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# CONVERSION OF α ACETYLENIC ALCOHOLS INTO αβ UNSATURATED ALDEHYDES

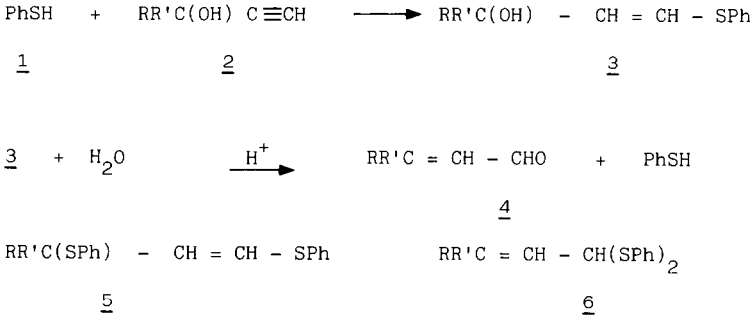
Marc Julia and Christian Lefebvre

Ecole Normale Supérieure, Laboratoire de Chimie

24, rue Lhomond, 75231 Paris Cédex 05. France.

Summary : *Very mild conditions have been found for the efficient regioselective addition of phenylthiol to ethynyl carbinols. A biphasic aqueous acid hydrolysis then leads to α,β-unsaturated aldehydes. The Meyer-Schuster rearrangement is thus brought about in two steps.*

In the course of other work it has been found that phenylthiol 1 adds to the triple bond of ethynyl carbinols 2 under very mild conditions, leading to high yields of phenyl thiovinyl carbinols 3. These in turn are easily hydrolysed to the valuable αβ-unsaturated aldehydes 4.




Good to excellent yields of 3 (R=R'=Me) were obtained at room temperature with an excess (5-10 to 1) of the acetylenic carbinol (Table 1). The unreacted alcohol is easily separated from the 1-1 adduct by distillation. On a larger scale phenylthiol was conveniently added in three portions which allowed the use of only a 4 fold excess. Several carbinols 2 underwent this addition efficiently (Table II). About 3% of the initial phenylthiol was converted into $(PhS)_2$.

Table I : Addition of PhSH to 2, R=R'=Me :

| equivalents of PhSH added | Temp. °C | Time (hrs) | conversion of 2 (%) | yields (%) adjusted for recovered 2 | | |
|---|---|---|---|---|---|---|
| | | | | 3 | 5 | 6 |
| 1 | 20 | 16 | 32 | 69 | 12 | 9 |
| 1 | 40 | 4 | 62 | 24 | 35 | 29 |
| 0.2 | 20 | 5 | 20 | 80 | 5 | 5 |
| 0.1 | 20 | 1 | 10 | 94 | -- | -- |

Table II : Addition of phenylthiol to various acetylenic carbinols 2

| R | R' | 2 mmoles | 1 mmoles | Temp. 0°C | Time hrs | Conversion of 2 (%) | Yield (%) of 3 adjusted for recovered 2 | E/Z |
|---|---|---|---|---|---|---|---|---|
| Me | Me | 1200 | 120+100+80[a)] | 20 | 2+4+10 | 26 | 91 | 94/6 |
| Me | Et | 500 | 50+40+35 | " | " | 25.8 | 90 | 93/7 |
| $-(CH_2)_5-$ | | 600 | 60+50+40 | 30 | " | 28 | 83 | 93/7 |
| $n-C_5H_{11}$ | H | 500 | 50 | 20 | 18 | 12 | 75 | 65/35 |
| Me | H | 1000 | 100 | " | " | 9.5 | 68.5 | 72/28 |
| H | H | 400 | 40 | " | " | 8.7 | 74 | 66/34 |

a) Addition in three portions.

The stereochemistry of the adducts 3 was found to be mainly E. However at the beginning of the reaction we observed by NMR a substantial proportion of the Z-isomer. In fact we have checked that phenylthiol catalyses the isomerisation Z⟶E. The isomerization (Z⟶E) by thiols of their antimarkovnikov adducts to simple acetylenic compounds has already been observed (1,2) but the main product was the Z-isomer.

The use of a more hindered thiol, 2,4,6-trimethyl phenylthiol, under the same conditions (20°C and a proportion 2/thiol=10/1), led to slower isomerisation : we could measure the Z/E initial ratio as 85/15 and the final one as 30/70 with a 80% Total Yield in 3.

It is to be noted that the secondary carbinols 2 gave larger proportion of the Z isomer than the tertiary ones.

The addition of thiols to acetylenic compounds has been carried out with added base (3) or free radicals initiators (4). For α-acetylenic carbinols the former mode can be made efficient and regioselective with t-BuSH (5).

In the present work the addition didn't need any base or radical initiator and was retarded by hydroquinone which points to a free radical mechanism, perhaps of the "molecule induced homolysis" type (6).

The hydrolysis of phenylthiovinylalcohol 3 (R=R'=Me) carried out with aqueous mineral acid under litterature conditions (7,8,9,10,11) gave prenal 4 (R=R'=Me), accompanied by non negligible amounts of 5 + 6.

Addition of pentane to remove phenylthiol as soon as it was formed proved beneficial. Under these conditions only a few per cent of 5 + 6 are formed and phenylthiol was partially recovered. The same conditions could be used with other phenylthiovinylalcohols 3 (Table III).

We have had to use dilute solution in the hydrolysis of 3 (R=R'=Me) because of the nucleophilicity of phenylthiol. With the more hindered 2,4,6-trimethylphenylthiol the hydrolysis of its addition product 3 with 2 (R=R'=Me) could be carried out in the same biphasic system in more concentrated solutions (10 to 20 times) with an isolated yield of 65% in 4 and 60% in recovered thiol.

Another way to carry out the hydrolysis was to heat a solution of 3 (R=R'=Me) in aqueous acid made homogenous by addition of sulfolane and to steam-distil the aldehyde 4 and phenylthiol.

It thus appeared possible to carry out in two steps under very mild conditions the Meyer Schuster isomerisation of carbinols 2 into aldehydes 4. Even cyclohexylidene-acetaldehyde could be obtained free of the endocyclic isomer that is formed by the classical Meyer-Schuster isomerisation techniques (13 to 16).

Table III : Hydrolysis of carbinols 3 (25 mmoles) to aldehydes 4 at r.t.

| R | R' | aq. $H_2SO_4$ Volume (l) Molarity(M/l) | Pentane vol. (l) | Time (h) | Yields [a] 4 | 1 |
|---|---|---|---|---|---|---|
| Me | Me | 0.5 0.0125 | 0.5 | 40 | 78(70) | 71(46) |
| Me | Et | 0.5 0.0125 | 0.5 | 40 | 75(67) | 71(46) |
| $-(CH_2)_5-$ | | 0.5 0.050 | 0.5 | 65 | 65(55) | 30(20) |
| $n-C_5H_{11}$ [c] | H | 0.14 [b] 0.10 | 0.2 | 72 | 60(45) | 30(20) |
| Me | Me 10mmole | 0.16 0.125 [d] | 0 | 1,60 1mmHg | 60 | 45 |

a) Determined by NMR (isolated)
b) 0.06 l of sulfolane added
c) 10 mmoles
d) 0.04l of sulfolane added ; the aldehyde was steam-distilled as soon as it was formed

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