Tetrahedron Letters, Vol.33, No.2, pp. 257-260, 1992
Printed in Great Britain

0040-4039/92 $3.00 + .00
Pergamon Press plc

SYNTHESIS AND CYCLOREVERSION OF BENZOCYCLOBUTENE- AND BENZOCYCLOBUTADIENE-ANTHRACENE ADDUCTS

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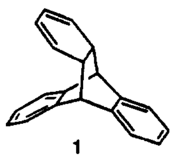
Abstract. The [4+2]-cycloadducts of anthracene and benzocyclobutene or benzocyclobutadiene were synthesized and their cycloreversion was investigated.

Cycloreversion of [4+2]-adducts of arenes is highly exothermic process. Although activation parameters of several cycloadducts of benzene and aromatic hydrocarbons (1 as a typical example) have been investigated,[1,2] such study for cycloadducts containing strained aromatic or anti-aromatic hydrocarbons has not been reported. We wish to report synthesis and cycloreversion of benzocyclobutene- and benzocyclobutadiene-anthracene adducts (2 and 3).



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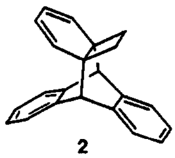

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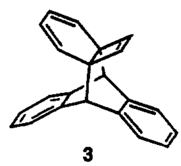

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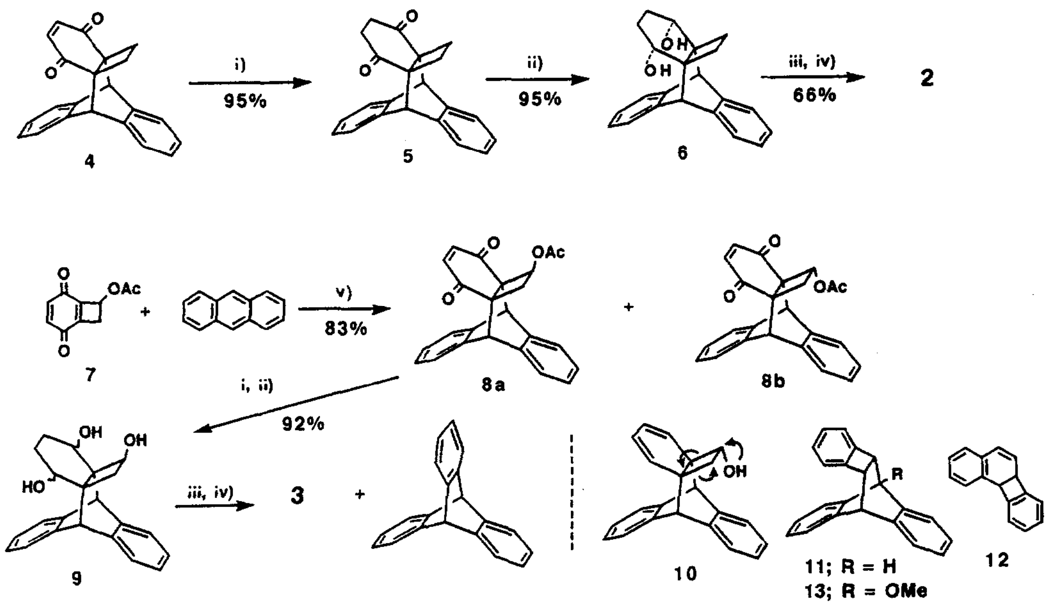
The diene 2 was synthesized from Diels-Alder adduct 4 of anthracene and benzocyclobutene-*p*-benzoquinone[3] through 5 and 6. The synthesis of triene 3 was performed similarly, but met with more difficulty because of more complicated stereochemical problems in the intermediates and rather poor yield of the final step. Thus, Diels-Alder reaction of the acetoxyquinone 7[4] and anthracene in the presence of $BF_3 \cdot OEt_2$ gave stereoisomers of the adducts **8a** and **8b**. The isomers were assigned as shown in Scheme 1 by shielding effect of benzene ring toward the proton attached to acetoxy substitututed carbon (see Table 3). Two step reductions of the major isomer **8a** afforded a mixture of two stereoisomers of triols 9 (91% in the ratio of 3.6 : 1). Treatment of the major isomer of triol 9 with CH_3SO_2Cl/py and subsequent elimination with *t*-BuOK/DMSO gave 3 (22%) along with triptycene (20%). Although the mechanism of formation of triptycene has not been pursued, we assume the dienol **10** which might arise from incomplete methanesulfonylation at the cyclobutanol moiety is responsible for the base induced fragmentation, because the similar procedure for the minor acetate **8b** produced triptycene exclusively.

Although the benzene-anthracene adduct **1** undergoes cycloreversion at reasonable rate below 80 °C, the cycloreversion of annelated diene **2** to benzocyclobutene and anthracene required higher temperature of 120 °C. The cycloreversion of triene **3** proceeded only at higher temperature, above 200 °C, producing **11** (40%),[5] benzocyclobutadiene-dimer **12** (trace), and anthracene (56%). Dissociation-recombination mechanism for the formation of **11** was proved by the trapping benzocyclobutadiene by 9-methoxyanthracene (2 eq), giving the adduct **13** (57%). Table 1 summarizes the activation parameters for **2** and **3** along with the reported values for **1**.[6] The activation energy (Ea) of cycloreversion of **3** is higher than that of **2** by about 7 kcal/mol, and the latter value is also higher than that of **1** by about 5 kcal/mol.

Scheme 1



i) Zn/AcOH, 60 °C; ii) $LiAlH_4$/THF, 0 °C; iii) CH_3SO_2Cl/py, rt, 2 h; iv) *t*-BuOK/DMSO, rt, 5 h; v) $BF_3 \cdot OEt_2$ (0.15 eq)/C_6H_6, rt, 5 h

Table 1. Activation parameters for the [4+2] cycloreversion of **1**, **2**, and **3**

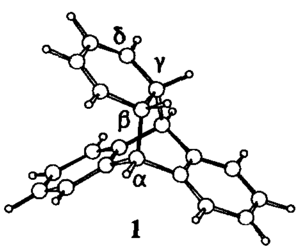
compound	temperature (°C)	log A	Ea (kcal/mol)	ΔG* (77 °C) (kcal/mol)
1[a]	56-80	15.5 ± 0.4	29.3 ± 0.7	25.3 ± 0.2
2[b]	119-149	13.7 ± 0.4	34.5 ± 0.5	33.2 ± 0.5
3[b]	223-253	14.2 ± 0.4	41.6 ± 0.7	39.8 ± 0.7

[a] reference 2; [b] reference 6

In a series of cycloreversion of [4+2] adducts of benzene and several aromatic hydrocarbons, Grimme and co-workers have reported linear relationship between the observed free energy of activation ($\Delta G^{\neq}$) and the calculated gain of resonance energies.[2] Since the difference of resonance energies of benzocyclobutene and benzene is small (heat of hydrogenation for benzocyclobutene is only 3 kcal/mol more negative than *o*-xylene),[7] Grimme's relationship alone cannot explain the large difference between **1** and **2**. The deviation may be mainly ascribed to the change of geometries. Inspection of molecular model indicates that the ethano-bridging of **1** at the ring junction would increase a dihedral angle of C_α-C_β-C_γ-C_δ. Such geometrical change is even larger for the etheno-bridging (see **1**, **2**, and **3** in Table 2). Increasing the dihedral angle would decrease the through bond interaction between cyclohexadiene and benzene orbitals through the σ^* orbital (C_α-C_β).[8] As a result the bond length (C_α-C_β) would be shortened in the sequence of **1**→**2**→**3**. This qualitative consideration is consistent with molecular mechanics calculation (MMP2).[9] The optimized geometries, the dihedral angle (C_α-C_β-C_γ-C_δ), and the bond length (C_α-C_β) are shown in Table 2. Obviously, the dihedral angle decreases and the bond length increases in the same order of **3**→**2**→**1**. Relatively small change of these structural parameters in the ground states would cause larger effects in the transition state.

In addition to the above geometrical factor, anti-aromatic destabilization of benzocyclobutadiene[10] may also affect the bond breaking process in **3**. For this reason, the cycloreversion of **3** may not be concerted and may proceed via the conceivable diradical intermediate.

Table 2. The calculated dihedral angle (C_α-C_β-C_γ-C_δ) and bond length (C_α-C_β) for **1**, **2**, and **3**



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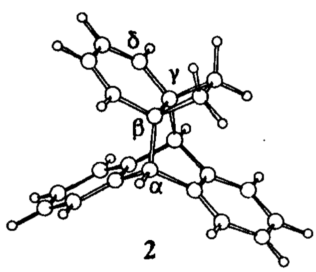

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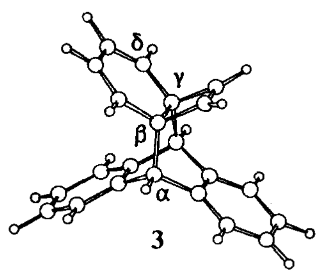

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compound	dihedral angle C_α-C_β-C_γ-C_δ (°)	bond length C_α-C_β (Å)
1	124.5 ± 0.1	1.548
2	127.7 ± 0.4	1.544
3	131.0 ± 0.1	1.540

Table 3. Mps and NMR ($CDCl_3$) data of some new compounds

2: 148-150 °C dec.; ^1H NMR, δ 1.40-2.10 (4H, AA'BB'), 3.94 (2H, s), 5.40 (4H, s), 6.93-7.40 (8H, m); ^{13}C NMR, δ 33.89, 45.32, 53.55, 120.78, 124.68, 125.06, 125.39, 125.55, 130.89, 142.07, 142.53

3: mp 176-177 °C; ^1H NMR, δ 4.00 (2H, s), 5.68 (6H, s), 6.95-7.45 (8H, m); ^{13}C NMR, δ 53.18, 53.51, 122.77, 124.85, 125.29, 128.92, 137.23, 141.73, 142.76

8a: Viscous oil; ^1H NMR, δ 1.63-2.15 (2H, m), 1.92 (3H, s), 4.45 (1H, dd, J = 8.0, 6.3 Hz), 4.80 (1H, s), 4.91 (1H, s), 6.46 (2H, s), 7.00-7.50 (8H, m)

8b: mp 233-235 °C; ^1H NMR, δ 1.67 (1H, dd, J = 14.0, 7.5 Hz), 1.90 (3H, s), 2.50 (1H, dd, J = 14.0, 9.0 Hz), 4.72 (1H, s), 4.97 (1H, dd,, J = 9.0, 7.0 Hz) 5.00 (1H, s), 6.39 (2H, s) 7.00-7.60 (8H, m)

13: mp 124-125 °C; ^1H NMR, δ 3.88 (2H, m), 4.12 (3H, s), 4.50 (1H, d, J = 2.8 Hz), 6.85-7.45 (11H, m), 7.67 (1H, m)

References and Notes

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4. The acetoxyquinone 7 was prepared in a similar method described in reference 3; mp, 97-98 °C; ^1H NMR ($CDCl_3$), δ 2.12 (3H, s), 2.98 (1H, dd, J = 15.6, 1.5 Hz), 3.51 (1H, dd, J = 15.6, 3.7 Hz), 5.88 (1H, dd, J = 3.7, 1.5 Hz), 6.66 (2H, s).
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(Received in Japan 17 October 1991)