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Efficient Hydrogenation of Sterically Hindered Olefins with Borane−Methyl Sulfide Complex

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Sterically hindered olefins are efficiently reduced to the corresponding alkanes by the borane−methyl sulfide (BMS) complex at room temperature (or below) in dichloromethane containing a mild one-electron oxidant (such as an aromatic cation radical) or by the passage of an anodic current. In an alternative procedure, the hydrogenation of the same (electron-rich) olefins with the BMS complex (in the absence of a one-electron oxidant) is also carried out in the presence of a strong Brønsted acid (such as HBF_4). In the oxidative activation, olefin cation radicals are the first observable intermediates, and separate experiments (including transient electrochemistry) confirm the facile reduction of the olefin cation radical by borane to produce the corresponding alkane. The direct protonation of olefins produces carbocationic intermediates which are also efficiently reduced by borane to the corresponding alkanes. The intermediacy of both olefin cation radicals and carbocations in the hydrogenation procedure with borane is discussed.

Introduction

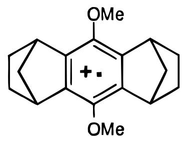
Catalytic hydrogenation (in the presence of transition metal catalysts) is the method most often used for olefin reduction,[1] but its application to alkenes multiply substituted with alkyl and aryl groups generally requires high temperatures and high pressures, and sometimes fails even under these forcing conditions.[2,3] For example, all our abortive attempts to reduce the double bond in 2,3-diarylbicyclo[2.2.2]oct-2-ene (**1**) by catalytic hydrogenation (even at high hydrogen pressures)[4] were attributed to the steric crowding around the double bond by the bicyclooctane framework and the vicinal aryl groups. Likewise, Nelsen and Teasley found that the sterically crowded adamantylideneadamantane was completely inert under the conditions of catalytic and ionic hydrogenations.[5]

Alkyl- and aryl-substituted olefins are known to be electron rich.[6] Therefore, the ready oxidation of the olefin **1** to the corresponding cation radical $\mathbf{1}^{\bullet+}$ with tris-(4-bromophenyl)aminium hexachloroantimonate, prompted us to employ the hydrogenation procedure of Mirafzal and Bauld[7] using tri-*n*-butyltin hydride as the hydrogen source. However, this procedure did not lead to the desired product in appreciable yield (< 5%),[8] despite the ready oxidation of olefin **1** to the corresponding cation radical.

An alternative hydrogenation procedure, especially suited for the sterically crowded olefins, was clearly needed. Our subsequent experimentation revealed that the hydrogenation of such sterically hindered olefins can be effected by replacing tri-*n*-butyltin hydride with the borane−methyl sulfide (BMS) complex[9] as a hydrogen source, and the oxidation brought about by the addition of a mild one-electron oxidant or by an equivalent electrochemical (anodic) method. We also find that the hydrogenation of the same olefins with borane−methyl sulfide complex can be carried out (without one-electron oxidant) in the presence of a strong Brønsted acid. Accordingly, we will discuss the role of olefin cation radicals (generated by oxidation using either *Orange* CRET$^{\bullet+}$ or by passage of an anodic current) and of carbocations (generated by protonation of olefins with an strong acid) as intermediates in the hydrogenation of sterically crowded (electron-rich) olefins with borane.

Results

We recently introduced a highly colored orange cation radical for electron transfer, hereinafter referred to as simply *Orange* CRET$^{\bullet+}$ as an excellent one-electron



(*Orange* CRET$^{+•}$)

oxidant with a reversible reduction potential $E^{o}_{red} = 1.11$ V vs SCE.[10] In order to examine the efficacy of *Orange*

[⊗] Abstract published in *Advance ACS Abstracts,* July 15, 1996.

(1) (a) Rylander, P. N. *Catalytic Hydrogenation in Oragnic Synthesis*; Academic Press: New York, 1979. (b) Freifelder, M. *Catalytic Hydrogenation in Oragnic Synthesis: Procedure and Commentary*; Wiley: New York, 1978. (c) *Catalysis of Organic Reactions*; Rylander, P. N., Greenfield, H., Augustine, R. L., Eds.; Marcel Dekker: New York, 1988.

(2) (a) March, J. *Advanced Organic Chemistry*, 4th ed.; Wiley: New York, 1992, pp 713. (b) Smith, M. B. *Organic Synthesis*; McGraw-Hill: New York, 1994; pp 430.

(3) (a) Butler, D. N.; Gupta, I.; Ng, W. W.; Nyburg, S. C. *J. Chem. Soc., Chem. Commun.* **1980**, 596. (b) Bolze, R.; Eierdanz, H.; Schluter, K.; Massa, W.; Grahn, W.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 924. (c) Arnett, E. M.; Bollinger, J. M.; Sanda, J. C. *J. Am. Chem. Soc.* **1965**, *87*, 2050.

(4) Catalytic hydrogenation of 2,3-bis(2,5-dimethoxy-4-methylphenyl)-bicyclo[2.2.2]oct-2-ene (**1**) in ethanol at 25 °C in the presence of 10% palladium on charcoal or platinum catalyst resulted only traces of the hydrogenated product after 48 h.

(5) Nelsen S. F.; Teasley, M. F. *J. Org. Chem.* **1986**, *51*, 3474. For other examples of ionic hydrogenation, see: Kursanov, D. N.; Parnes, Z. N.; Loim, N. M. *Synthesis* **1974**, 633.

(6) Nelsen, D. J.; Cooper, P. J.; Soundararajan, R. *J. Am. Chem. Soc.* **1989**, *111*, 1414.

(7) Mirafzal, G. A.; Bauld, N. L. *J. Am. Chem. Soc.* **1992**, *114*, 5457. Also see Mirafzal, G. A.; Liu, J.; Bauld, N. L. *J. Am. Chem. Soc.* **1993**, *115*, 6072.

(8) The major product obtained upon reduction of bicyclooctene **1**, according to the procedure of Mirafzal and Bauld,[7] was a demethylated compound which could not be identified.

(9) Borane−methyl sulfide complex is available from Aldrich Chemical Co. and has been extensively utilized for the hydroboration of alkenes, see: Brown, H. C. *Organic Synthesis Via Boranes*; Wiley: New York, 1975.

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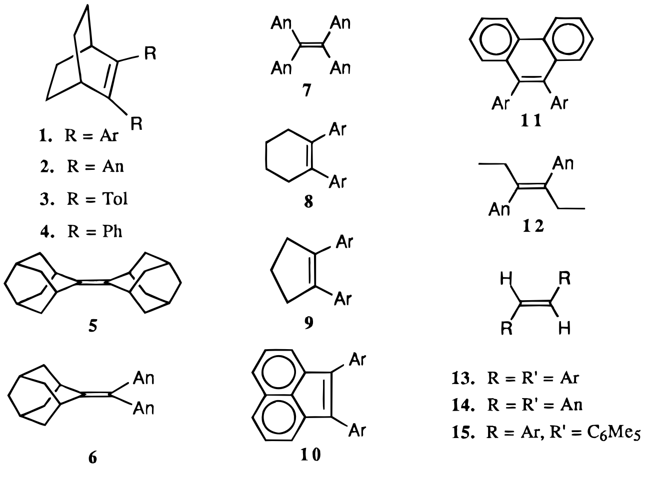
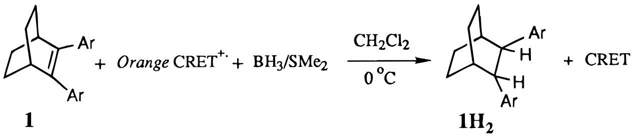
CRET$^{•+}$ with the borane−methyl sulfide complex, we prepared a series of highly encumbered olefins, such as diarylbicyclooctenes (**1**−**4**), adamantylidene-based olefins (**5**[11] and **6**[12]), tetraanisylethylene[13] (**7**), diarylcycloalkene derivatives (**8**−**11**),[14] *etc.* The 2,3-diarylbicyclo[2.2.2]oct-2-enes were prepared for the first time by the reaction of arylmagnesium bromide with 2,3-dibromobicyclo[2.2.2]-oct-2-ene[15] in the presence of a palladium catalyst[16] (see Experimental Section).



Ar = p-MeC$_6$H$_2$-2,5-(OMe)$_2$; An = p-MeOC$_6$H$_4$; Tol = p-MeC$_6$H$_4$; Ph = C$_6$H$_5$

I. Hydrogenation of Olefins with the Borane−Methyl Sulfide (BMS) Complex in the Presence of *Orange* CRET$^{•+}$. When a colorless solution of 0.1 M 2,3-diarylbicyclo[2.2.2]oct-2-ene (**1**) in dichloromethane was treated with a 1 equiv of *Orange* CRET$^{•+}$ at 0 °C, under an argon atmosphere, the solution immediately turned dark brown. This brown solution was stable for hours at 0 °C, as monitored by UV−vis spectroscopy. Upon the addition of 2 equiv of the borane−methyl sulfide complex, the highly colored reaction mixture progressively bleached to afford a pale yellow solution (~1 h). In a simple work-up procedure, the reaction mixture was quenched with aqueous potassium carbonate, and the dichloromethane layer was washed with water and dried over anhydrous magnesium sulfate. Evaporation of the solvent *in vacuo* and chromatographic purification afforded the 2,3-diarylbicyclo[2.2.2]octane **1H$_2$**, as a single isomer, in excellent yield, *e.g.*[17]



1 **1H$_2$** (1)

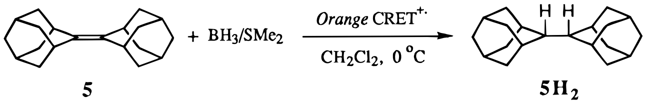
In a control experiment, olefin **1** was treated (in the absence of *Orange* CRET$^{•+}$) with excess BMS complex in dichloromethane at 0 °C under an argon atmosphere. The reaction mixture was stirred for 2 h and the GC and GC−MS analysis of an aliquot (see Experimental Section for the aqueous workup with hydrogen peroxide) indicated that only unreacted olefin **1** was present. Even after refluxing overnight, the unreacted olefin **1** was recovered quantitatively.[18] In another experiment, a prechilled (0 °C) solution of *Orange* CRET$^{•+}$ in dichloromethane was treated with excess borane−methyl sulfide complex under an argon atmosphere. The bright orange-red solution was stable for prolonged periods (4−6 h) at 0 °C, and it was only slowly bleached when brought to room temperature to afford the reduced (neutral) CRET in quantitative yields.

Table 1. Hydrogenation of Olefins with the BMS Complex in the Presence of *Orange* CRET$^{•+}$ in Dichloromethane[a]

olefin	E$_{1/2}$ (V vs SCE)[b]	*t* (h)	alkane yield[c] %
1	0.99	1.0	88
2	0.98	0.5	97
3	1.36	6.0	86
4	1.47	6.0	79
5	1.45	2.0	98
6	1.17	1.0	82
7	1.08	12.0	48[d]
8	1.01	1.0	91
9	1.01	0.5	84
10	1.04	0.5	89
11	1.16	14.0	e
12	1.15	1.0	96
13	0.90	0.3	97
14	1.05	0.3	98
15	1.04	0.5	94

[a] A 0.1 M solution of olefin containing *Orange* CRET$^{•+}$ (1.1 equiv) and BMS complex (2 equiv) in dichloromethane at 0 °C. [b] In dichloromethane containing 0.2 M n-Bu$_4$N$^+$ PF$_6^-$ at $\nu = 100$ mV s^{-1} and 25 °C. [c] Isolated yields. [d] Starting material recovered. [e] See text.

With this simple procedure, a variety of olefins were hydrogenated to the corresponding alkanes in excellent yields (see Table 1). It is especially noteworthy that adamantylideneadamantane (**5**), which resisted ionic hydrogenation in strongly acidic media,[5] was efficiently reduced using *Orange* CRET$^{•+}$ and the BMS complex to yield the saturated biadamantane[19] **5H$_2$** in quantitative yield, *i.e.*



5 **5H$_2$** (2)

Also note that the severely crowded tetranisylethylene[20] (**7**) on treatment with *Orange* CRET$^{•+}$ produced a dark blue solution, the UV−vis spectral analysis of which confirmed the formation of the corresponding cation radical **7**$^{•+}$ with the characteristic absorbances at $\lambda_{\max} =$

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(10) Rathore, R.; Kochi, J. K. *J. Org. Chem.* **1995**, *60*, 4399. Also see: Rathore, R.; Bosch, E.; Kochi, J. K. *J. Chem. Soc., Perkin Trans. 2* **1994**, 1157.

(11) Tolstikov, G. A.; Lerman, B. M.; Belogaeva, T. A. *Synth. Commun.* **1991**, *21*, 877.

(12) Bosch, E.; Kochi, J. K. *J. Am. Chem. Soc.* **1996**, *118*, 1319.

(13) Buckles, R. E.; Womer, W. D. *J. Am. Chem. Soc.* **1958**, *80*, 5055.

(14) Baumstark, A. L.; McCloskey, C. J.; Witt, K. E. *J. Org. Chem.* **1978**, *43*, 3609. Also see: McMurry, J. E. *Chem. Rev.* **1989**, *89*, 1513 and references therein.

(15) Komatsu, K.; Aonuma, S.; Jinbu, Y.; Tsuji, R.; Hirosawa, C.; Takeuchi, K. *J. Org. Chem.* **1991**, *56*, 196.

(16) Kumada, K. *Pure Appl. Chem.* **1980**, *52*, 669 and references therein.

(17) The hydrogenation of olefin **1** (in eq 1) with 1 equiv of the borane−methyl sulfide complex proceeded sluggishly with incomplete reduction. Since the boron-containing products were not identified, the complete stoichiometry in eq 1 was not established.

(18) Sterically crowded olefins are known to resist hydroboration, see: Zweifel, G.; Brown, H. C. *Org. React.* **1963**, *13*, 1. Also see Butler *et al.* in ref 3.

(19) Van Zorge, J. A.; Strating, J.; Wynberg, H. *Recl. Trav. Chim. Pays-Bas* **1970**, *89*, 781.

(20) (a) Suzuki, H. *Bull. Chem. Soc. Jpn.* **1960**, *33*, 389. (b) Suzuki, H.; Koyano, K.; Shida, T.; Kira, A. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 2794.

565 and 920 nm.[21] The dark blue solution bleached very slowly (~12 h) in the presence of the BMS complex at room temperature. Workup of the resultant pale yellow solution afforded the reduced tetranisylethane[22] **7H$_2$** in 48% yield together with recovered **7** (51%). Furthermore, 1,2-bis(2,5-dimethoxy-4-methylphenyl)acenaphthylene (**10**) reacted with *Orange* CRET$^{\bullet+}$ and the BMS complex to selectively yield 1,2-dihydroacenaphthylene **10H$_2$** as a single product,[23] in excellent yield (see Table 1). The mild reaction conditions and the simplicity of the procedure prompted us to employ this method for the reduction of electron-rich stilbenes. As shown in Table 1, the various substituted stilbenes could be cleanly reduced to the corresponding diarylethanes in excellent yields. Under similar reaction conditions, the (unsubstituted) *trans*-stilbene (E_p^{ox} = 1.59 V vs SCE)[24] itself was not hydrogenated to 1,2-diphenylethane. Moreover, the dichloromethane solution of the highly colored 9,10-diarylphenanthrene radical cation **11**$^{\bullet+}$ (generated *in situ* using *Orange* CRET$^{\bullet+}$) was sluggishly decolorized in the presence of the BMS complex after prolonged stirring at 0 °C, and aqueous workup of the pale yellow solution afforded the unreacted phenanthrene **11** in quantitative amounts.

The hydrogenation of the various olefins listed in Table 1 generally afforded only one of the two possible isomers.[25] For example, 2,3-bis(2,5-dimethoxy-4-methylphenyl)bicyclo[2.2.2]oct-2-ene (**1**) yielded a single isomer of the corresponding 2,3-diarylbicyclo[2.2.2]octane **1H$_2$**. The ^{1}H NMR spectrum showed that the signals of the benzylic 2,3-methine protons were relatively shifted downfield (3.87 ppm). Such a downfield shift of the benzylic protons in various 2,3-diarylbicyclooctanes (*i.e.* 3.55 ppm, **2**; 3.64 ppm, **3**; 3.71 ppm, **4**) suggested a cis arrangement of the two aryl groups, since the benzylic resonances in the corresponding trans isomer were expected to show a distinctive upfield shift due to the ring current effect of the neighboring aryl groups.[26] In order to further establish the stereochemistry of **1H$_2$**, a colorless crystal of **1H$_2$** suitable for X-ray crystallographic analysis was grown from methanol at −20 °C. The crystals belonged to the monoclinic space group P2$_1$/C. The intensity data were collected on a Nicolet R3m/V automatic diffractometer, and the structure was determined using the direct method program SHELXTL. The perspective ORTEP views of the molecular structure in Figure 1, parts A and B, clearly show that the two aryl groups are arranged in a cis configuration, although such an arrangement of the aryl groups resulted in a considerable twisting of the bicyclo[2.2.2]octane framework (see Figure 1B). In addition, torsional strain imposed by the cis aryl groups resulted in a considerable lengthening of the C1−C2 bond (1.581 Å).

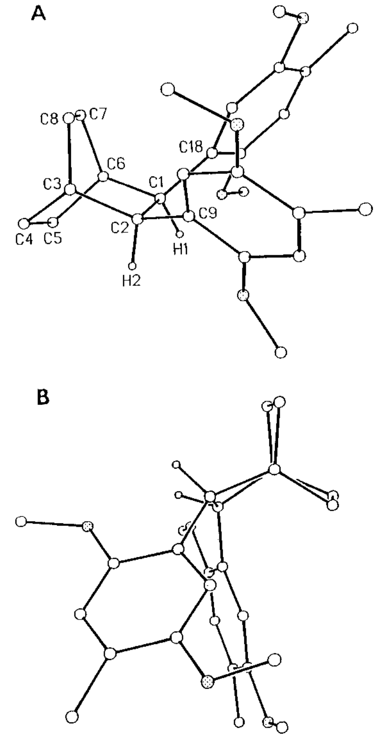

Figure 1. ORTEP perspective of 2,3-diarylbicyclo[2.2.2.]-octane **1H$_2$** showing (A) the *cis* arrangement of the two aryl groups and (B) the twisting of the bicyclooctane framework.

Table 2. Hydrogenation of Olefins with the BMS Complex via Electrochemical (Anodic) Oxidation[a]

olefin	$E_{1/2}$ (V vs SCE)	olefin$^{\bullet+}$ λ_{max} (nm)[b]	alkane yield[c] %
1	0.99	315, 445, 550	97
2	0.98	492, 546, >800	91
5	1.45	540	99
6	1.17	406, 426, 660	93
8	1.01	430	98
13	0.90	500, 590	96

[a] A 0.02 M solution of olefin and the BMS complex (2 equiv) in anhydrous dichloromethane (containing 0.1 M *n*-Bu$_4$N$^+$ PF$_6^-$) electrolyzed at a constant potential (~$E_{1/2}$) and 25 °C. [b] See Experimental Section. [c] Isolated yields.

II. Hydrogenation of Olefins with the Borane-Methyl Sulfide (BMS) Complex via Electrochemical Oxidation. The conversion of olefins to the corresponding alkanes was also readily effected by electrochemical means in the presence of the BMS complex. Thus, passing an anodic current at a constant potential of 1.0 V through a colorless mixture of 2,3-dianisylbicyclo[2.2.2]-oct-2-ene (1 mmol) and the BMS complex (2 equiv) in 50 mL of dichloromethane (containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate as the supporting electrolyte) under an argon atmosphere at 25 °C caused the solution to turn magenta (red) [λ_{max} = 546, 492 (sh), and >800 nm] immediately in the vicinity of the electrode. The red color which appeared at the electrode surface was rapidly dissipated into the solution, as the initial rapid flow of the current slowly dropped to a negligible rate. The amount of passed current was recorded with the aid of a digital coulometer and found to be 103 C during this period. The reaction mixture was evaporated under reduced pressure, and the residue was digested in anhydrous ether and then filtered through a short pad of silica gel. A simple removal of the solvent from the filtrate afforded the 2,3-dianisybicyclooctane **2H$_2$** in quantitative yields. The other olefins listed in Table 2

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[21] Svanholm, U.; Jensen, B. S.; Parker, V. D. *J. Chem. Soc., Perkin Trans. 2* **1974**, 907. Also see: Bard, A. J.; Phelps, J. *J. Electroanal. Chem.* **1970**, *25*, App. 2.

[22] (a) Mitchell, R. H.; Mazuch, L.; Shell, B.; West, P. R. *Can. J. Chem.* **1978**, *56*, 1246. (b) Luh, T.-Y. *Synth. Commun.* **1981**, *11*, 829.

[23] The catalytic hydrogenation of acenaphthylene **10** in ethanol with dihydrogen in the presence of 10% Pd on charcoal, yielded a mixture of 1,2-dihydroacenaphthlene **10H$_2$** (72%) and unidentified tetrahydro- and hexahydroacenaphthlenes (~28%).

[24] Bauld, N. L.; Yueh, W. *J. Am. Chem. Soc.* **1994**, *116*, 8845.

[25] The reduction of olefins **2**−**4**, **8**, and **10** also indicated (by GC−MS analysis) the presence of a trace amount (<2%) of a second isomer of the hydrogenated product. In the case of olefin **1**, the single isomer obtained was clearly identified by X-ray crystallography to be the *cis* isomer. However, the stereochemistry of the other hydrogenated alkanes in Table 1 is not known.

[26] (a) Dodson, R. M.; Zielske, A. G. *J. Org. Chem.*, **1967**, *32*, 28. (b) Bauld, N. L.; Hudson, C. E. *Tetrahedron Lett.* **1974**, *36*, 3147 and references therein.

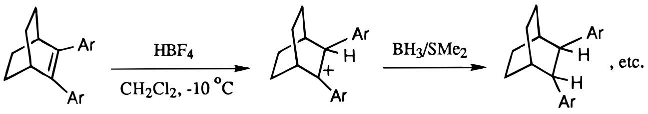
Table 3. Hydrogenation of Olefins with the BMS Complex in the Presence of Tetrafluoroboric acid[a]

olefin	olefin-H$^+$ [λ_{max}(nm)][b]	t (h)	alkane yield[c] %
1	518	0.08	98
2	507	0.17	97
12	510	0.17	98
5	480	3.00	38[d]
7	508	12.0	8[d]

[a] A 0.1 M solution of olefin containing HBF_4 (2 equiv) and the borane−methyl sulfide complex (2 equiv) in dichloromethane at −10 °C. [b] See Experimental Section. [c] Isolated yields. [d] Starting material recovered.

were similarly reduced to the corresponding alkanes in essentially quantitative yields.

III. Hydrogenation of Olefins with the Borane-Methyl Sulfide Complex in the Presence of Tetrafluoroboric Acid (HBF_4). Since other cation−radical-induced reactions were also effectively promoted by an acid catalyst,[27] we employed tetrafluoroboric acid for the hydrogenation of olefins with borane. Thus, a colorless solution of 0.1 M diarylbicyclooctene **1** in dichloromethane at −10 °C (in an ice−salt bath) was treated with 2 equiv of HBF_4, under an argon atmosphere. The solution immediately turned bright red. The UV−vis spectral analysis of the highly colored solution showed that the red color arose largely from a species with a distinctive absorption band at $\lambda_{max} = 518$ nm (*vide infra*). When the red solution was treated with the borane−methyl sulfide complex (2 equiv), the color of the reaction mixture rapidly faded (3−5 min) to yield a pale yellow solution. In a simple work-up procedure, the reaction mixture was treated with aqueous sodium bicarbonate, followed by removal of the solvent *in vacuo* to afford the corresponding reduced 2,3-diarylbicyclooctane **1H$_2$** in quantitative yields, *i.e.*[28]



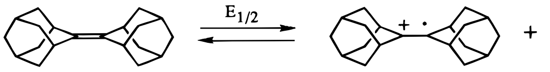
1 **1H$^+$** **1H$_2$**

(3)

The spectral properties and the GC−MS behavior of the **1H$_2$** coincided with those of an authentic sample obtained via the cation−radical-induced reaction of **1** with the BMS complex. Similarly, the bicyclooctene **2** and stilbene **12** on treatment with HBF_4 developed a strong red coloration. The red solution upon treatment with borane, afforded good yields of hydrogenated products (see Table 3). However, adamantylideneadamantane (**5**) and tetraanisylethylene (**7**) gave only poor yields of hydrogenated products (see Experimental Section) under similar reaction conditions (compare entries 5 and 7 in Table 1 and 3).

IV. Cation Radical *Versus* Carbocation as the Critical Reactive Intermediate in the Hydrogenation of Olefin with Borane. Transient colorations were observed in both oxidative procedures described above for the hydrogenation with borane, *i.e.* by the addition of *Orange* CRET$^{•+}$ or by the passage of an anodic current. In a similar vein, the protonation of olefins with tetrafluoroboric acid was accompanied by the development of a strong red coloration owing to the formation of carbocations, which rapidly reacted with the borane−methyl sulfide complex to yield hydrogenated products. Since such transient colorations were the earmarks of the reactive intermediates, we further examined the behavior of these intermediates in the hydrogenation procedure with borane in the following way.

a. Cyclic Voltammetry of the Adamantylidene-adamantane (5) and Neutral CRET in the Presence of the Borane-Methyl Sulfide (BMS) Complex. As described above, the bulk electrolysis of a mixture of **5** and the BMS complex in dichloromethane afforded quantitative yields of biadamantane (**5H$_2$**). The efficiency of this reaction prompted us to investigate the transient electrochemical behavior of **5** at a platinum electrode in the presence of the BMS complex. Thus, the cyclic voltammetric oxidation of 0.01 M **5** in anhydrous dichloromethane (containing 0.2 M tetra-*n*-butylammonium hexafluorophosphate as the supporting electrolyte) at 25 °C under an argon atmosphere showed a well-defined anodic wave at $E_p{}^a = 1.49$ V vs SCE and a coupled cathodic wave at 1.42 V on the reverse scan. The cyclic voltammogram showed a cathodic/anodic peak current ratio of $i_a/i_c = 1.0$ (theoretical) at a scan rate of $\nu = 200$ mV s^{-1} (see Figure 2B). Calibration of the peak currents with ferrocene provided the oxidation potential of $E_{1/2} =$ 1.45 V vs SCE[29] for the reversible production of the cation radical, *i.e.*



5 **5$^{+·}$**

(4)

The same solution was then subjected to the anodic oxidation in the presence of the BMS complex (2 equiv) under otherwise identical electrochemical conditions. The presence of the BMS complex caused a distortion of the CV wave ($E_p{}^a = 1.49$ V vs SCE), which was highly irreversible, and the coupled cathodic wave was not observed (compare Figure 2, parts C and B). [The irreversible cyclic voltammogram of 0.02 M borane−methyl sulfide complex alone in dichloromethane (containing 0.2 M supporting electrolyte) at a scan rate of $\nu = 200$ mV s^{-1}, is shown in Figure 2A.]

In contrast, the electrochemical oxidation of neutral CRET (9,10-dimethoxy-octahydro-1,4:5,8-dimethanoanthracene),which is known to be reversibly oxidized ($E_{1/2} = 1.11$ V vs SCE)[10] to the corresponding cation radical (*Orange* CRET$^{•+}$) in dichloromethane ($\nu = 200$ mV s^{-1}), also showed a well-defined reversible cyclic voltammogram, despite the presence of the borane−dimethyl sulfide complex (compare Figure 3, parts B and C).

b. Reaction of Cation Radical 2$^{•+}$ with Borane. The observation of the strong coloration in both the *Orange* CRET$^{•+}$ and electrochemical hydrogenation procedures prompted us to separately prepare an olefin cation radical in order to directly examine its reactivity with borane. The cation radical of the 2,3-dianisylbicyclooctene (**2**) was generated as a persistent species by direct oxidation with the well-known one-electron oxi-

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[27] (a) Lopez, L.; Troisi, L. *Tetrahedron Lett.* **1989**, *30*, 3097. (b) Ciminale, F.; Lopez, L.; Mele, G. *Tetrahedron* **1994**, *50*, 12685. (c) Gassman, P. G.; Singleton, D. A. *J. Am. Chem. Soc.* **1984**, *106*, 7993. (d) Rathore, R.; Kochi, J. K. *J. Org. Chem.* **1995**, *60*, 7479 and references therein.

[28] Although boron-containing products in eq 3 were not identified, the formation of alkane by the alternative sequence (involving hydroboration of alkene followed by protonolysis) is disfavored since it requires the presence of a carboxylic acid (such as propionic acid) and is usually carried out at elevated temperatures. See, Brown, H. C. in ref 9, pp 81.

[29] Nelsen, S. F. *Acc. Chem. Res.* **1987**, *20*, 269.

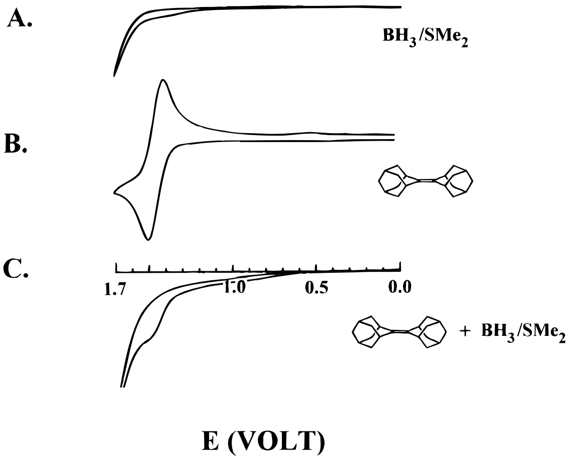


Figure 2. Initial positive scan cyclic voltammograms in dichloromethane containing 0.2 M n-Bu_4N^+ PF_6^- at a sweep rate of $\nu = 200$ mV s^{-1} for the (A) solution of 0.02 M BH_3/SMe_2 alone, (B) solution of 0.01 M olefin **5** alone, and (C) combined solutions of 0.01 M **5** and 0.02 M BH_3/SMe_2.

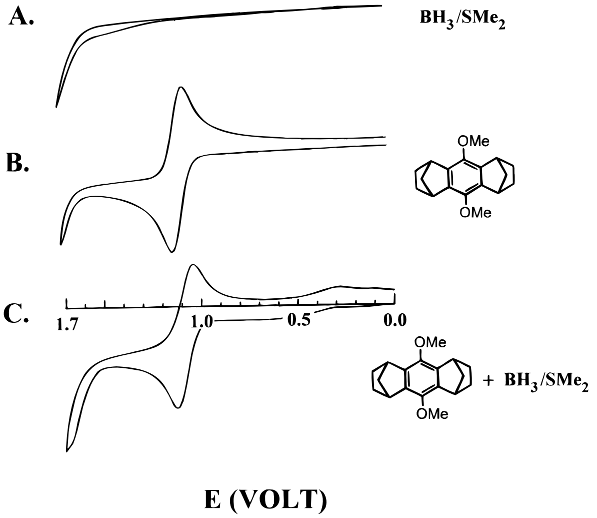
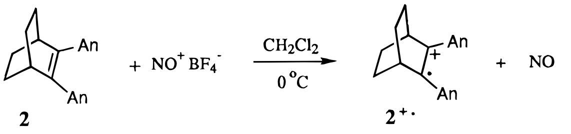


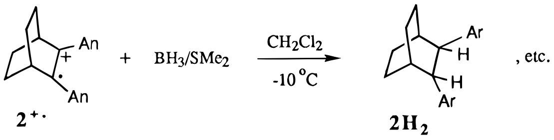
Figure 3. Cyclic voltammograms for the oxidation of (neutral) CRET in dichloromethane containing 0.2 M n-Bu_4N^+ PF_6^- at $\nu = 200$ mV s^{-1}: (A) Solution of 0.02 M BH_3/SMe_2 alone, (B) solution of 0.01 M CRET alone, and (C) combined solutions of 0.01 M CRET and 0.02 M BH_3/SMe_2.

dant, nitrosonium tetrafluoroborate (NO^+ BF_4^-)[30] according to eq 5. The dichloromethane solution of the cation



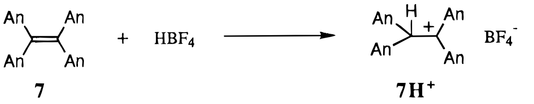
(5)

radical $2^{\bullet+}$, which was free of nitric oxide (NO), was prepared according to the eq 5 by entrainment of NO from the solution with a stream of oxygen-free argon (see Experimental Section). The resultant magenta (red)-colored solution containing only $2^{\bullet+}$ was stable for prolonged periods.[31] The dichloromethane solution of $2^{\bullet+}$ was cooled to −10 °C in an ice−salt bath, and 2 equiv of the BMS complex was added. The red color of the reaction mixture faded within 10 min to yield a pale yellow solution, which upon workup with aqueous sodium carbonate afforded the 2,3-dianisylbicyclooctane $2H_2$ in quantitative yield according to eq 6.[32]



(6)

c. Carbocation as the Reactive Intermediate. Highly colored carbocations are readily generated by protonation of aryl-substituted olefins, which is an approach that has been widely utilized in spectroscopic investigations of carbocations.[33] Thus, the mixing of a colorless solution of bicyclooctene **1** with tetrafluoroboric acid (HBF_4) in dichloromethane (at −10 °C), immediately produced a dark red solution. The UV−vis spectral analysis showed that the red color arose largely from a species with a well-resolved absorption band at $\lambda_{max} = 518$ nm. Furthermore, the protonation of tetranisylethylene (**7**) with HBF_4 produced a similar red coloration which upon UV−vis spectral analysis showed an absorption maximum at $\lambda_{max} = 508$ nm. This UV−vis absorption maximum was readily assigned to the corresponding carbocation $\mathbf{7H^+}$ in eq 7 by comparison with the absorption spectra ($\lambda_{max} = 505$ nm) previously observed for protonated 1,1-dianisylethylene.[34] Similarly, other olefins in Table 3 showed strong red colorations with HBF_4 due to the formation of corresponding carbocations, and the UV−vis absorption maxima are listed in Table 3.



(7)

Discussion

We have developed a one-pot procedure for the reduction of sterically encumbered olefins in which the prior exposure of olefin to either a cation−radical salt (such as *Orange* $CRET^{\bullet+}$) or strong acid (such as HBF_4) in dichloromethane at room temperature (or below), followed by treatment with the borane−methyl sulfide (BMS) complex readily leads to the corresponding hydrogenated alkanes in excellent yields (see Tables 1 and 3). Furthermore, the use of electrochemical oxidation of the olefins in the presence of the BMS complex provides yet another inexpensive alternative to cation−radical salts[35] for the hydrogenation procedure (see Table 2). The mild reaction conditions in both approaches combined with the simplicity of the workup procedure (especially in the case of electrochemical oxidation) makes this method an ideal choice for the facile reduction of sterically crowded olefins, which are otherwise not readily

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(30) Kim, E. K.; Kochi, J. K. *J. Am. Chem. Soc.* **1991**, *113*, 4962. Also see: Bandlish, B. K.; Shine, H. J. *J. Org. Chem.* **1977**, *42*, 561.

(31) Note that the original olefin **2** was readily regenerated in a quantitative yield by the reduction of cation radical $2^{\bullet+}$ with zinc dust.

(32) The complete stoichiometry in eq 6 was not established due to the difficulty in identifying boron-containing products.

(33) (a) Freedman, H. H. In *Carbonium Ions*: Olah, G. A., Schleyer, P. v. R., Eds.; Wiley: New York, 1973; Vol. IV, p 1501. (b) Olah, G. A.; Pittman, C. U., Jr. In *Carbonium Ions;* Olah, G. A., Schleyer, P. v. R., Eds.; Wiley: New York, 1968; Vol. I, p 153. (c) Olah, G. A. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 173. (d) Deno, N. C; Jaruzelski, J. J.; Schreisheim, A. *J. Am. Chem. Soc.* **1955**, *77*, 3044.

(34) (a) Al-Ekabi, H.; Kawata, H.; de Mayo, P. *J. Org. Chem.* **1988**, *53*, 1471. (b) Azarani, A.; Berinstain, A. B.; Johnston, L. J.; Kazanis, S. *J. Photochem. Photobiol. A: Chem.* **1991**, *57*, 175 and references therein.

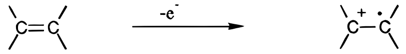
(35) Similar yields of hydrogenated alkanes were obtained with tris-(4-bromophenyl)aminium hexachloroantimonate ("magic blue") as the one-electron oxidant.

reduced. However, note that the sterically encumbered electron-rich ($E_{1/2}$ = 1.27 V vs SCE) 2,3-bis(pentamethylphenyl)bicyclo[2.2.2]oct-2-ene (**16**), in which the double bond is entombed by the bicyclooctane framework and two phenyl groups containing four *ortho* methyl groups, does not undergo reduction with the borane−methyl sulfide complex in the presence of either *Orange* CRET$^{+\cdot}$ or a strong Brønsted acid (such as HBF_4 or CF_3SO_3H), and the starting olefin **16** is recovered quantitatively (see the Experimental Section).

The activation of the olefin (with either *Orange* CRET$^{+\cdot}$ or HBF_4) is a prerequisite for the reduction with borane, since the individual olefins are completely unreactive[18] toward the borane−methyl sulfide complex in dichloromethane in the absence of an activator. Furthermore, the efficient hydrogenation of hindered olefins with the BMS complex by facile chemical promotion with cation radicals, such as *Orange* CRET$^{+\cdot}$, or by electrochemical (anodic) promotion, indicates that the process can be initiated by one-electron oxidation. On the other hand, the protonation of the olefin (with a strong acid such as HBF_4) indicates that the corresponding carbocation can also lead to the rapid reduction of olefins by the BMS complex.

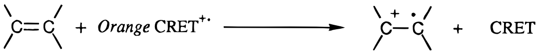
In order to reconcile these apparently discordant observations, let us first focus on the oxidative promotion, in particular with regard to the appearance of transient olefin cation radicals and their subsequent conversion to the corresponding hydrogenated alkanes with borane.

I. Observation of Olefin Cation Radical. The bicyclooctene cation radical $\mathbf{2}^{\bullet+}$, generated immediately upon either (a) the introduction of *Orange* CRET$^{+\cdot}$ or (b) by the passage of an anodic current through the dichloromethane solution of the olefin **2**, *i.e.*



2 $\mathbf{2}^{+\cdot}$ (8)

is the first observable intermediate in the activation of the olefin toward its reaction with borane. In general, such an activation depends on the ability of the olefinic donors to undergo one-electron transfer, *e.g.*



(9)

The various olefins listed in Table 1 qualitatively follow a reactivity trend in accord with their one-electron oxidation potentials (E°_{ox}). For example, most olefins in Table 1 are relatively strong electron donors by virtue of their low oxidation potentials ($E_{1/2}$ = 0.90−1.47 V vs SCE). As a result, the free energy change ΔG_{et} for eq 9 is exergonic (on the basis of the reduction potential of the *Orange* CRET$^{+\cdot}$ of E°_{red} = 1.11 V vs SCE)[10] and sufficient to promote electron transfer and lead to the efficient hydrogenations in Table 1. It is noteworthy that the parent (unsubstituted) stilbene with a more positive potential of E°_{ox} = 1.59 V vs SCE[24] is not hydrogenated by borane under these conditions.

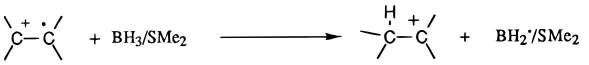
II. Olefin Cation Radical as the Critical Reactive Intermediate. There are two independent sets of experiments that provide further support for the olefin cation radical as a critical reactive intermediate in the hydrogenation procedure, namely (a) the generation of cation radicals via transient electrochemistry and its reaction with borane, and (b) the ready transformation of the isolated salts of olefin cation radical to the hydrogenated product with borane. Let us consider these two sets of experiments separately in the following way.

a. Transient Electrochemistry. The cyclic voltammetric (CV) oxidation of adamantylideneadamantane (**5**) in dichloromethane at room temperature is readily reversible, as indicated by the anodic/cathodic CV peak current ratio of unity even at ν = 25 mV s^{-1}.[29] In contrast, the cyclic voltammogram measured for the oxidation of **5** in the presence of the borane−methyl sulfide complex is highly irreversible as evidenced by the complete absence of the cathodic reduction wave of $\mathbf{5}^{\bullet+}$ on the return scan (see Figure 2C). This result indicated that electrochemically generated cation radical $\mathbf{5}^{\bullet+}$ reacts rapidly with borane in the diffusion layer, and thus it is not available for reduction on the return scan. Such a fast reaction of $\mathbf{5}^{\bullet+}$ with borane is consistent with the observed high yield of the corresponding hydrogenated product from the bulk electrolysis of a mixture of **5** and the BMS complex in dichloromethane (see Table 2).

On the other hand, the cyclic voltammograms of the aromatic donor (neutral) CRET with and without added borane (in Figure 3, parts C and B) are both completely reversible, *i.e.* the electrochemically generated *Orange* CRET$^{\bullet+}$ does not react with borane at an appreciable rate. This result is in line with the very sluggish bleaching of the highly colored solution of *Orange* CRET$^{\bullet+}$ in dichloromethane at room temperature. Furthermore, the quantitative recovery of the resulting neutral CRET suggests that borane does react slowly with *Orange* CRET$^{\bullet+}$ via electron transfer. Likewise, the cation radical $\mathbf{11}^{\bullet+}$ generated from an aromatic donor 9,10-diarylphenanthrene **11**, is not subject to hydrogenation with the borane−methyl sulfide complex (see Table 1, entry 11).

b. Direct Hydrogenation of Olefin Cation Radical with Borane. The formulation of the olefin cation radical as the critical reactive intermediate in the hydrogenation with borane requires that it be quantitatively converted to the corresponding alkane after it is formed either via *Orange* CRET$^{\bullet+}$ or anodic oxidation. Indeed, this process is demonstrated by independent preparation of 2,3-dianisylbicyclooctene cation radical ($\mathbf{2}^{\bullet+}$) in eq 5 and its facile reduction with the borane−methyl sulfide complex to the corresponding bicyclooctane $\mathbf{2H_2}$ in quantitative yields according to the eq 6.

The conversion of an olefin cation radical to the corresponding alkane with borane may be formulated in two discrete steps. First, we note that the borane−methyl sulfide complex (BH_3/SMe_2 as the least reactive hydroborating agent[36]) is capable of rapid hydrogen atom transfer to various radicals, and thereby generates a boryl radical complexed to dimethylsulfide ($BH_2^{\cdot}/Me_2S$).[36] Such a facile hydrogen-atom transfer from BH_3/Me_2S when applied to the olefin cation radical would result in a carbocation intermediate according to eq 10. The subsequent transfer of a "hydridic" hydrogen from the borane−methyl sulfide complex to the carbocation intermediate leads to the desired alkane, *i.e.*



(10)

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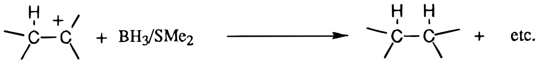
[36] (a) Baban, J. A.; Roberts, B. P. *J. Chem. Soc., Perkin Trans. 2* **1987**, 497. (b) Paul, V.; Roberts, B. P. *J. Chem. Soc., Perkin Trans. 2* **1988**, 1183. (c) Baban, J. A.; Roberts, B. P. *J. Chem. Soc., Perkin Trans. 2* **1988**, 1195. See also: Lucarini, M.; Pedulli, G. F.; Valgimigli, L. *J. Org. Chem.* **1996**, *61*, 1161.



(11)

The same carbocationic intermediate is also produced upon the direct protonation of the olefin. It is thus particularly illuminative that such a protonated olefin also reacts with borane and leads to high yields of reduced products as described in eq 3. Thus, the tandem results obtained from the cation radical and proton-induced procedures support the formulation in eqs 10 and 11.[37]

III. Cation Radical vs Carbocation as Intermediates in the Hydrogenation Procedure with Borane. The intermediacy of both cation radicals and carbocations in the hydrogenation of olefin with borane as presented in eqs 10 and 11 does explain the preparative results observed in Table 1−3. However, there exists a general problem of delineating electron transfer from the electrophilic (*i.e.* acid-catalyzed) pathways in a variety of other transformations.[27] Experimentally, the problem resolves into distinguishing the chemical behavior of paramagnetic cation radicals from that of diamagnetic cations as reactive intermediates. However, as applied to the reactive intermediates pertinent in the hydrogenation procedure with borane, we have shown that both cation radicals and carbocations can lead to the efficient hydrogenation (compare Table 1 and 3). Thus, an efficient hydrogenation of adamantylideneadamantane (**5**)- and tetranisylethylene (**7**) to the corresponding alkane by borane in the presence of *Orange* CRET$^{+\cdot}$ (or by passage of anodic current), but not so efficiently by acid (compare entries 5 and 7 in Tables 1 and 3), may serve to distinguish between the cation radical and carbocation pathways. However, we add the caveat that such a distinction is severely compromised in the acid-catalyzed pathway in which both species (*i.e.* carbocations and cation radicals) can coexist.[38] We hope that further studies in progress will resolve this subtle (but important) dissonance.

Experimental Section

Materials. Adipoyl chloride, glutaryl dichloride, 2-adamantanone, acenaphthenequinone, phenanthroquinone, 4′-methoxypropiophenone, bis(triphenylphosphine)palladium(II) chloride, tetra-*n*-butylammonium hexafluorophosphate, borane−methyl sulfide (BMS) complex, tetrafluoroboric acid (HBF_4), and 4,4′-dimethoxystilbene (**14**) were purchased from Aldrich and used without further purification. Adamantylideneadamantane[11] (**5**), (4,4′-dimethoxy-benzhydrylidene)adamantane[12] (**6**), 1,1,2,2-tetrakis(4-methoxyphenyl)ethylene[13] (**7**), 3,4-bis(4-methoxyphenyl)hex-3-ene[39] (dimestrol) (**12**), 1,2-bis-(2,5-dimethoxy-4-methylphenyl)ethylene[40] (**13**), and 2,3-dibromobicyclo[2.2.2]oct-2-ene[15] were prepared according to the literature procedure. The radical cation *Orange* CRET$^{\bullet+}$ was readily isolated as the stable hexachloroantimonate ($SbCl_6^-$) and tetrafluoroborate (BF_4^-) salt in a quantitative yield from the reaction of hydroquinone methyl ether CRET (9,10-dimethoxy-1,4:5,8-dimethano-1,2,3,4,5,6,7,8-octahydroanthracene) with antimony pentachloride ($SbCl_5$) and nitrosonium tetrafluroborate, respectively.[10] CRET (precursor for *Orange* CRET$^{\bullet+}$) can be easily prepared in multigram quantities from the corresponding bis-annulated hydroquinone which was easily obtained by the Diels−Alder condensation of *p*-benzoquinone with cyclopentadiene followed by hydrogenation over palladium/carbon and aromatization with bromine in excellent yield.[10] Nitrosonium tetrafluoroborate (Strem) was stored in a Vacuum Atmospheres HE-493 dry box kept free of oxygen. Dichloromethane was repeatedly stirred with fresh aliquots of concentrated sulfuric acid until the acid layer remained clear. After separation, it was washed successively with water, aqueous sodium bicarbonate, water, and brine and then dried over calcium chloride. It was distilled from phosphorus pentoxide followed by calcium hydride under an argon atmosphere and stored in a Schlenk flask equipped with a Teflon valve fitted with Viton O-rings. Tetrahydrofuran was distilled from sodium metal under an argon atmosphere with benzophenone ketyl as the indicator.

Preparation of Olefins. Synthesis of 2,3-Diarylbicyclo-[2.2.2]oct-2-enes. The synthesis of various 2,3-diarylbicyclo-[2.2.2]oct-2-enes (**1**−**4**) was accomplished by coupling of the arylmagnesium bromide with 2,3-dibromobicyclo[2.2.2]oct-2-ene[15] in the presence of bis(triphenylphosphine)palladium(II) chloride as a catalyst,[16] according to the general procedure described below:

General Procedure. A solution of (2,5-dimethoxy-4-methylphenyl)magnesium bromide was prepared from 4-bromo-2,5-dimethoxytoluene[41] (2.88 g, 12.5 mmol) and magnesium turnings (0.48 g, 20 mmol) in anhydrous tetrahydrofuran (25 mL) under an argon atmosphere. The Grignard solution thus obtained was transferred via a cannula to a Schlenk flask containing a mixture of 2,3-dibromobicyclo[2.2.2]oct-2-ene[15] (1.33 g, 5.0 mmol) and a catalytic amount of bis(triphenylphosphine)palladium(II) chloride (0.10 g, 0.15 mmol) in anhydrous tetrahydrofuran (20 mL) under an argon atmosphere. The pale yellow reaction mixture was refluxed for 10−16 h and cooled to room temperature. It was then poured into a saturated aqueous ammonium chloride solution (100 mL), and the organic phase was separated. The aqueous layer was further extracted with ether (3 × 50 mL). The combined organic extracts were dried over anhydrous magnesium sulfate. Evaporation of the solvent *in vacuo* afforded an oily residue which was purified by flash chromatography on silica gel with ether−hexanes (1:1) as the eluent. The resultant product was further recrystallized from methanol at −20 °C, to afford the desired olefin **1** in the form of ivory crystals (1.51 g, 74%). The characteristic spectral data for various 2,3-diarylbicyclo[2.2.2]oct-2-enes are given below:

2,3-Bis(4-methyl-2,5-dimethoxyphenyl)bicyclo[2.2.2]-oct-2-ene (1): yield 74%; mp 110 °C; IR (KBr) 2931, 2854, 1504, 1462, 1398, 1208, 1040, 850, 794, 688 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.64 (br s, 8H), 2.13 (s, 6H), 2.78 (s, 2H), 3.41 (s, 6H), 3.72 (s, 6H), 6.25 (s, 2H), 6.64 (s, 2H); ^{13}C NMR ($CDCl_3$) 16.09, 26.27, 36.30, 55.77, 56.34, 113.80, 114.34, 124.84, 128.83, 140.01, 151.17, 151.30; GC−MS *m/z* 408 (M^+), 408 calcd for $C_{26}H_{32}O_4$. Anal. Calcd for $C_{26}H_{32}O_4$: C, 76.44; H, 7.90. Found: C, 76.24; H, 7.92.

2,3-Bis(4-methoxyphenyl)bicyclo[2.2.2]oct-2-ene (2): yield 94%; mp 72−73 °C (EtOH); ^1H NMR ($CDCl_3$) δ 1.62 (br d, 4H), 1.74 (br d, J = 7.2 Hz, 4H), 2.94 (s, 2H), 3.79 (s, 6H), 6.77 (d, J = 8.7 Hz, 4H), 7.09 (d, J = 8.7 Hz, 4H); ^{13}C NMR ($CDCl_3$) 26.23, 37.44, 54.97, 113.23, 129.44, 133.63, 138.60, 157.59; GC−MS *m/z* 320 (M^+), 320 calcd for $C_{22}H_{24}O_2$. Anal. Calcd for $C_{22}H_{24}O_2$: C, 82.46; H, 7.55. Found: C, 82.38; H, 7.53.

2,3-Bis(4-methylphenyl)bicyclo[2.2.2]oct-2-ene (3): yield 92%; oil; ^1H NMR ($CDCl_3$) δ 1.70 (d, J = 7.5 Hz, 4H), 1.81 (d, J = 7.5 Hz, 4H), 2.40 (s, 6H), 3.04 (br s, 2H), 7.10 (d, J = 8.4 Hz, 4H), 7.14 (d, J = 8.4 Hz, 4H); ^{13}C NMR ($CDCl_3$) 21.10, 26.23, 37.52, 128.28, 128.56, 135.26, 138.23, 139.52; GC−MS *m/z* 288 (M^+), 288 calcd for $C_{22}H_{24}$. Anal. Calcd for $C_{22}H_{24}$: C, 91.61; H, 8.39. Found: C, 91.45; H, 8.35.

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(37) The formulation in eqs 10 and 11 does account for the hydrogenation of both olefin cation radicals and carbocations with borane to form the corresponding alkanes. However, the fate of the boron-containing products could not be identified, and thus eqs 10 and 11 may merely represent a simplified scheme for a rather complex reaction.

(38) (a) Johnston, L. J.; Kanigan, T. *J. Am. Chem. Soc.* **1990**, *112*, 1271. (b) Hart, H.; Teuerstein, A.; Babin, M. A. *J. Am. Chem. Soc.* **1981**, *103*, 903. (c) Eberson, L.; Radner, F. *Acta Chem. Scand.* **1991**, *45*, 1093 and references therein. (d) Also see Al-Ekabi *et al.* in ref 34.

(39) McMurry, J. E.; Fleming, M. P. *J. Am. Chem. Soc.* **1974**, *96*, 4708.

(40) Hunt, S. E.; Lindsey, A. S. *J. Chem. Soc. (C)* **1968**, 3049.

(41) (a) McHale, D.; Mamalis, P.; Green, J.; Marcinkiewicz, S. *J. Chem. Soc.* **1958**, 1600.

2,3-Diphenylbicyclo[2.2.2]oct-2-ene (4): yield 96%, mp 126−127 °C (EtOH); ^{1}H NMR ($CDCl_3$) δ 1.68 (sym m, 4H), 1.82 (sym m, 4H), 3.03 (s, 2H), 7.14−7.28 (m, 10H); ^{13}C NMR ($CDCl_3$) 26.20, 37.49, 125.85, 127.83, 128.43, 140.23, 141.02; GC−MS *m/z* 260 (M^+), 260 calcd for $C_{20}H_{20}$. Anal. Calcd for $C_{20}H_{20}$: C, 92.26; H, 7.74. Found: C, 91.98; H, 7.78.

2,3-Bis(pentamethylphenyl)bicyclo[2.2.2]oct-2-ene (16): yield 94%; mp 239−240 °C (EtOH); ^{1}H NMR ($CDCl_3$) δ 1.77 (br d, J = 7.4 H_z, 4H), 1.91 (br d, J = 7.4 H_z, 4H), 2.14 (s, 12H), 2.18 (s, 6H), 2.19 (s, 12H), 2.63 (br s, 2H); ^{13}C NMR ($CDCl_3$) 16.63, 16.81, 19.83, 27.28, 37.79, 131.96, 132.08, 132.54, 139.45, 142.71; GC−MS *m/z* 400 (M^+), 400 calcd for $C_{30}H_{40}$. Anal. Calcd for $C_{30}H_{40}$: C, 89.94; H, 10.06. Found: C, 89.77; H, 10.01.

1,2-Bis(2,5-dimethoxy-4-methylphenyl)cyclohexene (8). Aluminum chloride (10.5 g, 78.6 mmol) was added in portions to a stirred solution of 2,5-dimethoxytoluene[42] (10.0 g, 65.8 mmol) and adipoyl chloride (5 mL, 34.4 mmol) in dichloromethane (100 mL) at 0 °C, under an argon atmosphere.[43] The dark brown reaction mixture was stirred at room temperature for 16 h, and then it was poured into a mixture of ice and concentrated hydrochloric acid. The organic layer was separated and washed several times with water followed by brine and dried over anhydrous magnesium sulfate. Evaporation of the solvent *in vacuo* afforded a pale yellow solid which was digested with hot isopropyl alcohol (150 mL). The resulting suspension was filtered hot, and the residue was further washed with hot isopropyl alcohol to yield pure 1,6-bis(2,5-dimethoxy-4-methylphenyl)hexane-1,6-dione as a colorless amorphous solid (8.7 g, 61%): mp 164−165 °C; IR (KBr) 2952, 2833, 1659, 1609, 1497, 1462, 1398, 1258, 1215, 1131, 1047, 878, 759, 702 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.74 (t, J = 7.5 Hz, 4H), 2.25 (s, 6H), 3.02 (t, J = 7.5 Hz, 4H), 3.81 (s, 6H), 3.86 (s, 6H), 6.77 (s, 2H), 7.23 (s, 2H); ^{13}C NMR ($CDCl_3$) 16.70, 24.40, 43.80, 55.80, 56.03, 111.16, 114.78, 125.61, 133.13, 151.69, 153.08, 201.64; GC−MS *m/z* 414 (M^+), 414 calcd for $C_{24}H_{30}O_6$.

According to the literature procedure,[14] titanium tetrachloride (2 mL, 18.4 mmol) was added dropwise to a prechilled (−20 °C) solution of the above 1,6-diarylhexanedione (2.12 g, 5.1 mmol) in anhydrous tetrahydrofuran (60 mL), under an argon atmosphere. To the resulting yellow suspension, zinc dust was added (2.3 g, 35 mmol) in one portion. The mixture was warmed to room temperature and was further refluxed for 16 h. The resulting gray slurry was cooled and treated with a saturated aqueous potassium carbonate solution (50 mL) followed by ether (100 mL). The organic phase was separated, and the aqueous layer was further extracted with ether (3 × 50 mL). The combined organic extracts were washed with water until neutral and dried over anhydrous magnesium sulfate. Evaporation of the solvent *in vacuo* and recrystallization from methanol afforded the pure 1,2-bis(2,5-dimethoxy-4-methylphenyl)cyclohex-1-ene (**8**) as an off-white amorphous solid (0.83 g, 42%): mp 110−112 °C; IR (KBr) 2931, 2826, 1504, 1462, 1398, 1208, 1047, 864, 787, 751, 611 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.82 (br s, 4H), 2.09 (s, 6H), 2.41 (br s, 4H), 3.51 (s, 6H), 3.72 (s, 6H), 6.35 (s, 2H), 6.53 (s, 2H); ^{13}C NMR ($CDCl_3$) 16.08, 23.10, 30.40, 55.73, 55.98, 113.24, 113.62, 124.57, 130.97, 133.75, 150.49, 151.01; GC−MS *m/z* 382 (M^+), 382 calcd for $C_{24}H_{30}O_4$. Anal. Calcd for $C_{24}H_{30}O_4$: C, 75.35; H, 7.91. Found: C, 75.02; H, 7.86.

1,2-Bis(2,5-dimethoxy-4-methylphenyl)cyclopent-1-ene (9). Friedel−Craft condensation[43] of glutaryl dichloride (4.4 mL, 34.5 mmol) and 2,5-dimethoxytoluene[42] (10 g, 65.8 mmol) using aluminum chloride (10.5 g, 78.6 mmol) as the catalyst in dichloromethane (100 mL), according to the procedure described above, afforded pure 1,5-bis(2,5-dimethoxy-4-methylphenyl)pentane-1,5-dione as a colorless carpet of tiny needles (9.22 g, 67%): mp 152−153 °C; IR (KBr) 2945, 2833, 1659, 1609, 1497, 1462, 1398, 1258, 1208, 1047, 878, 787, 702 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.08 (q, J = 7.2 Hz, 4H), 2.25 (s, 6H), 3.07 (t, J = 7.2 Hz, 4H), 3.81 (s, 6H), 3.84 (s, 6H), 6.76 (s, 2H), and 7.25 (s, 2H); ^{13}C NMR ($CDCl_3$) 16.67, 19.43, 43.16, 55.75, 56.00, 111.11, 114.76, 125.55, 133.15, 151.64, 153.11, 201.34; GC−MS *m/z* 400 (M^+), 400 calcd for $C_{23}H_{28}O_6$. The 1,5-diarylpantanedione (2.05 g, 5.1 mmol) thus obtained was converted to the corresponding 1,2-diarylcyclopentene (**9**) via McMurry reaction, according to the procedure described above. The crude material was slowly recrystallized from methanol at −20 °C to yield pure 1,2-bis(2,5-dimethoxy-4-methylphenyl)-cyclopent-1-ene (**9**) as an off-white solid (1.13 g, 60%): mp 74−76 °C; IR (KBr) 2924, 2826, 1504, 1462, 1391, 1208, 1047, 864, 787, 709 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.06 (q, 2H, J = 7.2 Hz, 2 H), 2.14 (s, 6H), 2.87 (t, J = 7.2 Hz, 4H), 3.48 (s, 6H), 3.64 (s, 6H), 6.41 (s, 2H), 6.61 (s, 2H); ^{13}C NMR ($CDCl_3$) 16.08, 23.01, 37.54, 55.67, 56.12, 112.80, 114.37, 125.32, 126.16, 137.38, 150.86, 151.22; GC−MS *m/z* 368 (M^+), 368 calcd for $C_{23}H_{28}O_4$. Anal. Calcd for $C_{23}H_{28}O_4$: C, 74.97; H, 7.66. Found: C, 74.51; H, 7.49.

1,2-Bis(2,5-dimethoxy-4-methylphenyl)acenaphthylene (10).[44] A solution of acenaphthenequinone (0.91 g, 5 mmol) in tetrahydrofuran (20 mL) was added dropwise to a stirred solution of arylmagnesium bromide [freshly prepared from 4-bromo-2,5-dimethoxytoluene (2.88 g, 12.5 mmol) and magnesium turnings (0.43 g, 18 mmol)] in tetrahydrofuran (50 mL) under an argon atmosphere. After completion of the addition the red-brown reaction mixture was refluxed for 16 h and was cooled to 0 °C. It was then treated with dichloromethane (100 mL) and water (100 mL). The organic phase was separated, washed with water, and dried over anhydrous magnesium sulfate. Evaporation of the solvents *in vacuo* produced an orange viscous oil which was digested with diethyl ether (20 mL) at 0 °C. A small amount of the monoadduct [GC−MS *m/z* 334 (M^+)] precipitated as a pale yellow solid which was removed by filtration. Evaporation of the filtrate *in vacuo* left a solid residue which was recrystallized from methanol at −20 °C to yield pure trans-1,2-bis(2,5-dimethoxy-4-methylphenyl)-1,2-dihydroacenaphthylene-1,2-diol as pale yellow crystals (1.56 g, 64%): mp 180−181 °C; IR (KBr) 3515, 2931, 2833, 1504, 1462, 1398, 1208, 1040, 885, 787 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.22 (s, 6H), 2.79 (s, 3H), 3.50 (s, 3H), 3.61 (s, 3H), 3.81 (s, 3H), 6.54 (s, 1H), 6.66 (s, 1H), 6.75 (s, 1H), 7.15 (s, 1H), 7.40−7.85 (m, 6H); GC−MS *m/z* 468 ($M^+ - H_2O$), 468 calcd for $C_{30}H_{23}O_6 - H_2O$.

A mixture of *trans*-diol (1.53 g, 3.15 mmol) from above and a catalytic amount of iodine (0.1 g, 0.4 mmol) in glacial acetic acid (40 mL) was refluxed for 1 h. The reaction mixture was cooled and poured into a saturated aqueous solution of sodium bisulfite (60 mL) and extracted with dichloromethane (2 × 100 mL). The dichloromethane layer was washed with water and dried over anhydrous magnesium sulfate. Evaporation of the solvent *in vacuo* yielded crude pinacolone [GC−MS *m/z* 468 (M^+)] which was used in next step without further purification. Thus, a mixture of the crude pinacolone and lithium aluminum hydride (0.06 g, 1.5 mmol) in tetrahydrofuran (60 mL) was refluxed for 1 h. The usual aqueous workup yielded the crude alcohol as an amorphous solid [GC−MS *m/z* 470 (M^+)]. The crude alcohol was rearranged to the corresponding 1,2-diarylacenaphthylene (**10**) using acetic acid (40 mL) and a catalytic amount of iodine (0.1 g, 0.4 mmol), as described above. Recrystallization from ethanol at −20 °C afforded pure **10** as an orange solid (1.17 g, 82% over three steps): mp 141−143 °C; IR (KBr) 2995, 2931, 2826, 1490, 1462, 1434, 1208, 1047, 871, 773, 695 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.24 (s, 6H), 3.54 (s, 6H), 3.60 (s, 6H), 6.75 (s, 2H), 6.76 (s, 2H), 7.51 (dd, J = 8.1 and 6.9 Hz, 2H), 7.61 (d, J = 6.9 Hz, 2H), 7.78 (d, J = 8.1 Hz, 2H); ^{13}C NMR ($CDCl_3$) 16.34, 55.89, 55.98, 113.95, 114.69, 122.95, 123.90, 126.47, 126.76, 127.50, 128.26, 136.73, 140.34, 148.51, 151.03, 151.48; GC−MS *m/z* 452 (M^+), 452 calcd for $C_{30}H_{28}O_4$. Anal. Calcd for $C_{30}H_{28}O_4$: C, 79.62; H, 6.24. Found: C, 79.25; H, 6.23.

9,10-Bis(2,5-dimethoxy-4-methylphenyl)phenanthrene[44] (11). Reaction of phenanthroquinone (1.04 g, 5 mmol) and arylmagnesium bromide (12 mmol) in tetrahydrofuran (50 mL) readily afforded the *trans*-1,2-bis(2,5-dimethoxy-4-methylphenyl)-1,2-dihydrophenanthrene-1,2-diol [(1.24 g, 48%): mp 240−242 °C; IR (KBr) 3500, 2931, 2833, 1504, 1469,

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1391, 1208, 1040, 850, 787, 752, 695 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.04 (s, 6H), 3.15 (s, 6H), 4.02 (s, 6H), 6.12 (s, 2H), 6.72 (s, 2H), 6.74 (s, 2H), 7.24 (dd, J = 7.5 and 7.2 Hz, 2H), 7.36 (dd, J = 7.5 and 7.2 Hz, 2H), 7.71 (d, J = 7.2 Hz, 2H), 7.85 (d, J = 7.5 Hz, 2H); GC−MS *m/z* 512 (M^+), 512 calcd for $C_{32}H_{32}O_6$] which was converted (with the same sequence of reactions as described for the corresponding acenaphthylene **10**) to 9,10-bis(2,5-dimethoxy-4-methylphenyl)phenanthrene (**11**). Recrystallization from isopropyl alcohol furnished pure **11** as an ivory powder (1.00 g, 88% over three steps): mp 224−226 °C; IR (KBr) 2931, 2826, 1504, 1462, 1398, 1208, 1047, 864, 758, 723, 632 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.21 (s, 3H), 2.22 (s, 3H), 3.48 (s, 3H), 3.58 (s, 6H), 3.59 (s, 6H), 6.59 (s, 1H), 6.64 (s, 3H), 7.44−7.63 (m, 6H), 8.77 (d, J = 8.4 Hz, 2H); ^{13}C NMR (CDCl$_3$) 16.37, 16.41, 55.74, 55.84, 56.01, 113.13, 113.80, 115.56, 122.48, 126.01, 126.27, 126.32, 126.62, 127.46, 127.72, 129.97, 130.21, 131.85, 131.97, 134.51, 134.71, 150.89, 151.20, 151.48; GC−MS *m/z* 478 (M^+), 478 calcd for $C_{32}H_{30}O_4$. Anal. Calcd for $C_{32}H_{30}O_4$: C, 80.31; H, 6.32. Found: C, 79.64; H 6.25.

(*E*)-1-(2,5-Dimethoxy-4-methylphenyl)-2-pentamethylphenylethene (15). To a suspension of sodium hydride (0.80 g, 60% dispersion in mineral oil, 20 mmol) in a mixture of *N*,*N*-dimethylformamido-dichloromethane (2:1, 60 mL) at 0 °C, was added (pentamethylbenzyl)triphenylphosphonium bromide [prepared by refluxing a solution of pentamethylbenzyl bromide[45] (5.59 g, 11.1 mmol) and triphenylphosphine (12 mmol) in toluene (50 mL) for 48 h] under an argon atmosphere. After the mixture was stirred for 5 min, 2,5-dimethoxy-4-methylbenzaldehyde[46] (2.0 g, 11.1 mmol) was added in one portion and the mixture was refluxed for 3 h. The usual aqueous workup and evaporation of the solvent *in vacuo* afforded a solid residue which upon chromatographic purification on silica gel with 1:1 chloroform−hexanes mixture as eluent and recrystallization from methanol afforded pure (*E*)-stilbene **15** as colorless plates (1.78 g, 50%): mp 113−114 °C; IR (KBr) 2924, 1504, 1464, 1398, 1208, 1047, 977, 850 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.23 (s, 9H), 2.25 (s, 3H), 2.28 (s, 6H), 3.76 (s, 6H), 3.86 (s, 6H), 6.71 (d, J = 16.8 Hz, 1H), 6.73 (s, 1H), 7.07 (s, 1H), 7.09 (d, J = 16.8 Hz, 1H); ^{13}C NMR (CDCl$_3$) 16.33, 16.59, 16.77, 18.08, 56.10, 56.74, 108.76, 115.67, 125.28, 127.39, 129.10, 129.39, 132.11, 132.76, 133.89, 136.46, 151.39, 152.54; GC−MS *m/z* 324 (M^+), calcd for $C_{22}H_{28}O_2$. Anal. Calcd for $C_{22}H_{28}O_2$: C, 81.44; H, 8.70. Found: C, 81.18; H, 8.59.

Hydrogenation of Olefins with the Borane-Methyl Sulfide (BMS) Complex in the Presence of Orange CRET$^{+\cdot}$ in Dichloromethane. General Procedure. Solid *Orange* CRET$^{+\cdot}$ (0.67 g, 1.1 mmol) was added to a prechilled (~0 °C) solution of the olefin **1** (408 mg, 1.0 mmol) in dichloromethane (20 mL), under an argon atmosphere. The highly colored mixture was stirred, and the BMS complex (0.20 mL, 2.0 mmol) was added with the aid of a hypodermic syringe. The highly colored solution was progressively bleached to afford a pale yellow solution. The reaction mixture was quenched with a saturated aqueous potassium carbonate solution (20 mL) and diluted with dichloromethane (20 mL). The organic layer was separated, washed with water (3 × 25 mL), and dried over anhydrous magnesium sulfate. Evaporation of the solvent *in vacuo* afforded a solid residue which upon GC and GC−MS analysis indicated that it consisted mainly of reduced 2,3-diarylbicyclooctane **1H$_2$** and neutral CRET together with traces of unreacted bicyclooctene **1**. Further purification by flash chromatography on silica gel using mixture of ether−hexanes (1:1) as eluent afforded the hydrogenated product **1H$_2$** in excellent yield (360 mg, 88%) together with unreacted diarylbicyclooctene **1** (33 mg, 8%). [Note that the neutral CRET (292 mg, 98%) was recovered quantitatively].

In a control experiment, a solution of olefin **1** (41 mg, 0.1 mmol) in dichloromethane (2 mL) was treated with excess BMS complex (0.02 mL, 0.2 mmol) under an argon atmosphere at 0 °C. The reaction mixture was stirred for 3 h at 0 °C and was further refluxed overnight. The cooled reaction mixture was treated with ethanol (1 mL) and hydrogen peroxide (30%, 1 mL). After stirring for 1 h, it was worked up in the usual manner to afford the unreacted olefin **1** in a quantitative yield (38 mg, 93%).

The various hydrogenation products listed below were prepared using the general procedure described above and the characteristic spectral data are given below.

2,3-Bis(2,5-dimethoxy-4-methylphenyl)bicyclo[2.2.2]octane (1H$_2$): mp 128−129 °C; IR (KBr) 2938, 2861, 1504, 1469, 1398, 1363, 1208, 1047, 871, 653 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.51−1.88 (m, 10H), 2.10 (s, 6H), 3.49 (s, 6H), 3.50 (s, 6H), 3.87 (br s, 2H), 6.42 (s, 2H), 6.49 (s, 2H); ^{13}C NMR (CDCl$_3$) 15.45, 21.58, 28.00, 28.67, 39.25, 55.61, 56.14, 112.15, 113.02, 123.23, 130.38, 150.53, 151.34; GC−MS *m/z* 410 (M^+), 410 calcd for $C_{26}H_{34}O_4$. Anal. Calcd for $C_{26}H_{34}O_4$: C, 76.06; H, 8.35. Found: C, 75.19; H, 8.35.

2,3-Bis(4-methoxyphenyl)bicyclo[2.2.2]octane (2H$_2$): mp 87−88 °C; ^{1}H NMR (CDCl$_3$) δ 1.44−1.94 (m, 10H), 3.55 (s, 2H), 3.69 (s, 6H), 6.60 (d, J = 8.7 Hz, 4H), 6.83 (d, J = 8.7 Hz, 4H); ^{13}C NMR (CDCl$_3$) 21.03, 27.82, 29.63, 45.54, 55.00, 112.66, 130.09, 135.33, 156.63; GC−MS *m/z* 322 (M^+), 322 calcd for $C_{22}H_{26}O_2$. Anal. Calcd for $C_{22}H_{26}O_2$: C, 81.95; H, 8.13. Found: C, 81.51; H, 7.98.

2,3-Bis(4-methylphenyl)bicyclo[2.2.2]octane (3H$_2$): mp 74−75 °C; ^{1}H NMR (CDCl$_3$) δ 1.52 (br d, J = 8.1 Hz, 2H), 1.77−1.91 (m, 8H), 1.97 (br s, 2H), 2.22 (s, 6H), 3.04 (s, 2H), 6.84 (d, J = 8.4 Hz, 4H), 6.89 (d, J = 8.4 Hz, 4H); ^{13}C NMR (CDCl$_3$) 20.88, 21.11, 27.88, 29.65, 45.97, 128.00, 129.05, 133.88, 140.17; GC−MS *m/z* 290 (M^+), 290 calcd for $C_{22}H_{26}$. Anal. Calcd for $C_{22}H_{26}$: C, 90.98; H, 9.02. Found: C, 90.42; H, 8.83.

2,3-Diphenylbicyclo[2.2.2]octane (4H$_2$): mp 93−94 °C; ^{1}H NMR (CDCl$_3$) δ 1.55−1.97 (m, 8H), 2.08 (br s, 2H), 3.71 (s, 2H), 6.97−7.14 (m, 10H); ^{13}C NMR (CDCl$_3$) 21.06, 27.87, 29.42, 46.42, 124.69, 127.23, 129.21, 143.14; GC−MS *m/z* 262 (M^+), 262 calcd for $C_{20}H_{22}$. Anal. Calcd for $C_{20}H_{22}$: C, 91.55; H, 8.45. Found: C, 90.97; H, 8.51.

Biadamantane (5H$_2$): mp 184−185 °C (lit.[19] mp 184−185 °C) ; ^{1}H NMR (CDCl$_3$) δ 1.38−1.88 (m, 30 H); ^{13}C NMR (CDCl$_3$) 27.91, 28.08, 28.25, 31.66, 38.44, 39.63, 42.41; GC−MS *m/z* 270 (M^+), calcd for $C_{20}H_{30}$.

2-(1,1-Dianisylmethyl)adamantane (6H$_2$): mp 135−136 °C; ^{1}H NMR (CDCl$_3$) δ 1.42−1.91 (m, 15H), 2.41 (d, J = 12.3 Hz, 1H), 3.75 (s, 6H), 6.82 (d, J = 8.4 Hz, 4H), 7.23 (d, J = 8.4 Hz, 4H); ^{13}C NMR (CDCl$_3$) 27.80, 28.04, 29.06, 31.25, 38.32, 39.29, 47.77, 51.34, 113.82, 128.59, 136.80, 157.60; GC−MS *m/z* 362 (M^+), 362 calcd for $C_{25}H_{30}O_2$. Anal. Calcd for $C_{25}H_{30}O_2$: C, 82.83; H, 8.34. Found: C, 82.48; H, 3.22.

1,1,2,2-Tetrakis(4-methoxyphenyl)ethane (7H$_2$): mp 188−189 °C (lit.[22] mp 189−190 °C) ; ^{1}H NMR (CDCl$_3$) δ 2.31 (s, 2H), 3.82 (s, 12H), 6.97 (d, J = 8.4 Hz, 8H), 7.19 (d, J = 8.4 Hz, 8H); ^{13}C NMR (CDCl$_3$) 49.30, 114.08, 129.27,137.05, 157.90; GC−MS *m/z* 227 (M^+ - 227), 227 calcd for $C_{30}H_{30}O_4$ - $C_{15}H_{15}O_2$.

1,2-Bis(2,5-dimethoxy-4-methylphenyl)cyclohexane (8H$_2$): mp 105−107 °C; IR (KBr) 2931, 2847, 1511, 1462, 1398, 1208, 1047, 857, 808, 681 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.67−1.82 (m, 4H), 1.97−2.00 (m, 4H), 2.11 (s, 6H), 3.47 (s, 6H), 3.58 (s, 6H), 3.69 (dd, J = 4.7 Hz, 2H), 6.48 (s, 2H), 6.59 (s, 2H); ^{13}C NMR (CDCl$_3$) 15.84, 24.84, 29.03, 36.09, 56.11, 56.32, 112.38, 113.60, 123.73, 131.97, 150.82, 151.38; GC−MS *m/z* 384 (M^+), 384 calcd for $C_{24}H_{32}O_4$. Anal. Calcd for $C_{24}H_{32}O_4$: C, 74.97; H, 8.39. Found: C, 74.64; H, 8.42.

1,2-Bis(2,5-dimethoxy-4-methylphenyl)cyclopentane (9H$_2$): mp 100 °C; IR (KBr) 2945, 2826, 1511, 1469, 1398, 1209, 1047, 864, 829, 681, 632 cm^{-1};^{1}H NMR (CDCl$_3$) δ 1.98−2.07 (m, 6H), 2.11 (s, 6H), 3.44 (s, 6H), 3.54 (s, 6H), 3.83 (dd, J = 4.8 Hz, 2H), 6.23 (s, 2H), 6.44 (s, 2H); ^{13}C NMR (CDCl$_3$) 15.87, 24.00, 30.72, 41.71, 56.00, 111.38, 113.22, 123.83, 129.84, 150.83, 151.43; GC−MS *m/z* 370 (M^+), 370 calcd for $C_{23}H_{30}O_4$. Anal. Calcd for $C_{23}H_{30}O_4$: C, 74.56; H, 8.16. Found: C, 74.51; H, 8.10.

1,2-Bis(2,5-dimethoxy-4-methylphenyl)-1,2-dihydroacenaphthylene (10H$_2$): mp 124−125 °C; IR (KBr) 2995, 2931, 2826, 1511, 1462, 1398, 1208, 1047, 857, 829, 787, 660 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.07 (s, 6H), 3.27 (s, 6H), 3.58 (s, 6H), 5.69 (s, 2H), 5.93 (br s, 2H), 6.43 (s, 2H), 7.15 (d, J = 6.9 Hz, 2H), 7.51 (dd, J = 8.1 and 6.9 Hz, 2H), 7.71 (d, J = 8.1

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Hz, 2H); ^{13}C NMR (CDCl$_3$) 16.02, 30.87, 55.81, 55.97, 112.67, 113.71, 120.62, 122.65, 124.81, 128.08, 131.20, 139.51, 147.65, 148.52, 150.72, 151.58; GC−MS *m/z* 454 (M$^+$), 454 calcd for $C_{30}H_{30}O_4$. Anal. Calcd for $C_{30}H_{30}O_4$: C, 79.27; H, 6.65. Found: C, 79.22; H, 6.69.

2,3-Bis(4-methoxyphenyl)hexane (12H$_2$): mp 144−145 °C (lit.[47] mp 146 °C); ^{1}H NMR (CDCl$_3$) δ 0.55 (t, 6H), 1.20−1.52 (m, 4H), 2.52 (sym m, 2H), 3.83 (s, 6H), 6.90 (d, $J = 8.7$ Hz, 4H), 7.12 (d, $J = 8.7$ Hz, 4H); ^{13}C NMR (CDCl$_3$) 12.20, 27.34, 53.47, 55.07, 113.20, 129.10, 136.52, 157.70; GC−MS *m/z* 298 (M$^+$), 298 calcd for $C_{20}H_{26}O_2$.

1,2-Bis(2,5-dimethoxy-4-methylphenyl)ethane (13H$_2$): mp 123−124 °C lit.[40] mp 124−125 °C); IR (CDCl$_3$) 2931, 2833, 1511, 1462, 1398, 1208, 1047, 857, 836, 653 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.20 (s, 6H), 2.84 (s, 4H,), 3.73 (s, 6H), 3.77 (s, 6H), 6.59 (s, 2H), 6.67 (s, 2H); ^{13}C NMR (CDCl$_3$) 16.05, 30.69, 56.07, 56.26, 113.00, 114.00, 124.45, 128.67, 151.23, 151.46; GC−MS *m/z* 330 (M$^+$), 330 calcd for $C_{20}H_{26}O_4$.

1,2-Bis(4-methoxyphenyl)ethane (14H$_2$): mp 124−125 °C (lit.[48] mp 125 °C); ^{1}H NMR (CDCl$_3$) δ 2.87 (s, 4H), 3.81 (s, 6H), 6.86 (d, $J = 8.6$ Hz, 4H), 7.12 (d, $J = 8.6$ Hz, 4H); ^{13}C NMR (CDCl$_3$) 37.21, 55.12, 113.59, 129.29, 113.85, 157.67; GC−MS *m/z* 242 (M$^+$) 242 calcd for $C_{16}H_{18}O_2$.

1-(2,5-Dimethoxy-4-methylphenyl)-2-(pentamethylphenyl)ethane (15H$_2$): mp 145−146 °C; IR (KBr) 2924, 1504, 1469, 1398, 1208, 1047, 850, 688 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.23 (s, 3H), 2.25 (s, 9H), 2.36 (s, 6H), 2.69 (m, 2H), 2.91 (m, 2H), 3.81 (s, 3H), 3.83 (s, 3H), 6.70 (s, 1H), 6.72 (s, 1H); ^{13}C NMR (CDCl$_3$) 16.11, 16.17, 16.80, 31.21, 31.74, 56.08, 56.28, 112.91, 113.97, 124.85, 125.23, 128.83, 131.93, 132.50, 136.10, 151.36, 151.64; GC−MS *m/z* 326 (M$^+$), calcd for $C_{22}H_{30}O_2$. Anal. Calcd for $C_{22}H_{30}O_2$: C, 80.94; H, 9.26. Found: C, 80.89; H, 9.10.

Attempted Hydrogenation of 2,3-Bis(pentamethylphenyl)bicyclooct-2-ene (16). To a prechilled (~0 °C) solution of the olefin **16** (200 mg, 0.5 mmol) in dichloromethane (10 mL) was added solid *Orange* CRET$^{+\cdot}$ (335 mg, 0.55 mmol), under an argon atmosphere. The dark brown mixture was stirred and the BMS complex (0.1 mL, 1 mmol) was added. The highly colored solution bleached slowly (~6 h) to afford a pale yellow solution. The standard aqueous quench/workup, as described above, afforded a solid residue, which upon GC and GC−MS analysis showed that residue to consist of unreated 2,3-bis(pentamethylphenyl)bicyclooctene **16** (198 mg, 99%) and neutral CRET (148 mg, 99%). Thus, no hydrogenation product derived from olefin **16** was detected.

Preparative-Scale Electrolysis of Olefins in the Presence of the Borane-Methyl Sulfide Complex in Dichloromethane. The electroxidations were carried out with a PAR Model 173 potentiostat/galvanostat equipped with PAR Model 179 digital coulometer which provided a feed-back compensation for ohmic drop between working and the reference electrodes. The voltage-follower amplifier (PAR Model 178) was mounted external to the potentiostat with a minimum length of high-impedance connection to the reference electrode. The electrochemical cell was of airtight design with high vacuum. The counter electrode was constructed of a double coil of nichrome wire with a large surface area. The working electrode consisted of a platinum-wire cage wrapped with a platinum gauze with a total surface area of ~1.1 cm^2. The electrooxidations were carried out at constant potential.

General Procedure. A solution of olefin **2** (320 mg, 1.0 mmol) in dichloromethane (50 mL) containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) was placed in the center compartment of the electrochemical cell. The reference electrode and counter electrode compartments were charged with the dichloromethane solution containing 0.1 M electrolyte. Thus, passing a small anodic current at a constant potential of 1.0 V for a short duration (~20 s) through the colorless solution of **2** caused it to turn bright magenta (red) immediately. UV−vis spectrometric analysis of the red solution showed a well-resolved band with a maximum at $\lambda_{max} = 546$ nm, a shoulder at 492 nm, and a broad band extending beyond > 800 nm. When the highly colored mixture in the central compartment of the cell was treated with the BMS complex (0.2 mL, 2 mmol) with the aid of a hypodermic syringe; the solution faded immediately. The mixture was further electrolyzed at a constant potential of 1.0 V for 3.5 h. The current flow was recorded by the digitized coulometer to be 103 C during this period. The current flow was stopped at this point, and the pale yellow reaction mixture was collected in a flask and the solvent was removed *in vacuo*. The solid residue was suspended in ether and filtered through a short pad of silica gel to afford the colorless crystalline 2,3-dianisylbicyclo[2.2.2]octane **2H$_2$** in an excellent yield (312 mg, 0.97 mmol). The various olefins listed in Table 2 afforded excellent yields of hydrogenated products.

Hydrogenation of Olefins with the Borane-Methyl Sulfide (BMS) Complex Using Tetrafluoroboric Acid (HBF$_4$) in Dichloromethane. General Procedure. A solution of bicyclooctene **1** (408 mg, 1 mmol) in anhydrous dichloromethane (10 mL) was cooled in an ice−salt bath (ca. −10 °C) and 2 equiv of tetrafluoroboric acid (Aldrich) was added under an argon atmosphere. The solution immediately turned bright red which upon spectral analysis (UV−vis) showed the formation of protonated olefin **1H$^+$** with the absorption maximum at $\lambda_{max} = 518$ nm. After the solution was stirred for 10 min (at −10 °C), the BMS complex (0.20 mL, 2.0 mmol) was added with the aid of a hypodermic syringe. The highly colored mixture progressively bleached to afford a pale yellow solution (~5 min). The reaction mixture was quenched with a saturated aqueous sodium bicarbonate solution (20 mL) and diluted with dichloromethane (20 mL). The organic layer was washed with water (3 × 25 mL) and dried over anhydrous magnesium sulfate. Evaporation of the solvent *in vacuo* afforded reduced 2,3-diarylbicyclooctane **1H$_2$** as a crystalline solid in excellent yield (402 mg, 98%). Similarly, the other olefins listed in Table 3 were reduced to the corresponding alkanes.

It is interesting to note that when a dark red solution of 0.1 M tetraanisylethylene (**7**) in dichloromethane (10 mL) containing 2 equiv of HBF$_4$ (~0 °C) was treated with the borane complex (2 equiv) under an argon atmosphere, the solution immediately turned dark blue. The UV−vis spectral analysis of the highly colored solution showed that the blue color coincided with that of tetraanisylethylene cation radical **7**$^{+\cdot}$ ($\lambda_{max} = 565$, 920 nm).[12,21] The dark blue solution was stirred at room temperature for 16 h and the aqueous workup of the resulting pale brown solution afforded a crude residue, which upon GC and GC−MS analysis (internal standard method) indicated a mixture of reduced tetraanisylethane **7H$_2$** (36 mg, 8%) and unreacted tetraanisylethylene **7** (414 mg, 92%). [This observation suggests that the carbocation (**7H$^+$**) formed in the HBF$_4$ treatment of **7** may undergo interconversion to the cation radical **7**$^{+\cdot}$ which is then (slowly) converted to **7H$_2$** by BH$_3$/SMe$_2$.]

Attempted Hydrogenation of 2,3-Bis(pentamethylphenyl)bicyclooct-2-ene (16) in the Presence of A Strong Brønsted Acid. A solution of bicyclooctene **16** (200 mg, 0.5 mmol) in dichloromethane (5 mL) was treated with tetrafluoroboric acid (0.075 mL, 1 mmol) at ~0 °C. The resulting pale brown reaction mixture was stirred for 10 min (at 0 °C), and the BMS complex (0.1 mL, 1 mmol) was added. The reaction mixture progressively bleached (~ 10 min) to afford a pale yellow solution. The aqueous workup afforded unreacted 2,3-bis(pentamethylphenyl)bicyclooct-2-ene (**16**), identified by GC and GC−MS, in essentially quantitative yield (197 mg). In another similar experiment, a solution of olefin **16** (200 mg, 0.5 mmol) in dichloromethane (5 mL) was treated with trifluoromethanesufonic acid (151 mg, 1 mmol) at 0 °C to yield a dark red solution. The resulting red solution was stirred for 10 min, and the BMS complex (0.1 mL, 1 mmol) was added with the aid of a hypodermic syringe. The highly colored reaction mixture rapidly bleached to afford a colorless solution. However, the standard aqueous workup as described above, afforded the unreacted olefin **16** in quantitative yield (198 mg, 99%).

Cyclic Voltammometry in the Presence of Added Borane-Methyl Sulfide Complex. Cyclic voltammetry (CV) was performed on a BAS 100A Electrochemical Analyzer. The

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CV cell was of an airtight design with high vacuum Teflon valves and Viton O-ring seals to allow an inert atmosphere to be maintained without contamination by grease. The working electrode consisted of an adjustable platinum disk embedded in a glass seal to allow periodic polishing (with a fine emery cloth) without significantly changing the surface area (~1 mm^2). The saturated calomel electrode (SCE) and its salt bridge was separated from the catholyte by a sintered glass frit. The counter electrode consisted of a platinum gauze that was separated from the working electrode by ~3 mm. The CV measurements were carried out in a solution of 0.2 M supporting electrolyte (tetra-*n*-butylammonium hexafluorophosphate) and 5×10^{-3} M olefin in dry dichloromethane under an argon atmosphere. The borane complex (1×10^{-2} M) was added to the same solution with the aid of a hypodermic syringe and the cyclic voltammogram was recorded. All the cyclic voltammograms were measured at the same sweep rate of 200 mV s^{-1} and were *iR* compensated. The potentials were referenced to SCE which was calibrated with added ferrocene (5×10^{-3} M). The oxidation potential ($E_{1/2}$) values were the average of the anodic and cathodic peak potentials and are listed in Table 1.

Spectral Observation of the Olefin Cation Radicals. Characteristic colorations were observed in both procedures for the hydrogenation of olefins with borane−methyl sulfide complex, *i.e.* via the addition of *Orange* CRET$^{+\cdot}$ or by the equivalent electrochemical method. Thus, the colors accompanying the hydrogenation of olefins with borane were identified as the olefin cation radicals in the following way.

By Electrochemical Oxidation. The olefin **2** (32 mg, 0.1 mmol) was dissolved in dichloromethane (30 mL) containing 0.1 M electrolyte (TBAH). This mixture was placed in the center compartment of the electrochemical cell. The reference electrode and counter electrode compartments were charged with the dichloromethane containing 0.1 M electrolyte. The mixture was electrolyzed at a constant potential of 1.0 V for 2 min. The current flow recorded with the aid of a digitized coulometer was 2.5 C. The current flow was stopped and dark magenta solution of $\mathbf{2}^{\cdot+}$ PF_6^- thus obtained was analyzed by UV−vis spectroscopy. The spectrum showed a well-resolved maximum at $\lambda_{max} = 546$ nm, a shoulder at 492 nm, and a broad band extending beyond >800 nm. The UV−vis absorption maxima for various olefin cation radicals, generated by similar electrochemical oxidation, are listed in Table 2.

By Chemical Oxidation with *Orange* CRET$^{+\cdot}$ $SbCl_6^-$. A 1-cm quartz cuvette equipped with a sidearm and Teflon needle valve (Schlenk adapter) was charged with a solution of *Orange* CRET$^{+\cdot}$ (2 mL, 0.0001 M) in anhydrous dichloromethane. The solution was cooled in an ice−salt bath (ca. −10 °C), and a prechilled dichloromethane solution of 2,3-dianisylbicyclooctene **2** (0.2 mL, 0.01 M) was added under an argon atmosphere with the aid of a hypodermic syringe. The color of the solution immediately turned magenta red and UV−vis absorption spectrum was recorded. The spectrum showed a maximum at $\lambda_{max} = 546$ nm, a shoulder at 492 nm, and a broad band extending beyond 800 nm. Note that the UV−vis absorption spectrum of $\mathbf{2}^{\cdot+}$ $SbCl_6^-$ was found to be identical with the $\mathbf{2}^{\cdot+}$ PF_6^- and BF_4^- salts (*vide infra*). [Also note that the UV−vis absorption spectra of various olefin cation radicals generated using *Orange* CRET$^{+\cdot}$ were identical in all respect to those generated either using tris(4-bromophenyl)aminium hexachloroantimonate or by electrochemical (anodic) oxidation in anhydrous dichloromethane.]

Preparation of 2,3-*Bis*(4-methoxyphenyl)bicyclo[2.2.2]-oct-2-ene Cation−Radical Salt ($\mathbf{2}^{\cdot+}$ BF_4^-) and its Reaction with Borane. A 100-mL flask fitted with a quartz cuvette and a Schlenk adapter was charged with NO^+ BF_4^- (118 mg, 1 mmol), and a prechilled (ice−salt bath) solution of olefin **2** (320 mg, 1 mmol) in anhydrous dichloromethane (50 mL) was added under an argon atmosphere. The heterogeneous mixture was vigorously stirred at −10 °C. The nitric oxide (NO) evolved [UV−vis spectral analysis of the gas revealed the characteristic absorbances of NO at $\lambda_{max} = 204$, 214, and 226 nm][10,49] was entrained by bubbling argon through the solution. The magenta (red) suspension was stirred for 30 min to yield a dark red solution of $\mathbf{2}^{\cdot+}$ [λ_{max} (nm) = 546, 492 (sh), >800 nm].

Reaction of $\mathbf{2}^{\cdot+}$ BF_4^- with the Borane-Methyl Sulfide Complex. To a prechilled (−10 °C) dark red solution of $\mathbf{2}^{\cdot+}$ BF_4^- [prepared from NO^+ BF_4^- (118 mg, 1 mmol) and olefin **2** (320 mg, 1 mmol) in dichloromethane (50 mL)] was added the borane−methyl sulfide complex (0.2 mL, 2 mmol) under an argon atmosphere. The reaction mixture was stirred for 10 min to afford a pale yellow solution. The aqueous workup, as above, afforded the dianisylbicyclo[2.2.2]octane $\mathbf{2H_2}$ in almost quantitative yield (306 mg, 0.95 mmol).

Reaction of $\mathbf{2}^{\cdot+}$ BF_4^- with Borohydride.[50] A cold solution of PPN^+ BH_4^- (0.22 mmol) in dichloromethane (5 mL) was added to a dark red solution of $\mathbf{2}^{\cdot+}$ BF_4^- (0.02 M, 10 mL) at −10 °C, under an argon atmosphere. The highly colored reaction mixture faded within a min to a colorless solution. The aqueous workup afforded the unreacted 2,3-dianisylbicyclo[2.2.2]oct-2-ene (**2**) in almost quantitative yield (62 mg, 0.19 mmol).

X-ray Crystallography of 2,3-Bis(2,5-dimethoxy-4-methyl)bicyclo[2.2.2]-octane ($\mathbf{1H_2}$). Slow evaporation of the diethyl ether−hexane solution of $\mathbf{1H_2}$ at room temperature yielded colorless prismatic blocks. A suitable crystal with the dimensions 0.40 × 0.45 × 0.60 mm was mounted in a random orientation on a glass fiber. The intensity data were collected with the aid of a Nicolet R3m/V automatic diffractometer under a stream of nitrogen at approximately −50 °C. The radiation used was Mo Kα, monochromatized by a highly ordered graphite crystal. The 25 standard reflections were used to refine the cell parameters. The crystal system was found to be monoclinic with the space group $P2_1/c$, $a = 9.184$ (3) Å, $b = 12.356$ (4) Å, $c = 20.117$ (6) Å, $\beta = 95.12$ (2)°, $V = 2274$ Å^3, $Z = 4$. The data were collected in the range $4^o \leq 2\theta \leq 50^o$. Two standard reflections monitored every 2 h during data collection showed no significant variations. A total of 3986 reflections were collected of which 3036 were found to satisfy the condition $I > 3\sigma(I_0)$. The structure was solved using the direct methods program (SHELXTL-PLUS), which revealed the positions of all non-hydrogen atoms in the molecule. Remaining atoms were located in the subsequent difference Fourier syntheses. The usual sequence of isotropic and anisotropic refinement was followed, after which all the hydrogen atoms were fixed in the ideal calculated positions. The two *p*-methyl groups on the phenyl moieties were refined as ideal rigid bodies and allowed to rotate independently. At the end of the refinement, the final $R = 0.046$ and $R_w = 0.046$ for 278 variables.

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(50) Note that a better hydride donor such as borohydride anion was completely ineffective as hydrogen donor. For example, it reacted with cation radical $\mathbf{2}^{\cdot+}$ exclusively via electron transfer owing to its low oxidation potential of $E^o_{ox} = -1.0$ V vs SCE.[51]

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