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SHORT COMMUNICATION

SYNTHESIS OF 1,1,1-TRIFLUORO-2-PENTEN-4-ONE

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SUMMARY

The 1,1,1-trifluoro-2-penten-4-one has been prepared from trifluoroacetaldehyde by two different ways. Its condensation with a cyclohexanone enamine leads, by annelation, to 4-trifluoromethyl- Δ -1,9 (and Δ -9,10)-octalin-2-one.

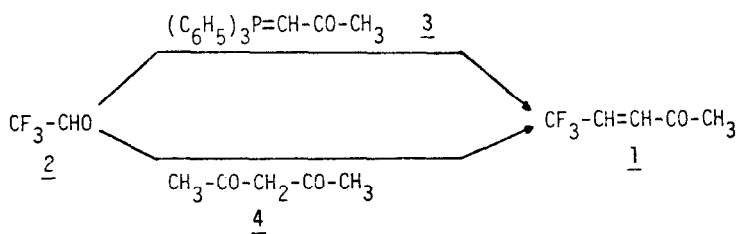
INTRODUCTION

The interest in fluorinated aliphatic α,β -ethylenic ketones has grown up recently. Several syntheses of monofluoromethyl vinyl ketones and their higher homologues have been described [1]. Polyfluorinated analogues are less studied; pentafluoroethyl- and 2,2,2-trifluoroethyl vinyl ketone have been prepared [2,3]. We report here the synthesis, by two different ways, of 1,1,1-trifluoro-2-penten-4-one 1 and its condensation with an enamine leading, by annelation, to a trifluoromethylcyclohexenone.

RESULTS

The two syntheses use trifluoroacetaldehyde 2 as starting material. Like trifluoromethylketones [4], this fluorinated aldehyde readily reacts with resonance stabilized alkylidene phosphorane 3. This Wittig reaction, performed in diethylether at 50° for 3 hours, produces 1 with 54 % yield (scheme 1). The other preparation of 1 is an extension to fluoral 2 of the recent reaction [5] between aldehydes and 2,4-pentanedione 4. This condensation, performed in dry diethylether at room temperature in the presence of anhydrous potassium carbonate gives 1 with 33 % yield (calculated from 4, scheme 1).

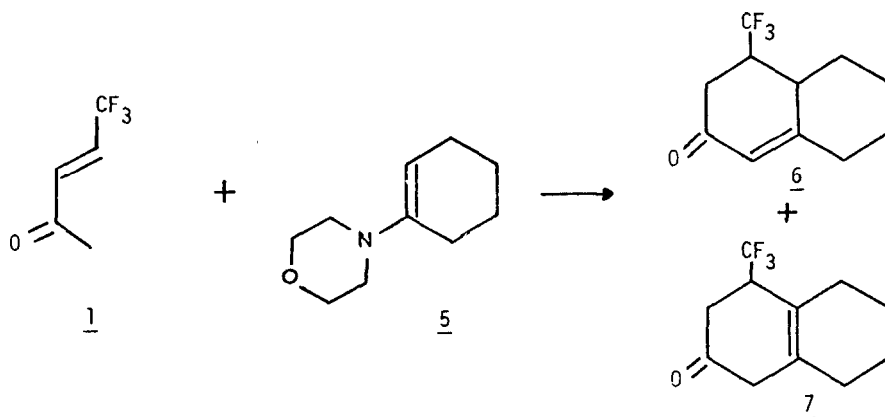
The second method gives a lower yield but is performed with commercially available products.



Scheme 1

The trifluorinated α,β -ethylenic ketone 1 can behave like a Michael acceptor in reaction with nucleophilic species. As an example, we describe the annelation with reagent 1 of the enamine 5, derived from cyclohexanone. The reaction is performed in pentane at room temperature ; hydrolysis with hot 5N hydrochloric acid leads to a mixture of two isomers : 4-trifluoromethyl- Δ -1,9-octalin-2-one and 4-trifluoromethyl- Δ -9,10-octalin-2-one (compounds 6 and 7, scheme 2) with a combined yield of 57 %.

This sequence constitutes a method to build up a ring bearing a trifluoromethyl group.



Scheme 2

EXPERIMENTAL

^1H and ^{19}F NMR spectra were recorded on a Jeol C 60 HL instrument. The chemical shift values δ have been expressed in ppm relative to Me_4Si (for ^1H NMR spectra) or CFCl_3 (for ^{19}F NMR spectra) as internal standard. IR spectra were recorded with a Perkin-Elmer 167 spectrometer. Mass spectra were obtained on a AEI MS 30 instrument at 70 eV. Preparative glc were performed with a Varian Aerograph model 920 chromatograph.

1,1,1-trifluoro-2-penten-4-one 1 (11c)(a) Wittig condensation

4 g (0.04 mole) of trifluoroacetaldehyde [6] and 13 g (0.04 mole) of acetylmethylenetriphenylphosphorane [7] in 60 ml of diethylether are placed in a 125 ml steel autoclave. The autoclave is shaken and heated at 50° for 3 hours, then cooled. The solid is filtered off and washed with diethylether. The solvent is removed from the filtrate by distillation with a spinning band apparatus. The 1,1,1-trifluoro-2-penten-4-one is separated from the residual mixture by a bulb to bulb distillation under 15 Torr. Distillation at $102\text{--}104^\circ$ under ca. 760 Torr gives 3 g of 1,1,1-trifluoro-2-penten-4 one 1 (54 % yield, calculated from 2). The reagent 1 is stable in the presence of small amounts of hydroquinone at -30° during several months.

^1H NMR (CDCl_3), $\delta = 2.35$ (3H, singlet, CH_3) and 6.65 ppm (2H, multiplet, $\text{CH}=\text{CH}$).

^{19}F NMR (CDCl_3) $\delta = 65$ ppm (doublet, $^3J_{\text{FH}} = 4$ Hz).

IR (CHCl_3) : 1710 and 1695 cm^{-1} ($\text{C}=\text{O}$) ; 1665 and 1655 cm^{-1} ($\text{C}=\text{C}$).

Mass spectrum : $m/e = 138$ (M), 123 (M- CH_3), 95 (M-CO CH_3), 69 (M- CF_3).

Analysis : found : C, 43.75 ; H, 3.47 ; F, 41.13 % ; $\text{C}_5\text{H}_5\text{F}_3\text{O}$ requires : C, 43.49 ; H, 3.65 ; F, 41.27 %.

(b) Condensation with 2,4-pentanedione

10 g (0.1 mole) of 2,4-pentanedione, 20 g (0.15 mole) of anhydrous potassium carbonate and 12 g (0.12 mole) of trifluoroacetaldehyde [6] in 80 ml of dry diethylether are placed in a 250 ml steel autoclave. After

shaking for 45 hours at room temperature, the reaction mixture is filtered and the solid washed with diethylether. The solvent is removed with a spinning band apparatus. Distillation of the residue gives 4.5 g of 1,1,1-trifluoro-2-penten-4-one 1 (33 % yield, calculated from 4).

4-trifluoromethyl- Δ -1,9 (and Δ -9,10)-octalin-2-one 6 and 7

3.4 g (0.02 mole) of 1-morpholinocyclohexene and 2.8 g (0.02 mole) of 1,1,1-trifluoro-2-penten-4-one in 15 ml of dry pentane are stirred for one day at room temperature. Then, the solvent is evaporated under vacuum and the residual liquid is refluxed with 5N hydrochloric acid for 6 hours. After cooling and extraction with diethylether, the organic layer is dried over magnesium sulfate. After removal of the solvent under vacuum, distillation gives 2.5 g of a mixture of 4-trifluoromethyl- Δ -1,9-octalin-2-one 6 and 4-trifluoromethyl- Δ -9,10-octalin-2-one 7 (57 % yield).

B.p. : 82-83° /0.2 Torr

Mass spectrum : m/e = 218 (M)

Analysis : found for the 2,4-dinitrophenylhydrazone (m.p. : 174°) : C, 51.23 ; H, 4.43 % ; $C_{17}H_{17}F_3N_4O_4$ requires : C, 51.26 ; H, 4.30 %.

The components are separated by preparative glc on a silicone SE 30 column in the ratio of 7 (1 part) to 6 (4 parts).

4-trifluoromethyl- Δ -9,10-octalin-2-one 7 (nc)

1H NMR ($CDCl_3$), δ = 1.6-2.9 ppm (multiplet).

^{19}F NMR ($CDCl_3$), δ = 68 ppm (doublet, $^3J_{FH}$ = 8.5 Hz).

IR ($CHCl_3$) : 1715 cm^{-1} (C=O) ; 1670 cm^{-1} (C=C).

4-trifluoromethyl- Δ -1,9-octalin-2-one 6 (nc)

1H NMR ($CDCl_3$), δ = 1.3-2.6 (12H, multiplet) and 5.8 ppm (1H, singlet; CH=C).

^{19}F NMR ($CDCl_3$), δ = 69 ppm (doublet, $^3J_{FH}$ = 7 Hz).

IR ($CHCl_3$) : 1670 cm^{-1} (C=O) ; 1625 cm^{-1} (C=C).

UV (cyclohexane) : λ_{max} = 229 nm ; ϵ = 13865 [8].

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