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Synthesis of unsymmetric trisannelated benzenes using a $SOCl_2$/EtOH reagent

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A simple and efficient method for the synthesis of unsymmetric trisannelated benzenes is presented. The dimers of cycloketones react with molecules of other cycloketones to form corresponding unsymmetric trisannelated benzenes in the presence of thionyl chloride in anhydrous ethanol.

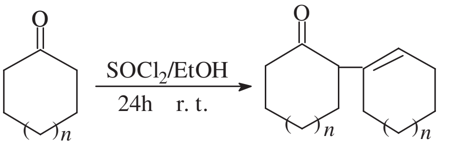
Keywords: unsymmetric trisannelated benzenes, thionyl chloride, catalyse, condensation

The study of trisannelated benzenes, such as 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12-dodecahydro-triphenylene (**1**), 2, 3, 4, 5, 6, 7, 8, 9-octahydro-1H-trindene (**2**), 2, 3, 4, 5, 6, 7, 8, 9, 10, 11-decahydro-1H-cyclopenta [*l*] phenanthrene (**3**) and 1, 2, 3, 4, 5, 6, 7, 8, 9, 10-decahydrobenz [*e*]-*as*-indacene (**4**) (structures in Scheme 2) is an active area of investigation. The di- and tri-anions of these trisannelated benzenes have been used as the ligands in the preparation of sandwich complexes with transition-metals.[1] Several approaches to the synthesis of unsymmetrical trisannelated benzenes have been described.[2-6] However, the literature methods involved multiple steps, unstable starting materials or reactions at high temperature.[4-11]

The preparation of 1, 3, 5-triarylbenzene,[12] asymmetric 1, 3, 5-triarylbenzene,[13] chalcones[14] and α, α'-bis(substituted benzylidene) ketones[15] can be catalysed by $SOCl_2$/EtOH. We have extended this approach to the synthesis of symmetric trisannelated benzenes. In the study of the synthesis of the symmetrical trisannelated benzenes **1** and **2**, we noticed that an oil with a high boiling point could be obtained as the main product if the amount of $SOCl_2$ was reduced and the reaction time was prolonged (see the synthesis of compound **5** and **6**). The oil was distilled and characterised by GC-mass, ^{1}H NMR, and the result showed that it was the intermediate of the triple condensation reaction (Scheme 1). Then the dimer reacted with another molecule of ketone to give the trimer. It follows that if the dimers reacted with another cycloketone, the unsymmetric trisannelated benzene could be obtained (Scheme 2). As we expected, the target products were found.

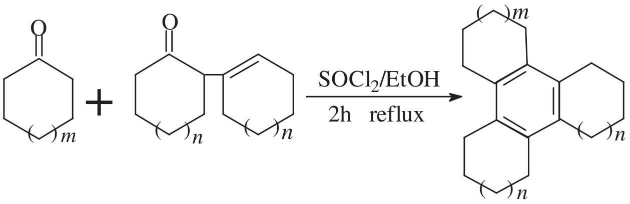
In the synthesis of the unsymmetric trisannelated benzenes, the di- or tri-condensations of ketones were side reactions. In order to prevent the side reactions, the dimers were used in an excess, while the thionyl chloride and betone were added dropwise and synchronously. Futhermore, we found that the amount of thionyl chloride was also an important factor to influence the yield of the products. Too much or too little of the thionyl chloride resulted in a poor yield of the products (for example, when the ratio of $SOCl_2$ to cyclopentanone was 1 to 1, the yield of **3** was 40% but when the ratio of $SOCl_2$ to cyclopentanone was 3 to 1, the yield was 45%). The optimal ratio of $SOCl_2$ to cyclopentanone was 2 to 1.

We also found that the alcohol was indispensable in the catalyst system as well as serving as reaction solvent. Other solvents such as toluene and pyridine were also used, but only alcohols catalysed the condensation reaction. There is no significant variation of yields between anhydrous CH_3OH and anhydrous C_2H_5OH. On the basis of these results, we think the reaction proceeds via the reaction of the enol sulfite ester of the ketones. The byproduct HCl may accelerate the reaction.[12,14,15] The detailed mechanism and further applications of this reaction are under study in our laboratory.



5:*n*=1; **6**:*n*=0

Scheme 1



1: *m*=1, *n*=1;
2: *m*=0, *n*=0;
3: *m*=0, *n*=1;
4: *m*=1, *n*=0

Scheme 2

Experimental

IR spectra were recorded on a PTS-40 IR spectrophotometer in KBr. ^{1}H NMR spectra were measured in $CDCl_3$ using TMS as internal standard on a BRUKER 80 MHz spectrometer. The mass spectra were performed on an Agilent GC-MS spectrometer.

Synthesis of *1,2,3,4,5,6,7,8,9,10,11,12-dodecahydro-triphenylene (DTP)* (**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 (0.2 mol, 14.56 ml) was added dropwise and the mixture was then refluxed for 2 h. Saturated aqueous Na_2CO_3 was added and the mixture was extracted twice with ethyl ether (20 ml), and the extract 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.

Synthesis of *2,3,4,5,6,7,8,9-octahydro-1H-trindene* (**2**): In a similar experiment as described for **1** (taking cyclopentanone as the starting material), the residue was purified by column chromatography on silica gel using petroleum ether as eluent.

Synthesis of 2, 3, 4, 5, 6, 7, 8, 9, 10, 11-decahydro-1H-cyclopenta [l] phenanthrene (**3**): a typical experimental procedure for the synthesis of unsymmetric trisannelated benzenes: To a stirred mixture of 2-(1-cyclohexenyl)-cyclohexanone (**5**) (9.79 g, 0.055 mol) and anhydrous ethanol (14.7 ml, 0.25 mol), thionyl chloride (7.2 ml, 0.1 mol) and cyclopentanone (4.23 ml, 0.05 mol) were dropped synchronously. The mixture was refluxed for 2 h. Then saturated aqueous Na_2CO_3 was added and the mixture was extracted three times with ethyl ether (20 ml) and the extract 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.

Synthesis of *2-(1-cyclohexenyl)-cyclohexanone* (**5**): 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 (0.1 mol, 7.28 ml) was added dropwise. The mixture was stirred for 24 h. After the reaction was finished, saturated aqueous Na_2CO_3 was added. The

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mixture was extracted three times with ethyl ether (20 ml) and the extract was finally dried over anhydrous MgSO$_4$. After evaporation of the volatiles, the residue was distilled in vacuum.

Synthesis of *bicyclopentyliden-2-one* (**6**): 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 (0.025 mol, 1.82 ml) was added dropwise. In a similar experiment as described for **5**, the residue was distilled in vacuum.

Spectroscopic data of the products

1: Isolated yield: 60%, m.p. 229°C (lit.[16] 230°C); IR(KBr, cm^{-1}): 2920, 2850, 1445, 1420; ^{1}H NMR (CDCl$_3$, ppm): 1.73 (s, 12H), 2.53(s, 12H); Mass (*m/z*, %): 240(M^{+},100).

2: Isolated yield: 52%, m.p. 95°C (lit.[17] 97.5 °C); IR(KBr, cm^{-1}): 2837, 1448, 1424, 1300, 1275; ^{1}H NMR (CDCl$_3$, ppm): 2.71(t,12H, *J*=7.3Hz), 1.82–2.32(m, 6H); Mass (*m/z*, %): 198(M^{+},100).

3: (lit.[5]): Isolated yield: 60%, IR (KBr, cm^{-1}): 2920, 2830, 1920, 1985, 1430; ^{1}H NMR(CDCl$_3$, ppm): 1.33–3.42(m, 22H); Mass (*m/z*, %): 226(M^{+}, 100);

4 (lit.[5]): Isolated yield: 55%, IR (KBr, cm^{-1}): 2920, 2830, 1920, 1985, 1430; ^{1}H NMR(CDCl$_3$, ppm): 1.81–2.22(m, 12H), 2.62–2.93 (m, 8H); Mass (*m/z*, %): 212(M^{+}, 100);

5: Total yield: 60%, b.p. 140–142°C/13tor. (lit.[18]: 142°C /13tor.); IR (KBr, cm^{-1}): 2930, 2870, 1717, 1450, 920, 830; ^{1}H NMR (CDCl$_3$, ppm): 1.91–2.42(m, 16H), 2.99(m, 1H), 5.45(m, 1H); Mass(*m/z*, %): 178(M^{+}, 60), 149(100);

6: Total yield: 55%, b.p. 120–122°C/12tor. (lit.[19]: 120–124°C /12tor.); IR (KBr, cm^{-1}): 2950, 2850, 1700, 1445, 1120; ^{1}H NMR (CDCl$_3$, ppm): 1.91–2.33(m, 12H), 2.78(m, 1H), 5.51(m, 1H); Mass (*m/z*, %): 150 (M^{+}, 55), 121(100);

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