

AN IMPROVED SYNTHESIS OF 1,2,3,4,5-PENTAMETHYLCYCLOPENTADIENE

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Summary

An inexpensive three-step synthesis for large-scale preparation of 1,2,3,4,5-pentamethylcyclopentadiene is reported. Improvement of Burger's route involving 2,3,5,6-tetrahydro-2,3,5,6-tetramethyl- γ -pyrone and 2,3,4,5-tetramethylcyclopent-2-enone raised the overall yield to about 34% of the desired compound (originally 8%).

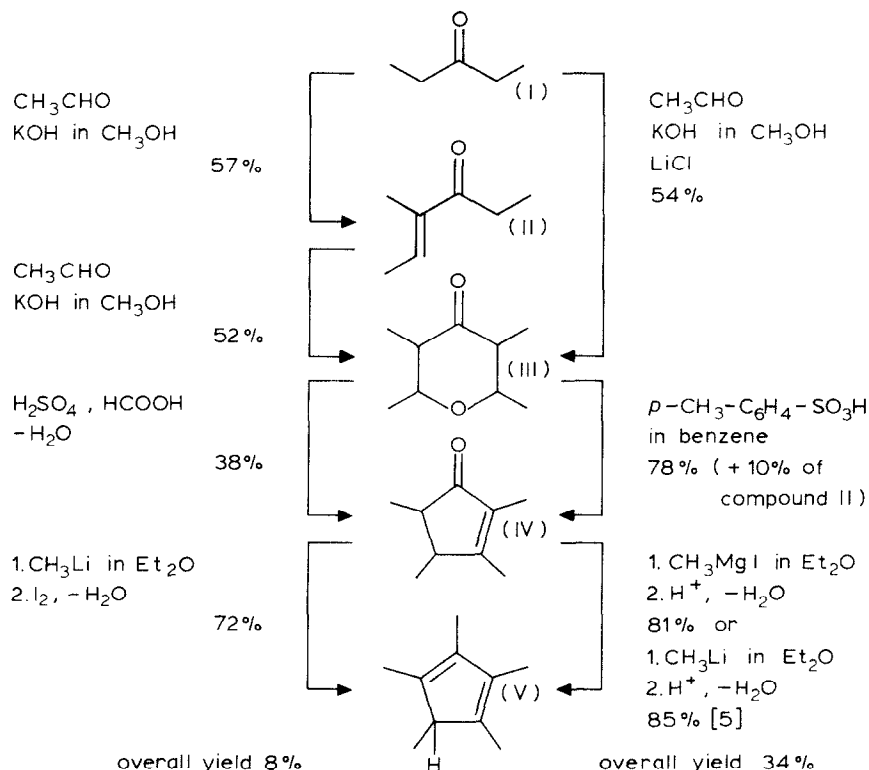
The permethylated cyclopentadienyl ligand seems to be one of the most important Cp-derivatives in main group and transition metal chemistry. Attempts to prepare the hydrocarbon $\text{Me}_5\text{C}_5\text{H}$ have led to a few convenient routes [1–4]. The least expensive materials are used in Burger's synthesis [1], involving 2,3,5,6-tetrahydro-2,3,5,6-tetramethyl- γ -pyrone and 2,3,4,5-tetramethylcyclopent-2-enone. Since the author reported that he made no attempts to improve this synthesis, we have done so.

We showed that the initial formation of the pyrone-derivative III via double Aldol-addition (Scheme 1) can also be carried out in one step. Adding a small amount of lithium chloride or lithium bromide (about 3 mol%) raises the yield to 54%; we suggest that the Li^+ -cation forms complexes with the carbonyl compounds, whose geometries favour conversion to the pyrone derivative III.

In the second step of the synthesis we found that refluxing of the pyrone derivative III in benzene in the presence of 10 mol% of *p*-toluenesulfonic acid leads to the formation of the pentenone derivative IV in good yields (78%). As a by-product, the α,β -unsaturated ketone II is obtained (10% yield), which can be used as additional starting material in the Aldol-addition-step (Scheme 1).

A convenient conversion of the pentenone IV to yield 85% of 1,2,3,4,5-pentamethylcyclopentadiene (V) has been reported [5]. We found, that reaction of IV with methylmagnesium iodide in ether and finally elimination of water with a few drops of fairly concentrated hydrochloric acid yields 81% of 1,2,3,4,5-pentamethylcyclopentadiene.

In comparison to the original work of Burger [1], this improvement of the



SCHEME 1. Synthesis of 1,2,3,4,5-pentamethylcyclopentadiene; Burger's original route [1] on the left.

synthesis raised the overall yield from 8 to about 34% (see Scheme 1), so that an efficient synthetic method is now available.

Experimental

2,3,5,6-Tetrahydro-2,3,5,6-tetramethyl- γ -pyrone (III)

To a solution of 56.1 g KOH in 375 ml methanol 258 g of diethylketone (I) (3.00 mol) are added. After addition of 8.50 g LiCl (0.20 mol) and gentle warming up to 30°C, 500 ml (392 g) of acetaldehyde (8.89 mol) are added very slowly (5–10 h) from an ice-cooled dropping-funnel. After 12 h, the deep red oily mixture is neutralized with HCl. The light red coloured organic layer is separated and washed twice with H₂O. Simple distillation under reduced pressure up to a boiling point of 100°C/16 Torr gives a crude product; redistillation through a 20 cm Vigreux-column yields 251.9 g of III (54%), b.p. 63–89°C/13 Torr.

2,3,4,5-Tetramethylcyclopent-2-enone (IV)

100.6 g *p*-Toluenesulfonic acid (0.53 mol) are added to 825.6 g of III (5.29 mol) diluted with 400 ml of benzene. While the mixture is refluxing the formed water is collected in a trap (a low boiling organic by-product is trapped before the separation of water begins). After about 20 h, the elimination of water is complete. The mixture

is neutralized with Na_2CO_3 solution and the organic layer is washed twice with water. Distillation under reduced pressure through a 20 cm Vigreux-column yields 570.4 g of IV (78%), b.p. $79\text{--}83^\circ\text{C}/13$ Torr and additional 60.0 g of the α,β -unsaturated ketone II (10%), b.p. $53\text{--}65^\circ\text{C} / 13$ Torr.

References

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