chromium(II) produced in reaction 1 does not significantly affect the rate of disappearance of $CrSCN^{2+}$. This was further checked by adding $Co(NH_3)_5F^{2+}$ to react with the chromium(II) produced in reaction 1.[20–22] A solution 0.42 M in V^{2+} and 1 M in perchloric acid was mixed with a solution $\sim 2 \times 10^{-3}$ M in $CrSCN^{2+}$, 1.2×10^{-2} M in $Co(NH_3)_5F^{2+}$, and 1 M in perchloric acid, and the formation of $VNCS^{2+}$ and its subsequent disappearance were followed at 400 mμ, an absorption minimum of $Co(NH_3)_5F^{2+}$. The value of t_{max}, the time required for the concentration of $VNCS^{2+}$ to reach its maximum value, was 0.83 sec, in very good agreement with the value of 0.83 sec calculated for reactions 1 and 2.[23,24] We conclude, therefore, that, in contrast to the iron(III)–vanadium(II) reactions, the reaction of $CrSCN^{2+}$ with vanadium(II) proceeds *via* an anion-bridged transition state, in which the thiocyanate is bonded to both the vanadium and the chromium. It is noteworthy that the rate constant for reaction 1 is very similar to the rate constant for the formation of thiocyanatopentaaquovanadium(II) from vanadium(II) and thiocyanate ions.[25,26]

---

(20) The rate constants for the reaction of $Co(NH_3)_5F^{2+}$ with vanadium(II) and chromium(II) are 2.6 and 9×10^5 M^{-1} sec^{-1}, respectively, at 25.0° and ionic strength 1.0 M.[21,22]

(21) J. P. Candlin, J. Halpern, and D. L. Trimm, *J. Am. Chem. Soc.*, **86**, 1019 (1964).

(22) J. P. Candlin and J. Halpern, *Inorg, Chem.*, **4**, 766 (1965).

(23) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1961, p 166.

(24) G. Friedlander, J. W. Kennedy, and J. M. Miller, "Nuclear and Radiochemistry," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1964, p 71.

(25) These studies do not establish the structure of the monothiocyanate complex of vanadium(III). However, the similarity of the spectra of the monoazide and monothiocyanate complexes of vanadium(III) (both have absorption maxima at 350 mμ) strongly suggests that the latter complex is nitrogen bonded. The observation that V^{2+} reacts 4×10^4 times more rapidly with $CrSCN^{2+}$ than with $CrNCS^{2+}$ is consistent with this view. Evidence has been previously presented[5,19,26] that the stable monothiocyanate complexes of chromium(III) and iron(III) are nitrogen bonded.

(26) T. J. Conocchioli and N. Sutin, *J. Am. Chem. Soc.*, **89**, 282 (1967).

Bernard R. Baker, Mato Orhanovic, Norman Sutin
Chemistry Department, Brookhaven National Laboratory
Upton, New York 11973

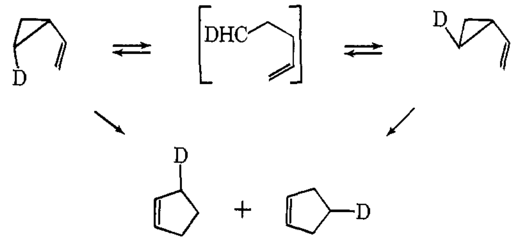
Received November 16, 1966

The Stereochemical Fate of the Cyclopropyl Ring in the Vinylcyclopropane Rearrangement

Sir:

Thermolysis of vinylcyclopropane to cyclopentene is a reaction whose course is securely established.[1–3] Interpretation of the kinetic parameters for the formation of cyclopentene have, on the one hand, led to the conclusion that the rearrangement is concerted,[2] and, on the other hand, that a discrete diradical intermediate is involved.[3] We present here experimental evidence that has a considerable bearing on this mechanistic question.

A 5:1 mixture of *cis*- and *trans*-2-bromo-1-vinylcyclopropane[4] was separated by vapor phase chromatography. These bromine compounds were reduced by sodium in moist methanol to vinylcyclopropane. Reduction of each isomer by sodium in methanol-O-*d* containing deuterium oxide produced vinylcyclopropane containing 1 deuterium atom/molecule. The upfield portion of the 100-MHz nmr spectrum of vinylcyclopropane consists of three complex multiplets centered at δ 1.3, 0.7, and 0.4, with intensities of 1:2:2. The nmr spectrum of the monodeuteriovinylcyclopropane prepared from the minor brominated isomer exhibits peaks with the same chemical shifts but having the intensities 1:1:2, while the spectrum of the compound prepared from the major brominated isomer exhibited intensities of 1:1.5:1.5. Since it is assured that the stereochemistry has been lost in the latter case, we turned our attention to the monodeuterio isomer with the 1:1:2 pattern of intensity.[5] Pyrolysis of this monodeuteriovinylcyclopropane at 300 mm in a base-washed Pyrex tube at 360° for 10 min caused a 6% conversion to cyclopentene. The intensities of the absorptions of the upfield portion of the nmr spectrum changed from 1:1.1:1.9 before pyrolysis to 1:1.5:1.5 in the recovered vinylcyclopropane. The precision and reproducibility of our integrated intensities are such that no more than 5% unrearranged deuteriovinylcyclopropane would have remained undetected. If both the scrambling of the deuterium label and the formation of cyclopentene are first-order reactions, we can then calculate that during the first 6% of the irreversible formation of cyclopentene complete equilibration of the stereochemistry at the labeled site occurred. We thus conclude that the loss of stereospecificity at the deuterium-labeled site in the cyclopropyl ring is at least five times as fast as the conversion to cyclopentene.



The most economical interpretation of this experiment is based on the trimethylene diradical model for the *cis*- and *trans*-1,2-dideuteriocyclopropane isomerization data of Rabinovitch, *et al.*[6,7] These authors assert that the geometrical and structural isomerization of cyclopropane involves formation of the trimethylene diradical as an intermediate, a process with an activation energy of 63 kcal/mole. The addition of a vinyl group to the cyclopropyl ring should lower the activation energy for formation of a diradical by

---

(1) C. G. Overberger and A. E. Borchert, *J. Am. Chem. Soc.*, **82**, 1007 (1960).

(2) (a) M. C. Flowers and H. M. Frey, *J. Chem. Soc.*, 3547 (1961); (b) C. A. Wellington, *J. Phys. Chem.*, **66**, 1671 (1962); (c) R. J. Ellis and H. M. Frey, *J. Chem. Soc.*, 4188 (1964); (d) C. J. Elliot and H. M. Frey, *ibid.*, 345 (1965); (e) C. J. Elliot and H. M. Frey, *ibid., Phys. Sect.*, 553 (1966).

(3) (a) B. Grzybowska, J. H. Knox, and A. F. Trotman-Dickenson, *ibid.*, 4402 (1961); (b) H. M. Frey, *Trans. Faraday Soc.*, **58**, Part I, 516 (1962); (c) H. M. Frey and D. C. Marshall, *J. Chem. Soc.*, 3981 (1962); (d) R. J. Ellis and H. M. Frey, *ibid.*, 959 (1964); (e) K. W. Egger, D. M. Golden, and S. W. Benson, *J. Am. Chem. Soc.*, **86**, 5420 (1964).

(4) D. Seyferth, Y. Yamazaki, and D. L. Alleston, *J. Org. Chem.*, **28**, 703 (1963).

(5) The *trans* relationship of the deuterium atom and the vinyl group can be inferred from the nmr spectrum. However, since the observations reported here do not depend on this assignment in any critical fashion, we have decided to defer a more rigorous assignment of structure.

(6) (a) The contributions to the question are summarized in D. W. Setser and B. S. Rabinovitch, *J. Am. Chem. Soc.*, **86**, 564 (1964); (b) S. W. Benson, *J. Chem. Phys.*, **34**, 521 (1961).

(7) (a) B. S. Rabinovitch, E. W. Schlag, and K. B. Wiberg, *ibid.*, **28**, 504 (1958); (b) B. S. Rabinovitch and E. W. Schlag, *J. Am. Chem. Soc.*, **86**, 5996 (1960).

about 13 kcal/mole (the resonance energy of the allylic radical[3e]), thus leading to a predicted and observed activation energy for formation of an intermediate in the vinylcyclopropane isomerization of 50 kcal/mole. The diradical can cause geometrical isomerization of the deuterium label just as it does in cyclopropane. In addition this diradical can by redistribution of electrons and slight movement of some carbon and hydrogen nuclei rearrange to cyclopentene. We propose this scheme as a logically structured, and presently acceptable, mechanism. However, we would also point out that an alternative scheme that would consider cyclopentene formation and geometrical isomerization to be in separate energy manifolds is only so slightly different both conceptually and experimentally from the diradical mechanism that we cannot discount it without further, and more subtle, experiments.[8]

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

---

(8) A suggestion that this alternative explanation may be quite reasonable is provided by Hoffmann's calculations of the stereochemical course of the closure of trimethylene diradicals,[9] Crawford's observations on the behavior of these diradicals generated from pyrazoline pyrolysis,[10] and Rabinovitch, Setser, and Wiberg's expanded ring model for cyclopropane isomerization.[6a,7]

(9) R. Hoffmann, Abstracts of the 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966, Paper 109K.

(10) R. J. Crawford and A. Mischra, *J. Am. Chem. Soc.*, **88**, 3963 (1966).

M. Robert Willcott, Virgil H. Cargle
Department of Chemistry, University of Houston
Houston, Texas 77004

Received October 31, 1966

Five-Coordinate Copper(II) in [Cu(tren)(NCS)](SCN)

Sir:

Raymond and Basolo[1] have recently reported the preparation of [Cu(tren)(NCS)](SCN)[2] and have suggested that one thiocyanate ion is coordinated to the copper(II) ion through the nitrogen atom and the other through the sulfur atom, in a *cis*-octahedral complex. Their conclusion was based upon two observations. First, the appearance of two C–N frequencies at 2094 and 2060 cm^{-1} and two C–S frequencies at 818 and 745 cm^{-1} in the infrared spectrum suggested that one thiocyanate is bonded to copper through the nitrogen atom and the other is either bonded through the sulfur atom or not coordinated to copper. Secondly, the similarity in cell dimensions and identity of space group of the crystalline copper and nickel compounds suggested that the two molecules have the same configuration, and Rasmussen[3] has shown $Ni(tren)(NCS)_2$ to have a *cis*-octahedral configuration.

Professor Basolo kindly furnished us a sample of [Cu(tren)(NCS)](SCN), and we have determined its crystal structure. The cell has dimensions $a = 9.16$, $b = 14.00$, $c = 11.29$ A and contains four molecules. Systematic absence of $h00$, $0k0$, and $00l$ with odd indices indicates the space group $P2_12_12_1$. (The cell dimensions for the nickel compound are $a = 8.62$, $b = 14.72$, $c = 10.82$ A, and its space group is also $P2_12_12_1$.) Three-dimensional X-ray diffraction intensities were collected on a Picker single-crystal diffractometer with Mo Kα radiation, out to a limit of $2\theta = 55°$. The positions of the copper atoms were determined from a sharpened Patterson synthesis, and the other atoms were found in a series of Fourier syntheses. The structure has been refined by full-matrix least squares, with isotropic temperature factors and without introduction of hydrogen atoms, to a value of $R = 0.08$. The refinement is being continued and the final results will be published later.

Table I. Bond Lengths (in Angstroms) and Angles (in Degrees)

Cu–N(1)	2.04	N(1)–Cu–N(2)	84
Cu–N(2)	2.07	N(1)–Cu–N(3)	85
Cu–N(3)	2.16	N(1)–Cu–N(4)	85
Cu–N(4)	2.06	N(5)–Cu–N(2)	95
Cu–N(5)	1.95	N(5)–Cu–N(3)	98
		N(5)–Cu–N(4)	94
		N(1)–Cu–N(5)	177
		N(2)–Cu–N(3)	114
		N(2)–Cu–N(4)	130
		N(3)–Cu–N(4)	113

The copper ion is surrounded by five nitrogen atoms from the tren molecule and one thiocyanate ion, in a somewhat distorted trigonal bipyramid, with the tertiary nitrogen atom, N(1), and the thiocyanate nitrogen atom, N(5), at the apices, and the three primary nitrogen atoms, N(2), N(3), N(4), in the equatorial positions. Bond lengths and angles in the coordination polyhedron are given in Table I. The nitrogen atom, N(6), of the second thiocyanate ion lies at a distance of 3.84 A from the copper ion in the equatorial plane of the trigonal bipyramid, near the bisector of the N(2)–Cu–N(3) angle. The Cu–N(6)–S(2) angle is 96°, bringing the S(2) atom to 3.7 A from N(3) but more than 5 A from Cu. The S(2) atom from another thiocyanate ion is 4.57 A from the copper ion, and this is the shortest Cu–S distance in the crystal. Thus the second thiocyanate ion is not coordinated to the copper ion.

The apparently reasonable, but incorrect, conclusions of Raymond and Basolo regarding the structure of [Cu(tren)(NCS)](SCN) illustrate the danger of drawing structural conclusions from comparisons of cell dimensions and the space group of crystals.

Acknowledgment. This work was supported in part by a grant from the National Science Foundation.

Prem C. Jain, E. C. Lingafelter
Department of Chemistry, University of Washington
Seattle, Washington 98105

Received December 1, 1966

---

(1) K. N. Raymond and F. Basolo, *Inorg. Chem.*, **5**, 1632 (1966).

(2) tren = $N(CH_2CH_2NH_2)_3$.

(3) S. E. Rasmussen, *Acta Chem. Scand.*, **13**, 2009 (1959).

Arylation by Aromatic Nitro Compounds at High Temperatures

Sir:

Since Berthelot in 1887 established the explosiveness of nitroaromatics at high temperatures,[1] there has been an understandable reluctance on the part of chemists to study the reactions of these derivatives at 400° and higher. What scant literature exists is concerned with determination of safe temperature limits, *e.g.*, for hydrogenation of nitroxylenes to xylidines.[2]

---

(1) M. Berthelot, *Compt. Rend.*, **105**, 1159 (1887).

(2) R. L. Datta and N. R. Chatterjee, *J. Chem. Soc.*, **115**, 1006 (1919); C. L. Brown, W. M. Smith, and W. G. Scharmann, *Ind. Eng. Chem.*, **40**, 1538 (1948); P. C. Condit and R. L. Haynor, *ibid.*, **41**, 1700 (1949).