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Novel Two-Step Synthesis of Homobarrelenones, Bicyclo[3.2.2]nona-3,6,8-trien-2-ones, from Tropones and 2,3-Bis(methoxycarbonyl)-7-oxabicyclo[2.2.1]heptadiene by High-Pressure Cycloaddition-Thermal Cycloreversion Procedure

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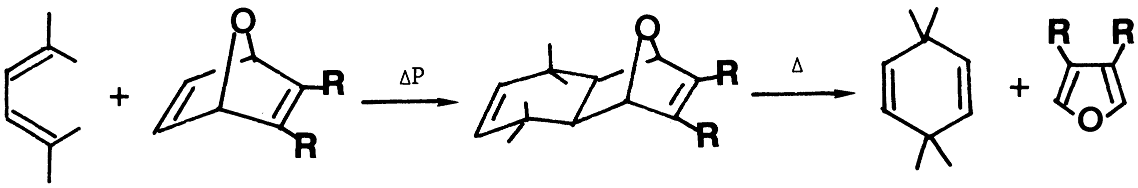
The Diels-Alder adduct of tropone with 2,3-bis(methoxycarbonyl)-7-oxabicyclo[2.2.1]hepta-2,5-diene formed homobarrelenone by heating at ca. 130 °C. Similarly prepared were 1-hydroxy-, 3-methoxy-, 1-chloro-, and 3-chlorohomobarrelenones. High-pressure cycloaddition improved the yields of the Diels-Alder adducts.

In organic synthesis, designing of an acetylene (**A**) synthon for cycloadditions in general is worth trying. Recent paper by N. Ono et al.1) described a remarkable two-step formation of 1,4-cyclohexadienes, Diels-Alder adducts of dienes with **A** in a formal sense; i.e., Diels-Alder reaction of β-nitrosulfonylethene with dienes and AIBN-initiated elimination of adducts with tributyltin hydride. Other than this, a) an oxidative decarboxylations of Diels-Alder adducts from maleic acid2) and b) reductive eliminations of halogens from dihaloethene adducts3) were frequently used, but a) was successful only in limited instances, and b) seems to have limitations depending on the other functional groups in the molecule. Therefore, still further development of versatile method is desired.

As the Diels-Alder adducts of furans readily cause the cycloreversion,4) 7-oxabicyclo[2.2.1]heptadiene, corresponds to the Diels-Alder adduct of furan with **A**,5) should serve as a substitute for **A**.



This was indeed the case when the Diels-Alder adducts of 2,3-bis(methoxycarbonyl)-7-oxabicyclo[2.2.1]heptadiene (**1**)6) with tropones (**2**a–d) prepared under high-pressure conditions were easily thermolyzed to homobarrelenones7) (**3**a,8) **3**b, **3**d, **4**c, and **4**d), of which the synthesis is still a current interest.9)

In 1972, Sasaki et al.10) described the Diels-Alder reaction of tropone (**2**a) with **1** to form a 1:1-adduct (**5**a). According to our repeated experiments, heating the mixture at 140 °C under ordinary pressure yielded not only formerly identified

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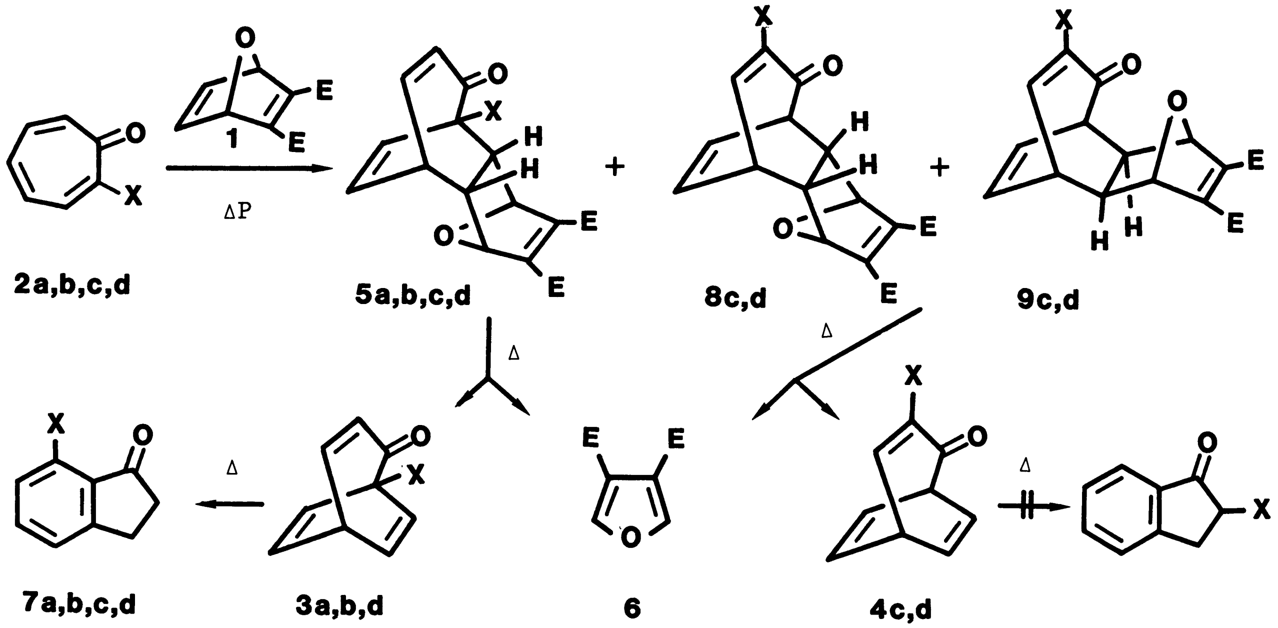
5a[10] [δ(H)[11]=2.50(1H, d, J=8 Hz), 2.70(1H, d, J=8 Hz), 3.44(1H, tm, J=8 Hz), 3.68(1H, d, J=8 Hz), 3.78(3H, s), 3.80(3H, s), 4.92(1H,d, J=1 Hz), 5.01(1H, d, J=1 Hz), 5.70(1H, dd, J=11, 2 Hz), 6.10(1H, t, J=8 Hz), 6.24(1H, t, J=8 Hz), and 7.18 (1H, dd, J=11, 8 Hz). δ(C)=39.7, 41.8, 48.2, 52.5(2C),57.0, 85.9, 86.7, 126.8, 129.5, 136.1, 145.7, 146.1, 153.7, 162.6, 163.1, and 196.3] but three other products (**3**a [δ(H)=3.85(1H, m), 4.15(1H, tq, J=6.5, 1.5 Hz), 5.04(1H, 1H, ddd, J=11, 2, 1 Hz), 6.33(2H, ddd, J=8, 6.5, 1.5 Hz), 6.67(2H, ddd, J=8, 6.5, 1.5 Hz), and 7.02(1H, dd, J=11, 8 Hz). δ(C)=41.5, 59.4, 124.9, 128.9(2C), 138.5(2C), 153.2, and 189.7], **6**, and **7**a). The NMR spectrum of **3**a was identical with that reported for homobarrelenone,[8] and **6** and **7**a were identified to be 3,4-bis(methoxycarbonyl)-furan and 1-indanone, respectively. Therefore, spontaneous retro-Diels-Alder fragmentation, **5**a to **3**a and **6**, already occurred.



a: X=H, b: X=OH, c: X=OMe, d: X=Cl, E=COOMe

Next, the reaction of tropolone (**2**b) with **1** at 130 °C under 1 bar also gave the adduct (**5**b [δ(H)=2.24(1H, d, J=8 Hz), 2.58(1H, d, J=8 Hz), 3.61(1H, tm, J=8 Hz), 3.77(6H, s), 4.70(1H, d, J=2 Hz), 5.52(1H, d, J=2 Hz), 5.88(1H, d, J=11 Hz), 5.92(1H, d, J=9 Hz), 6.32(1H, dd, J=9, 8 Hz), and 7.30(1H, dd, J=11, 8 Hz)]) in 50% yield together with the fragmentation products, 1-hydroxyhomobarrelenone (**3**b [δ(H)=4.04(1H, dtm, J=8, 6 Hz), 4.7(1H, OH), 5.42(1H, dd, J=11, 1 Hz), 6.28(2H, dd, J=7.5, 2 Hz), 6.66(2H, dd, J=7.5, 6 Hz), and 7.22(1H, dd, J=11, 8 Hz). δ(C)= 41.9, 86.0, 121.9, 134.4(2C), 137.7(2C), 155.2, and 189.9], 11% yield), 7-hydroxy-1-indanone (**7**b [δ(H)=2.6–2.8(2H, m), 3.0–3.2(2H, m), 6.71(1H, d, J=7.5 Hz), 6.89 (1H, d, J=7.5 Hz), 7.43(1H, t, J=7.5 Hz), and 9.02(1H, s)], 2%), and **6** (8%). The reaction under high-pressure conditions gave better results; under the pressure of ca. 3000 bar, the yields of Diels-Alder adducts were improved to 88% for **5**a and 66% for **5**b without any cycloreversion products. The reaction was further extended to 2-methoxytropone (**2**c) and 2-chlorotropone (**2**d) with **1**; in both cases, three adducts (**5**c, **8**c, and **9**c from **2**c, and **5**d, **8**d, and **9**d from **2**d) formed without any cycloreversion product. Table 1 summarizes the high-pressure Diels-Alder reaction.

Table 1. Diels-Alder Reactions of **1** with Tropones under 3000 bar

Tpn	Conditions	Adduct (Yields/%; mp/°C)
2a	100 °C, 11 h	**5**a(88; 100-102[10])
2b	120 °C, 12 h	**5**b(66; 114-115[10])
2c	120 °C, 12 h	**5**c(34; 102-103) **8**c(12; 129-131) **9**c(4; 76.5-78)
2d	120 °C, 12 h	**5**d(44; 146-147) **8**d(20; 122-123) **9**d(7; 157-159)

Table 2. Cycloreversion of the Diels-Alder Adducts of Tropones

Adducts	Conditions	Thermolysates (Yields/%)			
		Homobarrelenones	mp/°C	Indanones	Furan (**6**)
5a	130 °C, 7 d	**3**a (26)	44[8]	**7**a (22)	(48)
5b	120 °C, 6 d	**3**b (39)	colorless oil	**7**b (36)	(81)
5c	120 °C, 7 d			**7**c (95)	(100)
8c+**9**c	120 °C, 7 d	**4**c (50)	colorless oil		(50)
5d	130 °C, 24 h	**3**d (17)	67-68	**7**d (17)	(62)
8d+**9**d	130 °C, 6 h	**4**d (88)	85-87		(88)

To obtain homobarrelenones, the adducts were thermolyzed at 130 °C for prolonged period; e.g., **5**a gave **3**a, **7**a, and **6** in 26%, 22%, and 48%, respectively. Although the yields of **6** were satisfactory, the isolated yields for **3** and **4** were relatively low; this was due to their volatility and a facile isomerizing tendency to indanone derivatives. This method provides a versatile two-step synthesis of these structurally interesting bicyclic ketones (Table 2).

However, an attempted fragmentation of the major product (**5**c [δ(H)=2.64(2H, s), 3.43(1H, ddm, J=8.5, 7 Hz), 3.58(3H, s), 3.78(3H, s), 3.80(3H, s), 4.91(1H, d, J=1.5 Hz), 5.41(1H, d, J=1.5 Hz), 5.74(1H, dd, J=11, 1 Hz), 6.06(1H, d, J=9 Hz), 6.37(1H, dd, J=9, 7 Hz), and 7.14(1H, dd, J=11, 8.5 Hz)]) from **2**c resulted only a formation of 7-methoxy-1-indanone (**7**c), but the major adduct (**5**d [δ(H)=2.62(1H, dd, J=7.5, 1 Hz), 2.76(1H, d, J=7.5 Hz), 3.48(1H, tm, J=8 Hz), 3.80(3H, s), 3.81 (3H, s), 4.96(1H, d, J=1.5 Hz), 5.69(1H, d, J=1.5 Hz), 5.90(1H, dd, J=11, 0.7 Hz), 6.04(1H, dt, J=9, 1 Hz), 6.44(1H, ddd, J=9, 8, 0.7 Hz), and 7.26(1H, dd, J=11, 8 Hz)]) of **2**d produced 1-chlorohomobarrelenone (**3**d [δ(H)=3.90(1H, dtm, J=8, 6.5 Hz), 5.34(1H, dd, J=11, 0.5 Hz), 6.34(2H, dd, J=7.5, 1.5 Hz), 6.76(2H, dd, J=7.5, 6.5 Hz), and 7.14(1H, dd, J=11, 8 Hz). δ(C)=40.2, 77.2, 123.7, 135.4(2C), 136.2 (2C), 153.6, and 181.6]) and 7-chloro-1-indanone (**7**d). Thus, the electron-releasing group on the bridge-head carbon tends to facilitate the indanone formation.

The by-products (**8**c [δ(H)=2.48(1H, d, J=8 Hz), 2.68(1H, dd, J=8, 1.5 Hz), 3.45(1H, m), 3.52(3H, s), 3.8(1H, m), 3.78(3H, s), 3.80(3H, s), 4.90(1H, s), 4.98 (1H, s), 6.08(1H, t, J=7.5 Hz), 6.16(1H, d, J=9.5 Hz), and 6.51(1H, t, J=7.5 Hz)] and **9**c [δ(H)=2.49(1H, dd, J=8.5, 4.5 Hz), 2.61(1H, dd, J=8.5, 4.5 Hz), 3.54(3H, s), 3.5–3.9(2H, m), 3.78(6H, s), 4.86(1H, s), 4.92(1H, s), 5.81(1H, d, J=9.5 Hz), 6.14(1H, ddd, J=8, 7.5, 0.5 Hz), and 6.64(1H, ddd, J=8, 7, 1 Hz)] from **2**c and **8**d [δ(H)=2.52(1H, d, J=8 Hz), 2.74(1H, dd, J=8, 1.5 Hz), 3.54(1H, ddm, J=9, 7.5 Hz), 3.79(3H, s), 3.81(3H, s), 3.94(1H, d, J=7.5 Hz), 4.90(1H, s), 5.02(1H, s), 6.16(1H, t, J=7.5 Hz), 6.48(1H, t, J=7.5 Hz), and 7.48(1H, d, J=9 Hz)] and **9**d [δ(C)=2.56 (1H, dd, J=8, 5.5 Hz), 2.68(1H, dd, J=8, 3.5 Hz), 3.65(1H, m), 3.78(6H, s), 3.98 (1H, ddm, J=7.5, 5.5 Hz), 4.90(1H, d, J=1 Hz), 4.95(1H, d, J=1 Hz), 6.22(1H, ddd, J=8.5, 7.5, 1 Hz), 6.64(1H, ddd, J=8.5, 7, 1 Hz), and 7.16(1H, d, J=9 Hz)] from **2**d) were respectively converted to 3-methoxyhomobarrelenone (**4**c [δ(H)=3.42(3H, s), 3.96(1H, dtt, J=9, 6.5, 1.5 Hz), 4.38(1H, tt, J=6.5, 1.5 Hz), 6.16(1H, d, J=9 Hz), 6.42(2H, ddd, J=7.5, 6.5, 1.5 Hz), and 6.82(2H, ddd, J=7.5, 6.5, 1.5 Hz). δ(C) =38.3, 54.5, 58.5, 120.1, 128.7(2C), 140.2(2C), 146.1, and 187.1]) and 3-chlorohomobarrelenone (**4**d [δ(H)=4.02(1H, dtt, J=9, 6.5, 1.5 Hz), 4.52(1H, tt, J=6.5, 1.5 Hz), 6.48(2H, ddd, J=7.5, 6.5, 1.5 Hz), 6.82(2H, ddd, J=7.5, 6.5, 1.5 Hz), and 7.36(1H, d, J=9 Hz). δ(C)=41.2, 58.4, 127.3, 129.0(2C), 138.7(2C), 149.6, and 183.9]) by cycloreversion.

Up to date, only a few derivatives of **3**a are prepared,[9,12] including a 6,7-bis(methoxycarbonyl)homobarrelenone by a direct Diels-Alder addition of **2**a to dimethyl butynedioate.[13]

This procedure, high-pressure cycloaddition and thermal fragmentation, may be widely applicable, and **1** will serve as a convenient substitute for acetylene.

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