Table I. Properties of Aromatic Carbon Atom Clusters

C_n species			Hückel MO		MNDO	
n	symm	ring types[a]	E_{res}[b]	p_{cc}[c]	ΔH_f[d]	r_{cc}[e]
24[f]	O_h	$6^8/4^6$	0.496	0.404, 0.686	34.0	1.502, 1.386
40[g]	D_{5d}	$6^{10}/5^{12}$	0.528	0.405-0.633	22.5	1.522-1.382
50[h]	D_{5h}	$6^{15}/5^{12}$	0.539	0.382-0.624	18.4	1.486-1.389
60[i]	I_h	$6^{20}/5^{12}$	0.553	0.476, 0.602	14.5	1.474, 1.400
60[j]			0.475	(0.52 ± 0.01)[k]	(19 ± 1)[l]	
60[m]	D_{6h}	$6^{20}/5^{12}$	0.542	0.393-0.691	18.3	1.493-1.370
70[h]	D_{5h}	$6^{25}/5^{12}$	0.554	0.470-0.596	13.5	1.49-1.39
q			0.574[n]	0.525[n]	(1.5)[o]	(1.421)[p]

[a] Superscripts indicate number of each polygon type. [b] Ethylene-based resonance energy per C in units of the resonance integral β. [c] Nearest-neighbor π-type bond orders (unique values or ranges). [d] MNDO[6,7] ΔH_f at 298 K (kcal/mol per C atom). [e] Nearest-neighbor values in Å, listed analogously to bond orders. [f] Truncated octahedron. [g] Formed from BF by deleting 10 hexagons from an equatorial belt. [h] C_{50} and C_{70} are formed from BF by rotating one hemisphere $2\pi/10$ radians relative to the other and then removing or adding an equatorial belt of 10 C atoms. [i] Buckminsterfullerene. [j] Finite graphite sheet: planar, polyaromatic C_{60} cluster with a minimal number (i.e., 20) of dangling bonds. [k] Mean for interior bonds. [l] Based on data in ref 9a for $C_{60}H_{20}$ and 101 ± 3 kcal for the mean CH bond energy (from the process, benzene → *o*-benzyne + 2H).[9a,13] [m] Graphitene.[5] [n] Reference 4. [o] Reference 9a. [p] Reference 14. [q] Infinite graphite sheet.

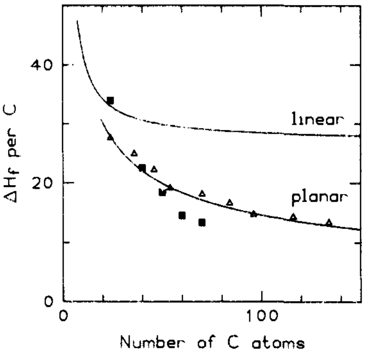

Figure 1. ΔH_f (per C atom) for various polyhedral, planar (graphite-like), and linear (C_{2n} triplet states) carbon clusters. Based, respectively, on MNDO results (solid squares; see Table I), empirical estimates (footnote 1, Table I), and UHF MNDO results. The linear results for n = 2-18 were extrapolated to larger n (limiting ΔH_f = 27.0 kcal/mol/C). Each planar cluster (triangles) has the minimal number m of "edge" atoms and is obtained by dehydrogenating the corresponding C_nH_m molecule. Use of $m = (6n)^{1/2}$ gives the exact stoichiometry for n = 6, 24, 54, ... (i.e., concentric "shells" about a benzene nucleus) and provides a smooth approximation (solid curve) for the general pattern.

Our principal results are as follows:

(1) BF is intrinsically stable. Its normal mode frequencies are all real and range from 186 to 1217 cm^{-1}. Included is a totally symmetric "double-bond" stretching mode at 1179 cm^{-1}, intermediate between that of benzene (990 cm^{-1}) and ethylene (1623 cm^{-1}).[11] The "double bonds" are those shared by hexagonal rings. These are shorter by 0.07 Å than the pentagonal edge bonds. This shortening is consistent with the Hückel prediction. (Hückel bond orders did not yield good predictions for relative bond lengths in other clusters, but these were well correlated with MNDO bond orders.)

(2) The graphitene form of C_{60} suggested by Haymet[5] is considerably less stable than the icosahedral form.

(3) Spheroidal C_{70} appears to be somewhat more stable than C_{60}, so that the greater abundance observed experimentally for C_{60} may reflect either kinetic conditions during cluster generation or the influence of the mass spectrometric detection method.

(4) The crossover (Figure 1) in energy preference from planar to polyhedral clusters occurs near n = 40. Since planar fragments with their unsatisfied valences are likely to be highly reactive, it is understandable that mass peaks with $n < 40$ diminish when NO is added to the reaction system.[1c]

(5) The MNDO ionization potentials for C_{50}, C_{60}, and C_{70} are 8.6, 9.1, and 8.7, respectively. Even when reduced by an estimated ~1-eV correction, they remain at variance with an early reported threshold of ≲5.0 eV for single photon ionization.[3a] However, they seem compatible with more recent[12] upper (7.9 eV) and lower (6.4 eV) bounds.

(6) The MNDO MO's in BF separate cleanly into π (≳97% radial 2p) and σ(2s and tangential 2p) types, and 21 of the 30 occupied π levels lie at the top of the occupied manifold. Thus, despite the obvious angle strain, it is reasonable to think of BF in conventional aromatic terms.

Acknowledgment. We are grateful to Professor R. E. Smalley for providing us with material prior to publication, and a probable structure for C_{70}, and to Dr. A. Kaldor for giving us information regarding ionization thresholds prior to publication. We thank Dr. John McKelvey for making available a VAX version of the MOPAC program. This research was carried out at Brookhaven National Laboratory under Contract DE-AC02-76CH00016 with the U. S. Department of Energy and supported by its Division of Chemical Sciences, Office of Basic Energy Sciences.

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Chemistry of Dioxiranes. 4. Oxygen Atom Insertion into Carbon-Hydrogen Bonds by Dimethyldioxirane[1]

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We have recently reported[2] that we have discovered a method of producing solutions of pure methyldioxiranes. This discovery has permitted us to record the spectroscopic properties of dimethyldioxirane (**1**), as well as to carry a number of very efficient O atom transfer reactions with a variety of substrates including olefins, polycyclic aromatic hydrocarbons, sulfides, tertiary amines, aldehydes, and triphenylphosphine. These reactions usually take place very rapidly and under extremely mild conditions with the oxidized product being obtained, usually in very high yield, as a

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(1) Part 3: Murray, R. W.; Jeyaraman, R. *Proceedings of the Tenth International Symposium on Polynuclear Aromatic Hydrocarbons*; Battelle Press, in press.

(2) Murray, R. W.; Jeyaraman, R. *J. Org. Chem.* **1985**, *50*, 2847-2853.

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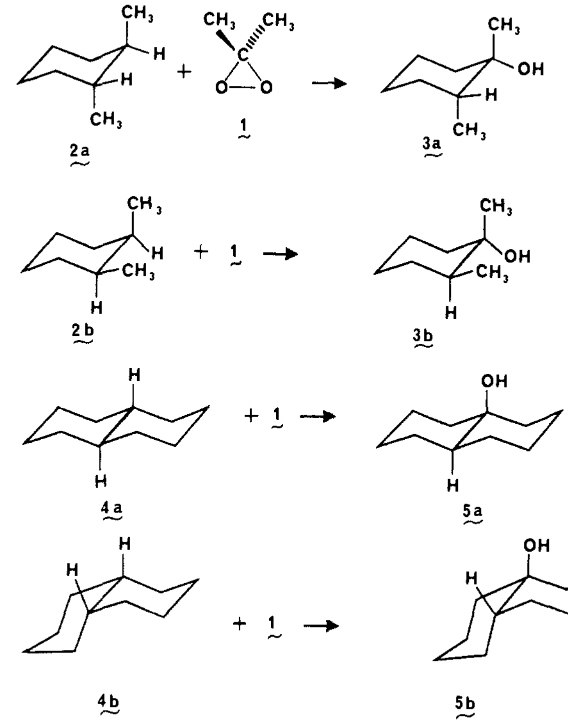
Scheme I



solution in the precursor ketone, i.e., acetone in the case of **1**.

We now wish to report that **1** inserts an O atom into carbon-hydrogen bonds of hydrocarbons to give alcohols or products derived from further oxidation of the alcohols. Furthermore, using suitable substrates, we have shown that the insertion reaction occurs stereospecifically with retention and displays a primary kinetic isotope effect ($k_H/k_D = 4.97$). Some examples of the reaction are the conversion of toluene to benzaldehyde, cyclohexane to cyclohexanol and cyclohexanone, cyclododecane to cyclododecanone, and *n*-decane to a number of products including 2-decanone and 3-decanone. Adamantane is conveniently converted to 1-adamantanol.[3]

In a typical reaction a solution of **1** in acetone (25 mL, 0.052 M) was added to a solution of adamantane (0.321 g; 2.35 mmol) in 25 mL of acetone. The solution was stirred at 22 °C while protected from light. Progress of the reaction was followed by periodic sampling and capillary GC analysis (DB-1701 fused silica column). In 4 h 1-adamantanol had been formed in ca. 40% yield. In 18 h the reaction was essentially complete giving an 87% yield of 1-adamantanol accompanied by 2-adamantanol and 2-adamantanone in 2.6% combined yield.

The stereochemistry of the insertion reaction was determined by studying the reaction of **1** with the stereoisomeric 1,2-dimethylcyclohexanes (**2a,b**) and the stereoisomeric decalins (**4a,b**) (Scheme I). In both cases the reaction is stereospecific with retention. Thus the trans compound, **2a**, gives only the corresponding trans alcohol, **3a**, while the isomer **2b** gives only alcohol **3b**.[4] Likewise *trans*-decalin (**4a**) gives only the trans alcohol **5a** and the *cis*-decalin gives only the cis alcohol **5b**.[9] The stereochemical results obtained with the 1,2-dimethylcyclohexanes are similar to those obtained by Hellman and Hamilton[11] when the same substrates were ozonized in the presence of $FeCl_3$ where the oxidation was found to be nearly stereospecific with retention. Likewise Durland and Adkins had earlier observed[10] that ozone converts the decalins stereospecifically to the corresponding alcohols albeit in only modest yield.[12]

Table I. Relative Reactivity in C–H Reactions[a]

substrate[b]	rel rate of insertion by **1**	rel reactivity toward H abstraction[c]
toluene	(1)	(1)
ethylbenzene	24	3.2
cumene	91	6.8

[a] Relative reactivities are given per H. [b] In all cases only benzylic H is involved. [c] Taken from ref 13. H abstraction is by *tert*-butoxy radicals at 40 °C.

The relative rate of the insertion reaction in a series of related substrates was determined and compared to that for a radical process[13,14] (Table I). The data indicate that **1** is considerably more selective than the *tert*-butoxy radical toward these substrates. The observed reactivity of **1** is more reminiscent of that observed by Hamilton and co-workers[15] for the ozone oxidation of 2-methylbutane, i.e., 1:13:110 for primary-secondary-tertiary C-H oxidation. We now plan a comparable study, i.e., using aliphatic C–H, with **1** as oxidant.

In order to gain further insight into the details of the mechanism of the C–H insertion a kinetic isotope study was carried out. An equimolar mixture of cyclododecane and cyclododecane-d_{24} (0.1 mmol of each) was added to a solution of **1** in acetone (0.124 M). The resultant solution was stirred at 25 °C in the absence of light.[16] The solution was sampled periodically and the samples analyzed by capillary GLPC using a precision syringe. Straight line plots were obtained for consumption of the hydrocarbons according to pseudo-first-order kinetics. The reaction was carried out over several half-lives and gave $k_H/k_D = 4.97$. This observed primary kinetic isotope effect indicates that the C–H bond is being broken in the rate-determining step of the oxidation. Furthermore the value observed suggests that the C–H bond is probably not completely cleaved in the transition state.

While dioxiranes are relatively unknown compounds, the chemistry they have displayed to date[1,2,17] indicates that they are

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(3) Products were identified by comparing physical, spectroscopic, and chromatographic properties with those of the authentic materials. Yields varied from 2% to 80%. Higher yields and shorter reaction times were obtained by using higher **1**:substrate ratios.

(4) The hydrocarbons **2a** and **2b** are converted to the respective alcohols, **3a** and **3b**, in 45% and nearly quantitative yield, respectively, in 18 h. The product alcohols were identified by comparing their physical properties with those previously reported: the cis alcohol had mp 22.8 °C, lit.[5] mp 23.2 °C; n_D^{22} 1.4610, lit.[6] n_D^{25} 1.4628; the trans alcohol had mp 2-4 °C,[7] lit.[5] mp 13.2 °C and -3.5 to -1 °C,[8] n_D^{22} 1.4565, lit.[6] n_D^{25} 1.4588. The crude reaction mixture was analyzed by capillary GC using a 30 M × 0.311 mm DB 210 column to give the reported results. The analysis used temperature programming as follows: temperature 1, 45 °C, time 5 min, then changed at rate of 20 °C/min to temperature 2, 180°, maintained for 15 min. Separately determined detection limits indicate that any contaminating alcohol present would not exceed 0.8%.

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(6) Nevitt, T. D.; Hammond, G. S. *J. Am. Chem. Soc.* **1954**, *76*, 4124-4127.

(7) The variation in melting point values for the trans alcohol may be due to a variable conformer makeup.

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(9) The cis isomer **4b** is converted to the cis alcohol **5b** in 84% yield in 17 h. The trans isomer **4a** gives **5a**, in 20% yield in the same reaction time. The trans hydrocarbon **4a** is contaminated with ca. 1% of **4b**. Since **4b** is the faster reacting material some **5b** is observed to form. The alcohol products were identified by mass spectra and ^1H NMR spectra. The trans alcohol had mp 51-52 °C, lit. [10] mp 50-52 °C; the cis alcohol had mp 64-65 °C, lit.[10] mp 64.5-65 °C. The reaction mixtures were analyzed by GC using a 30 M × 0.311 mm DB column with temperature programming as follows: temperature 1, 60 °C, time 5 min then to temperature 2, 100 °C at a rate of 20 °C/min, time, 5 min, then to temperature 3, 160 °C, same rate, time 5 min.

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(12) A referee has suggested that O_3, produced by reaction of **1** with O_2, might be responsible for the chemistry observed here. This possibility would seem to be ruled out by the observation[2] that **1**, produced in the same manner as in the current work, reacts with olefins to give high yields of epoxides. Under the same conditions O_3 would be expected to lead to ozonolysis, i.e., cleavage of the olefin.

(13) Walling, C.; Thaler, W. *J. Am. Chem. Soc.* **1961**, *83*, 3877-3884.

(14) The relative reactivities were determined by oxidizing an equimolar mixture of the hydrocarbons with **1** and determining hydrocarbon consumption in 24 h by using GLPC.

(15) Hamilton, G. A.; Ribner, B. S; Hellman, T. M. *Adv. Chem. Ser.* **1968**, *No. 77*, 15-25.

(16) Dimethyldioxirane is a very volatile peroxide. Reactions should be carried out in the hood and behind a shield.

very powerful oxidants. In particular they are very powerful O atom donors in which respect they resemble certain monooxygenase enzymes.[18] Since the parent dioxirane has been indentified as a product of gas-phase ozonolysis of ethylene, it also seems likely that dioxiranes could be involved in air pollution chemistry and particularly the environmental health aspects of this chemistry.

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Generation of $^1\Delta_g$ O_2 from Triethylsilane and Ozone

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Trialkylsilanes are known to react with ozone at 0 to −60 °C in inert organic solvent to form trialkylsilanols as major products by a pathway that is thought to involve trialkylsilyl hydrotrioxides as intermediates.[1] We became interested in this reaction as a possible chemical method for the generation of $^1\Delta_g$ O_2 at sufficiently low temperatures to allow the synthesis of unstable endoperoxides since it seemed that the silyl hydrotrioxide → silanol + O_2 reaction could be a source of singlet dioxygen. Despite the existence of an extensive literature on the reaction of ozone with silanes,[1] the possible production of $^1\Delta_g$ O_2 in this process has not been proposed. Physical and chemical evidence is presented herein that triethylsilyl hydrotrioxide can be generated at −78 °C by the reaction of ozone with triethylsilane and that it decomposes to give $^1\Delta_g$ O_2 in preparatively useful yield.

The color of a cold (−78 °C), saturated methylene chloride solution of ozone (ca. 0.04 M) was discharged within 45 s upon treatment with 2 equiv of triethylsilane (TES). Addition of a methylene chloride solution (at −78 °C) of excess 2,5-diphenyl-3,4-benzofuran (DPBF) at once and further reaction at −78 °C for 1 h produced (after warming to 0 °C and analysis by HPLC) 45% yield of *o*-dibenzoylbenzene (based on O_3).[2] In a parallel preparative experiment[3] *o*-dibenzoylbenzene was isolated in 91% yield,[4a] using 1 equiv of ozone, 2 equiv of TES, and 0.33 equiv of DPBF. This chemical evidence for the generation of $^1\Delta_g$ O_2 was further confirmed by the demonstration of a number of characteristic transformations including α-terpinene → ascaridole (90% yield),[4b] 9,10-dimethylanthracene → 9,10-endoperoxide (92%),[4c] 1,3-cyclohexadiene → 1,4-endoperoxide (46%),[4d] tetraphenylcyclopentadienone → (*Z*)-1,2-dibenzoylstilbene (62%),[4e] tetramethylethylene → 3-hydroperoxy-2,3-dimethyl-1-butene (40%),[4f] citronellol → 1:1 mixture of 3,7-dimethyloct-5-ene-1,7-diol and 3,7-dimethyloct-7-ene-1,6-diol (after reduction with $NaBH_4$–CH_3OH, 25%),[4g] and 2-[(trimethylsilyl)oxy]bicyclo[2.2.1]hept-2-ene → 3-[(trimethylsilyl)peroxy]bicyclo[2.2.1]heptan-2-one (50%).[4h,5]

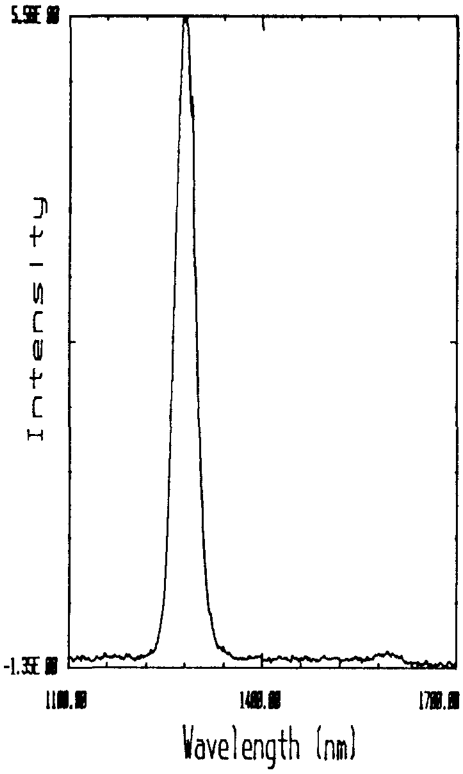

Figure 1. Near-infrared emission spectrum from decomposition of triethylsilyl hydrotrioxide at −60 °C in CH_2Cl_2.

The approximate rate of decomposition of the intermediate which gives rise to $^1\Delta_g$ O_2, clearly best formulated as triethylsilyl hydrotrioxide, was evaluated at −78 °C by generating the hydrotrioxide at that temperature, adding an excess of DPBF (in CH_2Cl_2 at −78 °C) at varying time intervals, and determining the extent of oxidation of DPBF to *o*-dibenzoylbenzene by HPLC analysis. In this way a half-life of a few minutes could be estimated. Equation 1 summarizes the process of $^1\Delta_g$ O_2 generation.

$$(C_2H_5)_3SiH + O_3 \xrightarrow[45\ \mathrm{s}\ (CH_2Cl_2)]{-78\ °\mathrm{C}} (C_2H_5)_3SiOOOH \xrightarrow[t_{1/2}\ \mathrm{ca.}\ 150\ \mathrm{s}]{\mathrm{ca.}\ -60\ °\mathrm{C}} (C_2H_5)_3SiOH + {}^1\Delta_g\ O_2 \quad (1)$$

The formation of $^1\Delta_g$ O_2 from triethylsilyl hydrotrioxide was also demonstrated spectroscopically. Solutions of ozone and triethylsilane were mixed in a small Pyrex Dewar vessel cooled by a dry-ice cold finger (to a temperature of ca. −60 °C) and placed before the entrance slit of an ultrasensitive near-infrared

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(1) (a) *Ozonation in Organic Chemistry*; Bailey, P. S., Ed.; Academic Press: New York. 1982; Vol. II, p 329. (b) Aleksandov, Yu. A.; Tarunin, B. I. *Russ. Chem. Rev.* (*Engl. Transl.*) **1977**, *46*, 905. (c) Spialter, L.; Pazdernik, L.; Bernstein, S.; Swansiger, W. A.; Buell, G. R.; Freeburger, M. E. *Adv. Chem. Ser.* **1972**, *No. 112*, 65. (d) For studies of the formation of carbon hydrotrioxides from the reaction of activated C–H bonds with ozone and the thermal decomposition of such C–hydrotrioxides, see: Stary, F. E.; Emge, D. E.; Murray, R. W. *J. Am. Chem. Soc.* **1976**, *98*, 1880. Pryor, W. A.; Ohto, N.; Church, D. F. *Ibid.* **1982**, *104*, 5813.

(2) HPLC analysis was performed under air-free conditions (because of facile air oxidation of DPBF), using a Du Pont Zorbax silica gel column with 3% tetrahydrofuran in hexane as solvent.

(3) Yield based on the limiting substrate. In preparative experiments the ratio of TES to O_3 was generally 2. The ratio of O_3 to substrate (O_3/S ratio) was 5 unless otherwise indicated.

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(5) Products were identified unambiguously by spectral and chromatographic comparisons with authentic samples prepared as previously described.[4] In all these reactions the material balance was excellent, the remainder being starting material.

0002-7863/86/1508-2472$01.50/0