tion is not sufficient to permit a complete analysis of the system.

To alleviate the spin–spin coupling problem we had also measured the spectra of the corresponding 2,2,6,6-tetradeuterio-4-alkylcyclohexanols. Deuteration in the β,β'-positions does indeed eliminate the spin–spin coupling problems, and the signals for the 1-protons now appear as sharp singlets.[7] With the deuterated alcohols in both solvents, our results show remarkable constancy of the chemical shift of the 1-proton in the four *trans*-4-alkylcyclohexanols which are expected[4] to exist nearly exclusively in the *ee*-conformation T. Also, the *cis*-alcohols exhibit a trend of decreasing chemical shift with decrease in the size of the alkyl group.

TABLE II

A VALUES (KCAL./MOLE) FROM N.M.R. AT 30°

Group	CCl_4	2-D-2-Propanol
i-Pr	2.28 ± 0.08	2.25 ± 0.08
Et	1.74 ± 0.06	1.77 ± 0.07
Me	1.74 ± 0.06	1.60 ± 0.06
OH	0.78 ± 0.02	0.88 ± 0.02

Using the chemical shifts for conformational analysis of cyclohexanol, K_{ae} is obtained with the aid of equation (1) and this leads to a value for A_{OH}, the free energy of preference of the hydroxyl group for an *equatorial vs.* an *axial* position.[4] Similar treatment of the *cis*-4-alkylcyclohexanols leads to A values which are differences between A_{R} and A_{OH}. As is clear from Table II, essentially identical values of A_{R} are obtained in both solvents, in spite of differences in the nature of the solvent and the cyclohexanol concentration. Even the A_{OH} values agree quite well. Also, A_{R} and A_{OH} concur with those obtained by other methods.[7,8] The figure for $A_{i\text{-Pr}}$ is much more reasonable than the previous rough estimate[4] (>3.3) based on old saponification rate constants[9] which we have remeasured[10] and found to be erroneous.

(7) As this manuscript was being submitted a Communication by F. A. L. Anet appeared [*J. Am. Chem. Soc.*, **84**, 1053 (1962)] reporting simplification of the spin–spin coupling pattern by remote deuteration at carbon atoms 3, 4 and 5 and the conformational analysis of cyclohexanol based on coupling constants.

(8) (a) E. L. Eliel, *J. Chem. Ed.*, **37**, 126 (1960); (b) H. Van Bekkum, P. E. Verkade, B. M. Wepster, *Koninkl. Ned. Akad. Wetenschap, Proc. Ser. B*, **64**, No. 1, 161 (1961).

(9) G. Vavon, *Bull. Soc. Chim. France*, [4] **49**, 1002 (1931).

(10) A. H. Lewin, unpublished work.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALIFORNIA
LOS ANGELES 24, CALIFORNIA

ANITA H. LEWIN
S. WINSTEIN

RECEIVED APRIL 6, 1962

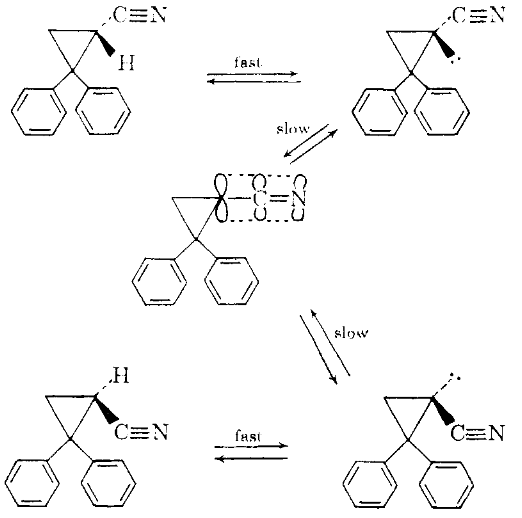
CYCLOPROPANES. XII. THE CYCLOPROPYL CARBANION

Sir:

A comparison of the rate of deuterium exchange with the rate of racemization in the phenyl 2-octyl sulfone system has revealed that the exchange rate is faster than the rate of racemization.[1-3] This has been interpreted in terms of "asymmetric solvation"[1] or by postulating that the intermediate carbanion has retained its asymmetry.[1,2] In the case of sulfones the asymmetry can be maintained by having the electron pair in a 2p or sp^3 orbital conjugating with the 3d orbital of sulfur in a Case II type[4] of structure.[2] In contrast to the work on sulfones the rates of deuterium exchange and rates of racemization of several optically active nitriles were found to be equal.[5] Apparently, "asymmetric solvation" is unimportant in these cases, presumably due to the ambident nature of the intermediate anion.[5]

We wish at this time to report our findings on the base-catalyzed deuterium exchange of 2,2-diphenylcyclopropylnitrile (I). In connection with our studies on the cyclopropyl carbanion[6] we had occasion to determine the pseudo first-order rate constants k_1 for the sodium methoxide catalyzed racemization of I. At 75.7° and at 92.6° the k_1's in methanol (0.09 M in I and 0.99 M in methoxide) are $0.363 \pm 0.007 \times 10^{-6}$ sec.$^{-1}$ and $3.25 \pm 0.05 \times 10^{-6}$ sec.$^{-1}$, respectively. The extrapolated k_1 at 50° is $6.78 \pm 0.13 \times 10^{-9}$ sec.$^{-1}$. Under comparable conditions (0.096 M in I and 0.88 M in methoxide) the rate of deuterium–hydrogen exchange at 50.0° using methanol-*d* as the solvent was found[7] to be $5.48 \pm 0.13 \times 10^{-5}$ sec.$^{-1}$. The ratio of $k_1$exc./$k_1$rac. is 8,080 with the half-life for racemization being 3.5 years and the half-life for exchange being 3.51 hours. The $k_{1\text{H}}/k_{1\text{D}}$ ratio for the exchange reaction was found to be 1.69 ± 0.04.

Since "asymmetric solvation" is not important when methanol is used as a solvent[8] and since



---

(1) D. J. Cram, C. A. Kingsbury and B. Rickborn, *J. Am. Chem. Soc.*, **83**, 3688 (1961).

(2) E. J. Corey and E. T. Kaiser, *ibid.*, **83**, 490 (1961).

(3) H. L. Goering, F. T. Towns and B. Dittmar, *J. Org. Chem.* **27**, 736 (1962).

(4) H. P. Koch and W. E. Moffitt, *Trans. Far. Soc.*, **47**, 7 (1951).

(5) D. J. Cram, B. Rickborn, C. A. Kingsbury and P. Haberfield, *J. Am. Chem. Soc.*, **83**, 3678 (1961); D. J. Cram and P. Haberfield, *ibid.*, **83**, 2354 (1961).

(6) (a) H. M. Walborsky and F. M. Hornyak, *ibid.*, **77**, 6026 (1955); (b) H. M. Walborsky and F. M. Hornyak, *ibid.*, **78**, 872 (1956).

(7) The rate was measured by infrared intensity analysis (at 1189 for I-D and at 1137 for I-H) and a number of points checked by the combustion method.

(8) D. J. Cram, D. A. Scott and W. D. Nielsen, *J. Am. Chem. Soc.*, **83**, 3696 (1961).

acyclic nitriles have been shown to yield symmetrical carbanions under these conditions[5] we feel that our results are best explained by assuming that the cyclopropyl carbanion retains its asymmetry. These results also indicate that there is indeed an energy barrier to the rehybridization of the electron pair from a hybridized orbital into a p-orbital (I-Strain).[9] However, in aprotic solvents such as ether the nitrile (I) racemizes very rapidly.[6a]

In a recent study it has been demonstrated[10] that the acidity of the α-hydrogen in isopropyl phenyl sulfone and cyclopropyl phenyl sulfone is nearly equal. In the nitrile system it appears that the α-hydrogen of the cyclopropyl nitrile is more acidic than it is in its acyclic analog 2-methyl-3,3-diphenylpropionitrile (II). Under the identical conditions used to study the racemization of I the k_1 at 50° for II was found to be $1.75 \pm 0.03 \times 10^{-6}$ sec.$^{-1}$. Since the rate of deuterium exchange and racemization have been found to be equal for 2-methyl-3-phenylpropionitrile,[5] one can assume that this will also be the case for II. On this basis the k^{I}exc./k^{II}exc. would equal 31.[11]

---

[9] H. C. Brown, R. S. Fletcher and R. B. Johannesen, *J. Am. Chem. Soc.*, **73**, 212 (1951); H. C. Brown and M. Barkowski, *ibid.*, **74**, 1894 (1952).

[10] H. E. Zimmerman and B. S. Thyagarajan, *ibid.*, **82**, 2505 (1960).

[11] This work was supported by a grant from the National Science Foundation, which is gratefully acknowledged.

DEPARTMENT OF CHEMISTRY
FLORIDA STATE UNIVERSITY
TALLAHASSEE, FLORIDA

H. M. WALBORSKY
A. A. YOUSSEF
J. M. MOTES

RECEIVED APRIL 16, 1962

BOOK REVIEWS

The Biosynthesis of Proteins. By H. CHANTRENNE, Free University of Brussels, Belgium Pergamon Press Ltd. Headington Hill Hall, Oxford, England. 1961. viii + 220 pp. 15 × 23.5 cm. Price, $6.50.

It takes courage to write a book on Protein Biosynthesis. For one thing, the field covered is so extensive: genetics, embryology, cytology, cell physiology, microbiology, immunology, crystallography—as well as chemistry. Another difficulty is that new developments are coming in this field at break-neck speed. Despite the odds against him, Professor Chantrenne has written an excellent book. It is both precise and broadly based.

In his preface he expresses concern lest much of what he has written will soon become obsolete. He need not fear that this would seriously impair the value of his book. It is true that the rush of events has already outdistanced parts of what he has written. A reader of the book is, however, well prepared for the next steps in discovery. It is indeed curious to see that one of Professor Chantrenne's readers was so well informed that he could be brought fairly well up to date (at the date on which this review is being written) simply by reading the January issue of the *Proceedings of the National Academy of Sciences*.

The reason that Chantrenne's book has a certain lasting quality is that when introducing most topics he usually first presents the fundamental concepts and the significant original observations and experiments. The only serious criticism of his book is that he does not always do this. Several examples may be mentioned: (1) The great concept of genetic continuity, reaching back to Mendel and Weismann, is frequently presumed but not explicitly stated. (2) The development of the concept relating genes to protein synthesis begins, of course, with Garrod and reaches a high-point in the work on hemoglobin. The account given is blurred by the inclusion of irrelevant material and by the failure to note that an important breakthrough was the discovery by Sumner, Northrop and Kunitz that enzymes are proteins. (3) One reason that human material has been so important for investigation of protein biosynthesis is that the proteins are often readily available, as Chantrenne says. Even more readily available, however, are the proteins of cattle. The special significance of human material is that individual human organisms mean far more to us than do any other individual organisms, so that a prodigious effort is made to recognize genetic individuality in man. The essence of the genetic procedure from Mendel down is that investigation of individual differences is the key to an understanding of fundamental processes. (4) In introducing the term *cistron* no mention is made of the original experiments by Edward Lewis on *cis–trans* position effects in Drosophila. My experience has been that a student grasps this subject more readily if the exposition begins with Lewis' work.

When a second edition of Professor Chantrenne's fine book is called for, as one may confidently expect, he will of course include the fascinating novelties that are now being discovered every month; one hopes that he will then do some pruning and so find space for more of the classical concepts and experiments that date back before the present decade.

PROFESSOR AND MEMBER
ROCKEFELLER INSTITUTE
NEW YORK 21, NEW YORK

ALFRED E. MIRSKY

Surface Activity. The Physical Chemistry, Technical Applications, and Chemical Constitution of Synthetic Surface-Active Agents. Second edition, revised and enlarged. By J. L. MOILLIET, B.S. (Rice), Ph.D. (Lond.), B. COLLIE, B.Sc., (Aberd.), Ph.D. (Lond.), and W. BLACK, B.Sc. (St. Andrews). D. Van Nostrand Company, Inc., 120 Alexander Street, Princeton, New Jersey. 1961. xvi + 518 pp. 16.5 × 25.5 cm. Price, $15.00.

Progress in the last decade in the field of surface and colloid chemistry and the rapid expansion in the applications in technology and in general consumer uses of surface-active agents have necessitated substantial changes in the subject matter treated in the first edition of this well-known book. Therefore, it is not surprising that the authors have found it necessary to expand the first edition by 132 pages.

Nearly half of the added material is in Part I ("The Physical Chemistry of Surface-Active Agents and Interfacial Processes"), which is in accordance with the authors' original objective of emphasizing "the unifying scientific discipline of colloid science." It is unfortunate that in their enlarged presentation of physical chemical principles, the authors have not taken the time to improve the general style and balance of the most poorly presented portion of their book. Also, as in the first edition, Part I represents an unbalanced treatment of the subject. This feature. coupled to excessive preoccupation with theoretical aspects needing more sophisticated discussion than is given in most books, results in making Part I of little value to anyone but a specialist. For example, little is said about constitutive effects on surface tension or interfacial tension, only a page is concerned with the nature of interfacial films, and the discussion of the surface viscosities of adsorbed films is so trivial as to be useless. No reader without a good background on the physical chemistry of surfaces and adsorbed