

SOCl₂/EtOH을 이용한 사이클로케톤과 아세톤의 효율적인 응축반응

Zhiguo Hu*, Zhibing Dong, Jun Liu, Wenjie Liu, and Xinling Zhu

College of Chemistry and Environmental Science, Henan Normal University, Xuxiang, 453007, Henan, P. R. China

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Efficient Condensation of Cycloketones and Acetone Using SOCl₂/EtOH

Zhiguo Hu*, Zhibing Dong, Jun Liu, Wenjie Liu, and Xinling Zhu

College of Chemistry and Environmental Science, Henan Normal University, Xuxiang, 453007, Henan, P. R. China

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요 약. 싸이오닐 클로라이드와 무수에탄올 존재 하에서 사이클로헥세논 또는 아세톤을 호모커플링 반응을 진행시켜서 회합물 2-(1-사이클로헥센일)사이클로헥산온(1), 바이사이클로펜틸이던-2-온(2) 그리고 4-메틸-3-펜텐-2-온(3)을 효율적으로 제조하였다.

주제어: 싸이오닐 클로라이드, 응축반응

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.

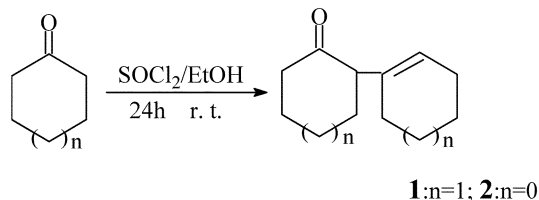
Keywords: Thionyl Chloride, Catalyst, Condensation

INTRODUCTION

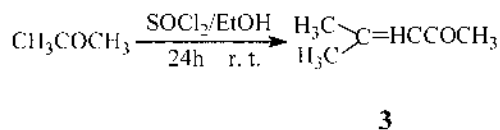
2-(1-Cyclohexenyl)-cyclohexanone (1) (Scheme 1) is an important intermediate for the synthesis of OPP (*o*-C₆H₃C₆H₄OH) which is used as antiseptic. Both 1 and bicyclopentyliden-2-one (2) (Scheme 1) are original materials for the synthesis of some unsymmetrical trisannulated benzenes (4) and (5)¹ (Scheme 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 1.² The condensation can be catalyzed by acids, bases, or by heat alone. A few methods, for instance, using tetraalkoxysilane in the

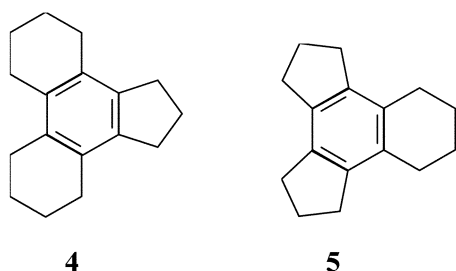
presence of fluoride ions,³ RuCl₃,⁴ CuCl₂^{1,5} as catalyst have been reported for the synthesis of 1 and 2, and several methods have been described for the



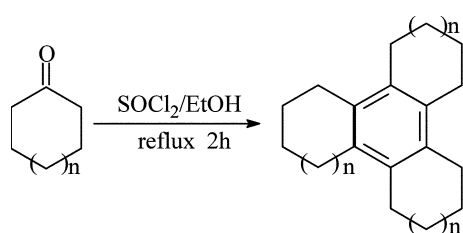
Scheme 1.



Scheme 2.



Scheme 3.



6: n=1; 7: n=0

Scheme 4.

preparation of 3.^{1,6} The literature synthetic methods involve some disadvantageous reaction conditions such as too high or too low temperature, high pressure and long reaction time.

RESULT AND DISCUSSION

On the basis of our previous reports the synthesis of 1, 3, 5-triarylbenzene,⁷ asymmetrical 1, 3, 5-triarylbenzene,⁸ chalcones⁹ and α , α' -bis(substituted benzylidene) ketones¹⁰ catalyzed by SOCl₂/EtOH, we expanded this method to the synthesis of symmetric trisannulated benzenes and 1, 3, 5-trimethyl benzene. During the study of synthesizing the symmetrical trisannulated benzenes 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12-dodecahydro-triphenylene (6) and 2, 3, 4, 5, 6, 7, 8, 9-octahydro-1H-trindene (7) (Scheme 4), we noticed that oil with high boiling point could be obtained as the main product (see the synthesis of compounds 1 and 2) if the amount of SOCl₂ was reduced and the reaction time was prolonged. The oil was isolated by distillation and characterized by GC-mass and ¹H NMR, and the analytical data showed that it was the intermediate of the triple

condensation reaction. We optimized the reaction conditions and found that SOCl₂/EtOH 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 catalyst system. Other solvents such as toluene and pyridine were not efficient for the reaction, only alcohols catalyzed the condensation reaction. There is no significant variation of yields between anhydrous CH₃OH and anhydrous C₂H₅OH. 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.^{7,9,10} 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 PTS-40 IR spectrophotometer in KBr. ¹H NMR spectra were measured in CDCl₃ 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-(1-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_2CO_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 on a rotaevaporator, the residue was distilled at reduced pressure (140-142°C/13 mmHg), total yield: 60%. b.p.: 140-142°C/13tor. (lit.³: 142°C /13tor.); IR (KBr, cm^{-1}): 2930, 2870, 1717, 1450, 920, 830; ^1H NMR (CDCl_3 , ppm): 1.9-2.4(m, 16H), 2.9(m, 1H), 5.5(m, 1H); Mass(m/z, %): 178(M⁺, 60), 149(100).

Synthesis of bicyclopentyliden-2-one (2):

To a stirred mixture of cyclopentanone (13.27 mL, 0.15 mol; freshly distilled) and anhydrous ethanol (43.7 mL, 0.75 mol), thionyl chloride (1.82 mL, 0.025 mol) was added dropwise. In a similar experiment as described for 1, the residue was distilled at reduced pressure (120-122°C/12mmHg), total yield: 55%. b.p.: 120-122°C/12tor. (lit.⁴: 120-124°C /12tor.); IR (KBr, cm^{-1}): 2950, 2850, 1700, 1445, 1120; ^1H NMR (CDCl_3 , ppm): 1.9-2.3(m, 12H), 2.8(m, 1H), 5.5(m, 1H); Mass (m/z, %): 150 (M⁺, 55), 121(100).

Synthesis of 4-methyl-3-penten-2-one (3):

To a stirred mixture of acetone (11 mL, 0.15 mol) and anhydrous ethanol (35 mL, 0.6 mol), thionyl chloride (3.64 mL, 0.05 mol) was added dropwise. In a similar experiment as described for 1, the residue was purified by column chromatography on silica gel using cyclohexane / EtOAc (10/1, v/v) as eluent, isolated yield: 40%. lit.¹¹ IR (KBr, cm^{-1}): 2990, 2910, 1690, 1620, 1440, 1350, 1210, 1160, 960, 620; ^1H NMR(CDCl_3 , ppm): 1.9(s, 3H), 2.2(s, 6H), 6.1 (s, 1H); Mass: (m/z, %): 98 (M⁺, 53), 83(100).

Synthesis of 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12-dodecahydro-triphenylene (DTP)(6):

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 (14.56 mL, 0.2 mol) was added dropwise, the mixture was refluxed for 2 hours. Then saturated aqueous Na_2CO_3 solution was added and the mixture was

extracted with ethyl ether (20 mL) twice, and finally 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.¹², 230°C); IR(KBr, cm^{-1}): 2920, 2850, 1445, 1420; ^1H NMR (CDCl_3 , ppm): 1.7 (s, 12H), 2.5(s, 12H); Mass (m/z, %): 240(M⁺, 100).

Synthesis of 2, 3, 4, 5, 6, 7, 8, 9-octahydro-1H-trindene (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.: 95°C (lit.¹³, 97.5 °C); IR(KBr, cm^{-1}): 2837, 1448, 1424, 1300, 1275; ^1H NMR (CDCl_3 , ppm): 2.7(t, 12H, J=7.3Hz), 1.9-2.4(m, 6H); Mass (m/z, %): 198(M⁺, 100).

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