Pyrolytic Aromatization of Dimethyl 3,5,6,7,8,8a-Hexahydro-5,5,8a-trimethyl-1,2-naphthalenedicarboxylate

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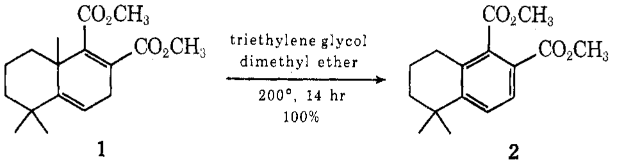
Received July 20, 1972

Pyrolytic aromatization reactions involving the elimination of a bridgehead methyl group are seldom of synthetic utility. Thus, the pyrolysis of steroidal 10-methyl ring A dienones to 19-norphenolic steroids are characterized by reaction temperatures between 300 and 700° and yields of less than 30%.[2] Similarly, pyrolytic aromatizations of bis-$\Delta^{5,8(9)}$-steroidal dienes to the corresponding ring B aromatic steroids are usually effected in low yields.[3-10]

We wish to report a high-yield pyrolytic aromatization involving the elimination of a bridgehead methyl group under exceptionally mild conditions. Previously unreported dimethyl 3,5,6,7,8,8a-hexahydro-5,5,8a-trimethyl-1,2-naphthalenedicarboxylate (**1**), prepared in 69% yield by the Diels-Alder reaction of 1-vinyl-2,6,6-trimethylcyclohexene with dimethyl acetylenedicarboxylate, is quantitatively aromatized to dimethyl 5,6,7,8-tetrahydro-5,5-dimethyl-1,2-naphthalenedicarboxylate (**2**) by heating in triethylene glycol dimethyl ether at 200° for 14 hr. At m/e greater than 178 (M^+ of solvent) the mass spectra of the reaction mixture and an analytical sample of **2** were identical. The nmr spectrum of the isolated product exhibited peaks due to a trace of residual solvent but was otherwise identical with the spectrum of the analytical sample. To the extent that the results of pyrolytic aromatization studies of various methyl-substituted 1,4-cyclohexadienes[11-14] apply to the aromatization of **1**, the reaction probably goes through a nonchain radical process.



1 2

Whereas **1** is a useful intermediate for the synthesis of many sesquiterpenes, **2** should prove to be useful for the synthesis of compounds such as the tanshinones[15] or 4,4-dimethyl ring B aromatic steroids.

Experimental Section

Dimethyl 3,5,6,7,8,8a-Hexahydro-5,5,8a-trimethyl-1,2-naphthalenedicarboxylate (1).—A mixture of 12.92 g (0.086 mol) of 1-vinyl-2,6,6-trimethylcyclohexene and 25 ml of dimethyl acetylenedicarboxylate was mechanically stirred and heated on a steam bath under nitrogen for 71 hr. Prolonged heating at higher temperatures causes the dimethyl acetylenedicarboxylate to tetramerize.[16] Vacuum distillation gave 17.35 g (69%) of **1** contaminated with a small amount of **2**: bp 135° (0.13 mm); uv max (MeOH) end absorption; ir (neat) 1725 (C=O), 1670, 1630 (C=C), 1250 cm^{-1} (CO); nmr (CCl_4) δ 5.92–5.49 (dd, 1, J = 3.0, 2.6, 3.0 Hz, =CH), 3.70 (s, 6, OCH_3), 3.00 (d, 1, J = 5.6 Hz, =$CHCH_2$), 2.8 (d, 1, J = 3.0 Hz, =$CHCH_2$), 1.70–1.27 [m, 6, $(CH_2)_3$], 1.37 (s, 3, bridgehead CH_3), 1.17 (s, 3, geminal CH_3), 1.13 (s, 3, geminal CH_3); mass spectrum (70 eV) m/e (rel intensity), 292 (2), 277 (13), 260 (26), 245 (100), 233 (37), 213 (98), 163 (37).

Anal. Calcd for $C_{17}H_{24}O_4$: C, 69.84; H, 8.27. Found: C, 70.03; H, 8.51.

Dimethyl 5,6,7,8-Tetrahydro-5,5-dimethyl-1,2-naphthalenedicarboxylate (2).—A solution of **1** (0.5 g) in 5 ml of triethylene glycol dimethyl ether was heated at 200° for 14 hr. The reaction mixture was diluted with chloroform and extracted with water. Concentration of the dried (sodium sulfate) chloroform solution gave a quantitative yield of **2**, as a pale yellow oil: uv max (pentane) 241 nm (ϵ 9400), 281 (1500), 289 (1450); ir (neat) 1725, 1735 (C=O), 1590 (aromatic CH), 1275, 1290 cm^{-1} (CO); nmr (CCl_4) δ 7.38 and 7.75 (ABq, 2, J = 9 Hz, aromatic H), 3.85 (s, 6, OCH_3), 2.86–2.54 (m, 2, benzyl CH_2), 2.13–1.50 [m, 4, $(CH_2)_2$], 1.33 [s, 6, $(CH_3)_2$]; mass spectrum (70 eV) m/e (rel intensity) 276 (4), 261 (9), 245 (37), 244 (100), 229 (49), 213 (4), 201 (8), 186 (21), 142 (8).

Anal. Calcd for $C_{16}H_{20}O_4$: C, 69.55; H, 7.30. Found: C, 70.00; H, 7.47.

Registry No.—**1**, 36963-51-6; **2**, 36963-52-7.

Acknowledgment.—The author acknowledges financial support from NSF Grant GP-10810 and fruitful discussions with Dr. William Reusch.

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The Enamine as a Cyclohexylidene Source

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Received July 18, 1972

The recent observation of Alt and Gallegos[1] that enamines react with cyanoacetic acid to produce alkylidenecyanoacetic acids has led us to examine the limitations of 1-morpholino-1-cyclohexene as an intermediate for the preparation of cyclohexylidene derivatives (Knoevenagel products).

Malonic acid derivatives which contain at least one cyano group (cyanoacetic acid derivatives) react with the enamine in an exothermic reaction within 30 min, producing the expected product in at least 59% yield. On the other hand, several other compounds having active methylene groups (phenylacetonitrile, ethyl malonate, acetylacetone, chloroacetic acid, and chloroacetonitrile) failed to give a condensation product even with extensive boiling. The limitation is essentially the same as documented so carefully by Hein, Astle, and

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