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A HIGHLY CONVENIENT PROCEDURE FOR THE HYDROLYSIS OF TERMINAL PHENYL VINYL SULFIDES

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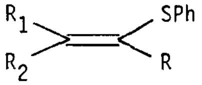
ABSTRACT: Terminal vinyl and chlorovinyl sulfides are hydrolyzed by 70% perchloric acid-thiophenol in benzene to the corresponding diphenyl thioacetals and thioesters in good yields.

Vinyl sulfides are very important class of compounds due to their versatility in organic synthesis[1]. Numerous methods are available for the hydrolysis of vinyl sulfides[1] 1 (R = alkyl or aryl) but few methods are available for the hydrolysis of the vinyl sulfides[2] where R = H or Cl.



1

R_1, R_2 = H, Alkyl, Aryl
R = H, Cl, Alkyl, Aryl

These terminal vinyl sulfides, in general, are quite difficult to hydrolyzed and the method of choice, so far, seems to be that reported by Cohen et.al.[2a] in which a combination of hydrogen chloride gas and thiophenol in benzene was employed.

In connection to our program to utilize vinyl sulfides and chlorovinyl sulfides in synthesis, we have developed a convenient method for the hydrolysis of vinyl sulfides 1 (R = H, Cl) The process involves the combination of thiophenol in benzene in the presence 70% perchloric acid or trifluoroacetic acid. We have found that the most convenient and the easiest to handle acid is 70% perchloric acid. Our results are summerized in Table I.

Table I

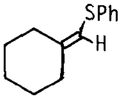
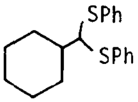
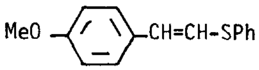
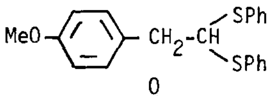
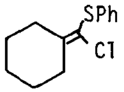
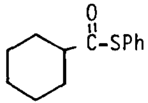
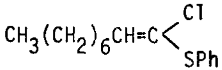
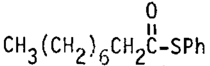
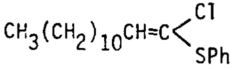
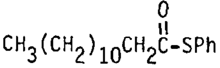
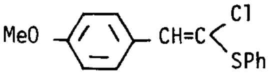
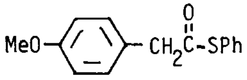
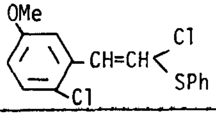
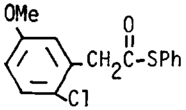
Entry	Vinyl sulfides	Products: Yields % (method)[a]	
1			60(1); 67(2); 67(3)
2			87(1)
3			60(1); 4(2); 0(3)[b]
4	 $CH_3(CH_2)_6CH{=}C(Cl)SPh$	 $CH_3(CH_2)_6CH_2C(=O)\text{-}SPh$	66(1); 64(2)
5	 $CH_3(CH_2)_{10}CH{=}C(Cl)SPh$	 $CH_3(CH_2)_{10}CH_2C(=O)\text{-}SPh$	62(1)
6			76(1)[c]

Table I (cont.)

Entry	Vinyl sulfides	Products : Yields (method)[a]	
7			72(1)[c]

[a] Method 1, The reaction was carried out with thiophenol (2 equiv.) and 70% perchloric acid (6 equiv.) in benzene at room temperature (RT) for 3 minutes.

2, The reaction conditions were thiophenol (2 equiv.) and trifluoroacetic acid (2 equiv.) in benzene at RT for 10 minutes.

3, A mixture of hydrogen chloride gas and thiophenol (1 equiv.) in benzene at RT for 10 minutes was employed.

[b] All starting material was recovered.

[c] Reaction time was 4 hours.

In the case of thioester formation, prolonged reaction time led to the formation of the corresponding carboxylic acid . For example, in entry 3, when the reaction time was prolonged to 4 hr., cyclohexanecarboxylic acid was isolated in 40% yield together with 20% yield of the thioester. The thioesters could be converted to the corresponding methyl esters in 70-80% yield by stirring overnight in anhydrous methanol and a catalytic amount of concentrated sulfuric acid[3].

Our hydrolytic procedure provides a convenient entry to thioesters which are of considerable synthetic interest[4]. In view of the fact that the relatively mild conditions were required in our reactions, this method should be applicable to the hydrolysis of various terminal vinyl sulfides.

References

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3. For methods of S → O ester conversion see: a) S. Masamune, Y. Hayase, W. Schilling, W.K. Chan and G.S. Bates, J.Am.Chem.Soc., **99**, 5756 (1977); b) S. Masamune, Aldrichimica Acta, **11**, 23 (1978) and references cited therein.
4. a) K.C. Nicolaou, Tetrahedron, **33**, 683 (1977); b) T.G. Back, ibid., **33**, 3041 (1977); c) S. Masamune, G.S. Bates and J.W. Corcoran, Angew.Chem.Int.Ed.Engl. **16**, 585 (1977); d) T. Imamoto, M. Kodera and M. Yokoyama, Synthesis, 134 (1982) and references cited therein.

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