Partial Conversion of 3a to Its Trans Epimer 5a. After compound **3a** had been heated in refluxing ethanol for 48 h, a new, higher running TLC component was detected. Compound **5a** and unreacted starting material were isolated after flash column chromatography of the crude mixture on silica-gel (hexane-EtOAc 4:1) (relative proportions *3a–5a*; 3:2). The same results were obtained if compound **3a** is treated with a catalytic amount (~ 10%) of $ZnBr_2$ in CH_2Cl_2 at room temperature for 2 h. **5a** (colorless oil): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (m, ArH), 3.63 (dd, J = 6.4 Hz, H-2,6), 3.50, 3.45 (2 d, J_{AB} = 13 Hz, $NCH_2C_6H_5$); ^{13}C NMR ($CDCl_3$) δ 19.7 (C-4), 29.0 (C-3,5), 50.4 (C-2,6), 58.2 (CH_2), 117.0 (CN) 128.4, 128.9, 129.3, 147.8 (Ar); MS, *m/e* (relative intensity) 225 ($M^{\bullet+}$, 5), 198 (5), 148 (5), 134 (10), 91 (100). Anal. Calcd for $C_{14}H_{15}N_3$: C, 74.64; H, 6.71; N, 18.65. Found: C, 74.35; H, 6.70; N, 17.64.

Acknowledgment. We would like to thank Dr. Robert Bucourt for fruitful discussions and Mme. F. Cossart for technical assistance.

Supplementary Material Available: Tables of atomic coordinates, thermal parameters, bond distances and angles, and torsional angles (6 pages). Ordering information is given on any current masthead page.

Reactions of Phenylethylenes with O(^{3}P) Atoms in Condensed Phases

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Oxidation of sytrene, α- and β-alkyl-substituted styrenes, *cis*- and *trans*-stilbene, triphenylethylene, allylbenzene, and its trans β-alkyl-substituted derivatives with O(^{3}P) resulted mainly in epoxides and carbonyl compounds formed by 1,2-H shifts. The O(^{3}P) atoms were produced by microwave discharge of O_2, CO_2, or N_2O/N_2 in the presence of He. The temperature effect on the relative yields of products was studied on *cis*-stilbene and the regioselectivity of the O(^{3}P) attack on the double bond in the series of β-alkylstyrenes and β-alkyl-substituted allylbenzenes. The mechanism of the oxidation is postulated to involve a diradical intermediate. The temperature effect is explained by the interconversion of different electronic states of this diradical and the steric effect by an early unsymmetric transition state for the addition of O(^{3}P) atoms to the double bond.

Oxygen atoms in their ground state [O(^{3}P) atoms] can be formed in several ways, three of which were used for reactions with olefins in the gas phase on a preparative scale: (1) photolysis of N_2O in the presence of Hg vapors,[1] (2) microwave discharge of a mixture of O_2 and He at low pressures,[2] and (3) γ-irradiation of substrates dissolved in liquid CO_2.[3] For reactions with olefins in condensed phases, we have utilized the microwave discharge method. We have enlarged its scope using, in addition to O_2, CO_2 and mixtures of N_2O and N_2.[4] The technique used by us is based on microwave discharge of a steady flow of mixtures of gases at 2–4 torr, which are passed through a U-tube containing the substrates.[4] The "after glow" gases, coming into contact with organic substrates, contain only neutral species, including O(^{3}P) atoms and $O_2(^1\Delta_g)$ molecules.

Results

This paper describes the reactions of O(^{3}P) with styrene, α- and β-substituted styrenes, and allylbenzene and its alkyl derivatives.[5] The reactions of styrene, α-substituted styrenes, and *cis*-stilbene were performed by using the three microwave discharge methods (discharge of O_2, CO_2, or N_2O/N_2 in the presence of He), and the reactions of β-alkyl styrenes and β-substituted allylbenzenes were carried out by using CO_2 discharge only. This latter method was found to be the simplest and most suitable for preparative uses. The other two methods are less convenient: on O_2 discharge, the undecomposed O_2 molecules may intervene with the reaction course, and the use of N_2O/N_2 discharge involves working with a mixture of three gases, which is technically cumbersome. Generally, the reaction was performed on neat liquids (ca. 0.05 mol of substrate) for 30–120 min at variable temperatures. In addition, some reactions were carried out in *n*-decane solution, in diethylene glycol suspensions, and with substrates in powdered form. The products were also isolated by column chromatography and identified by comparison with authentic samples.

***cis*-Stilbene.** The reactions of *cis*-stilbene (1) were performed by using the three discharge methods which

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(1) (a) Cvetanovic, R. J. *Adv. Photochem.* **1963**, *1*, 115. (b) Cvetanovic, R. J.; Ring, D. F.; Doyle, L. C. *J. Phys. Chem.* **1971**, *75*, 3056. (c) Atkinson, R.; Cvetanovic, R. J. *J. Chem. Phys.* **1971**, *55*, 659. (d) Hirokami, S.; Cvetanovic, R. J. *J. Am. Chem. Soc.* **1974**, *96*, 3738. (e) Singleton, D. L.; Cvetanovic, R. J. *J. Am. Chem. Soc.* **1974**, *96*, 6812. (f) Gaffney, J. S.; Atkinson, R.; Pitts, J. N., Jr. *J. Am. Chem. Soc.* **1976**, *98*, 1828. (g) Havel, J. J. *J. Am. Chem. Soc.* **1974**, *96*, 530. (h) Havel, J. J.; Chamberlain, W. T.; Krautter, P. M. *J. Am. Chem. Soc.* **1974**, *96*, 632. (i) Havel, J. J.; Chan, K. H. *J. Org. Chem.* **1974**, *39*, 2439; *J. Am. Chem. Soc.* **1975**, *97*, 5800. (j) Havel, J. J. *J. Org. Chem.* **1978**, *43*, 762.

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(3) (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) Karasawa, H.; Samamoto, T.; Yugeta, R.; Sato, S. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 902.

(4) (a) Zadok, E.; Amar, D.; Mazur, Y. *J. Am. Chem. Soc.* **1980**, *102*, 6369. (b) Zadok, E.; Sialom, B.; Mazur, Y. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 1004. (c) Zadok, E.; Mazur, Y. *Tetrahedron Lett.* **1980**, *21*, 4955. (d) Zadok, E.; Mazur, Y. *J. Org. Chem.* **1982**, *47*, 2233. (e) Zadok, E.; Rubinraut, S.; Mazur, Y. *Isr. J. Chem.* **1983**, *23*, 457. (f) Zadok, E.; Aronovitch, C.; Mazur, Y. *Nouv. J. Chim.* **1982**, *6*, 699 (g) Zadok, E.; Rubinraut, S.; Frolow, F.; Mazur, Y. *J. Am. Chem. Soc.* **1985**, *107*, 2489. (h) Zadok, E.; Rubinraut, S.; Frolow, F.; Mazur, Y. *J. Org. Chem.* **1985**, *50*, 2647.

(5) Part of this work was published as a communication to the Editor, ref 4a.

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Table I. Relative Yields (%) and Ratios of Products in the Reaction of *trans*-β-Alkylstyrenes and Allylbenzenes with O(^{3}P) Atoms

	products					ratios of products	
	epoxides		carbonyl products				
substrate	6	7	8	9	10	epoxides/ carbonyl cmpds	β/α^a
5a	61.5	10.5	8	20	-	2.6	2.5
5b	71	4	8	16	1	3.0	2.1
5c	70	3	15	10	2	2.7	0.8
5d	74	1	17	5	3	3.0	0.5
5e	61		7	32			
5f	55	11	6	22	6	1.9	1.8
5g	59	9	8	17	7	2.1	1.1
5h	66	3	13	9	9	2.2	0.4

[a] Ratios of carbonyl compounds having oxygen at α and β positions [(**9** + **10**)/**8**] for **5a–d** and [**9**/(**8** + **10**)] for **5f–h**.

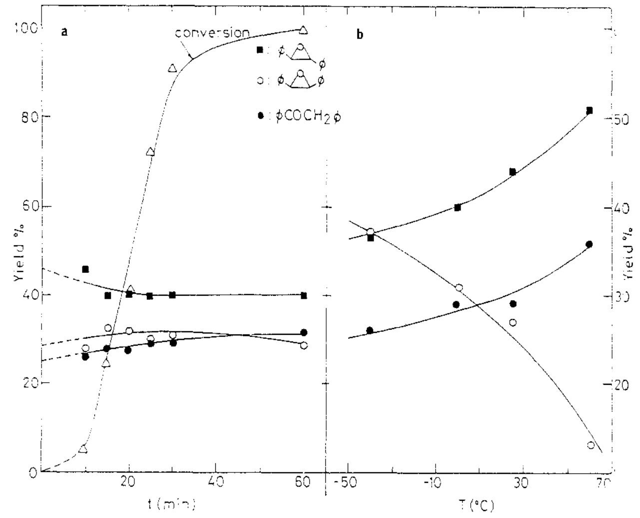
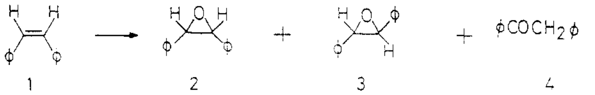


Figure 1. Variation in the amounts of products formed in the reaction of *cis*-stilbene (**1**) with O(^{3}P) atoms as a function of (a) time and (b) temperature.

gave similar results: the formation of *cis*-stilbene oxide (**2**), *trans*-stilbene oxide (**3**), and benzyl phenyl ketone (**4**).



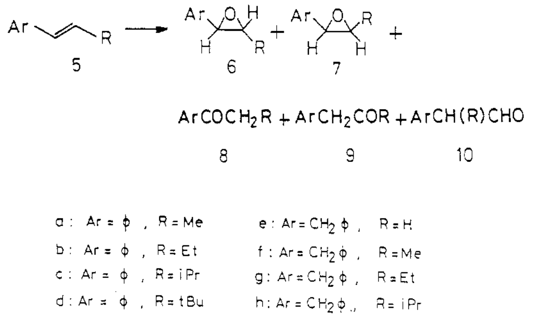
(1)

At 0 °C, in neat liquid, the conversions were almost complete after 60 min of reaction. The yields of the three products ranged between 70 and 90%, their ratio being independent of the reaction time, indicating that they are primary reaction products (Figure 1a). The rest consisted of unidentified insoluble material and traces of diphenylacetaldehyde (<0.5%). At conversions of less than 30%, the three main products accounted for almost all the material consumed. *cis*-Stilbene (**1**) was also reacted in *n*-decane solution at 0 °C. *N*-Decane was chosen as a solvent because of its relatively low volatility and low reactivity toward O(^{3}P) atoms. We have obtained the same relative ratios of products as in neat liquid which were, however, accompanied by solvent oxidation products, i.e., carbonyl compounds and alcohols. On the other hand, in solution, the amount of unidentified products was drastically reduced. The relative yields of the three products were temperature dependent: lowering the temperature resulted in a higher yield of cis epoxide **2** and lower yields of trans epoxide **3** and benzyl phenyl ketone (**4**) (Figure 1b).

***trans*-β-Alkylstyrenes.** The four compounds *trans*-β-methyl-, β-ethyl-, β-isopropyl-, and β-*tert*-butylstyrene (**5a–d**) were allowed to react separately, by using CO_2 discharge as the source of O(^{3}P) atoms. The reactions were performed in neat liquids at -25 °C for 90 min. The main products were trans and cis epoxides **6a–d** and **7a–d**, respectively, and ketones **8a–d** and **9a–d**, derived from oxygen attack on both α- and β-olefinic carbon atoms, respectively (eq 2). In all four reactions, the ratio of epoxides to ketones was ca. 3:1 (Table I). In addition, ethyl-, isopropyl-, and *tert*-butylstyrene (**5b–d**) gave low yields of rearranged aldehydes **10b–d**. However, β-methylstyrene (**5a**) did not yield the rearranged aldehyde **10a**. All four substrates also formed small amounts (<2%) of benzaldehyde.

Table II. Relative Yields (%) of Products in the Reaction of Styrene with Different Sources of O(^{3}P) Atoms

		products			
	O(^{3}P) source	PhCHCH$_2$O	PhCH$_2$ CHO	PhCO- CH$_3$	Ph- CHO
1	O_2 (15% in He)	60	20	7	13
2	CO_2 (100%)	59	22	5	14
3	CO_2 (15% in He)	59	28	4	9
4	CO_2 (5% in He)	62	31	2	5
5	N_2/N_2O (6:1, 40% in He)	62	31	2	5
6	N_2/N_2O + O_2	56	25	3	12



$$ArCOCH_2R + ArCH_2COR + ArCH(R)CHO \quad (2)$$

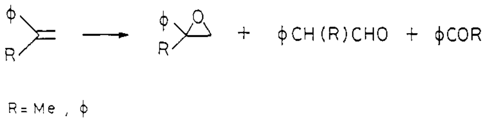
8 9 10

a : Ar = ϕ , R = Me
b : Ar = ϕ , R = Et
c : Ar = ϕ , R = iPr
d : Ar = ϕ , R = tBu
e : Ar = CH$_2$ϕ , R = H
f : Ar = CH$_2$ϕ , R = Me
g : Ar = CH$_2$ϕ , R = Et
h : Ar = CH$_2$ϕ , R = iPr

Allylbenzene and Its Trans β-Alkyl Derivatives. These compounds were allowed to react with O(^{3}P) atoms under the same conditions as above. The major products in the reaction of allylbenzene (**5e**) were its epoxide (**6e**) (61%) and β-phenylpropionaldehyde (**10e**) (32%), and the minor one was benzyl methyl ketone (**8e**) (7%). *trans*-(β-alkylallyl)benzenes **5f–h** gave, as major products, trans epoxides **6f–h** (55–66%). In addition, cis epoxides **7f–h** and ketones **8f–h** and **9f–h** (formed by attack of O(^{3}P) atoms on both olefinic C atoms) and low yields of rearranged aldehydes **10f–h** were isolated (eq 2, Table I).

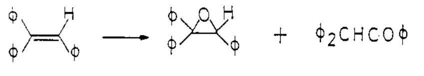
Styrene, α-Methylstyrene, and 1,1-Diphenylethylene. The reactions of styrene in neat liquid with O(^{3}P) atoms at -25 °C for 2 h resulted in a conversion of ca. 50% to give two main products: styrene oxide and phenylacetaldehyde (in 2:1 to 3:1 ratios), as well as benzaldehyde and acetophenone, which were formed in smaller amounts (Table II). In addition, 30% of the starting material was recovered, the rest consisting of unidentified polymeric products. The relative yields of the products depended on the source of $O(^3P)$ atoms: using O_2 discharge, the relative yields of acetophenone and benzaldehyde were the largest (20%, entry 1), while N_2O/N_2 discharge resulted in smaller yields of these compounds (7%, entry 5). When, however, a stream of O_2 was introduced after the N_2O/N_2 discharge zone, the relative yield of benzaldehyde increased by a factor of 2 (entry 6). Low yields of benzaldehyde were also formed with CO_2 (5% in He) discharge under the conditions generally applied (entry 4). However, on raising the CO_2 partial pressure the relative yield of benzaldehyde increased, reaching 14% with pure CO_2 (entry 2). The amount of acetophenone also increased in the presence of pure CO_2, but to a lesser extent.

Reaction of α-methylstyrene and 1,1-diphenylethylene with $O(^3P)$ atoms generated by the three microwave sources (discharge of O_2, N_2O/N_2 and CO_2) gave the respective epoxides and aldehydes (eq 3). In addition, acetophenone and benzophenone were formed from α-methylstyrene and 1,1-diphenylethylene, respectively, when the source of $O(^3P)$ was O_2 discharge. In all three cases the amount of insoluble polymeric material was much higher when an O_2 discharge was utilized, than with the other two sources.



(3)

trans-Stilbene and Triphenylethylene. These compounds, which are sparingly soluble solids were reacted with $O(^3P)$ atoms (He/O_2 discharge) in the form of fine powder. *trans*-Stilbene gave, under these conditions, 15% of *trans*-stilbene oxide (**3**) and benzyl phenyl ketone (**4**) in 2.5:1 ratio. Triphenylethylene was converted in 35% yield to triphenylethylene oxide and benzhydryl phenyl ketone in 4:1 ratio (eq 4). *trans*-Stilbene, reacted as a 15% suspension in diethylene glycol, gave, in 25% yield, a 1:1 mixture of *trans*-stilbene oxide (**3**) and benzyl phenyl ketone (**4**). In all of these reactions unidentified polymeric material was also formed.

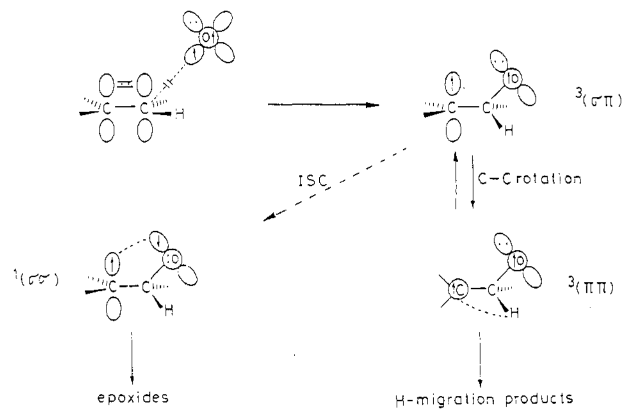


(4)

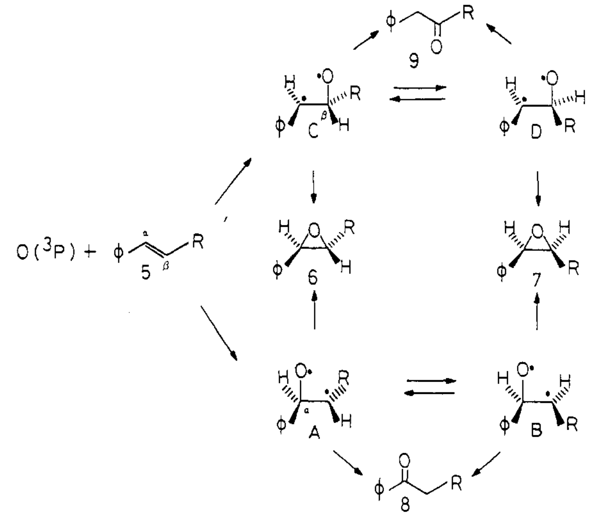
Discussion

Our results can be interpreted by using the generalized scheme for the reaction of $O(^3P)$ atoms with alkylethylenes in the gas phase, as proposed by Cvetanovic.[1,2,6] The initial step in this scheme is the addition of $O(^3P)$ atoms to the double bond forming triplet diradicals which undergo intersystem crossing followed by cyclization to give epoxides. According to this mechanism, the formation of trans epoxide **3** from *trans*-stilbene and both cis and trans epoxides **2** and **3** from *cis*-stilbene (**1**) indicate the intermediacy of two distinct diradical species. The cis diradical which possesses an unfavorable conformation because of the steric repulsion of the two phenyl groups, may interconvert to the more stable trans diradical by rotation around the single C–C bond, which occurs faster than the ring closure to give the epoxide. The reverse process, the interconversion of the trans to the cis diradical is, however, sterically unfavorable. Furthermore, the increase in the proportion of trans epoxide in relation to the cis isomer at a higher temperature may be due to the decrease in the internal rotation in the primarily formed triplet diradical.

Scheme I



Scheme II



The explanation for the steric and the temperature effects observed in the reaction of *cis*-stilbene (**1**) on the relative yields of the two epoxides can be deduced from theoretical calculations described by Dupuis et al.[7a] and Yamaguchi et al.[7b] These calculations define eight electronic states of the C–C–O diradical, derived from ethylene and $O(^3P)$ atoms based on Hartree–Fock wave functions, as having triplet or singlet $\sigma\sigma$, $\sigma\pi$, $\pi\sigma$, and $\pi\pi$ configurations. The terms σ and π define singly occupied orbitals in the C–C–O plane or perpendicular to it, respectively; the first character in each pair referring to an odd electron on C atom and the second one to an odd electron on O atom. Out of the eight states, the $^3(\sigma\pi)$ (Scheme I) is the most stable, while the $^3(\pi\pi)$ is only slightly above it in energy (<2 kcal/mol).[7] These two states can interconvert by rotation around the C–C bond. The small energy gap between these two states indicates a comparatively low-energy barrier for rotation around the C–C bond. Furthermore, the $^3(\sigma\pi)$ state can undergo a potential energy surface crossing to the $^1(\sigma\sigma)$ state,[7] whose geometry allows ring closure to give an epoxide.

$O(^3P)$ atom attack on unsymmetrically substituted olefins in the series of *trans*-β-alkylstyrenes **5a–d** and of trans β-alkyl-substituted allylbenzenes **5e–h** occurs at both olefinic C atoms (Scheme II). The formation of cis epoxides **7** involves the intermediacy of cis diradicals B and D and that of trans epoxides **6** of trans diradicals A and C. The other process originating from the initially formed

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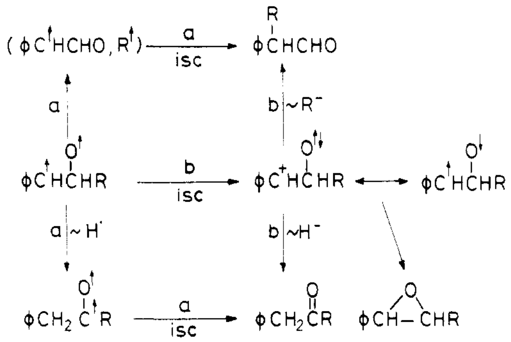
[6] Cvetanovic, R. J. *J. Phys. Chem.* **1970**, *74*, 2730.

[7] (a) Dupuis, M.; Wendoloski, J. J.; Takada, T.; Lester, W. A. *J. Chem. Phys.* **1982**, *76*, 481. (b) Yamaguchi, K.; Yabushita, S.; Fueno, T. *Chem. Phys. Lett.* **1980**, *70*, 27.

Scheme III



diradicals is the 1,2-H migration to give carbonyl compounds. Thus, phenyl ketones **8** are formed by 1,2-H migration from diradicals A and B, while benzyl ketones **9** are formed from diradicals C and D (Scheme II). Analogous H shifts also occur in all other olefins studied. In order to show their intramolecular natrue, we have reacted a mixture of *trans*-β-methylstyrene (**5a**) and its dideuteriated analogue. The resulting benzyl methyl ketones showed, in the mass spectrum, a mixture of dideuteriated and nondeuteriated species only. This 1,2-H shift takes place, according to Cvetanovic mechanism,[1,2,6] from triplet diradical (pathway a, Scheme III) which implies the previously mentioned facile interconversion of the initially formed $^3(\sigma\pi)$ to the $^3(\pi\pi)$ state. The latter state has a favorable configuration for 1,2-H migration, since its C–H orbital overlaps the half occupied p orbital at the vicinal C atom (Scheme I). Thus, the decrease in the relative yield of benzyl phenyl ketone at lower temperatures can be accounted for by the increase in the rotation around the C–C bond in the diradicals.

The formation of small amounts of aldehydes in the two series of olefins **5b–d** and **5f–h** can be interpreted by the cleavage of the initially formed triplet diradicals, followed by the recombination of the resulting free radicals (pathway a, Scheme III). The increasing amounts of aldehydes obtained in the sequences **5b–d** and **5f–h** may be related to the increasing ease of the C–C bond cleavage. Since no fragmentation products derived from free radicals were identified, as in analogous reactions in the gas phase,[1a] it can be assumed that the recombination of the free radicals takes place in a solvent cage.

It may also be argued that either H migration or the rotation around the C–C bond or both processes occur from the singlet and not from the triplet state (pathway b, Scheme III). This implies an efficient intersystem crossing from the latter to the former state, which is likely to possess a high degree of dipolar character. This ionic character of the singlet state may facilitate an intersystem crossing.[8] Such an intermediate may have sufficient lifetime for the rotation around the C–C bond, which is faster than the C–O bond-forming step.[9] Furthermore, the ionic intermediate may undergo a facile H$^-$ shift to give carbonyl compounds.

The formation of small amounts of rearranged aldehydes implies according to this mechanism, C–C bond migration from the dipolar intermediate (pathway b, Scheme III). Thus, in the series of β-alkylstyrenes (**5b–d**), the relative amounts of aldehydes increase in the sequence $C_2H_5 < (CH_3)_2CH < (CH_3)_3C$, in accordance with the increasing migratory aptitudes of these groups. In the allylbenzene series **5f–h** the relative yields of the corresponding aldehydes increased in similar sequence and the relatively larger amounts of aldehydes formed (6–9%) may be due to the higher propensity of migratory aptitude of benzyl group.

Table III. Relative Rates of O(^{3}P) Atoms Attack on *trans*-β-Alkylstyrenes

	substrate			
relative rates	**5a**	**5b**	**5c**	**5d**
measured	1.00	0.90	0.54	0.48
calculated[a]	$1.00k_\alpha^{\mathrm{Me}}$	$0.89k_\alpha^{\mathrm{Et}}$	$0.51k_\alpha^{i\text{-}\mathrm{Pr}}$	$0.43k_\alpha^{t\text{-}\mathrm{Bu}}$

[a] Using eq 5 and normalized.

The steric effect of the substituents on the regioselectivity of O(^{3}P) addition to the double bond can be deduced from the product distribution in the β-alkylstyrene series (Table I). The constant ratio of epoxides to carbonyl compound in this series, shows that the same fractions of the two diradical pairs (A + B and C + D, Scheme II) are converted into epoxides and ketones, indicating that the rates of cyclizations and 1,2-H migration, which are temperature dependent, do not depend either on the β-alkyl substituent or on the structure of the diradical. On the other hand, the different ratios of the carbonyl compounds indicate that the population of the initially formed diradicals (A and C) is different, depending on the β-alkyl substituent. Furthermore, the ratio of the rate constants for the attack of O(^{3}P) atoms on the β- and α-vinylic C atoms, k_β/k_α, may be assumed to be equal to the ratio of the respective carbonyl products (β/α, Table I). The rate constant, k, for the attack of O(^{3}P) on the double bond C atoms is thus given in eq 5.

$$k = k_\alpha + k_\beta = k_\alpha + (\beta/\alpha)k_\alpha = [1 + (\beta/\alpha)]k_\alpha \qquad (5)$$

Experimental relative rate constants were obtained from the reactions of 1:1 mixtures of *trans*-β-methylstyrene with each of the other three β-substituted styrenes, respectively, and the calculated rate constants were obtained with the above equation. The comparison of the experimental and the calculated values shows (Table III) that the rate of addition of O(^{3}P) atom to the olefinic α-C atom, k_α, is constant for all the four compounds investigated. Thus, it may be concluded that the ratios of carbonyl compounds having oxygen at the β and α position (β/α) reflect the rates of O(^{3}P) attack on the β-C atoms. We can thus assume that the rate-determining step in the reaction of O(^{3}P) atoms with olefins, which defines the product distribution, is the first step involving O(^{3}P) addition to the double bond. It can also be seen (Table I) that these rates depend to some extent on the steric effects of the substituents at the olefinic C atoms. Thus, replacing CH_3 by $(CH_3)_3C$ group in β-alkylstyrene decreases the ratio of carbonyl compounds (β/α), and with it the rate of O(^{3}P) addition to the β-C atom by a factor of ca. 5. This steric effect is much smaller than that generally found in radical attack on corresponding substituted olefinic carbon atoms in related olefins.[10] The influence exerted by the β-alkyl substituent on the rate of addition of an O(^{3}P) atom to the β-C atom and the lack of influence on the addition to the α-C atom is consistent with an unsymmetrical approach of the O atom to the double bond. Related unsymmetrical transition states are postulated also for the attack of alkyl radicals on double bonds.[10] Theoretical calculations also indicate that O(^{3}P) atoms approach the olefin, making an

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[8] Wirz, J. *Pure Appl. Chem.* **1984**, *56*, 1289. Caldwell, R. A. *Pure Appl. Chem.* **1984**, *56*, 1167. Wilson, R. M. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1985; Vol. 7, pp 340–453.

[9] Ukachukwa, V. C.; Blumenstein, J. J.; Whalen, D. L. *J. Am. Chem. Soc.* **1986**, *108*, 5039.

[10] Cf.: Giese, B. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 753 and references therein.

obtuse angle of ca. 107° with the C=C bond.[7] The subsequent decrease of the C=C π bond order occurs simultaneously with an increase in the C–O σ bond order, and the development of a 1,3-diradical character.[11]

The relatively small steric effect points to an early transition state on the reaction coordinate. This is supported by the observation of a low inverse isotope effect (k_H/k_D = 0.92) in the reaction of $O(^3P)$ with a mixture of β-methylstyrene (**5a**) and its α,β-dideuteriated analogue (determined by the relative rates of their disappearance) which is indicative of a small extension of rehybridization (sp^2–sp^3) for the β-C atom in this early transition state.[12] The total kinetic isotope effect for this reaction (determined from MS of the product **9a**) was found to be 1.33.

Accordingly, the primary isotope effect of the hydrogen migration (the total kinetic isotope effect divided by the inverse effect) is evaluated to be 1.45. This comparatively low value of this effect for hydrogen migration indicates high energy content of an intermediate and a low activation energy for its collapse and is in accord with a triplet diradical state.[13] In the gas phase, the corresponding primary effect was found to be even smaller (1.17).[14] The early transition state and the electrophilic character of $O(^3P)$ atoms suggest that the rate of $O(^3P)$ addition will be related to the energy difference between HOMO of the olefin and SOMO of $O(^3P)$ atom. Since the energies of HOMO's of β-alkylstyrenes are dominated by the strong electronic influence of the phenyl group, the alkyl substituent has only a limited influence on the polarity of this system. This dominant influence of the phenyl substituent is also reflected in the small differences of the ionization potentials (IP) between styrene and *tert*-butylstyrene (0.29 eV).[15a] By comparison, the IP difference between ethylene and *tert*-butylethylene is higher than 1 eV and that between ethylene and styrene higher than 2 eV.[15b]

The influence of the electronic effect on the regioselectivity of $O(^3P)$ attack can be seen by comparing the reactions in the styrene series with those in the allylbenzene series (Table I). In the former series, the ratios of the carbonyl compounds derived from O attack at β- and α-olefinic C atoms (β/α) were found to be much higher than in the latter (Table I). Since the steric effect of phenyl is much smaller than that of the benzyl group,[16] the higher regioselectivity in styrene series is the result of the electronic factor.

Most of the reactions of $O(^3P)$ atoms described here were performed by a CO_2 discharge, since O_2 discharge leads to formation of substantial amounts of oxidative cleavage products. This is particularly evident in the reaction of styrene where the relative yield of benzaldehyde was more than twice as high with O_2 discharge than with either CO_2 or N_2O/N_2 discharges (Table II). A similar increase was observed under the latter conditions when O_2 was introduced to the reaction vessel, after the discharge zone or when higher proportions of CO_2 (or pure CO_2) were used for the formation of $O(^3P)$ atoms. It is plausible that in the presence of O_2, O_3 is formed, which is responsible for the formation of benzaldehyde. However, the absence of ozonides in the reaction mixture may point to an alternative pathway which involves reaction of O_2 with the initially formed diradical to give an intermediate which decomposes leaving an aldehyde without the intermediacy of an ozonide.

Experimental Section

General. ^1H NMR spectra were recorded on a Varian FT-80A (80 MHz) and MS spectra on a Finnigan GC-MS 4000 spectrometer. GC measurements were performed on a Varian Aerograph Series 1400 instrument, equipped with a flame ionization detector. GC analysis were carried out on (a) 20% SE 30 on Chromosorb W AW 60–80 mesh 3-m and (b) 5% FFAP on Chromosorb G AW DMCS 100–200 mesh 3-m columns. GC–MS separations were performed on a SE-54 capillary column (0.25-mm film thickness, 30 m, 0.24 mm i.d.). Microwave discharge reactions were performed on neat liquids or in 10% solutions (2 mL total volume). Microwaves were generated by using a Kiva MPG-4 generator (2450 MHz, 100 W) transmitted to the discharge cavity using an air-cooled antenna. The vessel for the liquid–phase reactions consisted of a quartz U-tube of 15-mm diameter, containing the magnetically stirred liquid. The discharge cavity was placed ca. 5 cm above the level of solution. The outlets of reaction vessels were connected via a diaphragm manometer and a liquid nitrogen trap to the vacuum pump. The mixture of gases submitted to the discharge consisted of (a) CO_2 and He (5:95) at a total flow rate of 0.6 L/min, (b) O_2 and He (1:7) at flow rate of 0.7 L/min, and (c) N_2O, N_2, and He (1:6:10) at flow rate of 1 L/min. The total pressure in all the experiments was 2 torr. All reactions were performed in a thermostatic bath.

Materials. β-Alkylstyrenes. **5a** was commercially available. **5b–d** were prepared by Grignard reactions of benzaldehyde and the respective alkyl bromides, followed by dehydration with sulfuric acid, according to the previously described procedure.[17] The *trans*-olefins obtained were accompanied by small amounts of the cis isomers (up to 3%) as determined by GC–MS.

Expoxides **6a–d** and **7a–d** were prepared by epoxidation of the respective olefins **5a–d** with *m*-chloroperbenzoic acid. The minor products (<3%) were identified by NMR and GC–MS as the cis epoxides. **7a** was prepared from the corresponding olefin, which was synthesized according to previously described procedure:[18] ^1H NMR δ 7.29 (5 H, br s), 4.04 (1 H, d, J = 4.2 Hz), 3.31 (1 H, dq, J = 5.4, 4.2 Hz), 1.07 (3 H, d, J = 5.4 Hz). **8a**, **8b**, **9a**, and **9b** were commercially available. **8c** was prepared by Jones oxidation of the respective alcohol: ^1H NMR δ 7.42–8.00 (5 H, m), 2.83 (2 H, d, J = 6.6 Hz), 2.29 (1 H, octet, J = 6.6 Hz), 0.99 (6 H, d, J = 6.5 Hz). **9c** was prepared as a mixture with its isomer **8c** by $LiAlH_4$ reduction in ether of **6c** followed by oxidation with Jones reagent (benzylic hydrogens: δ 3.64). **8d** was prepared by Jones oxidation of the respective alcohol: ^1H NMR δ 7.41–8.00 (5 H, m), 2.86 (2 H, s), 1.05 (9 H, s). **9d** was prepared as a mixture with **8d** from **6d** in analogoy to the procedure described above (benzylic hydrogens: δ 3.78).

Allylbenzene 5e and Its β-Alkyl Derivatives 5f–h. Allylbenzene (**5e**) and *trans*-1-phenyl-2-butene (**5f**) were commercially available. **5g** and **5h** were prepared according to the previously reported methods.[19] **5g**: ^1H NMR δ 7.20 (5 H, br s), 5.54 (2 H, m), 3.31 (2 H, br d, J = 3.6 Hz), 1.90–2.10 (2 H, m), 0.98 (3 H, t, J = 7.2 Hz); IR ($CHCl_3$, cm^{-1}) 965; MS, *m/e* (relative intensity) 146 (60, M^+), 117 (100, $M^+ - C_2H_5$), 91 (50, $C_7H_7^+$). **5h**: ^1H NMR δ 7.22 (5 H, br s), 5.51 (2 H, m), 3.31 (2 H, br d, J = 4.7 Hz), 2.68 (1 H, br heptet, J = 6.6 Hz), 0.98 (6 H, d, J = 6.6 Hz).

Trans epoxides **6f–h** and epoxide **6e** were prepared by epoxidation of **5e–h** with *m*-chloroperbenzoic acid. Cis epoxides

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7f–h were prepared by similar epoxidation of the corresponding *cis*-olefins, which were obtained by Wittig reaction.[20] *cis*-1-Phenyl-2-butene: bp 66–68 °C (9 mm): ^{1}H NMR δ 7.22 (5 H, br s), 5.57 (2 H, m), 3.89 (2 H, br d, J = 5.5 Hz), 1.72 (3 H, d, J = 5 Hz). *cis*-1-Phenyl-2-pentene: bp 75–77 °C (8 mm); ^{1}H NMR δ 7.21 (5 H, br s), 5.52 (2 H, m), 3.39 (2 H, d, J = 6.3 Hz), 2.13 (2 H, m), 1.01 (3 H, t, J = 7.1 Hz). *cis*-1-Phenyl-4-methyl-2-pentene: bp 82–85 °C (8 mm); ^{1}H NMR δ 7.23 (5 H, br s), 5.40 (2 H, m), 3.39 (2 H, d, J = 5.8 Hz), 2.77 (1 H, d-heptet, J = 6.7, 1.8 Hz), 1.00 (6 H, t, J = 6.7 Hz). These products contained, according to GC, 14–20% of the trans isomers. **8f–h** and **9f–h** were prepared from the corresponding epoxides **6f–h** by reduction with $LiAlH_4$ followed by Jones oxidation.

***trans*-β-Methylstyrene-α,β-d_2 (5a-d_2)** was prepared by $LiAlD_4$ reduction of methylphenylacetylene[21] followed by decomposition with D_2O: MS (13 eV), m/e (relative intensity) 121 (10.6, $M^+ + 1$), 120 (100, M^+, $C_9H_8D_2^+$), 119 (9.8, $C_9H_8D^+$); MS (CI), m/e (relative intensity) 121 (100, $M^+ + 1$), 120 (53.1), 119 (12.5), 106 (87.9), 105 (8.7). The product composition was found to be 91% d_2 and 9% d_1, according to the ratio of the peaks at m/e 106 and 105 in the CI spectrum.

Reactions with O(^{3}P) Atoms. *cis*-Stilbene (1). Oxidations were performed in neat liquid at −40, 0, 25, and 60 °C, with O(^{3}P) atoms formed by O_2 discharge. The total reaction mixtures were analyzed at 10-min intervals for a 1-h reaction time, by NMR. The reaction products were separated after 1 h by column chromatography using SiO_2 and identified by comparison with authentic materials. Oxidation under similar conditions were also performed with O(^{3}P) atoms formed by CO_2 and N_2O/N_2 discharge at 0 °C.

β-Alkylstyrenes 5a–d. Oxidations were performed on 1 g of substrate at −25 °C for 90 min. Analyses of reaction products were carried out by NMR, GC–MS, and GC (column a at 160 °C, and column b at 145 °C). The products were isolated on SiO_2 column and identified by comparison with authentic samples. **10b–d** were identified by their ^{1}H NMR signals at δ 9.60–9.75 (d, J = 1.4–1.5 Hz).

Allylbenzene (5e) and Its β-Alkyl Derivatives 5f–h. Oxidations were performed as described above for β-alkylstyrenes. Analyses were performed by using NMR, GC–MS, and GC (column b at 150–185 °C). Aldehydes **10e–h** were identified by the signals at δ 9.6–9.7 (d, J = 1.1–1.4 Hz), and by GC–MS, according to their specific fragmentations. The other products were identified by comparison to authentic samples.

Styrene, α-Methylstyrene, and 1,1-Diphenylethylene. Oxidations were performed on 1.5 g of the neat substrate at −25 °C for 2 h using the three types of discharge. Products composition was determined by comparison to authentic samples, after chromatographic separation.

***trans*-Stilbene and Triphenylethylene. (a) Powdered Substrates.** Oxidations were performed on the solid substrates deposited from ether solution of 5 cm long, 2 cm diameter quartz boat. The boat was introduced into the flow system after the discharge zone. Reactions were conducted for 2 h at room temperature, by using He/O_2 discharge. The products were dissolved in ether, isolated by column chromatography and compared with authentic samples.

(b) Diethylene Glycol Suspension. *trans*-Stilbene (0.5 g, 2.8 mmol) was ground for 1 h in the presence of diethylene glycol (5 mL) by using a small ball-mill. The suspension obtained was reacted at room temperature for 3 h, by using He/O_2 discharge. The resulting mixture was adsorbed on silica gel from acetone solution and chromatographed. A small amount of starting material was isolated (0.02 g) along with **3** (0.07 g, 12.5%) and **4** (0.07 g, 12.5%). The rest consisted of unidentified polymeric material.

***trans*-β-Methylstyrene (5a) and Its Dideuteriated Analogue (5a-d_2).** A mixture of **5a** (0.36 g, 3 mmol) and **5a**-d_2 (0.57 g, 4.83 mmol) was reacted with O(^{3}P) formed by CO_2 discharge for 1 h. The conversion was 40% as determined by GC. The reaction mixture was analyzed in GC–MS. The substrates mixture showed MS (CI) m/e (relative intensity) 121 (59.1), 120 (39.2), 119 (100), 118 (46.5), 106 (56.8), and 105 (85.4), before the reaction and MS (CI) m/e (relative intensity) 121 (46), 120 (30.9), 119 (86.4), 118 (39.3), 106 (63.7), and 105 (100) after the reaction. The inverted kinetic isotope effect (k_H/k_D = 0.92) was calculated from the molar ratios of **5a** and **5a**-d_2 before (1.66, corrected for the natural abundance of ^{13}C) and after the reaction (1.52, corrected for ^{13}C natural abundance and 40% conversion). The reaction product **9a** showed MS (CI) m/e (relative intensity) 137 (45.5, $C_9H_8D_2O^+ + 1$), 136 (13, $C_9H_{10}O^+$), and 135 (100, $C_9H_{10}O_+ + 1$). The total isotope effect was calculated by dividing m/e 137 and 135 peak intensities ratio with the molar ratio of the starting materials **5a** and **5a**-d_2 (k_H/k_D = 2.20/1.66 = 1.33).

Registry No. 5a, 873-66-5; **5b**, 1005-64-7; **5c**, 15325-61-8; **5d**, 3846-66-0; **5e**, 300-57-2; **5f**, 935-00-2; **5g**, 51795-73-4; **5h**, 51795-76-7; **6a**, 23355-97-7; **6b**, 69140-50-7; **6c**, 94719-35-4; **6d**, 40102-58-7; **6e**, 4436-24-2; **6f**, 32215-84-2; **6g**, 105882-77-7; **6h**, 105882-78-8; **7a**, 4541-87-1; **7b**, 69140-51-8; **7c**, 94719-34-3; **7d**, 40102-59-8; **7f**, 36004-03-2; **7g**, 105882-79-9; **7h**, 105882-80-2; **8a**, 93-55-0; **8b**, 495-40-9; **8c**, 582-62-7; **8d**, 31366-07-1; **8e**, 103-79-7; **8f**, 1007-32-5; **8g**, 6683-92-7; **8h**, 5349-62-2; **9a**, 103-79-7; **9b**, 1007-32-5; **9c**, 2893-05-2; **9d**, 6721-67-1; **9e**, 104-53-0; **9f**, 2550-26-7; **9g**, 20795-51-1; **9h**, 40463-09-0; **10b**, 2439-43-2; **10c**, 2439-44-3; **10d**, 86429-26-7; **10f**, 5445-77-2; **10g**, 24569-60-6; **10h**, 105337-06-2; O, 17778-80-2; D_2, 7782-39-0.

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