Synthesis of symmetric trisannelated benzenes and 1,3,5-trimethylbenzene using a $SOCl_2$/EtOH reagent

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A simple and efficient method for the synthesis of symmetric trisannelated benzenes and 1,3,5-trimethylbenzene is presented. Two trisannelated benzenes and 1,3,5-trimethylbenzene were synthesised from cyclohexanone, cyclopentanone and acetone respectively in the presence of thionyl chloride in anhydrous ethanol.

Keywords: trisannelated benzenes, thionyl chloride, catalysis, condensation

The trisannelated benzene derivatives, such as dodecahydrotriphenylene(**1**), *2,3,4,5,6,7,8,9-octahydro-1H-trindene*(**2**) and 1,3,5-triphenylbenzene have been extensively studied from the point of view of their physical and chemical properties.[1] It has been noted that the presence of **1** and **2** in nylon 66 produced fluorescence.[2] The photochemical properties of many films such as phetalate and siloxan have been modified by the addition of a few percent of **1** in their composition[3] and it is also utilised as a η^6-aryl ligand.[4] The trianion derivated from **2** is a useful di- or trinucleating ligand.[5] 1,3,5-trimethyl-benzene (**3**) is a very important raw material for the preparation of some anti-oxidation reagents, dyes, UV radiation absorbing reagents and is an intermediate for the preparation of alkyd.

Self-condensation of ketones using different reagents including Lewis acids has attracted a great deal of attention. Compounds **1** and **2** were first prepared as minor products of the acid-catalysed condensations of cyclohexanone and cyclopentanone, respectively. Several methods, for example, using anhydrous $CuCl_2$,[6b,c] zirconium halide[6a] or tetrachlorosilane[7] as the catalysts have been reported for the preparation of **1**, **2** and **3**. However, they usually involve the use of high temperature, high pressure, and long reaction times and give somewhat poor yields. We have extended the method used for the preparation of 1,3,5-triarylbenzene (**4**),[8] asymmetric 1,3,5-triarylbenzene (**5**),[9] chalcones[10] and α, α'-bis(substituted benzylidene) ketones[11] catalysed by $SOCl_2$/EtOH, to the synthesis of symmetric trisannelated benzenes (Scheme 1) and 1,3,5-trimethylbenzene (Scheme 2).

In the trimerisation of the ketones, the amount of thionyl chloride is a key factor. We found that if the amount of thionyl chloride was too high, a black sticky substance would be obtained which made the succeeding manipulation difficult. The yield of the trimers was also low. If the amount of thionyl chloride was too low, oil would be obtained (maybe dimers). The reaction time also influenced the yield of the trimers, and the optimal reaction time is 2 h.

The mechanism of trimerisation of cyclohexanone in the presence of $SOCl_2$/EtOH presumably involved the sequence as depicted in Scheme 3. Compound **7** (the enol structure of **6**) further reacted with another molecule of cyclohexanone to give the unstable ketoalcol **8**. Dehydration of **8** led to the formation of the unsaturated ketone **9**. Thermally superfacial [1, 7] sigmatropic rearrangement of **9** led to the formation of the trienol **10**. Dehydration of **11** led to the formation of **1**. All of these reactions were catalysed by $SOCl_2$/EtOH. The mechanisms for the preparations of **2** and **3** might also reasonably go through a similar sequence.

In summary, we have reported a novel and efficient method for the synthesis of symmetric trisannelated benzenes and 1,3,5-trimethylbenzene. The advantages of this method are a cheap catalyst, short reaction time, and simple manipulation.

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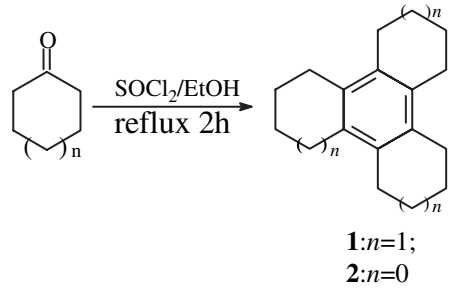
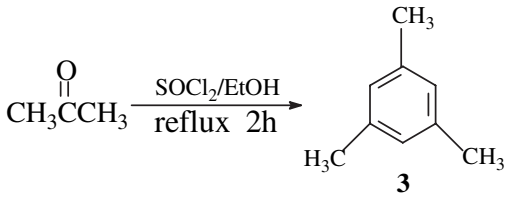


1:*n*=1;
2:*n*=0

Scheme 1



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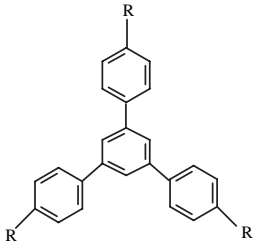
Scheme 2



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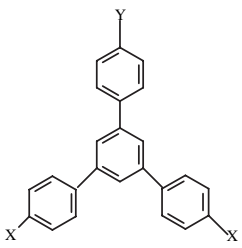

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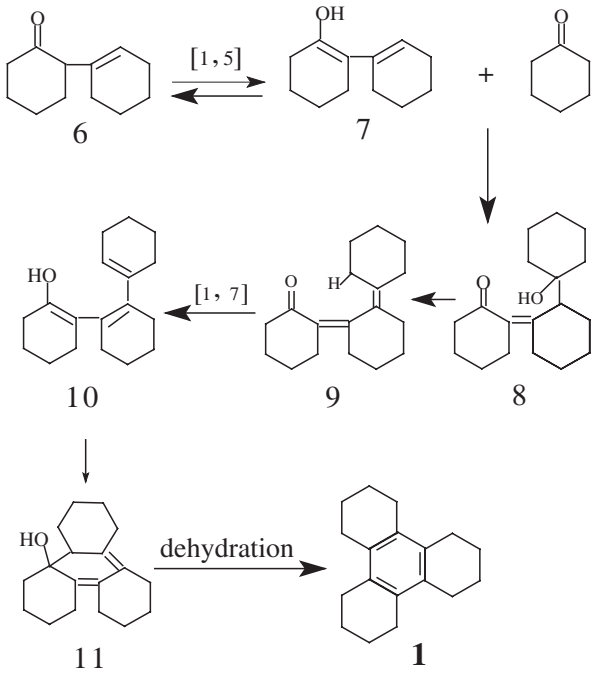
We believe this reaction expands the application of the thionyl chloride in organic synthesis.

Experimental

Melting points were determined on a Kofler micro melting point apparatus without correction. Infrared spectra were recorded on a PTS-40 IR spectrophotometer in KBr. ^{1}HNMR spectra were measured in $CDCl_3$ using TMS as internal standard on a Bruker 80 MHz spectrometer. The mass spectra were determined on 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 refluxed for 2 h. The colour of the mixture changed from yellow orange to dark purple after 15–20 min of refluxing. Saturated Na_2CO_3 was added and the mixture was extracted with diethyl ether (20 ml) twice, and dried over anhydrous $MgSO_4$. After evaporation of the volatile material, the residue was purified by column chromatography on silica gel using petroleum ether as eluent, isolated yield:



Scheme 3

45–60%. 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 (**2**): In a similar experiment (the starting material was cyclopentanone) as described for **1**, 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): 2.9–2.5(t,12H, *J*=7.3Hz), 1.8–3.2(m, 6H); Mass (*m/z*, %): 198(M^+,100).

Synthesis of 1,3,5-trimethylbenzene (**3**): To a stirred mixture of acetone (11 ml, 0.15 mol) and anhydrous ethanol (43.7 ml, 0.75 mol), thionyl chloride (0.15 mol, 10.98 ml) was added dropwise, the mixture was refluxed for 2 h. After extraction, the residue was purified by column chromatography on silica gel using petroleum ether as eluent, isolated yield: 35–45%. IR[14] (KBr, cm^{-1}): 3010, 2910, 1610, 1520, 840, 690; ^1H NMR[15] ($CDCl_3$, ppm): 2.2(s, 9H), 6.7(s, 3H); Mass (*m/z*, %): 120(M^+, 100)

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14 IR spectrum is compatible with Sadtler Reference Spectra (Vol. 1-2, 407K).
15 ^1H NMR spectrum is compatible with Sadtler Reference Spectra (Vol. 13-15, 9910M).