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O-CYCLISATION OF ALLENIC β-KETOESTERS

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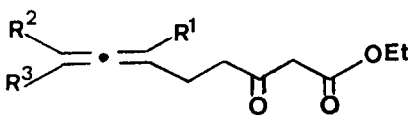
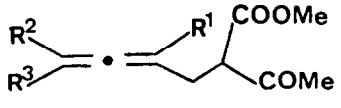
Summary : Allenic β-ketoesters 1 and 2, readily prepared from allenic alcohols, lead respectively to the compounds 6 and 7 under the action of catalytic amounts of yellow mercury (II) oxide and p-toluenesulfonic acid.

In our continuing study on the reactivity of allenic compounds, we are, in particular, dealing with nucleophilic attacks on the allenic linkage.

Cyclisations of various functionnalized allenes have previously been reported, both by our group (1) and by others (2). To our knowledge, nothing yet is known on the behaviour of allenic β-ketoesters. The cyclisation of their ethylenic (3) and acetylenic (4) conterparts is well documented and leads to either heterocyclic or carbocyclic compounds. Therefore, we decided to undertake the study of β-ketoesters 1 and 2 :

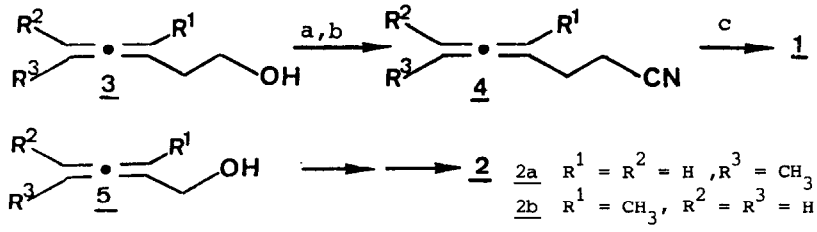


1



2

Linear compounds 1 are obtained in three steps from the corresponding β- allenic alcohols, using the recent improvement of the Blaise reaction (5) on nitriles 4.(Yields of purified products,calculated from alcohols 3 , are : 1a : 54 % ; 1b : 58 % ; 1c : 55 %). Compounds 2 can be prepared from α-allenic alcohols 5 via a palladium catalysed substitution of the corresponding phosphates by the sodium salt of methyl-acetylacetate (6) (Scheme 1).



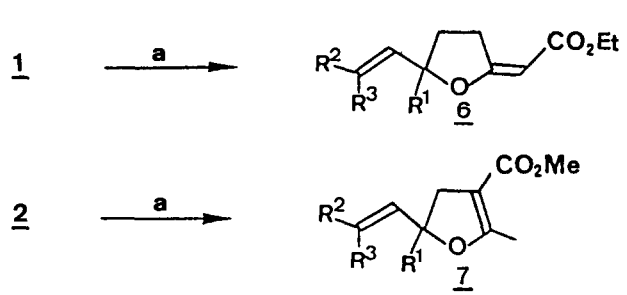
1a $R^1 = H, R^2 = R^3 = CH_3$
1b $R^1 = R^3 = H, R^2 = CH_3$
1c $R^1 = C_2H_5, R^2 = R^3 = H$

2a $R^1 = R^2 = H, R^3 = CH_3$
2b $R^1 = CH_3, R^2 = R^3 = H$

a) MsCl, Et_3N (Et_2O/-5°C) b) NaCN (EtOH/H_2O-80/20-),reflux
c) Zn,Br-CH_2-COOEt,THF reflux.

SCHEME 1

Treatment of the ketoesters 1 and 2 with catalytic amounts of yellow mercury (II) oxide and p-toluenesulfonic acid in refluxing cyclohexane, affords respectively the heterocyclic compounds 6 and 7 (7) (Scheme 2).



6a* 56%**
6b 68% (Z/E = 20/80)
6c*** 31%

7a 72% (Z/E = 25/75)
7b 74%

a) HgO/PTSA 5 % molar. Reaction times(hrs) 7a :8 ; 7b :2.25 ; 7c :0.7 ; 8a :1.25 ; 8b : 1.5
* oxalic acid is used instead of PTSA to prevent isomerisation of 1a into diene ; ** Yields of purified (neutral alumina) products ; *** Contamined by a small amount of the 6-membered heterocycle resulting from the attack of the enol on the central allenic carbon.

SCHEME 2

The heterocycles obtained can be useful synthetic tools as they have already been rearranged into various functionnalized carbocycles. Thus compounds 6 can lead thermally to 7-membered ring (8) or 5-membered ring via π-allylic species (9) and analogs of compounds 7 have been photochemically isomerised into cyclopropanic products (10).

Further investigations on the scope of our cyclisation and on the reactivity of compounds 6 and 7 are presently underway.

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(7) In the absence of acidic catalysis, no reaction occurs. The role of the acid may be as well to increase the enol-ratio in the starting malerial (4) as to break the carbon-mercury bond in the intermediate, since we noticed that the cyclisations of Y-allenic alcohols using catalytic amounts of mercury oxide require acidic catalysis. ^{1}H NMR, Infra-Red, Mass spectrometry spectra of all new compounds are in accordance with proposed structures. The ratio of Z/E isomers of 6b and 7a have been determined by 350 MHz ^{1}H NMR.
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