J. Org. Chem. **1998,** *63,* 4587−4593 **4587**

Reactions of Microwave-Generated O(^{3}P) Atoms with Unsaturated Hydrocarbons

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Received November 13, 1997

The reactions of neat olefins or solutions of olefins in acetone at low temperature with oxygen atoms were examined. O(^{3}P) atoms were produced by microwave irradiation of He/O_2 mixtures, followed by contact of the plasma with the fluid at low pressure and temperature. Addition of oxygen atoms to olefins results in skeletal rearrangements involving hydrogen and alkyl migration reactions and ring rearrangements of the intermediate oxygen adducts in competition with epoxide formation. While epoxide formation predominates for simple olefins such as 1- and 4-octene with minor yields of rearrangement products, for highly substituted or strained olefins, such as norbornadiene, skeletal rearrangement dominates following oxygen atom addition. When oxidation of norbornadiene is carried out in the presence of a radical inhibitor to suppress secondary oxidation leading to benzene, the novel ring-rearrangement product, bicyclo[$3.^{2,3}1.0$]hex-3-ene-*endo*-6-carboxaldehyde, is produced from norbornadiene in significant yields.

Introduction

It is clear from our previous work on the solution-phase reactions of atomic ($H^{\bullet}$)[4] and more complex radical species ($CH_3^{\bullet}$)[5] formed using a microwave discharge that the conditions produce thermalized reactants whose products are the result of the reactions of the primary intermediates. Kinetic studies show that addition of oxygen to olefins at room temperature is nearly diffusion-controlled, whereas hydrogen abstraction is more than a factor of 10^3 slower per hydrogen than addition to an olefin.[6] Thus, low temperatures will further enhance selectivity for addition, in addition to producing thermalized intermediates. A number of publications have reported the vapor- phase reactions of atomic oxygen, O(^{3}P) generated by the mercury-photosensitized decomposition of nitrous oxide[7] or by a microwave plasma promoted by O_2/He at low pressures.[8] The vapor-phase reactions in general show deep-seated fragmentation and rearrangements of substrates, indicative of energetically enriched intermediates.

A number of studies that generate ground-state oxygen, O(^{3}P), have reported reactions carried out in the condensed phase or on solid surfaces.[9−11] The liquid-phase reactions have been carried out using γ-irradiation of substrates dissolved in liquid CO_2,[8] by the microwave discharge of CO_2,[10] with oxygen atoms generated by an O_2/He plasma,[11] or with a plasma formed from a mixture of N_2 and N_2O.[12]

The mechanism proposed for the addition of O(^{3}P) atoms to an olefin was shown to proceed via a triplet diradical since *cis*- or *trans*-stilbene yielded both *cis*- and *trans*-stilbene oxide as well as benzyl phenyl ketone.[9a,b] The use of a O_2/He plasma to generate O(^{3}P) atoms has been questioned since the reactive species produced by the plasma were possibly contaminated with O_2, $O_2(^1\Sigma g)$, or O_3.[9i] When O(^{3}P) atoms were generated using a microwave discharge of O_2/He, the product ratios formed

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(4) (a) Tanner, D. D.; Zhang, L. *J. Am. Chem. Soc.* **1994**, *116*, 6683. (b) Tanner, D. D.; Zhang, L.; Vigneswaran, M.; Kandanarachchi, P. *J. Org. Chem.* **1995**, *60*, 4481. (c) Tanner, D. D.; Zhang, L.; Kandanarachchi, P. *J. Phys. Chem.* **1996**, *100*, 11319. (d) Tanner, D. D.; Zhang, L.; Hu, L. Q.; Kandanarachchi, P. *J. Org. Chem.* **1996**, *61*, 6818. (e) Tanner, D. D.; Koppula, S.; Kandanarachchi, P. *J. Org. Chem.* **1997**, *62*, 4210.

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(6) Bucher, G.; Scaiano, J. C. *J. Phys. Chem.* **1994**, *98*, 12471−1. For example, cyclopentene reacts with O(^{3}P) at 1.6×10^{10} M^{-1} s^{-1} at room temperature in acetonitrile, compared to cyclopentane, 3.8×10^8 M^{-1} s^{-1}, both rate constants on a per molecule basis.

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(8) (a) Bell, A. T. In *Techniques and Applications of Plasma Chemistry;* Hollahan, J. R., Bell, A. T., Eds.; Wiley-Interscience: New York, 1974; Chapter 1, pp 1−55. (b) Sato, S.; Cvetanovic, R. J. *Can. J. Chem.* **1959**, *37*, 953. (c) Cvetanovic, R. J. *Can. J. Chem.* **1960**, *38*, 1678. (d) Huie, R. E.; Herron, J. T. *Int. J. Chem. Kinet.* **1972**, *4*, 521.

(9) (a) Sakurai, H.; Akimoto, K.; Toki, S.; Takamuku, S. *Chem. Lett.* **1975**, 469. (b) Goto, S.; Hori, A.; Takamuku, S.; Sakurai, H. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 2965. (c) Hirokami, S.; Wojnarovits, L.; Sato, S. *Bull Chem. Soc. Jpn.* **1979**, *52*, 299. (d) Karawawa, H.; Samamoto, T.; Yugeta, R.; Sato, S. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 902.

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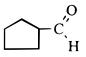
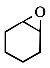
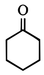
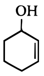
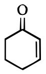
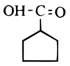
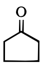
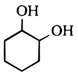
S0022-3263(97)02083-5 CCC: $15.00

Table 1. Reaction Products of Cyclohexene with Atomic O(^{3}P), −78°C

[Reactant] Cyclohexene	Products (mole % reaction) 								Others (10 products)[a]	% Reaction
9.88	13.1	21.3	31.1	3.2	2.0	1.7	2.2	17.7	7.0	23.5
9.88	13.8	50.0	17.4	2.03	1.6	1.27	1.16	5.18	5.4	2.0
1.0[b]	13.9	45.9	22.9	1.17	1.05	0.82	2.64	5.78	5.72	9.8
1.0[b]	11.2	46.2	29.2	2.87	1.27	0.85	1.65	2.09	4.60	21.9
1.0[b]	13.4	38.3	20.5	2.82	2.12	3.44	1.45	5.05	13.0	44.0

[a] Area % of products. [b] Acetone solutions.

from the oxidation of styrene[9i] or *cis*-stilbene[9a] were not appreciably different. However, with all three of the microwave-promoted methods for the generation of O(^{3}P) atoms, an appreciable amount of benzaldehyde (5−13%) was formed from the oxidation reactions of styrene.[9i] The formation of a cleavage product, benzaldehyde, suggested that under the reaction conditions in all three cases ozone is formed.

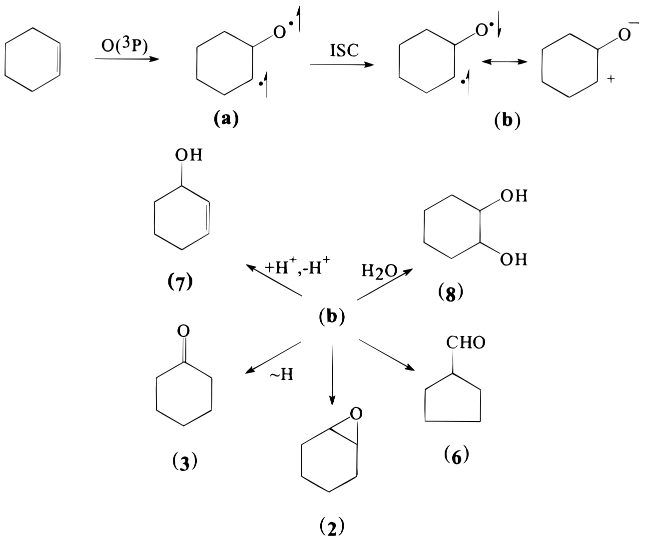
To establish the identity of the reactive reagent and to compare some of the more striking differences between the vapor-phase and solution-phase reactions of O(^{3}P) atoms, the reaction of a number of olefins was investigated. The model substrates chosen are examples of vapor-phase or condensed-phase chemistry that involved extensive molecular rearrangement or fragmentation.

Results and Discussion

Cyclohexene. The vapor-phase oxidation of cyclohexene (**1**) by O(^{3}P) atoms was reported[6] to give epoxycyclohexane (**2**), cyclohexanone (**3**), 5-hexenal (**4**), 2-hexenal (**5**), and cyclopentanecarboxaldehyde (**6**). In the present solution-phase study, neat and acetone solutions of cyclohexene (−78 °C) formed **2**, **3**, **6**, and several cyclohexyl and cyclopentyl products, but did not form open-chain materials in appreciable yields; see Table 1.

A mechanism that accounts for the products is consistent with the intermediacy of a triplet diradical (**a**). The reactive intermediate **b** formed after intersystem crossing (ISC) can rationalize the formation of the other products; see Scheme 1. Cyclohexenol (**7**) may be formed by deprotonation/reprotonation of **b**; cyclohexanone is formed by a 1,2-hydrogen shift of **b**. Products **3** and **6** are formed by hydrogen migration and skeletal rearrangement of **b**. We prefer to attribute some zwitterionic character to **b** in the polar solvent, acetone, because the skeletal rearrangement leading to the production of cyclopentanecarboxaldehyde, **6**, and in particular, the formation of 1,2-cyclohexanediol, **8**, by hydration, are both suggestive of a dipolar character for **b** in Scheme 1. The possibility that **3**, **6**, and **8** could form by acid-catalyzed hydrolysis of **2** was also considered. Titration of a reaction mixture following 60% conversion of cyclohexene revealed 0.01−0.04 M acid content following exposure to the plasma. However, when the reaction mixture resulting from exposure of cyclohexene to oxygen atoms was analyzed by GC and NMR over a period of 18 h, a negligible decrease in the concentration of cyclohexene oxide or change in product ratios was observed. Finally, the possibility that the products were formed from reactions of ozone was ruled out by exposing cyclohexene to ozone under identical reaction conditions. The formation of ketones and aldehydes in the gas-phase addition of oxygen atom to olefins has been suggested to involve 1,2-hydrogen, -alkyl, and -aryl migrations.[13] The photolysis of epoxides, presumably leading to the same diradical intermediates, may involve 1,2-alkyl and -hydrogen migration reactions for simple alkene oxides.[14] The present results are consistent with rapid 1,2-hydrogen and 1,2-alkyl (ring contraction) shifts involving the diradical intermediate.

Scheme 1



1-Octene. The reaction of 1-octene with the O$_2$/He plasma yields five major products accounting for 99% of the substrate that reacts. Several (approximately five) minor products could also be detected; see Table 2. A mechanism that rationalizes the production of 96−98% of the products formed proceeds by a single intermediate, a diradical, formed from the addition of O(^{3}P) to the olefin, Scheme 2. Products reflecting the participation of O$_2$ or ozone account for several percent of the products. The hydrogen shift leading to RCH$_2$CHO may occur by hydride shift to carbon, proton shift to oxygen, or deprotonation/reprotonation involving solvent or equivalently may be described as a direct 1,2-hydrogen atom migration

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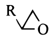
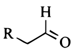
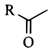
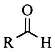
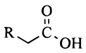
(13) Suhr, H. *Plasma Chem. Process.* **1982**, *3*, 1.

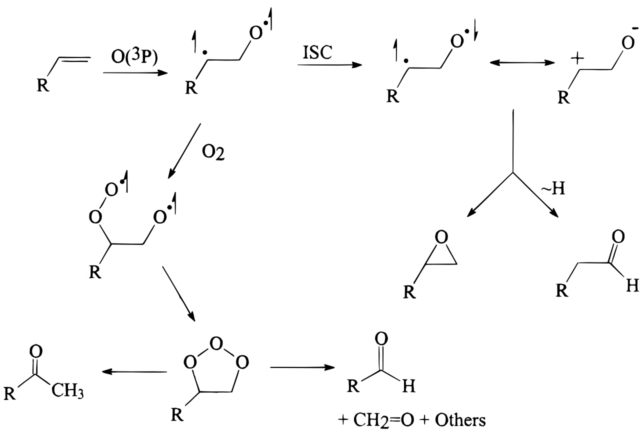
(14) (a) Nastasi, M.; Streith, J. In *Rearrangements in Ground and Excited States*, De Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, p 445. (b) Gritter, R. J.; Sabatino, E. C. *J. Org. Chem.* **1964**, *29*, 1965.

Table 2. Products from the Reaction of 1-Octene with a O_2/He Plasma, ~78°C[a]

[Reactant] 1-Octene	Products (mole %), R = C_6H_{13}						% Reaction
						Other[b]	
1.27 M (acetone)	85.7	10.3	0.72	0.52	0.70	<1(5)	76
6.37 M (neat)	81.8	16.0	0.43	0.23	1.53	<1(5)	45.1
6.37 M (neat)	71.4	25.0	0.53	0.37	0.19	<1	8.0

[a] He/O_2 ratio 4.5/1. [b] Five other products, area (%).

Scheme 2



of the singlet diradical, reminiscent of photochemical ring-opening reactions of epoxides[14,15] in solution that produce ketones and aldehydes. The singlet diradical may be expected to exhibit a greater degree of zwitterionic character in the polar solution phase than in the gas phase. As with cyclohexene, polar diradical characteristics will effect alkyl and hydrogen migration reactions and reactions with nucleophiles such as water. Activation barriers for 1,2-alkyl and 1,2-hydrogen migration on the singlet surface must be very nearly barrierless, since they must compete with ring closure of the diradical to the epoxide on the singlet surface. In one theoretical study of the biradical from addition of oxygen atom to $CH_2{=}CH_2$, attempts to optimize the geometry of the singlet diradical led only to collapse to acetaldehyde, suggestive of the relative facility of the 1,2-hydrogen shift compared to oxirane formation.[15] Finally, we note that the major product observed from 1-octene, octene oxide, was not formed by reaction of ozone with the olefin, as demonstrated in control ozonolysis experiments.

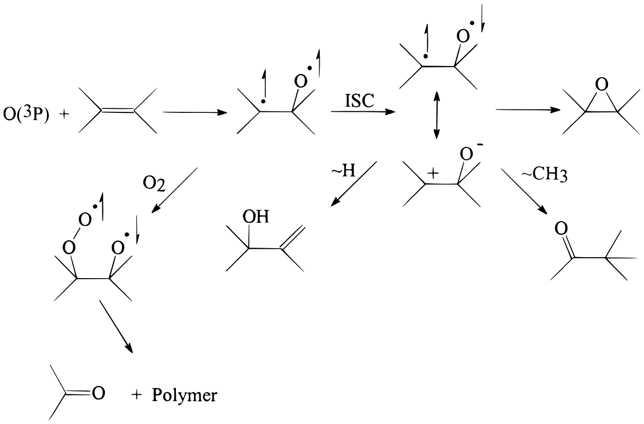
***cis*-4-Octene.** To confirm the observations previously reported that cis- or trans 1,2-disubstituted ethylenes yielded, among other products, both *cis*- and *trans*-epoxides, in the condensed phase,[9i] or in the vapor phase,[16] the reaction of *cis*-4-octene was carried out using an O_2/He plasma; see Table 3. The yield of epoxides (99%) formed at moderate (36%) conversion is fully consistent with the proposed mechanism, formation of the triplet diradical adduct, which undergoes internal rotation on a comparable or shorter time scale than intersystem crossing and epoxide formation. With extensive conversion (70−85%), lower yields of epoxides (60−70%) and higher yields of 4-octanone are observed. The latter product may reflect secondary attack on the epoxide at extensive conversion.

Table 3. Products of the Reactions of *cis*-4-Octene with Atomic Oxygen (−78 °C)

			product yield (%)		
[*cis*-4-octene][a] (mol L^{-1})	time (min)	conversion (%)	*cis*-4,5-epoxyoctane	*trans*-4,5-epoxyoctane	4-octanone
0.71	2	35.9	59.1	39.8	1.09
0.71	10	70.1	42.2	27.6	30.2
0.18	5	85.0	35.7	24.1	40.2

[a] Acetone solutions (oxygen flow rate = 6 mL/min).

Scheme 3



2,3-Dimethyl-2-butene. The products from the reaction of a tetrasubstituted ethylene include both addition, rearrangement, and fragmentation as well as further oxidation; see Table 4. The fragmentation to acetone accounted for approximately 22% of the products at −42 °C and can be tentatively proposed as arising from the further reaction of the diradical with undissociated O_2; see Scheme 3. While the participation of O_2 or ozone provides a pathway for acetone production, the majority of the products can be rationalized by rearrangements of the biradical intermediate resulting from oxygen atom addition. The production of methyl *tert*-butyl ketone suggests that 1,2-alkyl migration competes with oxirane formation in the biradical system.

Norbornene. The reaction of norbornene with an O_2/He plasma yields three major products (95−98% yield); see Table 5. The product ratios do not appear to change as a function of the percentage reaction, indicating that the three products, epoxide, ketone, and alcohol, are primary products. The formation of the three oxidation products can be rationalized as occurring from a common intermediate see Scheme 4. The triplet oxygen atom adduct undergoes intersystem crossing to the singlet adduct followed by ring closure to the epoxide or hydrogen migration to form the ketone, path c. The formation of the ketone can be rationalized as occurring via c or by formation and disproportionation (path d) of hydroxynorbornyl radical. However, formation of hydroxynorbornyl

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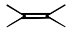
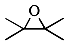
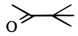
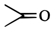
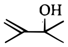
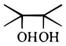
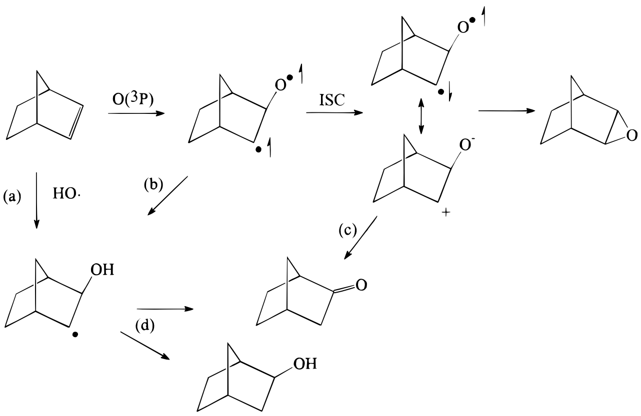
(15) Belbruno, J. J. *J. Phys. Org. Chem.* **1997**, *10*, 113−120.
(16) Cvetanovic, R. J. *Can. J. Chem.* **1958**, *36*, 623.

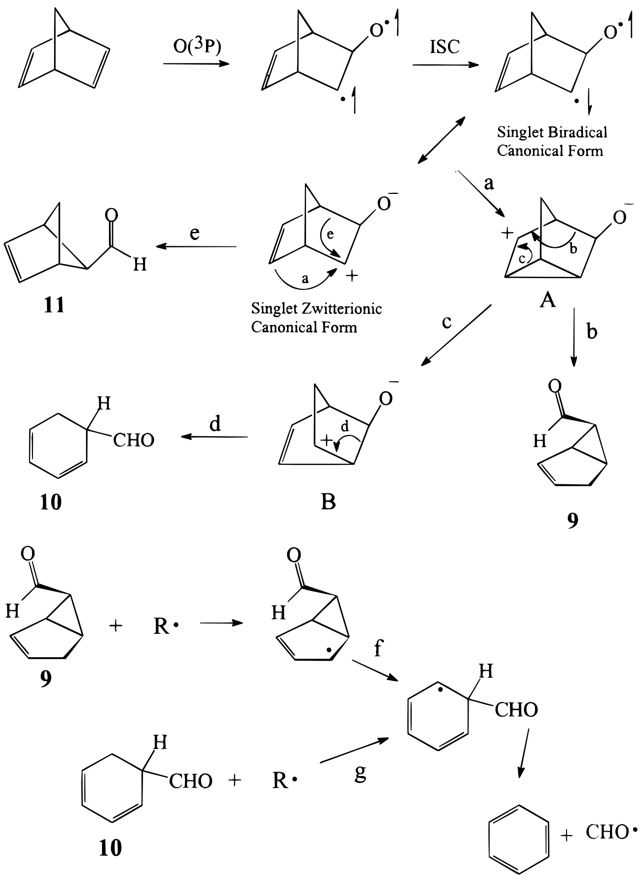
Table 4. Products from the Reaction of 2,3-Dimethyl-2-butene with $O(^3P)$ Atoms

Temp (°C)	Rxn (%)	Reaction (M)	Products (mole %)					
								Others (6)
-42	26.2	8.40	55.3	13.0	20.6	7.79	3.27	6.2 (area %)

Scheme 4



Scheme 5



$R\bullet = O,\ HO\bullet,\ CHO\bullet, CH_3COCH_2\bullet$

radical from disproportionation of the initial oxygen adduct would require oxygen adduct diradicals to exhibit unrealistically long triplet lifetimes and to exist at suitably high adduct concentrations, for the triplet biradicals to undergo bimolecular disproportionation, an unlikely situation.[17] Thus, the participation of hydroxyl radical is depicted in the production of 2-hydroxynorbornane in Scheme 4, although the source of hydroxyl radical is uncertain. The formation of hydroxyl radical by $O(^3P)$ abstraction of hydrogen is unlikely in the presence of olefins.[6]

Norbornadiene. The reaction of norbornadiene with $O(^3P)$ gave benzene as the primary product, see Table 6. At higher conversion (2−90%), a number (~10) of other minor products can be detected. Seven aldehydes with the molecular formula C_7H_8O were detected, along with traces of phenol. All of the aldehyde protons exhibited coupling to an adjacent proton in the ^1H NMR spectra; none of the cyclic aldehydes was conjugated with an olefinic system. No benzaldehyde was present in the reactions before workup, although benzaldehyde was detected following chromatographic workup of the reaction. The aldehyde formed in dominant yield (up to 63% of the total aldehydes produced) was bicyclo[3.^{2,3}1.0]hexene-6-*endo*-carboxaldehyde, **9**. An aldehyde comprising 8−23% of the total aldehydes present was tentatively identified by GC/IR[18] and GC/MS[19] as 1,2-dihydrobenzaldehyde, **10**. Bicyclo[3.^{2,3}1.0]hexene-6-*endo*-carboxaldehyde, **9**, was always detected in low absolute yields, but when a small amount of a radical inhibitor, 2,6-di-*tert*-butyl-4-methyl phenol, was added, **9** became the major product at the expense of benzene; see Table 6.

A mechanism that is consistent with the formation of benzene, but that forms bicyclic aldehyde, **9**, as a major isolable product, is given in Scheme 5. Addition of $O(^3P)$ to norbornadiene produces the triplet diradical adduct. After intersystem crossing, the singlet diradical undergoes typical cationic rearrangements involving the two intermediates, **A**[20] and **B**.[21] Because of the similarity of the products to cationic transformations, we depict a zwitterionic characteristic of the biradical in Scheme 5. Structure **11** is a possible candidate for one of the seven product aldehydes but was not positively identified. The inhibitor suppresses the disappearance of **9**, which then accumulates as a major product at the expense of benzene. Oxidation at the 7-carbon of norbornadiene is not the source of benzene. While it is known that reactions leading to the formation of norbornadien-7-one result in the efficient formation of benzene,[22] the much higher rate constants for reaction of oxygen atoms with

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[17] The 254-nm photolysis of propylene oxide gave acetone, isopropyl alcohol, and hexane-2,5-dione as major products (ref 14b). The authors propose a mechanism in which the diradical from the epoxide abstracts hydrogen from the epoxide ring carbon, leading to acetonyl radicals and the observed products. Thus, the biradicals are assumed to have a sufficient lifetime for abstraction of hydrogen from the solvent (neat epoxide).

[18] Aldrich/HP Vapor-Phase IR Database.

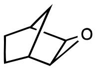
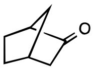
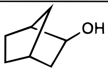
[19] MIST/EPA/MSDS Mass Spectral Data Base, 1990, PC Version 3.0.

[20] (a) Winstein, S.; Shatavsky, M. *J. Am. Chem. Soc.* **1956**, *78*, 592. (b) Winstein, S.; Walborsky, H. M.; Schreiber, K. **1950**, *72*, 5795.

[21] Story, P. R. *Tetrahedron Lett.* **1962**, 401.

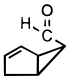
[22] (a) Landsberg J. M.; Sieczkowski J. *J. Am. Chem. Soc.* **1971**, *93*, 972. (b) Hunt D. F.; Lillya C. P.; Rauch M. D. *J. Am. Chem. Soc.* **1968**, *90*, 2561.

Table 5. Product Distribution from the Reaction of norbornene[a] with Atomic Oxygen (−72 °C)

Oxygen Flow Rate (mL/min)	Reaction Time (min)	Conversion (%)	Product Yield (%)			
						Others
2	40	7.1	73.2	14.5	7.13	5.10
2	60	12.6	76.6	13.6	7.70	2.11
6	15	3.0	67.3	20.4	8.55	3.74
6	20	5.5	72.5	12.0	11.8	3.75
6	80	33.2	74.0	15.4	8.39	2.32
30	25	12.5	55.9	28.8	10.5	4.62
30	45	22.2	68.8	20.8	8.67	1.80

[a] 1 M solution in acetone.

Table 6. Products from the Reaction of Atomic Oxygen with Norbornadiene (−72 °C)[a]

Reaction[b]	Oxygen Flow Rate (mL/min)	Added Inhibitor (%)	Time (min)	Conversion (%)	Product Yield (%)			
							C_7H_8O[c]	Others[d]
1	2	-	30	6.8	95.7	-	tr	4.30
2	6	-	40	8.3	82.3	tr	3.87	13.8
3	30	-	5	2.0	96.3	-	1.69	2.03
4	30	-	15	5.6	90.4	tr	3.32	6.28
5	30	-	30	20.5	76.6	6.36	6.55	10.5
6	30	0.025	20	12.3	68.8	15.8	5.87	9.49
7	30	0.025	40	25.2	42.9	42.9	5.39	8.81
8	30	4.0	20	15.8	60.9	27.3	7.55	4.21
9	30	4.0	40	26.6	43.2	45.9	5.14	5.76

[a] An acetone solution of 1 M norbornadiene [b] Reactions 1−5 were performed using norbornadiene fractionally distilled before use. Reactions 6−9 were carried out with an added radical inhibitor, 2,6-di-*tert*-butyl-2-methylphenol. [c] The GC/IR spectra indicated the presence of an unsaturated nonconjugated aldehyde, tentatively assigned structure of **10**. The molecular formula was assigned on the basis of the GC/MS spectra. [d] Several minor and trace compounds were detected, including phenol and several carbonyl compounds with the molecular formulas C_7H_8O and $C_7H_8O_2$.

olefins relative to hydrocarbon CH abstraction[6] make a pathway involving the norbornadien-7-yl or norbornadien-7-oxyl radical unlikely. The absence of norbornadien-7-ol argues against a Russell-type autoxidative mechanism[23] leading to benzene (via a tetraoxide precursor of norbornadien-7-one and norbornadien-7-ol). When a radical inhibitor is added to the oxidation reaction, aldehyde **9** and benzene account for approximately 90% of the total reaction. Formaldehyde accompanies the formation of benzene. These results suggest that some of the aldehyde products **9** and probably **10** (and other minor aldehydes) are converted in an oxidative radical chain decomposition to give benzene. In an attempt to reproduce the conditions for the chain decomposition, **9** was exposed to atomic oxygen. A number of dioxygenated and polymeric products were produced, but benzene was produced in only trace quantities. However, when **9** was heated at 60 °C in acetone in the presence of AIBN (10% of concentration of **9**) for ∼1 half-life, 24 h, benzene was formed as the only product. For each equivalent of AIBN, approximately 20 molecules of benzene are formed, corresponding to a chain length of ∼10. When an identical solution was irradiated at −78 °C with a 200-W incandescent lamp, benzene was produced as the only product. In Scheme 5, both **9** and **10** are depicted as benzene precursors involving a common intermediate. However, **9** is clearly the primary source of benzene, since it is the major aldehydic product.

Conclusions

This study has shown that olefins react with atomic oxygen in solution at reduced temperature to give predominately epoxides. Unlike gas-phase oxygen-atom reactions, reactions in the liquid phase at low temperature produce synthetically useful quantities and distributions of products. Epoxide formation was shown to be accompanied by apparent 1,2-hydrogen and 1,2-alkyl migrations and ring contraction reactions in competition with ring closure of the diradical to oxiranes. The results suggest that both hydrogen and alkyl migration must be nearly barrierless processes in order for them to compete with oxirane formation on the singlet surface.

Experimental Section

General Method for the O(^{3}P) Atom Reactions. The substrate was placed in the Pyrex reactor and maintained at −42 to −78 °C. Helium and oxygen were introduced into the system at the desired flow rate, and the pressure of the system was maintained at 2−4 Torr. The O_2/He plasma was generated in the microwave cavity, and the oxygen atoms were swept over the stirred solution; see Figure 1.

Instrumentation. The ^{1}H, ^{2}H, and ^{13}C NMR spectra were obtained using either a Bruker AM-400 (400 MHz), Bruker AM-300 (300 MHz), or Bruker WH-200 (200 MHz) NMR spectrometer. Unless otherwise noted, the ^{1}H NMR spectra are referenced to TMS as an internal standard at 0.00 ppm or $CHCl_3$ as an internal standard at 7.26 ppm. The ^{13}C NMR chemical shifts are reported in δ (ppm) relative to chloroform (δ $CDCl_3 = 77.0$). The ^{13}C spectra were determined using APT

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[23] Russell, G. A. *J. Am. Chem. Soc.* **1957**, *79*, 3871.

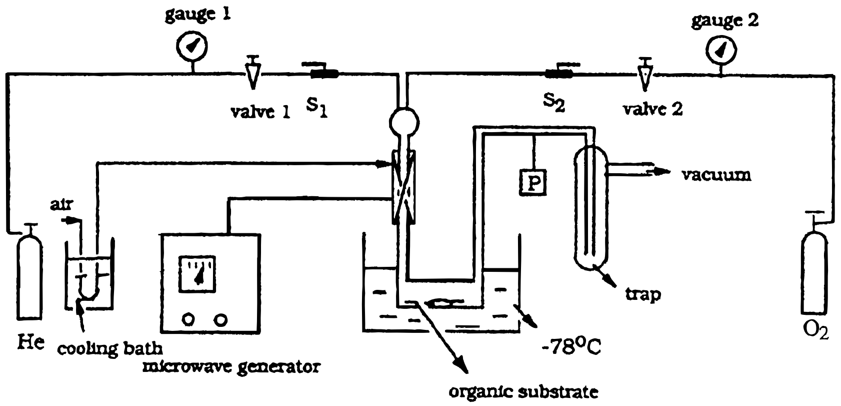

Figure 1. Diagram of apparatus for O(^{3}P) atom reactions.

(attached proton test) to determine the number of protons attached to each carbon.

GC/IR data were obtained using a HP 5965A IRD GC/FTIR interfaced to a HP 5890 gas chromatograph fitted with a DB-5 (30 m × 0.25 mm) glass capillary column.

GC/MS data were obtained using a VG-70E EI$^+$ spectrometer fitted with a Varian Vista 6000 gas chromatograph having a glass capillary column (DB-5, 30 m × 0.25 mm, J. & W. Scientific) and interfaced to a 1125 data system.

GC analyses were carried out using a Varian Vista 6000, FID, gas chromatograph fitted with a glass capillary column (PONA, 30 m × 0.25 mm, Hewlett-Packard) and interfaced to a Varian Vista CDS 401 chromatographic data system. The yield of the reaction products was determined by GC analysis using a standard calibration solution of known concentrations of the authentic materials and an added internal standard (1-chlorooctane or *o*-dichlorobenzene).[7] The purity of the reactants (1-octene, cyclohexene, norbornene, and 2,3-dimethyl-2-butene, Aldrich Chemical Co.) was checked by GC and found to be >99% pure. Norbornadiene (Aldrich Chemical Co.) was washed several times with a solution of sodium hydroxide (10%), dried over magnesium sulfate, and fractionally distilled (bp 89 °C) before use. The product was found to be >99% pure by GC. *cis*-4-Octene (TCI America) was used as received.

The products were identified by a comparison of their GC retention times, GC/IR spectra, and GC/MS spectra with those of authentic samples.

Cyclohexene. Acetone solutions (1 M, 10 mL) or neat liquid were subjected to the oxygen/helium plasma (oxygen flow rate 6–30 mL/min, −78 °C total pressure 2.0–2.5 Torr). Samples were withdrawn and analyzed by gas chromatography. The total acid content of the reaction mixtures was determined by titration with a standardized sodium hydroxide solution (0.104 mol/L) and found to be 0.007 and 0.03 M for neat cyclohexene and 1 M solutions in acetone, respectively. The product distributions of the acidic reaction mixtures were monitored for 18 h at room temperature by gas chromatography. A reaction mixture was neutralized by adding $NaHCO_3$ and analyzed by gas chromatography. A reaction performed in deuterated acetone was analyzed by both ^{1}H NMR and gas chromatography, and the product ratios between cyclohexene oxide, cyclohexanone, and cyclopentanecarboxaldehyde were compared in both analysis methods. The concentration of cyclohexene oxide decreased by 4% in 18 h, and the ratio of the products remained constant within experimental error over that period of time.

Bicyclo[2.2.1]hepta-2,5-dien-7-ol was synthesized according to the literature procedure[24] by the reaction of 7-acetonylnorbornadiene with methylmagnesium bromide in THF: ^{1}H NMR ($CDCl_3$) δ 6.50–6.60 (m, 4H), 3.40–3.50 (m, 2H), 3.05 (d, 1H), 2.15 (s, 1H); IR (vapor phase) ν 2586, 3079, 2997, 1545, 1398, 1320, 1202, 1088, 807, 738, 663 cm^{-1}; MS *m/z* 107.0 (M$^+$), 91.0, 79.1, 77.0, 64.4, 44.2. Bp 169–170 (750 mmHg). Its reaction with the oxygen plasma did not yield benzene (0.6 M in acetone, oxygen flow rate 6 mL/min, −72 °C for 8–30 min).

Norbornene. A acetone solution of norbornene (1 mol/L, 10 mL) was subjected to the oxygen/helium plasma (oxygen flow rate 2–40 mL/min, total pressure 2.0–2.5 Torr, −72 °C). Samples were withdrawn at intervals and analyzed by gas chromatography. The products were identified by comparison of their GC retention times and GC/IR and GC/MS spectra with those of authentic compounds.

Norbornadiene. An acetone solution of norbornadiene (1 M, 10 mL) was exposed to a He/O_2 plasma in the same manner as was norbornene. Several oxidations were carried out with an added inhibitor, 2,5-di-*tert*-butyl-4-methyl phenol; see Table 6. At low conversion (2–7%), the major product was benzene (95.7%), with traces of other higher boiling compounds detected. At higher conversion (>20%), benzene was still the major product (82%), and several other compounds (>8) were formed (18%). Phenol was identified as one of the minor (<1%) products. Formaldehyde was detected by trapping in acetone at −72 °C by GCIR and identified by its reaction with resorcinol.[25] The aldehyde bicyclo[3.^{2,3}1.0]hexa-2-en-6-carboxaldehyde (**9**) was detected and isolated (see below). With added inhibitor, **9** became the major product at the expense of benzene; see Table 5. Norbornadien-7-ol was not detected among the products. Six other aldehydes were also detected. Aldehyde peaks for the seven products were detected by ^{1}H NMR at δ 9.1 (d, 5 Hz), 9.15 (**10**, d, 5 Hz), 9.25 (**9**,d, 5 Hz), 9.44 (d, 5 Hz), 9.84 (d, 7.5 Hz), 9.96 (d, 7.5 Hz), and 10.19 (d, 7.5 Hz). In a reaction carried out to 25% conversion of norbornadiene, the percent composition of the aldehydes (relative to the total aldehyde concentration) was 7.3, 8.4, 62.5, 8.8, 4.4, 2.2, and 6.6%, respectively. At 90% conversion, the composition of the aldehydes was 11.4, 23.0, 44.5, 2.84, 1.6, trace, 16.6%, respectively. In both of the latter reactions, the yield of benzene was greater than 90% and the sum of other products less than 10%.

Bicyclo[3^{2,3}.2.0]hex-2-ene-6-carboxaldehyde (9) was separated from the reaction mixture by concentration under reduced pressure to remove benzene and acetone, followed by chromatography of the remaining residue on a silica gel column using methylene chloride/hexane (3:1) as eluent. The product was identified by NMR (^{13}C (APT), proton-coupled and -decoupled spectra), GC/IR, and GC/MS: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.32 (d, 1H, $J = 5.0$ Hz), 6.45 (m, 1H), 5.60 (m, 1H), 2.62 (m, 2H), 2.60 (m, 1H), 2.38 (m, 1H), 1.26 (m, 1H); ^{13}C (300 MHz, $CDCl_3$) δ 200.6 (1H), 131.8 (1H), 130.9 (1H), 40.4 (1H), 36.2 (2H), 35.4 (1H), 26.9 (1H); IR (vapor phase ν 3070, 2921, 2819, 2722, 1720, 1392, 1170, 1006, 922, 834, 708 cm^{-1}; E$^+$ (GC/MS, VG 70) *m/z* 108.1 (M$^+$), 79.0, 77.1, 63.0, 51.0; HRMS calcd for C_7H_8O 108.057 52, found 108.058 09.

Reaction of Bicyclo[3^{2,3}.1.0]hex-2-ene-6-carboxaldehyde (9) with Atomic Oxygen. A solution of **9** in acetone

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[24] Story, P. R. *J. Org. Chem.* **1961**, *26*, 287.

[25] Feigl, F. *Spot Tests in Organic Analysis*, 5th Engl. ed.; Elsevier: Amsterdam, 1956; p 331.

(0.2 M, 2 mL) was subjected to a O_2/He plasma at −72 °C for 10 min (oxygen flow rate = 6 mL/min). Benzene was only formed in trace amounts, along with dioxygenated products.

Reaction of Bicyclo[3^{2,3}.1.0]hex-2-ene-6-carboxaldehyde (9) with AIBN. A solution of **9** was heated at 60 °C in acetone in the presence of AIBN (10% of concentration of **9**) for ∼1 half-life, 24 h. Benzene was formed as the only product. When an identical solution was irradiated at −72 °C with a 200-W incandescent lamp, benzene was produced in quantitative yield.

Ozonolysis Experiments. Ozonolysis control experiments were performed using an ozone generator (Welsbach Corp., Pittsburgh, PA) at −78 °C (0.06−0.07 SCFM of oxygen flow, 14−16 mg of O_3/min at 8 lbs per in.^{2} O_2 pressure) using 5 g of neat substrate or 10 mL of a 1 M solution of substrate in acetone over a 20-minute exposure. The products were analyzed by gas chromatography. **Cyclohexene.** Neat cyclohexene (5 g) was taken to 1.5% conversion in the liquid phase. A white precipitate formed. No cyclohexene oxide, cyclopentanone, or cyclopentane carboxaldehyde was observed. A 1 M solution of cyclohexene in acetone (10 mL) was taken to 90.5% conversion by exposure to O_3. A cloudy precipitate formed that dissolved. No cyclohexene oxide, cyclopentanone, or cyclopen-tanecarboxaldehyde was observed. **Octene.** Neat 1-octene (5 g) was exposed to ozone until 43.4% reaction had occurred. A white precipitate was formed that dissolved as the solution was brought to room temperature. No epoxide of 1-octene was observed. Heptanaldehyde was detected as the major product (∼58%). A 1 M solution of 1-octene in acetone (10 mL) was exposed to ozone to 96.3% conversion of 1-octene. No epoxide of 1-octene was observed. Heptanaldehyde was detected as a major product (∼49%).

Acknowledgment. This work was supported in part by the U.S. Department of Energy, Office of Energy Research, Office of Basic Energy Sciences, under Contract No. DE-ACO6-76RLO 1830 with Battelle Memorial Institute, which operates the Pacific Northwest National Laboratory for the U.S. Department of Energy.

JO972083G