was contacted with the solid at 80°, an anisotropic ESR signal was observed at room temperature. The g values of the spectrum ($g_\parallel$ = 2.010. $g_\perp$ = 2.002; g_{av} = 2.005) suggest that it could be assigned either to the sulfonyl radical (SiSO$_2$·) or to sulfur dioxide anion radical (SO$_2$·$^-$). The reported isotropic g values for arylsulfonyl[10] and alkylsulfonyl radicals[11] lie in the range of $g \simeq$ 2.004–2.005. Observed $g_{m\parallel}$ and $g_\perp$ values are also very close to those reported for SO$_2^-$ radicals adsorbed on solid surfaces.[12,13] The number of the SO$_2^-$ radicals was 5 × 10^{16}/g. which was much larger than the number of spins from the original solids. This means that the most of spin centers in siloxene were not detectable by ESR, probably because of the short relaxation time. The fact that the siloxene is capable of producing free radicals is further demonstrated by the polymerization of styrene. By stirring ca. 200 mg of the solid with 20 ml of styrene at 30°, ethanol insoluble polymer of 0.48 g/g and 1.7 g/g were obtained after 4.5 and 19 hr, respectively. Without the solid, polymer was not obtained in the same conditions.

Though the free radical mechanism through vinyl rearrangement is well established in the homogeneous isomerization,[5–9] to our knowledge, isomerization of butene-2 over pyrolytic carbon has been only one example, in which a free radical mechanism was claimed in the field of heterogeneous catalysis.[14]

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[2 + 2] Cycloadditions of Tetracyanoethylene to Enol Ethers. Structure of the Product of Interception with Alcohol

Sir:

Numerous mechanistic criteria evidence the occurrence of zwitterionic intermediates in the cyclobutane formation from tetracyanoethylene (TCNE) and enol ethers.[1–5] The stereoselectivity depends on the polarity of the solvent; one obtains from TCNE and *cis*-propenyl methyl ether the cis adduct 2 and the corresponding trans adduct in the ratio of 95:5 in benzene, 92:8 in ethyl acetate, and 84:16 in acetonitrile.[1] The fast trapping reaction of the zwitterionic intermediate with alcohols suppresses the ring closure,[6] while six-membered rings are formed in the slow interception of the zwitterion (in equilibrium with the cyclobutane derivative) by multiple bond systems in 1,4-dipolar cycloadditions.[7]

The reaction of the zwitterion from TCNE and *cis*-propenyl *methyl* ether with *ethanol* at 0° creates a second chir-

al center in the acetalic trapping product. A 95% stereoselectivity was observed (80% 3 + 4% 4 + 16% 2 under conditions of kinetic control).[6] The analogous reaction of *trans*-propenyl methyl ether proceeds likewise with 95% stereospecificity, but now in favor of 4. The slow ethanolysis of 2 at 25° produces 98% 3 + 2% 4.[6] Thus, the same conformation of the zwitterion is formed from the $_\pi$2 reactants and by opening of the four-membered ring.

The stereoselectivity of ring closure and trapping reaction argues strongly for the U-shaped zwitterionic intermediate 1, favored by Coulombic attraction. charge transfer interaction, and through-bond coupling[8] of the π orbitals at carbon atoms 1 and 4 with the 2,3 bond. A gauche conformation at the 2,3 bond with a slight twisting about the 1,2 and 3.4 bonds (to guarantee through-space interaction of the π orbitals at 1 and 4) may constitute the best model for the intermediate.
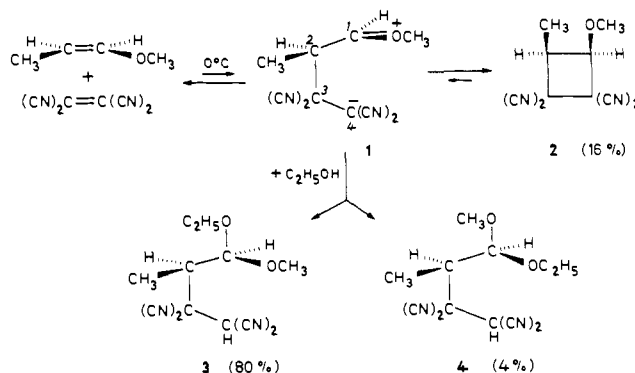
The zwitterion 1 may be compared with an intimate ion pair, one side of the carboxonium ion solvated by the malodinitrile anion group. The configurations 3 and 4 are based on the assumption of transition state 5 where the alcohol molecule enters from "outside". However, an alternative mechanism via the proton chelate 6 (solvent separated ion pair) would lead to opposite structural assignments of the acetals.
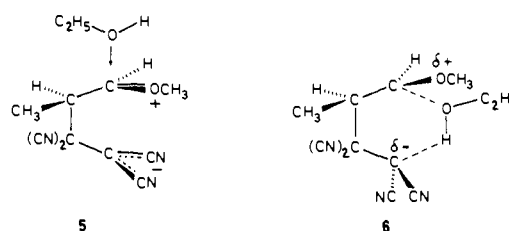
The crystals of the methylethylacetal, mp 95–96°. were unsuitable for X-ray analysis because of twinning[9] and, probably, variable content of optical antipodes.[10] Therefore, we treated the *cis*-cyclobutane (2) with (S)-(+)-2-butanol at 25° in the expectation that the minor component (2% in the methyl ethyl case above) would remain in the mother liquor. Regardless of asymmetric induction. the diastereomeric acetals 7 and 8 should be the main products if the optically active butanol attacks from "outside". Each should suit the X-ray analysis because the relative configuration at C-1 and C-2 is the same.

Table I. Fractional Coordinates and Thermal Parameters ^{a} with Standard Deviations ^{b}

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	0.6871 (6)	0.6403 (2)	0.7259 (3)	4.2 (2)	5.9 (2)	3.9 (2)	0.4 (2)	−0.2 (2)	−1.6 (2)
O (1A)	0.6516 (5)	0.6264 (1)	0.8401 (2)	6.5 (2)	4.0 (1)	3.4 (1)	−0.1 (1)	−0.0 (1)	−0.7 (1)
C (1B)	0.4959 (9)	0.6330 (4)	0.5605 (4)	6.6 (3)	10.4 (4)	4.7 (2)	−1.2 (3)	−1.4 (2)	−2.5 (2)
O (1B)	0.5088 (4)	0.6558 (2)	0.6732 (2)	4.2 (1)	6.2 (1)	3.9 (1)	−0.6 (1)	−0.5 (1)	−0.9 (1)
C (2)	0.8285 (6)	0.7001 (3)	0.7189 (3)	3.2 (2)	8.8 (3)	3.5 (2)	−0.6 (2)	0.4 (1)	−1.5 (2)
C (2A)	1.0284 (8)	0.6770 (4)	0.7514 (5)	3.6 (2)	11.4 (4)	7.5 (3)	1.0 (3)	−0.0 (2)	−3.4 (3)
C (3)	0.7706 (6)	0.7638 (2)	0.7902 (3)	4.1 (2)	6.2 (2)	2.3 (1)	−1.4 (2)	0.1 (1)	−0.5 (1)
C (3A)	0.7904 (6)	0.7530 (2)	0.9159 (3)	3.8 (2)	5.2 (2)	3.0 (1)	−0.7 (2)	−0.2 (1)	−0.2 (1)
N (3A)	0.8053 (6)	0.7488 (2)	1.0088 (3)	5.5 (2)	6.5 (2)	2.6 (1)	−0.1 (2)	−0.7 (1)	−0.4 (1)
C (3B)	0.9040 (8)	0.8200 (3)	0.7590 (4)	5.8 (2)	9.5 (3)	3.2 (2)	−3.6 (3)	0.5 (2)	−0.0 (2)
N (3B)	1.0020 (10)	0.8624 (4)	0.7301 (4)	11.4 (4)	14.2 (5)	5.4 (2)	−8.6 (4)	1.2 (2)	−0.3 (3)
C (4)	0.5568 (6)	0.7895 (2)	0.7693 (3)	4.9 (2)	5.2 (2)	2.6 (2)	−0.7 (2)	−0.0 (1)	0.0 (1)
C (4A)	0.5190 (8)	0.8009 (2)	0.6493 (3)	6.6 (3)	6.3 (2)	3.1 (2)	−1.2 (2)	−0.7 (2)	0.5 (2)
N (4A)	0.4943 (9)	0.8123 (3)	0.5555 (3)	9.8 (3)	8.3 (3)	4.0 (2)	−0.6 (3)	−1.7 (2)	1.1 (2)
C (4B)	0.5180 (8)	0.8551 (3)	0.8286 (4)	6.5 (3)	5.7 (2)	4.2 (2)	−0.3 (2)	−0.3 (2)	−0.1 (2)
N (4B)	0.4898 (9)	0.9050 (3)	0.8763 (5)	9.3 (3)	6.6 (2)	8.3 (3)	−0.0 (3)	−1.0 (3)	−1.4 (2)
C (5)	0.5755 (9)	0.5578 (2)	0.8649 (5)	7.6 (3)	3.9 (2)	6.2 (2)	−0.2 (2)	−0.5 (2)	−0.5 (2)
C (5A)	0.7407 (14)	0.5075 (4)	0.8643 (7)	11.3 (5)	6.5 (3)	11.3 (5)	3.0 (3)	0.7 (5)	0.3 (3)
C (5B)	0.4773 (12)	0.5649 (3)	0.9787 (6)	11.9 (5)	5.0 (2)	9.5 (4)	−0.7 (3)	4.9 (4)	0.1 (2)
C (5C)	0.3832 (16)	0.5000 (4)	1.0188 (9)	18.2 (9)	6.6 (3)	16.9 (8)	−0.4 (5)	8.6 (8)	1.9 (4)

^{a} The thermal parameters are of the form $T = \exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$. ^{b} Standard deviations are based solely on least-squares parameters.

Figure 1. Stereodrawing based on the experimentally determined coordinates and thermal factors.

Figure 2. Bond distances and angles. Standard deviations are on the order of 0.006 Å for the bond lengths and 0.4° for the bond angles.

While the separation of the diastereomers by fractional crystallization from the usual solvents was tedious, one obtained by gentle cooling of the solution in (S)-2-butanol a first crop of mp 95–100° which after two further crystallizations from dichloromethane–cyclohexane showed mp 99–101° and the constant $[\alpha]^{25}$D 75.2° (dichloromethane, 0.02 M):[11] NMR (CDCl$_3$, 60 MHz) τ 4.73 (4-H, s), 5.44 (1-H, d, J_{12} = 2.5 Hz), 6.52 (OCH$_3$ s), 7.37 (2-H, dq, J = 7, 2.5 Hz).

The substance crystallizes in the orthorhombic space group $P2_12_12_1$ with a = 6.985 (4) Å, b = 19.353 (9) Å, c = 11.854 (7) Å, Z = 4, and d_{calcd} = 1.09 gm/cm^3. Data were collected with an automatic diffractometer. Cu Kα radiation, Ni filter, λ 1.54178 Å. $2\theta_{max}$ = 126.5°. As data collec-

tion progressed, the crystal became discolored in the X-ray beam and a slight decrease in the intensity of the monitored standards was noted. The structure was solved by the symbolic addition procedure for noncentrosymmetric crystals,[12] and the results are displayed in Figure 1.[13] Full-matrix least-squares refinement on the 1434 independent reflections, minimizing the function $\sum w_F(|F_o| - |F_c|)^2$, led to an R factor of 0.068.[14] Hydrogen atoms were located in a difference map and included in the refinement as constant parameters. Coordinates are listed in Table I. The bond lengths and angles in the tetracyanoethyl moiety agree well with the average values found for the comparable grouping in the anthracene–TCNE adduct,[15] including the 1.594 Å value for the C(3)–C(4) bond. Atoms C(1), C(2), C(3), and C(4) are close to the gauche conformation with a torsional angle of 50.8° about the C(2)–C(3) bond.

Of the two possible sets of X-ray diffraction coordinates that set was chosen which conformed with (S)-butanol. The structure corresponds to 7, which has the 1R,2R configuration. Thus, the data confirm the mechanism of model 5: the contact ion pair is attacked by the nucleophilic alcohol from "outside".

Retention of configuration in [2 + 2] cycloadditions does not necessarily require U (i.e., cisoid or gauche) conformation of tetramethylene type intermediates. Through-bond coupling[8] could impede 1,2 and 3,4 rotations while the 2,3 rotations are not influenced; even 2,3-trans conformations (Z shape) could cyclize after 2,3 rotation to cyclobutanes with retention. *The high stereoselectivity by which the zwitterion 1 is intercepted with alcohol argues against both*

1,2 and 2,3 rotations during the process. Any Z conformation of the zwitterion should collapse with alcohol more or less randomly.

[2 + 2] Cycloadditions via diradical intermediates show lower stereospecificity[16] than those through 1,4 zwitterions which are often completely stereospecific.[17] Our finding emphasizes that the zwitterions *must be created from the π 2 reactants in U conformations* which are favored by Coulomb potential and CT interactions.[18]

Supplementary Material Available. A listing of calculated coordinates for hydrogen and structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Business Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number JACS-75-5285.

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(9) It was easier to grow fingernail size crystals than well-shaped small ones.
(10) Some big crystals gave levo- or dextrorotary solutions, others turned out to be racemic.
(11) Anal. Calcd for $C_{14}H_{18}N_4O_2$: C, 61.29; H, 6.61; N, 20.43. Found: C, 61.27; H, 6.59; N, 20.60. Stable under dry nitrogen, the colorless crystals develop a brown amorphous coat on longer exposure to air.
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New Evidence in the Mechanism of Ozonolysis of Olefins

Sir:

Considerable controversy has surrounded the mechanism of ozonolysis. The most accepted mechanism today is a refinement of the Criegee mechanism,[1] the Bauld–Bailey syn-

anti zwitterion mechanism.[2] Since this paper does not involve syn and anti zwitterions, only the basic Criegee mechanism (2 + 3 exchange reaction) is shown below.
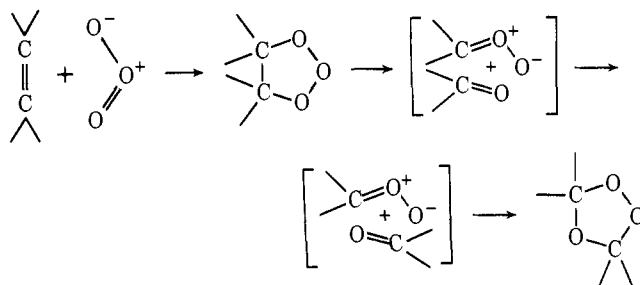

This mechanism was challenged by Story[3] and given the most serious blow by some exchange experiments.[3c] When *trans*-diisopropylethylene was ozonized in the presence of an excess of ^{18}O enriched acetaldehyde, some 75% of the ^{18}O label ended up in the peroxide bridge.

Such results cannot be accommodated by the Criegee mechanism since all the label should end up in the ether position.
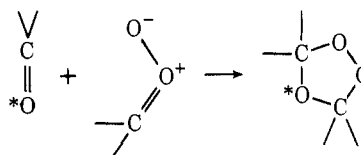
On the basis of this and other evidence, Story suggested various alternative mechanisms for ozonolysis. His aldehyde interchange mechanism illustrating the incorporation of ^{18}O into the peroxide bridge is shown below.
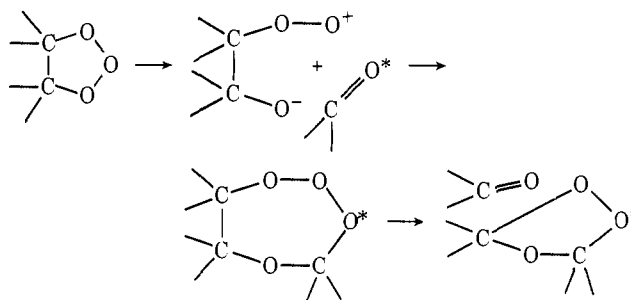
Since then numerous experimentalists[4] have tried to confirm these results by other methods but failed to find the high proportions reported by Story. However, under some specific conditions, ^{18}O is undoubtedly incorporated into the peroxide bridge as was shown by several researchers using various olefins and ^{18}O enriched aldehydes.[5]

With the exception of the preceding piece of disturbing evidence, however, the Criegee mechanism, with refinements, has held up quite well. It is supported not only by molecular orbital symmetry considerations[6] but also by a large accumulation of experimental data.[7]

The fact that, on the other hand, the mechanism advocated by Story invokes an unfavorable 2 + 2 concerted path prompted us to reexamine the supporting experimental facts. In the process of doing this, we found and present here evidence that the disturbing observations reported above might be simple artifacts and cannot be used as evidence against the Criegee mechanism.

We hypothesized that aldehydes may react with ozone in the same fashion as olefins, i.e., via a favorable (2 + 3) exchange reaction.[6]