

indicates that coupling is weaker in the latter ion. Charge density differences on the  $sp^2$  carbon atom in ions I and II could be responsible for this behavior.

Despite the long-recognized ability of fluorine to form  $p-p(\pi)$  double bonds (as compared to chlorine and bromine), any manifestations of this behavior, especially in  $SN1$  type reactions, have been nullified by its inductive effect.<sup>5</sup> The stabilization accrued to carbonium ions with fluorine attached directly to the  $sp^2$  carbon attests to its great resonance-electron-donating ability despite its high electronegativity.<sup>6</sup> Further studies of other carbonium ions with fluorine attached directly to the positive center are now in progress.

**Acknowledgment.** The authors wish to express their gratitude to the National Science Foundation for support of this research and for a grant to Western Reserve University for the acquisition of nmr equipment.

(5) See J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 168, and references therein cited.

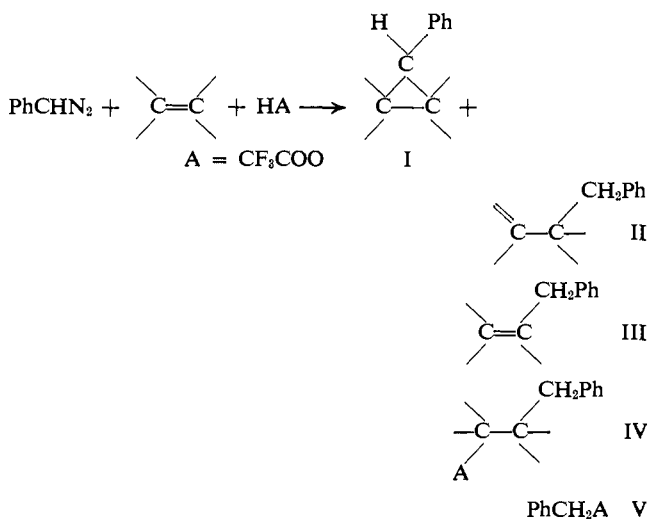
(6) In contrast to the stability of ion I in solution at  $-60^\circ$ , benzyl cation undergoes rapid polymerization at this temperature.

George A. Olah, Chris A. Cupas, Melvin B. Comisarow  
Department of Chemistry  
Western Reserve University, Cleveland, Ohio 44106  
Received November 5, 1965

### Formation of Cyclopropanes in Acid-Catalyzed Decomposition of Phenyl diazomethane in Olefins<sup>1</sup>

Sir:

Our interest in the mechanism of carbenoid cyclopropane formation<sup>2</sup> led us to examine the acid-catalyzed decomposition of phenyl diazomethane in olefinic solvents. Typical experiments involved the addition of trifluoroacetic acid to solutions of phenyl diazomethane in olefins at  $-70^\circ$ .<sup>3</sup> Thermal decomposition of phenyl diazomethane was shown to be negligible under these conditions. Phenylcyclopropanes (I), benzylated olefins (II and III), and trifluoroacetates of structure IV constituted the main products besides 30–40% benzyl



(1) This work was supported by National Science Foundation Grant GP-4214.

(2) Cf. G. L. Closs and R. A. Moss, *J. Am. Chem. Soc.*, **86**, 4042 (1964); G. L. Closs and J. J. Coyle, *ibid.*, **87**, 4270 (1965).

(3) Although trifluoroacetic acid was studied in greater detail, other acids such as formic acid and anhydrous hydrochloric acid gave qualitatively similar results.

trifluoroacetate (V). Table I lists the product distribution obtained from reactions with olefins of various substitution patterns.<sup>4</sup> It should be noted that major fractions of cyclopropanes are formed only from olefins containing no tertiary carbon atoms. Furthermore, additions to *cis*- and *trans*-2-butene are completely stereospecific, leading to cyclopropanes in which the alkyl groups have the same geometrical relationship as in the olefins. The trifluoroacetates IV, however, are mixtures of *threo* and *erythro* isomers.<sup>5</sup>

Table I. Product Distribution

Olefin	Product type (per cent of total I-IV)			
	I	II	III	IV
2,3-Dimethyl-2-butene	1	98	...	1
Isobutene	2	64	20	14
<i>trans</i> -2-Butene	61	8 <sup>a</sup>	...	31 <sup>b</sup>
<i>cis</i> -2-Butene	51 <sup>c</sup>	21	6	22 <sup>b</sup>
1-Butene	38	32 <sup>a</sup>	...	30

<sup>a</sup> This olefin may contain small amounts of III, due to imperfect glpc separation. <sup>b</sup> Mixtures of *threo* and *erythro* isomers. <sup>c</sup> Mixture of *syn* and *anti* isomers formed in a ratio of 1.2:1.

The use of excess deuteriotrifluoroacetic acid in the reaction with *trans*-2-butene led to incorporation of 21 atom % deuterium in I while II, IV, and V contained over 80%.<sup>6</sup> Similarly, when phenyldiazomethane- $\alpha$ -*d* was allowed to react with unlabeled acid, the deuterium content of I remained over 85%.

Mechanism studies on the acid-catalyzed decomposition of diphenyldiazomethane in polar solvents have established rate-limiting proton transfer as the first step.<sup>7</sup> The conjugate acid of the diazo compound, usually formulated as diphenylmethyldiazonium ion, is assumed to lose nitrogen in a fast step, yielding benzhydryl cation. An equivalent reaction scheme, however, cannot account for formation of I and the remaining products. If either benzyldiazonium ion or benzylcarbonium ion were precursors of the cyclopropane, the deuterium content of I as produced in the reaction with deuteriotrifluoroacetic acid should at least be one-half that of II and IV, and, most likely, should be significantly larger because of the expected isotope effect in the deprotonation step.<sup>8</sup> We therefore suggest that in the nonpolar medium of our experiments the diazo carbon functions as acceptor in hydrogen-bond formation with the acid, but that complete proton transfer is slow or comparable in rate with subsequent steps. Reaction of the olefin solvent with the hydrogen-bonded complex VI may lead either to I via the transition state VII or, through a less symmetrical transition state, to the ion pair VIII which then collapses to give

(4) The cyclopropanes were identified by direct comparison with previously prepared samples.<sup>2</sup> The trifluoroacetates IV were saponified, and the alcohols were compared with samples synthesized by standard methods. The structures of the olefins are fully supported by their infrared, nmr, and mass spectral data.

(5) The compositions of the isomer mixtures obtained from the two olefins are not identical. Configurations have not yet been assigned.

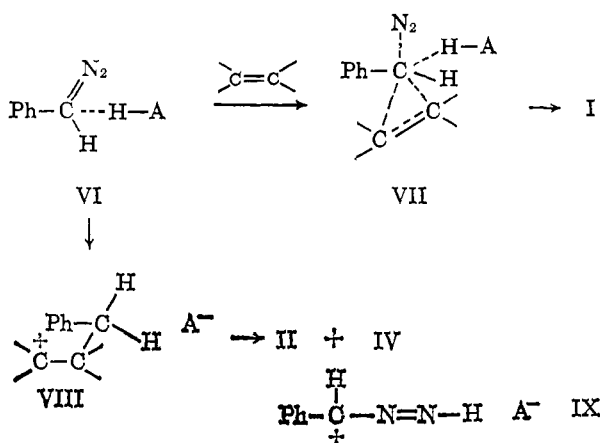
(6) The deuterium incorporation changes somewhat with the excess of acid employed, although the ratios of deuterium content of the various products remains practically constant. The trifluoroacetic acid was better than 95% deuterated as determined by nmr.

(7) D. Bethell and J. D. Callister, *J. Chem. Soc.*, 3801, 3808 (1963), and earlier references cited therein.

(8) A. A. Aboderin and R. L. Baird, *J. Am. Chem. Soc.*, **86**, 2300 (1964), estimate  $k_H/k_D$  for the loss of a proton from a bridged ion as  $\sim 3$ . The stereospecificity of the reaction requires that the ion produced from the addition of benzyl cation to the olefin would be bridged.

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.



(9) A. P. Sloan Fellow, 1962-1966.

G. L. Closs,<sup>9</sup> R. A. Moss, S. H. Goh  
Department of Chemistry, The University of Chicago  
Chicago, Illinois 60637  
Received November 23, 1965

### On the Mechanism of the Conversion of Cyclopropanecarboxyaldehyde Tosylhydrazone to Bicyclobutane<sup>1</sup>

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,<sup>2</sup> whereas in the presence of alcohols it is bicyclobutane.<sup>3,4</sup> The normal reaction of the cyclopropylcarbinyl carbene appears to be rearrangement to cyclobutene.<sup>4</sup> It has been suggested that the role of the alcohol in the bicyclo-

(1) This investigation was supported by the Army Research Office, Durham.

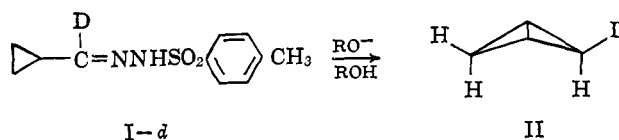
(2) L. Friedman and H. Shechter, *J. Am. Chem. Soc.*, **82**, 1002 (1960).

(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).

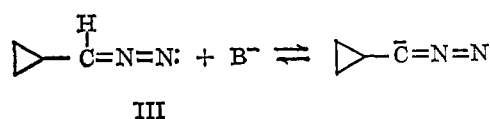
butane formation is to provide a proton source which will convert diazomethylcyclopropane to the diazonium ion which then may lose nitrogen and lead to bicyclobutane *via* the "bicyclobutonium" ion.<sup>4</sup>

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.<sup>5</sup> When the reaction was



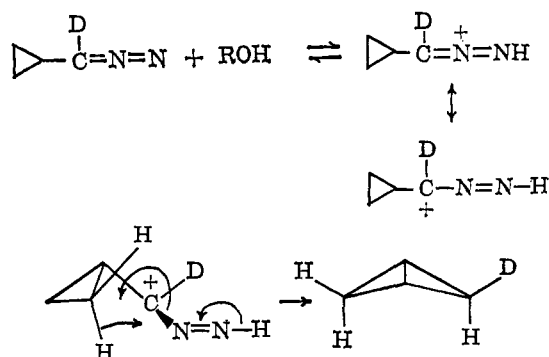
carried out using an excess of base, the bicyclobutane contained significantly less deuterium. Similarly, when unlabeled I was heated with an excess of base in ethylene glycol-*d*<sub>2</sub> the product was the same as that obtained from I-*d*. Finally, when unlabeled I was treated with a deficiency of base in deuterium-labeled solvent, no significant amount of deuterium was found in the product.

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,<sup>6</sup> the next step probably involves the loss of *p*-toluenesulfonic acid and the formation of diazomethylcyclopropane (III). This might be expected to undergo a facile base-catalyzed hydrogen exchange,<sup>7</sup> 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

### Scheme I



(5) In bicyclobutane, the *exo* hydrogens give a signal at  $\tau$  8.56 and the *endo* hydrogens give a signal at  $\tau$  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.