

XIII

seems unlikely that this type of interaction is important.

Experimental

Melting points are uncorrected. Analyses were performed by Weiler and Strauss, Oxford, England. Gas chromatographic analyses were performed using a Perkin-Elmer model 154-C vapor Fractometer. The column used for the analysis of the alcohols was a 1 m. \times 6 mm. Pyrex tube packed with 9% by weight THEED (tetra-(hydroxyethyl)-ethylenediamine) on 60-80 mesh Celite. The column used in preparative runs was a 1 m. \times 15 mm. tube packed with 20% by weight THEED on Celite.

endo-7-Isopropylidene-bicyclo-(2,2,1)-5-hepten-2-ol (Ia), m.p. 74-75°, was prepared by the method of DePuy and Story.⁴

exo-7-Isopropylidene-bicyclo-(2,2,1)-5-hepten-2-ol was obtained by equilibration of Ia. The *endo*-alcohol (5 g., 0.03 mole), aluminum isopropoxide (6.8 g., 0.03 mole) and acetone (0.1 ml.) were dissolved in 100 ml. of dry isopropyl alcohol and the solution heated under reflux for 72 hours. Dilute acid was added, the products extracted with ether, the extracts washed and dried over anhydrous MgSO₄. The solvent was carefully removed (the alcohols are very volatile) and the resulting oil analyzed by g.p.c. It contained about 43% *exo*-alcohol. The mixture was dissolved in pentane and as much *endo*-alcohol as possible allowed to crystallize, leaving a mixture containing about 60% *exo*-alcohol. A single pass through the preparative column was sufficient to separate about 200 mg. of the oil into two crystalline alcohols. Recrystallization from pentane gave the *exo*-alcohol in the form of long white needles, m.p. 56-57°.

Anal. Calcd. for C₁₀H₁₄O: C, 79.95; H, 9.39. Found: C, 79.65; H, 9.27.

endo-7-Isopropylidene-bicyclo-(2,2,1)-2-heptanol, m.p. 81-82°, was prepared by the method of DePuy and Story.⁴

exo-7-Isopropylidene-bicyclo-(2,2,1)-2-heptanol was prepared by equilibration of the corresponding *endo*-alcohol as described above. After isolation by g.p.c. and recrystallization from pentane it had a m.p. 62.5-63°.

Anal. Calcd. for C₁₀H₁₆O: C, 78.89; H, 10.59. Found: C, 78.64, 78.02; H, 9.07, 10.13.

Tosylates.—All tosylates were prepared from the alcohols by the method of Tipson.¹³ The *endo*-tosylates have been described earlier.⁴ The *exo*-tosylates decomposed on standing or heating and accurate melting points could not be obtained.

Kinetic Measurements.—The technique used was that of Winstein.¹⁴ The bath temperatures were 49.99 \pm 0.02° and 30.00 \pm 0.03°. The acetolyses were run in sealed tubes each containing 5 ml. of solution, approximately 0.035 *M* in tosylate and 0.040 *M* in sodium acetate. The reactions gave good first-order plots over at least 50% of the reaction, but some curvature was observed at long reaction times. Several infinity points checked with calculated values to within a few per cent.

Product Analysis.—About 1.5 g. of each of the tosylates was allowed to solvolyze at 50° for 24 hours in 40 ml. of dry acetic acid which was 0.2 *M* in sodium acetate. The reaction mixture was poured into cold water and extracted with pentane. The extracts were washed with water, dried and the pentane removed. The product in each case showed only a single peak on g.p.c. analysis, under conditions which readily separated mixtures of the acetates of all four compounds. The acetates were hydrolyzed, the hydrolysis products extracted with pentane, dried and the solvent carefully removed. In each case the products crystallized immediately, and the alcohol was obtained in 85-90% yield after chromatography or recrystallization. The *endo*-tosylates gave these high yields of the corresponding *endo*-alcohols, identified by their infrared spectra and mixture melting points with authentic samples. The *exo*-tosylates gave two new alcohols.

Alcohol from Acetolysis of Vb.—This alcohol melted at 102.5-103.5°. It readily absorbed hydrogen over palladium-on-carbon and had infrared peaks at 6.36 and 13.7 μ , characteristic of the dehydronorbornyl system.

Anal. Calcd. for C₁₀H₁₄O: C, 79.95; H, 9.39. Found: C, 80.22; H, 9.38.

After the uptake of one molar equivalent of hydrogen the resultant dihydro alcohol was identical with that described below from the solvolysis of VI.

The alcohol from the acetolysis of VI melted at 86-87°.

Anal. Calcd. for C₁₀H₁₆O: C, 78.89; H, 10.59. Found: C, 78.64; H, 10.80.

(13) R. S. Tipson, *J. Org. Chem.*, **9**, 235 (1944).

(14) S. Winstein, C. Hansen and E. Grunwald, *J. Am. Chem. Soc.*, **70**, 812 (1948).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE PENNSYLVANIA STATE UNIVERSITY, UNIVERSITY PARK, PENNA.]

The Proton Nuclear Magnetic Resonance Spectra of Cyclohexane, *cis*- and *trans*-Decalin, *cis*- and *trans*-Hydrindan and *cis*-Bicyclo[3.3.0]octane

BY WILLIAM B. MONIZ AND JOSEPH A. DIXON

RECEIVED NOVEMBER 3, 1960

The 40 mc. proton n.m.r. spectra of six alicyclic hydrocarbons have been studied over a range of temperatures. From changes in the spectrum of *cis*-hydrindan at low temperature, it has been possible to obtain an approximate value of 6.4 kcal./mole for the energy barrier to chair-chair interconversion of the molecule. The lack of change in the *cis*-decalin spectrum at low temperature indicates that the chair-chair interconversion energy barrier is lower than that of *cis*-hydrindan, presumably because of non-bonded proton interactions. The spectra of *trans*-decalin, *trans*-hydrindan and *cis*-bicyclo[3.3.0]octane change little with temperature. The unusually low-field absorption present in the last, and attributed to the bridgehead protons, is qualitatively explained in terms of C-C bond anisotropy.

Introduction

For some time, much interest has centered around the preferred conformations of cyclohexane, the isomeric decalins and related compounds containing the six-membered ring. Conformational analysis has supplied some qualitative answers to the problems of carbon skeleton flexibilities and favored arrangements of the atoms in these systems.¹⁻⁵

(1) D. H. R. Barton and R. C. Cookson, *Quart. Revs. (London)*, **10**, 44 (1956).

The use of n.m.r. techniques to obtain conformational information about some of these systems appeared promising because of the marked dif-

(2) W. G. Dauben and K. S. Pitzer in "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, Chap. 1.

(3) W. Klyne in "Progress in Stereochemistry," Vol. 1, Academic Press, Inc., New York, N. Y., 1954, Chap. 2.

(4) S. J. Angyal and J. A. Mills, *Revs. Pure and Appl. Chem. (Australia)*, **2**, 185 (1952).

(5) H. D. Orloff, *Chem. Revs.*, **54**, 347 (1954).

ference between the spectra of the flexible alicyclic and the rigid alicyclic hydrocarbons. If the motions of the flexible molecules could be slowed sufficiently, it should be possible to observe concomitant changes in the spectra, as, for example, has been the case for rotational isomers of sterically hindered amides.⁶ The effect recently has been observed in cyclohexane by Jensen, Noyce, Sederholm and Berlin.⁷

Experimental

Samples.—The *cis*-hydrindan (99.95 mole %) and *trans*-hydrindan (99.71 mole %) are API Research hydrocarbons.⁸

The *cis*-decalin, *trans*-decalin and *cis*-bicyclo[3.3.0]octane are PSU hydrocarbons⁹ of minimum purity 95 mole %. Fisher Scientific Co. "spectranalyzed" cyclohexane was used for the chloroform studies; Phillips pure grade cyclohexane (99.0 mole % minimum purity) for the carbon disulfide studies.

The solvents used were J. T. Baker analyzed reagent chloroform and carbon disulfide. The tetramethylsilane was obtained from Peninsular Chemresearch, Inc., Gainesville, Fla.

Sample Preparation.—Solutions (20% by volume) of each sample were prepared, in chloroform and in carbon disulfide. The CS₂ solutions were freeze-thaw degassed before being sealed under nitrogen in cleaned 5 mm. o.d. Pyrex sample tubes. The internal reference in all cases was tetramethylsilane, 1–5% by volume.

For studies below –130°, a quantity of CCl₂F₂ was added to the *cis*-hydrindan and *cis*-decalin CS₂ sample solutions. These samples remained liquid down to approximately –150°. It was found, however, that resolution deteriorated rapidly below –130°, due either to viscous broadening or instrument instabilities (caused, e.g., by excessive frost formation), or both.

Spectrometer.—A Varian Associates model 4300-2 n.m.r. spectrometer operating at 40 mc. was employed for all measurements.

Variable Temperature Accessory.—The Varian variable temperature accessory, model V-4340, and spinning sample Dewar insert were employed for all non-ambient temperature studies. The temperature was monitored by means of a copper-constantan thermocouple located near the sample. The apparatus was calibrated in the following manner, using a dummy sample: a second thermocouple was immersed in the sample, and the temperatures of both thermocouples were recorded under simulated operating conditions over the temperature range studied (60° to approximately –140°). The resulting calibration curve allowed determination of the true sample temperature to an estimated accuracy of ±0.5°. All temperatures reported herein are true sample temperatures.

Calibration of Spectra.—For calibrations, image peaks were imposed upon the spectrum¹⁰ with a Hewlett-Packard model 202-A low frequency function generator. The frequency was continuously monitored with a Hewlett Packard industrial electronic counter, model 521C, using the 10-second gate. A total of six to ten sweeps was made for each calibration, usually at two or more imposed frequencies. The temperature was determined at frequent intervals.

(6) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).

(7) F. R. Jensen, D. S. Noyce, C. H. Sederholm and A. J. Berlin, *J. Am. Chem. Soc.*, **82**, 1256 (1960); F. R. Jensen and D. S. Noyce, private communication.

(8) These samples of API Research hydrocarbons have been made available by the American Petroleum Institute through the API Research Project 44 at the Carnegie Institute of Technology. The samples were purified by the API Research Project 6 from material supplied by the API Research Project 45 at the Ohio State University. Description of the purification and purity of these samples is given by A. J. Streiff, A. R. Hulme, P. A. Cowie, N. C. Krouskop and F. D. Rossini, *Anal. Chem.*, **27**, 411 (1955).

(9) The *cis*-decalin and *trans*-decalin were generously supplied by API Research Project 45 at the Ohio State University; the *cis*-bicyclo[3.3.0]octane was supplied by API Research Project 42 at The Pennsylvania State University.

(10) J. T. Arnold and M. E. Packard, *J. Chem. Phys.*, **19**, 1608 (1951).

The locations of prominent peaks were computed with respect to the internal standard of tetramethylsilane to 0.1 c./s. Standard deviations were calculated for all measured peaks; values whose deviation from the mean exceeded twice the standard deviation were discarded. The standard error was computed for each mean value. Standard deviations were generally below 1 c./s. and standard errors about 0.4 c./s.

Anisotropy Calculations for *cis*-Bicyclo[3.3.0]octane.—The ring system was constructed from one piece of 1/32-inch sheet aluminum, assuming planar rings and 108° angles. The sheet was bent at the ring fusion to an angle of 109.5°. The C–H bonds, 1/8-inch-wide aluminum strips cut to appropriate length, were secured to the rings with masking tape. The C–C–H angles were adjusted to 109.5° with the aid of paper gussets whose angles were carefully measured with a protractor. The scale of the model was one inch to one ångström, with the following bond lengths assumed: C–C, 1.54 Å.; C–H, 1.09 Å. It is estimated that the angles in the model were accurate to ±2° and the bond lengths to ±0.05 inch.

Thread was strung between the proton being measured and the centers of the various C–C bonds. Paper gussets were cut to fit the acute angle between the thread and the C–C bond, and measured with a protractor. The distances were measured to 1/16 of an inch with a ruler.

All measured angles and distances are listed in Table I, along with the frequency shifts calculated by means of the equation¹¹

$$\sigma_{av} = \frac{(3 \cos^2 \theta - 1)(\chi_T - \chi_L)}{3r^3}$$

taking $(\chi_T - \chi_L)$ equal to -5.5×10^{-30} cm.³/molecule.¹² The common elements which arise because of symmetry were not carried through the calculations. The numbering of the protons and C–C bonds is shown in Fig. 1. It is estimated that the calculated shielding values are accurate to ±15%.

Results and Conclusions

Cyclohexane.—The cyclohexane signal observed at 40 mc. begins to broaden rapidly below –60°. At –71.0 ± 0.5° a distinct flattening of the top of the signal is noticeable. The signal becomes an unsymmetrical doublet at slightly lower temperature. At –77.5 ± 0.5° additional structure begins to appear in the wings. Further decrease in temperature causes the resulting unsymmetrical quartet (Fig. 2) to become well defined. The flattening of the signal at –71° can be attributed to the first appearance of distinct signals from axial and equatorial protons. The rate of chair–chair interconversion is of the same order of magnitude as the chemical shift. However, the observed frequency separation of the initial doublet peaks, 8.6 c./s., cannot be taken as the true chemical shift because of the appearance of the additional structure at –77.5°.

Since the cyclohexane protons constitute an A₆B₆ (or perhaps even more complex) system, a rigorous spectral analysis is impossible, particularly in view of the few resolved components in the observed spectrum.

Jensen, *et al.*,⁷ have calculated an energy barrier to chair–chair interconversion of 10.1 kcal./mole from 60 mc. low-temperature data.

Several n.m.r. studies of six-membered ring systems^{13,14} have shown that, with few exceptions, the

(11) H. M. McConnell, *ibid.*, **27**, 226 (1957).

(12) A. A. Bothner-By and C. Naar-Colin, *Ann. N. Y. Acad. Sci.*, **70**, 833 (1958).

(13) R. U. Lemieux, R. K. Kullnig, H. J. Bernstein and W. G. Schneider, *J. Am. Chem. Soc.*, **79**, 1005 (1957); **80**, 6098 (1958).

(14) R. U. Lemieux, R. K. Kullnig and R. Y. Moir, *ibid.*, **80**, 2237 (1958).

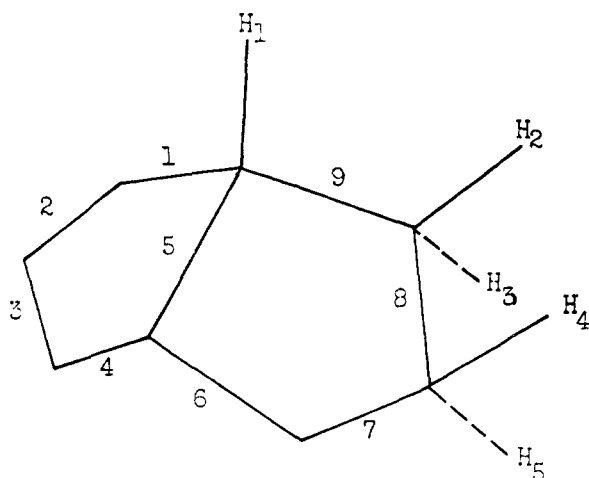


Fig. 1.—Numbering of the C-C bonds and protons designated in Table I.

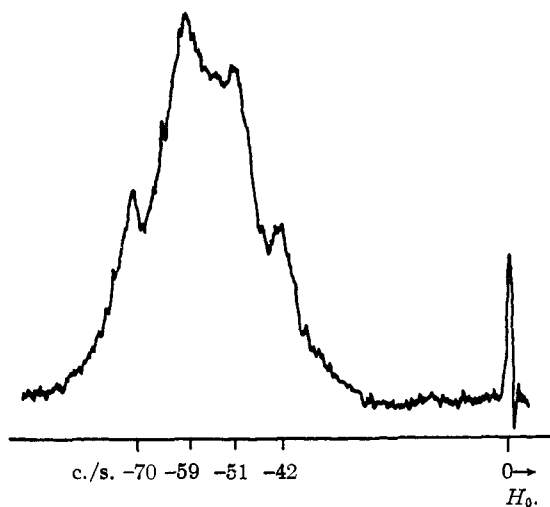


Fig. 2.—N.m.r. spectrum of cyclohexane 20% in CS₂ at -101° (tetramethylsilane internal reference = 0).

signals from axial protons appear at higher fields than those from equatorial protons. Calculations by Jackman¹⁵ based upon the anisotropy of the C-C bond predict a higher shielding value for the axial protons. It is therefore reasonable to assign the high-field signals in the low temperature cyclohexane spectrum to the axial protons.

cis-Hydrindan.—The more intense (high-field) component of the *cis*-hydrindan spectrum is located at about the same position as the cyclohexane signal. Consequently, the signal at -55 c/s. (Fig. 3) is assigned to the protons of the six-membered ring. At temperatures below -110°, this signal begins to broaden rapidly, eventually coalescing with the low-field component so that only one broad signal is observed below -127°. Unfortunately, even at the lowest temperature reached, -140°, no structure becomes visible, preventing a firm calculation of the chair-chair interconversion energy barrier.

If it is assumed that the Eyring equation¹⁶ is

(15) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, Inc., New York, N. Y., 1959, p. 117.

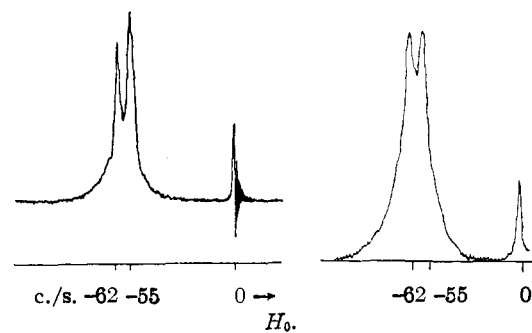


Fig. 3a.

Fig. 3b.

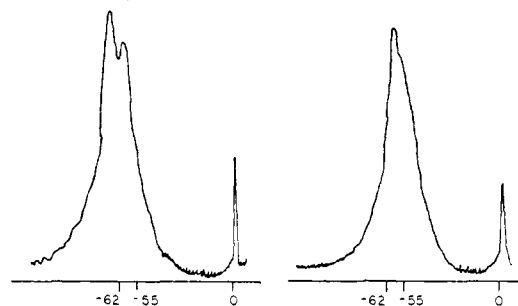


Fig. 3c.

Fig. 3d.

Fig. 3.—N.m.r. spectrum of *cis*-hydrindan 20% in CS₂: a, 25°; b, -114°; c, -122°; d, -127° (tetramethylsilane internal reference = 0).

applicable, it is possible to calculate a probable maximum value of the energy barrier to chair-chair interconversion of *cis*-hydrindan

$$\Delta F^* = 2.3RT \left(\log \frac{kT}{h} - \log k' \right)$$

where k' is the specific reaction rate. If a value of $k' = 100$ (corresponding to a chemical shift of 22 c/s.) is chosen, and a temperature of -133°, a value of ΔF^* of 6.4 kcal./mole is obtained. It can be seen that varying k' by a factor of ten will change ΔF^* by 0.6 kcal./mole. The temperature is subject to error, but probably by not more than ten degrees. Calculations for -143° give a value for ΔF^* of 6.0 kcal./mole.

The enthalpy of activation (ΔH^*) may be estimated by assuming that the entropy of activation is small: $\Delta H^* \cong \Delta F^* = 6.4$ kcal./mole.

It is likely that ring-fusion strains present in *cis*-hydrindan bring about the relatively low energy barrier.

cis-Decalin.—The comparison of *cis*-hydrindan with *cis*-decalin is informative; in the latter, no strains are introduced as a result of the ring fusion. However, there are present in the two-chair conformation of *cis*-decalin two pairs of protons in close proximity.² The spectrum of *cis*-decalin at temperatures as low as -121° shows no indication of the broadening which occurs in the case of *cis*-hydrindan at higher temperatures. It is therefore reasonable to assume that ΔH^* of *cis*-decalin is lower than that of *cis*-hydrindan and that the non-bonded interactions present in *cis*-decalin raise the

(16) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 195.

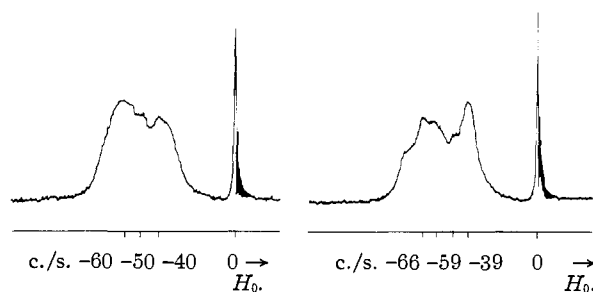


Fig. 4.—N.m.r. spectrum of *trans*-decalin 20% in CHCl_3 at 25° (tetramethylsilane internal reference = 0). Fig. 5.—N.m.r. spectrum of *trans*-hydrindan 20% in CHCl_3 at 25° (tetramethylsilane internal reference = 0).

ground state energy to a greater extent than do the strains present in the six-membered ring of *cis*-hydrindan.

***trans*-Decalin and *trans*-Hydrindan.**—The broad, ill-defined spectra of *trans*-decalin and *trans*-hydrindan resemble the low temperature spectrum of cyclohexane. The nature of the ring fusion does not allow chair-chair interconversion of these molecules. The low temperature spectra are not very revealing; at temperatures below -115° some broadening of the high-field component of the *trans*-decalin spectrum occurs. The spectrum of *trans*-hydrindan changes little with temperature.

Some general assignments of signals are possible, based upon the low temperature cyclohexane spectral interpretation. The signals at -60 c/s. (Fig. 4) and -63 c/s. (Fig. 5) may be attributed to the equatorial protons of *trans*-decalin and *trans*-hydrindan, respectively. The high-field signals in each spectrum may be attributed to the axial protons. It is likely that inter-ring anisotropy effects will not contribute greatly to the observed shifts.

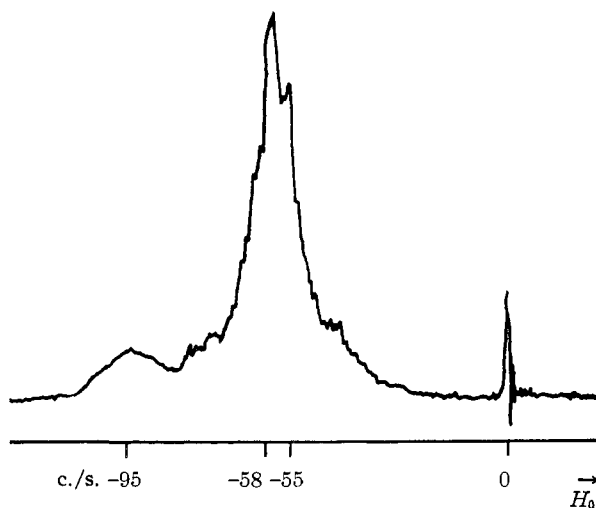


Fig. 6.—N.m.r. spectrum of *cis*-bicyclo[3.3.0]octane 20% in CHCl_3 at 25° (tetramethylsilane internal reference = 0).

The distinct differences in the character of the n.m.r. spectra of *cis* and *trans* fused systems containing the six-membered ring is of analytical value.

TABLE I
ANISOTROPY CALCULATIONS FOR *cis*-BICYCLO[3.3.0]OCTANE

Proton	C-C bond	Nr. ident. ^a C-C bonds	θ ($^\circ$)	r , Å.	σ_{av} , p.p.m.	$\Sigma\sigma_{av}$, p.p.m.
1	1	1(3)	42.5	1.54	-0.315	-0.38
	2	2(4)	44	2.56	- .122	
	3	1(2)	90	3.13	+ .060	
2	1	1	43	2.56	- .064	-0.12
	2	1	40	3.75	- .027	
	3	1	90	4.31	+ .023	
	4	1	30	3.69	- .047	
	5	0(2)	44	2.56	
3	6	0(1)	90	3.13	+0.16
	8	0(2)	42.5	1.54	
	1	1	78	2.13	+ .166	
	2	1	41	2.94	- .054	
	3	1	77	3.69	+ .031	
	4	1	62	3.56	+ .014	
	5	0(2)	44	2.56	
	6	0(1)	90	3.13	
4	8	0(2)	42.5	1.54	-0.07
	1	2	32	3.75	- .082	
	2	2	64	4.69	+ .015	
	5	0(1)	90	3.13	
5	6	0(2)	44	2.56	+0.08
	7	0(2)	42.5	1.54	
	1	2	63	3.44	+ .036	
	2	2	77	4.00	+ .048	
	5	0(1)	90	3.13	
	6	0(2)	44	2.56	
	7	0(2)	42.5	1.54	

^a The number in parentheses indicates the number of identical C-C bonds prior to cancellations because of symmetry.

It appears that the spectra of compounds containing a rigid *trans* fused cyclohexane ring will consist of broad, overlapping signals, while *cis* fused systems will show sharp, narrow resonances, if rigidity is not forced upon the molecule by other factors.

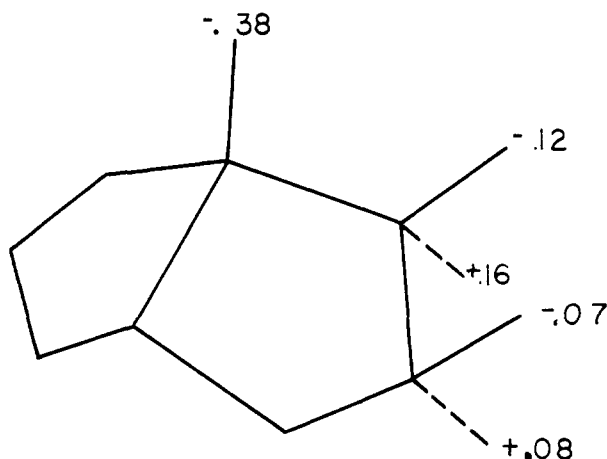


Fig. 7.—Results of the anisotropy calculations for *cis*-bicyclo[3.3.0]octane. The chemical shifts in p.p.m. are indicated adjacent to the appropriate protons.

cis-Bicyclo[3.3.0]octane does not properly belong in a consideration of six-membered ring systems. However, because the molecule is ex-

pected to be rather rigid, and a preliminary examination of its n.m.r. spectrum aroused interest, it was included in this study.

The most interesting aspect of the spectrum (Fig. 6) is the unusually low-field signal at -95 c./s. which is attributed to the bridgehead protons. The direction of shift corresponds to that of the cyclohexane equatorial protons, but the magnitude of the shift (1.0 p.p.m.) is unexpected. Calculations (Table I) based upon the anisotropy of the C-C bond resulted in the chemical shifts (p.p.m.) indicated in Fig. 7. Although the calculated shift of 0.6 p.p.m. is only about half of the observed shift, the low-field position of the bridgehead protons is qualitatively explained. Because of the ring strains and non-bonded interactions of the protons below the planes of the ring, it is very likely that the shape of the five-membered rings and the bond angles are appreciably different from those assumed for the

model. Additionally, changes of bond angles and bond lengths will alter electron densities and hybridization.

It is evident that the carbon skeleton of *cis*-bicyclo[3.3.0]octane is quite rigid; otherwise there would be little resolved structure in the n.m.r. spectrum.

It is probable that only the β -methylene groups enter appreciably into the puckering motions of the rings.

Acknowledgment.—The American Petroleum Institute is thanked for the donation of the bicyclic compounds which were employed in this study. The authors express their appreciation to Dr. William A. Steele and to Dr. Richard E. Glick for several helpful discussions. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

[CONTRIBUTION FROM THE DANIEL SIEFF RESEARCH INSTITUTE, THE WEIZMANN INSTITUTE OF SCIENCE, REHOVOTH, ISRAEL]

Unsaturated Macrocyclic Compounds. XVII.¹ The Prototropic Rearrangement of Linear 1,5-Enynes to Conjugated Polyenes. The Synthesis of a Series of Vinylogs of Butadiene

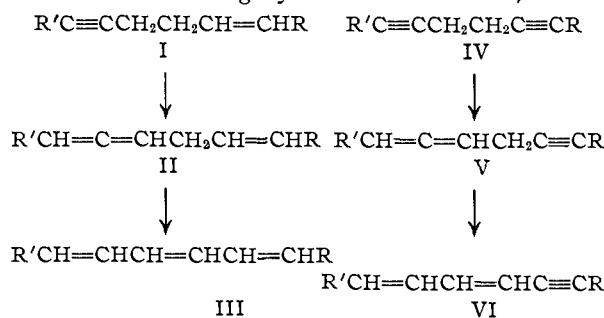
BY FRANZ SONDHEIMER, DAVID A. BEN-EFRAIM AND REUVEN WOLOVSKY

RECEIVED NOVEMBER 9, 1960

It is shown that 1,5-enynes are rearranged to conjugated polyenes by means of potassium *t*-butoxide in *t*-butyl alcohol. The method is used for the synthesis of a series of vinylogs of butadiene, containing 3, 5, 6, 8 and 10 conjugated double bonds. The ultraviolet spectra data of this simplest possible class of conjugated polyene are discussed briefly.

Large-ring compounds containing α,γ -diacetylene units have recently become available through the oxidative coupling of aliphatic α,ω -diacetylenes.³ These highly unsaturated cyclic substances promised to be suitable intermediates for the synthesis of completely conjugated cyclic polyenes, systems which are of considerable theoretical interest.

For instance if 1,5-enyne units (I) could be introduced into a ring by the above method, it was



(1) For Part XVI, see F. Sondheimer, Y. Gaoni and J. Bregman, *Tetrahedron Letters*, **26**, 25 (1960). Although the present paper and the subsequent one² are concerned only with acyclic compounds, they have been included in this series since reactions are described which served as models for analogous ones applied subsequently in the macrocyclic series.

(2) F. Sondheimer, D. A. Ben-Efraim and Y. Gaoni, *J. Am. Chem. Soc.*, **83**, 1682 (1961).

(3) F. Sondheimer, *et al.*, *ibid.*, **78**, 4178 (1956); **79**, 4247, 5817, 6263 (1957); **81**, 4600, 6301 (1959); G. Eglinton and A. R. Galbraith, *Chemistry & Industry*, 737 (1956); *J. Chem. Soc.*, 889 (1959).

considered possible that subsequent base treatment would result in rearrangement *via* the allenes II to 1,3,5-trienes III with the consequent formation of a completely conjugated cyclic polyene. Alternatively a cyclic substance incorporating 1,5-diyne units (IV) might be isomerized *via* the allenes V to a conjugated system containing 1,3-dien-5-yne units (VI), which could then be hydrogenated to a conjugated cyclic polyene. In fact this second route to the latter class of compound has proved to be realizable, as described so far in preliminary reports.⁴

Before studying the rearrangement of I to III and IV to VI in the cyclic series, it was decided first to work with more accessible linear models. Related isomerizations of acids of type I and IV where R = COOH to conjugated polyene and polyenyne acids by means of potassium hydroxide had been carried out previously.⁵ It was not known however whether removal of the conjugating influence of the carboxylic acid grouping would not cause the rearrangements to proceed differently or to require such drastic conditions as to result in polymerization of the products. Indeed the fact that a number of hydrocarbons of type I and IV had been prepared by dehydrohalogenation of halo-compounds with alcoholic potassium hydrox-

(4) F. Sondheimer and R. Wolovsky, *J. Am. Chem. Soc.*, **81**, 1771, 4755 (1959); *Tetrahedron Letters*, No. 3, 3 (1959); F. Sondheimer, R. Wolovsky and Y. Gaoni, *J. Am. Chem. Soc.*, **82**, 754, 755 (1960).

(5) E. R. H. Jones, B. L. Shaw and M. C. Whiting, *J. Chem. Soc.*, 3212 (1954); B. L. Shaw and M. C. Whiting, *ibid.*, 3217 (1954).