Efficient Condensation of Cycloketones and Acetone Using SOCl$_2$/EtOH

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ABSTRACT. A simple and efficient method for homocoupling of cycloketones and acetone is described. 2-(1-Cyclohexenyl)-cyclohexanone (1), bicyclopentyliden-2-one (2) and 4-methyl-3-penten-2-one (3) were synthesized from cyclohexanone, cyclopentanone and acetone respectively, in the presence of thionyl chloride in anhydrous ethanol.

Keywords: Thionyl Chloride, Catalyst, Condensation

INTRODUCTION

2-(1-Cyclohexenyl)-cyclohexanone (1) (Scheme 1) is an important intermediate for the synthesis of OPP ($\alpha$-C$_6$H$_5$C$_6$H$_4$OH) which is used as antiseptic. Both 1 and bicyclopentyliden-2-one (2) (Scheme 1) are original materials for the synthesis of some unsymmetrical trisannelated benzenes (4) and (5) (Scheme 3). 4-Methyl-3-penten-2-one (3) (Scheme 2) is a common solvent for some colophony and fibrin, an important intermediate of some drugs and pesticides.

Cyclohexanone has long been known to undergo self-condensation to 1. The condensation can be catalyzed by acids, bases, or by heat alone. A few methods, for instance, using tetraalkoxy silane in the presence of fluoride ions, as catalyst have been reported for the synthesis of 1 and 2, and several methods have been described for the
condensation reaction. We optimized the reaction conditions and found that SOCl\_2/H\_2O reagent is also a good catalyst for synthesizing the dimers of these ketones.

Furthermore, we found that the alcohol serving as reaction solvent was indispensable for the catalytic system. Other solvents such as toluene and pyridine were not efficient for the reaction, only alcohols catalysed the condensation reaction. There is no significant variation of yields between anhydrous CH\_3OH and anhydrous C\_6H\_5OH. On the basis of these results, we think the reaction proceeds via the reaction of the enol sulfite ester of the ketones, and the byproduct HCl may accelerate the reaction.\[^{6,10}\]

The detailed mechanistic investigation and further applications of this reaction are under study in our laboratory.

**CONCLUSION**

In this paper, an efficient and simple method for the synthesis of the dimers of cycloketones and acetone in the presence of thionyl chloride in anhydrous ethanol has been reported. Comparing with other methods, this method is easily available with cheap catalyst, simple manipulation under mild conditions. We believe this reaction will expand the application of the thionyl chloride in organic synthesis.

**EXPERIMENTAL**

Melting points were determined on the Kofler micro-melting point apparatus without correction. Infrared spectra were recorded on a PFT-40 IR spectrophotometer in KBr. \(^{1}\)H NMR spectra were measured in CDCl\_3 using TMS as internal standard on a BRUKER 80 MHz NMR spectrometer. The mass spectra were performed on an Agilent GC-MS spectrometer.

Synthesis of 2-(\-cyclohexenyl\)cyclohexanone (1):
To a stirred mixture of cyclohexanone (15.54 mL, 0.15 mol; freshly distilled) and anhydrous ethanol (43.7 mL, 0.75 mol), thionyl chloride (7.28 mL, 0.1 mol) was added dropwise. The mixture was stirred
for 24 hours, saturated aqueous Na$_2$CO$_3$ solution was added. The mixture was extracted with ethyl ether (20 mL) three times, and the combined solution was dried over anhydrous MgSO$_4$. After evaporation of the volatiles, the residue was purified by column chromatography on silica gel using petroleum ether as eluent. Isolated yield: 60%. m.p.: 229°C (lit$^1$, 230°C); IR(KBr, cm$^{-1}$): 2920, 2850, 1445, 1420; $^1$H NMR (CDCl$_3$, ppm): 1.7 (s, 12H), 2.5 (s, 12H); Mass (m/z): 240(M, 100).

Synthesis of bicyclopentadiene-2-one (7):

The similar synthetic procedure was applied as described for 6 (taking cyclopentanone as the starting material). The residue was purified by column chromatography on silica gel using petroleum ether as eluent, isolated yield: 52%. m.p.: 97°C (lit$^2$, 97.5°C); IR(KBr, cm$^{-1}$): 2837, 1448, 1424, 1300, 1275; $^1$H NMR (CDCl$_3$, ppm): 2.7 (t, 12H, J=7.3 Hz), 1.9-2.4 (m, 6H); Mass (m/z, %): 146(M, 100).

REFERENCES

11. IR spectrum is compatible with the Sadler Reference Spectra (Vol. 19, 20, 3800K); $^1$H NMR spectrum is compatible with the Sadler Reference Spectra (Vol. 19-21, 1321M).