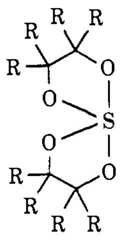
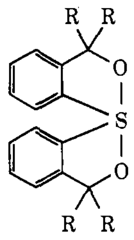
markable compound, tetrakispentafluorophenylsulfurane, recently reported by Sheppard[20] may be an exception, since it showed only one pentafluorophenyl group in the nmr spectrum, but here also an intermolecular mechanism could be operative.



10, $R = CF_3$



11, $R = CF_3$

Conceptually, sulfuranes and selenuranes have an isomerization pathway open to them which is not available to phosphoranes, *i.e.*, the possibility of lone pair inversion through a square planar transition state. Clearly, the relatively high configurational stability of the selenuranes reported here suggests that such a pathway is no more, and perhaps less energetically accessible than the intermediates required for isomerization *via* Berry pseudorotation.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

(20) W. A. Sheppard, *J. Amer. Chem. Soc.*, **93**, 5597 (1971).

Hans J. Reich
Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706
Received August 24, 1972

Isomerization of Cyclopropane. A Molecular Orbital Study on Alternative Mechanisms

Sir:

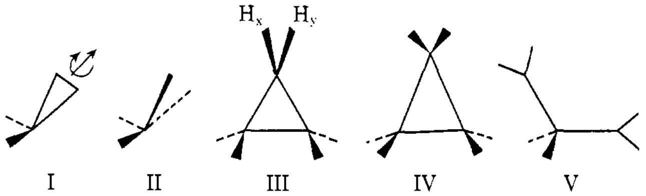
Recently the mechanism of the stereoisomerization of cyclopropane was investigated with EHT[1] and with *ab initio* methods.[2,3] In these studies the attention was focused on trimethylene biradical-like transition states characterized by one long C–C distance.

During our MO studies on carbene insertion reactions,[4] we found that alternative mechanisms involving transition states with two long and one short C–C bonds or with three C–C bonds of about equal length are feasible according to the calculated activation energies. The results of these calculations are presented in this preliminary communication.

The method used in this study is our modified[5] CNDO[6] procedure. In general it yields satisfactory heats of atomization together with reasonable equilibrium geometries for hydrocarbons,[5] hydrocarbon radicals,[7] and carbocations.[8] The ability of the method to allow a complete minimization of the energy of a molecular system with respect to its geometrical parameters is essential for the calculation of reaction coordinates.

As MO theoretical calculations have shown,[4,9] insertion reactions of carbenes proceed *via* a concerted two-step mechanism. In the first step, the empty orbital of the carbene attacks a bonding orbital of the substrate forming a three center bond as in I. (I corresponds to the prototype reaction $CH_2 + H_2$.[4b]) In the second phase of the reaction the lone pair of the carbene combines with the antibonding substrate orbital leading to the final product orbitals. The addition of methylene to double bonds[10] proceeds analogously.[9b,10]

We found that in the methylene adduct I the original H_2 has a low rotational barrier about the axis perpendicular to the H–H bond. Thus, a mechanism for the thermal enantiomerization process at a tetragonal C atom *via* II as the transition state is conceivable.



According to our calculations this mechanism describes the minimum energy path for the interchange of two H atoms in methane. Analogous mechanisms are conceivable for the cis–trans isomerization of cyclopropane. We have investigated three different mechanisms for the interchange of two hydrogens at the same C atom of cyclopropane characterized by the structures of the corresponding transition states.

1. The transition state III can be described as an adduct of cyclopropylidene and H_2. III is characterized by three C–C bonds of comparable length (C1–C2 = 1.50 Å; C2–C3 = 1.51 Å; C–C in cyclopropane: 1.51 Å[5]). The three-center bond in III leads to a short H_x–H_y distance (0.82 Å as compared with the calculated value for H_2 of 0.73 Å) and to stretched C–H_x and C–H_y bonds (1.36 Å). Energetically III comes out to be 73 kcal/mol above cyclopropane. A different and probably less favorable[1,11] transition state with an intact cyclopropane ring was proposed previously.[12]

2. The transition state IV can be described as an adduct of methylene and ethylene. In IV, the three carbon atoms participate in the three-center bond. Thus, two stretched and one shortened C–C bonds (1.61 and 1.42 Å, respectively) are obtained. The mechanism involving IV entails an activation energy of 67 kcal/mol.

A transition state which is analogous to IV but with the restriction of the CCC plane to be a symmetry plane was also considered by Salem, *et al.*,[2b] but found

---

(1) R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 1475 (1968).

(2) (a) J. A. Horsley, Y. Lean, C. Moser, L. Salem, R. M. Stevens, and J. S. Wright, *ibid.*, **94**, 279 (1972); (b) Y. Lean, L. Salem, J. S. Wright, J. A. Horsley, C. Moser and R. M. Stevens, "Proceedings of the 23rd IUPAC Congress, Boston 1971," Butterworths, Washington, D. C., 1971.

(3) P. J. Hay, W. J. Hunt, and W. A. Goddard III, *J. Amer. Chem. Soc.*, **94**, 638 (1972).

(4) (a) H. Kollmar and H. O. Smith, *Angew. Chem.*, **84**, 680 (1972); (b) H. Kollmar, *Tetrahedron*, in press.

(5) H. Fischer and H. Kollmar, *Theor. Chim. Acta*, **13**, 213 (1969).

(6) J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, **43**, 5129 (1965).

(7) H. Kollmar, *Chem. Phys. Lett.*, **8**, 533 (1971).

(8) H. Kollmar and H. O. Smith, *Theor. Chim. Acta*, **20**, 65 (1971), and references therein.

(9) (a) R. C. Dobson, O. M. Hayes, and R. Hoffmann, *J. Amer. Chem. Soc.*, **93**, 6189 (1971); (b) N. Bodor, M. J. S. Dewar, and J. S. Wasson, *ibid.*, **94**, 9095 (1972).

(10) R. Hoffmann, R. Gleiter, and F. B. Mallory, *ibid.*, **92**, 1460 (1970).

(11) S. W. Benson, *J. Chem. Phys.*, **34**, 521 (1961).

(12) F. T. Smith, *ibid.*, **29**, 235 (1958).

to be unstable with respect to its dissociation into methylene and ethylene. For the heat of dissociation of cyclopropane into ethylene and methylene we calculate a value of 105 kcal/mol (exptl value 93 kcal/mol).

By appropriate variation of geometrical parameters it was ensured that III and IV are energetically the highest points on the corresponding paths for the isomerization of cyclopropane. The two structures III and IV are of like symmetry (C_s) and the occupied orbitals can be correlated. Thus, III can be transferred to IV passing a barrier for which we calculated an upper limit of only 7 kcal/mol.

3. In addition, one of the possible trimethylene transition states was also calculated. According to the *ab initio* results,[2,3] the different conformations of trimethylene are of only slightly different energies. We have chosen for our study the trimethylene with two coplanar CH_2 groups (V).

Its ground state cannot be described adequately with one determinant. Hence, the interaction with one doubly excited configuration was taken into account (corresponding to the transfer of two electrons from the highest π to the lowest π^* orbital). As was shown earlier,[7] such a configuration interaction treatment of a "broken" bond is equivalent to the half-electron method.[13] This method yields consistent heats of formation and geometries of radicals.[7,13] Thus, one can expect to get reasonable results for the trimethylene by the procedure described above.

In this manner, an energy of 63 kcal/mol above cyclopropane was obtained for trimethylene. This value compares well with those calculated with *ab initio* methods (61[3] and (with a 3×3 CI treatment) 52[2] kcal/mol). Since CI was used in the calculation of V, and also because of the artificial favoring of small ring stability by the modified CNDO method,[5] the direct comparison of its energy with the energies of III and IV is subject to some reservations. In IV the interaction with the most important doubly excited configurations lowers the energy by an additional 8 kcal/mol. The corresponding value for cyclopropane is only 6 kcal/mol. The optimized structure of V is characterized by a C–C bond length of 1.50 Å and a CCC valence angle of 120°.

Although the quantitative results of our calculations may be of questionable accuracy, the following conclusions can be drawn. According to the calculations, the transition states III, IV, and V have comparable energies, *i.e.*, 73, 67, and 63 kcal/mol, respectively, relative to cyclopropane. The experimental value for the activation energy of the isomerization process of cyclopropane is reported to be 64 kcal/mol.[14]

Thus, one can expect that the mechanism for the isomerization of a substituted cyclopropane derivative will be determined by electronic factors as given by its substituents. An electron withdrawing substituent R might favor the transition state IV because of the stabilization of the lone pair in the carbene CHR. On the other hand, appropriate 1,2 substitution could stabilize the trimethylene. Finally, carbenoids might isomerize *via* a state which is analogous to III.

More generally, reactions proceeding with a high activation energy (50 kcal/mol) may be expected to involve a greater variety of possible transition states than do thermally "allowed" reactions.

H. Kollmar
Battelle Institut e.V.
Frankfurt (Main), Germany
Max Planck Institut für medizinische Forschung
Heidelberg, West Germany

Received May 6, 1972

---

[13] (a) M. J. S. Dewar, J. A. Hashmall, and G. Venier, *J. Amer. Chem. Soc.*, **90**, 1953 (1968); (b) M. J. S. Dewar and E. Haselbach, *ibid.*, **92**, 590 (1970).

[14] B. S. Rabinovitch, E. W. Schlag, and K. B. Wiberg, *J. Chem. Phys.*, **28**, 504 (1958).

Vinyloxyboranes as Synthetic Intermediates

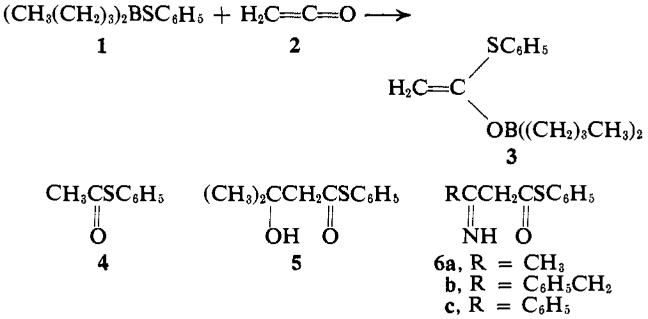
Sir:

We recently reported a convenient method for preparation of β-hydroxyalkanethioates by the reaction of thioboronite and carbonyl compounds with ketene, and it was suggested that the reaction proceeded by initial formation of a coordination complex of a carbonyl compound with thioboronite, followed by a nucleophilic attack of the thiolate anion on ketene.[1] However, the present investigation shows that the key intermediate of this reaction is vinyloxyborane (**3**) formed from thioboronite and ketene.

When nearly 1 equiv of gaseous ketene (**2**) was passed into a solution of phenyl di-*n*-butylthioboronite (**1**) in CCl_4 at -20 to $-30°$ under argon, the formation of **3** was confirmed by the pmr spectrum of the reaction mixture which displayed two doublets for the vinyl hydrogens (H_A and H_B) at δ 4.57 and 4.63 ($J_{AB} = \sim 1.5$ Hz). On hydrolysis of this reaction mixture, phenyl thioacetate (**4**) was isolated by preparative tlc.

It was further established that the treatment of **3** with acetone in ether, followed by hydrolysis and preparative tlc of the crude product, afforded phenyl β-hydroxyisovalerothioate (**5**, oil, ir 3410, 1685 cm^{-1}; pmr (CCl_4) δ 1.22 (s, 6 H), 2.70 (s, 2 H), 3.28 (s, 1 H), 7.23 (s, 5 H)) in 67% yield.

In a similar way, β-imino thiol esters (**6a–c**) were obtained by the reaction of **3** with nitriles at room temperature under argon (**6a**, 35%, oil; **6b**, 39%, mp 74°; **6c**, 37%, mp 111–112°). On the other hand, it was found that a coordination complex[2] formed from **1** and benzyl cyanide did not react with ketene.



$(CH_3(CH_2)_3)_2BSC_6H_5 + H_2C{=}C{=}O \longrightarrow H_2C{=}C(SC_6H_5)OB((CH_2)_3CH_3)_2$

1 **2** **3**

$CH_3C(=O)SC_6H_5$ **4**

$(CH_3)_2C(OH)CH_2C(=O)SC_6H_5$ **5**

$RC(=NH)CH_2C(=O)SC_6H_5$

6a, R = CH_3
b, R = $C_6H_5CH_2$
c, R = C_6H_5

Next, in order to study further the reactions of vinyloxyborane, the preparation of the borane from thioboronite and vinyl methyl ketone was tried. Vinyl methyl ketone was allowed to react with an equimolar

---

[1] T. Mukaiyama and K. Inomata, *Bull. Chem. Soc. Jap.*, **44**, 3215 (1971).

[2] (a) T. Mukaiyama, K. Inomata, and S. Yamamoto, *Tetrahedron Lett.*, 1097 (1971); (b) T. Mukaiyama, S. Yamamoto, and K. Inomata, *Bull. Chem. Soc. Jap.*, **44**, 2807 (1971).