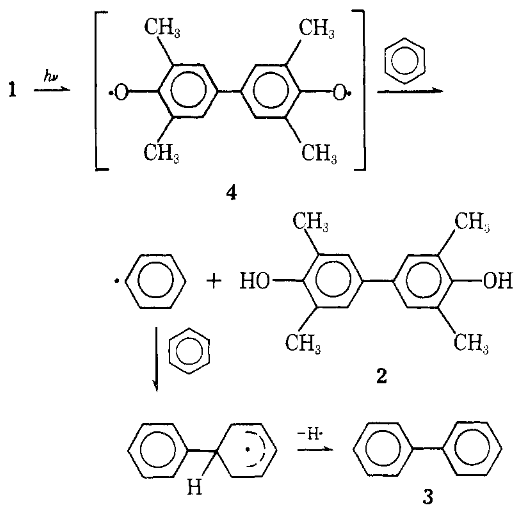

of a dipolar transition state[6] consisting of diphenoquinone and benzene in place of 4 cannot be ruled out at present.

Experimental Section

Melting points are uncorrected. Infrared spectra were run on a Hitachi Model 215 grating spectrophotometer. Nmr spectra were recorded on a Varian HR-220 apparatus. Chemical shifts of the nmr spectra are reported in parts per million downfield from internal TMS. Mass spectra were obtained on a double-focusing mass spectrometer, Model JMS-01SG.

3,3′,5,5′-Tetramethyldiphenoquinone (1) was prepared by the oxidation of 2,6-xylenol with a copper(I) chloride–acetonitrile system. A solution of 0.5 g (0.005 mol) of copper(I) chloride in 50 ml of acetonitrile was stirred under an oxygen atmosphere, followed by addition of 1.22 g (0.01 mol) of 2,6-xylenol to the resulting homogeneous solution. The mixture was stirred for 2 hr at 30° while oxygen was being bubbled in and was chilled with an ice-water mixture. The resulting red crystals were filtered to yield 0.7 g of 1, mp 207–208° (lit.[12] mp 208–210°). The elementary analysis, ir, and nmr spectra were all in agreement with the reported structure. Reduction of 1 with zinc dust in acetic acid gave the corresponding biphenol (2): mp 220–223° (lit.[12] mp 223–225°); mass spectrum M^+ m/e 242 (calcd for $C_{16}H_{18}O_2$, 242); nmr ($CDCl_3$) 8.15, 8.26 (CH_3, s), 6.63 (OH, s), and 3.14 and 3.25 ppm (ring H, s); ir (KBr) 3380 (OH), 860 cm^{-1} (phenyl).

Irradiation of 3,3′,5,5′-Tetramethyldiphenoquinone. A solution of 0.4 g of diphenoquinone (1) in 1000 ml of benzene was purged with nitrogen for 2 hr and then irradiated by means of a 200-W high-pressure mercury arc surrounded by a quartz filter for 100 hr under a stream of nitrogen gas. After removal of the solvent *in vacuo*, the chloroform solution of the reaction mixture was chlomatographed over silica gel (300 g) using chloroform as eluent. The first fraction (50 ml of eluent) obtained contained 0.02 g of 3, whose ir (KBr) and nmr spectra were completely identical with those of authentic diphenyl. The second fraction (0.072 g, 75 ml of eluent) was identified as biphenol (2) by comparison with spectra of an authentic specimen. Starting material (0.250 g) was recovered as the third fraction by elution with 250 ml of chloroform.

Registry No.—1, 4906-22-3; 2, 2417-04-1; 3, 92-52-4; 2,6-xylenol, 576-26-1.

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Atomic Oxygen. III. Reaction of 1,3-Butadiene with Oxygen(^{3}P) Atoms[1]

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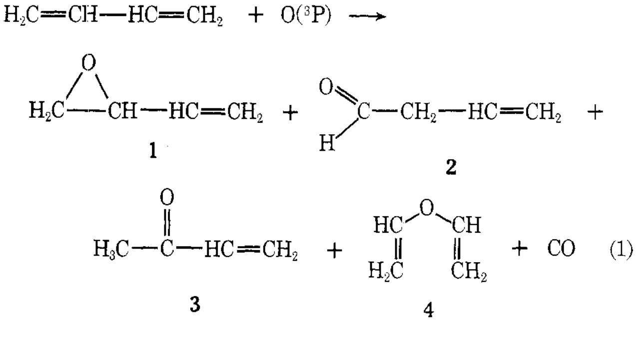
Received December 17, 1973

Atomic oxygen in its ground (triplet) state is produced by the gas-phase mercury-photosensitized decomposition of nitrous oxide.[2] The reaction of oxygen atoms with organic compounds is accomplished by photolysis of a mixture of mercury vapor, organic acceptor, and a large excess of nitrous oxide.[3] The generation of oxygen atoms by this technique produces one molecule of nitrogen per oxygen atom. Yields given below were calculated on the basis of nitrogen evolved during photolysis. Reactions were stopped with less than 25% of the reactant diene converted to products.

The reaction of 1,3-butadiene with O(^{3}P) has been studied by Cvetanovic and Doyle.[4] The oxygenated products that they isolated were carbon monoxide, 3,4-epoxy-1-butene, and crotonaldehyde. Crotonaldehyde may have been produced by rearrangement of 3-butenal during work-up.

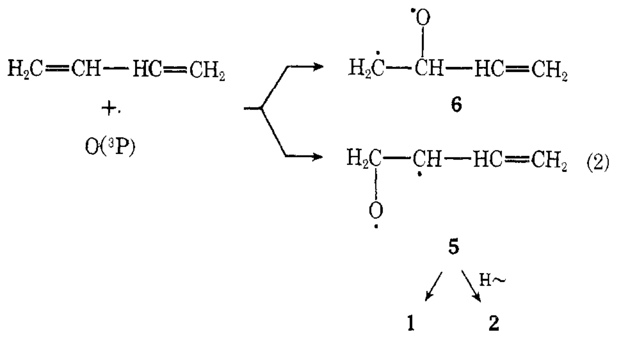
We have examined the reaction of 1,3-butadiene with O(^{3}P) and have determined the product composition with very mild analytical techniques (*vide infra*). The oxygen-containing products of the reaction were carbon monoxide (14% yield); 3,4-epoxy-1-butene (1, 41%); 3-butenal (2, 23%); 3-buten-2-one (3, 1.5%); and vinyl ether (4, 0.5%) (eq 1). Total recovery of oxygenated material was 80%.



The hydrocarbons produced by formation of carbon monoxide were not quantitatively analyzed; however, propene was the major product of low molecular weight. Cvetanovic and Doyle[4] have shown that at a constant total pressure, product yields from the reaction of 1,3-butadiene with O(^{3}P) are independent of reactant ratio in the range nitrous oxide:1,3-butadiene = 9.6:137.

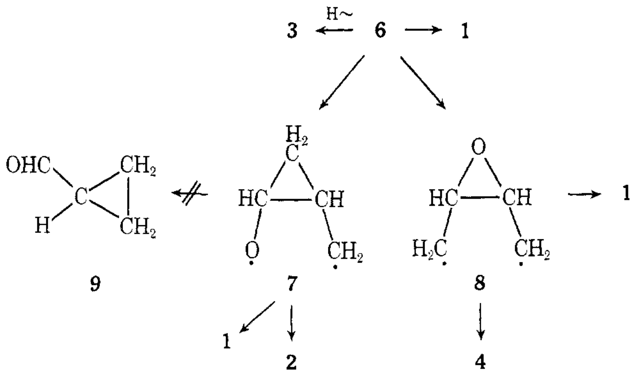
A search was made for the presence of 2,5-dihydrofuran in the product mixture. None of this product was detected upon injection of the product mixture on a vpc column known to separate an authentic sample of 2,5-dihydrofuran from products **1**–**4**. **5** would be the product of a 1,4-cycloaddition of atomic oxygen to the diene. 1,4-Cycloaddition products have been reported from the reactions of atomic sulfur[5] and nitrogen[6] with 1,3-butadiene.

The initial reaction of atomic oxygen with a conjugated diene is addition of the atom to a double bond to form 1,3 biradicals.[7] This process is illustrated in eq 2. Addition can occur either to an external carbon atom to produce biradical **5**, or to an internal carbon atom to make biradical **6**. Of these two competing processes, production of biradical **5** is favored over production of **6**. The carbon radical site of **5** is both secondary and allylic, whereas the carbon radical of **6** is primary and without allylic stabilization. The addition of $O(^3P)$ to olefins also shows preferential formation of the more stable biradical.[7] Product formation from **5** is accomplished by either ring closure to yield epoxide **1** or rearrangement of a hydrogen atom to give aldehyde **2**.



The transformation of biradical **6** to products is more complex (Scheme I). Ring closure and hydrogen migration produce epoxide **1** and ketone **3**, respectively. Another mode of reaction of **6** is intramolecular addition of the carbon and oxygen radical sites to the double bond to produce new 1,4 biradicals, **7** and **8**. The intermediates formed in this process are similar to those produced in triplet di-π-methane rearrangements. Photoinduced oxadi-π-methane rearrangements of β,γ-unsaturated carbonyl compounds appear to take place solely from the triplet state.[8]

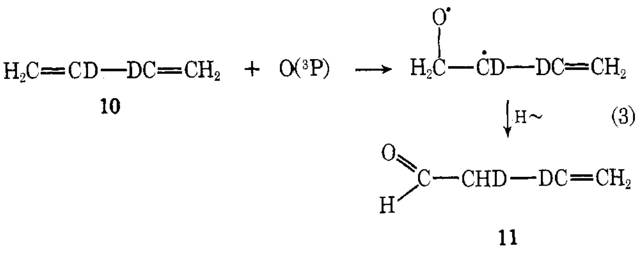
Scheme I

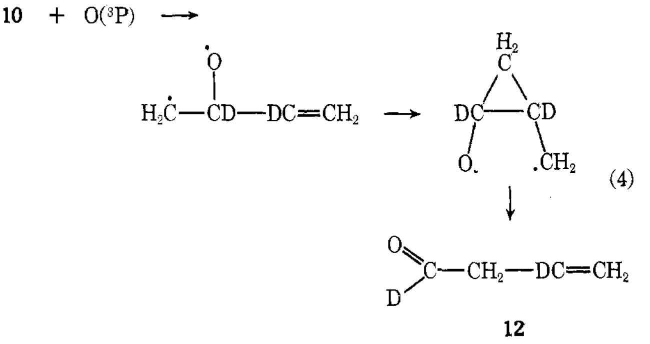


Possible reactions of biradical **7** include rearrangement either by β-cleavage to 3-butenal (**2**), or by a di-π-methane-like process to give epoxide **1** and cyclopropanecarboxaldehyde (**9**). However, no trace of **9** was detected among the products from the reaction of 1,3-butadiene with oxygen atoms.[9] Biradical **8** can decompose to the ether **4** (an observed product) or to epoxide **1**.

The β-cleavage reactions of 1,4 biradicals **7** and **8** (yielding **2** and **4**, respectively) are not without precedent. Pitts and Hess[10] have generated an analogous biradical by photolytic decarbonylation of bicyclo[3.1.0]hexan-3-one.

As is seen from the preceding discussion, epoxide product **1** can be made from four separate intermediates, while aldehyde **2** can arise by two pathways. It is possible to determine how much 3-butenal arises from each of the biradicals **5** and **7** by studying the reaction of 1,3-butadiene-*2,3*-d_2 (**10**) with oxygen atoms. 3-Butenal formed from intermediate **5** would be labeled at carbons 2 and 3 (eq 3), while aldehyde from intermediate **7** would have deuterium in positions 1 and 3 (eq 4).





The ratio of 3-butenal-*2,3*-d_2 (**11**) to 3-butenal-*1,3*-d_2 (**12**) was determined by mass spectrometry. At 70 eV, the mass spectrum of undeuterated 3-butenal shows a large HCO^+ ion (*m/e* 29) and a small H_2CO^+ ion (*m/e* 30). The intensity of the ion at *m/e* 30 is only 1% of that of HCO^+ (corrected for the natural abundance of carbon-13 in HCO^+). This observation makes it possible to determine the ratio of **11** to **12** from the reaction of deuterated butadiene by measuring the intensities of the HCO^+ and DCO^+ ions. The corrected[11] ratio of HCO^+ to DCO^+ was 19:1. Thus, 95% of the 3-butenal arises by the mechanism of eq 3. No more than 5% is made by the di-π-methane process (eq 4).

In conclusion, it should be noted that 3-butenal is difficult to prepare by other methods. Isomerization to the conjugated isomer can be catalyzed by acid or base[12] or can occur under some vpc conditions.[4] 3-Butenal has been made in unspecified yields by the chromium trioxide oxidation of 3-buten-1-ol[13] and by the thermolysis of vinyl ether.[14] The reactions of other dienes with $O(^3P)$ and the independent production of biradicals **5** and **6** are currently being examined in these laboratories.

Experimental Section

Materials. All reactants were purified by trap-to-trap distillation before reaction. 1,3-Butadiene-*2,3*-d_2 (**10**) was prepared by the method of Craig and Fowler.[15] Mass spectrometric analysis at 10 eV indicated that the sample of **10** contained 9% monodeuterated and 1% undeuterated butadiene. Integration of the nmr spectrum of **10** showed that the area of absorptions in the region of the internal protons (τ 3.3–4.1) was <3% of the area of the terminal protons (τ 4.6–5.2).[16] This observation is consistent with specific deuteration in the 2 and 3 positions and with the isotopic purity determined by mass spectrometry.

Cyclopropanecarboxaldehyde (**9**) was made by the method of

Young and Trahanovsky.[17] Comparison samples of products **1**, **3**, and **4** and 2,5-dihydrofuran were obtained commercially.

Reaction Procedures. The apparatus and techniques used for the reactions of hydrocarbons with O(^{3}P) have been described previously.[3] Reactions were run to less than 25% completion to avoid secondary oxidation of products. A high ratio of nitrous oxide to diene reactant (>25) was used in all reactions. Under these reaction conditions, no products of the direct[18] or mercury-sensitized[19] photorearrangement of the diene were observed (0.3% conversion could have been detected). The product composition from the reaction of 1,3-butadiene with O(^{3}P) is not affected by the duration of photolysis.[4]

During photolysis, a thin, pale-yellow polymer formed on the surface of the immersion lamp. Irradiation of a mixture of nitrogen (586 Torr), 1,3-butadiene (24 Torr), and mercury vapors resulted in the loss of 2% of the butadiene by polymerization on the lamp.

Vpc analysis of the product mixture from the reaction of 1,3-butadiene was performed by injection of gas-phase aliquots onto either a 5-ft column of 10% dinonyl phthalate or an 11-ft column of 20% tricresyl phosphate in polyethylene tubing at 25°. Double vpc purification of individual products gave samples of >98% purity.

Spectra of products **1**, **3**, and **4** closely corresponded to spectra of authentic commercial samples of these compounds. Spectrometric data on 3-butenal (**2**) include ir (vapor phase) 3110, 3020, 2910, 2830, 2740, 1740, 1645, 1405, 1300, 1125, 990, and 915 cm^{-1}; uv (vapor phase) λ_{max} 300 mμ (ϵ 22); nmr (CDCl$_3$ solvent) 0.21 (1 H, triplet, J = 1.8 Hz), 3.9–5.0 (3 H, multiplet), 6.8 (2 H, multiplet); mass spectrum (70 eV) m/e (rel intensity) 70 (54), 69 (9), 42 (88), 41 (100), 40 (53), 39 (96), 38 (34), 29 (60), 27 (60), 26 (19); high-resolution mass spectrum of parent peak, observed mass 70.0421 (calcd for C$_4$H$_6$O, 70.0418).

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We thank Dr. P. S. Engel for the use of a vapor-phase uv cell.

Registry No.—**1**, 930-22-3; **2**, 7319-38-2; 1,3-butadiene, 106-99-0.

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Multipathway Bromination of Stilbenes. Competition between Carbonium and Bromonium Ion Intermediates

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Received March 19, 1974

A recent thermodynamic–kinetic approach to the transition state structure of the electrophilic bromination of olefins[1] leads to the conclusion that tensions in the ground state are preserved or even enhanced in the activated complex whatever the structure, bromonium or carbonium, of the intermediate. Therefore, it was proposed that bridged transition states are involved in all cases and that they lead to either bridged or open cationic intermediates. These results prompt us to report an extension of our study on the bromination of substituted stilbenes[2] which confirms that carbonium ion like and bromonium ion like transition states differ in their charge distribution.

We have shown elsewhere[2] that the bromination of stilbenes, XC$_6$H$_4$C$_x$H=C$_y$HC$_6$H$_4$Y, in methanol is a dual-path addition leading competitively to carbonium ions C$_x^+$ and C$_y^+$ through transition states where the charge is on one of the olefinic carbon atoms, without significant participation of the bromine atom. In this note, we investigate a new series of substituted stilbenes to determine how bromine participation modifies the carbonium pathway mechanism and to measure the differences between carbonium and bromonium ion like transition states. To establish the carbonium ion mechanism, we had selected stilbenes where one substituent at least was electron donating, favoring thus charge development on the benzylic carbon atom, α to the donor ring. Here, we attempt to determine whether bromonium ions occur in the bromination of stilbenes where both rings contain deactivating groups which disfavor formation of benzyl cations.

Bromination rate constants for X,Y-disubstituted stilbenes where X and Y are both electron attracting are given in Table I. The elementary rate constants for molecular bromine addition, k_{Br_2}, were measured in methanol at 25° either by the conventional method[3] (kinetic effects of the bromide ion concentration) or by an empirical equation established previously.[2a]

The reactivities of the deactivated stilbenes are first calculated as if the addition proceeds *via* the dual-path mechanism: the overall rate constant is the sum of the two partial rate constants k_x and k_y. Each partial rate constant follows the two-parameter equation log $(k_x/k_0) = \rho_\alpha\sigma_X^+ + \rho_\beta\sigma_Y$ (eq 1) and log $(k_y/k_0) = \rho_\alpha\sigma_Y^+ + \rho_\beta\sigma_X$ (eq 2), where ρ_α and ρ_β are −5.07 and −1.41, respectively. Comparison of the calculated and experimental values (Table II) reveals that the two carbonium ion scheme is inadequate for strongly deactivated stilbenes and that these latter react more rapidly than expected by the dual-carbonium path mechanism.

Bromonium Ion Intermediates. The attenuation of the effects of strongly electron-attracting substituents can most reasonably be interpreted in terms of an increase in the substituent–charge distance, so that the charge is on the bromine atom, *i.e.*, the transition states resemble bromonium ions **3**. In this case, the two substituents X and Y should have identical kinetic effects and there should be a linear free energy relationship between the reactivities, log k, and the sum of the Hammett constants: log $k = \rho_{Br^+}(\sigma_X + \sigma_Y) + \log k_0'$. For the four stilbenes which deviate most