

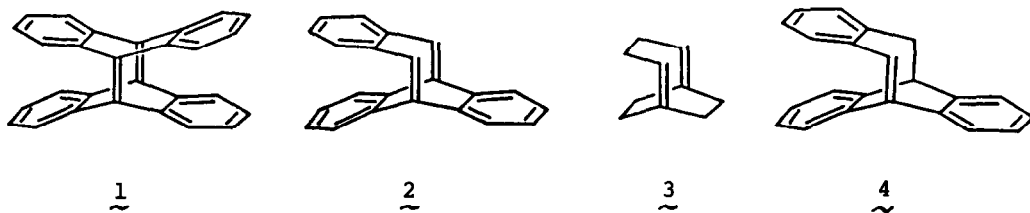
SYNTHESIS OF 3,4;7,8;9,10-TRIBENZOBICYCLO[4.2.2]DECA-
1,3,7,9-TETRAENE: A NEW STRAINED BRIDGEHEAD OLEFIN

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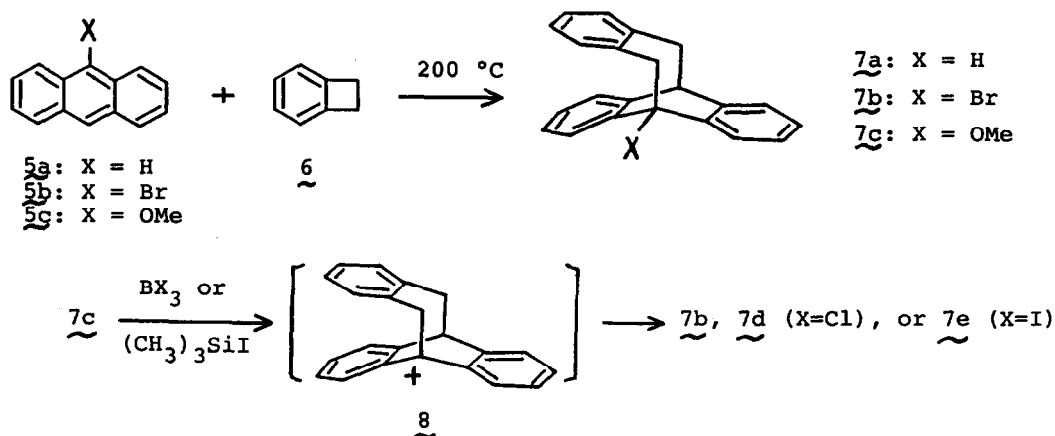
Summary: The title compound which incorporates a strained bridgehead double bond and highly deformed *cis* and *trans* stilbene structures in bicyclo[4.2.2]-decane ring system was synthesized in good yield as an air-sensitive substance. Some reactions pertinent to strain were examined.

Bridgehead olefins have received substantial attention in relation to the limits of applicability of Bredt's rule.¹⁻³⁾ There are now numerous examples of bridgehead olefins in various ring systems. However, there are far fewer examples of bridgehead olefins with high degree of unsaturation such as dienes, trienes, and so on. The most notable example is 9,9',10,10'-tetrahydrodianthracene (1) which consists of sp² carbons only and has two "syn-bent" carbon-carbon double bonds at the bridgeheads.⁴⁾ This compound is thermally remarkably stable and little is known on the chemical properties of the strained double bonds. We have been interested in the related molecule 2, because its less symmetric and less hindered structure would allow examination of the properties pertinent to strain such as cycloadditions, *cis-trans* isomerization, and possible valence isomerization to the elusive [2.2.2]propellane structure. The parent bridgehead diene 3 has been synthesized as a thermally labile and very air-sensitive substance.⁵⁾ In the course of our synthetic studies towards 2, we have prepared the title olefin 4, the dihydro-compound of 2, which has a strained bridgehead double bond too as well as highly deformed *cis* and *trans* stilbene structures.



Nozaki and co-workers have reported that reaction of anthracene (5a) and *o*-quinodimethane yields 5,12[1',2']-benzenodibenzo[a.e]cyclooctene (bishomotriptycene) (7a) which has the required carbon skeleton of 2 and 4.⁶⁾ Application of this reaction to 9-bromoanthracene (5b) under thermolytic conditions of 1,2-dihydrobenzocyclobutene (6) resulted, however, in the formation of a

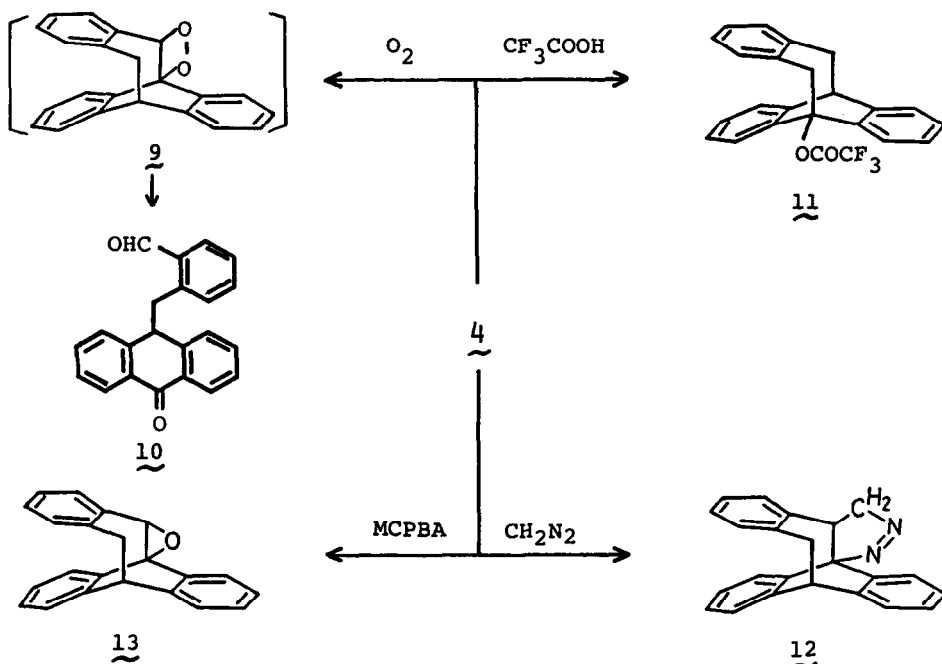
hardly separable, complex mixture containing the expected adduct 7b only as a minor component. Yield of the cycloaddition was much improved when 9-methoxyanthracene (5c) was used as a substrate, and the adduct 7c⁷⁾ was obtained in 70% yield (based on 0.5 equiv. of 6, *o*-dichlorobenzene as solvent, 200 °C, 15.5 h). The clean transformation of 7c to 7b was achieved by treatment with boron tribromide (1.0 equiv., CH₂Cl₂, -78 °C to room temp.). Similarly, 7c yielded the chloride 7d with boron tribromide quantitatively. The iodide 7e⁷⁾ could be also obtained in high yield by reaction of 7c with iodotrimethylsilane (3.0 equiv., CH₂Cl₂, room temp.). These halogenations by the replacement of methoxyl group contrast with normal cleavage of the O-CH₃ bond of 9-methoxytriptycene under the similar conditions, which must reflect higher stability of the bridgehead carbocation 8 relative to rather destabilized 9-triptycyl cation.⁸⁾ Dehydrohalogenation of 7b, 7d, and 7e were effected by *t*-BuOK-18-Crown-6 in benzene or *t*-BuOK in THF around room temperature to give, after chromatographic purification on silica gel, the desired bridgehead olefin 4 as an air-sensitive substance in more than 90% yield (white solid, mp 150 °C). The use of lithium diisopropylamide in THF was unsuccessful resulting in metal-halogen exchange.



While the aliphatic protons of bishomotriptycene 7a appear in the ¹H NMR spectrum as an A₂B system owing to rapid inversion of conformation, those of 4 (at 500 MHz) do as an ABX system at δ 2.89 (d, J = 14.4 Hz), 3.31 (dd, J = 14.4 and 10.3 Hz), and 4.37 (d, J = 10.3 Hz) in accordance with fixation of the conformation. The olefin proton is observed as a singlet at δ 6.83 among the signals of the aromatic protons (δ 6.76-7.46). In the ¹³C NMR spectrum, C-1 and C-2 are observed at δ 150.8 and 120.3, respectively.⁷⁾ The considerably large difference in these chemical shifts may suggest some polarization of the bridgehead double bond in addition to change of hybridization. The UV absorption observed at 260 nm (broad in cyclohexane, ε = 6300) is no more red-shifted than that of 7a but is appreciably blue-shifted than that of *trans* stilbene, although tailing reaches beyond 300 nm. Accordingly, conjugation between the

benzene rings through the bridgehead double bond is severely reduced owing to nearly perpendicular arrangement of the p-orbitals of the benzene rings and those of the double bond.

The olefin 4 is thermally stable at least up to 150 °C in contrast to the ready thermal rearrangement of the dihydro-compound of 1 at 80 °C.⁹⁾ It is unstable, however, in solutions under air, gradually suffering autoxidation: stirring a benzene solution of 4 under oxygen at room temperature for 21 h lead to 70% decomposition of 4 giving rise to the ketoaldehyde 10⁷⁾ in 38% yield. Intermediacy of the dioxetane 9 explains the formation of 10, although its confirmation needs further studies. Formation of dioxetane through reaction of olefins with ground state triplet oxygen is rare and has been reported in the autoxidation of antiaromatic cyclobutadienes.¹⁰⁾ No matter what the mechanism is, the easy autoxidation of 4 is a reflection of strain in the bridgehead double bond.



While inert to acetic acid (pK_a 4.75) at room temperature, 4 is reactive to more acidic trifluoroacetic acid (pK_a 0.23) to give the addition product 11⁷⁾ in 77% yield, probably via the carbocation 8. This result indicates that 4 is less reactive towards electrophilic additions than the fairly extensively studied bicyclo[1.m.n.]nonenes having a bridgehead double bond, the latter readily adding acetic acid.^{11,12)} Diazomethane also added to 4 smoothly and regioselectively at room temperature to form the 1,3-dipolar adduct 12⁷⁾ in 74% yield. Finally, the olefin 4 shows a high reactivity to epoxidation: treatment of a 1:1 mixture of 4 and *trans* stilbene with 0.4 equivalents of *m*-chloroperbenzoic acid at 0 °C yielded the epoxide 13⁷⁾ almost exclusively. In this case, the deconjugation as well as the strain in 4 may be responsible for the

higher reactivity.

Further studies on 4 and attempts on the synthesis of 2 are in progress.

References and Notes

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- 7) 7b: mp 154 °C; $^1\text{H NMR}$ (CDCl_3), δ = 3.18 (2H, d, $J=6.5$ Hz), 4.00 (2H, s), 4.38 (1H, t, $J=6.5$ Hz), 6.83 (4H, m), 7.10 (6H, m), 8.10 (2H, m).
7c: mp 141 °C; $^1\text{H NMR}$ (CDCl_3), δ = 3.08 (2H, d, $J=6.5$ Hz), 3.28 (3H, s), 3.37 (2H, s), 4.32 (1H, t, $J=6.5$ Hz), 6.80 (4H, m), 7.14 (6H, m), 7.47 (2H, m).
7d: mp 144 °C; $^1\text{H NMR}$ (CDCl_3), δ = 3.22 (2H, d, $J=6.5$ Hz), 3.82 (2H, s), 4.21 (1H, t, $J=6.5$ Hz), 6.84 (4H, m), 7.14 (6H, m), 7.97 (2H, m).
7e: mp 160 °C; $^1\text{H NMR}$ (CDCl_3), δ = 3.14 (2H, d, $J=6.5$ Hz), 4.17 (2H, s), 4.38 (1H, t, $J=6.5$ Hz), 6.80 (4H, m), 7.12 (6H, m), 8.20 (2H, m).
10: liquid; IR (liquid), ν = 2730, 1695, 1670 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3), δ = 3.39 (2H, d, $J=6.8$ Hz), 4.51 (1H, t, $J=6.8$ Hz), 6.38 (1H, dd, $J=7.2, 1.5$ Hz), 7.13-7.53 (8H, m), 7.79 (1H, dd, $J=7.5, 1.8$ Hz), 8.20 (2H, m), 9.93 (1H, m).
11: mp 153 °C; $^1\text{H NMR}$ (CDCl_3), δ = 3.12 (2H, d, $J=6.8$ Hz), 3.58 (2H, s), 4.34 (1H, t, $J=6.8$ Hz), 6.65-7.25 (12H, m).
12: mp 156 °C; $^1\text{H NMR}$ (CDCl_3), δ = 3.11 (1H, dd, $J=14.4, 2.0$ Hz), 3.48 (1H, dd, $J=14.4, 10.4$ Hz), 3.91 (1H, s), 4.43 (1H, dd, $J=10.4, 2.0$ Hz), 6.71-7.51 (12H, m).
13: mp 185 °C; $^1\text{H NMR}$ (CDCl_3), δ = 3.12 (1H, dd, $J=14.4, 1.9$ Hz), 3.51 (1H, dd, $J=10.0, 6.0$ Hz), 3.54 (1H, dd, $J=14.4, 11.2$ Hz), 4.45 (1H, dd, $J=11.2, 1.9$ Hz), 4.80 (1H, dd, $J=19.2, 10.0$ Hz), 5.43 (1H, dd, $J=19.2, 6.0$ Hz), 6.68-7.54 (1.9 H, m).
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- 12) Direct comparison with bicyclo[1.m.n]nonenes in regard to strain energy is difficult because the stability of the intermediate carbocation 8 should be different from that of the carbocations from bicyclononenes.

(Received in Japan 12 February 1988)