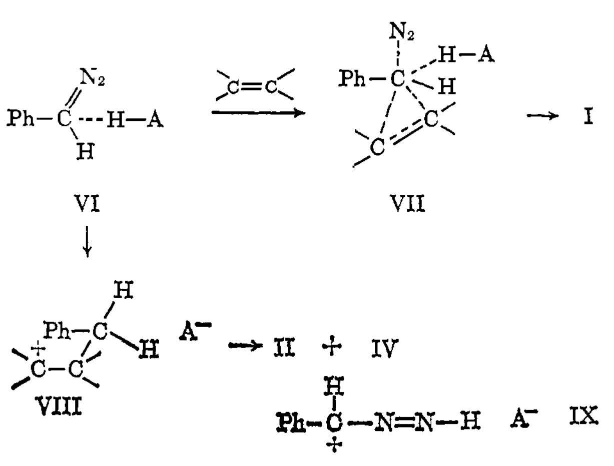
II and IV. The latter path, of course, should be strongly favored when the carbonium ion VIII is tertiary. This mechanism is able to account for (i) the stereochemistry of formation of both I and IV, (ii) the variation in yield of I with structural changes of the olefin, and (iii) the observed deuterium incorporation. The fact that some deuterium gets incorporated into I indicates that proton transfer and its reverse reaction proceed with comparable rate as the reaction of VI with the olefin. On the basis of this mechanism the deuterium content of I should vary with acid strength and polarity of the reaction medium. Experiments to test this hypothesis are in progress.

An alternative mechanism which cannot be ruled out with the data at hand would involve protonation on nitrogen leading to the ion pair IX. This intermediate could then react with the olefin to give I and VIII. Incorporation of some deuterium into I, and the change in product distribution with variation of olefin substitution, however, are less readily explained on the basis of this mechanism.



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[9] A. P. Sloan Fellow, 1962–1966.

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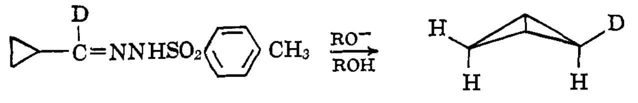
On the Mechanism of the Conversion of Cyclopropanecarboxyaldehyde Tosylhydrazone to Bicyclobutane[1]

Sir:

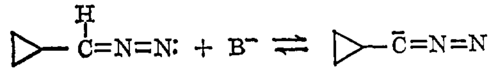
The thermal conversion of the anion derived from cyclopropanecarboxyaldehyde tosylhydrazone (I) to bicyclobutane (II) is of interest because of the unique solvent dependence. In the absence of a proton source, such as an alcohol, the product is cyclobutene,[2] whereas in the presence of alcohols it is bicyclobutane.[3,4] The normal reaction of the cyclopropylcarbinyl carbene appears to be rearrangement to cyclobutene.[4] It has been suggested that the role of the alcohol in the bicyclobutane formation is to provide a proton source which will convert diazomethylcyclopropane to the diazonium ion which then may lose nitrogen and lead to bicyclobutane *via* the "bicyclobutonium" ion.[4]

We have further investigated the reaction using a deuterium-labeled substrate and a deuterium-containing solvent. The reaction of I-*d* in the presence of a limited amount of base gave II, which contained 92% of one deuterium, essentially all in the *exo* position as shown by the nmr spectrum.[5] When the reaction was carried out using an excess of base, the bicyclobutane contained significantly less deuterium. Similarly, when unlabeled I was heated with an excess of base in ethylene glycol-d_2 the product was the same as that obtained from I-*d*. Finally, when unlabeled I was treated with a deficiency of base in deuterium-labeled solvent, no significant amount of deuterium was found in the product.



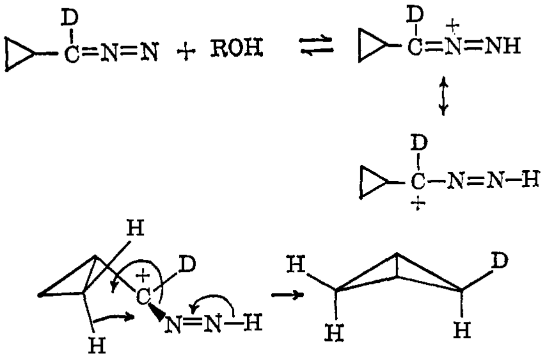
I-*d*   II

The deuterium exchange cannot involve either I or its anion since I is completely converted to its anion by the addition of base, and no exchange is found unless excess base is added. In accord with other studies of the decomposition of tosylhydrazones,[6] the next step probably involves the loss of *p*-toluenesulfinic acid and the formation of diazomethylcyclopropane (III). This might be expected to undergo a facile base-catalyzed hydrogen exchange,[7] and such a process is probably responsible for the exchange which was observed. The further reaction of III cannot involve protonation at carbon by solvent for, if it did, additional deuterium would be introduced when the reaction was carried out in ROD as solvent. Therefore, the reaction cannot involve the cyclopropylcarbinyl cation or any ion derived from it. Since it seems reasonably clear that a proton



III

Scheme I



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[1] This investigation was supported by the Army Research Office, Durham.

[2] L. Friedman and H. Shechter, *J. Am. Chem. Soc.*, **82**, 1002 (1960).

[3] H. M. Frey and I. D. R. Stevens, *Proc. Chem. Soc.*, 144 (1964).

[4] J. A. Smith, H. Shechter, J. Bayless, and L. Friedman, *J. Am. Chem. Soc.*, **87**, 659 (1965); J. Bayless, L. Friedman, J. A. Smith, F. B. Cook, and H. Shechter, *ibid.*, **87**, 661 (1965).

[5] In bicyclobutane, the *exo* hydrogens give a signal at τ 8.56 and the *endo* hydrogens give a signal at τ 9.56. The deuterium content was determined mass spectrometrically.

[6] L. Friedman and H. Shechter, *J. Am. Chem. Soc.*, **81**, 5512 (1959).

[7] *Cf.* H. Zollinger, "Azo and Diazo Chemistry," Interscience Publishers, Inc., New York, N. Y., 1961, p 45.

is in some way involved (for in its absence cyclobutene is the product), and since a mechanism must explain *both* the stereochemistry of the product and the intramolecular transfer of a proton from one carbon to another, the mechanism shown in Scheme I is suggested. Conventionally, the proton is placed at carbon in acid-catalyzed reactions of diazoalkanes. However, there appears to be no reason to believe that the carbon should be more basic than nitrogen. A mechanism of this sort may have other applications to reactions of diazoalkanes.

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Structure of and Bonding in $HCr_2(CO)_{10}^-$. The First Known Linear Electron-Deficient X–H–X Molecular System Stabilized by a Three-Center, One-Electron-Pair Bond[1]

Sir:

We wish to report that a detailed investigation by X-ray, infrared, and nmr methods has revealed the structure of the $HCr_2(CO)_{10}^-$ anion which represents the first known example of a *linear* X–H–X molecular system (where X in this case is the $Cr(CO)_5$ fragment) stabilized by a three-center, one-electron-pair bond (Figure 1).[2]

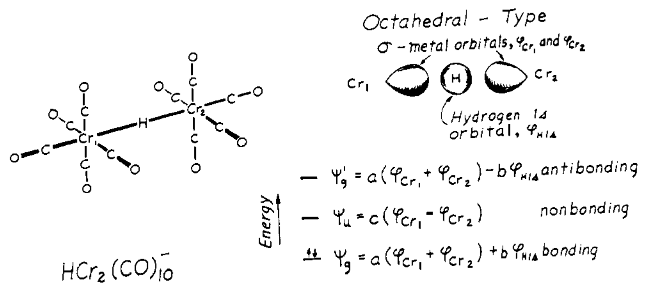

Figure 1. Molecular configuration and MO's for a symmetrical three-center, electron-pair Cr–H–Cr bond. The weighting coefficients *a*, *b*, *c* are taken as positive parameters. The use of such a delocalized three-center bond by which the two electrons in the bonding orbital are distributed over both chromium atoms (as well as the hydrogen atom) results in a closed-shell, electronic configuration for each chromium atom.

The salt $[(C_2H_5)_4N^+][HCr_2(CO)_{10}^-]$ was isolated as the major product in the reduction of $Cr(CO)_6$ by $(C_2H_5)_4NBH_4$ in THF when the gross reaction products were extracted into and crystallized from ethanol. The salt also was isolated from the reaction product of $NaBH_4$ and $Cr(CO)_6$ in THF on addition of an ethanolic solution of $(C_2H_5)_4NBr$. *Anal.* Calcd for $C_{18}H_{21}NO_{10}Cr_2$: C, 41.9; H, 4.1; N, 2.7; O, 31.1; Cr, 20.2. Found: (C, 42.4; H, 4.2; N, 2.7; O, 31.0; Cr, 19.6)[3] and (C, 41.2; H, 4.1; N, 3.1; O, 30.2).[4]

Behrens and Klek[5] first synthesized the dimeric hydrogen decacarbonyldichromate monoanion by oxidation of $Na_2Cr(CO)_5$ with water. Later Behrens and Haag[6] obtained $HCr_2(CO)_{10}^-$ by hydrolysis of $Cr_2(CO)_{10}^{-2}$ which was prepared from the reaction of $Cr(CO)_6$ with $NaBH_4$ in liquid ammonia. These authors[7] reported that the same reactants in THF yielded $Cr_3(CO)_{14}^{-2}$. Haworth and Huff[8] also showed the reduction of $Cr(CO)_6$ with $NaBH_4$ in diglyme to give solutions containing carbonyl chromates.

The infrared spectrum of $[(C_2H_5)_4N^+][HCr_2(CO)_{10}^-]$ in KBr pellet form shows three distinct absorption bands in the terminal carbonyl region at 2033 (m), 1943 (vs), and 1881 (s) cm^{-1}. Since these absorption maxima are essentially unaltered in the infrared spectra of the tetraethylammonium and sodium salts in THF solutions, the molecular configuration of the monohydrogen anion is preserved on dissolution. The observed infrared carbonyl pattern is consistent with a $(OC)_5Cr–H–Cr(CO)_5^-$ system having D_{4h} (or D_{4d}) symmetry. The presence of a chromium-coordinated hydrogen atom was established from the nmr spectrum of $[(C_2H_5)_4N^+][HCr_2(CO)_{10}^-]$ in THF solution which gives a sharp singlet resonance line at τ 29.47 ppm[9] in the region expected for transition metal bonded hydrogen atoms.[10]

A three-dimensional single crystal X-ray investigation of the salt revealed the coordinates of all nonhydrogen atoms. The present isotropic least-squares refinement, based on 829 reflections collected photographically with Mo Kα radiation, gives an unweighted reliability index of 9.8%. The yellow crystals are triclinic with symmetry P1 and with reduced cell parameters a = 6.82, b = 8.91, c = 10.13 Å, α = 78.0°, β = 86.3°, γ = 78.4°; ρ_{obsd} 1.50 g cm^{-3} *vs.* ρ_{calcd} = 1.45 g cm^{-3} for one formula species per unit cell. Although the tetrahedral configuration of the one tetraethylammonium cation (which arbitrarily was placed at the origin of the unit cell with fixed nitrogen coordinates of 0, 0, 0) requires the noncentrosymmetric space group P1, to a first approximation the dinuclear chromium carbonyl anion is disposed about the midpoint of the unit cell with the two halves of the anion related to each other by a center of symmetry.

Although not directly established from the X-ray work, stereochemical and bonding considerations are completely consistent with the hydrogen of $HCr_2(CO)_{10}^-$ being collinear with and equidistant from the two symmetry-equivalent chromium atoms.[11] A sym-

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(1) L. B. H. and L. F. D. gratefully acknowledge the financial support of the X-ray work by the National Science Foundation; the use of the CDC 1604 and 3600 computers at the Computing Center was made possible through the partial support of NSF and WARF through the University of Wisconsin Research Committee.

(2) The symmetrical O–H–O hydrogen bonds and the linear HF_2^- anion are examples of three-center, two-electron-pair bonds.

(3) Shell Development Co. from sample prepared by R. G. H.

(4) Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., from sample prepared by L. B. H. and P. M. T.

(5) H. Behrens and W. Klek, *Z. Anorg. Allgem. Chem.*, **292**, 151 (1957).

(6) H. Behrens and W. Haag, *Naturforsch.*, **14b**, 600 (1959); *Chem. Ber.*, **94**, 312 (1961).

(7) H. Behrens and W. Haag, *ibid.*, **94**, 320 (1961).

(8) D. T. Haworth and J. R. Huff, *J. Inorg. Nucl. Chem.*, 17, 184 (1961).

(9) For the corresponding sodium salt in THF solution, τ 29.17 ppm.

(10) *Cf.* (a) H. D. Kaesz, W. Fellmann, G. R. Wilkes, and L. F. Dahl, *J. Am. Chem. Soc.*, 87, 2753 (1965), and references cited therein; (b) R. J. Doedens and L. F. Dahl, *ibid.*, **87**, 2576 (1965), and references cited therein.

(11) The existence of a symmetrical *bent* hydrogen bridging between two transition metals was ascertained from an X-ray investigation of $HMn_3(CO)_{10}(BH_3)_2$[10a] for which a molecular mirror plane (demanded crystallographically) passes through the hydrogen and relates the two equivalent manganese atoms of the Mn–H–Mn moiety to each other.[12] X-Ray evidence for other similar *bent* three-center electron-pair bonds in which the hydrogen occupies a regular coordination site between two transition metals was acquired for $[(C_5H_5)_2Mo_2H\{P(CH_3)_2\}(CO)_4]$[10b] and