Figure 2. Schematic reaction sequence for $(Cl_2)_2 + Br_2$, illustrating the formation of van der Waals bonds (shown dashed), six-center exchange, and three successive bond scissions.

Figure 2 outlines the reaction sequence we infer from the scattering data. The sharp peaking of the BrCl and ICl angular distributions shows these molecules are emitted with very high centrifugal angular momentum; the broader distribution of Cl_2 shows it emerges with lower centrifugal momentum.[14] These properties indicate a chain structure for dissociative configurations of the reaction complex, $X-Cl\cdots Cl-Cl\cdots Cl-Y$. This presumably results from quick scission of the $X\cdots Y$ bond as the complex traverses a cyclic configuration.[16] The nonstatistical character of the reactive scattering indicates that at least one of the two weak $Cl\cdots Cl$ bonds also breaks quickly (within $\gtrsim 10^{-12}$ sec). The comparable velocities found for the Cl_2 and the $X-Cl$ products suggest that the second $Cl\cdots Cl$ bond persists longer, at least until $X-Cl\cdots Cl-Cl$ and $Cl-Y$ separate sufficiently to approach their asymptotic exit translational momenta (equal and opposite). For (R1) the first $Cl\cdots Cl$ bond to break might be either one. For (R2) the asymmetry of the Cl_2 distribution indicates it is usually the bond which releases HCl and $ICl\cdots Cl_2$. There is some Cl_2 corresponding to the opposite case, however, and this portion (at right in Figure 1) shows higher velocities consistent with the different mass distribution of the initial fragments (ICl and $HCl\cdots Cl_2$). Several aspects of the data thus offer evidence that three sequential bond scissions can be resolved in these single-collision experiments.

Few reaction mechanisms have postulated termolecular processes involving molecules rather than atoms, radicals, or ions. Apparently only two such examples are known with near-zero activation energies, reactions involving two nitric oxide molecules with oxygen and with halogens, and participation of van der Waals mole-

(16) Velocity spectra of $(Cl_2)_2$ scattered by Br_2 or HI without reaction show a very large inelastic component. Much of this may come from break-up of the six-atom complex to re-form the reactants, as an initial $Cl-Cl\cdots Cl-Cl\cdots X-Y$ chain complex probably often fails to attain the cyclic configuration.

cules is suspected.[17] Potential surface calculations show a termolecular hydrogen reaction *via* H_6 is possible and indicate it would involve coupling H_2 to an H_4 chain.[18] Our results suggest that many analogous six-center reactions may be found by exploiting the nozzle-beam technique.

(17) K. J. Laidler, "Chemical Kinetics," McGraw-Hill, New York, N. Y., 1965, p 137.
(18) J. S. Wright, *Chem. Phys. Lett.*, **6**, 476 (1970).

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Oxidation of Diazo Compounds with Singlet Oxygen. Formation of Ozonides

Sir:

As part of our continuing studies of the mechanism of ozonolysis[1] we earlier reported[2,3] that ozonides can be prepared by photooxidizing diazo compounds in the presence of aldehydes. The formation of ozonides in such cases was interpreted as involving the reaction of a carbonyl oxide, or Criegee[4] zwitterion, with the excess aldehyde present. The zwitterion was seen as arising from the reaction of a methylene with ground state oxygen.[2,3] This method has also been extended to cases where either the aldehyde or the oxygen is enriched with ^{18}O and has provided[5] information which is extremely valuable to the problem of the mechanism of ozonolysis. The method used in these earlier reports was successful only for diaryl-substituted diazo compounds, and thus the usefulness of this approach to our ozonolysis mechanism studies was somewhat limited.

We now wish to report that diazo compounds can be converted to ozonides by allowing them to react with singlet oxygen in the presence of aldehydes. The reaction is observed with both aryl and alkyl diazo compounds and can be used to produce ozonides capable of existing as stereoisomers.

In a typical reaction 5.0 mmol of diphenyldiazomethane in acetonitrile solution containing 4 ml of a Methylene Blue stock solution[6] and 20 mmol of benzaldehyde were photolyzed using a General Electric DWY 650-W lamp operated at 50 V. The reaction mixture was worked up by removing solvent, washing with sodium bisulfite to remove excess benzaldehyde, and analyzing the residue by thin-layer chromatography. The major products were triphenylethylene ozonide (26% yield) and benzophenone (67% yield). Using a similar procedure the photosensitized oxidation of isopropyldiazomethane in the presence of isobutyraldehyde and of phenyldiazomethane in the presence of

(1) R. W. Murray, *Accounts Chem. Res.*, **1**, 313 (1968).
(2) R. W. Murray and A. Suzui, *J. Amer. Chem. Soc.*, **93**, 4963 (1971).
(3) R. W. Murray and A. Suzui, *J. Amer. Chem. Soc.*, **95**, 3343 (1973).
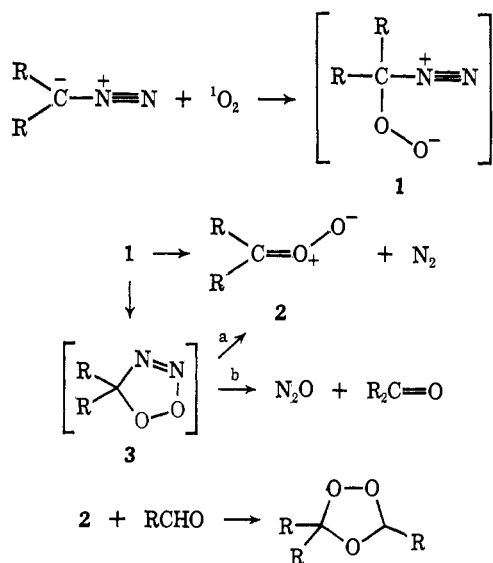(4) R. Criegee, *Rec. Chem. Progr.*, **18**, 111 (1957).
(5) R. W. Murray and D. P. Higley, *J. Amer. Chem. Soc.*, **95**, 7886 (1973).
(6) The stock solution of Methylene Blue was prepared by dissolving 10 mg of Methylene Blue in 10 ml of methylene chloride.

benzaldehyde led to the formation of 1,2-diisopropyl-ethylene ozonide (3.5% yield)[7] and stilbene ozonide (3.1% yield), respectively.

Evidence that the reaction involves singlet oxygen comes from the observations (1) that the destruction of diphenyldiazomethane in a Methylene Blue-sensitized photooxidation occurs at a rate approximately 25 times that of the unsensitized oxidation,[2,3] (2) that when the photooxidation is attempted in the presence of 25 mmol of 1,4-diazabicyclo[2.2.2]octane (DABCO), a known[8] singlet oxygen quencher, the concentration of the diazo compound remains essentially unchanged, and (3) that a sensitized photolysis using N_2 instead of O_2 leads to only minor decomposition of the diazo compound.

A possible mechanism for the reaction involves attack by the electrophilic singlet oxygen at an electron-rich center of the diazo compound.[9,10] The resulting intermediate 1 may decompose to give nitrogen and the zwitterion, 2, or it may cyclize to give an additional intermediate, the heterocycle 3. This latter interme-

$$R_2\overset{-}{C}-\overset{+}{N}{\equiv}N + {}^1O_2 \longrightarrow \left[R-\underset{\underset{\underset{O^-}{|}}{\overset{|}{O}}}{\overset{|}{\underset{R}{C}}}-\overset{+}{N}{\equiv}N \right]$$

1

$$1 \longrightarrow R_2C{=}\overset{+}{O}{-}O^- + N_2$$

2

$$\left[R_2C\underset{O{-}O}{\overset{N{\equiv}N}{\diagup}} \right] \overset{a}{\underset{b}{\longrightarrow}} N_2O + R_2C{=}O$$

3

$$2 + RCHO \longrightarrow R_2C\underset{O}{\overset{O{-}O}{\diagup}}CHR$$

diate may decompose to give (a) N_2 and **2** or (b) N_2O and a carbonyl compound. The intermediacy of **3** is suggested by mass spectral and infrared data[11] indicating the presence of N_2O in the gaseous products.

We have also found that ozonides can be formed by allowing diazo compounds to react with triphenyl phosphite ozonide,[12] **4**, and the ozonide of 4-ethyl-2,6,7-tri-

Table I. Formation of Ozonides

Method[a]	Ozonide	% trans ozonide[b]
(structure) → (structure)	(structure)	38.4 ± 0.4
(structure) + (structure) → (structure)	(structure)	45.6 ± 1.5
(structure) + (structure) → (structure)	(structure)	51.5 ± 0.8
(structure) + (structure) → (structure)	(structure)	55.2 ± 1.4
(structure) + (structure) + 4 → (structure)	(structure)	36.8 ± 0.4
(structure) + (structure) + 5 → (structure)	(structure)	53.2 ± 1.5
(structure) + C_6H_5CHO → (structure)	(structure)	53.3 ± 0.8
(structure) + C_6H_5CHO → (structure)	(structure)	53.2 ± 0.5
(structure) + C_6H_5CHO → (structure)	(structure)	49.0 ± 0.6
(structure) + C_6H_5CHO → (structure)	(structure)	51.6 ± 0.9
(structure) + C_6H_5CHO + 5 → (structure)	(structure)	50.0 ± 0.9

[a] Methylene chloride was the solvent in all cases. Values in parentheses are moles per liter. [b] In each case the % trans ozonide reported is the result of at least three separate determinations. [c] The dye was made soluble in methylene chloride by the addition of 1 equiv of benzyldimethylphenylammonium chloride.

oxa-1-phosphabicyclo[2.2.2]octane,[13] **5**, in the presence of aldehydes. Thus, reaction of isopropyldiazomethane with **5** at ca. 3° in the presence of isobutyraldehyde led to an 11.1% yield of 1,2-diisopropylethylene ozonide. A similar reaction of **4** and isopropyldiazomethane at −40° gave 1,2-diisopropylethylene ozonide (18% yield) and of **5** with phenyldiazomethane and benzaldehyde gave stilbene ozonide (1% yield). While both **4** and **5** have been shown to be sources of singlet oxygen,[12a-d,13] these reactions could

(7) Methylene chloride was used as solvent in this case. The yield of ozonide is thought to have suffered substantially from a competitive reaction of the diazo compound with aldehyde to give 2,5-dimethyl-3-hexanone, the major reaction product (64% yield).

(8) C. Ouannès and T. Wilson, *J. Amer. Chem. Soc.*, **90**, 6527 (1968).

(9) This proposal is similar to those made recently[10] for the case of singlet oxygen oxidation of anions.

(10) (a) H. H. Wasserman and J. E. Van Verth, *J. Amer. Chem. Soc.*, **96**, 585 (1974); (b) R. H. Young and H. Hart, *Chem. Commun.*, 827 (1967); (c) R. H. Young, *ibid.*, 704 (1970); (d) D. Bethell and R. G. Wilkinson, *ibid.*, 1178 (1970).

(11) When the exit gases from the photooxidation of diphenyldiazomethane were passed through a −160° trap and O_2 and N_2 were removed by pumping, a solid remained which upon warming gave a gas whose infrared spectrum was identical with that of N_2O. The mass spectrum of this gas had peaks at m/e 44 (N_2O^+), 30 (NO^+, base peak), and 28 (N_2^+). It is concluded that this gas is N_2O and that it is produced in 21% yield.

(12) (a) R. W. Murray and M. L. Kaplan, *J. Amer. Chem. Soc.*, **90**, 537 (1968); (b) *ibid.*, **90**, 4161 (1968); (c) *ibid.*, **91**, 5358 (1969); (d) P. D. Bartlett and G. D. Mendenhall, *ibid.*, **92**, 210 (1970); (e) Q. E. Thompson, *ibid.*, **83**, 845 (1961); (f) A. P. Schaap and P. D. Bartlett, *ibid.*, **92**, 6055 (1970).

(13) M. E. Brennan, *Chem. Commun.*, 956 (1970).

involve a bimolecular reaction[12d] between the diazo compound and the ozonide. Work on this aspect of these results is continuing. A summary of the photosensitized oxidations, phosphite ozonide oxidations, and some comparable experiments in which the desired ozonides were obtained by ozonolysis of the appropriate olefins is given in Table I.

The similarity of the ozonide stereoisomer distributions in a given ozonide obtained by the photosensitized oxidations and the phosphite ozonide oxidations[14] suggests a common precursor to ozonide, most likely the zwitterion 2. The results in Table I also indicate that for 1,2-diisopropylethylene ozonide the photosensitized oxidations and the oxidation with phosphite ozonide 5 give an ozonide stereoisomer distribution which is closer to that obtained by ozonolysis of the trans olefin and distinctly different from that obtained from the cis olefin. These results thus parallel similar results reported earlier[3] in the case of 1-(1-naphthyl)-1-phenyl-1-propene. In the case of the stilbene ozonides the new oxidations reported here give an ozonide stereoisomer distribution which is approximately the same as that obtained by ozonolysis of either olefin isomer. The relationship of these results to studies of the ozonolysis mechanism involving an ^{18}O tracer[15-20] is under investigation.

The results obtained here suggest that singlet oxygen may react with a number of other systems containing an electron-rich center (e.g., azides, ylids, etc.). In addition, these new methods for producing zwitterions, uncomplicated by the conditions of the ozonolysis method, may permit us to examine other reactions of zwitterions (including other 1,3-dipolar additions) as well as to examine their nmr spectra and possibly obtain evidence for the existence of syn and anti isomers.

(14) The one exception to this statement is the reaction of isopropyldiazomethane with 4 at −40°. In this case the variation is believed to be a temperature effect which is being explored further.

(15) S. Fliszár and J. Carles, *J. Amer. Chem. Soc.*, 91, 2637 (1969).

(16) P. R. Story, C. E. Bishop, J. R. Burgess, R. W. Murray, and R. D. Youssefyeh, *J. Amer. Chem. Soc.*, 90, 1907 (1968).

(17) R. W. Murray and R. Hagan, *J. Org. Chem.*, 36, 1103 (1971).

(18) P. R. Story, J. A. Alford, J. R. Burgess, and W. C. Ray, *J. Amer. Chem. Soc.*, 93, 3042 (1971).

(19) C. W. Gillies and R. L. Kuczkowski, *J. Amer. Chem. Soc.*, 94, 7609 (1972).

(20) C. W. Gillies, R. P. Lattimer, and R. L. Kuczkowski, *J. Amer. Chem. Soc.*, 96, 1536 (1974).

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A New Synthesis of Allylic Sulfones and Their Conversion to Polyolefins. β-Carotene from Vitamin A

Sir:

The well-known Ramberg-Bäcklund olefin synthesis[1] should allow a conversion of diallylic sulfones to the corresponding trienes. Because none of the existing

(1) L. A. Paquette in "Mechanisms of Molecular Migrations," Vol. I, B. S. Thyagarajan, Ed., Interscience, New York, N. Y., 1968, p 121.

syntheses appeared to be suitable for the preparation of such sulfones, we have prepared them by a new method from allyl alcohols and sulfur transfer agents. Some precedent for the chemistry to be discussed was available. Treatment of allyl alcohol with sulfur dichloride at −95° gave 2-propene 1-sulfinate (2) by rearrangement of the anticipated diallyl sulfoxylate (1).[2] 1,1'-Thiodimidazole (3) combines with alcohols to yield alkyl sulfoxylate esters,[3] and the more stable N,N'-thiodiphthalimide (4)[4] was found to react with a number of nucleophiles.[5]
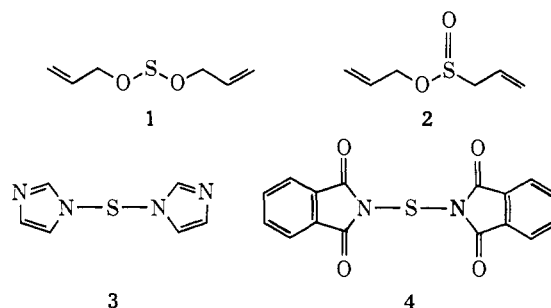
Three experimental procedures were followed for the synthesis of allylic sulfones. In method A an allylic alcohol in ether or methylene chloride is added to sulfide 3 in the same solvent at 0-20°. Sulfide 3 may be prepared *in situ* from 1 equiv of sulfur dichloride and 4 equiv of imidazole and used directly as was done for the synthesis of sulfone 7a. With vitamin A, however, better yields are obtained using sulfide which had been isolated. In method B the lithium alkoxide is preformed with n-butyllithium in methylene chloride at 0° followed by addition of a slight excess of sulfide 4 at room temperature and stirring for 1 hr. Finally, a mixture of sulfide 4 and the allylic alcohol in either benzene or methylene chloride is stirred at room temperature for a few hours in the presence of suspended potassium carbonate or 1 equiv of triethylamine (method C). Sulfinates 6a, b, c, and 10 with intense ir absorption at 1120-1150 cm^{-1} are initially formed from the allylic (5a, b, c) and propargylic (9) alcohols presumably by [2,3]sigmatropic rearrangement of the sulfoxylic amide esters or the sulfoxylates. The sulfinate-sulfone rearrangement, accompanied by the appearance of intense ir absorption at 1300-1330 cm^{-1} proceeds only slowly at room temperature. More rapid transformation was accomplished by stirring methylene chloride solutions of crude sulfinates over silica gel at room temperature or by refluxing toluene solutions over potassium carbonate for approximately 40 min. Sulfoxylate esters were never encountered and no 3-sulfonylfuran was produced by [2,3] rearrangement of the sulfinate 13.[6] Sulfones 7b and 7c were found to be mixtures of geometric isomers, but it is not clear yet whether this is the result of nonstereospecific 2,3-sigmatropic rearrange-

(2) Q. E. Thompson, *J. Org. Chem.*, 30, 2703 (1965); N. S. Zefirov and F. A. Abdulvaleeva, *Vestn. Mosk. Univ., Khim.*, 24, 135 (1969); *Chem. Abstr.*, 71, 112345 (1969). Since submission of this manuscript, sulfone 11 has been prepared by a similar method; see S. Braverman and D. Segev, *J. Amer. Chem. Soc.*, 96, 1245 (1974).

(3) L. Birkofer and H. Niedrig, *Chem. Ber.*, 99, 2070 (1966); L. Birkofer, P. Richter, and A. Ritter, *ibid.*, 93, 2804 (1960).

(4) M. V. Kalnins, *Can. J. Chem.*, 44, 2111 (1966).

(5) D. N. Harpp and T. G. Back, *Tetrahedron Lett.*, 1481 (1972).

(6) S. Braverman and T. Globerman, *Tetrahedron Lett.*, 3023 (1973), reported the thermal isomerization of furfuryl arenesulfinates to phenyl-3-furfuryl sulfones.