(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.

References and Notes

(1) G. N. LaMar and F. A. Walker in "The Porphyrins", Vol. IV, D. Dolphin, Ed., Academic Press, New York, 1979, pp 61–157, and references therein.
(2) G. N. LaMar and F. A. Walker, *Ann. N.Y. Acad. Sci.*, **206**, 328 (1973); *J. Am. Chem. Soc.*, **95**, 1782 (1973).
(3) G. N. LaMar, T. J. Bold, and J. D. Satterlee, *Biochim. Biophys. Acta*, **498**, 189 (1977); G. N. LaMar, T. J. DelGaudio, and J. S. Frye, *ibid.*, **498**, 422 (1977); G. N. LaMar, D. B. Viscio, K. M. Smith, W. S. Gaughey, and M. L. Smith, *J. Am. Chem. Soc.*, **100**, 8085 (1978).
(4) A. Kowalsky, *Biochemistry*, **4**, 2382 (1965); K. Wuthrich, *Struct. Bonding (Berlin)*, **8**, 53 (1970).
(5) R. G. Shulman, S. H. Glarum, and M. Karplus, *J. Mol. Biol.*, **57**, 93 (1971).
(6) A. Mayer, S. Ogawa, R. G. Shulman, T. Yamane, J. A. S. Cavaleiro, A. M. d'A. Rocha Consalves, G. W. Kenner, and K. M. Smith, *J. Mol. Biol.*, **86**, 749 (1974).
(7) G. N. LaMar, M. Overkamp, H. Sick, and K. Gersonde, *Biochemistry*, **17**, 352 (1978); G. N. LaMar, D. B. Viscio, K. Gersonde, and H. Sick, *ibid.*, **17**, 361 (1978).
(8) Y.-Y. H. Chao, R. Bersohn, and P. Aisen, *Biochemistry*, **18**, 774 (1979).
(9) R. M. Keller and K. Wuthrich, *Biochim. Biophys. Acta*, **285**, 326 (1972); R. Keller, O. Groudinsky, and K. Wuthrich, *ibid.*, **328**, 233 (1973); R. Keller, O. Groudinsky, and K. Wuthrich, *ibid.*, **427**, 497 (1976).
(10) H. C. Longuet-Higgins, C. W. Rector, and J. R. Platt, *J. Chem. Phys.*, **18**, 1174 (1950).
(11) F. S. Matthews, P. Argos, and M. Levine, *Cold Spring Harbor Symp. Quant. Biol.*, **36**, 387 (1971).
(12) T. G. Traylor and A. P. Berzinis, *J. Am. Chem. Soc.*, **102**, 2844 (1980).
(13) F. A. Walker and M. Benson, *J. Am. Chem. Soc.*, in press.
(14) M. Benson, unpublished work.
(15) F. A. Walker and D. Reis, manuscript in preparation.
(16) 4(5)-Phenylimidazole is a mixture of the two molecular structures resulting from rapid tautomerism of the N–H proton between the two nitrogens. It is probable that only the 5-phenylimidazole tautomer can bind to compounds **1–5** to produce non-sterically-hindered complexes.
(17) F. A. Walker, M.-W. Lo, and M. T. Ree, *J. Am. Chem. Soc.*, **98**, 5552 (1976).
(18) T. Mashiko, J.-C. Marchon, D. T. Musser, C. A. Reed, M. E. Kastner, and W. R. Scheidt, *J. Am. Chem. Soc.*, **101**, 3653 (1979).
(19) M. A. Bobrik and F. A. Walker, *J. Am. Chem. Soc.*, in press.
(20) J. L. Hoard, Abstracts of Papers, the 175th National Meeting of the American Chemical Society, Anaheim, Calif., March 13–17, 1978, INOR 15.
(21) D. M. Collins, R. Countryman, and J. L. Hoard, *J. Am. Chem. Soc.*, **94**, 2066 (1972).
(22) F. Parak, M. Buckl, and F. A. Walker, unpublished work.
(23) H. Goff, *J. Am. Chem. Soc.*, preceding paper in this issue.
(24) Recipient, NIH Research Career Development Award, 1976–1981.
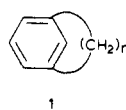
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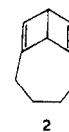*San Francisco, California 94132*

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Tricyclo[6.1.1.0³,⁹]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[6.1.1.0³,⁹]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-


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[4.3.1.0¹,⁶]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 Me₂SO afforded 6-syn which, upon treatment at room temperature with an excess of *t*-BuOK in Me₂SO, slowly polymerized. However, 3-anti could be converted into its mesylate **5** (90%), which on treatment with 1 equiv of *t*-BuOK in Me₂SO afforded 6-anti (70%). The reaction of **5** or of 6-anti with 3 to 5 equiv of *t*-BuOK in Me₂SO (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 (H₂, 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[6.1.1.0³,⁹]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

Scheme I

Scheme II

A:

11-syn   1a   POLYMERS

B:

11-anti   12   2

partially opened   backside attack
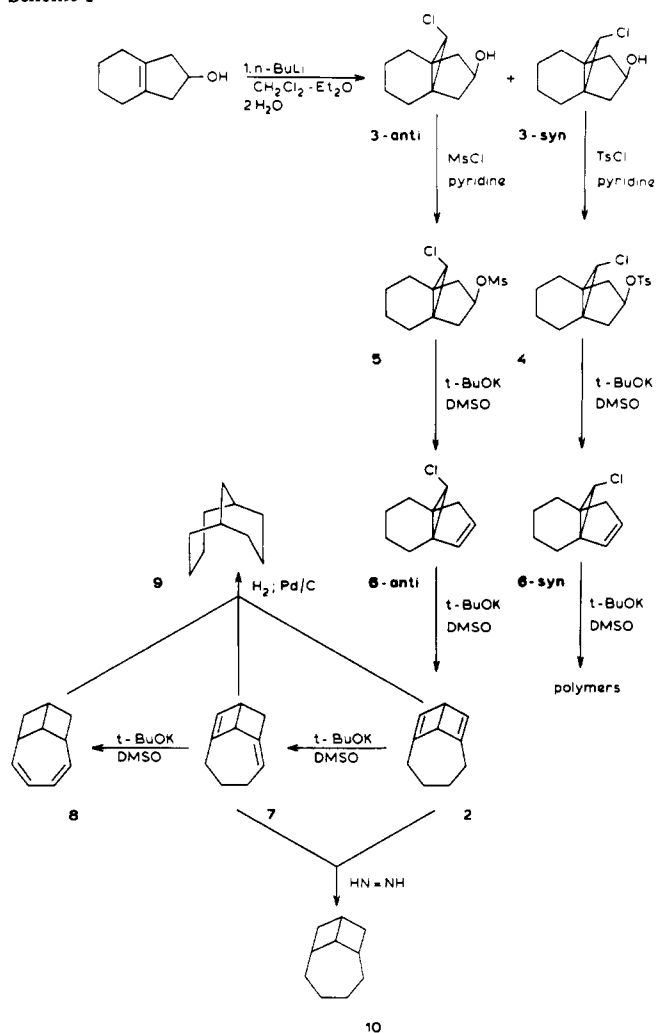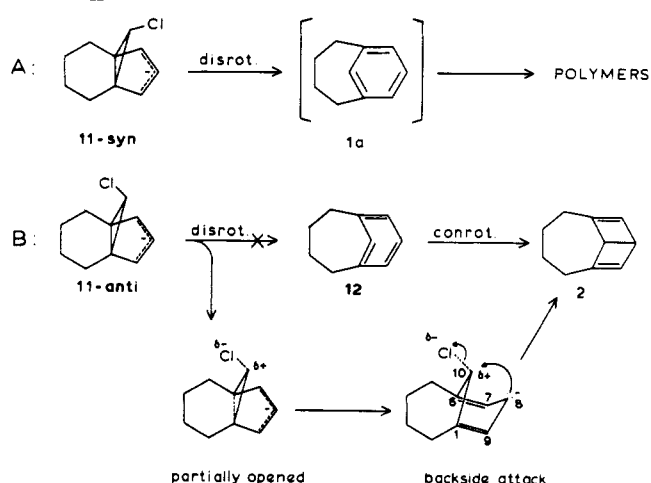
corresponding anions, **11-syn** and **11-anti**, respectively (Scheme II). **11-syn** might yield **1a** by loss of chloride ion in a symmetry-allowed disrotatory opening of the cyclopropane ring, unless strain in **1a** is prohibitive; it is feasible that either instability of **1a** or escape reactions 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 Me₂SO 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.

References and Notes

(1) van Straten, J. W.; de Wolf, W. H.; Bickelhaupt, F. *Tetrahedron Lett.* **1977**, 4667.
(2) Hirano, S.; Hara, H.; Hiyama, T.; Fujita, S.; Nozaki, H. *Tetrahedron* **1975**, *31*, 2219.
(3) Starr, J. E.; Eastman, R. H. *J. Org. Chem.* **1966**, *31*, 1393.
(4) Fleming, I.; Thomas, E. J. *Tetrahedron* **1972**, *28*, 5003.
(5) The X-ray analysis was performed by Dr. C. H. Stam from the University of Amsterdam and is to be published.
(6) Fieser, L. F.; Fieser, M. "Reagents for Organic Synthesis"; Wiley: New York, London, Sydney, 1967; Vol. 1, p 1180.
(7) Tricyclo[6.1.1.0^{3,9}]deca-2,8(10)-diene (**2**): ^{1}H NMR (CDCl₃, δ in ppm) 6.27 (m, 2 H), 3.82 (m, 1 H), 3.71 (m, 1 H), 2.28 (m, 4 H), 1.78 (m, 4 H); ^{13}C NMR (CDCl₃, δ in ppm) 164.6 (s, C₃,₈), 137.9 (d, C₂,₁₀), 56.4 (d, C₉), 44.6 (d, C₁), 31.6 (t, C₄,₇), 28.3 (t, C₅,₆); MS *m/z* (% fragment) 132 (22, C₁₀H₁₂$^{+}$·) (found 132.0936, C₁₀H₁₂ calcd 132.0939), 91 (100, C₇H₇$^{+}$·); UV (cyclohexane) 242 nm (sh), end absorption. Tricyclo[6.1.1.0^{3,9}]deca-2,7-diene (**7**): ^{1}H NMR (CDCl₃) 5.59 (d of d, *J* = 2, 1.5 Hz, 1 H), 5.49 (m, 1 H), 3.83 (m, 1 H), 3.05 (d of d of d, *J* = 7.5, 2, 1.5 Hz, 1 H), 2.9–1.9 (m, 6 H), 1.85–1.45 (m, 2 H); ^{13}C NMR (CDCl₃) 157.6 (s, C₃), 147.1 (s, C₈), 126.8 (d, *J* = 172 Hz, C₂), 126.0 (d, *J* = 154 Hz, C₇), 54.5 (d, *J* = 156 Hz, C₉), 35.4 (d, *J* = 154 Hz, C₁), 31.8 and 31.2 (d, *J* = 124 Hz, C₄ and C₆), 30.2 (t, *J* = 136 Hz, C₁₀), 27.3 (t, *J* = 126 Hz, C₅); MS 132 (46, C₁₀H₁₂$^{+}$·) (found 132.0936, C₁₀H₁₂ calcd 132.0939), 117 (100, C₉H₉$^{+}$·); UV (cyclohexane) 229 nm (sh), end absorption. Tricyclo[6.1.1.0^{3,9}]deca-4,6-diene (**8**): ^{1}H NMR (CDCl₃) 5.85 (m, 4 H), 3.41 (m, 2 H), 2.55 (m, 4 H), 2.10 (m, 2 H); ^{13}C NMR (CDCl₃) 137.3 (d, C₄,₇), 124.6 (d, C₅,₆), 46.4 (d, C₉), 38.4 (d, C₃,₈), 34.2 (t, C₂,₁₀), 28.6 (d, C₁); MS 132 (65, C₁₀H₁₂$^{+}$·) (found 132.0939, C₁₀H₁₂ calcd 132.0939), 104 (100, C₈H₈$^{+}$·); UV (cyclohexane) 265 nm.
(8) del Cima, F.; Pietra, F. *J. Chem. Soc., Perkin Trans. 1* **1974**, 1710.
(9) Tricyclo[6.1.1.0^{3,9}]decane (**10**): ^{1}H NMR (CDCl₃) 1.3–2.1 (m, 10 H), 2.3–3.1 (m, 6 H); ^{13}C NMR (CDCl₃) 41.9 (d, *J* = 140 Hz, C(9) or C(1)), 36.0 (d, *J* = 136 Hz, C₃,₈), 34.8 (t, *J* = 133 Hz, C₂,₁₀), 31.4 (t, *J* = 124 Hz, C₄,₇), 29.6 (d, *J* = 150 Hz, C(1) or C(9)), 26.4 (t, *J* = 126 Hz, C₅,₆); MS 136 (2, C₁₀H₁₆$^{+}$·) (found 136.1249, C₁₀H₁₆ calcd 136.1252), 95 (100, C₇H₁₁$^{+}$·).

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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 FSO₃H yielding the stable cation **2**, the structure of

1   2   3   4