APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2007; **21**: 373–376

(www.interscience.wiley.com) DOI:10.1002/aoc.1216

Studies on the reaction of organotin phenoxides with ethyl propiolate catalysed by triethylamine and tin(IV) chloride

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Received 14 December 2006; Revised 4 January 2006; Accepted 8 January 2007

Different tributyltin phenoxides react at room temperature with ethyl propiolate in benzene, in the presence of tin(IV) chloride, triethylamine and their mixture to give the derivatives of 3-phenoxyacrylic acid ethyl ester. Exceptionally, 3-(2-hydroxyphenyl)acrylic acid ethyl ester and 3-(2-hydroxy-5-methylphenyl)acrylic acid ethyl ester have been obtained from the reaction of tributylphenoxytin and tributyl(*p*-tolyloxy)tin, respectively catalysed by $SnCl_4$, and they have been easily hydrolysed to coumarin and 6-methylcoumarin. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: tin phenoxides; ethyl propiolate; tin(IV) chloride; triethylamine

INTRODUCTION

In 1908, pure *ortho*-vinylphenol was synthesized for the first time by decarboxylation of *ortho*-hydroxycinnamic acid.[1] Since then, a number of methods have been developed for the synthesis of vinylphenols. Electrophilic acylation of phenol followed by reduction and dehydration was employed in the commercial production of *p*-vinylphenol by Maruzen Petrochemicals Co.[2,3] Another method which utilized benzylic oxidation of ethylphenol was reported.[4] Halophenol derivatives could be vinylated by the Heck reaction.[5] Yamaguchi[6–9] reported the ethenylation reaction of phenol using the $SnCl_4$–Bu_3N reagent system. This reaction has a drawback of employing elevated temperatures. Kobayashi and Yamaguchi[10] also described the catalytic version of the reaction using silylethyne. Phenyl vinyl ethers were obtained for the first time by Ruhemann and Beddow[11] using chlorofumaric acid diethyl ester and the appropriate phenol sodium salt. Rosnati[12,13] observed that the reaction of ethyl 2-bromopropionate with phenol in the potassium carbonate-acetone system led to ethyl (*E*)-3-phenoxypropenoate with 10% yield.

Also, recently, the authors have reported that organotin phenoxides react at room temperature with diethyl acetylenedicarboxylate in diethyl ether, in the presence of lithium perchlorate to give a mixture of corresponding phenyl vinyl ethers and ring ethenylated phenols.[14] Strazisar and Wolczanski[15] studied the possibility of application of vinyl ethers (including phenyl vinyl ethers) for production of commercially important polymers generated using single-site Ziegler–Natta catalysts. Cleavage of the C–O bond of phenyl vinyl ethers by transition metal complexes is attracting much interest with regard to catalysis as well as organic and organometallic synthesis.[16] Also, derivatives of coumaric acid serve as valuable materials in the organic synthesis. For example, Ullrich presented an efficient route from coumarins to highly functionalized *N*-phenyl-2-quinolinones via Buchwald–Hartwig amination.[17] The use of O-metallation of alcohols or enols to enhance their reactivity towards electrophiles such as aldehydes or alkyl or acyl halides is a familiar process[18] and we suspected that the O-metallation of phenols could be exploited to enhance the rate of electrophilic substitution in the ring. The polarity of the $M^{\delta+}$–$O^{\delta-}$–Ar bond would be expected to promote the reaction with ethyl propiolate, whatever the detailed structure of the metal phenoxide (which may be associated in solution). We have chosen to work with organotin phenoxides (Bu_3SnOAr) because it is easy to introduce or remove the organotin group and because of the pronounced polarity of the Sn–O bond.[19]

RESULTS AND DISCUSSION

We believe that the reaction between studied organotin phenoxides and ethyl propiolate may proceed according

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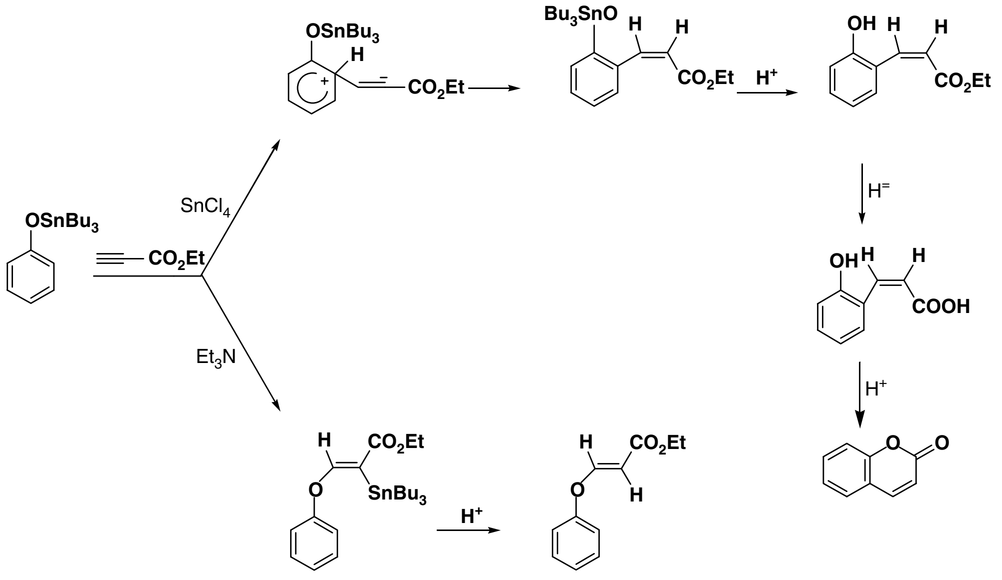
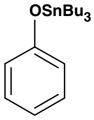
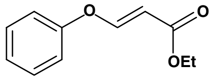
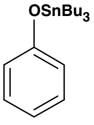
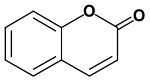
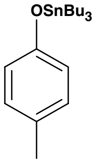
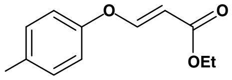
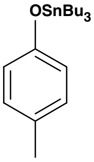
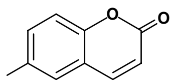
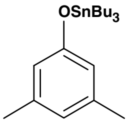
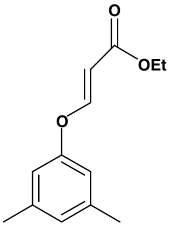


Scheme 1. Reaction of tributylphenoxytin with ethyl propiolate catalysed by $SnCl_4$ and Et_3N.

to two possible mechanisms, which may compete. As the result 3-(2-hydroxyphenyl)acrylic acid ethyl ester and 3-(2-hydroxy-5-methylphenyl)acrylic acid ethyl ester have been obtained from tributylphenoxytin and tributyl(*p*-tolyloxy)tin, respectively, when $SnCl_4$ or $SnCl_4$–Et_3N mixture has been used as a catalyst, as shown in Scheme 1. Their recognition as the *cis*-alkenes was based on comparison of values of coupling constants of vinyl protons equal to 9.1 Hz and identification of products of their hydrolysis, i.e. coumarin and 6-methylcoumarin. However, other tin phenoxides under studied conditions gave only the appropriate phenyl vinyl ethers (see Table 1). The formation of selectively phenyl vinyl ethers from these tin phenoxides is governed mainly by a steric hindrance of 2- or 3-Me groups. The method which we adopted seems to be the most favorable out of all known procedures for synthesis of analogous compounds which require high temperatures and often require the use of concentrated sulfuric acid.[20]

Isolation of products (**1**–**6**) was carried out by column chromatography. All the reactions that we studied were carried out in benzene in the presence of Et_3N, $SnCl_4$ or their mixture. No addition products were detected for a reaction carried out without addition of the above-mentioned catalysts or with simple phenols used instead of tin phenoxides. The elemental analysis as well as ^1H NMR and IR studies of products (**1**–**6**) confirmed their composition. Identification of coumarin and 6-methylcoumarin was based on comparison of their NMR and IR spectra with the commercial samples.

Table 1. Reaction of different organotin phenoxides with ethyl propiolate catalysed by $SnCl_4$ and Et_3N

Organotin phenoxide	Catalyst	Product after hydrolysis and purification by column chromatography	Yield of the reaction
	Et_3N	 **1**	80%
	$SnCl_4$	 **2**	60%
	Et_3N	 **3**	80%
	$SnCl_4$	 **4**	60%
	Et_3N	 **5**	80%

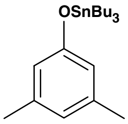
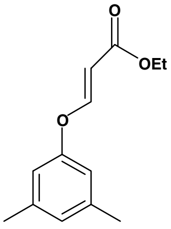
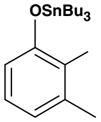
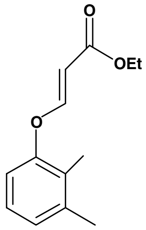
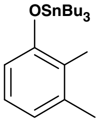
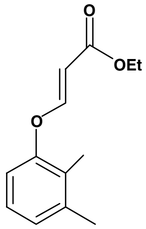
(*continued overleaf*)

EXPERIMENTAL

NMR spectra were recorded using an Avance DRX 500 Bruker and a Varian Gemini 200 BP spectrometers. The tributyltin

DOI: 10.1002/aoc

Table 1. (*Continued*)

Organotin phenoxide	Catalyst	Product after hydrolysis and purification by column chromatography	Yield of the reaction
	$SnCl_4$	 **5**	60%
	Et_3N	 **6**	80%
	$SnCl_4$	 **6**	60%

The reaction between four studied tributyltin phenoxides and ethyl propiolate carried out in benzene, in the presence of the $SnCl_4$–Et_3N mixture, gave analogous products and yields as for $SnCl_4$ used as a catalyst.

phenoxides were prepared by the azeotropic dehydration of a mixture of the appropriate phenol and bis(tributyltin) oxide in toluene.[19] All chemicals were purchased from Aldrich.

Typical examples of reactions under study are as follows: tributyl-(*p*-tolyloxy)tin (1259 mg, 3.17 mmol) and ethyl propiolate (311 mg, 3.17 mmol) were added to benzene (15 cm^3). Next, the equimolar amount of triethylamine (320 mg, 3.17 mmol) or tin(IV) chloride (824 mg, 3.17 mmol) or their mixture was added and the mixture was left for 4 days. The progress of the reaction was monitored by TLC [using light petroleum–ethyl acetate mixture (4 : 1, v/v) as eluent] and by NMR spectroscopy, which showed that product was formed. All products of reactions were separated in nearly the same way. First, benzene was evaporated under reduced pressure and, in order to hydrolyze the remaining unreacted tributyltin phenoxides, the reaction mixture was stored over aqueous 0.1 M solution of HCl for 24 h. Exceptionally, in the case of the reactions of tribuylphenoxytin or tributyl(*p*-tolyloxy)tin and ethyl propiolate catalyzed by $SnCl_4$, the product of the reaction was stored for 4 days over aqueous 0.5 M solution of HCl. The organic materials were extracted with diethyl ether, which was dried over Na_2SO_4. Isolation of products of reactions under study was carried out by column chromatography using petroleum–ethyl acetate mixture (7 : 3, v/v as eluent). The elemental analysis as well as ^{1}H NMR studies of obtained products confirmed their composition. The identification of vinyl ethers (**1**), (**3**), (**5**) and (**6**) as ethyl esters of *trans*-β-phenoxyacrylic acid and its derivatives was based on comparison of their spectra with the literature proton chemical shifts of *cis*- and *trans*-β-phenoxyacrylic acid.[21] Ethyl (*E*)-3-phenoxypropenoate (**1**) and ethyl (*E*)-3-(p-tolyloxy)propeonate (**3**) were previously obtained.[12,13,22] However, their ^{1}H NMR spectra as well as those of other two other vinyl ethers (**5**) and (**6**) are not available. Therefore, we decided to attach their ^{1}H NMR characteristic. The reaction products have shown the following values of chemical shifts.

*Ethyl (E)-3-phenoxypropenoate (**1**) oil*

$C_{11}H_{12}O_3$ requires: C 68.74, H 6.29. Found: C 68.68, H 6.25. $\delta_H(CDCl_3)$: 1.28 (3H, t, $J = 7.1$ Hz), 4.19 (2H, q, $J = 7.1$ Hz), 5.54 (1H, d, $J = 12.4$ Hz), 7.14 (2H, dd, $J_1 = 7.5$ and $J_2 = 2.0$ Hz), 7.27 (1H, m), 7.46 (2H, m), 7.78 (1H, d, $J = 12.4$ Hz).

*Ethyl (E)-3-(p-tolyloxy)propenoate (**3**) oil*

$C_{12}H_{14}O_3$ requires: C 69.88, H 6.84. Found: C 69.74, H 6.76. $\delta_H(CDCl_3)$: 1.24 (3H, t, $J = 7.1$ Hz); 2.28 (3H, s); 4.14 (2H, q, $J = 7.1$ Hz); 5.47 (1H, d, $J = 12.4$ Hz); 6.89 (2H, d, $J = 8.5$ Hz); 7.10 (2H, d, $J = 8.5$ Hz); 7.74 (1H, d, $J = 12.4$ Hz).

*Ethyl (E)-3-(3,5-dimethylphenoxy)propenoate (**5**) oil*

$C_{13}H_{16}O_3$ requires: C 70.89, H 7.32. Found: C 70.77, H 7.28. $\delta_H(CDCl_3)$: 1.29 (3H, t, $J = 7.1$ Hz); 2.31 (6H, s); 4.19 (2H, q, $J = 7.1$ Hz); 5.52 (1H, d, $J = 12.2$ Hz); 6.68 (2H, s); 6.82 (1H, s); 7.78 (1H, d, $J = 12.2$ Hz).

*Ethyl (E)-3-(2,3-dimethylphenoxy)propenoate (**6**) oil*

$C_{13}H_{16}O_3$ requires: C 70.89, H 7.32. Found: 70.80, H 7.29. $\delta_H(CDCl_3)$: 1.27 (3H, t, $J = 7.3$ Hz); 2.06 (3H, s); 2.22 (3H, s); 4.10 (2H, q, $J = 7.3$ Hz); 5.26 (1H, d, $J = 12.4$ Hz); 6.77 (1H, d, $J = 7.9$ Hz); 7.05 (2H, m); 7.69 (1H, d, $J = 12.4$ Hz).

REFERENCES

1. Fries K, Fickewirth G. *Chem. Ber.* 1908; **41**: 367.
2. Corson BB, Heintzelman WJ, Schwartzman LH, Tiefenthal HE, Lokken RJ, Nickles JE, Atwood GR, Pavlik FJ. *J. Org. Chem.* 1958; **23**: 544.
3. Everhart ET, Craig JC. *J. Chem. Soc., Perkin Trans. I* 1991; 1701.
4. Emerson WS, Heyd JW, Lucas VE, Cook WB, Owens GR, Shortridge RW. *J. Am. Chem. Soc.* 1946; **68**: 1665.
5. Rollin Y, Meyer G, Troupel M, Fauvarque J-F, Perichon J. *J. Chem. Soc. Chem.Commun.* 1983; 793.
6. Yamaguchi M, Hayashi A, Hirama M. *J. Am. Chem. Soc.* 1995; **117**: 1151.
7. Yamaguchi M, Arisawa M, Kido Y, Hirama M. *J. Chem. Soc. Chem. Commun.* 1997; 1663.

8. Yamaguchi M, Arisawa M, Omata K, Kabuto K. Hirama M, Uchimaru T. *J. Org. Chem.* 1998; **63**: 7298.
9. Yamaguchi M. *Pure Appl. Chem.* 1998; **70**: 1091.
10. Kobayashi K, Yamaguchi M. *Organic Lett.* 2001; **3**: 241.
11. Ruhemann S, Beddow F. *Chem. Soc.* 1900; **77**: 1119.
12. Rosnati V, Saba A. *Tetrahedron Lett.* 1981; **22**: 167.
13. Rosnati V, Saba A, Salimbeni A, Vettori U. *Gazz. Chim. Ital.* 1981; **111**: 249.
14. Kinart WJ, Kinart CM. *J. Organomet. Chem.* 2006; **691**: 1441.
15. Strazisar SA, Wolczanski PT. *J. Am. Chem. Soc.* 2001; **123**: 4728.
16. Planas JG, Marumo T, Ichikawa Y, Hirano M, Komiya S. *J. Chem. Soc., Dalton Trans.* 2000; 2613.
17. Ulrich T, Giraud F. *Tetrhedron Lett.* 2003; **44**: 4207.
18. Davies AG. *J. Chem. Soc. Perkin Trans. I* 2000; 1997.
19. Davies AG. *Organotin Chemistry*. VCH: Weinheim, 1997; 166–190.
20. Thompson TJ, Edee RH. *J. Am. Chem. Soc.* 1925; **47**: 2556.
21. Kajimoto O, Kobayashi M, Fueno T. *Bull. Chem. Soc. Jpn* 1973; **46**: 1425.
22. Fujinami M. *Agric. Biol. Chem.* 1970; **34**: 1157.

DOI: 10.1002/aoc