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ELECTROPHILE-INDUCED BERSON-WILLCOTT REARRANGEMENT OF 11-CARBOXYL-1,6-METHANO[10]ANNULENE METHYL ESTER

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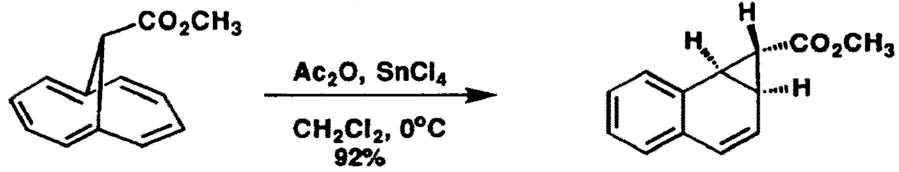
Abstract: Attempted electrophilic acylation of bridged annulene **1** leads instead to an efficient Berson-Willcott rearrangment.

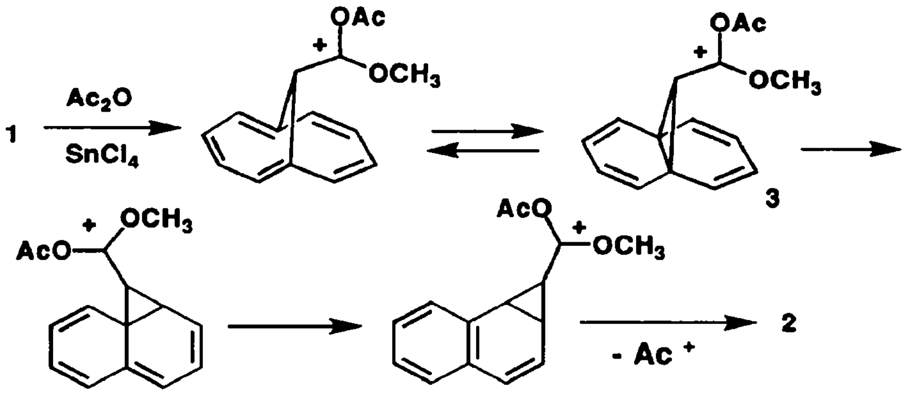
We have recently reported an efficient new synthetic route to 11-carboxyl-1,6-methano[10]-annulene methyl ester (**1**), as part of an effort to gain access to derivatives bearing substituents on both the bridge and the annulene ring.[1] We report here that attempted electrophilic acylation of **1** leads instead to a Berson-Willcott rearrangement,[2] to produce the known[3] tricyclic ester **2**.



1 **2**

Treatment of **1** under standard electrophilic acylation conditions (2 eq $SnCl_4$, 1 eq acetic anhydride, CH_2Cl_2, 0°C, 0.5 hr) followed by aqueous work-up and chromatography on silica afforded **2** in 92% yield.[4,5] In contrast, treatment of **1** with only $SnCl_4$ under these conditions for 2 hr had no effect. A possible mechanism for this rearrangement is shown below. According to this mechanistic hypothesis, O-acylation generates a species with considerable cationic character at the carbon adjacent to the bridging methylene. From the bisnorcaradiene tautomer, **3**, this cation can undergo two successive 1,5-sigmatropic rearrangements. The resulting cation is deacylated upon work-up to generate benzonorcaradiene derivative **2**.

Precedent for this rearrangement may be found in the reactions of 1,6-methano[10]annulene itself and its 11,11-dicyano derivative. The parent hydrocarbon undergoes a single 1,5-sigmatropic rearrangment upon flash vacuum pyrolysis at 500°C, to generate a benzocycloheptatriene isomer.[6] The 11,11-dicyano derivative undergoes a single 1,5-sigmatropic rearrangement rapidly



at room temperature, to generate a dicyano benzocycloheptatriene;[7] when heated to 99°C, this initial product further rearranges to a benzonorcaradiene that is analogous to **2**.[8]

The rearrangement of **1** to **2** is more facile than either of these precedents. It has been proposed that electron-withdrawing substituents favor norcaradiene tautomers over cycloheptatriene forms.[9] This hypothesis is supported by our observations: the high reactivity can be attributed to the strongly electon-withdrawing character of the cationic center attached to the bridging methylene in the initial O-acylation product, which stabilizes bisnorcaradiene tautomer **3** and thereby promotes rearrangement.

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4. Compound **2** was isolated as a yellow oil: ^{1}H NMR ($CDCl_3$): d 0.86 (t, 3.9 Hz, 1H), 2.60-2.68 (m, 1H), 3.08 (dd, 8.3, 3.9 Hz, 1H), 3.74 (s, 3H), 6.35 (AB of ABX, 9.6, 4.8, 0.0 Hz, 2H), 7.11-7.44 (m, 4H); ^{13}C NMR ($CDCl_3$): d 22.62, 27.65, 30.52, 52.10, 125.79, 125.91, 126.74, 127.89, 128.62, 130.64, 132.49, 175.90; EI MS: *m/z* 200.0836 (calcd. for $C_{13}H_{12}O_2$ (M+) 200.0837).
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