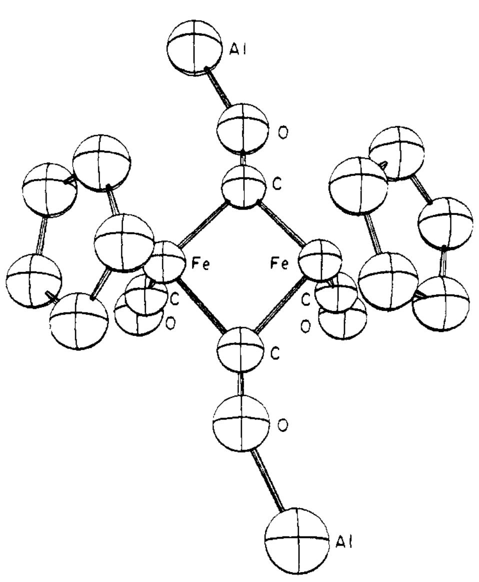

Figure 1. The structure of $Fe_2(\pi\text{-}C_5H_5)_2(CO)_2(COAl(C_2H_5)_3)_2$ viewed along a line which is 20° from the twofold axis. Ethyl groups and hydrogen atoms are not included.

Anal. Calcd for $C_{48}H_{80}Al_4Fe_4O_4$: C_2H_5, 31.14; Al, 10.25; Fe, 21.22; $Fe_4(\pi\text{-}C_5H_5)_4(CO)_4$, 56.61; mol wt, 1052. Found: C_2H_5, 32.30; Al, 10.68; Fe, 20.64; $Fe_4(\pi\text{-}C_5H_5)_4(CO)_4$ (after hydrolysis), 57.26; mol wt (cryoscopy in benzene), 1056.

This adduct displays a single CO stretching frequency at 1527 cm^{-1} (heptane solution) which represents a 125-cm^{-1} decrease from that of the parent carbonyl compound. This large decrease indicates that the 4 moles of aluminum triethyl are coordinated to the oxygens of the bridging carbon monoxide. Both molecular weight and solution infrared data indicate little dissociation. Thus the bridging carbonyl groups of the iron tetramer are significantly more basic than those of the iron dimer. In summary, the present results introduce a new structural feature in carbonyl chemistry and indicate that Lewis basicity may be a general property of the bridging carbonyl ligand.

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of a tetrahedral array of iron atoms with a π-cyclopentadiene at each vertex and bridging carbon monoxide projecting from each face.

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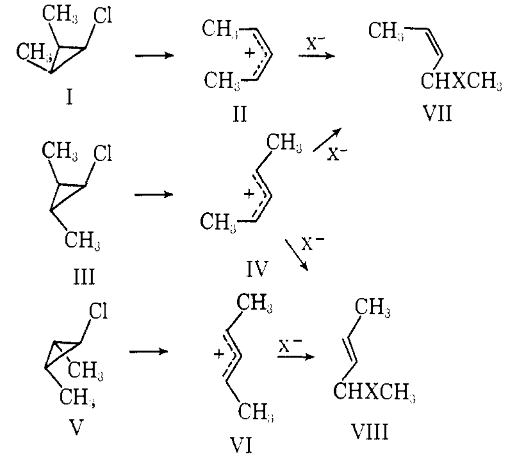
The Stereochemistry of Allyl Cations from the Isomeric 2,3-Dimethylcyclopropyl Chlorides. The Stereomutation of Allyl Cations

Sir:

In 1965 Woodward and Hoffmann predicted that the ring opening of cyclopropyl cations to allyl cations should follow either of two possible disrotatory paths.[1] Following a suggestion by DePuy,[2] the relationship of the mode of opening—outward or inward—to the orientation of the leaving group in a cyclopropyl derivative was examined.[2] Extended Hückel MO calculations indicated that concerted ionization–ring opening should be stereospecific: the groups at C_2 and C_3 *trans* to the leaving group should move outward, and the *cis* groups inward.[2] Specifically, the isomeric 2,3-dimethyl-1-cyclopropyl chlorides[3] should react as shown in Scheme I.

Scheme I



Experimental tests of these predictions have demonstrated their validity.[2,4,5] However, the evidence has been indirect, being based on the interpretation of kinetic data. For example, the tosylates corresponding to I, III, and V acetolyze at 150° with relative rates 1, 65, and 4500, respectively, an order corresponding to the expected steric strain changes in going from reactants to transition states.

Direct, complete stereochemical verification of the Woodward–Hoffmann prediction has been lacking. Under the usual solvolytic conditions, one of the two asymmetric centers present in the intermediate allyl cations (II, IV, and VI) inevitably is lost in going to covalent products (VII and VIII). It is therefore difficult to exclude the possibility that I may react to give IV, which could give VII by preferential reaction at the *trans* center. For this reason we have examined the stereochemistry of the ring-opening ionization of the cyclopropyl chlorides (I, III, and V) in strong acid media, in which the carbonium ion products (II, IV, and VI) are stable and the stereochemical fate of both

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[1] R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 395 (1965). For further calculations on the cyclopropyl cation–allyl cation interconversions, see W. Kutzelnigg, *Tetrahedron Lett.*, 4965 (1967); D. T. Clark and G. Small, *Tetrahedron*, **25**, 13 (1969).

[2] *Cf.* C. H. DePuy, *Accounts Chem. Res.*, **1**, 33 (1968); C. H. DePuy, L. G. Schnack, J. W. Hausser, and W. Wiedemenn, *J. Amer. Chem. Soc.*, **87**, 4006 (1965); S. J. Cristol, R. M. Sequeira, and C. H. DePuy, *ibid.*, **87**, 4007 (1965).

[3] G. L. Closs, *ibid.*, **82**, 5723 (1960).

[4] P. von R. Schleyer, G. W. Van Dine, U. Schollkopf, and J. Paust, *ibid.*, **88**, 2868 (1966); U. Schollkopf, K. Fellenberger, J. Paust, P. von R. Schleyer, T. Su, and G. W. Van Dine, *Tetrahedron Lett.*, 3639 (1967); P. von R. Schleyer, Abstracts, 20th National Organic Chemistry Symposium, Burlington, Vt., June 1967, p 5; U. Schollkopf, *Angew. Chem. Intern. Ed. Engl.*, **7**, 588 (1968).

[5] Bibliographies can be found in ref 4. Several more recent works are: J. A. Landgrebe and C. W. Becker, *J. Org. Chem.*, **33**, 1173 (1968); G. H. Whitham and M. Wright, *Chem. Commun.*, 294 (1967); M. S. Baird and C. B. Reese, *Tetrahedron Lett.*, 1379 (1967); J. W. Hausser and N. J. Pinkowski, *J. Amer. Chem. Soc.*, **89**, 6981 (1967); W. F. Parham and R. J. Spesley, *J. Org. Chem.*, **32**, 924, 926 (1967).

centers determined. Our results verify the Woodward–Hoffmann predictions and indicate that the prior kinetic work has been correctly interpreted.[4]

We prepared carbonium ions from the cyclopropyl chlorides (I, III, and V) in SbF_5SO_2ClF at −100° using vacuum line techniques already described.[6] The species present were clearly stereoisomeric 1,3-dimethylallyl cations, *a different isomer being produced* from each starting material (I, III, and V). These ions are assigned structures II, IV, and VI, respectively, on the basis of the nmr spectra (assignments are given in Figure 1).

The chemical shifts, determined with external TMS reference, agreed well with those reported by Olah for various methyl-substituted allyl cations.[7] Since the chemical shifts of allyl cation methyl groups, whether *cis* or *trans*, are known to be virtually identical,[7] stereochemical assignments were made on the basis of the coupling constants of the C_1 and C_3 hydrogens with the C_2 hydrogen. The *trans* coupling constants should be larger than the *cis*, as is found in other allyl derivatives.[8] Olah has reported the nmr spectrum of a 1,3-dimethylallyl cation (presumed to be the *trans,trans* isomer VI) with J = 14.0 Hz,[7] and Pittman[9] more recently reported its preparation with J = 13.8 Hz. This spectrum (except for the solvent band) is identical with that from V (Figure 1); we find J = 14.0 Hz (the C_1 and C_2 hydrogens appear at τ 0.12 and 1.76, respectively). The ion from III can easily be assigned the *cis,trans* structure IV since the C_2 hydrogen atom (τ 1.69) is coupled to the two nonequivalent vinyl hydrogens at C_1 (τ 0.03) and C_3 (τ −0.61) with J = 9.0 and 14.0 Hz. As expected, the *cis,cis* ion II formed from I has only two kinds of vinyl hydrogens (τ 1.70 and 0.00) with J = 9.0 Hz. The methyl doublet (J is about 5.7 Hz for all three ions) appears at τ 6.62, 6.54, and 6.42 for VI, IV, and II, respectively. Apparently, the shifts of the methyl peaks in IV (*cis,trans*) are very close and only one doublet is observed. The small downfield and upfield peaks in the II (*cis,cis*) spectra are due to a small amount of IV (*cis,trans*) probably formed by local overheating during preparation of the ion.

These results provide convincing evidence that ring opening is concerted with ionization and follows the Woodward–Hoffmann predictions:[1,2] I → II, III → IV, and V → VI. The formation of three individual 1,3-dimethylallyl cation isomers from the three isomeric starting materials excludes the intermediacy of cyclopropyl cations, for it would be expected that the cyclopropyl ion produced from either I or V would open to give largely VI, perhaps accompanied by some II. No evidence for the presence of cyclopropyl cations was found in the spectra we have observed. Our results also exclude the alternative bridged chloronium ion mechanism of Olah and Bollinger,[7] which could not lead to stereochemical integrity.

Although stable for long periods at low temperatures, II (*cis,cis*) was converted cleanly to IV (*cis,trans*) at −10° with a half-life of about 10 min and IV (*cis,trans*) was further isomerized to VI (*trans,trans*) at +35° with about the same half-life. Rates of the allyl cation isomerizations were followed by measuring the increase or decrease of the area of the downfield vinyl hydrogen of the *cis,trans* isomer (IV). Analysis of the data gave the following activation parameters

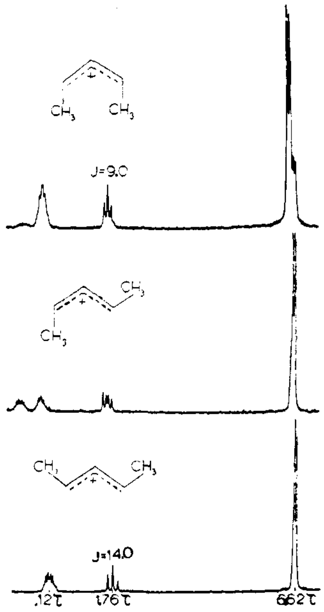

Figure 1.

	E_a, kcal/mol	log A
II (*cis,cis*) ⟶ IV (*cis,trans*)	17.5 ± 1.0	11.8 ± 0.8
IV (*cis,trans*) ⟶ VI (*trans,trans*)	24.0 ± 1.0	14.0 ± 1.0

The direction of the observed sequence II → IV → VI provides additional support for the stereochemical assignments of the dimethylallyl cations because of their expected stabilities. The difference in stabilities of II and IV, 6.5 kcal/mol, is in good agreement with 6.0 kcal/mol predicted from naphthalene models.[4]

We have considered three pathways for the isomerization: (a) rotation around only one of the allyl bonds at a time; (b) recombination to the allyl halide, rotation, then dissociation; and (c) disrotatory closure to the cyclopropyl cation as intermediate or transition state, followed by disrotatory opening in the opposite sense.

While paths a and b allow stepwise conversion of II → IV → VI *as found*, path c would require II to be converted directly to VI, and IV would remain IV. Path c is therefore ruled out. Experiments to distinguish paths a and b are in progress.

The large difference between our activation parameters and Olah's may be due to differences in the substitution of the allyl ions or the fact that Olah's observed spectral change was in fact due to a change in chemical shift between the methyls with temperature, and has no relation to any kinetic process. Further investigation should clarify this situation.

Acknowledgments. This work was supported at both Yale and Princeton by grants from the National Science Foundation, and at Princeton by a Petroleum Research

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[6] M. Saunders and E. L. Hagen, *J. Amer. Chem. Soc.*, **90**, 2436 (1968).

[7] H. A. Olah and M. Bollinger, *ibid.*, **90**, 6082 (1968).

[8] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 242.

[9] C. U. Pittman, *Chem. Commun.*, 122 (1969).

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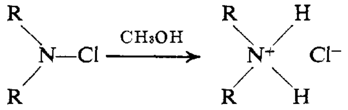
The Discrete Existence of Singlet and Triplet Nitrenium Ions[1]

Sir:

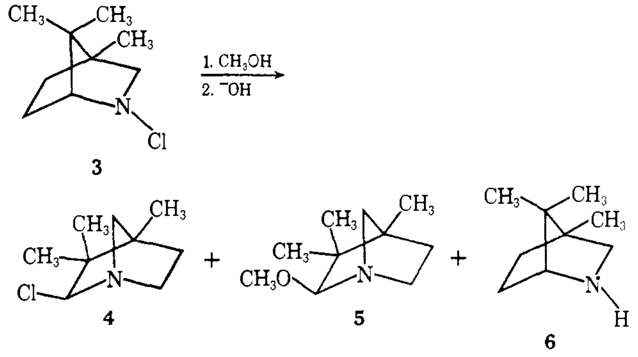
Although the principles of nitrenium ion (divalent electron-deficient nitrogen) theory have proven invaluable in predicting the reaction products which result from the heterolytic cleavage of the N–X bond,[2] no evidence existed to indicate whether a nitrenium ion could have a discrete existence. We wish to present preliminary findings which not only show that divalent electron-deficient nitrogen species are true intermediates, but also indicate that *nitrenium ions exist in both singlet and triplet spin states.*

When N-chloramines (**1**) are solvolytically ionized, small amounts of secondary amine salts (**2**) are often observed among the reaction products.[1b] For instance,



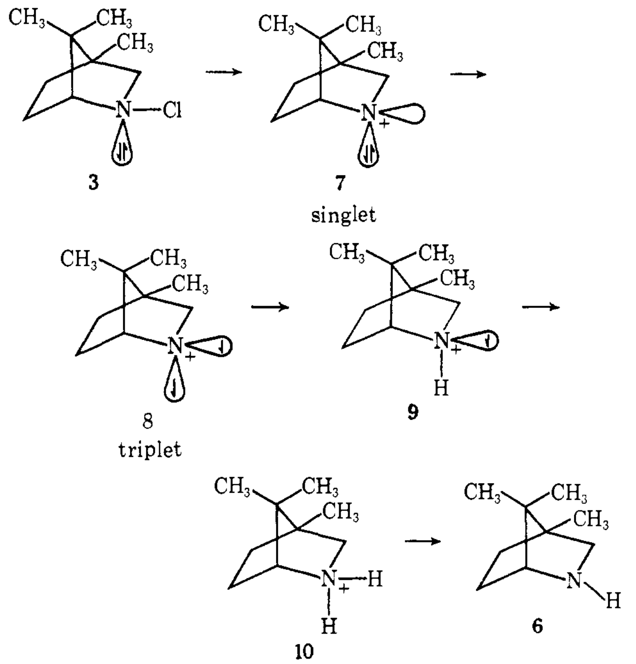
1 **2**

in the methanolysis of 4,7,7-trimethyl-2-chloro-2-azabicyclo[2.2.1]heptane (**3**) we found 59% **4**, 20% **5**, and 7% **6**. Although the formation of **4** and **5** was to be expected on the basis of nitrenium ion theory, the presence of **6** appeared to be anomalous because **6** is not the type of product expected from a positively charged species.[1b]



3 **4** **5** **6**

However, an important factor which requires consideration is that the nitrenium ion differs from most positive ions of interest to the organic chemist in that it possesses a nonbonding pair of electrons. Thus an attractive rationale for the formation of **6** would involve initial ionization of **3** to give **7**[3] which by virtue of its mode of generation would be in the singlet state. Spin inversion could then occur, converting **7** into the triplet species **8**. This triplet might be expected to behave more like a nitrogen cation radical than like a carbonium ion or singlet nitrenium ion. Since nitrogen cation radicals are excellent hydrogen abstractors[4] and methanol is a good source of hydrogen atoms, **8** would be expected to react with methanol to yield **9**. A second hydrogen abstraction from methanol by **9** would yield **10** which on neutralization with base would give **6**.



3 **7** singlet **8** triplet **9** **10** **6**

In order to test the validity of this hypothesis we investigated the effect of heavy atom solvents on the product composition observed in the methanolysis of **3**. Since heavy atoms are known to enhance the probability of singlet to triplet inversion through coupling of spin and orbital angular momenta,[5,6] the amount of **6** should increase in the presence of heavy atoms if our hypothesis is correct. Table I presents the results of our investigation. As shown in Table I the presence of heavy atoms has a very dramatic effect on the product ratios. A comparison of the products from methanol–bromoform and pure methanol showed that the presence of bromoform resulted in a 500-fold change in product ratio! Smaller effects were noted for chloroform (180-fold change) and carbon tetrachloride (50-fold change). *p*-Dibromobenzene also showed a very significant heavy atom effect when the relative percentage of heavy atoms present in the methanol-*p*-dibromobenzene solvent was taken into consideration.

The change in product ratios cannot be attributed to an effect of solvent polarity since methanol–hexane, the least polar solvent mixture, gave a product mixture very

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[1] Paper IX in a series on the chemistry of nitrenium ions. For the preceding papers see (a) P. G. Gassman and A. Carrasquillo, *Chem. Commun.*, 495 (1969); (b) P. G. Gassman and R. L. Cryberg, *J. Am. Chem. Soc.*, **91**, 2047 (1969).

[2] P. G. Gassman and D. K. Dygos, *ibid.*, **91**, 1543 (1969); P. G. Gassman, G. Campbell, and R. Frederick, *ibid.*, **90**, 7377 (1968), and references contained therein.

[3] The filled and empty orbitals in structures **3**, **7**, **8**, and **9** are not intended to imply any stereochemical relationships.

[4] Nitrogen cation radicals are considered to be the reactive hydrogen-abstracting intermediates in the Hofmann–Löffler–Freytag reaction: M. Wolff, *Chem. Rev.*, **63**, 55 (1963).

[5] C. D. Dijkgraaf and G. J. Hoijtink, *Tetrahedron Suppl.*, **2**, 179 (1963). See also J. N. Murrell, "The Theory of the Electronic Spectra of Organic Molecules," John Wiley & Sons, Inc., New York, N. Y., 1963, pp 294–300.

[6] A. G. Anastassiou, *J. Am. Chem. Soc.*, **88**, 2322 (1966).