

Acknowledgments.—The authors thank Miss P. A. Carney, R. M. Murch, and F. A. Kramer for assistance in determining n.m.r. spectra, and the Air Force Office of Scientific Research for financial support.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF WISCONSIN
MADISON, WISCONSIN

ROBERT E. BAILEY
ROBERT WEST

RECEIVED SEPTEMBER 12, 1964

Base-Catalyzed Intramolecular 1,3- and 1,5-Proton Transfers

Sir:

Since the report of the first base-catalyzed intramolecular 1,3-proton transfer,¹ enough other examples² have appeared in the literature to suggest that the phenomena might be rather general. Support for this view is found in a number of examples of enzyme-catalyzed intramolecular proton transfers that have been observed.³

molecular proton transfers which lend substantial support to these "conducted tour" mechanisms.

Compound III,⁵ when treated with various bases in a variety of deuterated solvents, gave IV⁶ with intramolecularity that varied from 17 to 98% (Table

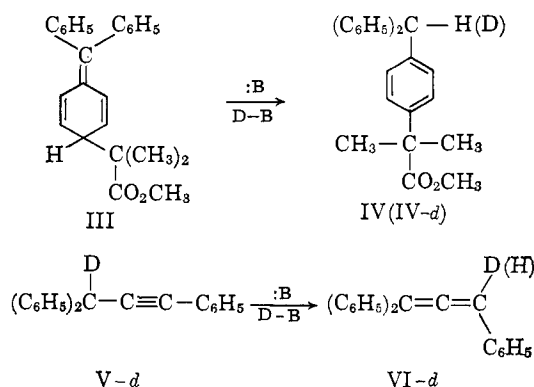


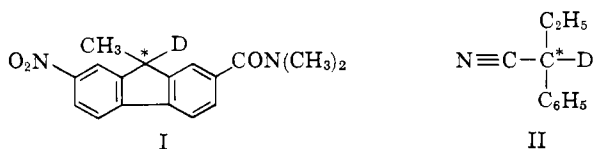
TABLE I

INTRAMOLECULARITY IN BASE-CATALYZED PROTON (DEUTERON) TRANSFERS IN TRIENE III TO GIVE TRIARYLMETHANE IV AND IN DEUTERATED ACETYLENE (V) TO GIVE ALLENE VI^a

Run no.	Compd.	Solvent ^b	Base	T, °C.	% intramolecular
1	III	$(\text{CH}_2\text{OD})_2$	$\text{DOCH}_2\text{CH}_2\text{OK}$	55	17
2	III	$(\text{CH}_2)_4\text{O}-10\% \text{D}_2\text{O}$	DONa	25	34
3	III	$(\text{CD}_3)_2\text{SO}-10\% \text{CH}_3\text{OD}$	CH_3OK	25	40
4	III	CH_3OD	CH_3ONa	25	47
5	III	<i>t</i> -BuOD	<i>t</i> -BuOK	25	50
6	III	$(\text{C}_2\text{H}_5)_3\text{COD}$	$(\text{C}_2\text{H}_5)_3\text{N}$	75	98
7	III	$(\text{C}_2\text{H}_5)_3\text{COD}^c$	$(\text{C}_2\text{H}_5)_3\text{N}$	75	97
8	III	$(\text{C}_2\text{H}_5)_3\text{COD}^d$	$(\text{C}_2\text{H}_7)_3\text{N}$	75	98
9	V	<i>t</i> -BuOD	<i>t</i> -BuOK	30	22 ± 3
10	V-d ^e	CH_3OH	CH_3OK	30	19
11	V-d ^e	$(\text{CH}_3)_2\text{SO}-1.6 \text{ M } t\text{-BuOH}$	$\text{N}(\text{CH}_2\text{CH}_2)_3\text{N}$	30	88
12	V-d ^e	$(\text{CH}_3)_2\text{SO}-3.9 \text{ M } \text{CH}_3\text{OH}$	$\text{N}(\text{CH}_2\text{CH}_2)_3\text{N}$	30	88
13	V-d ^e	$(\text{CH}_3)_2\text{SO}-3.9 \text{ M } \text{CH}_3\text{OH}^f$	$\text{N}(\text{CH}_2\text{CH}_2)_3\text{N}$	30	85
14	V-d ^e	$(\text{CH}_3)_2\text{SO}-3.9 \text{ M } \text{CH}_3\text{OH}^f$	$(\text{CH}_2)_5\text{NH}$	30	58

^a All deuterium analyses were made by combustion and falling drop method (J. Nemeth). Products once formed underwent little if any exchange under conditions of their formation. ^b Solvents 97–100% deuterated where deuterium is indicated. ^c Solution was 0.1 M in $(\text{C}_4\text{H}_9)_4\text{NI}$. ^d Solution was 0.1 M in $(\text{C}_2\text{H}_7)_3\text{NDI}$. ^e 95% of 1 atom of deuterium. Results were corrected accordingly. ^f Solution was 0.14 M in $\text{N}(\text{CH}_2\text{CH}_2)_2\text{NHI}$.

In studies of the stereochemistry of base-catalyzed hydrogen–deuterium exchange of I and II, examples of intramolecular racemization (isoracemization) were interpreted as occurring by a series of intramolecular proton transfers (conducted tour mechanism).⁴ Some of the steps involved 1,6-proton transfers across an aromatic system (I), others 1,3-proton transfers from carbon α to a cyano group to nitrogen and back to



carbon. We have now observed examples of intra-

I). This rearrangement involves proton transfer across the face of a benzene ring. Compound V (deuterated) under similar conditions with base in protonated solvents gave VI with intramolecularity that varied between about 20 and 88% (Table I).

The isomerization of triene III to aryl compound IV can be visualized as occurring by one 1,5-rearrangement, or by two successive 1,3-rearrangements. Evidence that the latter type of mechanism makes little, if any, contribution is shown by the fact that no deuterium could be detected in the aromatic rings of IV (combination of n.m.r. and combustion techniques) produced in those runs which gave low intramolecularity (1–5). Had intermediates such as VII-d intervened, some deuterium should have been incorporated into the *ortho* position of the *para*-substituted ring of IV.

These rearrangements are interpreted as occurring largely through ion-pair intermediates whose carbanion is hydrogen bonded to the molecule of oxygen or nitrogen acid generated by proton (deuterium) abstract-

(5) R. Heck, P. S. Magee, and S. Winstein, *Tetrahedron Letters*, **30**, 2033 (1964).

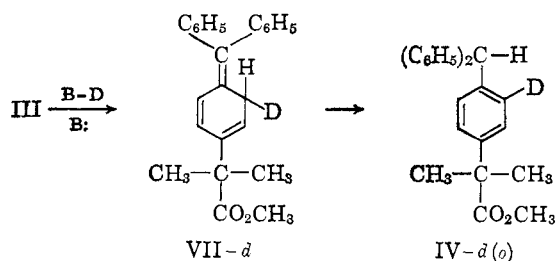
(6) All new compounds used in this investigation gave carbon and hydrogen analysis within 0.3% of theory. All old compounds gave physical properties which corresponded to literature values.

(1) D. J. Cram and R. T. Uyeda, *J. Am. Chem. Soc.*, **84**, 4358 (1962).

(2) (a) S. Bank, C. A. Rowe, Jr., and A. Schriesheim, *ibid.*, **85**, 2115 (1963); (b) R. B. Bates, R. H. Carnighan, and C. E. Staples, *ibid.*, **85**, 3032 (1963); (c) W. von E. Doering and P. P. Gaspar, *ibid.*, **85**, 3043 (1963); (d) G. Bergsen and A. M. Weidner, *Acta Chem. Scand.*, **17**, 862, 1798 (1963); (e) G. Bergsen, *ibid.*, **17**, 2601 (1963); (f) D. J. Cram and R. T. Uyeda, *J. Am. Chem. Soc.*, in press.

(3) (a) F. S. Kawahara and P. Talalay, *J. Biol. Chem.*, **235**, PC 1 (1960); (b) B. W. Agranoft, H. Eggerer, U. Henning, and F. Lynen, *ibid.*, **235**, 326 (1960); (c) H. C. Rilling and M. J. Coon, *ibid.*, **235**, 3087 (1960).

(4) D. J. Cram and L. Gosser, *J. Am. Chem. Soc.*, **86**, 2950 (1964).



tion by base. Although the carbanion might be hydrogen bonded by external deuteron (proton) donors in the medium, deuteron (proton) capture at sites distant from the cation of the ion pair would generate dissociated ions. Such a process is favorable only in solvents of high dielectric constant. Recapture by a new site of the proton (deuteron) originally abstracted to form the carbanion produces an ion pair when metal alkoxides serve as bases, and a neutral molecule when amines are used.

The intramolecular rearrangements of III to IV and of V to VI probably occur by migration of protons

(deuterons) as conjugate acids of the catalyst across the face of a π -cloud of electrons containing a negative charge. Migration from the front face of the π -cloud to the rear face by the migrating group would involve breakage of the hydrogen bond and at least partial dissociation of the ion pair, and is an unlikely process in those solvents which exhibit high intramolecularity. Therefore, these results imply that if suitable optically active analogs of III and V were submitted to conditions that gave high intramolecularity, the products would be of high optical purity. Thus asymmetric induction over several bond lengths is anticipated. The stereochemical experiments of Bergsen and Weidler^{2d,e} and of Jacobs and Dankner⁷ give force to this expectation, which is currently being tested.

(7) T. L. Jacobs and D. Dankner, *J. Org. Chem.*, **22**, 1424 (1957).

CONTRIBUTION NO. 1760

DEPARTMENT OF CHEMISTRY

UNIVERSITY OF CALIFORNIA AT LOS ANGELES

LOS ANGELES, CALIFORNIA

DONALD J. CRAM

F. WILLEY

H. P. FISCHER

DONALD A. SCOTT

RECEIVED SEPTEMBER 28, 1964

BOOK REVIEWS

Divalent Carbon. By J. HINE, Professor of Chemistry, Georgia Institute of Technology. The Ronald Press Co., 15 East 26th St., New York 10, N. Y. 1964. vii + 206 pp. 15 × 21 cm. Price, \$7.00.

Considering the volume of published material on the chemistry of methylenes, it is amazing that the publication of the first comprehensive and acceptable review in English appeared only after this field has enjoyed an immense popularity for more than a decade. It is fortunate that the first book entirely devoted to methylenes has been written by an author who has revitalized the interest in divalent carbon compounds through his pioneering studies on the mechanisms of haloform hydrolyses.

The book consists of eight chapters which proceed from a discussion of the physical and physical-organic chemistry of methylene itself to a treatment of the chemistry of a variety of methylene derivatives. Included in the latter are dihalomethylenes, alkoxy-, alkylthio-, and monohalomethylenes, double-bonded derivatives of divalent carbon, and miscellaneous other substituted methylenes. The last three chapters present a discussion of mechanisms of α -eliminations, of pyrolytic and photolytic decompositions of diazo compounds, and of a number of other reactions which may proceed through the intermediacy of divalent carbon species. The 218 references are taken from the literature available to the author to mid-1962. This includes some material with publication dates of 1963. Throughout the book, Hine has avoided the term "carbene"; instead he seems to prefer the Chemical Abstracts system which names all divalent carbon compounds as derivatives of methylene.

In the author's own words, the emphasis of the book is on "mechanisms of reactions involving methylenes and the effect of structure on reactivity in these reactions." As a consequence of this guideline, many references of interest mainly to the synthetic chemist are dealt with rather briefly, or are omitted entirely. Undoubtedly other books on divalent carbon will be published soon, and since it is likely that synthetic aspects will be stressed in one or the other, this restriction cannot be considered a shortcoming. The real strength of this monograph lies in its attempt to develop a general and consistent framework into which the vast volume of experimental data may be fitted. In the discussion Hine does not shy away from giving his own interpretations of many experimental observations even if his conclusions are not the same as those of the original authors. Another enjoyable aspect is the large number of suggestions of experiments which should be done to solve remaining problems. Considering

the size of the book, most aspects of mechanistic methylene chemistry in solution have been covered adequately. A somewhat more detailed description of the vapor phase work might have added to the value of the book. The only severe criticism must be directed towards the publisher. A production time of 18 months cannot be tolerated when the subject of the monograph is in a state of dynamic development. As a result of this time lag, the most exciting recent developments in methylene chemistry, such as the information on ground-state properties of divalent carbon compounds obtainable from e.s.r. studies, are only mentioned in a few words.

In conclusion, Hine succeeded in writing a very useful and stimulating book. Acquisition can be highly recommended to any one interested in organic reaction mechanisms. It should be included in the reading list for organic graduate students. They will profit not only from being familiarized with divalent carbon chemistry, but, more important, they will be given an excellent view on the methods and techniques used to study short-lived reactive intermediates in general.

DEPARTMENT OF CHEMISTRY
THE UNIVERSITY OF CHICAGO
CHICAGO 37, ILLINOIS

GERHARD L. CLOSS

Electronic Spectra and Quantum Chemistry. By C. SANDORFY, Professor of Chemistry, University of Montreal. Prentice-Hall, Inc., Englewood Cliffs, N. J. 1964. xiii + 385 pp. 16 × 23 cm. Price, \$14.95.

This book was originally published in French in 1959 as "Les Spectres Electroniques en Chimie Theorique," and its German translation (1961) was previously reviewed in this journal (*J. Am. Chem. Soc.*, **84**, 2656 (1962)). The present volume, as the author remarks in his preface, is a greatly augmented version of these previous editions.

After a short introduction on units, and a somewhat longer one on the basis of the variation and perturbation methods in quantum mechanics, there is a short chapter on energy calculations by the Hückel MO method, and another considerably longer one on the corresponding valence bond technique using "structures." The emphasis is on the presentation of complete detail of each treatment, so that not even the smallest arithmetic steps are passed over.