168.2°) and all intermediates were assayed for deuterium content by n.m.r. on a Varian A-60. The isotopic purity of the CD_3 group is estimated to be 99.5 atom %.

Deamination of the 3,3,3-d_3-1-aminopropane was carried out under the conditions of Roberts.[7,8] The gaseous products evolved were collected in a −140° trap and separated by gas chromatography.[9] The cyclopropane fraction was analyzed by low voltage mass spectrometry[10] on a Consolidated Electrodynamics Model 21-103C mass spectrometer. The cyclopropane (after correction for normal isotopic abundances) was found to consist solely of 43 ± 1% cyclopropane-d_2 and 57 ± 1% cyclopropane-d_3.

It has previously been assumed that the rearranged 1-propanol observed in the deamination of 1-aminopropane was derived from a rearranged 1-propylcarbonium ion.[5,8] The 1-propylcarbonium ion was also believed to be the immediate precursor of the cyclopropane formed in "deoxideation" and deamination reactions,[5] the rearranged ion leading to formation of some cyclopropane-d_1 on "deoxideation" of 1,1-d_2-1-propanol.[5] Implicit in these assumptions was the assumption that the rearranged carbonium ion undergoes the same reactions as does the unrearranged ion, and it has been implied that the loss of deuterium on formation of cyclopropane in the above "deoxideation" should mirror the extent of rearrangement observed in the formation of 1-propanol in deaminations.[5] A straightforward application of these principles to our system leads to the prediction that no more than 6% cyclopropane-d_3 should be formed if there is no isotope effect on deprotonation,[5] and no more than 31% for k_H/k_D as large as 7. Since the observed fraction of cyclopropane-d_3 is far in excess of this amount, the above principles would not appear to be valid.

The above experimental result can readily be accommodated by our mechanism,[1] which involves equilibration of the initially formed I with isomeric methyl-bridged ions. By invoking an isotope effect for proton loss of from ca. 2.7 to 3.0[11] one can arrive at the observed ratios of cyclopropane-d_2 and -d_3.[12]

A variation of our mechanism has recently been suggested to us,[13] however, which we feel is important enough to merit separate discussion. This mechanism involves the equilibration of hydrogen-bridged ions, I, II, III, etc., by a process which can be viewed as the (hindered) rotation of quasi-methyl groups. If the lifetimes of the bridged ions are sufficiently long, the deuterium and hydrogen will be statistically distributed among the five positions involved. Loss of the bridging hydrogen or deuterium would lead to cyclopropane-d_3 or -d_2,[14] respectively, and solvolytic opening to (rearranged) 1-propanols.[15] With longer

lifetimes, subsequent rearrangement to involve the remaining two hydrogens can occur via a transition state resembling our methyl-bridged ion.

The Wiberg mechanism may be considered to involve equilibration of hydrogen-bridged ions via methyl-bridged ions which differ from those postulated by us in that they have a "memory" (provided by a barrier to internal rotation) as to which side the hydrogen was originally bridged on. Although one would expect some differences between the two, most of these are small enough that experimental differentiation is not possible at present.[16]

Irrespective of the intimate details of the above mechanisms, it would appear that 1,3-rearrangements in the 1-propyl system are more readily interpreted as occurring via protonated cyclopropane intermediates than via equilibration of primary carbonium ions, but that great care must be exercised in extrapolation of these results to related systems (and vice versa).[17]

(16) For example, one can also rationalize the different extents of rearrangement of 1-propanol[15] *within the observed experimental error* via our mechanism.

(17) See, for example, G. J. Karabatsos and J. D. Grahm, *J. Am. Chem. Soc.*, **82**, 5250 (1960).

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(8) G. J. Karabatsos and C. E. Orzech, Jr., *J. Am. Chem. Soc.*, **84**, 2838 (1962).

(9) R. L. Baird and A. Aboderin, *Tetrahedron Letters*, 235 (1963).

(10) K. Biemann, "Mass Spectrometry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, Chapter 5.

(11) In view of the observed isotope effect (k_H/k_D = 1.5) on the protonation of cyclopropane,[1] it is not unreasonable to expect an isotope effect of this magnitude on the reverse reaction.
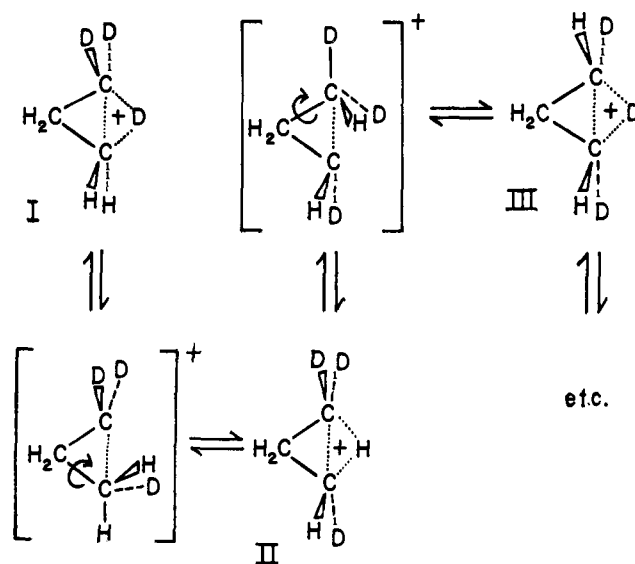
(12) The lower isotope effect is for proton transfers involving the methyl-bridged ions and the higher one for those involving the hydrogen-bridged ions.

(13) Private communication from Professor K. B. Wiberg.

(14) In this case an isotope effect for deprotonation of k_H/k_D = 2.0 would account for the product ratio.

(15) This mechanism also affords an explanation for the different extents of rearrangement observed in the 1-propanol obtained on deamination of labeled 1-aminopropane,[7,8] since one would expect more mixing of hydrogens[8] than of carbons[7] in an intermediate analogous to I.

Cyclobutane Compounds. I. Formation of a Four-Membered Ring during the Electrophilic Addition of Hydrogen Bromide to Allene

Sir:

Electrophilic additions of HX compounds to allene are generally considered to occur according to Markovnikov's rule[1,2] leading to 2-substituted propenes and/or 2,2-disubstituted propanes.

$$CH_2=C=CH_2 \xrightarrow{HX} CH_3-CX=CH_2 \xrightarrow{HX} CH_3-CX_2-CH_3$$
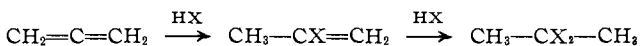
(1) A. A. Petrov and A. V. Fedorova, *Uspekhi Khim.*, **33**, 1, 3 (1964).

(2) T. L. Jacobs and R. N. Johnson, *J. Am. Chem. Soc.*, **82**, 6397 (1960).
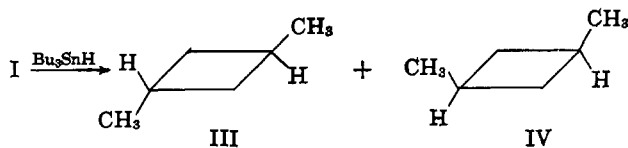
Examples are the hydration of allene in the presence of sulfuric acid to yield acetone,[3] the addition of hydrogen fluoride to yield 2,2-difluoropropane,[4] and the bismuth trichloride catalyzed addition of hydrogen chloride to form a mixture of 2-chloropropene and 2,2-dichloropropane.[2]

We have now observed that the ionic addition of hydrogen bromide to allene leads to a more complex product mixture. Reaction of equimolar amounts of hydrogen bromide and allene at $-80°$ produced an adduct mixture that contained four components according to capillary g.l.c. Fractional distillation of this mixture afforded the conventional adducts 2-bromopropene and 2,2-dibromopropane in the distillate and a semisolid residue. Repeated recrystallization of the latter from cold pentane and subsequent sublimation yielded a colorless, crystalline material, m.p. 54–55°.

Elemental analysis of this solid suggested the empirical formula $(C_3H_5Br)_n$. *Anal.* Calcd. for C_3H_5Br: C, 29.78; H, 4.16; Br, 66.05. Found: C, 29.81; H, 4.27; Br, 66.05. Its mass spectrum showed the characteristic 1-2-1 pattern (m/e 240-242-244, respectively) of a dibromo compound[5] for the parent peak, thus establishing the formula, $C_6H_{10}Br_2$ (calcd. mol. wt. for $C_6H_{10}Br_2$, 242). The compound had, therefore, either an acyclic unsaturated or a cyclic structure. Its infrared spectrum was very simple [bands at 3.45, 6.92, 7.10, 7.29, 7.9, 8.63, 9.16 μ (in CCl_4) and 12.62 μ (in KBr) describe the entire spectrum] and did not indicate any vinylic hydrogen atoms. This was confirmed by the n.m.r. spectrum which showed only two singlet peaks at $\delta = 2.13$ and 3.19 p.p.m. (CCl_4 as solvent, TMS as internal standard), in the ratio of 3:2 (6:4), respectively. Consideration of all these data limited the possible structures for our allene–hydrogen bromide adduct to the two alternatives *trans*-1,3-dibromo-1,3-dimethylcyclobutane (I) and *trans*-1,4-dibromo-2,3-dimethylbutene-2 (II).[6]

I   II
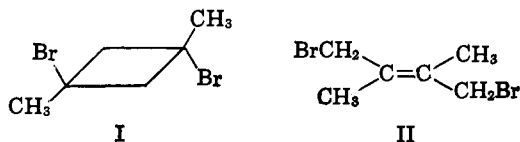
Reduction of our dibromo compound with tributyltin hydride favored the cyclic structure I since it produced in good yield a mixture of the isomeric 1,3-dimethylcyclobutanes III and IV.[7]

III   IV

The mass spectrum of the isomer mixture exhibited a parent peak of m/e 84 (calcd. mol. wt. of III or IV, 84). Its infrared spectrum showed all the bands—although in a slightly different intensity ratio—which were present in the published spectrum of a similar mixture of III and IV, obtained from the hydrogenation of 1,3-dimethylenecyclobutane.[8] The n.m.r. spectrum of the isomer mixture had a more complex pattern than one would expect for tetramethylethylene, the corresponding reduction product of II which could fit our mass spectrometric results.

The fourth component which was detected by g.l.c. in the hydrogen bromide–allene adduct mixtures has not yet been unambiguously identified. In view of the similarity of its retention time to that of I, we believe it to be an isomer of I, possibly the corresponding *cis* compound.

Therefore, on the basis of the data presented above, it appears that the ionic addition of hydrogen bromide to allene leads to the following over-all result.[9]
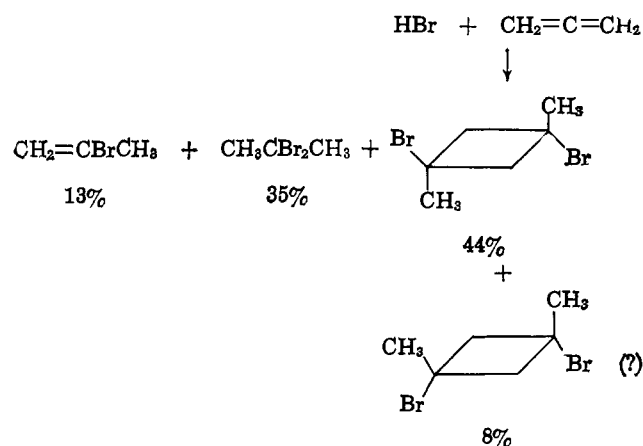
While several reports have appeared on the thermal dimerization of allene,[10-15] the present case is, to our knowledge, the first example of a cationically induced cyclodimerization. Unlike the thermal reaction which brings about a predominantly 1,2–1,2 dimerization of allene,[14] hydrogen bromide addition at low temperatures causes a formal 1,2–2,1 dimerization.

Regarding the reaction mechanism, we were able to show that it is not a simple dimerization of 2-bromopropene. Reaction of the latter with hydrogen bromide under the conditions of the allene addition reaction led to 2,2-dibromopropane exclusively. It was also established that our cycloaddition is indeed an

(3) G. Gustavson and N. Demjanoff, *J. prakt. Chem.*, [2] **88**, 201 (1888).

(4) P. R. Austin, U. S. Patent 2,585,529 (1952).

(5) J. H. Beynon, "Mass Spectrometry and Its Application to Organic Chemistry," Elsevier Publishing Co., Amsterdam, The Netherlands, 1960, p. 299.

(6) The corresponding *cis* isomer can be ruled out since it was reported to be a liquid, while the reported melting point of the *trans* isomer is 47–47.5°. See O. J. Sweeting and J. R. Johnson, *J. Am. Chem. Soc.*, **68**, 1057 (1946), and literature cited there.

(7) Reduction reactions of organic halides with organotin hydrides have been reported to occur by a free-radical mechanism [H. G. Kuivila, L. W. Menapace, and C. R. Warner, *ibid.*, **84**, 3584 (1962)]. It is, therefore, not surprising that the reduction of the *trans* dibromide III led to a mixture of the corresponding hydrocarbons III and IV.
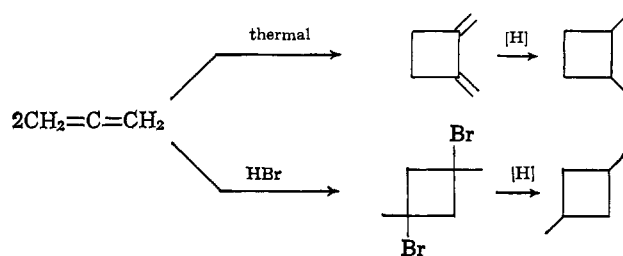
(8) F. F. Caserio, S. H. Parker, R. Piccolini, and J. D. Roberts, *ibid.*, **80**, 5507 (1958).

(9) The product distribution is based on g.l.c. analysis.

(10) S. Lebedev, *J. Russ. Phys. Chem. Soc.*, **45**, 1357 (1913).

(11) R. N. Meinert and C. D. Hurd, *J. Am. Chem. Soc.*, **52**, 4540 (1930).

(12) K. Alder and O. Ackermann, *Chem. Ber.*, **87**, 1567 (1954).

(13) A. T. Blomquist and J. A. Verdol, *J. Am. Chem. Soc.*, **78**, 109 (1956).

(14) J. K. Williams and W. H. Sharkey, *ibid.*, **81**, 4269 (1959).

(15) B. Weinstein and A. H. Fenselan, *Tetrahedron Letters*, **22**, 1463 (1963).

ionic reaction since no cyclic product was observed in the free-radical addition of hydrogen bromide to allene,[16] while the presence of an inhibitor did not prevent the formation of I.

Experiments are under way to examine the reaction mechanism in more detail and to define the scope of this novel cyclization with regard to other electrophilic reagents, other unsaturates, and possible crossover experiments between different unsaturates. The results of these investigations and the chemistry of the 1,3-dihalocyclobutanes obtained will be discussed in forthcoming papers.

Acknowledgment.—The author is indebted to Dr. G. G. Wanless for providing the mass spectrometric data and Mr. A. M. Palmer for valuable technical help.

(16) K. Griesbaum, A. A. Oswald, and D. N. Hall, *J. Org. Chem.*, in press.

Central Basic Research Laboratory   Karl Griesbaum
Esso Research and Engineering Company
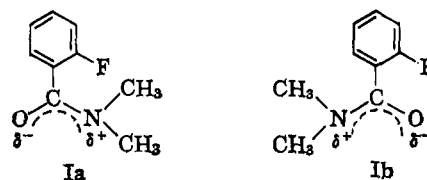Linden, New Jersey

The Question of Long/Range Spin-Spin Coupling through Space: H–F Splitting over Six Bonds[1]

Sir:

It has been noted that long-range spin–spin couplings, namely over more than three consecutive bonds, are not necessarily negligibly small.[2] Special geometries are required in order for the splitting to be observable,[3] but proximity of the nuclei is not always required. Thus, four-bond H–H coupling has been observed by Meinwald[4] between an *endo*-2-proton and the 7-proton *anti* to it, which are further apart than the corresponding *exo*-2-proton and the 7-proton *syn* to it in a bicyclo-[2.2.1]heptane skeleton; the geometry, however, is such as to favor four-bond H–H coupling.[3] On the other hand, Roberts, who has reported a number of cases of H–F spin–spin coupling over four and five bonds,[5,6] has suggested that possibly the five-bond H–F couplings observed by him may take place through space rather than through the bonds. Spin–spin coupling between H and F nuclei over more than five bonds seems to be unknown.

The proton n.m.r. spectrum of *o*-fluoro-N,N-dimethylbenzamide shows the following signals: an aromatic multiplet centered at τ 2.75 p.p.m. area = 4), a methyl singlet at τ 6.97 p.p.m. (area = 3), and a methyl doublet at τ 7.22 p.p.m. (area = 3). The nonequivalence of the two N-methyl groups arises from restricted rotation around the C–N bond, of which many examples are known.[7]

The conformations of this amide which maximize resonance interactions could be flat, all the atoms (except the methyl hydrogens) being coplanar as in Ia and Ib. Although these forms would be consistent

(1) Work supported by grant G-23705 from the National Science Foundation.

(2) Only the most pertinent references will be given.

(3) A. Rassat, C. W. Jefford, J. M. Lehn, and B. Waegell, *Tetrahedron Letters*, No. 5, 233 (1964).

(4) J. Meinwald and Y. C. Meinwald, *J. Am. Chem. Soc.*, **85**, 2514 (1963).

(5) D. R. Davis, R. P. Lutz, and J. D. Roberts, *ibid.*, **83**, 246 (1961).

(6) M. Takahashi, D. R. Davis, and J. D. Roberts, *ibid.*, **84**, 2935 (1962).

(7) (a) W. D. Phillips, *J. Chem. Phys.*, **23**, 1363 (1955); (b) J. C. Woodbrey and M. T. Rogers, *J. Am. Chem. Soc.*, **84**, 13 (1962); (c) The magnitude of the barrier to rotation in this system and related ones will be discussed separately.

Ia   Ib

with the observed n.m.r. spectrum, it seems more reasonable to assume that, due to nonbonded and electrostatic repulsive forces, the dimethylamido group is flat but turned out of the plane of the benzene ring.[8] In order to estimate the interplanar angle θ (between the benzene ring and the dimethylamido group) acetophenone derivatives were used as models. Application of the method of Braude and Nachod[9] to the values of the extinction coefficients reported by Horton and Robertson[10] for the primary absorption bands of *o*- and *p*-fluoroacetophenone indicates that the angle θ is *ca.* 25°. Consequently contributions from the resonance form II must be small and the system can be considered as rotating sufficiently fast between

II
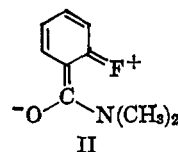
the limiting structures IIIa and IIIb, at room temperature, to result in a n.m.r. spectrum which is the average of the two forms. On the average, then, one methyl

IIIa   IIIb
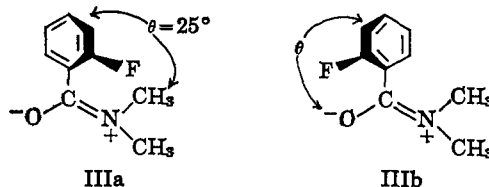
group is closer to the π-electron cloud of the aromatic ring and to the *o*-fluorine than the other one, and is constrained by the *ortho* substituent to lie above (or below) the plane of the phenyl ring.

In trying to assign the methyl resonances the anisotropy of both the phenyl ring and the carbonyl group must be considered and assignment on theoretical grounds becomes questionable. It seemed that an unsymmetrically N,N-disubstituted benzamide, in which one of the methyl groups had been replaced by a bulkier group, might exist in a preferred conformation. Such a system would, then, enable unequivocal assignment of the methyl resonances in *o*-fluoro-N,N-dimethylbenzamide. The compound prepared for this purpose was *o*-fluoro-N-cyclohexyl-N-methylbenzamide. Its proton n.m.r. spectrum shows, in addition to the aromatic and cyclohexyl multiplets, two discrete methyl resonances, 0.2 p.p.m. apart, the high field one being a doublet with J = 1.3 c.p.s. The integrated areas, in this case, are in the ratio of 3:2, the high field resonance having the larger area. This can be interpreted as being due to the rotational isomers IVa and IVb; it seems reasonable to assume that IVa will be the energetically preferred form. Since the high

(8) This argument is strengthened by current studies in ring-substituted benzamides to be published separately.

(9) E. A. Braude and F. C. Nachod, "Determination of Organic Structures by Physical Methods," Academic Press, Inc., New York, N. Y., 1955, pp. 173–174.

(10) W. J. Horton and D. E. Robertson, *J. Org. Chem.*, **25**, 1016 (1960).