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## Reactions with Olefins in Condensed Phases of $\text{O}(^3\text{P})$ Atoms Produced by Microwave Discharge

Sir:

The reactions of ground-state oxygen atoms with olefins in the gas phase have been investigated extensively by Cvetanović,<sup>1</sup> Havel,<sup>2</sup> and their co-workers, but only limited knowledge exists on these reactions in the condensed phases.<sup>1b</sup> Recently, Sakurai et al.<sup>3</sup> and Sato et al.<sup>4</sup> reported on oxidations of olefins dissolved in liquid  $\text{CO}_2$  and irradiated with  $\gamma$  rays, which was attributed to  $\text{O}(^3\text{P})$  atoms formed from  $\text{CO}_2$ .

We have found a simple and clean way to react  $\text{O}(^3\text{P})$  atoms with olefins in condensed phases, including neat liquids, solutions, suspensions, and solids, thus enabling utilization of oxygen atoms as reagents for preparative organic chemistry.

Ground-state oxygen atoms were generated by discharge of either  $\text{O}_2$ <sup>1cd,5</sup> or a mixture of  $\text{N}_2$  and  $\text{N}_2\text{O}$ .<sup>6</sup> In the first method, the  $\text{O}(^3\text{P})$  atoms formed are accompanied by  $\text{O}_2$  molecules in their singlet and triplet states, and by  $\text{O}(^1\text{D})$  atoms,<sup>7</sup> but the second method gives only almost pure  $\text{O}(^3\text{P})$  atoms.<sup>6</sup>

The reaction vessel consisted of a quartz U-tube of 15-mm diameter, containing 1–5 g of magnetically stirred substrate, and connected to a microwave generator (Kiva, MPG-2, operating at 2450 MHz with 100-W output) by a gas-discharge cavity (15-mm diameter) placed ca. 5 cm above the level of the substrate. A steady flow of a mixture of gases consisting of He and  $\text{O}_2$  in a 7:1 ratio (total flow 0.7 L/min) or a He,  $\text{N}_2$ , and  $\text{N}_2\text{O}$  mixture in a 10:6:1 ratio (total flow 1 L/min), maintained by means of a high-vacuum pump operating at a constant pressure of 4 torr, was passed through the U-tube; the temperature and the duration of the reaction were variable.

Reaction of neat *cis*-stilbene (1) with O atoms produced by  $\text{O}_2$  discharge resulted in a mixture of *cis*-stilbene oxide (3), *trans*-stilbene oxide (4), and benzyl phenyl ketone (5).<sup>8</sup> At 0 °C, all

Table I. Reactions of  $\text{O}(^3\text{P})$  with *cis*-Stilbene 1

conditions <sup>a</sup> °C	yield, %	conversion, %	product distribution, %		
			3	4	5
-40 <sup>b</sup>	85	50	37	37	26
0 <sup>b</sup>	75	100	31	40	29
0 <sup>c</sup>	71	60	36	41	29
0 <sup>d</sup>	90	65	31	36	33
25 <sup>b</sup>	72	63	27	44	29
60 <sup>b</sup>	e	e	13	51	36

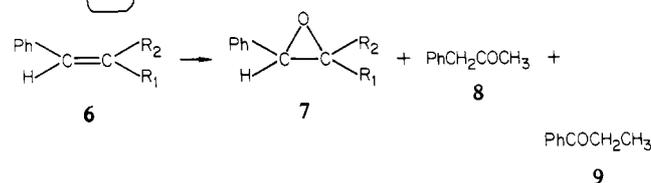
<sup>a</sup> Performed on 1.5 g of substrate for 30 min, except in solution where reaction time was 2 h. <sup>b</sup> Neat liquid,  $\text{O}_2$  discharge. <sup>c</sup> Neat liquid,  $\text{N}_2/\text{O}/\text{N}_2$  discharge. <sup>d</sup> 30% decane solution,  $\text{O}_2$  discharge. <sup>e</sup> Not determined.

Table II. Product Distributions (%) in the Reaction of  $\text{O}(^3\text{P})$  with Styrene at -25 °C

conditions	$\text{Ph}-\text{C}(\text{O})-\text{CH}=\text{CH}_2$	$\text{PhCH}_2-\text{CHO}$	$\text{PhCOCH}_3$	$\text{PhCHO}$
$\text{O}_2$ (neat) <sup>a</sup>	44	25	12	19
$\text{O}_2$ (decane) <sup>a</sup>	57	27	9	7
$\text{N}_2/\text{O}/\text{N}_2$ (neat)	62	31	2	5

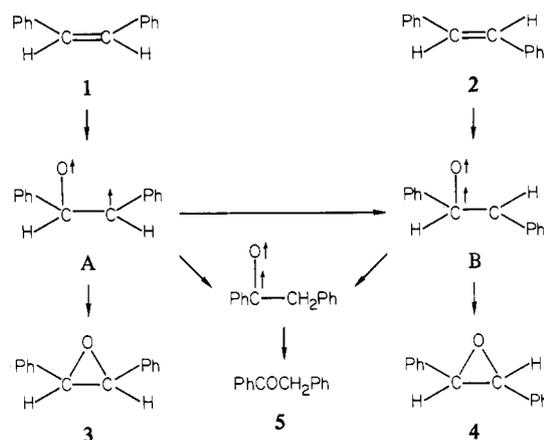
<sup>a</sup> In addition, a small amount (<3%) of 1-phenylethanol and  $\alpha$ -hydroxyacetophenone was isolated.

Scheme I



<sup>a</sup> a,  $\text{R}_1 = \text{CH}_3$ ,  $\text{R}_2 = \text{H}$ ; b,  $\text{R}_1 = \text{H}$ ,  $\text{R}_2 = \text{CH}_3$ . 6a  $\rightarrow$  7a (58) + 7b (8) + 8 (18) + 9 (12). 6b  $\rightarrow$  7a (36) + 7b (16) + 8 (23) + 9 (12). Product distribution percentage in parentheses.

Scheme II



the starting material (1.5 g) was consumed within  $1/2$  h; the total yield of characterized products was 75%, the rest consisting of an insoluble material (Table I). With shorter reaction times, the conversion was lower, but the relative yields were unchanged. As shown in Table I, similar product ratios were also obtained in a 30% *n*-decane solution, or when O atoms were produced by  $\text{N}_2/\text{N}_2\text{O}$  discharge. The product ratios were dependent on the reaction temperature: at higher temperatures, larger relative yields of both 4 and 5 were observed (Table I). In addition, we found a decrease in the reaction rate when the temperature was increased from 0 to 60 °C.<sup>9</sup>

(9) Negative temperature dependence of the reaction of  $\text{O}(^3\text{P})$  atoms with several olefins was observed previously; ref 11 and Atkinson, R.; Pitts, J. N., Jr. *J. Chem. Phys.* 1977, 67, 38.

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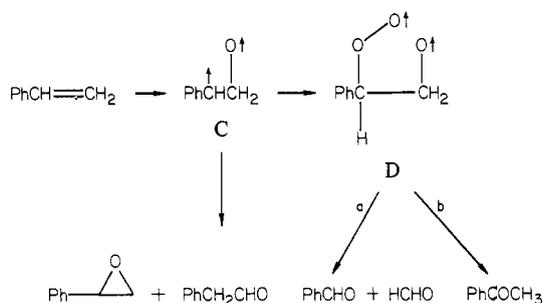
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(8) Diphenylacetaldehyde, the product of phenyl migration, was detected only in trace amounts (<0.5%).

Scheme III



Since *trans*-stilbene (**2**) is a sparingly soluble solid, its oxidation was performed in the powder, resulting in a 15% yield of **4** and **5**, formed in a 2.5:1 ratio. When the oxidation was done in 15% diethylene glycol suspension, these two compounds were formed (25%) in a 1:1 ratio.<sup>10</sup> Triphenylethylene was also oxidized in the solid state, yielding triphenyl ethylene oxide and phenyl benzhydryl ketone in a 4:1 ratio (35% total yield).

Oxidation of *trans*- and *cis*- $\beta$ -methylstyrene (**6a**) and (**6b**) with O(<sup>3</sup>P) atoms produced by O<sub>2</sub> discharge gave after 2 h at -25 °C two epoxides, **7a** and **7b**, and two ketones, **8** and **9**. The product of methyl migration, 2-phenylpropanal, was formed in minute amounts only (<1%). The product ratios (Scheme I) indicated a small preference for O attack on the  $\beta$ -C atom. However, when the source of the O atoms was N<sub>2</sub>O/N<sub>2</sub> discharge, this preference was increased (2.5 vs. 1.5 for **6a**).

These differences in the regioselectivity were more distinct in oxidation of styrene. With N<sub>2</sub>O/N<sub>2</sub> discharge, the major products were styrene oxide and phenylacetaldehyde while acetophenone and benzaldehyde were formed in small amounts (Table II). The relative abundance of the last two compounds increased when O<sub>2</sub> discharge was used, particularly in neat liquid, suggesting that O<sub>2</sub> also contributes to the formation of these products (Table II).

It is to be emphasized that in all the cases studied no products resulting from oxygen atom attack on the phenyl rings were detected.<sup>11,12</sup>

The suggested pathway for the reaction of O(<sup>3</sup>P) atoms with *cis*- and *trans*-stilbenes **1** and **2** involves the intermediacy of triplet diradicals A and B, respectively (Scheme II). The *trans*-diradical B possesses the geometrical requirements for both cyclization and H migration, giving *trans*-epoxide **4** and the ketone **5** (presumably as a triplet), respectively.<sup>16</sup> The steric interactions of the phenyl groups in the *cis*-diradical A lead, in addition, to rotation about the C-C bond forming the *trans*-epoxide **4**.

When the temperature is lowered, the increased viscosity of the liquid slows down the rotation, resulting in a higher relative yield of *cis*-epoxide **3** and lower yields of *trans*-epoxide **4** and benzyl phenyl ketone **5**. It follows that in the solid state the relative yield of **3** will be the highest.

We assume that in the case of styrene, the molecular oxygen present in the O<sub>2</sub> discharge interferes by interaction with the primary diradical C to form peroxy diradical D (Scheme III). The latter undergoes either cleavage of the C-C bond to form benzaldehyde<sup>13</sup> and formaldehyde (path a), or rearranges by H migration with evolution of O<sub>2</sub> to give acetophenone (path b).

Investigations of O(<sup>3</sup>P) atom reactions in condensed phases with aromatic and other unsaturated systems are in progress.

**Acknowledgment.** Support of this research by the U.S.-Israel

(10) Different products were reported to be formed in the  $\gamma$  radiolysis of *trans*-stilbene in liquid CO<sub>2</sub>, ref 3a.

(11) It was claimed, however, that O(<sup>3</sup>P) atoms attack both the styrene ring and the styrene side chain: Sloane, T. M.; Brudzynski, R. J. *J. Am. Chem. Soc.* **1979**, *101*, 1495.

(12) O(<sup>3</sup>P) atom reactions with  $\alpha$ -methylstyrene, 1,1-diphenylethylene, and 1-phenyl-2-butene resulted in an attack on the double bond only, giving the expected epoxides, ketones, and aldehydes.

(13) The formation of benzaldehyde by ozonolysis is less likely since only negligible amounts of ozone are produced in O<sub>2</sub> discharge: ref 1c and Herron, J. T.; Schiff, H. T. *Can. J. Chem.* **1958**, *36*, 1159. Moreover, we did not detect among the reaction products either styrene ozonide or benzoic acid.

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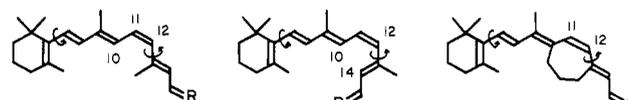
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## Nonbleachable Rhodopsins Retaining the Full Natural Chromophore

Sir:

The visual pigments rhodopsins<sup>1</sup> consist of 11-*cis*-retinal (I)<sup>2</sup> bound to the  $\epsilon$ -amino group of the apoprotein lysine moiety through a protonated Schiff base (II, SBH<sup>+</sup>).<sup>3,4</sup> The key event



I R: O

II R: N<sup>+</sup>H-lys-OPSIN

III R: N<sup>+</sup>H-n-Bu

IV R: N<sup>+</sup>H-lys-OPSIN

V R: O (≠I)

VI R: N<sup>+</sup>H-lys-OPSIN

in the visual transduction is the photoisomerization of the 11-*cis*-ene to *trans* geometry,<sup>2</sup> which eventually yields *all-trans*-retinal and opsin ("bleaching"). In this communication, we report the preparation and properties of rhodopsins, e.g., VI, in which this key step is blocked.

We had previously reported that 11,12-dihydrorhodopsin<sup>5</sup> formed from retinal lacking the crucial 11-ene gave a "nonbleachable" pigment.<sup>6</sup> The data on this pigment and other dihydrorhodopsins led to the external point-charge model<sup>7</sup> to account for the variance in  $\lambda_{\max}$  of visual pigments. In contrast to dihydrorhodopsins,<sup>7b</sup> the present pigments retain the full retinal chromophore.

We have shown that of the two possible conformations for 11-*cis*-retinal, 12-*s-trans*-II and 12-*s-cis*-IV, both of which are nonplanar (indicated by curved arrows) due to the interaction between 10-H/13-Me and 10-H/14-H, the chromophore in rhodopsin adopts the *transoid* conformer II.<sup>8</sup> In order to mimic the nonplanar 12-*s-trans*-retinal, but more importantly to prepare an 11-*cis*-locked chromophore, we conceived the model retinal V

(1) In view of the recent preparations of various artificial pigments from synthetic model retinals, we propose the use of the generic name "rhodopsin" prefixed by the specific modification carried out with the chromophore, e.g., 11,12-dihydro-9-*cis*-rhodopsin.

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(3) The protonated Schiff base theory is the one generally accepted, especially on grounds of resonance laser Raman studies: Callender, R.; Honig, B. *Annu. Rev. Biophys. Bioeng.* **1977**, *6*, 33. Eyring, G.; Mathies, R. *Proc. Natl. Acad. Sci. U.S.A.* **1979**, *76*, 33.

(4) There are, however, still some controversial views regarding the protonated Schiff base theory; see: Favrot, J.; Leclercq, J. M.; Roberge, R.; Sandorfy, C.; Vocelle, D. *Photochem. Photobiol.* **1979**, *29*, 99.

(5) Gawinowicz, M. A.; Balogh-Nair, V.; Sabol, J. S.; Nakanishi, K. *J. Am. Chem. Soc.* **1977**, *99*, 7720, and references cited therein.

(6) The 11,12-dihydrorhodopsin,  $\lambda_{\max}$  315 nm, was not affected by room light, and hence was "nonbleachable" in the classical sense of the terminology. When irradiated with UV light, the pigment underwent irreversible photo-decomposition of the chromophore rather than detachment of the chromophore from the opsin.

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