$(CO)_5^-$ resembles the spectrum of $Fe(CO)_5$ and might indicate a similar structure. The spectrum of $HFe(CO)_4^-$ correlates nicely with those of $Fe(CO)_4^{=}$ and $H_2Fe(CO)_4$. The decrease in molecular symmetry with addition of hydrogen is clearly evident.

Professor J. Richardson is thanked for helpful discussions on orbital theory.

RICHARD B. WETHERILL LABORATORY
PURDUE UNIVERSITY
LAFAYETTE, INDIANA

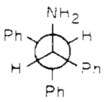
W. F. EDGELL
J. HUFF
J. THOMAS
H. LEHMAN
C. ANGELL
G. ASATO

RECEIVED DECEMBER 18, 1959

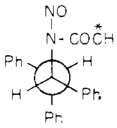
A RADIOCHEMICAL CRITFRION FOR CONFIGURATIONAL RELATIONSHIP

Sir:

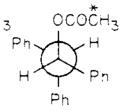
It has been shown[1] that N-nitrosoamides undergo thermal decomposition in polar and in non-polar solvents with net retention of configuration. To our knowledge, however, such decompositions have not yet been used as criteria for configurational relationships. In connection with studies of the stereochemical course of the deamination of 1,2,2-triphenylethylamine (I), it became necessary to relate the configuration of (+)-I with that of (+)-1,2,2-triphenylethanol [(+)-IV].[2] In order that the N-nitrosoamide decomposition could be used for this purpose, additional verification of its stereochemical course in the decomposition of (—)-N-acetyl-N-nitroso-1,2,2-triphenylethylamine [(—)-II] was necessary. In combination with appropriate tracer studies, such verification now has been obtained. Thus, D-(—)-II, labeled with carbon-14 in the acetyl group, was prepared from D-(+)-I, and thermally decomposed in purified acetic acid at 40.5°. The product, consisting of 70% (+)-III and 30% (—)-III, was fractionally crystallized and each fraction [(+) and (±)] was assayed for carbon-14. It was shown that (+)-III contained 29.2% of the carbon-14 originally in D-(—)-II, whereas (—)-III contained only 3.3% of the original radioactivity. In a repetition of this experiment with D-(+)-II, (—)-III contained 29.5% and (+)-III 3.7% of the original carbon-14. Since the labeled acetate group in II should be expected to remain preferentially in the same configuration during the decomposition to III, whereas solvent acetate should attack preferentially with inversion, the D-configuration now can be assigned without hesitation to (+)-I, (—)-II, (+)-III and (+)-IV.[3,4]



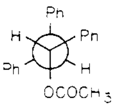
D-(+)-I



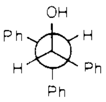
D-(-)-II



D-(+)-III



L-(-)-III



D-(+)-IV

In a typical experiment, 3.0 g. of D-(+)-N-acetyl-C^{14}-1,2,2-triphenylethylamine,[4] $[\alpha]^{25}D$ 109° (dioxane) (molar radioactivity, 7.941 mc. carbon-14) was converted to 3.15 g. of D-(—)-II, $[\Delta]^{25}D$ — 320° (benzene), by the method of France, Heilbron and Hey.[5] The material could not be obtained free from contaminating amide, as efforts to crystallize the sample resulted in its decomposition. Carbon and hydrogen determinations gave variable, unsatisfactory results. The purest sample obtained exhibited a molecular weight of 343.8 ± 1.3 (calcd. 344.4), as determined by radioactivity assay. A solution of 2.12 g. of D-(—)-II in 200 ml. of acetic acid was kept at 40.5° until reaction was complete, as shown by optical rotation of the solution. Samples of (+)-III and (±)-III were obtained by fractional crystallization of the product from 95% ethanol, and their purity was checked by infrared analyses. The sample of (+)-III showed on radioactivity assay 3.353 mc. carbon-14 per mole, whereas the (±)-III showed on radioactivity assay 2.168 mc. per mole, allowing the calculation that (—)-III contained 0.982 mc. of carbon-14 per mole.[6,7,8]

Acknowledgment.—The authors wish to acknowledge the encouragement and support given J. B. C. by the late Professor Cash B. Pollard of the University of Florida.

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(1) (a) R. Huisgen and H. Nakaten, *Ann.*, **586**, 84 (1954); R. Huisgen and Ch. Rüchardt, *ibid.*, **601**, 21 (1956); (b) E. H. White, THIS JOURNAL, **76**, 4497 (1954); **77**, 6008, 6011, 6014 (1955); E. H. White and C. A. Aufdermarsh, *ibid.*, **80**, 2597 (1958).

(2) C. J. Collins, W. A. Bonner and C. T. Lester, *ibid.*, **81**, 466 (1959).

(3) (+)-1,2,2-Triphenylethyl acetate (III) has been converted to (+)-1,1,2-triphenylethylene glycol by treatment with N-bromosuccinimide and alkaline hydrolysis [C. J. Collins, unpublished work]. The (+)-glycol is obtainable from D-(—)-mandelic acid by treatment with phenylmagnesium bromide [A. McKenzie and H. Wren, *J. Chem. Soc.*, **97**, 473 (1910)], and the absolute configuration of mandelic acid has been established by Mislow [K. Mislow, THIS JOURNAL, **73**, 3954 (1951)].

(4) D-(+)-III yields D-(+)-IV upon treatment with lithium aluminum hydride.[2]

(5) H. France, I. M. Heilbron and D. H. Hey, *J. Chem. Soc.*, 369 (1940).

(6) A detailed study of the stereochemistry and radiochemistry of the thermal decomposition of D- and L-II will be reported at a later date. Since chain-labeling experiments similar to those previously[2] reported indicate phenyl migration during the decomposition of II, the rather considerable amount of labeled acetoxyl associated with D-(—)-III may be attributed to inversion arising through phenyl migration through a *cis*-transition state in the ionic intermediates involved.

(7) Taken from the Ph.D. dissertation of Dr. Joan B. Christie, University of Florida, Gainesville, August, 1959. Predoctoral Fellow of the Oak Ridge Institute of Nuclear Studies.

(8) This paper is based upon work performed at Oak Ridge National Laboratory, which is operated by Union Carbide Corporation for the Atomic Energy Commission.

CHEMISTRY DIVISION
OAK RIDGE NATIONAL LABORATORY
OAK RIDGE, TENNESSEE CLAIR J. COLLINS
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF FLORIDA JOAN B. CHRISTIE

RECEIVED JANUARY 18, 1960

THE ENERGY DIFFERENCE BETWEEN THE BOAT AND CHAIR FORMS OF CYCLOHEXANE

Sir:

It is well accepted that the chair is more stable than the boat form of cyclohexane; however, attempts to estimate the magnitude of this energy difference have yielded values ranging from as little as 1.31[1] to as much as 10.6[2] kcal./mole. We re-

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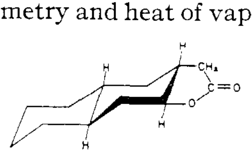
(1) The lower value of the range calculated by D. H. R. Barton, *J. Chem. Soc.*, 340 (1948).

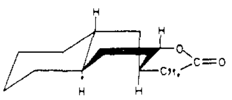
(2) The higher value of a range calculated by the Turner semi-empirical method as described by W. G. Dauben and K. S. Pitzer in M. S. Newman's "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 15.

port herewith experiments which establish the enthalpy difference between these two forms in the vapor phase at 25° as 5.3±0.3 kcal./mole.

The *trans–syn–trans* and *trans–anti–trans* lactones I and II, like the corresponding stereoisomers in the perhydroanthracene series,[3,4] differ in that the central ring assumes the chair conformation in the former and a boat in the latter. We have prepared this pair of lactones in quantity and in a high state of purity for precision combustion calorimetry and heat of vaporization determinations.



I



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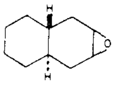
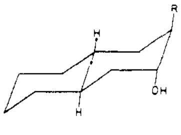
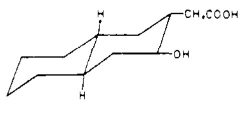


III



IV



V

The known[5] *trans*-Δ^2-octalin oxide III on reaction with sodiomalonic ester afforded the diaxial[6] adduct IV (R = $CH(COOEt)_2$), m.p. 60–63° (C, 65.5; H, 9.01). Saponification yielded the corresponding diacid, m.p. 166–167° dec., which, on heating in pyridine solution, underwent decarboxylation to give the diaxial hydroxy acid IV (R = CH_2COOH), m.p. 107.5–108° and 116–117° (C, 67.8; H, 9.25). Lactonization, which can occur only if the substituted ring flips into the boat form, required somewhat forcing conditions, *i.e.*, treatment with N,N′-dicyclohexylcarbodiimide or with *p*-toluenesulfonic acid in refluxing xylene. The lactone, II, thus obtained, melted at 49.6–50.3° (C, 74.2; H, 9.19), and on hydrolysis regenerated the 117° hydroxy acid showing that no rearrangement had occurred during lactonization.

Mild chromic acid oxidation of IV (R = CH_2-COOH) afforded the corresponding keto acid, m.p. 97.5–98.5° and 106–107° (C, 68.6; H, 8.67), which retained the axial orientation of the acetic acid residue as shown by its ready isomerization with aqueous sodium hydroxide into an isomeric keto acid V (=O in place of —OH), m.p. 75–77° and 91.5–92° (C, 68.8; H, 8.36). Reduction of this substance with sodium and isopropyl alcohol afforded the diequatorial hydroxy acid V, m.p. 156–156.3° (C, 68.1; H, 9.47) which on treatment with *p*-toluenesulfonic acid in refluxing benzene was transformed into the corresponding lactone I, m.p. 41.8–42.5° (C, 73.9; H, 9.33). Hydrolysis of I regenerated the original hydroxy acid V.

From four combustions of each lactone (0.5–0.8 g. samples) in high precision calorimeters[7] (accuracy 0.02% or better) the enthalpy of II was found to be greater than that of I by 5.5 ± 0.2 kcal./mole. The vapor pressures of I and II were measured by the Knudsen effusion technique over the range 240 to 310° K. with a vacuum microbalance[8] and the heats of sublimation evaluated from the slopes of log P *vs.* $1/T$. The values thus determined were practically identical, that for I being 0.2±0.2 kcal./mole greater than that of II. Hence, the enthalpy of the vapor of I is less than that of II by 5.3±0.3 kcal./mole at 25°. This value is considered to represent ΔH for the conversion of the chair to the boat form of cyclohexane. The *non*-cancelling interactions (produced by the terminal rings on the central ring of I and II) appear to be small and are probably within the experimental error. A critical analysis of these interactions will be given in a future definitive publication.[9]

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[3] W. S. Johnson, *Experientia*, **7**, 315 (1951).

[4] W. S. Johnson, THIS JOURNAL, **75**, 1498 (1953).

[5] W. Hückel and H. Naab, *Ann.*, **502**, 136 (1933).

[6] *Cf.* E. L. Eliel in M. S. Newman's "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 130.

[7] (a) To be described by Margaret A. Frisch, Ph.D. dissertation, University of Wisconsin, 1960. (b) Some of the runs were performed at the Argonne National Laboratory in collaboration with W. N. Hubbard.

[8] L. H. Spinar, Ph.D. Thesis, University of Wisconsin, 1957.

[9] This work was supported, in part, by grants from the National Institutes of Health, the National Science Foundation, and the Wisconsin Alumni Research Foundation.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF WISCONSIN
MADISON, WISCONSIN

WILLIAM S. JOHNSON
JOHN L. MARGRAVE
VICTOR J. BAUER
MARGARET A. FRISCH
LLOYD H. DREGER
WARD N. HUBBARD[7b]

RECEIVED DECEMBER 5, 1959

THE ENERGY BARRIER FOR THE CHAIR-CHAIR INTERCONVERSION OF CYCLOHEXANE

Sir:

One of the questions of conformational analysis regarding cyclohexane is the energy barrier for the chair–chair interconversion.[1] We have obtained evidence from low temperature studies of the nuclear magnetic resonance spectrum of cyclohexane which provides a reliable estimate of this barrier.[2] At low temperatures, the n.m.r. spectrum of cyclohexane shows progressive broadening and ultimate separation into two broad peaks. A solution of cyclohexane (3 M) in carbon disulfide remains liquid below −110°. Below −50° the single C–H peak of cyclohexane (−85.2 c./s. from tetramethylsilane internal standard) begins to broaden rapidly. At a temperature of −64.9°, the peak has changed to a single broadly rounded peak with a half-width of 31 cycles. At −70° two distinct peaks are observed, which are incompletely resolved. This character persists to the lowest temperatures studied. Care was taken throughout to observe a sharp peak for the internal standard tetramethylsilane in order to eliminate any possible band broadening due to viscosity effects.

These results clearly show that the rate of the chair–chair interconversion has been slowed to the point that the average lifetime τ at −66.5° is of the same order of magnitude as the difference ($\nu_a - \nu_e$) for the equatorial and axial protons. From

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[1] Estimates of 9–10 kcal./mole (C. W. Shoppee, *J. Chem. Soc.*, 1138 (1946)) and 14 kcal./mole (C. S. Beckett, K. S. Pitzer and R. Spitzer, THIS JOURNAL, **69**, 2488 (1947)) have been made.

[2] The measurements were carried out with a Varian Associates n.m.r. spectrophotometer, Model No. V-4311, operated at 60 mc.