at 100° in liquid sulfur dioxide; $K_{cis/trans} = 1.5$, determined by nmr spectroscopy.[7]

These results demonstrate the following points. (1) The dissociation of these adducts is a concerted process (or nearly so). The alternative would be a two-step mechanism involving dipolar[8] or diradical intermediates. That such intermediates would not result in the observed stereospecificity has been demonstrated.[4] (2) This 1,4 elimination is *cis* or disrotatory. This direction is that predicted by the principles presented by Woodward and Hoffmann[1] (assuming an elementary molecular orbital description of sulfur dioxide[9]).

We note, however, that for this particular ring system electronic factors may not be expected to be dominant. We envisage as the vibrational deformation leading to the transition state folding of the five-membered ring with the departing SO_2 fragment out of the plane of the four ring carbon atoms.[10] This model is in accord with the steric factors previously mentioned. Any conrotatory process would require relatively greater C–S bond rupture before appreciable overlap is developed within the incipient conjugated system. It is difficult to assess how the difference in activation energy between the processes thus represented compares with that expected from symmetry considerations alone. Since decomposition of thiirane 1,1-dioxide is also a stereospecific *cis* elimination[7] and is therefore presumably concerted, the role of stereoelectronic factors in electrocyclic transformations involving sulfur dioxide cannot yet be conclusively adjudged.

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[7] This isomer distribution is perhaps another manifestation of the factors which preferentially yield *cis*-substituted olefins from α-chlorosulfones and base: N. P. Neurieter and F. G. Bordwell, *J. Am. Chem. Soc.*, **85**, 1210 (1963).

[8] O. Crummitt, A. E. Ardis, and J. Fick, *ibid.*, **72**, 5167 (1950).

[9] W. Moffitt, *Proc. Roy. Soc.* (London), **A200**, 409 (1950).

[10] A geometrically similar transition state has been postulated in the decomposition of 1-pyrazolines: R. J. Crawford and A. Mishra, *J. Am. Chem. Soc.*, **87**, 3768 (1965).

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Fragmentations. The Thermal 5 → 4 + 1 Reaction[1]

Sir:

Although there exist many examples of thermal five-membered ring fragmentations of the type **1** → **2** where Y = $>C{=}O$, $>N^+{=}N^-$, and $>SO_2$,[3] the question of ring-opening stereochemistry has been answered only in part. If concerted, decomposition must occur in either of two modes: disrotatory or conrotatory,[2] illustrated below. All three systems are predicted on the basis of orbital symmetry arguments to fragment thermally *via* the former pathway.[2c] This has been verified for the diazene.[4] Rigid model compounds have afforded evidence that 3-cyclopentenones and 3-sulfolenes *can* fragment with disrotation,[5] but clear-cut stereochemical experiments on unconstrained ketones and sulfones have not been reported. We now wish (1) to describe such experiments in the sulfolene series, and (2) to consider the behavior of **1** (Y = >NNO), for which only the conrotatory mode is symmetry allowed.[2c]

1 **2**

disrotation conrotation

trans,trans-2,4-Hexadiene was allowed to react at room temperature with excess sulfur dioxide in the presence of pyrogallol to give a single sulfolene (**3**), 70% after sublimation, mp 44–44.2° after recrystallization of the sublimate from carbon tetrachloride (lit.[6] mp 43–43.5°). The much slower addition of sulfur dioxide to *cis,trans*-2,4-hexadiene required elevated temperatures, and isomerization occurred. After 12 hr at 96° **3** and an isomeric 3-sulfolene (**4**, isolated by fractional crystallization from carbon tetrachloride, mp 64.8–65.2°)[7,8] were obtained in roughly equal amounts.

Pyrolyses of **3** and **4** were carried out most conveniently in the injection chamber of a vapor chromatograph fitted with a Ucon Polar on Chromosorb W (HMDS-treated) column operated at 35°. At normal flow rates and an injector temperature of 155°, **3** was completely cleaved while **4** was left unscathed; this contrast in lability made separation of **4** from mixtures of the isomers extremely easy. For complete destruction of **4** it was necessary to raise the injector temperature to about 245°. In addition to sulfur dioxide, the only pyrolysis product of sulfolene **3** detectable by vapor chromatography was *trans,trans*-2,4-hexadiene, and **4** gave only the *cis,trans* diene. Intercontamination to the extent of 1% would have been observed in these experiments. Thus fragmentation and, by the principle of microscopic reversibility, formation of these sulfolenes as well are cleanly stereospecific processes.

cis-2,5-Dimethyltetrahydrothiophene, prepared from *meso*-2,5-dibromohexane and purified *via* its mercuric chloride complex, was oxidized with peracetic acid to the sulfone.[9] This sulfolane was identical with the product from hydrogenating **3** and easily distinguishable from the hydrogenation product of **4**. Hence **3**

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[1] The nomenclature is based on Huisgen's classification of cycloaddition reactions (R. Huisgen, R. Grashey, and J. Sauer in "The Chemistry of the Alkenes," S. Patai, Ed., Interscience Publishers, Inc., London, 1964, p 739). In terms of the number of electrons primarily involved, these fragmentations would be designated "6 → 4 + 2."[2b]

[2] (a) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395 (1965); (b) R. Hoffmann and R. B. Woodward, *ibid.*, **87**, 2046 (1965); (c) Abstracts of the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965, p 8S; private communication.

[3] See, for example: (for ketones) M. A. Ogliaruso, M. G. Romanelli, and E. I. Becker, *Chem. Rev.*, **65**, 261 (1965); (for diazenes) W. Baker, J. F. McOmie, and D. R. Preston, *J. Chem. Soc.*, 2971 (1961); L. A. Carpino, *J. Am. Chem. Soc.*, **84**, 2196 (1962); ref 4; (for sulfones) O. Grummitt, A. E. Ardis, and J. Fick, *ibid.*, **72**, 5167 (1950); W. L. Bailey and E. W. Cummings, *ibid.*, **76**, 1936, 1940 (1954); M. P. Cava and A. A. Deana, *ibid.*, **81**, 4266 (1959); M. P. Cava, M. J. Mitchell, and A. A. Deana, *J. Org. Chem.*, **25**, 1481 (1960).

[4] D. M. Lemal and S. D. McGregor, *J. Am. Chem. Soc.*, **88**, 1335 (1966).

[5] Baldwin has concluded from a kinetic study that thermal decarbonylation of cyclopentadienone dimer is concerted. The process is necessarily disrotatory, then, because of the geometrical requirements of the fused ring system (J. E. Baldwin, private communication). The facility with which Diels–Alder adducts of thiophene dioxide with itself and other dienophiles lose sulfur dioxide suggests that their decomposition is also concerted, and thus disrotatory (Bailey and Cummings, ref 3).

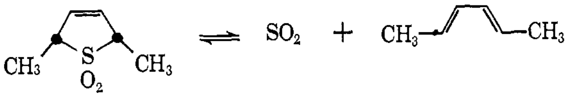
[6] H. J. Backer, J. Strating, and C. M. H. Kool, *Rec. Trav. Chim.*, **58**, 778 (1939).

[7] All new compounds prepared in this study gave correct elemental analyses.

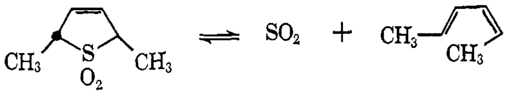
[8] Their nmr spectra established that both sulfolenes were Δ^3 isomers.

[9] E. V. Whitehead, R. A. Dean, and F. A. Fidler, *J. Am. Chem. Soc.*, **73**, 3632 (1951).

and **4** possess the *cis* and *trans* configuration, respectively; it follows that *these sulfolenes interconvert with their components in the disrotatory manner.*[10] The high thermal stability of sulfolene **4** relative to **3** is traceable primarily to repulsion in the transition state between the methyl and hydrogen which overlap so greatly in the *s-cis* conformation of the product.[11]



3



4

N-Nitroso-3-pyrroline (**1**, Y = >N—N=O, mp 34.5–36°, mol wt found, 100) was less than half decomposed by heating for 1 hr at 200° in benzene solution. Of the fraction destroyed roughly one-third was accounted for as pyrrole, and polymer was formed in considerable amount. Thus fragmentation to butadiene and nitrous oxide is a sluggish reaction if it occurs at all.[12]

Were heat of reaction the determining factor, N-nitroso-3-pyrroline would be expected to dissociate more readily than the labile 3-sulfolene ($t_{1/2}$ = 43 min. at 125°).[13,14] We attribute its reluctance to fragment chiefly to the fact that disrotation is symmetry forbidden.[2c] Compared with this pathway, the conrotatory counterpart suffers from these disadvantages: (1) C–N orbital overlap decreases to low values before the new C–C bonds are well developed; (2) the ring twists strongly, reducing π overlap between C-3 and C-4; and (3) the leaving group interferes sterically with the hydrogens which come to occupy the "inside" positions at the termini of the diene. In certain larger rings the severity of these effects is sharply diminished, so the possibility of observing conrotatory fragmentations remains an attractive one.

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(10) The same conclusion has been reached independently by W. L. Mock, *J. Am. Chem. Soc.*, **88**, 2857 (1966).

(11) In principle, disrotatory fragmentation of **3** could have given *cis,cis* diene as well as *trans,trans*. The fearful methyl–methyl repulsion which blocks approach to the transition state for formation of the *cis,cis* isomer explains its absence.

(12) No more than a trace of butadiene was present, though some may have polymerized under the reaction conditions. In another pyrolysis (neat at 212°, 1 hr) nitrous oxide was detected, but the yield was very low and, in fact, its origin is equivocal.

(13) O. Grummitt, ref 3.

(14) This statement is based on the model compounds dimethyl nitrosamine and dimethyl sulfone, for which $(\Delta H^\circ_{N_2O} - \Delta H^\circ_{(CH_3)_2N_2O}) = (\Delta H^\circ_{SO_2} - \Delta H^\circ_{(CH_3)_2SO_2}) - 16$, where the ΔH°'s are standard heats of formation in kcal/mole at 25°. The value for dimethyl sulfone (crystalline) is not corrected for heat of fusion. ("Selected Values of Chemical Thermodynamic Properties," Circular 500 of the National Bureau of Standards, U. S. Government Printing Office, Washington, D. C., 1952, pp 37, 53, 139, and 144.)

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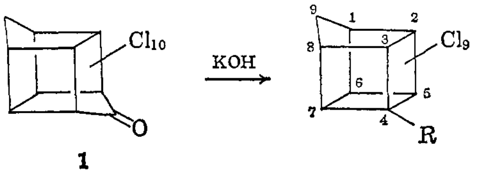
Bridgehead Reactivity in a Perchlorinated Cage Compound[1]

Sir:

Studies of reactions at or adjacent to bridgehead carbon have been instrumental in establishing the preferred geometry of trivalent carbon species,[2] in illuminating the mechanisms of reactions,[3] and in preserving for study otherwise fleeting intermediates.[4] We wish to call attention to the ready availability and favorable properties of a new bridgehead system and to make a preliminary report of its transformations.



1

2, R = COOH
3, R = $CO_2C_2H_5$
4, R = $C(CH_3)_2OH$
5, R = H
6, R = Cl
7, R = Br
8, R = NH_2
9, R = OH

Nonachloropentacyclo[4.3.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]nonane-4-carboxylic acid[5] (**2**), the precurser of all the compounds to be described, may be prepared in 80–90% yield by the Favorskii rearrangement of decachloropentacyclo[5.3.0.$0^{2,6}$.$0^{3,9}$.$0^{4,8}$]decan-10-one (**1**).[6] Dissolving the hydrated **1** in xylene (1 l./100 g), azeotropically removing water, adding powdered 85% potassium hydroxide (50 g/100 g of **1**) in portions to the refluxing solution, and refluxing the mixture with efficient stirring for 12–18 hr conveniently effect rearrangement. The potassium salt of **2**, collected by filtration, was converted to **2** by acidification. Crude product may be freed of the unchanged weakly acidic[1b] **1** hydrate by digesting it with aqueous ammonia, filtering, and reacidifying the filtrate.

The chlorinated pentacyclic cage skeleton of **2–8** confers on its simple derivatives several properties useful in physicochemical studies, in particular good solubility in organic solvents, nonabsorption through the ultraviolet, visible, nmr, and much of the infrared spectral regions, and sufficient volatility and thermal stability to allow gas chromatographic analysis.[7]

(1) (a) Presented in part at the 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965. (b) Transformations of Cage Chlorocarbons. II; for paper I see *Tetrahedron Letters*, 1199 (1965). (c) Supported in part by Public Health Service Research Grant No. GM-12731 from the National Institute of General Medical Sciences and by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

(2) (a) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, Chapter 13; (b) U. Schöllkopf, *Angew. Chem.*, **72**, 147 (1960); (c) P. von R. Schleyer and R. D. Nicholas, *J. Am. Chem. Soc.*, 83, 2700 (1961); (d) D. E. Applequist and L. Kaplan, *ibid.*, **87**, 2194 (1965).

(3) (a) P. D. Bartlett and L. H. Knox, *ibid.*, **61**, 3184 (1939); (b) P. T. Lansbury, V. A. Pattison, and J. W. Diehl, *Chem. Ind.* (London), 653 (1962); (c) P. T. Lansbury and J. D. Sidler, *Tetrahedron Letters*, 691 (1965).

(4) J. C. Kauer and W. W. Henderson, *J. Am. Chem. Soc.*, **86**, 4732 (1964).

(5) In our initial report on the formation of this substance[1b] the pentacyclic skeleton was incorrectly numbered.

(6) (a) J. S. Newcomer and E. T. McBee, *J. Am. Chem. Soc.*, **71**, 946 (1949); (b) E. T. McBee, C. W. Roberts, J. D. Idol, Jr., and R. H. Earle, Jr., *ibid.*, **78**, 1511 (1956); (c) E. E. Gilbert and S. L. Giolito, U. S. Patent 2,616,928 (1952); *Chem. Abstr.*, **47**, 2424 (1953); U. S. Reissue Patent 24,435 (1958); (d) G. W. Griffin and A. K. Price, *J. Org. Chem.*, **29**, 3192 (1964); (e) available as H-1 ketone monohydrate from Hooker Chemical Corp., Niagara Falls, N. Y.

(7) Typically at 200° on a 5 to 20 ft column packed with 5% SE-30 or Dow-11 on Chromosorb W.