, M. *Tetrahedron Lett.* **2009**, *50*, 3639; Arisawa, M.; Yamaguchi, M. *Tetrahedron Lett.*, doi:10.1016/j.tetlet.2010.07.040.
9. A related observation on acylphosphonates. Afarinkia, K.; Echenique, J.; Nyburg, S. C. *Tetrahedron Lett.* **1997**, *38*, 1663.
10. Arisawa, M.; Suwa, K.; Yamaguchi, M. *Org. Lett.* **2009**, *11*, 625.