

ether solution causes quantitative conversion to the hydrazone **6**, injection of a benzene solution of **4** into a hot (200°) evacuated Pyrex chamber and collection of the products in a trap at -196° give a mixture of 60% of hydrazone **6** and 40% of pure *cis,cis*-octa-2,6-diene (**10**). Similarly, the trans azo compound **5** gives pure *cis,trans*-octa-2,6-diene (**11**) as the hydrocarbon product. The potential ring-closure products, the dimethylbicyclo[2.2.0]hexanes **13**, **14**, or **15**, are not observed. Moreover, control experiments (Table I) show that neither any of the hydrocarbons **13**–**15**

Table I. Per Cent Yields^a of C₈H₁₄ Hydrocarbons in the Vapor-Phase Pyrolysis of **4** and **5**

Reactant	Products					
	10	11	12	13	14	15
4 ^b	>99	<i>f</i>	<i>f</i>	<i>f</i>	<i>f</i>	<i>f</i>
5 ^b	<i>f</i>	>99	<i>f</i>	<i>f</i>	<i>f</i>	<i>f</i>
6 ^b	0.6 ^c	0	0	0	0	0
13 ^{c,d,h}	0	63	1.2	0	0	35.8
14 ^{c,h}	8	0	92	0	0	<i>e</i>

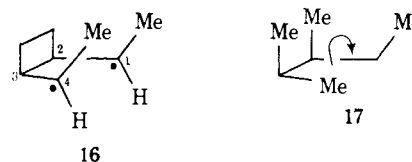
^a Yield relative to total of volatile products as determined by electronically integrated vpc analysis using 20 ft × 1/8 in. γ-methyl-γ-nitropimelonitrile column. ^b Chamber pyrolysis (120 sec at 200°). ^c Pyrolysis at 197.4° in sealed capillary tubes. ^d *t*_{1/2} = 10,000 sec; pyrolysis for 2.5 half-lives. ^e **14** and *dl*-3,4-dimethylhexa-1,4-diene not resolved by vpc. Yields do not include any of the latter formed. ^f Less than 0.1%. ^g Yield estimated by comparison to the trace peak relative to amount of **13** formed in pyrolysis of **4**. ^h Compare W. R. Roth, personal communication, as cited by R. G. Bergman in "Free Radicals," Vol. I, J. Kochi, Ed., Wiley-Interscience, New York, N. Y., 1973, p 229. We are indebted to Professor Roth for a reference spectrum of **13**. Compound **14** was synthesized independently (ref 8).

nor the hydrazone **6** is an intermediate in the formation of the dienes. The stereospecificities **4** → **10** and **5** → **11** are each >99.9%.

Azo compounds **4** and **5** of the cyclobutane series lose nitrogen at rates (*t*_{1/2} ~ 70 sec at 200°) about five times those of Allred's compound **3b**⁶ but much slower than the cyclopropane analogs **1a**–**c** (*t*_{1/2} ~ 30 min at -10°).² The rate decrease may result from less bent character in the bridge bond. Although the stereospecificity for **4** and **5** also should decline relative to that for **1a**–**c**, it remains higher than the upper limit of our analysis.

An interpretation of the results for **4** and **5** in terms of a 1,4-diradical intermediate would require that the

intermediate be formed specifically in conformation **16** and that cleavage of the bridge bond (C₂–C₃) in **16** be at least 1000 times faster than stereorandomizing bond rotations. There are good reasons to believe¹⁰ that there would be no significant rotational barriers introduced by conjugation of the 1,4 orbitals with the cyclobutane ring orbitals of **16**. In the absence of such special effects, rotational barriers about C_α–C_β bonds in hydrocarbon radicals may be estimated to be not more than about one-sixth of those in the corresponding hydrocarbons.¹¹ The barrier for the rotation shown in the model hydrocarbon 2,3-dimethylpentane **17** is 7



kcal/mol,¹⁴ from which it may be estimated that the barrier to rotation about the C₁–C₂ bond of **16** would be ≤1.2 kcal/mol. The 1000-fold stereospecificity of diene formation at 200° corresponds to ΔΔ*F*[‡] ≥ 6.5 kcal/mol, which thus would require that C₂–C₃ bond cleavage in the hypothetical diradical **16** have a *negative* activation energy. It is conceivable that "through-bond" coupling might increase the rotational barrier,¹⁵ but the peculiar requirements that the diradical be formed exclusively in conformation **16** and that it fail to cyclize to 2,3-dimethylbicyclo[2.2.0]hexanes¹⁶ would remain. We therefore interpret the decompositions of **4** and **5** as concerted reactions.

(10) R. Hoffmann and R. B. Davidson, *J. Amer. Chem. Soc.*, **93**, 5699 (1971).

(11) (a) The following values (in kcal/mol) are illustrative: propane (2.8), propyl radical (0.4–0.5); isobutane (3.6), isobutyl radical (0.3).^{12,13}

(12) H. E. O'Neal and S. W. Benson in "Free Radicals," Vol. II, J. Kochi, Ed., Wiley-Interscience, New York, N. Y., 1973, Chapter 17, and references cited therein.

(13) H. Fischer, ref 12, p 483 and references cited therein.

(14) U. Zirnits and M. M. Sushchinskii, *Opt. Spectrosc. (USSR)*, **16**, 489 (1964), as cited in ref 12.

(15) L. M. Stephenson and T. A. Gibson, *J. Amer. Chem. Soc.*, **94**, 4599 (1972).

(16) The pyrolysis of 5,6-dimethyl-2,3-diazabicyclo[2.2.2]oct-2-ene gives substantial quantities of **13** and **15**: W. R. Roth and M. Martin, *Tetrahedron Lett.*, 3865 (1967).

(17) National Science Foundation Graduate Fellow, 1969–1972; National Science Foundation Trainee, 1972–1973.

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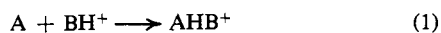
Chemical Consequences of Strong Hydrogen Bonding in the Reactions of Organic Ions in the Gas Phase. Base Induced Elimination Reactions

Sir:

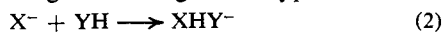
The strong hydrogen bond, formed by the binding of two n-donor bases to a labile proton, is an important structural moiety which warrants consideration in a variety of gas-phase ion-molecule reactions. Bimolecular¹ processes in which strong hydrogen bonding has been observed to play an important role include

(1) For a discussion of intramolecular interactions of remote functional groups in which strong hydrogen bonding is important, see T. H. Morton and J. L. Beauchamp, *J. Amer. Chem. Soc.*, **94**, 1369 (1972).

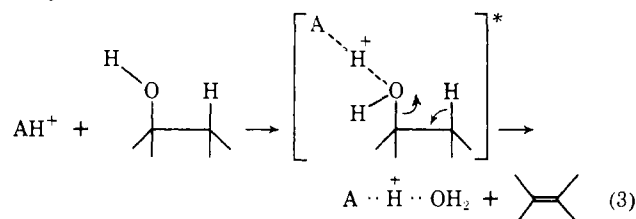
nucleophilic substitution reactions,²⁻⁴ acid-induced elimination reactions,⁴⁻⁶ and a novel class of associative fragmentation reactions.⁷ These reactions involve at one or more stages the binding of the base A to the conjugate acid of the base B, forming AHB⁺ (eq 1).



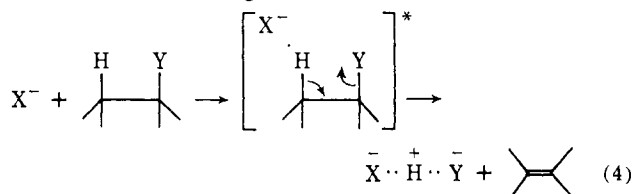
Equally strong is the binding of the conjugate base of the acid XH to the acid YH, forming XHY⁻ (eq 2).⁸⁻¹⁰ Strong hydrogen bonding of the type illustrated



in eq 1 is, for example, effective in promoting gas-phase acid-induced elimination reactions such as the dehydration of alcohols illustrated in eq 3.⁴⁻⁶ By



analogy we expected the type of strong hydrogen bonding illustrated in eq 2 to participate in the base-induced elimination reaction generalized in eq 4.



To investigate the possibility of such an elimination process we examined the reactions of CD₃O⁻, a relatively strong base in the gas phase,^{11,12} with a series of alkyl halide substrates. The reactant ion can be conveniently generated from CD₃ONO by low energy electron attachment.¹² In a typical experiment CD₃ONO was admitted to the analyzer of the ion cyclotron resonance spectrometer at a pressure of 10⁻⁶ Torr. The alkyl halide was admitted through a second sample inlet such that its pressure could be varied independently. Reactions were identified both by double resonance experiments and by the variation of relative single resonance peak intensities with the partial pressure of the alkyl halide.¹³ The results are summarized in Table I.

(2) D. Holtz, J. L. Beauchamp, and S. D. Woodgate, *J. Amer. Chem. Soc.*, **92**, 7484 (1970).

(3) J. L. Beauchamp, D. Holtz, S. D. Woodgate, and S. L. Patt, *J. Amer. Chem. Soc.*, **94**, 2798 (1972).

(4) J. L. Beauchamp and M. C. Caserio, *J. Amer. Chem. Soc.*, **94**, 2638 (1972).

(5) J. L. Beauchamp, *J. Amer. Chem. Soc.*, **91**, 5925 (1969).

(6) J. L. Beauchamp and R. C. Dunbar, *J. Amer. Chem. Soc.*, **92**, 1477 (1970).

(7) D. P. Ridge and J. L. Beauchamp, *J. Amer. Chem. Soc.*, **93**, 5925 (1971).

(8) M. Arshadi, R. Yamdagni, and P. Kebarle, *J. Phys. Chem.*, **74**, 1475 (1970); M. Arshadi and P. Kebarle, *ibid.*, **74**, 1483 (1970).

(9) R. Yamdagni and P. Kebarle, *J. Amer. Chem. Soc.*, **93**, 7139 (1971).

(10) Strong hydrogen bonding of the type illustrated in eq 2 has been implicated in gas-phase decarbonylation reactions: L. K. Blair, P. C. Isolani, and J. M. Riveros, *J. Amer. Chem. Soc.*, **95**, 1057 (1973).

(11) J. I. Brauman and L. K. Blair, *J. Amer. Chem. Soc.*, **92**, 5896 (1970).

(12) D. Holtz, J. L. Beauchamp, and J. R. Eyler, *J. Amer. Chem. Soc.*, **92**, 7045 (1970).

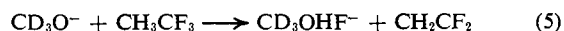
(13) For a description of the experimental techniques, see J. L. Beauchamp, *Annu. Rev. Phys. Chem.*, **22**, 527 (1971).

Table I. Reactions of CD₃O⁻ with Fluoroethanes

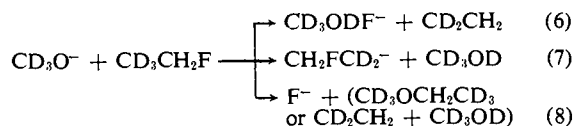
Reaction	k ^a (10 ⁻¹⁰ cm ³ molecule ⁻¹ sec ⁻¹)
CD ₃ O ⁻ + CH ₃ CH ₂ F	$\begin{cases} \text{CD}_3\text{OHF}^- + \text{CH}_2\text{CH}_2 & 0.38 \pm 0.12 \\ \text{CH}_2\text{FCH}_2^- + \text{CD}_3\text{OH} & 0.44 \pm 0.09 \\ \text{F}^- + \text{CH}_3\text{CH}_2\text{OCD}_3^b & 0.47 \pm 0.06 \end{cases}$
CD ₃ O ⁻ + CH ₃ CHF ₂	$\begin{cases} \text{CD}_3\text{OHF}^- + \text{CH}_2\text{CHF} & 9.0 \pm 2.4 \\ \text{CHF}_2\text{CH}_2^- + \text{CD}_3\text{OH} & 3.6 \pm 1.5 \end{cases}$
CD ₃ O ⁻ + CH ₃ CF ₃	$\begin{cases} \text{CD}_3\text{OHF}^- + \text{CH}_2\text{CF}_2 & 14.4 \pm 2.0 \\ \text{CF}_3\text{CH}_2^- + \text{CD}_3\text{OH} & 1.1 \pm 0.4 \end{cases}$
CD ₃ O ⁻ + CHF ₂ CH ₂ F	$\begin{cases} \text{CD}_3\text{OHF}^- + \text{C}_2\text{H}_2\text{F}_2 & 8.4 \pm 1.0 \\ \text{C}_2\text{H}_2\text{F}_3^- + \text{CD}_3\text{OH} & 5.6 \pm 0.4 \\ \text{F}^- + \text{CD}_3\text{OC}_2\text{H}_3\text{F}_2^b & 2.8 \pm 0.3 \end{cases}$
CD ₃ O ⁻ + CH ₂ FCF ₃	$\begin{cases} \text{CD}_3\text{OHF}^- + \text{CHF}_2\text{CF}_2 & 5.4 \pm 0.8 \\ \text{CF}_3\text{CHF}^- + \text{CD}_3\text{OH} & 3.4 \pm 0.5 \end{cases}$
CD ₃ O ⁻ + CHF ₂ CHF ₂	$\begin{cases} \text{CD}_3\text{OHF}^- + \text{CF}_2\text{CHF} & 2.5 \pm 0.4 \\ \text{CHF}_2\text{CF}_2^- + \text{CD}_3\text{OH} & 2.9 \pm 0.1 \end{cases}$
CD ₃ O ⁻ + CHF ₂ CF ₃	$\begin{cases} \text{CD}_3\text{OHF}^- + \text{CF}_3\text{CF}_2 & 19.0 \pm 2.0 \end{cases}$

^a Thermal energy rate constants and standard deviations determined using the analysis given by A. G. Marshall and S. E. Buttrill, Jr., *J. Chem. Phys.*, **52**, 2752 (1970). All experiments were performed at ambient temperature (295°K). Accuracy of total rate constants estimate to be ±30% as limited by uncertainties in drift times, pressures, and approximations inherent in the analysis employed. See, for example, M. B. Comisarow, *J. Chem. Phys.*, **55**, 205 (1971). ^b Neutral products uncertain. See text and footnote 14 for discussion.

In the interaction of CD₃O⁻ with CH₃CF₃, the elimination process (5) is the most important reaction



channel. Three competitive channels are observed in the interaction of CD₃O⁻ with CD₃CH₂F, including elimination (reaction 6), proton transfer (reaction 7), and fluoride ion production (reaction 8).¹⁴ Subsequent



reaction of F⁻ with CD₃CH₂F leads exclusively to elimination of DF and formation of FDF⁻ (reaction 9).



Kinetic analysis indicates reactions 5-9 are single-step bimolecular processes.

These results are consistent with the proposed general reaction (4) in which anionic attack occurs at the acidic β-hydrogen. The reaction depicted in eq 4 can be classified as an E2 elimination reaction in which the components of leaving group (HY) are in a cis configuration.¹⁵ In solution such processes are known to be promoted by strong bases, poor leaving groups, sub-

(14) The two possible sets of neutral products in reaction 8 are not distinguished in the present experiments. Thermochemical estimates indicate both to result in an overall exothermic process. The latter set could result from breakup of the elimination product. The former would result from a nucleophilic substitution reaction of the type reported by D. K. Bohme and L. B. Young, *J. Amer. Chem. Soc.*, **92**, 7354 (1970).

(15) For recent discussions of related processes in solution, see J. F. Bunnett, *Surv. Progr. Chem.*, **5**, 53 (1969); F. G. Bordwell, *Accounts Chem. Res.*, **5**, 374 (1972); A. Fry, *Chem. Soc. Rev.*, **1**, 163 (1972); and H. F. Koch, D. B. Dahlberg, A. G. Toczko, and R. L. Solsky, *J. Amer. Chem. Soc.*, **95**, 2029 (1973).

stituents which acidify β -hydrogen, and factors which promote the cis configuration of the intermediate base-substrate complex. Thus it is not surprising that $\text{CH}_3\text{-CF}_3$ is an ideal substrate for observing base-induced elimination reactions in the gas phase. In addition, the long range ion-dipole interaction between CH_3O^- and CH_3CF_3 facilitates attack of base at hydrogen.¹⁶

Gas-phase base-induced elimination reactions afford the means to study the selectivity and stereochemistry of E2 processes in the absence of complicating solvation phenomena. Efforts are now in progress to better characterize the thermochemical changes associated with these reactions, to extend the identification of elimination reactions to include substrates other than alkyl fluorides, and to provide better understanding of the factors determining the relative importance of pro-

(16) For a discussion of ion-dipole interactions, see J. V. Dugan and J. L. Magee, *J. Chem. Phys.*, **47**, 3103 (1967).

ton transfer, nucleophilic substitution, and elimination processes. Also of interest is the prevalence of proton transfer in several of the cases indicated in Table I, leading to β -substituted carbanions which recent theoretical calculations have suggested to have strongly preferred conformational stability.¹⁷

Acknowledgment. This work was supported in part by the United States Atomic Energy Commission under Grant No. AT(04-3)767-8.

(17) R. Hoffmann, L. Radom, J. A. Pople, P. von R. Schleyer, W. J. Hehre, and L. Salem, *J. Amer. Chem. Soc.*, **94**, 6221 (1972).

(18) D. P. Ridge was supported by the Department of Health, Education and Welfare, National Defense Education Act.

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Book Reviews*

Catalysis. Edited by J. W. HIGHTOWER. North Holland/American Elsevier, New York, N. Y. 1973. xxv + 1483 pp (in two volumes). \$79.00.

The Proceedings of the Fifth International Congress on Catalysis (August 1972) are reported here in the form of 107 papers reproduced from the authors' typescripts. Inasmuch as the papers are mostly reports of original research, one cannot help wondering how many of them represent redundant (and expensive) publication. There is an index of authors and commentators, and a minute subject index.

The Chemical Basis of Life. With Introductions by P. C. HANAWALT and R. H. HAYNES. W. H. Freeman and Co., San Francisco, Calif. 1973. 405 pp. \$12.00 (cloth); \$5.95 (paper).

This is a volume of 38 articles reprinted from "Scientific American" and is stated to be an updated version of "The Molecular Basis of Life", published in 1968. The articles originally appeared from 1953 to 1973; they are reproduced with full illustrations and figures, with liberal use of color.

Fundamental Aspects and Recent Developments in Optical Rotatory Dispersion and Circular Dichroism. Edited by F. CIARDELLI and P. SALVADORI (University of Pisa). Heyden and Son, Ltd., London. 1973. xvii + 419 pp. \$30.25.

In September 1971, a NATO Advanced Study Institute was held at Pisa on ORD and CD; the twenty-two main papers make up this volume. The topics range from "Basic Principles, Definitions, and Applications" to such specific subjects as "ORD and CD in Conformational Analysis of Synthetic High Polymers". Although the authors are an international group, all papers are printed in English. They are carefully edited, fully illustrated, and accompanied by extensive bibliographies, and are, in effect, review chapters, with emphasis on the authors' own research. There is a modest subject index.

Rodd's Chemistry of Carbon Compounds. Supplement to Volume I. Parts C and D. Edited by M. F. ANSELL (University of London). Elsevier Publishing Co., New York, N. Y. 1973. xix + 464 pp. \$48.50.

With this volume, the policy is being introduced of issuing supplements rather than completely rewritten volumes, with the goal of keeping the subject up to date without the high cost and large bulk that would otherwise be entailed. This volume thus carries the

subject on from the second edition (1964/5). Unfortunately, it is not stated when the coverage of the literature terminated for the contributions to this volume, so we are left in the dark about how up to date they are. The preface is dated March 1973, but the latest references apparent to casual scanning of the text appear to be from 1970. It is hard to understand this serious oversight in an important work of reference.

This volume covers aldehydes and ketones, dihydric alcohols, hydroxy aldehydes and ketones, carbon monoxide, isocyanides and fulminic acid, carbonic acid and derivatives, and carboxylic acids, simple and substituted (including amino acids). A welcome improvement over the early volumes is the inclusion of a good selection of general references (reviews and monographs). The index is, as heretofore, highly detailed. These supplements should effectively maintain the effectiveness of this valuable reference work.

Organic Reactive Intermediates. Edited by S. P. MCMANUS (University of Alabama in Huntsville). Academic Press, New York, N. Y. 1973. x + 539 pp. \$39.50.

The editor has classified reactive intermediates according to type, each being the subject of a contributed chapter: Free Radicals (E. S. Huyser); Carbenes (D. Bethall); Nitrenes (R. A. Abramovitch); Carbonium Ions (S. P. McManus and C. U. Pittman, Jr.); Carbanions (E. M. Kaiser and D. W. Slocum); Radical Ions (G. A. Russell and R. K. Norris); and Arynes (E. K. Fields). The authors have been appropriately chosen. The book is a selective review, designed, it is said, for readers who have had a basic course in organic chemistry, and particularly for advanced undergraduates and graduate students. The editor recommends it as a textbook for a graduate course, but the publishers evidently did not take this point seriously when setting the price.

This book is, in fact, a useful orienting reference work, with extensive bibliographies (eleven pages of references in the chapter on Carbonium Ions, for example). The coverage of the literature extends through 1971, with a few later references. There is an author index of 24 pages; it is a pity that the subject index is relatively skimpy.

Among the many pleasant features of this book is the way the generally untidy matter of nomenclature of carbenes has been neatly handled. Bethall cleanly states his principle that "carbene" will be used only in the generic sense, and "methylene" will be used in naming specific compounds; the structure $\text{R}_2\text{C:}$ will be used non-committally for singlet or triplet carbenes, and $\text{R}_2\text{C}\uparrow$ and $\text{R}_2\text{C}\uparrow\uparrow$ will be used to specify singlet or triplet species, respectively. Much confusion would be avoided if these principles would be followed in all the literature.

* Unsigned book reviews are by the Book Review Editor.