acetonitrile, acetic anhydride, etc., are treated here as one two-carbon reagent with *f* list 30, yielding an attached two-carbon unit (acetyl) of *f* list 20 in the product of a $3_1$ half-reaction (acylation, Tables IV and VI).

(21) R. E. Ireland "Organic Synthesis", Prentice-Hall, Englewood Cliffs, N.J., 1969.

(22) (a) E. J. Corey, W. T. Wipke, R. D. Cramer, and W. J. Howe, *J. Am. Chem. Soc.*, **94**, 421 (1972), and adjacent papers; (b) E. J. Corey, *Q. Rev. Chem. Soc.*, **25**, 455 (1971).

(23) "Computer Representation and Manipulation of Chemical Information", W. T. Wipke, S. R. Heller, R. J. Feldman, and E. Hyde, Ed., Wiley, New York, N.Y., 1974.

(24) There are a few cases in Table V–IX in which the half-span is different in substrate and product, essentially in $\bar{1}_2$ and one variant each of $A_3$ and $B_3$. The labeled half-span is always the greater. The *f* lists for $A_1$ and $B_1$ are sometimes listed with $f_\beta = 0$ since any function of $\beta$ is either disallowed or changes the label. See Appendix for discussion.

(25) The eight possible *f*′ lists for half-reactions yield $\binom{9}{2} = 36$ possible combinations of full *f*′ lists of six digits for the full six-carbon product strand. Excluding $f' = 101$, there are only $\binom{8}{2} = 28$ combinations. In Table XII, the rarely accessible $f' = 000.000$ (cf. Wurtz reaction) is omitted.

(26) A few oxidative and reductive couplings with reasonable precedent, as $A_2 \cdot A_2$ or $C_2 \cdot C_2$ (Table IV), have been added to the list of constructions, to make 196 full products and 367 reactions.

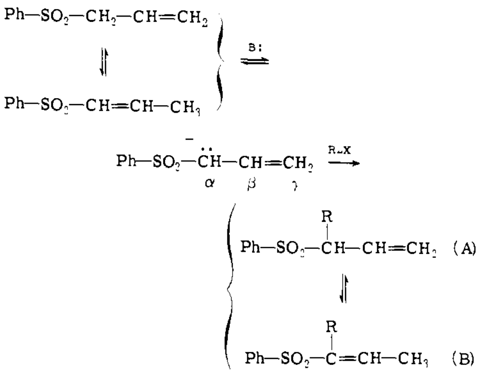
(27) N. Anand, J. S. Bindra, and S. Ranganathan, "Art in Organic Synthesis", Holden-Day, San Francisco, Calif., 1970, provides a convenient summary collection for examining how many syntheses have utilized this principle of functionality dissection; the Torgov and related steroid syntheses are found on pp 96, 170, 177.

(28) The leftmost construction is found in Table XIII only by assuming the double bond to be extraneous off-strand and looking up 000.2 instead of $000.2\overline{11}$.

(29) The sequence includes a Robinson annelation (steps 1 and 2). Another option for step 2, construction of bond 5–6 for the other $A_2 \cdot \bar{1}_3$ (Michael addition), is precluded by the maximum $\sigma$ list in Table XI which disallows $\sigma = 4$ at the $\beta$ atom of $\bar{1}_3$ (atom 4).

(30) Cyclization constructions may be further circumscribed by restricting the half-reactions that are viable for given ring sizes; in the particular case in Figure 3, reactions $A_1$ or $\bar{2}_2$ would presumably be disallowed.

(31) An example of half-reaction $B_3$ is the alkylation of unsaturated sulfones:



If there were no hydrogen on $\alpha$, the first tautomer (A) must be the product ($\sigma_\alpha = 3$) but, if (as shown) $\sigma_\alpha = 2$ in the product, then the product structure is expected to be the conjugated (B). Properly the lower substrate should be labeled $C_3$, but both are subsumed under the $B_3$ label because they are so clearly one reaction family and both yield the same products.

(32) Reactions $1_1$ and $1_2$ are further restricted in the tables to $\sigma_\alpha \leq 2$ in the substrate, forbidding displacements at tertiary carbons as characteristic of S<sub>N</sub>2 reactions. The few such constructions which occur at tertiary carbons are usually olefinic cyclizations to tertiary leaving groups. The catalog can be adapted in use to include these but their exclusion here is justified by their rarity: if tertiary $1_1$ and $1_2$ $\alpha$ carbons were allowed, too many nonviable constructions would turn up in the general sets of routes derived from them in any systematic search protocol.

(33) Presented at the Synthesis Design Symposium, Louvain, Belgium, March 1974; *Top. Curr. Chem.*, in press.

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# Atomic Oxygen. IV. Rearrangements in the Reactions of Oxygen ($^3P$) Atoms with Cyclic and Bicyclic Hydrocarbons[1]

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*Contribution from the Department of Chemistry, Rice University, Houston, Texas 77001.* *Received February 24, 1975*

**Abstract:** The gas phase reactions of ground state ($^3P$) oxygen atoms with several cyclic and bicyclic hydrocarbons have been examined. The atomic oxygen was produced by the mercury photosensitized decomposition of nitrous oxide. The organic substrates studied were: cyclohexene, norbornene, 1,4-cyclohexadiene, norbornadiene, cyclobutene, and bicyclo[1.1.0]butane. Extensive rearrangements occur during these reactions. Spectra of a novel compound, *endo*-bicyclo[2.1.1]hexane-5-carboxaldehyde, are reported.

The reactions of atomic oxygen are of demonstrated importance in the chemistry of the upper atmosphere[2] and of combustion.[3] Synthetic applications of oxygen atom reactions are also being explored.[1] Cvetanovic has made a number of interesting mechanistic observations about these atomic processes.[4]

Ground state ($^3P$) oxygen atoms are conveniently produced in the gas phase by the mercury photosensitized decomposition of nitrous oxide (eq 1 and 2).[4,5]

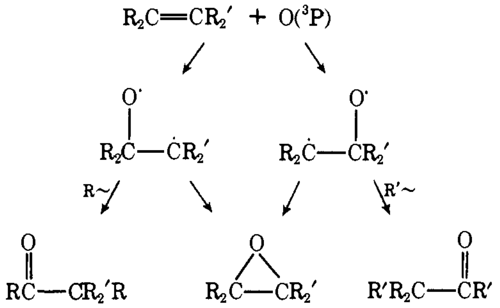
$$\mathrm{Hg}(^1S_0) + h\gamma \longrightarrow \mathrm{Hg}(^3P_1) \quad (1)$$

$$\mathrm{Hg}(^3P_1) + \mathrm{N_2O} \longrightarrow \mathrm{Hg}(^1S_0) + \mathrm{N_2}(^1\Sigma) + \mathrm{O}(^3P) \quad (2)$$

While $O(^3P)$ reacts sluggishly with most alkanes, the reaction with alkenes is quite efficient. The reaction of atomic oxygen with acyclic olefins produces approximately equal quantities of epoxides and carbonyl compounds. The latter products are of particular interest, because their formation must involve rearrangement of a substituent of the olefin.

Cvetanovic has proposed[4] that $O(^3P)$ atoms add to olefins to form short-lived 1,3 biradicals (Scheme I). These

Scheme I



biradicals can either close to epoxides or rearrange to aldehydes and ketones. The 1,2 migration of a hydrogen atom is intramolecular, but alkyl groups become at least partially detached during rearrangement. The migrating alkyl radicals can be scavenged by molecular oxygen. The rearrangement of hydrogen atoms and alkyl radicals in 1,3 biradicals is significant, because these groups do not commonly migrate in monoradical systems.

The reactions of O($^3$P) with molecules which contain more complex patterns of unsaturation than acyclic olefins have shown some unusual rearrangements or fragmentations. Product studies on the reactions of allenes,[6] cyclopropenes,[7] cyclopentene,[8] and 1,3-butadiene[1] have been published. We report here the products of the reactions of atomic oxygen with cyclohexene, norbornene, 1,4-cyclohexadiene, norbornadiene, cyclobutene, and bicyclo[1.1.0]butane.

## Results and Discussion

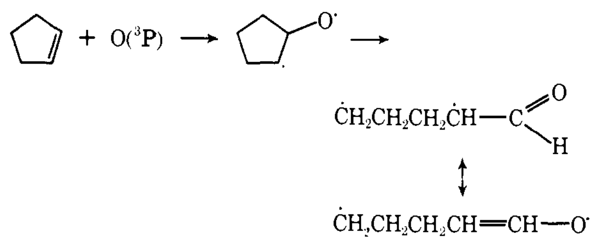
**A. Reaction Conditions.** The apparatus for the production and reaction of oxygen ($^3$P) atoms has been described previously.[6] The atoms are made by gas phase photolysis of a mixture of nitrous oxide, the hydrocarbon substrate, and mercury vapor. The total pressure before photolysis was about 0.9 atm, and the reaction temperature was 25–29°.

Product yields reported below are based on the quantity of nitrogen produced (eq 2). While total product yields from atomic oxygen reactions are usually quite good, substrates which polymerize rapidly, i.e., norbornadiene, exhibit limited conversions of substrate to oxygenated product. In these cases, the photolysis is self-terminated when the lamp becomes coated with a thin film of uv-opaque material.

Two experimental conditions are used to limit the reactions to primary processes. First, a high ratio of nitrous oxide to substrate (>15) is maintained in order to minimize mercury photosensitized reactions of substrate or products. Second, conversion of organic substrate was limited to <30% to minimize secondary oxidations of products.

**B. Atomic Oxygen Reactions. 1. Cyclohexene.** The reaction of cyclohexene with triplet oxygen atoms produces cyclopentanecarboxaldehyde (**1**) (27% yield), 1,2-epoxycyclohexane (**2**) (17% yield), cyclohexanone, (**3**) (16% yield), 5-hexenal (**4**) (7.5% yield), and *trans*-2-hexenal (**5**) (6.1% yield). No carbon monoxide was detected. Total recovery of oxygen atoms is 74%, based on nitrogen evolved.

In postulating a mechanism for this reaction, a review of the reaction of cyclopentene with O($^3$P) is useful.[8] The major products of the cyclopentene reaction are 1,2-epoxycyclopentane, cyclopentanone, cyclobutanecarboxaldehyde, and equal amounts of ethylene and acrolein. The key intermediate (**6**) in the formation of the last three major products and of several minor products (dihydropyran, 4-pentenal, and 2-pentenals) is a species in which the five-membered ring has opened (eq 3). The formation of **6** is consistent with earlier experiments,[9] which indicated that alkyl groups become detached from the molecule during rearrangement. Intermediate **6** is a 1,4 biradical. As such, it can form products by $\beta$ cleavage (ethylene and acrolein), by ring closure at either carbon (cyclobutanecarboxaldehyde) or oxygen (dihydropyran), and by hydrogen abstraction (2- and 4-pentenals).

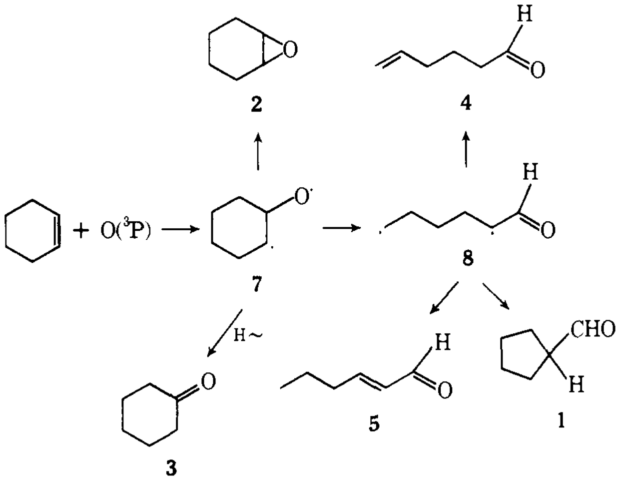


$$\dot{C}H_2CH_2CH_2\dot{C}H{-}C(=O)H \longleftrightarrow \dot{C}H_2CH_2CH_2CH{=}CH{-}O\cdot \qquad (3)$$

**6**

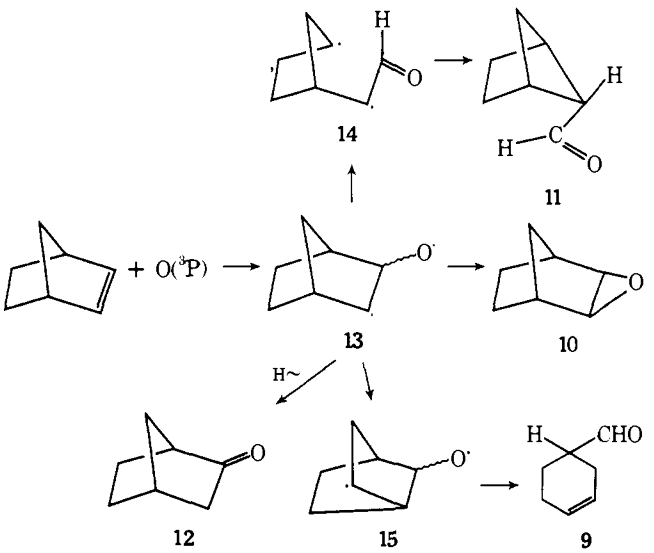
An extension of this mechanism to the reaction between cyclohexene and atomic oxygen is shown in Scheme II. 1,2-Epoxycyclohexane and cyclohexanone are formed from the initially produced 1,3 biradical **7**. Intermediate **8** is a 1,5 biradical, and so it does not have the $\beta$ cleavage option which is the major reaction from 1,4 biradical **6**. Instead, species **8** forms products by ring closure and hydrogen abstraction.

Scheme II



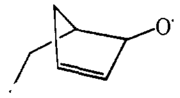
**2. Norbornene.** The reaction of norbornene with atomic oxygen produces 3-cyclohexene-1-carboxaldehyde (**9**) (39% yield), *exo*-2,3-epoxynorbornane (**10**) (25%), *endo*-bicyclo[2.1.1]hexane-5-carboxaldehyde (**11**) (8.3%), 2-norbornanone (**12**) (2.8%), and carbon monoxide (5%). The total yield of oxygenated material is 80%. A mechanism for the formation of $C_7H_{10}O$ products is shown in Scheme III.

Scheme III



Products **10**, **11**, and **12** are expected products of oxygen atom reactions. The less crowded endo form of aldehyde **11** is produced from biradical **14**. 2,6-Heptadienal was an expected product from $\beta$ cleavage of intermediate **14**, which is a 1,4 biradical. The formation of 2,6-heptadienal from the norbornene reaction would be analogous to the formation of acrolein and ethylene from the cyclopentene reaction.[7] A search was made for this aldehyde and for its Cope rearrangement product (1,5-hexadiene-3-carboxaldehyde), but neither compound was detected.

There is a precedent in the literature for the rearrangement of biradical **13** to product **9** via intermediate **15.** Garin[10] has reported that the pyrolysis of 2,3-epoxynorbornane (**10**) at 550° produces **9** in 62-67% yield. Other pyrolysis products reported are 2-norbornanone (**12**) (5-10%) and 2-cyclopentenone (5-10%). The reaction of norbornene with O($^3$P) produced no 2-cyclopentenone (detection limit ~0.5% yield). Garin proposed that 2-cyclopentenone was formed from biradical **16,** a possible precursor to intermediate **15.** However, since cyclopentenone is not a product of the atomic oxygen reaction, it is likely that the pyrolysis of epoxynorbornane makes cyclopentenone via the retro-Diels–Alder reaction of the enol of 2-norbornanone.

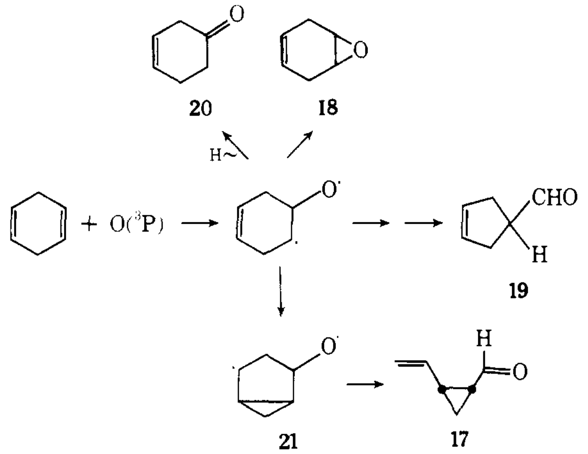


**16**

The peracid oxidation of norbornene yields 94% exo and 6% endo epoxides.[11] The production of only exo epoxide from the atomic oxygen reaction is not unusual since the addition of monoradicals to norbornene shows a large preference for *exo*-addition.[12]

3. **1,4-Cyclohexadiene.** Identified products from the reaction of 1,4-cyclohexadiene with atomic oxygen were *cis*-2-vinylcyclopropanecarboxaldehyde (**17**) (28% yield), 1,2-epoxy-4-cyclohexene (**18**) (20%), 3-cyclopentene-1-carboxaldehyde (**19**) (11%), 3-cyclohexen-1-one (**20**) (7.4%), and carbon monoxide (2%). In addition, two unidentified products were detected in 1-2% yield each. These unidentified materials had a low resolution mass spectrometric parent peak at *m/e* corresponding to $C_6H_8O^+$. The total yield of identified oxygenated material was 68%. The 1,4-cyclohexadiene recovered after reaction showed <5% isomerization to 1,3-cyclohexadiene. A mechanism for the formation of the observed $C_6H_8O$ products is shown in Scheme IV.

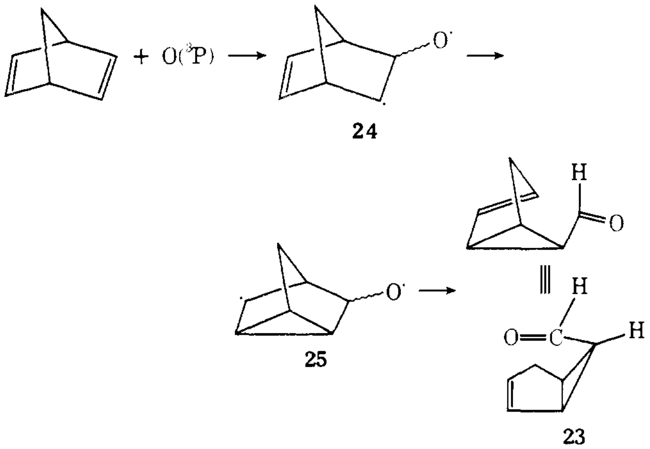
Scheme IV



*cis*-2-Vinylcyclopropanecarboxaldehyde (**17**) is formed by *β* cleavage of 1,4 biradical (**21**). Compound **17** has been reported[13] to partially isomerize under mild conditions to 2,5-dihydrooxepin (**22**). The equilibrium mixture at room temperature is 95% of aldehyde **17** and 5% of **22.** The NMR spectrum of VPC purified *cis*-2-vinylcyclopropanecarboxaldehyde from the atomic oxygen reaction does show a small amount of 2,5-dihydrooxepin.

4. **Norbornadiene.** Only one product of formula $C_7H_8O$ was found from the reactions of norbornadiene with O($^3$P). This product was *endo*-bicyclo[3.1.0]hexane-6-carboxaldehyde (**23**) in 55% yield. Carbon monoxide was made in 5% yield. Compound **23** is formed by a nortricyclane-type rearrangement (Scheme V).

Scheme V



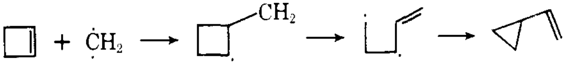
Rearrangements of the type **24** → **25** have been reported during the additions of various monoradicals to norbornadiene.[14] While product **23** gives no information about the direction of the initial O($^3$P) addition to norbornadiene, monoradicals add predominantly to the exo face of the double bond.

The peracetic acid epoxidation of norbornadiene at 0.5° yields *exo*-2,3-epoxy-5-norbornene (**26**).[15] However, epoxide **26** is thermally unstable. It slowly rearranges at room temperature or above to aldehyde **23.** In order to check for possible formation and isomerization of **26** during the reaction of atomic oxygen with norbornadiene, a sample of norbornadiene, doped with 10 mol % of **26,** was subjected to the atomic oxygen reaction conditions. After trap-to-trap distillation, the NMR of the product showed recovery of ~70% of epoxide **26.** Thus, **26** was relatively stable to the reaction, distillation, and NMR analysis conditions used. If **26** were formed from the atomic oxygen reaction, its detection limit by NMR analysis was estimated to be a 5% yield, based on nitrogen formation.

Product **23** is in equilibrium with 2-oxabicyclo[3.2.1]octa-3,6-diene.[16] However, the equilibrium mixture at room temperature is predominantly aldehyde **23.**

5. **Cyclobutene.** The reaction of cyclobutene with atomic oxygen shows an extensive and complex pattern of rearrangement and fragmentation. Products of the reactions are: carbon monoxide (25% yield), cyclopropanecarboxaldehyde (**27**) (17%), 3-butenal (**28**) (3.5%), cyclobutanone (**29**) (2.6%), acrolein (1.6%), 2-buten-3-one (**30**) (1.0%), crotonaldehyde (**31**) (1.0%), 1,2-epoxycyclobutane (**32**) (0.6%), vinyl ether (**33**) (0.4%), and 3,4-epoxy-1-butene (**34**) (0.3%). The total yield of oxygenated material is 53%. The multitude of products indicates that the reaction proceeds by several diverging pathways. While the mechanism shown in Scheme VI may contain too many branches, it adequately explains the formation of all observed $C_4H_6O$ products.

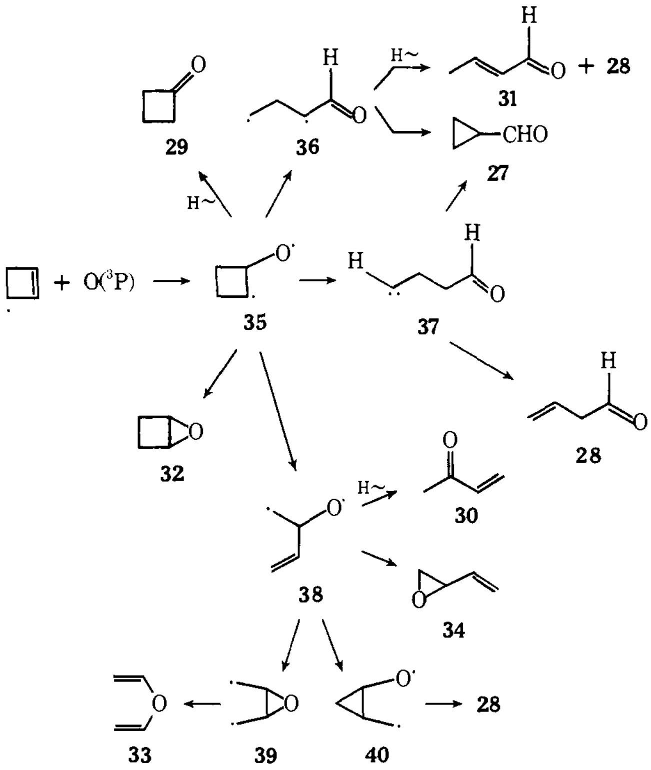
Precedence for the cleavages and rearrangements shown above can be found in the literature. A ring opening similar to the conversion of biradical **35** to **36** has been reported from the reaction of cyclopentene with atomic oxygen.[7] A close parallel to this ring opening is also seen from the reaction of cyclobutene with triplet methylene (eq 4).[17] Carbon–carbon 1,3 biradicals (like **36**) form products by ring closure and hydrogen rearrangement.[18]



(4)

Bergman and coworkers[19] have studied the pyrolysis of 2,3-diazabicyclo[3.2.0]hept-2-ene (**41**) a pyrazoline whose decomposition produces a carbon–carbon biradical similar

Scheme VI



to **35**. Pyrolysis of **41** also produces 1-carbena-4-pentene $(\mathrm{H\ddot{C}CH_2CH_2CH{=}CH_2}$. The formation of this carbene is postulated to proceed by rearrangement of **41** to 4-diazo-1-pentene; however, the experimental evidence does not exclude rearrangement of the biradical to the carbene. Such a rearrangement would be analogous to the conversion of biradical **35** to carbene **37**.

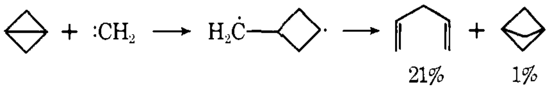
Biradical **38** has also been produced from the reaction of oxygen atoms with 1,3-butadiene.[1] In the 1,3-butadiene case, **38** is a minor adduct made by addition of O($^3$P) to one of the internal carbons. Compounds **28**, **30**, **33**, and **34** are products of reaction of 1,3-butadiene with atomic oxygen.

In the reactions of acyclic butenes with O($^3$P), the epoxide product(s) are formed in relative yields of about 50%. The relative yield of unrearranged 1,2-epoxycyclobutane (**32**) from the cyclobutene reaction is quite low (2% of the recovered $C_4H_6O$ product). The low yield of **32** indicates that this epoxide, which is initially formed in a vibrationally excited state, rearranges to other products. This rearrangement may occur by reversion of excited epoxide **32** to biradical **35**. Compound **32** is stable to the conditions of reaction and analysis. The gas phase reaction of singlet methylene with cyclobutene produces vibrationally excited bicyclo[2.1.0]pentane, which rearranges to a complex mixture of products.[17]

**6. Bicyclo[1.1.0]butane.** The product mixture from the reaction of O($^3$P) with bicyclobutane is simple compared with that obtained from the cyclobutene reaction. Three oxygen-containing compounds are produced: 3-butenal (**28**) (43% yield); carbon monoxide (26% yield); and an unidentified compound (**42**) (10% yield). Recovery of oxygenated material was 79%. Recovered bicyclobutane showed no isomerization to cyclobutene or 1,3-butadiene.

Unidentified product **42** was very sensitive to water. After VPC purification, its mass spectrum showed a parent peak at *m/e* 88 ($C_4H_6 + O + H_2O$). However, the VPC retention time of **42** on several columns was similar to that of four-carbon monoethers. Insufficient material was available for further spectral characterization of **42** or its hydrolysis product.

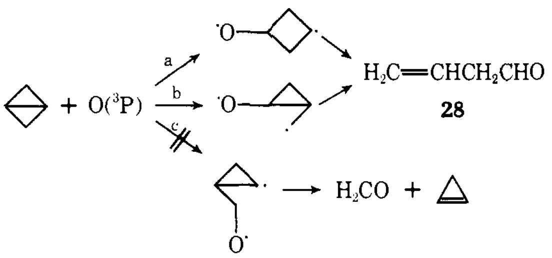
An interpretation of the reaction of bicyclobutane with atomic oxygen can be based on two literature precedents—the reaction of cyclopropane with O($^3$P) and the reaction of bicyclobutane with methylene. Scala and Wu[20] have reported that the initial process in the reaction of O($^3$P) with cyclopropane is attack upon a carbon-carbon bond to open the ring and form a carbon-oxygen 1,4 biradical. Wiberg and coworkers[21] have reported that methylene attacks the central carbon-carbon bond of bicyclobutane (eq 5).



(5)

Scheme VII shows the three possible modes by which oxygen atoms can open bicyclobutane. Pathways a and b would both yield 1,4 biradicals whose $\beta$ cleavage would produce 3-butenal. The 1,4 biradical made in pathway c would be expected to $\beta$-cleave to cyclopropene and formaldehyde. Neither of these compounds was observed. By analogy with the reaction of methylene with bicyclobutane,[21] it is possible that the unidentfied compound **42** is 2-oxabicyclo[1.1.0]pentane. This tentative assignment would be consistent with the short retention time of **42**.

Scheme VII



### Summary

The products obtained from the reactions of oxygen ($^3$P) atoms with various cyclic and bicyclic hydrocarbons show that extensive rearrangements occur during these gas phase reactions. Several of these rearrangements involve deep-seated structural changes. In some cases, product formation proceeds by $\beta$ cleavage of 1,4 biradical intermediates. The reaction of atomic oxygen with bicyclotane illustrates that O($^3$P) will readily attack not only carbon-carbon double bonds but also strained carbon-carbon single bonds.

In addition to the rearrangement processes, the occurrence of fragmentation reactions has been observed. These fragmentations lead to carbon monoxide and other oxygen-containing organic molecules. The nature of the fragmentation reactions in O($^3$P) systems is being examined in our laboratories.

### Experimental Section

**Materials.** All organic substrates and nitrous oxide were purified by trap-to-trap distillation before reaction. Cyclobutene was prepared by the method of Roberts and Borcic.[22] Bicyclo[1.1.0]butane was made by the method of Lampman and Aumiller.[23] Both of these $C_4H_6$ substrates were VPC purified before reaction.

Whenever feasible, samples of expected products were purchased or prepared for comparison with product mixtures. Products **2**, **3**, **5**, **9**, **12**, **23**, **29**, **30**, **33**, and **34** were obtained commercially. Epoxides **10**, **18**, and **32** were synthesized by reaction of the corresponding olefins with *m*-chloroperbenzoic acid. 5-Hexenal (**4**) was made by the method of Viola and Levasseur.[24] Cyclopropanecarboxaldehyde (**27**) was prepared by the method of Young and Trahanovsky.[25] 3-Butenal (**28**) was available from the reaction of 1,3-butadiene with atomic oxygen.[1] *exo*-2,3-Epoxy-5-norbornene (**26**) was synthesized by the method of Meinwald *et al.*[15]

**Reaction Procedure.** Techniques and conditions for atomic oxygen reactions have been described previously.[5,26] In the reactions reported above, a clean separation of unreacted substrate from products by trap-to-trap distillation was not possible. The organic reactant-product mixture was analyzed by VPC after removal of excess nitrous oxide.

Most VPC analysis was conducted on various columns of dinonylphthalate. Other VPC columns used were: 5A molecular sieves for noncondensable gases, saturated silver nitrate in benzyl cyanide for unreacted 1,4-cyclohexadiene, and propylene carbonate for purification and analysis of cyclobutene and bicyclobutane.

**Product Identification.** Major reaction products were identified by ir, NMR, and mass spectrometry and, when possible, by comparative VPC retention times. Minor reaction products (those formed in <7% yield) were identified by ir and mass spectrometry and by comparative VPC retention times. Isolated samples of product **17**, **19**, and **20** showed good correspondence to literature spectra.[13,27,28]

Spectra of *endo*-bicyclo[2.1.1]hexane-5-carboxaldehyde (**11**) are: high resolution mass of parent peak 110.0733 (obsd), 110.0731 (calcd); mass spectrum (70 eV) $m/e$ 110 ($I_R$ = 14), 109 (13), 95 (19), 92 (13), 91 (8), 81 (*100*), 79 (47), 66 (54); ir (thin film) 3002, 2915, 2802, 2705, 1735 cm$^{-1}$; NMR ($C_3D_6O$ solvent) $\delta$ 0.88 (1 H, d, $J$ = 6 Hz), 1.74 (3 H, s over m), 2.48 (1 H, m), 2.88 (2 H, m), 3.13 (2 H, m), 9.58 (1 H, d, $J \sim 1$ Hz).[29]

**Acknowledgment.** Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

## References and Notes

(1) Part III: J. J. Havel and K. H. Chan, *J. Org. Chem.*, **39**, 2439 (1974).
(2) The proceedings of a symposium on this subject have been recently published: *Can. J. Chem.*, **52**, 1381–1634 (1974).
(3) P. G. Ashmore, "Tenth International Symposium on Combustion", The Combustion Institute, Pittsburgh, Pa., 1965, pp 377–386, and references therein.
(4) R. J. Cvetanovic, *Adv. Photochem.*, 1, 115 (1963).
(5) R. J. Cvetanovic, *J. Chem. Phys.*, **23**, 1203 (1955).
(6) J. J. Havel, *J. Am. Chem. Soc.*, **96**, 530 (1974).
(7) J. J. Havel, W. T. Chamberlain, and P. M. Krautter, *J. Am. Chem. Soc.*, **96**, 632 (1974).
(8) R. J. Cventanovic, D. F. Ring, and L. C. Doyle, *J. Phys. Chem.*, **75**, 3056 (1971).
(9) R. J. Cvetnaovic, *Can. J. Chem.*, **36**, 623 (1958). This paper also presents preliminary data on the cyclohexene plus O($^3$P) reaction.
(10) D. L. Garin, *Can. J. Chem.*, **47**, 4071 (1969).
(11) H. Kwart and T. Takeshita, *J. Org. Chem.*, **28**, 670 (1963).
(12) D. I. Davies, L. T. Parfitt, C. K. Alden, and J. A. Claisse, *J. Chem. Soc. C*, 1585 (1969).
(13) S. J. Rhoads and R. D. Cockroft, *J. Am. Chem. Soc.*, **91**, 2815 (1969).
(14) (a) S. J. Cristol, G. C. Brindell, and J. A. Reeder, *J. Am. Chem. Soc.*, **80**, 635 (1958); (b) D. J. Trecker and J. P. Henry, *ibid.*, **85**, 3204 (1963).
(15) J. Meinwald, L. L. Labana, L. Q. Labana, and J. H. Wahl, Jr., *Tetrahedron Lett.*, 1789 (1965).
(16) M. Rey and A. S. Dreiding, *Helv. Chim. Acta*, **48**, 1985 (1965).
(17) (a) C. S. Elliot and H. M. Frey, *Trans. Faraday Soc.*, **64**, 2352 (1968). (b) A referee has pointed out that the results presented herein do not exclude formation of some fraction of ring-contracted product by direct rearrangement rather than by ring opening and recyclization.
(18) B. H. Al-Sadar and R. J. Crawford, *Can. J. Chem.*, **46**, 3301 (1968).
(19) D. H. White, P. B. Condit, and R. G. Bergman, *J. Am. Chem. Soc.*, **94**, 7931 (1972), and references therein.
(20) A. A. Scala and W. Wu, *J. Phys. Chem.*, **74**, 1852 (1970).
(21) K. B. Wiberg, G. M. Lampman, R. P. Ciula, D. S. Connor, P. Schertler, and J. Lavanish, *Tetrahedron*, **21**, 2749 (1965).
(22) S. Borcic and J. D. Roberts, *J. Am. Chem. Soc.*, **87**, 1056 (1965).
(23) G. M. Lampman and J. C. Aumiller, *Org. Synth.*, **51**, 55 (1971).
(24) A. Viola and L. A. Levasseur, *J. Am. Chem. Soc.*, **87**, 1150 (1965).
(25) L. B. Young and W. T. Trahanovsky, *J. Org. Chem.*, **32**, 2349 (1967).
(26) The bicyclobutane reaction was run at one-third the scale described in ref 5.
(27) A. Viola and J. H. MacMillan, *J. Am. Chem. Soc.*, **90**, 6141 (1968).
(28) D. S. Noyce and M. Evett, *J. Org. Chem.*, **37**, 394 (1972).
(29) NMR spectra of several 5-substituted *exo*-bicyclo[2.1.1]hexane systems were kindly provided by Professor K. B. Wiberg. The exo spectra show a characteristic triplet (1 H) at $\delta$ 0.9 and singlet (2 H) at $\delta$ 1.7.

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# Enthalpies of Solvent Transfer of the Transition States in the Cis–Trans Isomerization of Azo Compounds. The Rotation vs. the Nitrogen Inversion Mechanism

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**Abstract:** The enthalpies of transfer from cyclohexane to cyclohexanone of the reactants, transition states, and products in the cis-trans isomerization of *cis*-azobenzene and *cis*-*p*-chlorobenzenediazocyanide were determined calorimetrically. The relative magnitudes of these solvent transfer enthalpies suggest that the isomerization proceeds via a nitrogen inversion mechanism rather than via a rotational mechanism.

The remarkably facile cis-trans isomerization of compounds having an N=N bond[1-3] may proceed via a rotation about the N=N bond, or via inversion of one of the nitrogens (i.e., by way of an sp hybridized transition state).[4] The latter mechanism would account for the much greater ease of isomerization of azo compounds as compared with olefins, where the second mechanistic possibility does not exist.

One way to distinguish between these two possible transition states for this isomerization reaction is to consider the enthalpy of transfer of the transition state in this reaction from one solvent to another. We have shown[5] that this property, i.e., the enthalpy of transfer of the transition state from one solvent to another, $\delta H^{t}$, can provide useful information concerning the mechanism of a reaction. In particular, with the appropriate choice of solvents, this property, $\delta H^{t}$, may yield information concerning the geometry and the electronic constitution of the transition state. We report here a study on the cis-trans isomerization of azobenzene and *p*-chlorobenzenediazocyanide in a nonpolar solvent, cyclohexane, and in one having a substantial dipole, cyclohexanone ($\mu$ = 3 D[6]).

## Results and Discussion

The enthalpy of transfer of a transition state from one solvent to another, $\delta H^{t}$, is obtained from the relation

$$\delta H^{t} = \delta \Delta H_s{}^{r} + \delta \Delta H^{\ddagger}$$

where $\delta \Delta H_s{}^{r}$ is the enthalpy of transfer of the reactants from one solvent to the other and $\delta \Delta H^{\ddagger}$ is the difference in the enthalpies of activation in the two solvents. To obtain