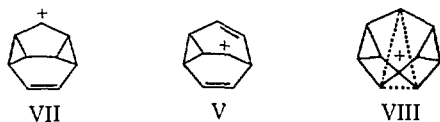


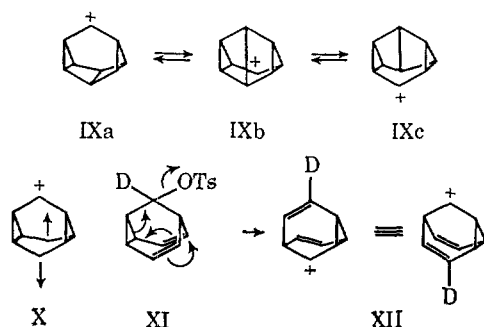
**Table II.** Deuterium Scrambling in Barbaralyl Solvolysis Products

| Compound                 | Solvolysis conditions  | % Deuterium in various positions ( $\pm 3\%$ ) |                      |                  |                |
|--------------------------|------------------------|--|----------------------|------------------|----------------|
|                          |                        | C <sub>1,5</sub>                               | C <sub>2,4,6,8</sub> | C <sub>3,7</sub> | C <sub>9</sub> |
| VI, X = OH               | 80% acetone, 18°, 1 hr | 5.2  | 1.7                  | 39.9             | 53.2           |
| VI, X = OAc              | HOAc, 25°, 30 min      | 7.4  | 18.2                 | 46.1             | 28.3           |
| Statistical distribution |                        | 22.2   | 44.4                 | 22.2             | 11.1           |

These results exclude the most obvious mechanistic possibilities: cyclopropylcarbinyl  $\rightarrow$  homoallylic rearrangement to the bicyclo[3.2.2]nonatrienyl cation (IV) and allylcarbinyl  $\rightarrow$  cyclopropylcarbinyl rearrangement to the interesting bishomotropylium system (VII). Such rearrangements would give rise to quite different deuterium distributions than were observed experimentally.



The observation that high percentages of deuterium, relative to a statistical distribution, appear at C<sub>3</sub>, C<sub>7</sub>, and C<sub>9</sub>, and low percentages over the remainder of the molecule suggests that the carbonium ion either has threefold symmetry (as in VIII) or undergoes an operation which leads to such threefold symmetry (such as the rapid equilibration IXa  $\rightleftharpoons$  IXb  $\rightleftharpoons$  IXc). Since distances between C<sub>3</sub>, C<sub>7</sub>, and C<sub>9</sub> probably are much too large to permit effective bonding, a better representation of VIII may be X, in which symmetrization by cyclopropylcarbinyl resonance is obvious. Alternatively, the observed deuterium distribution can be rationalized by a "synchronous" formulation (XI  $\rightarrow$  XII), but it is not clear why this should be favored.



Besides this "threefold symmetrization" mechanism, there must be a second, less rapid, process, e.g., through IV or VII, which distributes deuterium more widely. Perhaps rearrangement through IV is disfavored because of "antibicycloaromaticity,"<sup>5</sup> while VII may not be a very favorable intermediate due to the enforced nonplanarity of the bishomotropylium system. Further work is planned to clarify these matters.

**Acknowledgments.** This work was supported by grants from the National Science Foundation, the National Institutes of Health (AI-07766), and the

Petroleum Research Fund, administered by the American Chemical Society.

(12) National Institutes of Health Postdoctoral Fellows: (a) 1969–1970; (b) 1968–1969.

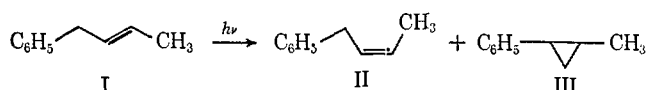
(13) NATO Postdoctoral Fellow, 1967–1968.

J. C. Barborak,<sup>12a</sup> J. Daub<sup>13</sup>  
D. M. Foltweiler,<sup>12b</sup> P. von R. Schleyer  
Department of Chemistry, Princeton University  
Princeton, New Jersey 08540  
Received October 17, 1969

### Molecular Rearrangement in the Gas Phase Photolysis of 1-Phenyl-2-butene

Sir:

We wish to report the photochemical rearrangement of a nonconjugated 1,4-diene to a cyclopropane derivative obtained for the first time in the gas phase by direct irradiation.<sup>1</sup> The effects of exciting wavelength and of foreign gas indicate that the cyclization proceeds *via* the formation of a vibrationally excited intermediate.



Irradiation of the *trans*-1-phenyl-2-butene (I) at four different wavelengths ( $\lambda$  266, 261, 252, 247 nm) with a 1000-W mercury-xenon lamp and at a pressure of 0.8 Torr leads to the formation of two products:<sup>2</sup> the *cis* isomer, II, already reported in the liquid phase photolysis<sup>3</sup> and a new photoproduct III eluting shortly after II on the MBMA<sup>4</sup> column of a capillary gas chromatograph. *t*-Butylbenzene was added to the photolysate mixture as an internal standard. Subsequent addition of bromine demonstrated that III reacted much more slowly than I and II as shown by successive injections in the capillary gas chromatograph. The new photoproduct, III, did not react at all with ozone while I and II completely disappeared to form the corresponding ozonides which did not elute from the column. During these chemical tests, the concentration of the *t*-butylbenzene in the mixture did not change, ruling out the possibility of an attack on the aromatic ring. The evidence then indicates that III lacks an aliphatic double bond. In earlier similar solution studies, it was shown that cyclopropane derivatives may be formed from irradiation of a nonconjugated 1,4-diene.<sup>1,5</sup>

*trans*-1-Phenyl-2-methylcyclopropane was prepared by treatment of *trans*- $\beta$ -methylstyrene with methylene iodide and a zinc-copper couple according to the Simmons-Smith procedure<sup>6</sup> and was identified by its nmr spectrum. Comparison of its retention time with the photoproduct III and direct comparison by glpc enhancement of a mixture of III and of *trans*-1-phenyl-2-

(1) H. E. Zimmerman and P. S. Mariano, *J. Amer. Chem. Soc.*, **91**, 1718 (1969).

(2) A third unidentified product with a lower boiling point is formed in only trace amount.

(3) H. Morrison and R. Peiffer, *J. Amer. Chem. Soc.*, **90**, 3428 (1968).

(4) *m*-Bis(*m*-phenoxy)benzene + Aplezon L.

(5) G. W. Griffin, J. Covell, R. C. Peterson, R. M. Dodson, and G. Klose, *J. Amer. Chem. Soc.*, **87**, 1410 (1965).

(6) H. E. Simmons and R. D. Smith, *ibid.*, **81**, 4256 (1959).

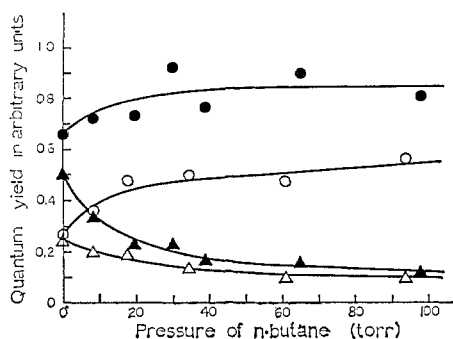


Figure 1. Variation of the quantum yield of isomerization of the *trans*-1-phenyl-2-butene with increasing pressure of *n*-butane. The circles correspond to *cis*-1-phenyl-2-butene and the triangles correspond to 1-phenyl-2-methyl cyclopropane. The open symbols denote runs with excitation at  $\lambda$  252 nm while the closed symbols denote excitation at  $\lambda$  266 nm.

methylcyclopropane showed the identity of these two compounds.

The effect of exciting wavelength upon the quantum yield of formation of the products is presented in Table I. The quantum yields of both II and III reach their

Table I. Effect of Exciting Wavelength on Photolysis of *trans*-1-Phenyl-2-butene<sup>a</sup>

| Wavelength <sup>b</sup><br>(nm) | $\Phi$ II<br>(in arbitrary units) | $\Phi$ III        | $\Phi$ II/ $\Phi$ III |
|---------------------------------|-----------------------------------|-------------------|-----------------------|
| 247                             | 0.090 $\pm$ 0.009                 | 0.088 $\pm$ 0.009 | 1.02                  |
| 252                             | 0.27 $\pm$ 0.03                   | 0.24 $\pm$ 0.025  | 1.13                  |
| 261                             | 0.57 $\pm$ 0.06                   | 0.46 $\pm$ 0.05   | 1.24                  |
| 266                             | 0.66 $\pm$ 0.07                   | 0.50 $\pm$ 0.05   | 1.32                  |

<sup>a</sup> Temperature = 26  $\pm$  1°, pressure = 0.8 Torr. <sup>b</sup> A Bausch and Lomb grating monochromator with linear reciprocal dispersion of 1.6 nm/mm was used with a slit width of 2 mm.

maximum at the wavelength corresponding to the 0-0 absorption band of I, and the ratio  $\Phi$  III: $\Phi$  II increases as the wavelength decreases.

The observed decrease of the quantum yields at shorter wavelengths may be due to an isomerization of I to a benzvalene-type intermediate<sup>7</sup> which rapidly reverts to the starting material and thereby results in a decrease of the other photochemical processes. Such processes have been shown to occur in the photolysis of benzene and its alkyl derivatives.<sup>8</sup> In the case of the xylenes, where isomerization is thought to involve a benzvalene-type intermediate, the quantum yield of isomerization in the gas phase does increase at the shorter wavelengths.

When *n*-butane is added at pressure up to 100 Torr, the quantum yield of II increases while the quantum yield of III decreases as shown in Figure 1. Formation of III does not occur in the liquid phase, which can be expected from our result, since collisional deactivation is probably complete in the liquid phase.

The behavior of  $\Phi$  II with respect to vibrational relaxation is quite normal in photochemical systems, but the contrasting effects of wavelength and pressure on  $\Phi$  III are unusual.

(7) L. Kaplan and K. E. Wilzbach, *J. Amer. Chem. Soc.*, **90**, 3291 (1968).

(8) W. A. Noyes, Jr., D. A. Harter, and D. Anderson, private communication.

While II may be formed by a conventional pathway, *i.e.*, *cis-trans* isomerization of a triplet, it is obvious that III is formed by a more complex mechanism. The effect of pressure on  $\Phi$  III suggests that vibrational relaxation of an intermediate leading to III is important. This intermediate is not the initially excited singlet, but, nevertheless, must be derived from it. It is possible that this intermediate could be a hot triplet or a hot ground state but at this stage neither can be ruled out.

More quantitative results and a detailed discussion of this work will appear soon.

**Acknowledgments.** The financial support of the National Science Foundation is gratefully acknowledged. The author wishes to thank Dr. W. Albert Noyes, Jr., for helpful discussions.

M. Comtet

Department of Chemistry, The University of Texas at Austin  
Austin, Texas 78712

Received September 27, 1969

### On the Nature of the Oxygen Species Adsorbed on Oxide Surfaces

Sir:

We wish to report here some interesting results directly bearing on the formation of  $O^-$  and  $O_2^-$  ions on a zinc oxide surface. High-purity ZnO, prepared by the vapor-phase oxidation of zinc in gaseous oxygen,<sup>1</sup> vacuum outgassed at elevated temperatures (>450°), and subsequently exposed at 25° to pure hydrocarbons (*e.g.*, *n*-butane, isobutane), in the range 100–700 Torr, revealed a decrease in the intensity of the esr signal at  $g = 1.96$  (attributed to either  $Zn^+$  or oxygen vacancies<sup>2</sup>), and the formation of a 3- $g$  valued signal shown in Figure 1a. An identical signal was also obtained on heating ZnO for 2 hr at 500° in a closed, static system, under a hydrogen or deuterium pressure of about 1 atm. While this signal is apparently similar to the triplet assigned in earlier studies<sup>3,4</sup> to an  $O_2^-$  species (Figure 1b), the formation of  $O_2^-$  ions on ZnO treated in a reducing atmosphere of either a hydrocarbon or hydrogen is extremely unlikely. We attribute this triplet (Figure 1a) to the formation of  $O^-$  species at the surface. A careful comparison of this signal with that obtained following low-pressure oxygen treatment of vacuum-heated ZnO (Figure 1b) reveals that the two are identical except for a slight difference between  $g_1$  and  $g_1'$ . A statistical analysis of the  $g$  values following the different treatments established the fact that  $g_1 = 2.042 \pm 0.001$  and  $g_1' = 2.039 \pm 0.001$ . It was also found that these two peaks are simultaneously and readily obtained (Figure 1c) upon oxygen treatment of a sample to which zinc dust has been added prior to the vacuum-heating treatment. That a slight shift in one of the three  $g$  values is all that makes the difference between

(1) ZnO samples furnished by the courtesy of New Jersey Zinc Co., Palmerton, Pa.

(2) (a) M. Codell, H. Gisser, J. Weisberg, and R. D. Iyengar, *J. Phys. Chem.*, **72**, 2460 (1968); (b) J. Schneider and A. Rauber, *Z. Naturforsch., A*, **16**, 712 (1961).

(3) Y. Fujita and J. Turkevich, *Discussions Faraday Soc.*, **41**, 407 (1966).

(4) J. H. Lunsford, *J. Chem. Phys.*, **44**, 1487 (1966).