8Ab (R = (*E*)-PhCH=CH, R′ = CH_3): mp 121–123 °C; ^1H NMR δ 7.38–7.13 (m, 12 H), 6.79 (d, 2 H, *J* = 7.8 Hz), 6.71 (t, 1 H, *J* = 7.3 Hz), 6.44 (d, 1 H, *J* = 15.9 Hz), 6.29 (dd, 1 H, *J* = 7.3, 15.9 Hz), 4.87 (m, 1 H), 4.67 (d, 1 H, *J* = 11.0 Hz), 4.26 (d, 1 H, *J* = 2.5 Hz), 1.05 (s, 9 H); ^{13}C NMR 146.55, 136.56, 134.32, 133.36, 129.77, 129.27, 128.99, 128.73, 128.49, 128.46, 127.70, 126.85, 126.58, 118.35, 114.85, 65.58, 58.68, 55.74, 23.81.

Anal. Calcd for $C_{26}H_{29}NOS$: C, 77.37; H, 7.26; N, 3.47. Found: C, 77.39; H, 7.18; N, 3.34.

8Ac (R = 2-furyl, R′ = Ph): mp 122–123 °C; ^1H NMR δ 7.32–7.30 (m, 4 H), 7.17–7.12 (m, 4 H), 6.83 (d, 2 H, *J* = 7.6 Hz), 6.72 (t, 1 H, *J* = 7.3 Hz), 6.20 (dd, 1 H, *J* = 1.8, 3.3 Hz), 6.02 (d, 1 H, *J* = 3.3 Hz), 5.58 (dd, 1 H, *J* = 2.7, 11.5 Hz), 4.42 (d, 1 H, *J* = 2.7 Hz), 4.23 (d, 1 H, *J* = 11.5 Hz), 1.08 (s, 9 H); ^{13}C NMR 153.30, 146.48, 141.66, 133.43, 129.74, 129.23, 128.76, 128.50, 118.97, 114.97, 110.47, 107.99, 64.57, 55.58, 52.94, 23.85; MS 367 (M^+, 2), 262 (M − S(O)-*t*-Bu, 24), 261 (65), 172 (100).

Anal. Calcd for $C_{22}H_{25}NO_2S$: C, 71.89; H, 6.87; N, 3.87. Found: C, 71.66; H, 6.82; N, 3.79.

8Ae (R = CH_3CH_2, R′ = Ph): viscous liquid; ^1H NMR δ 7.41–7.13 (m, 6 H), 6.86 (d, 2 H, *J* = 8.2 Hz), 6.71 (q, 2 H, *J* = 7.6 Hz), 4.29 (m, 1 H), 4.01 (d, 1 H, *J* = 2.3 Hz), 3.47 (d, 1 H, *J* = 11.3 Hz), 1.59 (m, 2 H), 1.00 (s, 9 H), 0.94 (t, 3 H, *J* = 7.4 Hz); ^{13}C NMR 147.92, 134.18, 129.98, 129.34, 128.87, 128.28, 117.80, 114.34, 65.08, 55.53, 55.43, 27.12, 23.86, 11.49; MS 329 (M^+, 3), 224 (M − S(O)-*t*-Bu, 34), 134 (100).

8Se (R = CH_3CH_2, R′ = Ph): ^{13}C NMR 146.71, 133.94, 130.14, 129.59, 128.55, 128.04, 117.63, 113.61, 60.76, 56.22, 53.89, 24.80, 23.56, 11.15.

Acknowledgment. S.G.P. thanks the staff and students of the Fachbereich Chemie at Philipps-Universität for their help and hospitality during the period January–June 1988. We thank a referee for helpful insights concerning transition states **6a′** and **6e′**. Financial support by the Deutsche Forschungsgemeinshaft, Soderforschungsbereich 260, is gratefully acknowledged.

Supplementary Material Available: Tables of all atomic positional and thermal parameters and all atomic distances and angles for the crystallographic structure **2c** (18 pages). Ordering information is given on any current masthead page.

Conversion of 1-Isopropylidene-4,4-dimethyl-2,5-cyclohexadiene to Its Crisscross Dimer

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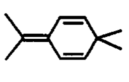
The title compound, **1**, gives only aromatization to **6** and polymerization upon treatment with acid in methylene chloride or when TFAA or TFA are added separately to the reaction mixture. When both TFAA and TFA are present at low temperatures, $HBF_4{\cdot}Et_2O$ causes remarkably efficient formation of the crisscross dimer **2**, which is isolated in up to 80% yield. Ozonolysis of **2** gives the diepoxide or rearranged compounds containing acetyl groups. One-electron oxidation of **2** produces a long-lived cation radical, which has its bis-allylic C–C bond intact, in contrast to less constrained 1,4-diene cation radicals.

Treatment of the monocyclic tetramethyl[3]dendralene[1] **1** under a rather specific set of acidic conditions causes formation of crisscross cage dimer **2**, as reported in a preliminary communication.[2] The four σ bonds shown as dotted ones on the structure of **2** are formed in one operation, which converts a monocyclic compound into a pentacyclic one having eight contiguous methyne carbons. This paper describes our work on this transformation as well as the oxygenation of **2** and spectral work on its cation radical.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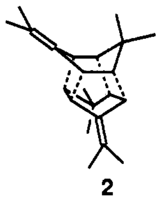
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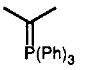
Results: Dimerization of 1

Desobry and Margaretha[3] previously prepared **1** by pyrolysis of the photoadducts of 2,3-dimethylbutene and 6-fluoro-4,4-dimethyl-2-cyclohexenone at 150 °C. We used Wittig addition of isopropylidenetriphenylphosphorane[4] (**3**) to 4,4-dimethylcyclohexa-2,5-dienone[5] (**4**). Pure **1** polymerizes rather rapidly, and we used batches as soon as possible after they were prepared; **1** may be stored at −20 °C for limited periods of time.



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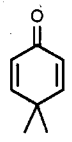

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Our original intent was to study the cation radical chain catalyzed[6] oxygenation of **1**. Cyclic voltammetry experiments under the conditions we usually use for study of unstable hydrocarbon cation radicals[7] gave only an irreversible oxidation wave peaking at 1.35 V at −78 °C with

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[1] (a) Hopf, H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 948. (b) Phelan, N. F.; Orchin, M. *J. Chem. Ed.* **1968**, *45*, 633.

[2] Nelsen, S. F.; Teasley, M. F. *J. Org. Chem.* **1986**, *51*, 4319.

[3] Desobry, V.; Margaretha, P. *Helv. Chim. Acta* **1975**, *58*, 2161.

[4] Wittig, G.; Wittenberg, D. *Liebigs Ann. Chem.* **1957**, *606*, 1.

[5] Zimmerman, H. E.; Hackett, P.; Juers, D. F.; McCall, J. M.; Schroder, B. *J. Am. Chem. Soc.* **1971**, *93*, 3653.

[6] Nelsen, S. F. *Acct. Chem. Res.* **1987**, *20*, 269.

[7] (a) Mixed acidic solvent consisting of a 20:1:1 v/v mixture of $CH_2Cl_2/(CF_3CO)_2O/CF_3CO_2H$ containing 0.1 M *n*-Bu_4NBF_4 as supporting electrolyte, at −78 °C. Potentials are reported versus a saturated calomel reference electrode. (b) For brevity, we shall refer to mixtures of volumes a, b, and c of methylene chloride, trifluoroacetic anhydride, and trifluoroacetic acid throughout this paper as a:b:c mixed acidic solvent.

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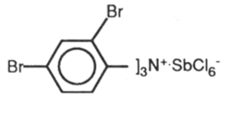
a 0.02 V/s scan rate, indicating that $1^{\bullet+}$ has a shorter lifetime than tetraalkylalkene cation radicals, which show chemically reversible oxidation waves under these conditions. Partial chemical reversibility was seen at a scan rate of 20 V/s, but the separation of the peak potentials observed was 0.26 V, precluding accurate measure of $E^{\circ\prime}$. Saturation of the CV solution with dioxygen diminished the oxidation current observed, but there was no evidence of ECbE character[6] for the wave. Although this indicated that chain oxygenation was unlikely, we attempted preparative oxygenation using tris(2,4-dibromophenyl)aminium hexachloroantimonate **5** as initiator. As expected from the CV experiments, the green color of **5** was rapidly discharged upon dropwise addition of **5** solutions to **1** (estimated $E^{\circ\prime}$ for **1** is about 1.3 V vs sce, so the electron transfer is about 8 kcal/mol exothermic). The major products are polymer, aromatization product **6**, dehydrodimer **7**, and the dimer shown below to be **2**. Chromatography on silica gel with hexane as eluant separated **2** (R_f 0.8) from **6**, **7**, and reduced initiator **5**, and also removed the polymer; **6** is the sole nonpolymeric product when **1** is treated with trifluoroacetic acid (TFA) in methylene chloride at room temperature. Dehydrodimer **7** was easily identified by comparison of its ^{13}C NMR spectrum with that of **6**. We observed no parent peak, P, by mass spectroscopy, but saw the $C_{11}H_{15}P/2$ peak.



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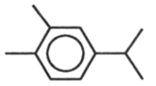

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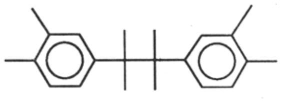

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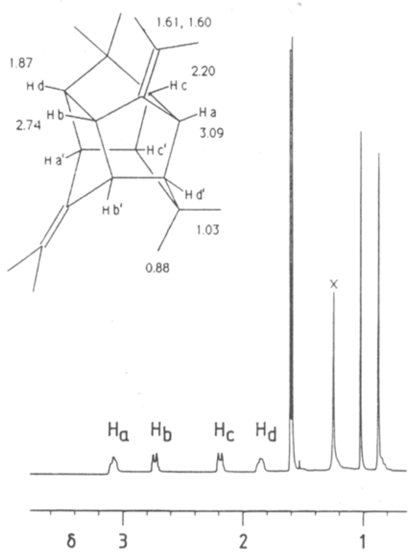

Figure 1. 270-MHz ^{1}H NMR spectrum of **2**, with chemical shifts and assignments.

Table I. Coupling Constants for the Tertiary Hydrogens of 2 (Hz)

	Ha′	Hb	Hb′	Hc	Hc′	Hd	Hd′
Ha	0.0	2.9	0.2	8.6	−0.1	0.0	4.9
Hb			5.5	0.0	0.0	9.1	0.2
Hc					4.7	3.4	0.2
Hd							0.0

The mass spectrum of **2** shows that it is a dimer of **1**. The ^{13}C NMR spectrum has 11 carbon signals, consisting of four methyl carbons, four methyne carbons, one quaternary carbon, and two disubstituted vinyl carbons. The ^{1}H NMR spectrum shows four different tertiary hydrogen signals between 1.8 and 2.2 δ, two methyls on vinyl carbons, and two methyls on saturated carbons. Dimerization of **1** destroys both of its symmetry planes and both of its endocyclic double bonds but keeps the $C{=}C(Me)_2$ units intact, and the dimer has a C_2 axis of symmetry. We were only able to write the crisscross cage structure shown as **2** as a reasonable possibility from these qualitative data, but desired firm evidence for formation of this unusual product. Presumably because of its nearly spherical shape, **2** is both slow to crystallize and forms a waxy solid; we have not obtained crystals of X-ray quality, and had to rely on the ^{1}H NMR data for proof of structure. Figure 1 shows the 270-MHz spectrum and letter assignments of the peaks to structure **2**. Most assignments in the spectrum are easy to make because of large shifts caused by the shielding cones of the double bonds. The upfield methyl singlets (0.88 δ) are assigned as those in the shielding cone of the double bonds, and those at 1.03 δ as the other pair on the saturated carbons. The allylic methyls have shifts of 1.60 and 1.61 δ, and we cannot assign which pair is which. The chemical shift difference between the allylic (downfield two) tertiary hydrogens H(a) and H(b) is 0.35 V, and between the nonallylic (upfield two) tertiary hydrogens H(c) and H(d) is 0.33 δ. The upfield hydrogens in each set, H(b) and H(d), are assigned as those in the shielding cone of a homoallylic double bond (see Figure 1). The striking resemblance of the patterns for H(a) to H(d) and H(b) to H(c) is easy to rationalize in terms of structure **2**,[2] but accurately determining the J values is more difficult because the spectrum is far from being first order. A 500-MHz 2D-J resolved[8] spectrum was obtained, but proved useless to us because spurious couplings appeared. As Bax has pointed out,[9] spurious peaks can appear in non-first-order multiplets in the 2D-J resolved experiment. The 500-MHz 2D-COSY spectrum[8] of **2** gave no off-diagonal peaks at all between H(b) and H(c), showing that both $^5J(bc)$ and $^5J(bc')$ are zero within the sensitivity of the experiment. Single-frequency irradiation decoupling experiments did not simplify the spectra sufficiently to allow analytical calculation of the coupling constants, and repeated attempts at simulation of the AA′MM′XX′ patterns resulting from such decoupling failed to give reliable values of the coupling constants. Two decouplers were not available, but the single available frequency was centered between the two peaks to be irradiated and split into two components at the proper frequencies. The resulting spectra contained spurious peaks which obscured some of the desired signals, and some of the collapsed multiplets proved too broadened for their couplings to be reliably measured, but the spectra obtained did lead to successful quantitative analysis of the couplings. Double-frequency decoupled spectra were successfully obtained for the aa′dd′, the aa′cc′, and the bb′cc′ spin systems remaining after decoupling at the other two frequencies, using the lettering of the hydrogens in Figure 1. The coupling constants were measured from the peak frequencies using the analytical solutions for AA′XX′ spectra,[10] and the signs verified by simulation of the double frequency decoupled spectra by using program RACCOON.[11] The measured couplings were

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(8) Morris, G. A. *J. Magn. Reson.* **1986**, 371.

(9) Bax, A. *Two-Dimensional Nuclear Magnetic Resonance in Liquids*; Delft University Press: Delft, Holland, 1982; pp 85 and 116.

(10) Becker, E. D. *High Resolution NMR*, 2nd ed.; Academic Press: New York, 1980; pp 167–171.

Table II. Optimization of Crisscross Dimer 2 Production in the Reaction of Dendralene 1 with Oxidant 5

						products,[b] %		
run	mg of 1	[1], mM	solv[a]	temp, °C	mol % 5	6	7	2
1	100	66	100:1:1	–78	11	20	13	20
2	100	66	100:1:1	–86	12	tr	17	20
3	100	66	100:1:1	–78	7	5[c]	7	20
4	100	66	100:1:1	–95	10	tr	12	13
5	100	67	100:0:0	–78	5.6	50	5	2
6	100	66	100:1:1	–78	11	19	18	25
7	100	67	500:1:1	–78	14	32	11	43
8	100	65	50:1:1	–78	14	55	14	43
9	100	300	100:10:1	–78	11	32	9	50
10	80	300	100:10:1	–95	11	tr[c]	7	28
11	100	240	100:10:1	–86	12	12	10	58
12	590	400	100:10:1	–86	8	14	8	58[d]
13	370	500	100:10:1	–86	12	16	4	68[e]
14	100	32	100:10:1	–78	51[f]	7	16	0

[a] Volumes of CH_2Cl_2:TFAA:TFA mixed at room temperature. [b] By NMR integration relative to reduced **5**. [c] Recovered **1** detected. [d] 52% of **2** isolated pure by chromatography. [e] 57% of **2** isolated pure by chromatography. [f] Inverse addition. [Note: TFAA = trifluoroacetic anhydride, TFA = trifluoroacetic acid, oxidant **5** = tris(2,4-dibromophenyl)aminium hexachloroantimonate.]

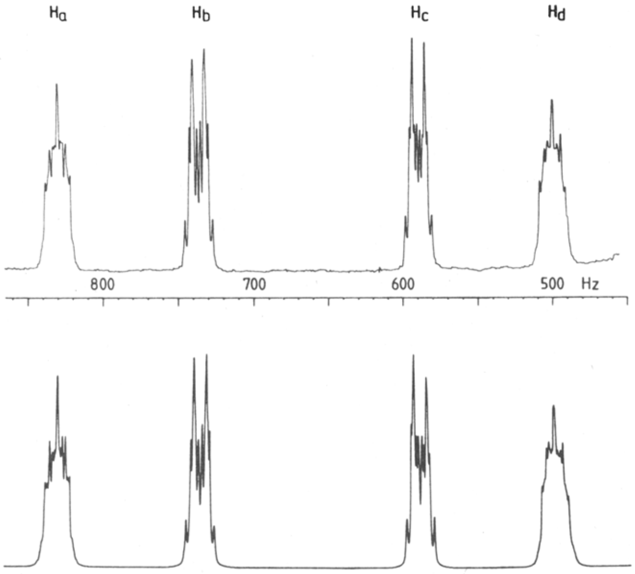

Figure 2. Comparison of the experimental 270-MHz NMR spectrum for the H(a)–H(d) region of **2** (top) with that calculated using the coupling constants of Table I.

used with educated guesses to simulate the AA′MM′XX′ patterns of the single frequency decoupled spectra, and the final set of couplings obtained shown in Table I was used to simulate the H(a)–H(d) region of the fully coupled spectrum, which is compared with the experimental spectrum in Figure 2, produced by using an expanded version[12] of LAOCN3.[13a] Changes of 0.1 Hz from the values quoted in Table I lead to greater distortion from the experimental spectrum. The vicinal couplings fit structure **2** well. The MM2 optimized structure[13b] of **2** has 0° dihedral angles for H(a)C,CH(c) and H(b)C,CH(d), and program 3JHH[14] calculates 9.1 Hz for both couplings (observed 8.6 and 9.1 respectively), and 33°, 34°, and 31° dihedral angles for H(a)C,CH(d′), H(b)C,CH(b′), and H(c)C,CH(c′), respectively, giving calculated couplings 6.3, 6.3, and 6.8 Hz (observed 4.9, 5.5, and 4.7 respectively). Although the observed vicinal couplings are slightly larger than the calculated ones, we believe the agreement is excellent. The four bond couplings differ significantly in size, as they ought to for structure **2**. Values of 2.9 and 3.4 Hz are observed for ^4J(ab) and ^4J(cd), which are fixed in *W* plan, and they are 1 order of magnitude larger than the non-*W* plan four-bond couplings, ^4J(ab′), ^4J(ac′), ^4J(bd′), and ^4J(cd′), which fall in the range 0.2 to –0.1 Hz. Calculations employing nonzero values for any of the five bond couplings (aa′, ad, bc, bc′, and dd′) fit the observed spectrum less well. We believe that the coupling constants establish **2** as the structure of this compound beyond any reasonable doubt.

The same products were found in the absence as in the presence of dioxygen, but the yields were higher under nitrogen, so most experiments were done under nitrogen. Table II includes experimental conditions of reactions used in maximizing the yield of the interesting product, crisscross dimer **2**. A solution of **5** was added dropwise until the green color of **5** persisted, indicating consumption of **1**. The reactions were quenched with triethylamine, and worked up as in the Experimental Section. Lowering the temperature decreases the amount of aromatization to **6**, but less **2** is formed at –95 °C than at –86 °C. Almost no **2** is formed in pure CH_2Cl_2 (run 5), and the ratio of **2**/**7** is larger in 100:10:1 solvent mixture than in 100:1:1. The relative yields of **2**, **6**, and **7** do not seem to be closely coupled. Because we did not see any **2** upon reaction of **1** with trifluoroacetic acid, TFA, we thought **2** came from **1**$^{\bullet+}$, but this did not prove to be the case. A stronger acid than TFA (pK_a –0.3) is required for significant amounts of **2** to be formed, and because **1**$^{\bullet+}$ deprotonates in producing **7**, its generation from **5** forms $HSbCl_6$, which doubtless protonates other compounds present rapidly. In the inverse addition experiment (run 14), where **1** was slowly added to the oxidant, no **2** was detected.

$HBF_4{\cdot}Et_2O$ (in the presence of trifluoroacetic anhydride [TFAA] and TFA) converts **1** to **2** and **6** without producing any dehydrodimer **7** at all, showing that a common intermediate is not involved in the formation of **2** and **7**. Table III includes the experimental conditions explored for this reaction. Extensive studies in which the amounts of trifluoroacetic anhydride (TFAA) and trifluoroacetic acid (TFA) were varied have not been done, but **2** was not detected in runs 3–5, where both were not present. We

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(11) Schatz, P. F. University of Wisconsin, Madison, Version 2.0, 1984.

(12) We thank Peter A. Petillo, University of Wisconsin.

(13) (a) Bothner-by, A. A.; Castellano, S. Program No. 111, Quantum Chemistry Program Exchange; Indiana University: Bloomington, IN. (b) Allinger, N. L. *J. Am. Chem. Soc.*, **1977**, *99*, 8127. Program No. 395, Quantum Chemistry Program Exchange; Indiana University: Bloomington, IN.

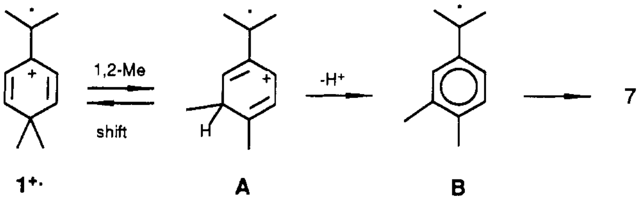
(14) (a) Haasnoot, C. A. G.; de Leeuw, F. A. M.; Altona, C. *Tetrahedron* **1980**, *36*, 2783. (b) Osawa, E.; Jaime, C. *3JHH:NMR Vicinal Coupling Constants*, QCPE 461; implementation of the 7-term Karplus equation of 14a. (c) Petillo, P. A., correction patch for 14b, submitted to QCPE. Reference 14b has a "bug" in the subroutine that calculates hydrogen atom positions from the heavy atom positions, which can cause incorrect coupling constants to be obtained.

Table III. $HBF_4 \bullet Et_2O$-Catalyzed Conversion of Dendralene 1 to Crisscross Dimer 2

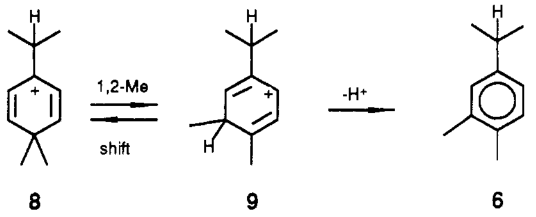
run	mg of 1	[1], mM	solv^a	temp, °C	mol % acid	product mixture,^{b} % 1	6	2
1	20	170	100:10:1	23	0	0	100^b	0
2	20	66	100:1:1	−78	0	100^c	0	0
3	20	190	100:0:0	−86	25	0	100^b	0
4	20	170	100:10:0	−86	25	0	100^b	0
5	20	190	100:0:3	−86	25	0	100^b	0
6	100	300	100:10:1	−86	10	0	12	88 [80]
7	370	500	100:10:1	−86	15	34	5	61 [41]
8	370	500	100:10:1	−86	20	11	13	66 [43]
9	300	450	100:10:1	−78	20	0	39	61 [60]

^{a} Volumes of CH_2Cl_2:TFAA:TFA mixed at room temperature. ^{b} Relative amounts by NMR integration. Number in brackets is yield of 2 isolated by chromatography. Polymer also present. ^{c} 1 recovered after 1 h without reacting.

Scheme I



Scheme II



believe it is quite striking that the presence of TFAA and TFA divert acid-catalyzed decomposition of 1 by $HBF_4 \cdot Et_2O$ from giving exclusively aromatization to 6 to giving mostly the crisscross dimer 2.

Discussion: Electron Loss and Acid-Catalyzed Reactions of 1

Dehydrodimer 7 is only found when oxidant 5 is added, clearly showing that it arises from cation radical $1^{\bullet+}$. The pathway shown in Scheme I, involving methyl shift to give rearranged cation radical A, its deprotonation to dimethylcumyl radical B, and dimerization of the dimethylcumyl radicals seems to us to be most likely. Because the inverse addition reaction (Table II, run 14), where 1 can only be present at very low concentrations, gave as much 7 as adding oxidant slowly to 1, addition of a radical or radical cation to neutral 1 is not a significant pathway to 7. C–C bond formation prior to deprotonation would require approach of two cations, and significant amounts of 7 are formed even at −95 °C, but we cannot rule out C–C bond formation from $1^{\bullet+}$ or A from our data.

Compound 1 isomerizes to 6 without observation of 2 when treated with 100:10:1 at room temperature (Table III, run 1) but does not react significantly within an hour when treated with 100:1:1 at −78 °C (run 2). Addition of $HBF_4 \cdot Et_2O$ causes 1 to be consumed even at −86 °C, but 2 was not observed as a product in pure CH_2Cl_2, or with addition of either TFA or TFAA (runs 3–5). These results are as expected. The thermodynamically favored protonation of 1 will occur at the exocyclic carbon to give pentadienyl cation 8 because protonation at other positions produces cross-conjugated or nonconjugated cations.[1] In addition, the HOMO of [3]dendralenes have their largest coefficient at the exocyclic carbon,[1b] so 8 is predicted to be the kinetically favored product as well. Aromatization presumably occurs as shown in Scheme II, by 1,2-methyl shift from position 4, generating 9, which deprotonates to 6. Some polymerization usually accompanies aromatization, but whether it is initiated by 8 or by less stabilized cations resulting from protonation at endocyclic carbons is not known.

Formation of 2 seems most easily rationalized as proceeding by the route outlined in Scheme III, [4 + 2] cycloaddition by pentadienyl cation 8 to a double bond of 1 to produce allyl cation 10, followed by intramolecular [2 + 2] cycloaddition to produce tertiary cation 11, which produces 2 upon loss of a proton. [4 + 2] cycloaddition of a pentadienyl cation to an alkene has been termed a class B cycloaddition by Woodward and Hoffman,[15] who pointed out that conversion of perezone 12 to pipitzols 13[16] may be formulated as an intramolecular example of a type B reaction, proceeding through the tautomeric zwitterion 12A. Katritzky and co-workers[17] have used zwitterionic class B cycloadditions of 3-oxidopyridinium ylides (14, X = NR) and Sammes and co-workers[18] those of 3-oxidopyrilium ylides (14, X = O), but the only cationic class B enophiles we have seen were employed by Büchi and coworkers,[19] who have generated several examples of cation 15 from the ketals using acid and added them to aryl activated alkenes. Conversion of 1 to 2 apparently is the first case involving hydrocarbon class B cycloaddition. Endo stereochemistry in the [4 + 2] cycloaddition is necessary to produce 2, and it should be noted that the *gem*-4,4′-dimethyls will greatly favor endo cycloaddition. [2 + 2] addition of an allyl cation to an alkene must proceed in stepwise fashion,[15] and the reaction has previously been observed to proceed reasonably well only for highly methyl substituted cases.[20] [2 + 2] cycloaddition is efficient in conversion of 1 to 2 despite the lack of methyl groups on the terminal positions of both the allyl and alkene components, presumably because it is intramolec-

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(15) Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781.

(16) (a) Walls, F.; Padilla, J.; Joseph-Nathan, P.; Giral, F.; Romo, J. *Tetrahedron Lett.* **1965**, 1577. (b) Walls, F.; Padilla, J.; Joseph-Nathan, P.; Giral, F.; Escobar, M.; Romo, J. *Tetrahedron* **1966**, *22*, 2387.

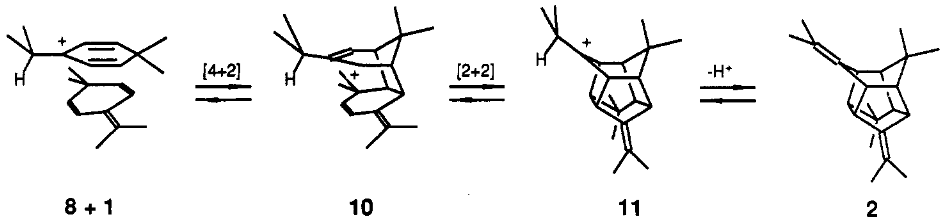
(17) (a) Dennis, N.; Ibrahim, B.; Katritzky, A. R.; Taulov, I. G.; Takeuchi, Y. *J. Chem. Soc., Perkin Trans. I* **1974**, 1883. (b) Katrizky, A. R.; Banerji, J.; Boonyarakvanich, A.; Cutler, A. T.; Dennis, N.; Abbas Rizvi, S. Q.; Sabongi, G. J.; Wilde, H. *Ibid.* **1979**, 399.

(18) (a) Sammes, P. G.; Street, L. J. *J. Chem. Soc., Chem. Commun.* **1982**, 1056. (b) Sammes, P. G.; Street, L. J. *J. Chem. Soc., Chem. Commun.* **1983**, 666. (c) Sammes, P. G.; Street, L. J. *J. Chem. Soc., Perkin Trans. I* **1983**, 1261. (d) Sammes, P. G.; Street, L. J. *J. Chem. Res. (S)* **1984**, 196. (e) Sammes, P. G.; Street, L. J.; Kirby, P. *J. Chem. Soc., Perkin Trans. I* **1983**, 2779. (f) Sammes, P. G.; Whitby, R. J. *J. Chem. Soc., Chem. Commun.* **1984**, 702.

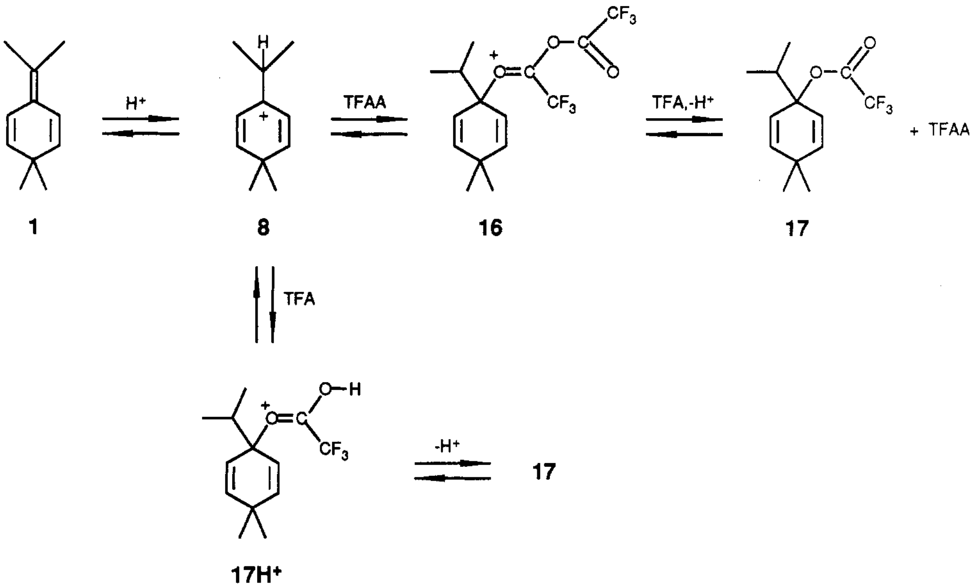
(19) (a) Büchi, G.; Chu, P.-S. *J. Am. Chem. Soc.* **1979**, *101*, 6767. (b) Büchi, G.; Chu, P.-S. *J. Org. Chem.* **1978**, *43*, 3717. (c) Büchi, G.; Mak, C.-P. *J. Am. Chem. Soc.* **1977**, *99*, 8073.

(20) Klein, H.; Mayr, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 1027.

Scheme III



Scheme IV



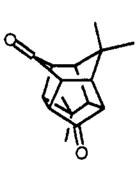
ular. Once **10** is formed, the allyl and alkene fragments cannot escape each other.

Although we believe that Scheme III qualitatively represents the conversion of **1** to **2**, the most puzzling aspects of this work are not addressed in it. Mixtures of TFAA and TFA divert the reaction of **1** with $HBF_4 \cdot Et_2O$ from giving exclusively aromatization product **6** and polymer to giving at least 80% **2** (the **2**/**6** ratio before chromatography was about 7.3 in our best reaction, run 6). Even at quite high initial **1** concentrations, little polymer is formed in the presence of TFAA and TFA, but neither TFAA nor TFA alone causes significant formation of **2**. Examination of Tables II and III shows that the ratio of **2**/**6** is greater with a substantial ratio of TFAA/TFA. This suggests to us that trifluoroacetyl groups trap **8** nucleophilically, as indicated in Scheme IV. Although we only show trapping at the central carbon of the pentadienyl cation, there is no evidence that this is true; **16** should form with only TFAA present, but no nucleophile would be available to allow formation of trifluoroacetate **17**. With only TFA present, $\mathbf{17H}^+$ should be formed, but no base capable of deprotonating it should be present in the reaction mixture; **16** and $\mathbf{17H}^+$ would be in rapid equilibrium with **8**, and substantial amounts of **8** may well be present. Almost exclusive aromatization instead of **2** formation occurs unless both TFAA and TFA are present, and for best yields of **2**, a substantial excess of TFAA over TFA is desirable. We propose that the reason a large ratio of TFAA/TFA favors **2** formation is that these conditions permit **1** to be converted to trifluoroacetate **17** as shown at the top of Scheme IV. Increasing the initial **1** concentration when TFAA and TFA are present raises the yield of **2** but does not increase the amount of polymer formed, which is nicely rationalized by Scheme IV, which provides a way of "storing" **1** under the very acidic reaction conditions. Schemes II–IV, however, cannot explain the partitioning of **1** between aromatization and dimer formation. If **8** really were a common intermediate in the aromatization of Scheme II and the dimerization of Scheme III, the aromatization, which is first order in **8**, would compete even better with dimerization if Scheme IV, which lowers the concentration of **1**, occurs. The only way we can see to rationalize the observed partitioning between **2** and **6** is to invoke at least two intermediates with the reactivity postulated for **8** in Schemes II and III, one of which aromatizes, and the other of which gives [4 + 2] cycloaddition efficiently. Free **8** ought to methyl shift most rapidly, and we see no reason not to write the precursor of **6** as **8**. We do not know how the intermediate which undergoes [4 + 2] cycloaddition actually differs from **8**; there seem to be several possibilities. Methylene chloride is a rather low polarity solvent, and ion pairing presumably is important. Perhaps tightly ion paired **8** would aromatize enough more slowly to be trapped by **1** as shown in Scheme III. Another possibility is that nucleophilic attack by **1** (or conceivably **17**) is concerted with ionization of an intermediate derived from a **1**, HX addition product like **17**. Alkene attack on $\mathbf{17H}^+$ (or an allylic isomer, or a compound with another leaving group), which is concerted with leaving group loss, could be required to achieve overall [4 + 2] cycloaddition. This would formally be an S_N2' reaction. We note that whatever intermediates may be involved, only aromatized product **6** is formed at room temperature in the 100:10:1 solvent mixture (Table III, run 1) while at low temperature the same solvent mixture gives the best yield of **2** when the reaction is initiated with $HBF_4 \cdot Et_2O$ (Table III, run 6). Successful competition of **2** formation with aromatization requires low temperature conditions. This is reasonable because $\Delta S^{\ddagger}$ should be substantially more negative for the second-order reaction leading ultimately to **2** than for the unimolecular methyl shift involved in aromatization.

There is little precedent for crisscross dimerization of skipped dienes as a reaction type. The only structurally analogous reaction we have found is the transition metal catalyzed crisscross dimerization of norbornadiene derivatives,[21] which proceeds in rather low yield, and clearly has nothing to do mechanistically with the chemistry considered here. The high yield obtained in the conversion of 1 to 2 makes this cage compound relatively easily available. If 2 could be functionalized properly and the bisallylic bond broken, the resulting molecular framework would be ideal for study of through-space interactions between functional groups, because the remaining three σ bonds between the six-membered rings would force the functional groups into each other.

Results and Discussion: Oxidation Chemistry of 1

Pentacyclic diketone 18 looks like it should be easily available from 2, but we have not yet found how to carry out this transformation. Ozonolysis of 1 at −78 °C in CH_2Cl_2 followed by methanol, trimethyl phosphite workup gave diepoxide 19, which was independently prepared in quantitative yield by using mCPBA. Only one diastereomer was detected, which we assign as that illustrated, with the oxygens introduced from the least hindered side of the double bonds. There is ample precedent for highly substituted alkenes producing epoxides instead of ketones upon ozonolysis.[22] Including methanol with the CH_2Cl_2 as a cosolvent in the ozonolysis, followed by a dimethyl sulfide workup changed the product to a mixture which we did not succeed in separating by TLC. Proton NMR showed several methyl singlets near 2.3 δ and several *gem*-dimethyl singlets between 0.9 and 1.3 δ, ^{13}C NMR showed a large number of peaks, including carbonyls at 218.6 and 211.4 δ, mass spectroscopy gave a parent ion of empirical formula $C_{22}H_{32}O_2$ and a base peak at $C_{21}H_{29}O$ (P − acetyl), and IR showed carbonyl stretches at 1734 and 1692 cm^{-1}. We conclude that the product is most likely to be a mixture of diastereomers of 20. Hydrogen bonding to methanol may slow formation of the second CO bond in molozonide formation, allowing the methyl shifts, which lead to acetyl group formation, to occur under these reaction conditions. Oxidation of 1 by RuO_4–$NaIO_4$ in H_2O/CCl_4 was also briefly investigated, but the product mixture formed was complex, of which the only compound identified was diepoxide 19. NMR indicated that the desired 18 was not present in significant amounts, and we abandoned this approach.



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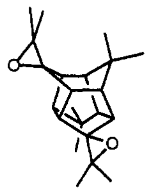

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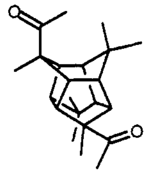
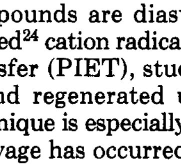


20

We dearly hoped that 2 could be converted to the bis(dioxetane) by cation radical chain catalyzed oxygenation[6] (which is what we had originally set out to study on 1); 2 structurally rather resembles isopropylideneadamantane, an excellent substrate for this reaction, and the bis(dioxetane) expected should cleave to 18. All successful CRCC substrates have shown ECbE cyclic voltammograms.[6] The CV of 2 under nitrogen in 20:1:1 mixed acidic solvent containing 0.1 M n-Bu_4NBF_4 shows reversibility at a 1 V/s scan rate, $E^{\circ\prime}$ 1.62 V vs sce, ΔE_{pp} 0.14 V, and at −78 °C, partially reversible waves were observed at $E^{\circ\prime}$ 1.56 V (ΔE_{pp} 0.074 V) and 1.85 V (ΔE_{pp} 0.15 V), 0.2 V/s scan rate. Both waves became chemically reversible at faster scan rates. This suggests that both the monocation and dication from 2 are reasonably long-lived at low temperature. Under dioxygen at −78 °C the first wave shows ECbE wave shape, and a second irreversible wave with E_p^{ox} 1.80 V appeared. Increasing the scan rate caused the first wave to grow in current, as expected for an ECbE wave, and the second wave became partially reversible at a scan rate of 2 V/s, $E^{\circ\prime}$ 1.78 V (ΔE_{pp} 0.13 V). A scan to higher potential showed the presence of an irreversible wave at E_p^{ox} 2.55 V. The CV results appeared encouraging, and we were hopeful that dioxetanes would be produced from 1. Once again, we were wrong. Our initial preparative run used 5 mol % 5 in 100:1:1 at −78 °C, but a significant amount of starting material was recovered. Long oxygenation chains do not occur, as they do in favorable cases of CRCC oxygenation. Use of 13 mol % 5 did consume 2, but the product mixture was quite complex, and its NMR spectrum did not look like either mono- or bis(dioxetane) was present in significant amount.

The failure of CRCC oxygenation of 2 to proceed as desired was a considerable disappointment, but 2 contains a 1,4-diene fragment. It is not even obvious that the bis-allylic C–C bond would remain intact upon electron removal. Cleavage of this bond would produce the bisallylic cation radical 21, which out to regenerate 2 upon reduction, as is implied by the CV results, because the allyl fragments are prevented from separating. Shida and coworkers[23] have carried out a detailed study of the optical spectra of cation radicals produced in freon matrices from cyclopentadiene and several $C_{10}H_{12}$ compounds derived from two cyclopentadiene units. They conclude that *endo*-dicyclopentadiene 22 produces the bond-cleaved cation radical 23 on the basis of MO calculations and PE spectrum considerations, and that *exo*- and *endo*-dicyclopentadiene give different bond-cleaved species (the cation radicals produced by bond cleavage from these compounds are diastereomeric). Roth has recently reviewed[24] cation radicals produced by photoinduced electron transfer (PIET), studied by CIDNP in the neutral compound regenerated upon back electron transfer. This technique is especially good for telling whether or not bond cleavage has occurred, because the CIDNP spectra which would result are very different. Roth points out that de-



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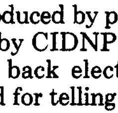

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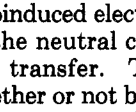

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[21] (a) Lemal, D. M.; Shim, K. S. *Tetrahedron Lett.* **1961**, 368. (b) Bird, C. W.; Colinese, D. L.; Cookson, R. C.; Hudec, J.; Williams, R. O. *Ibid.* **1961**, 373. (c) Acton, N.; Roth, R. J.; Katz, T. J.; Frank, J. K.; Maier, C. A.; Paul, I. C. *J. Am. Chem. Soc.* **1972**, *94*, 5446. (d) Marchand, A. P.; Earlywine, A. D. *J. Org. Chem.* **1984**, *49*, 1660.

[22] (a) Enzell, C. R. *Acta Chem. Scand.* **1961**, *15*, 1191. (b) Enzell, C. R. *Ibid.* **1962**, *16*, 1553. (c) Enzell, C. R.; Thomas, B. R. *Ibid.* **1965**, *19*, 1875. (d) Enzell, C. R.; Thomas, B. R. *Tetrahedron Lett.* **1965**, 225. (e) Munavalli, S.; Ourisson, G. *Bull. Soc. Chem. Fr.* **1964**, 729. (f) Henrick, C. A.; Jefferies, P. R. *Austr. J. Chem.* **1964**, *17*, 915. (g) Hochstettler, R. *J. Org. Chem.* **1975**, *40*, 1536.

[23] (a) Shida, T.; Momose, T.; Ono, N. *J. Phys. Chem.* **1985**, *89*, 815. (b) For a study in argon matrices, see: Andrews, L.; Dunkin, I. R.; Kelsall, B. J.; Lorito, J. T. *Ibid.* **1985**, *89*, 821, who accept the C–C bond cleaved structures suggested by Shida (footnote 8).

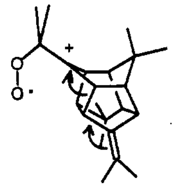
[24] (a) Roth, H. D. *Acct. Chem. Res.* **1987**, *20*, 343. (b) Roth, H. D.; Schilling, M. L. M. *J. Am. Chem. Soc.* **1985**, *107*, 716.

spite their considerably higher temperature, PIET–CIDNP experiments offer milder conditions for some bond-cleavage reactions than do matrix-isolation experiments, because the initial electron transfer is considerably less exothermic than that to matrix cation radical, and the cation radical lifetime is quite short. For example, unrearranged cation radicals have been detected by CIDNP from quadricyclane, Dewar benzene, and benzvalene. Even with CIDNP detection, the structure of the cation radical from **22** is the bond-cleaved species **23**, and the lifetime of a possible precursor cation radical with the doubly allylic bond intact would have to be under 10^{-9} s.[24b]

We examined the unusually long-lived cation radical obtained from **2** to determine if we could tell whether the bis-allylic bond is intact or cleaved from its spectral properties. The ESR spectrum of this species was obtained by electrolytic oxidation at −93 °C in 100:1:1/0.1 M n-Bu_4NBF_4. It has $g = 2.0037$ and shows 13 lines split by 8.5 G, which have intensity ratios close to the 1.00:0.86:0.53:0.24:0.07:0.014:0.002 (center line to outer lines) for 12 equivalent hydrogens. The observed linewidth is 4.5 G, with no resolved fine structure. This spectrum is reasonable for bond-closed $\mathbf{2}^{\bullet+}$ (the two pairs of methyl groups would show very similar splittings, which would not be resolved at the observed linewidth), and is not compatable with the bond-cleaved structure **21**, for which large splittings for the two terminal allylic hydrogens as well as for the methyl groups would be observed. Solutions containing this cation are reddish in color, and its generation in 200:1:1 solution at −90 °C with oxidation by **5** gave a broad maximum at 502 nm (ϵ >630), with a shoulder at 460 nm. The Neutral in Cation Geometry (NCG) approximation used with MNDO optimized cation radical geometries has proven useful for interpreting optical spectra of both alkene[25a] and 1,3-diene[25b] cation radicals. We carried out such calculations on cations derived from **2** to see if different optical spectra would be expected for species with the bis-allylic C–C bond broken and intact, and if the observed spectrum was reasonable for either. MNDO–UHF calculations optimizing $\mathbf{2}^{\bullet+}$ in C_2 symmetry starting from the C_2-optimized geometry of neutral **2** gave ΔH_f 205.5 kcal/mol, a C=C distance 1.379 Å, and NCG prediction of 499 and 413 nm for σ,π^+ transitions. The charge was calculated to be unsymmetrical at the symmetrical C_2 geometry enforced, an indication that this symmetry is too high (according to MNDO–UHF), and a π,π^+ charge transfer transition at 4877 nm (2050 cm^{-1}) is predicted. Allowing relaxation of this cation radical to C_1 symmetry lowered the heat of formation by 2.3 kcal/mol, and gave distinctly different bond lengths for the neutral and cation radical C=C bonds, 1.341 and 1.415 Å, respectively. NCG predicts σ,π^+ transitions at 477 and 403 nm, and the π,π^+ intervalence transition is calculated to occur at 2577 nm (3880 cm^{-1}). Use of Marcus–Hush theory[26] on a charge-transfer band at this wavelength gives an internal electron transfer barrier of 2.8 kcal/mol, not extremely far from the 2.3 kcal/mol MNDO–UHF obtained for the energy gap between the C_1 geometry and the C_2 geometry that represents the transition state for intervalence electron transfer. The low calculated barrier for electron transfer would make this species appear delocalized on the ESR timescale. We succeeded in getting into the energy well for this bis-allylic bond cleaved cation **21** by starting from the geometry of the optimized dication. Optimized **21** has about a 2.6-Å distance between its allyl units (the *C*H,C=*C*Me$_2$ distance is 2.614 Å, the *C*H,*C*H distance 2.652, and the *C*=CMe$_2$,*C*=CMe$_2$ distance 3.215) and delocalized charge and spin, but it is 18.2 kcal/mol destabilized with respect to MNDO–UHF optimized (C_1) $\mathbf{2}^{\bullet+}$. NCG does not predict a red color for **21** (it gives predicted absorption at 378 and 363), but we do not attribute any significance to this because the NCG method apparently is not able to handle bond cleaved bis-allylic cation radicals. It also predicts no visible absorption for **23**, which is experimentally untrue.[23] It is not clear what the problem is with the calculations, but we have been unable to find optimized structures for which a long wavelength band is predicted, or which have significantly different bond lengths for the cationic and neutral allyl systems of **23**. The visible band in the experimental spectrum has been assigned as a charge resonance band by Shida and co-workers.[23]

It is not obvious that MNDO would be able to get the correct energy gap between bis-allylic C–C bonded and bond cleaved cation radicals, but it does predict that the bond-cleaved species **23** is 17.4 kcal/mol stabler than $\mathbf{22}^{+}$. This is both the experimental stability order[23,24] and the opposite of the prediction for $\mathbf{2}^{\bullet+}$ and **21**, which the ESR results above establish is also experimentally the correct prediction. The calculated energy differences between bond closed and bond cleaved cation radicals from **2** and **22** are so large that even though MNDO probably does a poor job on the energies of these compounds, it obtained the experimentally correct answer.

The polycyclic structure of **2** clearly makes separation of the allyl groups much more difficult than for less constrained cases like **22**; $\mathbf{2}^{\bullet+}$ does not undergo bis-allylic bond cleavage. The CRCC oxygenation of **2** does not, however, produce dioxetanes. Mechanistic work has shown that the two C–O bonds formed in going from alkene to dioxetane in CRCC oxygenation are formed sequentially,[6] which means that **24** will be an intermediate. The cleavage indicated by the arrows on the structure of **24** might well be fast relative to trapping of the C^+ center by the peroxy radical, which is required for dioxetane formation.



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Conclusion

The cation radical $\mathbf{1}^{\bullet+}$ does not undergo oxygenation under any conditions we tried. It was, however, use of the mixed solvent containing TFAA and TFA, originally chosen to increase $\mathbf{1}^{\bullet+}$ lifetime by eliminating basic impurities, which led to discovery of the unprecedented conversion of **1** to **2**. The conclusion that formation of **2** probably occurs because **17** is formed under the reaction conditions has the interesting implication that it may prove unnecessary to work directly with the unstable dendralene **1** to accomplish the transformation of **4** to **2**. This hypothesis remains to be tested.

Experimental Section

1-Isopropylidene-4,4-dimethylcyclohexadiene (1). To a slurry of 2.81 g of isopropyltriphenylphosphonium bromide[4] (6.50

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[25] (a) Clark, T.; Teasley, M. F.; Nelsen, S. F.; Wynberg, H. *J. Am. Chem. Soc.* **1987**, *109*, 5719. (b) Nelsen, S. F.; Teasley, M. F.; Kapp, D. L. *J. Am. Chem. Soc.* **1986**, *108*, 5503.

[26] For reviews on application of Marcus–Hush theory to inorganic intervalence complexes, see: (a) Robin, M. B.; Day, P. *Adv. Inorg. Radiochem.* **1967**, *10*, 247. (b) Allen, G. C.; Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 357.

mmol) in 20 mL of THF at 0 °C was added by syringe 4.0 mL (6.00 mmol) of 1.5 M solution of *n*-butyllithium in hexane, producing a dark red-orange solution of **3**. After the solution was stirred for 30 min, 0.61 g (5.00 mmol) of **4**[5] in 10 mL of THF was added dropwise, and the reaction mixture was stirred overnight under a slow stream of nitrogen. The turbid solution was diluted with a small volume of acetone and stirred until excess **3** was destroyed; the mixture was diluted with pentane, filtered, and evaporated. The crude oil was filtered through a plug of alumina with pentane as eluant and evaporated to give 737 mg of pure **1** as an oil (99%): ^{1}H NMR ($CDCl_3$) δ 6.42 (d, J = 10.2 Hz, 2 H), 5.57 (d, J = 10.2 Hz, 2 H), 1.84 (s, 6 H), 1.08 (s, 6 H). This material polymerizes easily; even attempted bulb-to-bulb distillation usually just polymerizes the material. Acidification, aqueous workup, or base extraction are unnecessary and only lower the yield.

General Procedure for Table II. Solutions of **1** in CH_2Cl_2 were cooled to the indicated temperatures, and TFAA and TFA were added at the indicated ratios; **5** was added by syringe, using concentrated CH_2Cl_2 solutions. The reactions become a dark copper color. The reaction mixtures were quenched with Et_3N, poured into water, and extracted with pentane or hexane. The organic phase was dried with $MgSO_4$, filtered, and evaporated. The product ratios reported were determined by NMR integration after filtration through alumina with pentane or hexane to remove polymer and evaporation.

General Procedure for Table III. Solutions of **1** in CH_2Cl_2 were cooled to the indicated temperatures, and TFAA and TFA were added at the indicated ratios. Addition of known amounts of $HBF_4{\cdot}Et_2O$ solutions by syringe gave orange solutions. The reaction mixtures were quenched with Et_3N after a minimum of 1 h, poured into aqueous Na_2CO_3 solution, and extracted with pentane. The organic phases were dried with K_2CO_3, filtered, and evaporated; **2** and **6**, and **7** were isolated by chromatography from such reactions. Conditions are only given for the best reaction producing **2**.

3,4-Dimethylcumene (6): ^{1}H NMR ($CDCl_3$) δ 7.00 (m, 3 H), 2.85 (sept, J = 6.5 Hz, 1 H), 2.25 (s, 3 H), 2.23 (s, 3 H), 1.23 (d, J = 6.5 Hz, 6 H).

Bi(3,4-dimethyl-α-cumyl) (7): MS *m/e* 147 (base peak, 12%); ^{1}H NMR ($CDCl_3$) δ 6.96 (d, J = 7.9 Hz, 2 H), 6.86 (dd, J = 7.9, 2.1 Hz, 2 H), 6.78 (d, J = 2.1 Hz, 2 H), 2.23 (s, 6 H), 2.18 (s, 6 H), 2.18 (s, 6 H), 1.26 (s, 12 H).

3,10-Bis(1-methylethylidene)-6,6,12,12-tetramethylpentacyclo[6.3.1.0^{2,7}.0^{4,11}.0^{5,9}]dodecane (2). One hundred milligrams of **1** (0.675 mmole) in 2 mL of CH_2Cl_2 was cooled to −86 °C under N_2 in a 2-butanone slush bath, and 200 μL of TFAA and 20 μL of TFA were added by syringe. Upon addition of 10 μL of $HBF_4{\cdot}Et_2O$ (70 μmol, 10 mol %), the solution became orange. After stirring for 30 min the solution had faded to yellow, and after an hour it was quenched with Et_3N, poured into aqueous $NaCO_3$, extracted with pentane, dried with K_2CO_3, filtered, and evaporated to 140 mg of a reddish oil, which was analyzed by NMR as 88:12 **2**:**7**. Preparative TLC with hexane as eluant gave 80 mg of pure **2** (80%) as an oil which slowly solidifies upon standing. Empirical formula $C_{22}H_{32}$ established by high-resolution MS: IR (cm^{-1}) 2960 (s), 2850 (s), 1446 (m), 1368 (m), 1322, 1285, 1243, 1159, 1130, 1091; ^{1}H NMR spectrum shown in Figure 1, shifts in text, and coupling constants in Table I; ^{13}C NMR ($CDCl_3$) δ 138.4 (C), 115.4 (C), 56.2 (CH), 55.6 (CH), 45.5 (CH), 45.3 (CH), 39.3 (C), 31.0 (CH_3), 20.8 (CH_3), 20.09 (CH_3), 20.05 (CH_3).

3,10-Bis(1-methylethylidene)-6,6,12,12-tetramethylpentacyclo[6.3.1.0^{2,7}.0^{4,11}.0^{5,9}]dodecane Dioxide (19). One hundred milligrams of **2** (340 μmol) in 10 mL of CH_2Cl_2 was treated with 220 mg of 80% *m*-chloroperbenzoic acid (1 mmol, 3 equiv); slight warming occurred. After the mixture was stirred overnight, KI was added, the reaction mixture was diluted with pentane and extracted with aqueous sodium bisulfite solution followed by sodium carbonate solution. The organic phase was dried with $MgSO_4$, filtered, and evaporated to 140 mg of an oil, which was sublimed at 150 °C, 0.1 Torr, to give an oil, which solidified in several days, giving 110 mg (100%) of **19**, mp 129–131 °C. Empirical formula $C_{22}H_{32}O_2$ established by high-resolution MS: ^{1}H NMR ($CDCl_3$) δ 2.30 (m, 8 H), 1.40 (s, 12 H), 1.20 (s, 6 H), 0.96 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 75.6 (C), 66.1 (C), 55.8 (CH), 54.7 (CH), 47.1 (CH), 46.4 (CH), 38.2 (C), 30.8 (CH_3), 22.1 (CH_3), 22.0 (CH_3), 21.7 (CH_3).

Ozonolysis of 2. (a) Fifty milligrams of **2** in 5 mL of CH_2Cl_2 was ozonated at −78 °C by bubbling the effluent from an ozone generator through the solution until it turned blue. After flushing with oxygen, 2 mL of methanol and 0.1 mL trimethyl phosphite were added, and the mixture was stirred 12 h at room temperature. Solvent removal gave 80 mg of a mixture of **19** and trimethyl phosphite.

(b) One hundred milligrams of **2** (0.34 mmol) in 10 mL each of CH_2Cl_2 and CH_3OH was ozonated as above. After the mixture was flushed with N_2, 0.5 mL of Me_2S was added, and the mixture was stirred for 2 days. Solvent evaporation annd chromatography on silical gel with 15% ethyl acetate/hexane as eluant gave 90 mg of material which moved as a single spot (R_f 0.3), which appears to be a mixture of diketones **20** from the spectral data (reported in the text). The same product was isolated upon ozonolysis at 0 °C. Attempted TLC separation of the isomers failed.

Equipment. A Kratos MS-80 RFA mass spectrometer and Bruker WP-200, WP-270, and AM-500 NMR spectrometers were employed. Calculations were done on IBM PC-XT or DEC VAX-8650 computers. The methods used to obtain CV curves[25] and optical spectra[25] have been described in detail previously. The electrochemical cell used to generate the sample of $2^{\bullet+}$ for ESR was similar to that published by Ohya-Nishiguchi[27] except that heat-shrink tubing was used to insulate the central platinum electrode from the outer gold electrode. A Varian E-15 ESR spectrometer was used.

Two-Site Decoupling. The rf input to the decoupler unit was modulated by an audio frequency which was half the frequency separation of the two peaks to be irradiated, with the decoupler offset adjusted so that the unmodulated output was midway between these two peaks. Mixing was accomplished with a Mini-circuits Labs type SRA-1 double-balanced mixer. The rf input was about 1 V peak to peak and independent of the decoupler power setting. The audio input was about 0.4 V rms, adjusted to the maximum level that did not distort the modulated rf signal on an oscilloscope. Audio frequency was set precisely with a frequency counter, and decoupler power was the minimum that would produce complete decoupling, which helped minimize spurious signals in the spectrum.

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Registry No. **1**, 63577-41-3; **2**, 104423-54-3; **4**, 1073-14-9; **5**, 58047-17-9; **6**, 4132-77-8; **7**, 104423-55-4; **19**, 119971-40-3; **20**, 119971-41-4; isopropyltriphenylphosphonium bromide, 1530-33-2.

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(27) Ohya-Nishigushi, H. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 2064.