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On the Regioselectivity of Lewis Acid Catalyzed Diels–Alder Reactions of Methylcyclopentadiene[1]

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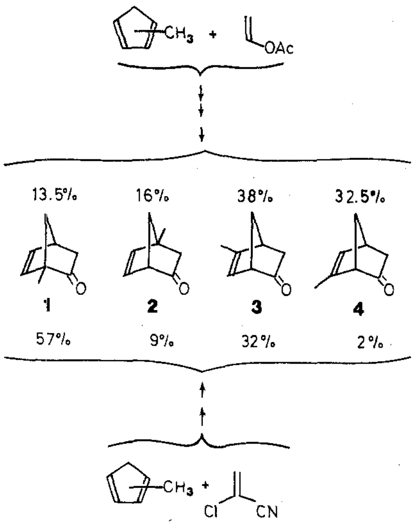
In connection with our investigation of bicyclic systems, 1-methyl-5-norbornen-2-one (**1**) was of interest as a precursor for 1,2-dimethyl-5-norbornen-2-yl derivatives. This compound had been obtained earlier, together with 4- (**2**), 5- (**3**), and 6-methyl-5-norbornen-2-one (**4**), by the Diels–Alder reaction of methylcyclopentadiene and vinyl acetate at 180° followed by a two-step conversion of the adduct to the ketone mixture (lithium aluminum hydride reduction followed by oxidation).[2] However, as shown by the upper part of Chart I, the desired isomer is the minor component of the mixture and thus this did not appear to be a suitable approach for preparing large amounts of **1**. From the **1**:**2** and **3**:**4** ratios it is clear that very little regioselectivity is observed for the uncatalyzed Diels–Alder addition of 1- and 2-methylcyclopentadiene.

Chart I



The equilibrium composition of the three isomeric methylcyclopentadienes is 45% 1-methyl-, 54% 2-methyl-, and 1% 5-methylcyclopentadiene.[3] The formation of over twice as much **3** + **4** as **1** + **2** shows that there is considerable isomerization of 1-methyl- to 2-methylcyclopentadiene which leads to unwanted isomers.

From various reports in the literature [4–6] it appeared that regioselectivity as well as rate should be increased by Lewis acid catalysts, and we now report that this is indeed the case. As shown by the lower part of Chart I, the cupric fluoroborate[7] catalyzed Diels–Alder reaction of the equilibrium mixture of the isomeric methylcyclopentadienes and α-chloroacrylonitrile in benzene at 0–5°, followed by hydrolysis, gives a mixture containing 57% of the desired ketone (**1**) together with 9% **2**, 32% **3**, and 2% **4**. Only trace amounts of unidentified contaminants were detected by GC. Satisfactory yields of pure **1** could be obtained by careful fractionation.

Comparison of the **1**:**2** and **3**:**4** ratios for the catalyzed and uncatalyzed reactions shows that cupric fluoroborate causes a remarkable increase in regioselectivity as well as in rate. Similar results have been reported for other dienes and the earlier interpretations[4,6] appear adequate for the present case.

It is noteworthy that the (**1** + **2**):(**3** + **4**) ratios show that 2-methylcyclopentadiene is more reactive than the 1-methyl isomer for the high-temperature uncatalyzed reaction whereas the reverse is true for the catalyzed reaction. Also, the amount of **1** + **2** obtained from the catalyzed reaction, relative to the amount of the 1-methyl isomer in the diene, suggests that there is isomerization of 2-methylcyclopentadiene to the 1-methyl isomer under the conditions of the catalyzed Diels–Alder reaction.

Experimental Section

1-Methyl-5-norbornen-2-one (1). Monomeric methylcyclopentadiene was prepared just before use by distillation of methylcyclopentadiene dimer. In a typical experiment a solution of 40 g (0.50 mol) of methylcyclopentadiene, 175 g (2 mol) of α-chloroacrylonitrile, and 75 ml of benzene[8] was cooled to 0–5° and 35.6 g (0.15 mol) of dry cupric fluoroborate was added slowly. The reaction mixture was stirred for 4 hr at 0–5°, after which brine containing sodium potassium tartrate was added. The resulting mixture was extracted with ether. After concentration of the ether extract under reduced pressure 500 ml of dimethyl sulfoxide was added to the residual oil. A hot solution of 1.25 mol of potassium hydroxide in 50 ml of water was added to the dimethyl sulfoxide solution and the resulting mixture was stirred at room temperature for 10 hr, after which the mixture was washed with water and extracted with ether. The ether extract was dried ($MgSO_4$) and the ether was removed under reduced pressure. Capillary GC (SE-30, 100 ft, 80°) showed that the residual oil consisted of **1**, 4- (**2**), 5- (**3**), and 6-methyl-5-norbornen-2-one (**4**) in a ratio of 57:9:32:2. Only trace amounts of unidentified contaminants were present. Distillation of the crude product, 46–53° (10 mm), gave 50 g (82%) of a colorless mixture of the four products. All ketones were isolated in pure form by preparative GC (10% Carbowax, 10 ft, 80°) and identified by the NMR spectra, which corresponded in detail to the NMR data reported earlier.[2b] The desired ketone (**1**) is the most volatile isomer and can be separated and purified by fractionation with a spinning band column, bp 46–47° (10 mm), NMR (CCl_4) δ 6.46 (q, 1 H), 5.72 (d, 1 H), 3.05 (s, 1 H), 1.68–2.24 (m, 4 H), 1.2 (s, 3 H).

Registry No.—**1**, 19740-13-7; **2**, 22405-38-5; **3**, 22405-40-9; **4**, 19740-15-9; methylcyclopentadiene, 26519-91-5; α-chloroacrylonitrile, 920-37-6.

References and Notes

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