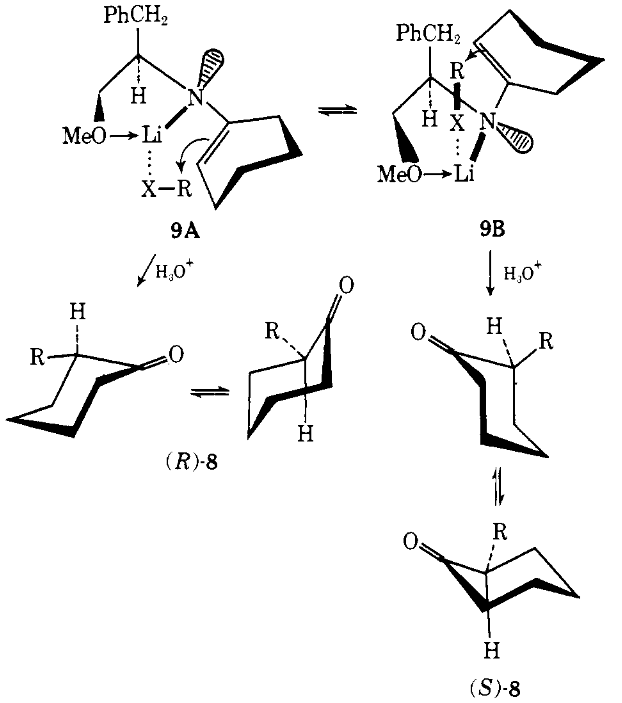
it appears to vindicate our earlier prediction for implementing an efficient enantioselective alkylation. The presence of the methoxyl group in **6** is undoubtedly playing a key role in this system. When **7** is metalated, the lithium ion becomes coordinated to the methoxyl ligand and results in essentially two conformers, **9A** and **9B**, related only by nitrogen lone pair inversion. Since **9A** represents, in effect, a *trans*-1,2-cyclopentane whereas **9B** represents a *cis*-1,2-cyclopentane, it would be expected that the equilibrium should lie heavily in favor of **9A**. If the valid assumption, based on earlier studies,[5] is made that the entering alkyl halide aligns itself so that the halogen is coordinated to the lithium ion while the alkyl group (R) is disposed so that the π-bond of the cyclohexenyl ring is directly behind it, this would provide the proper orientation for alkylation. To fulfill this alignment, it can be seen that **9A** allows RX to reside in a much less encumbered arena than that shown for **9B**. These approaches (**9A** and **9B**) to the transition state should be sufficiently different to provide a large $\Delta\Delta G^{\ddagger}$. If RX enters **9A** as shown, this would lead to the *R*-ketone as is actually found to be the case in this study.



Further studies are in progress to utilize this useful new alkylation to provide more complex chiral ketones via annelations as well as other carbonyl derivatives.

Acknowledgment. The authors are grateful to the National Science Foundation (MPS 73-04792) and the National Institutes of Health for generous financial support of our program.

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(6) We have recently prepared (−)-**6** from (*S*)-(−)-ethyl phenylalinate hydrochloride ([α]D −8.45° (*c* 3.04, H_2O)) by sodium borohydride reduction to (*S*)-(−)-phenylalinol ([α]D −25.3 (*c* 1.4, EtOH); lit.[7] reports [α]D −25.6° (*c* 1.04, EtOH)) followed by treatment with potassium hydride–methyl iodide, [α]D −14.4° (*c* 6.2, benzene). This route to (−)- or (+)-**6** is presumably more convenient and will allow the asymmetric synthesis of *either* optical antipode of 2-alkylcyclohexanones (Dr. G. Poindexter, research in progress).

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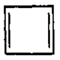
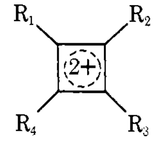
Novel Aromatic Systems. 5.[1] The 1,2-Dimethylbenzocyclobutadiene Dication, an 8C-6π Hückeloid System

Sir:

Cyclobutadiene **1** and its derivatives are known to be very reactive and can only be isolated via photosynthesis using matrix isolation techniques at low temperatures.[2] The removal of two electrons from **1** should result in the formation of 2π Huckeloid cyclobutadiene dication **2** with aromatic character.[3]


1

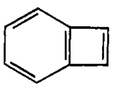

2



3

Although the parent dication **2** to date was not yet obtained, a number of substituted cyclobutadiene dications, **3**, have been prepared and directly studied by spectroscopic methods.[1,4]

The monobenzo derivative of cyclobutadiene, benzocyclobutadiene (**4**), has also been subjected to extensive search,[3a,5] but its isolation was only successful recently[6] despite the fact that several of its substituted derivatives were known for years.[3a,7] Benzocyclobutadiene, in principle, should also give a stable 6π aromatic dication **5** by two-electron oxidation. The 10π benzocyclobutadiene dianion **6** is also predicted to be aromatic.[3c,5b,8] We now wish to report the preparation and NMR spectroscopic characterization of the 1,2-dimethylbenzocyclobutadiene dication **7**, the first 6π-aromatic benzocyclobutadiene dication.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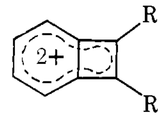
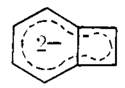
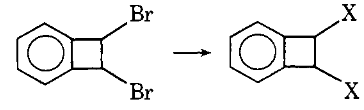


5, R = H
7, R = CH_3



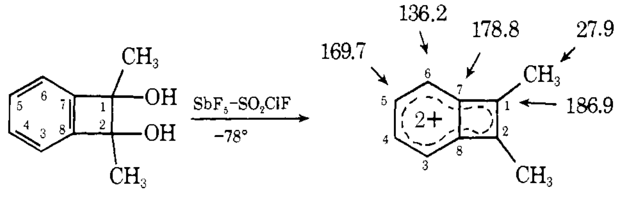
6

Although the acetolysis of *trans*-1,2-dibromobenzocyclobutene (**8**), in the absence of water, gave the corresponding *trans*-1,2-diacetate **9**,[9] ionization of 1,2-dibromo- (**8**), 1,2-diiodo- (**10**), and 1,2-dihydroxybenzocyclobutenes (**11**) in either SbF_5-SO_2ClF, FSO_3H-SbF_5-SO_2ClF, or HF-SbF_5-SO_2ClF solutions at −120° failed to give any evidence



8
9, X = OAc
10, X = I
11, X = OH

for the formation of the parent 1,2-benzocyclobutadiene dication **5**, and resulted only in the formation of unidentifiable polymeric products.[10] The 1,2-dimethylbenzocyclobutadiene dication **7**, however, could be prepared by careful addition of a suspension of *cis*- or *trans*-1,2-dimethylbenzocyclobutene-1,2-diols (**12** and **13**)[11] in SO_2ClF to a saturated solution of SbF_5 in SO_2ClF at dry ice-acetone bath temperature (ca. −78°). The resulting deep red solution of **7** is only stable below −30° and decomposes at higher temperatures.

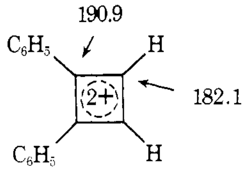


12, cis-
13, trans-

7

The 60-MHz proton NMR spectrum of **7** shows two equivalent methyl group absorption at δ 4.42 (singlet), and two broad deshielded two-proton aromatic resonances at δ 9.70 (overlaping with the hydronium ion peak) and at δ 10.08.[12] The natural abundance carbon-13 NMR spectrum obtained by Fourier transform technique (proton decoupled) consists of five carbon resonances at $\delta_{^{13}C}$ 27.9 (quartet, J_{C-H} = 136.8 Hz), 136.2 (doublet, J_{C-H} = 172.4 Hz), 169.7 (doublet, J_{C-H} = 182.8 Hz), 178.8 (singlet), and 186.9 (singlet). Carbon shift assignments are shown on structure **7**.[13]

Comparing the chemical shifts of cyclobutadiene ring carbons, $\delta_{^{13}C}$ 178.8 (C_7 and C_8) and 186.9 (C_1 and C_2), obtained for the 1,2-dimethylbenzocyclobutadiene dication **7** to those for the 1,2-diphenyl- (**14,** $\delta_{^{13}C}$ 182.1 and 190.9), tetraphenyl- (**15,** $\delta_{^{13}C}$ 173.4) and tetramethylcyclobutadiene (**16,** $\delta_{^{13}C}$ 209.7) dications[1] confirms that ion **7** is indeed also a fully delocalized 6π aromatic system, as are the compared cyclobutadiene dications.



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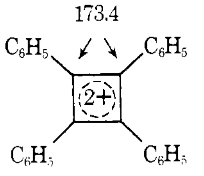

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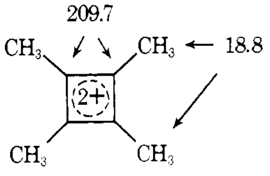

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Acknowledgement. Support of our work by the National Science Foundation is acknowledged.

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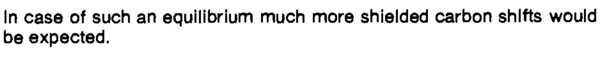
(10) Ionization of secondary dialcohol or dihalide derivatives, **8**, **10**, and **11** apparently was complicated by complexation of SbF_5 with the benzo ring. On the other hand, ionization of tertiary alcohols **12** and **13** proceeded without difficulty.

(11) (a) M. P. Cava, D. R. Napier, and R. J. Pohl, *J. Am. Chem. Soc.*, **85**, 2076 (1963); (b) M. P. Cava, R. J. Pohl, and M. J. Mitchell, *ibid.*, **85**, 2080 (1963); *Tetrahedron Lett.*, 825 (1962).

(12) ^1H and ^{13}C NMR shifts are given in parts per million from external (capillary) tetramethylsilane.

(13) The observation of symmetrical NMR spectra for the dication **7** with substantially deshielded proton and carbon shifts seems to eliminate the possibility of an equilibrium between a mono- and dication such as



In case of such an equilibrium much more shielded carbon shifts would be expected.

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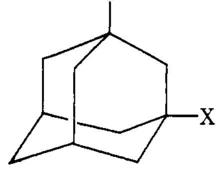
Fluorination at Saturated Carbon. 1. Direct Substitution of Adamantanes

Sir:

While investigating the fluorination of amides[1] we exposed *N*-trifluoroacetyladamantadine (**1a**) to CF_3OF. Surprisingly, the substrate underwent clean fluorination to 3-fluoro-*N*-trifluoroacetyladamantadine (**1b**). Adamantane itself with CF_3OF afforded 1-fluoroadamantane (**2b**). The substrates **4** and **5** afforded mixtures of fluorinated products which from fluorine NMR clearly bore secondary fluorine substituents.



1a, X = CF_3CONH; Y = H
1b, X = CF_3CONH; Y = F
2a, X = Y = H
2b, X = H; Y = F
3a, X = $OCOCF_3$; Y = H
3b, X = $OCOCF_3$; Y = F
3c, X = OH; Y = H
3d, X = OH; Y = F

Inasmuch as direct replacement of unactivated hydrogen atoms has appeared generally to be a consequence of a free radical reaction,[2] we sought to influence the initiation of this mild, selective, presumed radical fluorination. It is appropriate to note at this point that radical fluorinations with CF_3OF