another. A positive rotation brings the methyl carbon towards eclipse with N–H, while a negative rotation brings the methyl carbon toward a methylene carbon. All angles are fairly near 0°, except for two near 120° which represent another staggered conformation in which one methyl carbon projects axially from the methylene carbon in a direction opposite from that of the N–H bond. No previous studies of the conformations of Et_3NH^+ ions have appeared, and we do not recommend them as ordered positive ions in the studies of structures of the negative ions, unless the location of H atoms is a critical part of the study.

Acknowledgments. We wish to thank Dr. M. F. Hawthorne for providing a sample of $(Et_3NH)_3B_{20}H_{18}NO$, Dr. R. L. Lewin for determining the unit cell and space group of this compound, the Office of Naval Research and the Advanced Research Projects Agency for grants supporting this work, and the National Science Foundation for a predoctoral fellowship for C. H. S.

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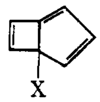
Detection of Cyclobutadienocyclopentadienyl Anion

Sir:

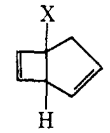
In principle, cyclic antiaromatic systems of four π electrons, such as cyclobutadiene, can be stabilized in two ways by fusion to other conjugated rings. Fusion to rings with six π electrons, as in biphenylene, is stabilizing because of diminished bond order in the cyclobutadiene ring even though the over-all system retains $4n$ π electrons.[1] On the other hand, fusion of two $4n$ π electron systems produces a composite with $4n + 2$ π electrons on the periphery; a number of examples are known[2] in which cyclooctatetraene is fused to another $4n$ π electron ring, but the energetic situation for such compounds is not yet completely clear.

The bicyclo[3.2.0.]heptatrienyl system is particularly interesting in this regard. The cation Ia, a bridged tropylium ion, is the formal product of fusion of cyclobutadiene and cyclopentadienyl cation; the anion Ib is on its periphery a cycloheptatrienyl anion, but it is also a cyclopentadienyl anion. HMO calculations predict a total π energy of 8.906β for both species, and a ΔDE of 1.918β for ionization of a covalent bicycloheptatriene (*e.g.*, Ic) to either species. The HMO calculated ΔDE for converting cyclopentadiene to its anion is only 2.000β, so Ic should be comparably acidic. As an approach to Ia and Ib we have generated the hydrocarbon Ic. This strained triene is so labile that we have not yet been able to isolate it undimerized, but it has still been possible to demonstrate that the ionization of Ic to the anion Ib is a facile process.

Treatment of 1-methoxybicyclo[3.2.0]hepta-3,6-diene (IIa)[3] with BCl_3 at −75° afforded the chlorodiene IIb[4] in 63% yield. On standing for 3 hr at 25° with 0.2 *M* KO-*t*-Bu in tetrahydrofuran, IIb eliminates HCl to produce a dimer of the triene Ic, *m/e* 180; the nmr data are consistent with a structure derived by 1,4 addition of the cyclopentadiene in Ic to the strained trisubstituted double bond of a second molecule of Ic. Triene Ic can also be trapped as an adduct with diphenylisobenzofuran, present during the base treatment of IIb. The adduct, *m/e* 360, is from the nmr data a mixture of the two stereoisomers formed by addition across the new strained double bond in Ic.



Ia, X = +
b, X = −
c, X = H



IIa, X = OCH_3
b, X = Cl

The same dimer, as well as the adduct with diphenylisobenzofuran, can be prepared by reaction of IIb with N-bromosuccinimide and dehalogenation of the resulting bromo-IIb[4] with Li (Hg) in ether.

Dimerization of Ic is fairly rapid: treatment of a 5×10^{-4} *M* solution of IIb with 0.1 *M* potassium *t*-butoxide in tetrahydrofuran for 5 min at 25°, followed by neutralization, leads to partial development of a new chromophore, λ_{max} 316 nm, which decays with second-order kinetics, $t_{1/2} \sim 3$ hr. Assuming that this uv absorption is due to triene Ic, at preparative concentrations it would have a half-life of a few minutes at best. Nonetheless, when the elimination of HCl from IIb is performed by stirring with 0.2 *M* KO-*t*-Bu in 74 ml of tetrahydrofuran and 6 ml of *t*-BuOD for 4 hr at 25°, a 40% yield of the dimer was formed containing 65% of 2.0 D/dimer. The 60% of recovered IIb has no deuterium, and the dimer does not exchange under these conditions. When some dimethyl-d_6 sulfoxide is added to the dehydrochlorination mixture the product dimer has 100% of 2.0 D/dimer. The nmr spectrum of deuterated dimer is consistent with dimerization of I (X = D). Apparently hydrocarbon Ic exchanges *via* anion Ib at a rate comparable to its rapid dimerization; while it is difficult to relate this observation to a precise pK_a for Ic, it does suggest that the HMO prediction of acidity in Ic is correct.

Acknowledgment. Support of this work by the National Institutes of Health and by the award of a NATO Postdoctoral Fellowship to R. G. B. is gratefully acknowledged.

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[4] Mass and nmr spectra consistent with the assigned structure.

Cations and Cation Radicals of Porphyrins and Ethyl Chlorophyllide *a*

Sir:

The polarographic oxidation of a variety of porphyrins has been studied in butyronitrile[1] and in methylene chloride.[2] Oxidation proceeds *via* two well-defined one-

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