

- (4) (a) S. Danishefsky and P. Cain, *J. Org. Chem.*, **39**, 2925 (1974). (b) Attempts to purify compound **7** lead, in our hands, to (racemic II) aldolization product **22**. Hence, the precise yield data are given from the tris an-relating agent **4**. The yield of crude **7** from **4** is essentially quantitative.
- (5) (a) C. H. Heathcock, J. E. Ellis, J. E. McMurry, and A. Coppolino, *Tetrahedron Lett.*, 4945 (1971). (b) Compound **6a** has been converted to *dl*-estrone by methods shown here in the optically active series. The details of this synthesis will be given in a full report.
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- (9) A fuller analysis of the mechanism of this reaction will be provided in our full paper.
- (10) The structural assignment to this compound is supported by (a) its infrared, Nu^2R , and mass spectra and (b) its elemental combustion analysis within 0.1% of theory.
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- (12) Attempted reduction of **6** (in both the racemic^{5b} and optically active series in alkaline medium ($Et_3N-EtOAc^2$) followed by ketalization gave **13** and **14** in 44 and 57% isolated yields, respectively. Hydrogenolysis is thus far avoided only by forfeiture of stereoselectivity. Under neutral conditions, the rate of α -reduction is extremely slow and is accompanied by other, undefined, reduction processes.
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Received May 5, 1975

Siloxene as a Unique Catalyst for Structural Isomerization of *n*-Butene

Sir:

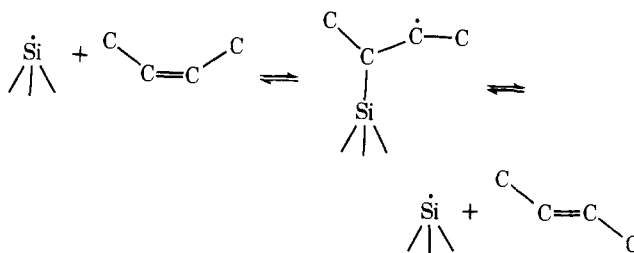
Siloxene ($Si_6O_3H_6$)_n is a unique solid with high surface area and contains reactive Si-H groups.¹⁻⁴ The reactivity of the Si-H groups of siloxene toward various substances has been studied in some detail,²⁻⁴ but its potentiality as a heterogeneous catalyst has never been explored. We have used

siloxene as the catalyst for isomerization of *n*-butenes and found it has a unique characteristic for the reaction. It catalyzes the *cis*-*trans* isomerization of butene-2, but it has no activity for double bond migration, i.e., 1-butene to 2-butene or vice versa.

Siloxene was prepared by the reaction of calcium silicide with hydrochloric acid and water in 1-propanol essentially according to the method described by Kautsky and Pflieger.² Calcium silicide (2.5 g) was added to the mixture of 300 ml of 1-propanol, 55 ml of water, and 10 ml of concentrated hydrochloric acid at 0°, and the system was continuously agitated in the dark under a nitrogen atmosphere. After 50-70 hr, the product was filtered under nitrogen and washed with 1-propanol and then with ethyl ether at 0°. The solid thus shows infrared bands due to Si-H stretching at 2120 and 2250 cm^{-1} and has a surface area of 560 m^2/g . Siloxene was then transferred to a reaction vessel of 44 ml and evacuated at 200° for 5 hr. This treatment caused a slight loss in the intensity of the 2120- cm^{-1} band. Then, the system was maintained at the reaction temperature and butene was introduced. After 1 hr, the product distribution was analyzed by gas chromatography. The results are summarized in Table I. It is clearly seen that siloxene has a catalytic activity for *cis*-*trans* isomerization, but no activity for double bond migration of butenes. The presence of hydrogen in the system does not alter the situation.

In the case of catalysis by metals or metal oxides, it is the usual observation that structural isomerization of butene-2 accompanies double bond migration. The unusual nature of the catalysis by siloxene seems to be explained by a free radical mechanism. Actually, in gas phase catalysis, free radicals such as I,^{5,6} RS,⁷ NO₂,⁸ or NO⁹ are known to promote structural isomerization without enhancing double bond migration.

We propose the following mechanism for the structural isomerization of butene-2, assuming the presence of hydrogen deficient silicon sites.



Though the presence of the hydrogen deficient sites could not be confirmed easily, the following information was obtained concerning the free radical character of the siloxene. The solid exhibits an ESR signal at $g = 2.004$ with the spin number of $1.3 \times 10^{15}/g$. Adsorption of *cis*-butene-2 does not alter the ESR spectrum, indicating that the above equilibrium much favors the side of the dissociated form at room temperature. However, after 50 mmHg of sulfur dioxide, which has much higher electron affinity than butene,

Table I. Product Distribution of Butene over Siloxene

Starting butene	Temp (°C)	Weight of catalyst (mg)	Butene pressure (mmHg)	Hydrogen pressure (mmHg)	Product distribution (%)			
					<i>cis</i> -C ₄ H ₈ -2	<i>trans</i> -C ₄ H ₈ -2	C ₄ H ₈ -1	C ₄ H ₁₀
<i>cis</i> -Butene-2	80	88	203	0	83	17	0	0
<i>cis</i> -Butene-2	80	184	146	60	88	12	0	0
<i>cis</i> -Butene-2	100	17	253	128	71	28	1	0
<i>cis</i> -Butene-2	150	35	106	52	63	36	0	1
Butene-1	100	77	388	0	0	0	100	0
Butene-1	100	90	257	106	0	0	100	0

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 ($\text{SiSO}_2\cdot$) or to sulfur dioxide anion radical ($\text{SO}_2\cdot^-$). The reported isotropic g values for arylsulfonyl¹⁰ and alkylsulfonyl radicals¹¹ lie in the range of $g \approx 2.004$ – 2.005 . Observed $g_{m\parallel}$ and g_{\perp} values are also very close to those reported for $\text{SO}_2\cdot^-$ radicals adsorbed on solid surfaces.^{12,13} The number of the $\text{SO}_2\cdot^-$ radicals was $5 \times 10^{16}/\text{g}$, 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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Received February 7, 1975

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

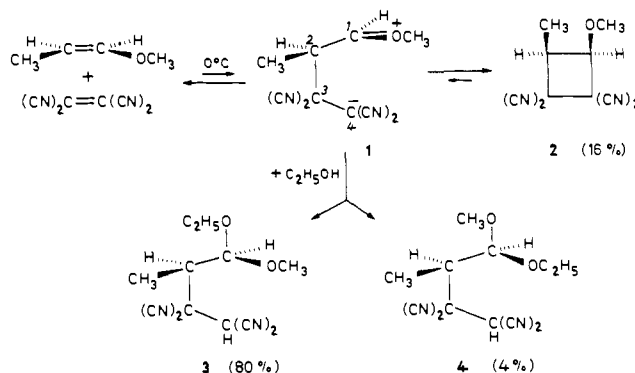
Sir:

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

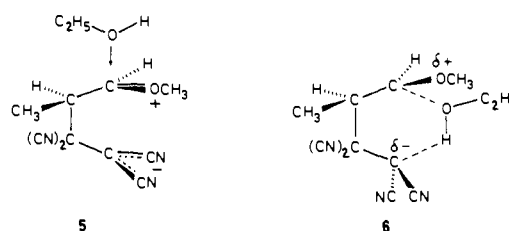
The reaction of the zwitterion from TCNE and *cis*-propenyl methyl ether with ethanol at 0° creates a second chir-

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 π -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 coupling⁸ 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 twinning⁹ 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.

