O–H bond in the transition state which implies a very "tight" transition state and hence a low A factor.

In general, the alkoxy–alcohol hydrogen transfer reaction may be of little significance in liquid-phase systems because of extensive hydrogen bonding. However, in the gas phase it may play a much more important role than has hitherto been recognized, *e.g.*, in alcohol oxidations.

Acknowledgment. We are grateful to Professor A. A. Zavitsas for a copy of his computer program.

(25) N.R.C.C. Postdoctoral Fellow, 1973.

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Atomic Oxygen. II.[1] The Reactions of Cyclopropenes with Oxygen (^{3}P) Atoms

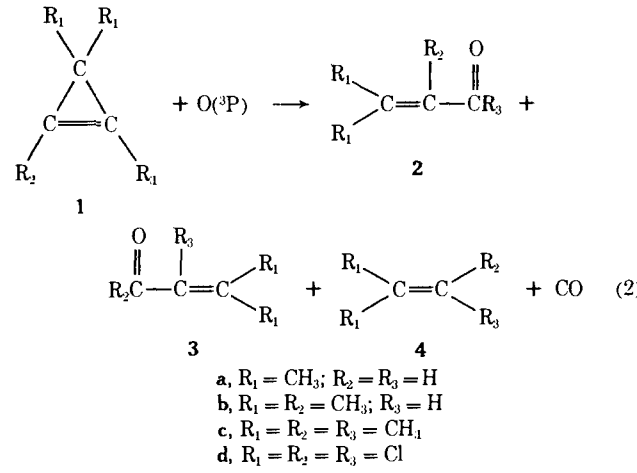
Sir:

A convenient source of ground-state (^{3}P) oxygen atoms is the mercury photosensitized decomposition of nitrous oxide (eq 1).[2] Gas-phase reactions of atomic

$$Hg(^3P_1) + N_2O \longrightarrow Hg(^1S_0) + N_2(^1\Sigma) + O(^3P) \qquad (1)$$

oxygen with organic compounds can be accomplished by photolysis at 2537 Å of a mixture of nitrous oxide (in large excess), the organic substrate, and mercury vapor.[3] The amount of nitrogen generated provides a basis for the determination of product yields.

We wish to report here the results of the reaction of O(^{3}P) with several substituted cyclopropenes, **1a–d**.[4] The products of these reactions are carbon monoxide, an olefin containing one carbon atom less than the reactant cyclopropene, and α,β-unsaturated carbonyl

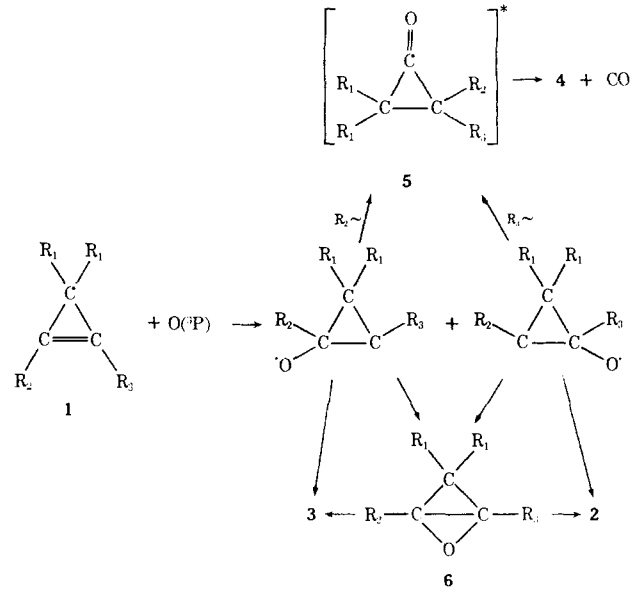


a, $R_1 = CH_3$; $R_2 = R_3 = H$
b, $R_1 = R_2 = CH_3$; $R_3 = H$
c, $R_1 = R_2 = R_3 = CH_3$
d, $R_1 = R_2 = R_3 = Cl$

compounds (eq 2).[5] Yields of products are listed in Table I.

It is proposed that the initial reaction of atomic oxygen is addition to the olefinic bond of the cyclopropene to form a 1,3-biradical (Scheme I).[6] The biradical

Scheme I



decomposes to products by three possible modes: (a) migration of a substituent on the original carbon–carbon double bond to produce a cyclopropanone (**5**) with excess energy, (b) rearrangement involving breaking of a carbon–carbon single bond to produce a carbonyl compound directly, or (c) closure of the 1,3-biradical to make a 2-oxabicyclo[1.1.0]butane derivative (**6**).[7] The excited cyclopropanone decomposes to carbon monoxide and olefin.[1,8] 2-Oxabicyclo[1.1.0]-butanes have not been isolated from the peracid oxida-

Table I. Products[a] of the Reaction of O(^{3}P) with Cyclopropenes

Cyclo-propene	Product yield, % 2	3	4	5
1a	53		13	15
1b	43	11	8	9
1c	57		6	7
1d[b]	46		41	44

[a] Product yields are based on the amount of nitrogen formed. The reaction temperature was 27–30°; initial pressure was 610 Torr. [b] A dark brown polymer formed on the photolysis lamp during reaction of cyclopropene, **1d**. Thus, while the product yield based on nitrogen evolution (eq 1) was good, the overall conversion of cyclopropene to products was poor. Nitrogen evolution with **1d** was one-seventh of that with **1a-c** for equal photolysis times.

(1) Part I: J. J. Havel, *J. Amer. Chem. Soc.*, **96**, 530 (1974).
(2) R. J. Cvetanovic, *J. Chem. Phys.*, **23**, 1203 (1955).
(3) See ref 1 for experimental details.
(4) (a) 3,3-Dimethylcyclopropene (**1a**) was prepared by the reaction of 1-chloro-3-methyl-2-butene with sodium amide in refluxing tetrahydrofuran; see F. Fisher and D. E. Applequist, *J. Org. Chem.*, **30**, 2089 (1965), for a similar procedure. (b) 1,3,3-Trimethylcyclopropene (**1b**) and tetramethylcyclopropene (**1c**) were prepared by the base-induced pyrolysis of the tosylhydrazones of 4-methyl-3-penten-2-one (**3b**) and 3,4-dimethyl-3-penten-2-one (**2c**); see G. L. Closs, L. E. Closs, and W. A. Boll, *J. Amer. Chem. Soc.*, **85**, 3796 (1963). (c) Tetrachlorocyclopropene (**1d**) was obtained from the Aldrich Chemical Co.
(5) Products were separated by trap-to-trap distillation and vpc and analyzed by comparison of vpc retention times and ir, nmr, and mass spectra with authentic samples. Trichloroacryloyl chloride (**2d**) was identified only by its comparative vpc retention time and mass spectrum.
(6) The chemistry of similar carbon–carbon 1,3-biradicals has been examined; see P. G. Gassman and W. J. Greenlee, *J. Amer. Chem. Soc.*, **95**, 980 (1973), and references therein.
(7) The reactions of atomic oxygen with acyclic olefins have been explained by a similar mechanism (addition of O(^{3}P) to the olefinic bond to form 1,3-biradicals, followed by closure or rearrangement); see R. J. Cvetanovic, *Advan. Photochem.*, **1**, 115 (1963).
(8) N. J. Turro, *Accounts Chem. Res.*, **2**, 25 (1969).

tion of cyclopropenes.[9] Instead, these strained systems isomerize to α,β-unsaturated carbonyl compounds (**2** and **3**) at 0°.

The observed yields of cyclopropanone derived products (carbon monoxide and olefin) are also consistent with the proposed scheme. The amount of these products decreases as the migrating group is changed from chlorine to hydrogen to methyl. It has been demonstrated in other 1,3-biradical and 1,1,3-triradical systems that chlorine migrates faster than hydrogen,[10] while hydrogen rearranges more readily than methyl.[11]

A comparison of the reactions of cyclopropenes and allenes with atomic oxygen is of interest. For example, the products from 3-methyl-1,2-butadiene are carbon monoxide (67% yield), 2-methylpropene (45%), and 3-methyl-3-buten-2-one (8.6%); no 3-methylcrotonaldehyde (**2a**) is observed.[1] Carbon monoxide and 2-methylpropene are formed by decomposition of excited 2,2-dimethylcyclopropanone, the same cyclopropanone formed by reaction of **1a** with $O(^3P)$. However, no 3-methyl-3-buten-2-one was detected from the reaction of cyclopropene, **1a**. This observation would be consistent with the hypothesis that carbonyl compounds from allene reactions are produced by rearrangement of initially formed biradicals and not by rearrangement of excited cyclopropanones.

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

(9) J. Ciabattoni and P. J. Kocienski, *J. Amer. Chem. Soc.*, **91**, 6534 (1969).
(10) J. J. Havel and P. S. Skell, *J. Amer. Chem. Soc.*, **94**, 1792 (1972).
(11) R. J. Cvetanovic, *Can. J. Chem.*, **36**, 623 (1958).

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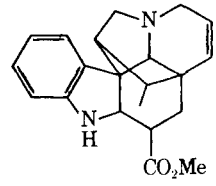
On the Structure of Vindolinine[1]

Sir:

Vindolinine is a $C_{21}H_{24}N_2O_2$ alkaloidal constituent of a variety of *Catharanthus* species[2] to which structure **1** had been assigned some time ago mostly on the basis of mass spectral analyses.[3] Since the structure analysis of a new dimeric indole alkaloidal constituent of *Catharanthus longifolius*[4] required a ^{13}C nmr analysis of vindolinine, the natural abundance, proton decoupled and single frequency, off-resonance decoupled cmr spectra of the alkaloid were recorded.[5] They revealed one more nonaromatic, nonprotonated carbon and one less nonaromatic methine signal than demanded by formula **1**. Since the missing signal was that of an aminomethine and the new nonprotonated carbon signal (81.4 ppm) that of an oxy or amino carbon site, formula **2a** was considered a reasonable alternative to the previous structure. The following cmr analyses of vindolinine derivatives **2b–e** and comparison of their shifts with those of the structurally related alkaloid venalstonine (**3**)[6] confirm the new structure.



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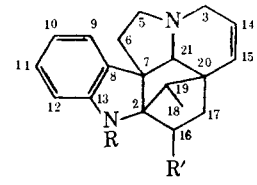
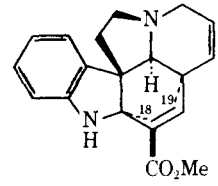


2a, R = H; R′ = CO_2Me
b, R = Me; R′ = CO_2Me
c, R = H; R′ = CH_2OH
d, 16-epi-**2a**
e, 14,15-dihydro-**2a**



3

The chemical shift assignments for compounds **2** were based on standard shift theory[7] and arguments made for alkaloids of the *Aspidosperma* type[8] and are listed in Table I. The aminomethylenes, C(3) and C(5), were differentiated by the expected change in their shifts on reduction of the olefinic bond,[8] while the C(6) and C(17) methylenes and C(16) and C(19) methines were recognized from the difference of their shifts in vindolinine (**2a**), alcohol **2c**, and 16-epivindolinine (**2d**). The shift contrast between **2a** and its N_a-methyl derivative (**2b**) supports strongly the C(2) attachment of the normal *Aspidosperma* 20-ethyl side chain. The C(2) and C(20) signals of vindolinine (**2a**) are 12–15 ppm downfield those of venalstonine (**3**) in analogy with the 13 ppm shift difference of the bridgehead carbons of norbornane[9] and bicyclo[2.2.2]octane.[10] The anomalous C(3) and C(21) shifts of vindolinine (**2a**) must reflect the extraordinary strain imposed on the piperideine ring by the norbornane unit.[11]

(1) Carbon-13 Nuclear Magnetic Resonance Spectroscopy of Naturally Occurring Substances. XXIII. For paper XXII see P. Mussini, F. Orsini, F. Pelizzoni, B. L. Buckwalter, and E. Wenkert, *Tetrahedron Lett.*, in press. Résonance Magnétique Nucléaire du ^{13}C de Produits Naturels et Apparentés XIV. For paper XIII see K. Tori, H. Ishii, Z. W. Wolkowski, C. Chachaty, M. Sangaré, F. Piriou, and G. Lukacs, *ibid.*, 1077 (1973).
(2) (a) M.-M. Janot, J. Le Men, and C. Fan, *Bull. Soc. Chim. Fr.*, 891 (1959); (b) M. Gorman, N. Neuss, G. H. Svoboda, and A. J. Barnes, Jr., *J. Amer. Pharm. Ass., Sci. Ed.*, **48**, 256 (1959); (c) P. Rasoanaivo, N. Langlois, and P. Potier, *Phytochemistry*, **11**, 2616 (1972); (d) N. Langlois and P. Potier, *ibid.*, **11**, 2617 (1972); (e) A. B. Segelmans, *Diss. Abstr. B*, **33**, 653 (1972); (f) H. Mehri, M. Koch, M. Plat, and P. Potier, *Ann. Pharm. Fr.*, **30**, 643 (1972).
(3) (a) C. Djerassi, S. E. Flores, H. Budzikiewicz, J. M. Wilson, L. J. Durham, J. Le Men, M.-M. Janot, M. Plat, M. Gorman, and N. Neuss, *Proc. Nat. Acad. Sci. U. S.*, **48**, 113 (1962); C. Djerassi, M. Cereghetti, H. Budzikiewicz, M.-M. Janot, M. Plat, and J. Le Men, *Helv. Chim. Acta*, **47**, 827 (1964).
(4) P. Rasoanaivo, N. Langlois, and P. Potier, unpublished results.
(5) In deuteriochloroform solution on a Fourier transform Bruker HX90E spectrometer operating at 22.63 MHz.
(6) Full justification for the shift assignment of **3** will be presented later.
(7) (a) G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists," Wiley-Interscience, New York, N. Y., 1972; (b) J. B. Stothers, "Carbon-13 NMR Spectroscopy," Academic Press, New York, N. Y., 1972.
(8) E. Wenkert, D. W. Cochran, E. W. Hagaman, F. M. Schell, N. Neuss, A. S. Katner, P. Potier, C. Kan, M. Plat, M. Koch, H. Mehri, J. Poisson, N. Kunesch, and Y. Rolland, *J. Amer. Chem. Soc.*, **95**, 4990 (1973).
(9) J. B. Grutzner, M. Jautelat, J. B. Dence, R. A. Smith, and J. D. Roberts, *J. Amer. Chem. Soc.*, 92, 7107 (1970).
(10) G. E. Maciel and H. C. Dorn, *J. Amer. Chem. Soc.*, **93**, 1268 (1971).
(11) As the similarity of the C(21) shift of vindolinine (2a) and its dihydro derivative (**2e**) indicates, the endocyclic homoallyl effect[8] is absent in this strained piperideine system.