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High-Pressure Diels-Alder Reaction of Tropone Acetal with Several Dienophiles

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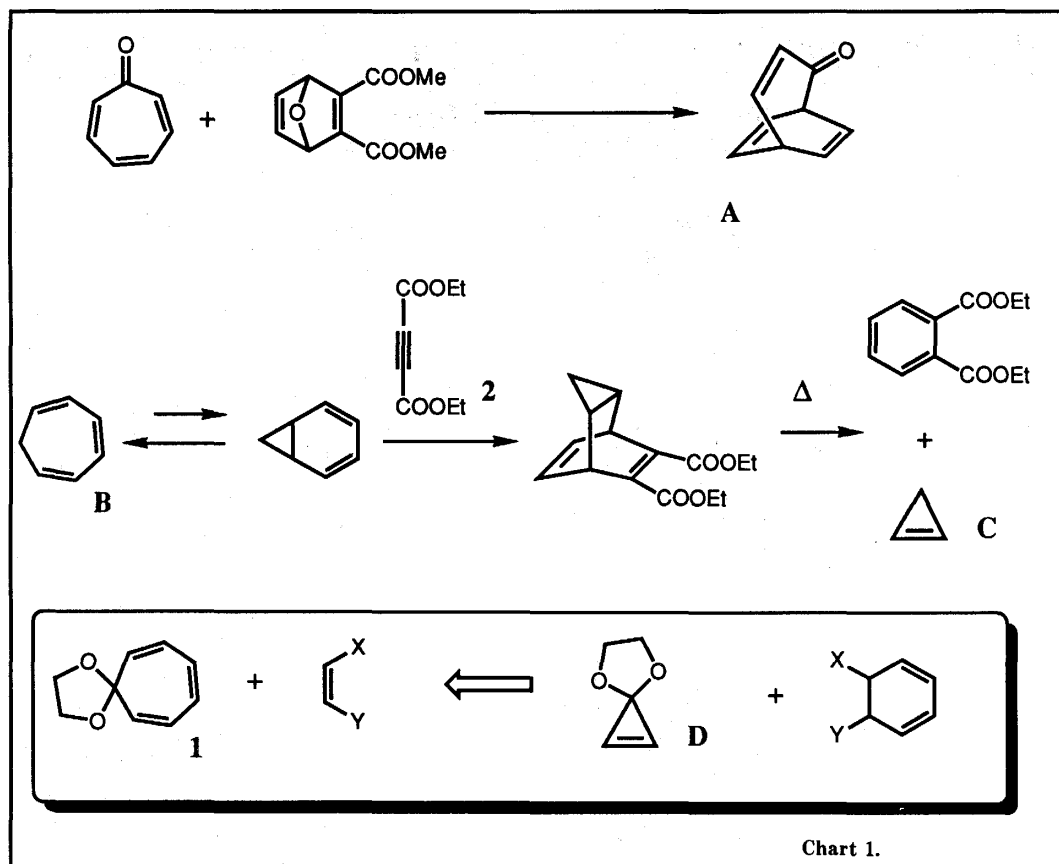
Abstract: The high-pressure (to 10000 bar) Diels-Alder reactions of tropone ethylene acetal with diethyl butynedioate, *N*-phenylmaleimide, and diphenylisobenzofuran afforded the single *endo*-Diels-Alder adducts, respectively. However, with less reactive dienophiles, pressure-accelerated sigmatropy of the acetal to a cycloheptadioxane occurred prior to cycloaddition.

High-pressure Diels-Alder reactions with tropones are recently becoming an important method of organic syntheses; we reported¹⁾ an improved synthesis of homobarrelenones (**A**)²⁾ from tropones and 2,3-bis-(methoxycarbonyl)-7-oxabicyclo[2.2.1]hepta-2,5-diene by combination of subsequent fragmentation.³⁾ However, the reaction of the tropone acetal, a masked tropone with tropyridene π -system, has not been investigated to date. Cycloheptatriene (tropyridene, **B**) is known to react with dienophiles as valence-isomeric norcaradiene (bicyclo[4.1.0]hepta-2,4-diene) form, and the Diels-Alder adduct with diethyl butyneditate (**2**) is a good precursor of cyclopropene (**C**). If this also occurred with tropone ethylene acetal (**1**), cyclopropenone acetal (**D**) could be easily obtained, and in the same time, the remaining C₄ moiety of **1** could serve as the 1,3-cyclohexadiene precursors. Since the substituted 1,3-cyclohexadienes are often found in terpenoid frameworks, their facile method of synthesis should be desirable. We now investigated the high-pressure Diels-Alder reaction of **1** with diethyl butynedioate (**2**)⁴⁾ and *N*-phenylmaleimide (**3**)⁵⁾ to furnish *endo*-Diels-Alder adducts exclusively.

Following the general procedure, **1** and **2** were heated in toluene at 80 °C for 10 h under 10000 bar. Collection of the resultant crystalline mass furnished (**4**) [colorless crystals, mp 92–93 °C. ¹H NMR δ =1.31 (6H, t), 3.66 (1H, t, *J*=7.7 Hz), 4.04 (5H, m), 4.27 (4H, q), 4.92 (1H, dd, *J*=11.0, 1.5 Hz), 6.36 (1H, t, *J*=7.7 Hz), 6.48 (1H, ddd, *J*=11.0, 8.4, 2.6 Hz), and 6.78 (1H, td, *J*=7.7, 1.5 Hz). ¹³C NMR δ =14.1 (2C), 39.1, 47.1, 61.2, 61.3, 64.6, 100.6, 127.6, 129.5, 136.0, 136.5, 139.3, 149.0, 166.0, 167.0. MS *m/z* (%): 230 (M⁺) Found: C, 64.01; H, 6.28%. (Calcd for C₁₇H₂₀O₆: C, 63.74; H, 6.29%)] in 55% yield. The structure of **4** was deduced from the ¹H and ¹³C NMR spectral analysis. The stability of **4** toward heat is outstanding in comparison with **A** which easily isomerized to dihydroindenone by heating.

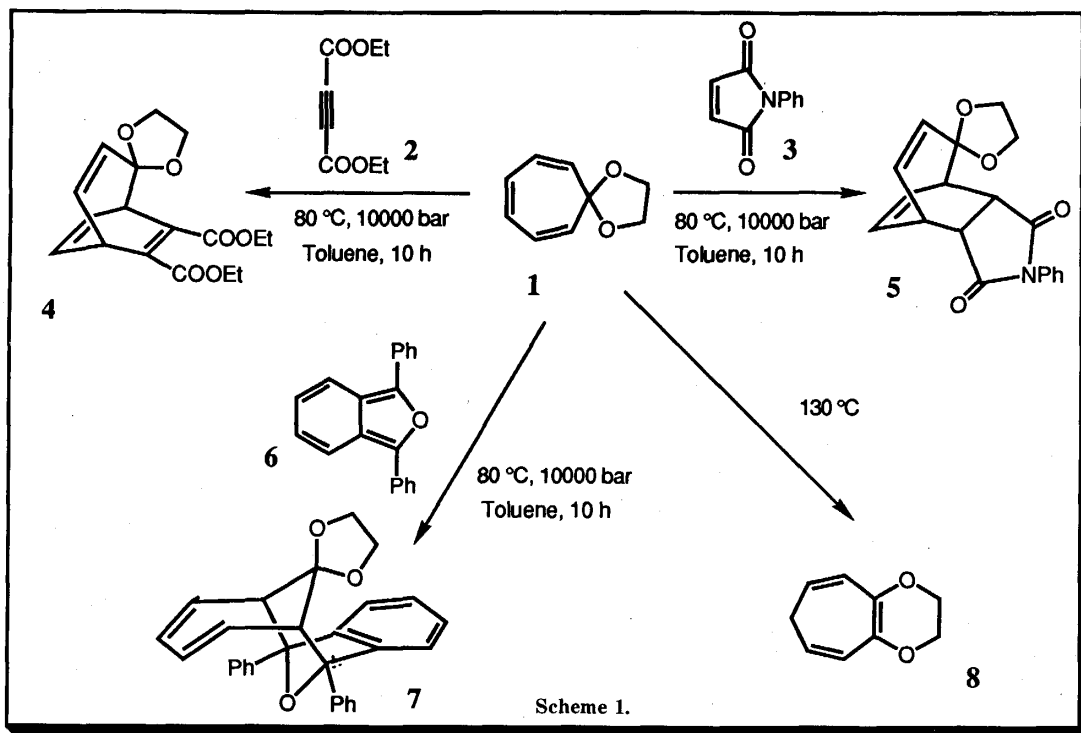
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On the other hand, the reaction of **1** and **3** by heating in a toluene solution under the same conditions as above also gave a single product, *endo*-4-phenyl-4-azatricyclo[5.3.2.0^{2,6}]dodeca-9,11-diene-3,5,8-trione ethylene acetal (**5**) [colorless crystals, mp 158-159 °C, ¹H NMR⁶⁾ δ =3.28 (1H, d, J =9.5 Hz), 3.45 (1H, dd, J =8.4, 2.2 Hz), 3.51 (1H, t, J =8.4 Hz), 3.67 (1H, dd, J =8.4, 1.8 Hz), 4.09 (4H, m), 5.34 (1H, dd, J =11.0, 2.5 Hz), 6.12 (1H, t, J =7.7 Hz), 6.34 (1H, dd, J =11.0, 8.4 Hz), 6.54 (1H, t, J =7.7 Hz), 7.21 (2H, m), and 7.42 (3H, m). ¹³C NMR δ =34.3, 41.2, 44.6, 47.0, 64.8, 65.4, 105.2, 126.4 (2C), 128.2, 128.7, 129.2 (2C), 130.4, 131.9, 134.8, 137.6, 177.0, and 178.1. MS m/z (%): 323 (M⁺). Found: C, 70.85; H, 5.30; N, 4.30%. (Calcd for C₁₉H₁₇O₄N: C, 70.57; H, 5.30; N, 4.33%)], in 93% yield. The ¹H and ¹³C NMR spectra of **5** were consistent with the structure depicted in Scheme 1.

The high-pressure reaction of **1** with diphenylisobenzofuran (**6**) afforded only 6% of a [6+4] cycloadduct (**7**) [colorless crystals, mp 296-297°C. ¹H NMR δ =3.40 (2H, d, J =6.8 Hz), 3.60 (2H, t, J =6.4 Hz), 3.75 (2H, t, J =6.4 Hz), 5.51 (2H, m), 5.93 (2H, m), 7.03 (2H, dt, J =8.7, 3.2 Hz), 7.14 (2H, dt, J =8.7, 3.2 Hz), 7.34 (2H, tt, J =7.5, 1.2 Hz), 7.47 (4H, t, J =7.5 Hz), and 7.71 (4H, dd, J =7.5, 1.2 Hz). ¹³C NMR δ =53.4 (2C), 63.3, 64.5, 90.0 (2C), 106.8, 120.9 (2C), 125.2 (4C), 127.2 (2C), 127.3 (2C), 127.5 (2C), 127.6 (2C), 128.6 (4C), 141.2 (2C), and 146.6 (2C). MS m/z (%): 420 (M⁺, 0.3), 283 (2), 727 (3), 271 (22), 720 (100), 241 (22), 239 (16), 165 (16), and 77 (20). Found: C, 82.96; H, 5.87%. (Calcd for C₂₇H₂₄O₃: C, 82.83; H, 5.75%)] whose stereochemistry was deduced to be *exo* from the chemical shifts of cycloheptadiene proton signals of AA'BB"-system; the observed chemical shifts revealed no anisotropic shift from the phenyl group of the isobenzofuran moiety.⁷⁾



The results showed the cycloaddition of **1** proceeded solely to form homobarrelenone acetals, but not as the norcaradiene acetal form. However, the reactivity of **1** was less reactive than tropone itself; heating the mixtures of **1** and **2** or **3** under 1 bar up to 135 °C caused no reaction to recover the starting material. Furthermore, prolonged heating of **1** resulted in the rearrangement to 3,4-dioxyethylenecyclohepta-2,4,6-triene (**8**) [^1H NMR δ =2.32 (2H, t, J =7.0 Hz), 4.14 (4H, s), 5.25 (2H, dt, J =9.5, 7.0 Hz), and 5.98 (2H, d, J =9.58 Hz). ^{13}C NMR δ =27.5 68.9 (2C), 118.0 (2C), 123.0 (2C), and 138.6 (2C)]. Attempted cycloadditions of cyclopentenone and ethoxyethene with **1** in toluene at 80 °C under 10000 bar for 10 h afforded no cycloadduct, but when the temperature was raised to 120 °C, **1** rearranged to **8**, which was isolated in 60% yield through a silica-gel column chromatography.

Consequently, in the high-pressure Diels-Alder reaction, **1** is less reactive than tropone. However, the masked carbonyl group of **1** was certainly advantageous to prepare light- and/or heat-sensitive Diels-Alder adducts, such as **4**.

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