(6) 2-Methylimidazole produces a significantly smaller pyrrole isotropic shift for **1** than do nonhindered imidazoles (Figure 3F). This fact, together with the lack of a resolved ESR spectrum for bis-2-methylimidazole tetraphenylporphinatoiron(III),[15] and differences in the low-temperature Mössbauer spectra of hindered vs. nonhindered imidazole complexes[22] suggest the possibility of different d-orbital energies for hindered and nonhindered imidazole complexes of **1**.

(7) The NMR resonance of the pyrrole protons of the mixed axial ligand complex of **1** can be obtained by titration of the bis-2-methylimidazole complex with *N*-methylimidazole (Figure 3F). The mixed-ligand complex also has its pyrrole resonance significantly downfield of that of the bis-*N*-methylimidazole complex of **1**.

(8) The pyrrole resonances of the mono-2-methylimidazole complex of **5** show the largest spread found so far, which may suggest a role for bond strain (tension) or lengthening of the Fe–N(2-methylimidazole) bond in increasing the spread, as suggested by Goff in the accompanying communication.[23] However, it is difficult to understand how two sterically hindered ligands can give rise to a decreased spread, while only one in combination with a nonhindered imidazole gives rise to an increased spread of the pyrrole-H resonances.

In summary, the single pyrrole-H resonance of bisimidazole tetraphenylporphinatoiron(III) is split into three or four peaks when one substituent is placed on an *o*-phenyl position. We speculate that this splitting and its magnitude are due to a sensitive balance of three factors: restricted rotation of one axial ligand by the *o*-phenyl substituent, the symmetry-breaking effect of that substituent, and, possibly, the axial ligand bond length and/or iron orbital energies. Further NMR, ESR, and structural studies now underway on these complexes and related bis covalently attached axially liganded iron(III) porphyrins may shed further light on the interrelationship of these effects.

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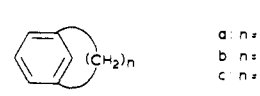
Tricyclo[6.1.1.0^{3,9}]deca-2,8(10)-diene, the Dewar Isomer of [4]Metacyclophane

Sir:

Recently, we reported the formation of [5]metacyclophane (**1b**), so far the smallest member of the metacyclophane series.[1] While our attempts to synthesize the next lower homologue [4]metacyclophane (**1a**) have so far not met with success, they led to the unexpected discovery of the highly strained Dewar isomer of **1a**, tricyclo[6.1.1.0^{3,9}]deca-2,8(10)-diene (**2**), which has the additional interesting feature of being a double Bredt olefin. Previously, [5]- and [6]metacyclophane had been ob-



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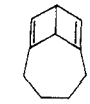

2

tained as byproducts in the synthesis of the corresponding 3,3′-bridged bicyclopropenyls. To make these interesting compounds more easily available, we devised a more rational approach. The new route resembles the general approach to [6]- and higher metacyclophanes of Hirano et al.,[2] however, with important modifications which make it more suitable for the preparation of the sensitive smaller members of the group such as **1a** and **1b**.

Addition of chlorocarbene to 5,6,7,8-tetrahydroindan-2-ol[3] yielded an ~2:1 mixture of isomeric endo alcohols **3** (94% yield) (Scheme I). The assignment of the stereochemistry of **3**-anti is based on the directing effect of the hydroxyl group in carbene additions, for which there is some precedent in literature[4] and which also manifests itself in the stereochemistry of **3**-syn; the latter follows from the X-ray crystal structure determination of **4**,[5] and **3**-anti and **3**-syn were correlated by reduction with sodium in liquid ammonia to the same *endo*-tricyclo[4.3.1.0^{1,6}]decan-8-ol.[3] When the mixture of **3** was treated with 2 equiv of tosyl chloride in pyridine,[6] **3**-syn, the minor component, was tosylated to yield **4** (70%), while the major isomer, **3**-anti, was hardly affected. Treatment of **4** with 1 equiv of *t*-BuOK in Me_2SO afforded **6**-syn which, upon treatment at room temperature with an excess of *t*-BuOK in Me_2SO, slowly polymerized. However, **3**-anti could be converted into its mesylate **5** (90%), which on treatment with 1 equiv of *t*-BuOK in Me_2SO afforded **6**-anti (70%). The reaction of **5** or of **6**-anti with 3 to 5 equiv of *t*-BuOK in Me_2SO (16 to 40 h at room temperature) yielded three isomeric dienes, **2**, **7**, and **8**. The structures of **2**, **7**, and **8** were assigned on the basis of their spectral[7] and chemical properties. Catalytic reduction (H_2, 10% Pd/C) of **2**, **7**, or **8** produced bicyclo[4.3.1]decane (**9**);[8] treatment of **2** or **7** with diimide afforded tricyclo[6.1.1.0^{3,9}]decane (**10**).[9]

The formation of **2**, though not fully understood at present, may be rationalized as follows. Upon treatment with *t*-BuOK, both **6**-syn and **6**-anti split off an allylic proton to give the

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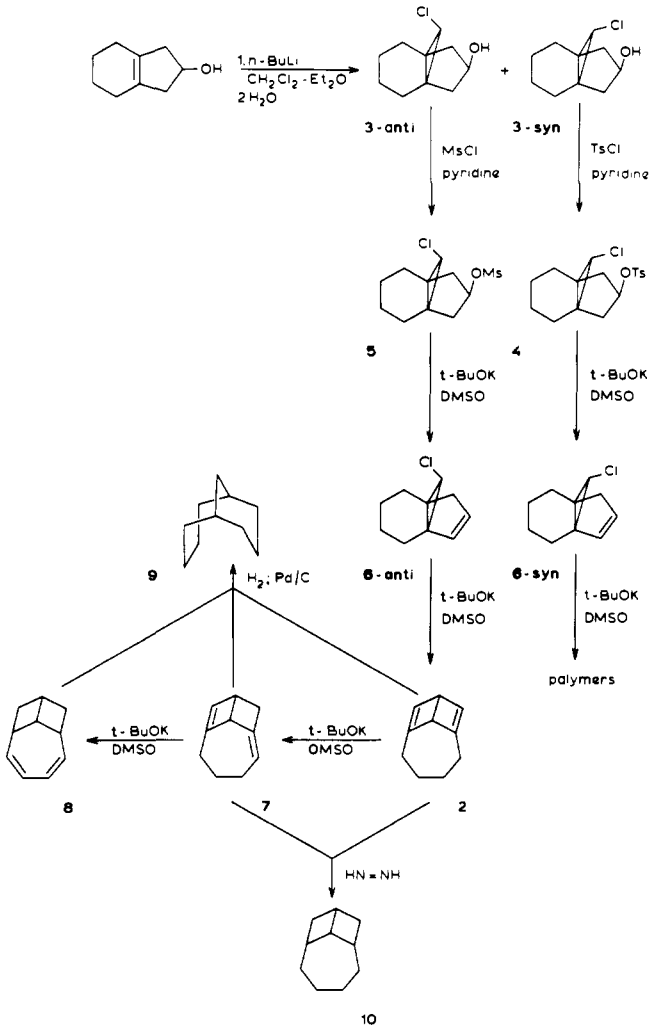
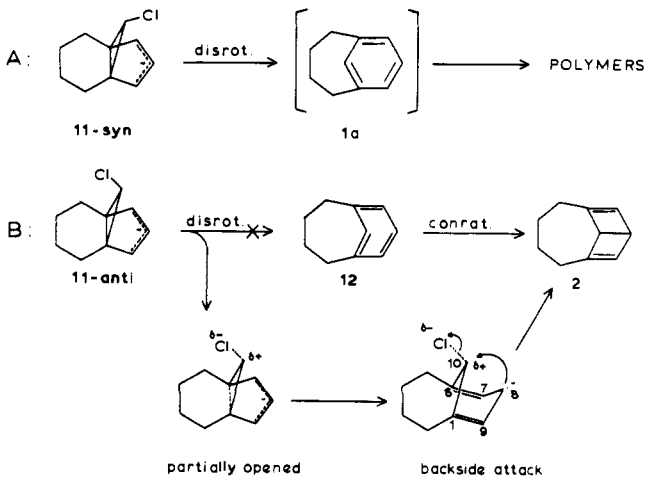
Scheme I



Scheme II



corresponding anions, **11**-syn and **11**-anti, respectively (Scheme II). **11**-syn might yield **1a** by loss of chloride ion in a symmetry-allowed disrotatory opening of the cyclopropane ring, unless strain in **1a** is prohibitive; it is feasible that either instability of **1a** or escape reactions are responsible for the observed formation of polymers. An analogous course of reaction is less probable for **11**-anti, as it would furnish the highly strained *trans*-benzene **12**; in principle, the latter could lead to **2** in a thermally allowed conrotatory process. It seems more likely that, while chloride ion is beginning to leave and the cyclopropane ring is partially opening, the developing negative charge at C(8) of the pentadienyl anion furnishes nucleophilic assistance toward C(10), while C(8) and C(10) move toward each other, thus establishing the central bond of the Dewar benzene. Alternative routes are conceivable and cannot be excluded; however, carbene formation, initiated by proton abstraction at C(10), is less likely in view of the difference in behavior between **6**-syn and **6**-anti. Isolation of **2** and **7** by preparative gas chromatography and separate treatment of both isomers with *t*-BuOK in Me_2SO proved that **2** rearranges to **7** and **7** to **8**. This may be explained by a sequence of deprotonations and reprotonations in allylic positions, leading consecutively to less strained isomers. While **7** is the result of one such sequence of reactions from **2**, it is remarkable that no further intermediates between **7** and **8** could be detected.

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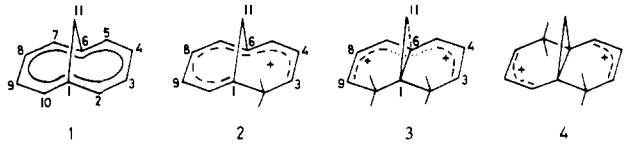
Aromatic Protonation. 5.[1] Diprotonated 1,6-Methano[10]annulene. NMR Evidence for a Cyclopropyldicarbinyl Dication Moiety

Sir:

Recently we reported on the high reactivity of the 1,6-methano[10]annulene system (**1**)[2] toward sulfonation.[3] For a better understanding of the electrophilic aromatic substitution of **1**[4] and in relation to our recent interest in arenium ions,[5] we were inspired to investigate the protonation of **1**. Winstein et al., already a decade ago, described the monoprotonation of **1** by FSO_3H yielding the stable cation **2**, the structure of



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