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# A SIMPLE SYNTHESIS OF 1-THIOPHENOXY-3-CHLOROALKENES USEFUL SYNTHONS FOR ACROLEIN AND METHACROLEIN

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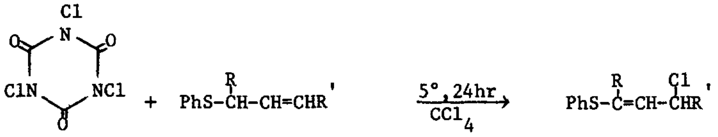
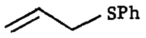
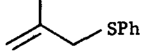
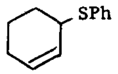
We wish to report that the inexpensive chlorinating agent trichloroisocyanuric acid (1, Aldrich) which is a component of some industrial deoderants and household cleansers under the trade name Chloreal,[2] is capable of converting allylic phenyl thioethers (2) into 1-thiophenoxy 3-chloroalkenes in yields approaching quantitative We also demonstrate the utility of two of the products as synthons for acrolein and methacrolein. A number of examples of the chlorination are given in Table I.



1 2 3

TABLE I. Chlorinations of Phenyl Allyl Sulfides[a]

| Thioether | Reagent | Yield of 3,% (%.E) |
|---|---|---|
|  | Chloreal | 98 (63) |
| " | NCS | 98 (97) |
|  | Chloreal | 97 (50) |
|  | NCS | 95 (95) |
|  | Chloreal | 88 |

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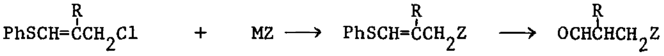
[a] A suspension of 3 mmol of Chloreal or 6 mmol of NCS in 15 ml of $CCl_4$ containing 6 mmol of thioether was stirred under nitrogen at 5° for 24 hr The product mixture was filtered and the filtrate evaporated.

The far more expensive reagent, N-chlorosuccinimide (NCS) is considerably less effective When R = alkyl, the same conditions afford mainly unreacted starting material and, in some cases, a small amount of a mixture of several unidentified products; even at room temperature, some unreacted starting material remains[3] Higher temperatures are frequently impractical since the substrates are prone to undergo allylic rearrangement[5] Furthermore, chlorinations of primary allylic thioethers (2, R = H) are significantly faster with Chloreal than with NCS, although the latter can be successfully used[6-8]

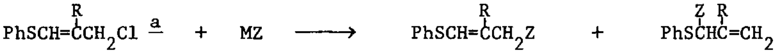
Since organometallic reagents frequently add to acrolein and methacrolein in a 1,2-fashion[9] or cause polymerization, we have demonstrated the utility of 1-thiophenoxy-3-chloropropene (4, R = H) and 1-thiophenoxy-2-methyl-3-chloropropene (4, R = Me), readily obtainable from phenyl allyl sulfide[10] and phenyl methallyl sulfide,[11] respectively, as synthons of these α,β-unsaturated aldehydes[12] in a Michael sense



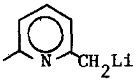
$$\underset{\mathbf{4}}{\mathrm{PhSCH{=}\overset{R}{C}CH_2Cl}} + \mathrm{MZ} \longrightarrow \underset{\mathbf{5}}{\mathrm{PhSCH{=}\overset{R}{C}CH_2Z}} \longrightarrow \underset{\mathbf{6}}{\mathrm{OCH\overset{R}{C}HCH_2Z}}$$

Table II lists some of the displacements which have been accomplished It can be seen that the displacements generally proceed in high yield and that only in the case of the phenyl Grignard reagent does the product of conjugate attack occur to an appreciable extent.

TABLE II



$$\underset{\mathbf{4}}{\mathrm{PhSCH{=}\overset{R}{C}CH_2Cl}}^{\underline{a}} + \mathrm{MZ} \longrightarrow \underset{A}{\mathrm{PhSCH{=}\overset{R}{C}CH_2Z}} + \underset{B}{\mathrm{PhS\overset{Z}{C}H\overset{R}{C}{=}CH_2}}$$

| R | MZ | Conditions | Yield [b] % | %A | %B |
|---|---|---|---|---|---|
| H | PhMgBr | Ether, reflux 45 min | 94 | 51 | 49 |
| H | PhCu[c] | Ether,25°,1 5 hr | 88 | 90 | 10 |
| H |  | THF,25°,2hr. | 95 | 100 | 0 |
| Me | PhMgBr | Ether,reflux, 45 min | 84 | 57 | 43 |
| Me | PhCu[c] | Ether,25°,1 5 hr | 86 | 91 | 9 |
| Me | $(PhS)_2CHLi$ | THF,0°,2 hr | 50 | 100 | 0 |

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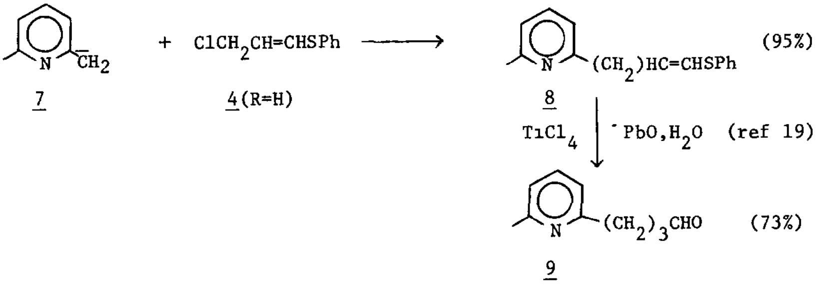
[a] 95-97% E. [b] Isolated material. [c] G. Costa, A. Camus, L. Gatti, and N Marsich J Organometal Chem , 5, 568 (1966).

A notable example is the preparation of the aldehyde 9, a key intermediate in Danishefsky's steroid synthesis,[13] by reaction of the anion 7 of 2,6-lutidine with 4(R=H) (25°, 2 hr) and hydrolysis of the vinyl sulfide 8 This conversion was previous accomplished[13] under far more vigorous conditions (reflux for 12 hr) by use of the alternative acrolein synthon 3-chloropropanal diethylacetal, which is available by a rather inefficient procedure [14]



In a subsequent publication,[15] we shall demonstrate the utility of 4(R=H or Me) as precursors of 1,3-dithiophenoxyalkenes, the anions of which are synthetic equivalents of the β-anions of acrolein and methacrolein [16]

As is pointed out in the accompanying article,[17] the hydrolysis of enol phenylthioethers of aldehydes under the usual conditions, mercuric chloride in wet acetonitrile,[18] is unsuccessful in the absence of certain neighboring groups and the titanium tetrachloride method[19] is also unsuccessful in many such cases (the conversion of 8 to 9 is an exception) However as indicated in that communication, rather efficient two step methods are available for the hydrolysis of 5(R=H, Z=Ph or *n*-But) to the corresponding aldehydes

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## References and Notes

1. Andrew Mellon Predoctoral Fellow.
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3. This difficulty with NCS was observed in both its attempted reaction with 3-thiophenoxycyclohexene and with 3-thiophenoxy-1-butene (as a mixture[4] with about 14% of phenyl crotyl sulfide)
4. E G Kataev, G A. Chmutova, and É G Yarkova, *Zhur Org Khim* **3**, 2188 (1967), *J Org Chem USSR*, **3**, 2139 (1967)

5. H Kwart and N Johnson, *J Am Chem Soc* , **92**, 6064 (1970) We have also noted allylic rearrangements of these thioethers, *on occasion*, the rates have been quite noticeable even at 5°

6. For example, phenyl crotyl sulfide (**2**, R=H, R'=Me) gives a 36% yield of **3** (R=H,R'=Me) after 24 hr at 5° whereas, under the same conditions, the yield is quantitative with Chloreal

7 NCS is, however, more stereoselective. See Table I

8. The only other report which we have been able to find of the chlorination of allylic thioethers involves the reaction of NCS with some primary allylic thioethers T B. Stephens, Ph D Thesis, Vanderbilt University, 1968

9 For example, see I Kuwajima, K. Sugimoto, and T Murofushi, *Chem Lett* , 625 (1974).

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11 H. Kwart and E R. Evans, *J Org Chem*., **31**, 413 (1966)

12 2-Thiophenoxy-4-chloro-2-butene has been explored as an equivalent of methyl vinyl ketone S Stournas, Ph D Thesis, Columbia University, 1971

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14 E J Witzemann, W. L. Evans, H Hass, and E. F Schroeder, "Organic Synthesis", Collect Vol. II, Wiley, New York, N Y., 1943, p. 137

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19. T Mukaiyama, K Kamio, S. Kobayashi and H Takei, *Bull Chem Soc Japan*, **45**, 3723 (1972)