The ruthenium catalyst was significantly superior to rhodium with respect to the selective formation of II rather than III under all conditions studied.

Conformations of Bicyclo[3.3.1]nonanes. 3-Methyl-2,4-dioxabicyclo[3.3.1]nonane

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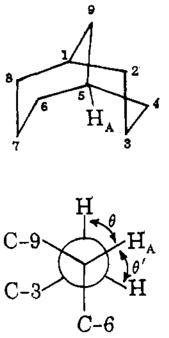
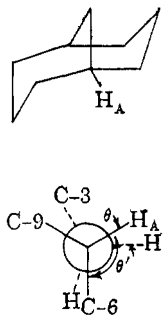
The bicyclo[3.3.1]nonane ring is interesting because the two "inside" hydrogens on C-3 and C-7 in the conformation (I) must have a considerable interaction. As a part of a program of study of the chemistry of the bridged medium rings it was important to ascertain the effect of this interaction on the preferred conformation of the ring. Until recently no information pertinent to this problem has been available, but it has been shown[1] *via* X-ray analysis that the hydrogen repulsion is relieved by flattening each ring *via* spreading the ring angles to 114°. The preferred conformation is the double chair (I) where the "inside" atoms at C-3 and C-7 are both hydrogen.

This paper describes an attempt to solve the conformational problem through the use of n.m.r. spectroscopy. Vicinal coupling constants are primarily dependent on the dihedral angle,[2] so that the bridgehead proton, H_A, should be nearly equivalently coupled to the two protons at C-4 in I ($\theta = \theta'$), but unequally coupled to the same pair in II ($\theta \neq \theta'$). For conformation I, H_A is expected to exhibit a triplet (AX_2) in the n.m.r. spectrum, whereas for II a quartet (doublets of a doublet, AXY with $J_{AX} \neq J_{AY}$) should appear. Thus the n.m.r. spectrum might be expected to differentiate between I and II in two ways: (a) the difference in the vicinal coupling constants and (b) the difference in the spectral patterns for the bridgehead proton, H_A.



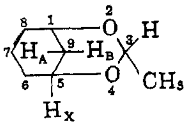
I



II

Actually the situation is considerably less favorable than this analysis would suggest. Unless the protons under consideration can be isolated from those in the remainder of the molecule, the spectrum would probably be too complex for analysis. Even then analysis would be troublesome unless the protons had a sufficiently large chemical shift difference. Distortion of the molecule from the symmetrical conformations I and II might tend toward a common spectrum intermediate between the extremes depicted above. Finally rapid interconversion of I and II would lead to a pair of coupling constants which are a weighted average of those characteristic of the protons in each environment.[4] Thus it is possible that an unambiguous conformational assignment might not be possible. Seeking a simple, readily accessible molecule to permit an experimental test of n.m.r. for conformational studies in this ring system we chose to study some 2,4-dioxabicyclo[3.3.1]-nonanes.

All attempts to prepare a cyclic acetal from cyclohexane-1,3-diol (predominantly the *cis* isomer) and various aldehydes failed. Exchange methods utilizing commercially available acetals or ketals fared no better. Apparently the equilibrium concentration of cyclic acetal is negligibly small, the reduced stability of the acetal undoubtedly being an effect of the hydrogen repulsions mentioned earlier. Eventually we prepared a sample of 3-methyl-2,4-dioxabicyclo[3.3.1]-nonane (III), albeit in low yield, by the method of Croxall, Glavis, and Neher.[5] III was clearly identified by (a) its molecular weight, which eliminates polymeric acetals, (b) its hydrolysis to give acetaldehyde, (c) its infrared spectrum which shows the absence of hydroxyl and carbonyl groups, and the presence of ether links, and (d) its n.m.r. spectrum which is discussed in detail below.



III

The n.m.r. spectrum of III exhibits peaks in three general groups, a sharp quartet at τ 4.74, a poorly resolved quintet at 5.79, some 16–20 peaks between 7.2 and 8.0 merging into a series of peaks between 8.0 and 9.0, and a sharp doublet at 8.8. Some of the bands are immediately and unequivocally assignable. The sharp quartet (1H) at τ 4.74 is due to the C-3 proton which is uniquely coupled (J = 5.0 c.p.s.) to the methyl protons as an AX_3 set. Accordingly the methyl group shows up as a clean doublet (3H) at τ 8.8 with the same coupling. The most important feature of the spectrum for our analysis is the incompletely resolved quintet (2H) at τ 5.79. A repetitive spacing of 2.5 c.p.s. and a width at half-height of 9.0 c.p.s. characterize the peak. It is certainly due to the bridgehead protons. The remainder of the spectrum is complex. It is pleasing to note that the τ 8–9 section of the spectrum bears a very strong resemblance to that of *cis*-1,3-

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(1) W. A. Brown, G. Eglinton, J. Martin, W. Parker, and G. A. Sim, *Proc. Chem. Soc.*, 57 (1964).

(2) M. Karplus, *J. Chem. Phys.* **30**, 11 (1959). It has been stressed recently[3] that other factors may also influence the coupling constants. Reliable results can be expected in a quantitative manner only with closely related species. In the present application where a theoretical value of J is compared with a measured one to provide an absolute test for conformation, it seems safe to apply the method where the predicted difference of J's for the conformations is large, or where good experimental models are available to provide confirmatory evidence.

(3) M. Karplus, *J. Am. Chem. Soc.*, **85**, 2870 (1963).

(4) For a clear discussion of this point, see J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., New York, N. Y., 1959, pp. 377–381.

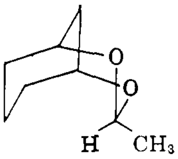
(5) W. J. Croxall, F. T. Glavis, and H. T. Neher, *J. Am. Chem. Soc.*, **70**, 2805 (1948).

dibromocyclohexane in the same region.[6] Significantly *cis*-1,3-dibromocyclohexane is a conformationally nearly uniform molecule.

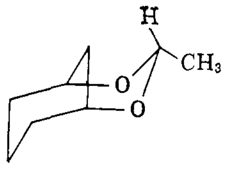
A series of some 16–20 peaks between τ 7.2 and 8.0 has been tentatively assigned to the protons on the bridge carbon. The group integrates roughly for two protons, and would be expected to show a downfield shift due to the deshielding of two β-oxygens. As a first approximation the spectrum was treated as the AB part of an ABX_2 spectrum.[7] The most reasonable fit gives an eleven-line pattern with $|J_{gem}| = 12.5$ c.p.s. and $\Delta\nu = 18.7$ c.p.s.[8] The values are in the expected ranges for a geminal coupling constant[11] and the chemical shift between axial and equatorial protons.[12] The conclusion that the bridge protons are coupled contrasts with the result reported by Zaugg[13] for a similar molecule.

These data do not permit us the luxury of a complete conformational assignment for III, but certain valuable conclusions can be reached. The appearance of a sharp quartet for the C-3 proton strongly suggests that III has only a single configuration at C-3. Whether the C-3 proton is *exo* or *endo*, and whether the *m*-dioxane ring has a single conformation or is rapidly converting between boat and chair forms is not discernable. The question of the conformation of the cyclohexane ring can be answered more clearly. Study of a number of oxygen- and halogen-substituted cyclohexanes shows that $J_{e,e} \cong J_{a,e} = 2.6$–$4.0$ c.p.s.[14] Using the bicyclo[2.2.1]heptane ring as a model for the boat conformation, we find that $J_{exo,exo} \cong J_{endo,endo} = 7.0$–$9.2$ c.p.s. and $J_{exo,endo} = 2.2$–2.3 c.p.s.[15] A series of drawings of hypothetical spectra for the chair and the boat forms using a variety of the above coupling constants shows that the best fit for the bridgehead protons is obtained for a rigid chair form. It is not possible however, to exclude a rapid interconversion of chair and boat forms with the chair predominating at equilibrium.

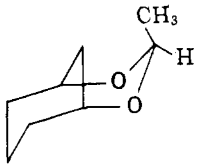
Two conformations have to be considered, IV and V. A third, VI, was excluded since scale drawings indicated that the flagpole methyl–flagpole hydrogen interaction was at least as severe as the C-3–C-7 hydrogen–hydrogen repulsion in IV. IV and V differ in configuration at C-3 and we hoped to be able to differentiate between the two possibilities by preparing a 7-keto derivative. The inside hydrogen in IV would then be within the shielding cone of the carbonyl group[16] while the C-3 proton in V would be virtually unaffected. We prepared an impure 7-hydroxy-3-methyl-2,4-dioxabicyclo[3.3.1]nonane (VII), but its extreme sensitivity to acid-catalyzed polymerization prevented our carrying the synthesis further. According to the n.m.r. spectrum, VII was not a single isomer. This was expected since its synthesis commenced with 1,3,5-cyclohexanetriol which was a mixture of *cis* and *trans* isomers.[17]



IV



V



VI

One further attempt to obtain evidence supporting one or the other of the two conformations was made. Kivelson and Winstein[18] have found the asymmetric methylene stretching frequency appears near or above 3000 cm.$^{-1}$ when that group is forced by molecular geometry into the very close proximity of a second C–H link. III and VII were examined in the C–H stretching region and each showed a cleanly delineated band at 2996 cm.$^{-1}$. This cannot be due to a coupled methylene because both compounds possess the same absorption. Doubtless this is merely another example of the influence of oxygen on C–H stretching frequencies.[19] Our results show that ring closure to cyclic acetals contributes to a further rise in the frequency, *i.e.* acetaldehyde diethyl acetal 2978 cm.$^{-1}$, 2-methyl-1,3-dioxolane[5] 2993 cm.$^{-1}$, 2-ethyl-1,3-dioxolane[20] 2979 cm.$^{-1}$, and 2-ethyl-1,3-dioxane 2972 cm.$^{-1}$

Difficulties with the preparation of the necessary cyclic acetals has led us to abandon further studies in this area. However, the present work shows that n.m.r. methods can be used to study the conformations of appropriately substituted bicyclo[3.3.1]nonanes.

Experimental

3-Methyl-2,4-dioxabicyclo[3.3.1]nonane.—A solution containing 50 g. (0.43 mole) of 1,3-cyclohexanediol,[21] 0.53 g. of mercuric oxide, and 0.5 ml. of boron trifluoride etherate in 200 ml. of anhydrous tetrahydrofuran was maintained at 25° (ice bath) while 111 g. (1.29 moles) of freshly distilled vinyl acetate was added. After the mixture had been stirred for 12 hr., it was poured into a solution of sodium carbonate. When no further carbon dioxide was evolved upon addition of sodium carbonate, the organic layer was separated, dried over anhydrous potassium carbonate, and distilled: b.p. 77–78° (17 mm.), n^{20}_D 1.4630, $\tilde{\nu}$ 1151 and 1108 cm.$^{-1}$. The yield was variable but did not exceed 10%.

Anal. Calcd. for $C_8H_{14}O_2$: C, 67.57; H, 9.92; mol. wt., 142. Found: C, 67.80; H, 9.99; mol. wt. (osmometer), 142.9.

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[6] H. M. van Dort and Th. J. Sekur, *Tetrahedron Letters*, **No. 20**, 1301 (1963).

[7] A. D. Cohen and N. Sheppard, *Proc. Roy. Soc.* (London), **A252**, 488 (1959).

[8] Assuming $J_{AX} = J_{BX}$ an ABX_2 spectrum simplifies to a set of four (generally overlapping) triplets of spacing J_{AX} for the AB part. Here $J_{AX} = 2.5$ c.p.s. Our spectrum deviates from the predicted in two respects. First it does not show the symmetry expected. We attribute this to a long-range coupling between a bridge proton and an equatorial proton at C-6 similar to those reported by the Meinwalds.[9] Second there are too many lines in the observed spectrum. This is probably due to virtual coupling effects,[10] since this is really an $ABX_2Y_2Z_2$ system.

[9] J. Meinwald and Y. C. Meinwald, *J. Am. Chem. Soc.*, **85**, 2514 (1963).

[10] J. I. Musher and E. J. Corey, *Tetrahedron*, **18**, 791 (1962).

[11] M. Barfield and D. M. Grant, *J. Am. Chem. Soc.*, **85**, 1899 (1963).

[12] H. Conroy, "Advances in Organic Chemistry: Methods and Results," Vol. 2, R. A. Raphael, E. C. Taylor, and H. Wynberg, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p. 280.

[13] H. E. Zaugg, R. W. deNet, and E. T. Kimura, *J. Med. Pharm. Chem.*, **5**, 432 (1960), as reported by H. E. Zaugg and R. J. Michaels, *J. Org. Chem.*, **28**, 1801 (1963).

[14] *Cf.* ref. 5; R. U. Lemieux, R. K. Kullnig, H. J. Bernstein, and W. G. Schneider, *J. Am. Chem. Soc.*, **80**, 6098 (1958); E. N. Marvell and H. Sexton, unpublished data.

[15] F. A. L. Anet, *Can. J. Chem.*, **39**, 789 (1961); E. N. Marvell and G. Caple, unpublished data.

[16] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, Inc., New York, N. Y., 1959, p. 124.

[17] H. Stetter and K. H. Steinacker, *Chem. Ber.*, **85**, 451 (1952).

[18] D. Kivelson, S. Winstein, P. Bruck, and R. L. Hansen, *J. Am. Chem. Soc.*, **83**, 2938 (1961).

[19] *Cf.*, for example, T. S. Wang, *J. Org. Chem.*, **28**, 245 (1963), and H. B. Henbest, G. D. Meakins, B. Nicholls, and A. A. Wagland, *J. Chem. Soc.* 1462 (1957).

[20] H. S. Hill and G. J. C. Potter, *J. Am. Chem. Soc.*, **51**, 1509 (1929).

[21] M. F. Clarke and L. N. Owen, *J. Chem. Soc.*, 2103 (1950).

Hydrolysis of 1 g. (7 mmoles) of the above acetal in aqueous ethanolic hydrochloric acid gave acetaldehyde, isolated as the 2,4-dinitrophenylhydrazone, m.p. 148°.[22]

3-Methyl-2,4-dioxa-7-bicyclo[3.3.1]nonanol.—A suspension of 16.1 g. (0.122 mole) of 1,3,5-cyclohexanetriol,[17] 0.4 g. of mercuric oxide, and 0.3 ml. of boron trifluoride etherate in 1500 ml. of anhydrous tetrahydrofuran was heated to reflux and 12.9 g. (0.15 mole) of freshly distilled vinyl acetate was added very slowly. The mixture was heated for 2 hr. after all of the triol had gone into solution. Aqueous sodium carbonate was added until gas evolution ceased and the organic layer was separated and dried over anhydrous potassium carbonate. Evaporation of the solvent gave a thick viscous liquid from which a small amount of more mobile liquid was separated by extraction with ether and chloroform. This was distilled at a bath temperature of 110° at 0.05 mm.: $\tilde{\nu}$ 3425, 1108, and 1093 (with a weak band at 1740 due to acetate impurity). The n.m.r. spectrum showed a quartet (1H) at τ 4.88, a poorly resolved but apparent triplet (2H) at τ 5.63, a singlet (1H) whose position varies between τ 5.9 and 7.5 depending on concentration, a doublet (*ca.* 3H) J = 5.5 c.p.s. at τ 8.88 and a group of unresolved peaks between τ 7.0 and 9.0. This product, obtained in less than 2% yield, polymerized before an analysis could be obtained.

2-Ethyl-1,3-dioxane.—A mixture of 19.3 g. (0.33 mole) of freshly distilled propionaldehyde, 95 g. (1.25 moles) of 1,3-propanediol, and 0.5 g. of *p*-toluenesulfonic acid was allowed to stand overnight, and then heated at reflux for 10 hr. After the addition of 300 ml. of methylene chloride and 10 ml. of 10% potassium hydroxide, the organic layer was separated, washed with saturated sodium sulfate solution, and dried. The product was distilled through a 24-in. helix-packed column, b.p. 130.5-131.5°, $n^{20}\text{D}$ 1.4219, giving 18.5 g. (48%) of a clear mobile liquid. Infrared absorption occurred at 1137, 1100, 1003, 973 cm.$^{-1}$.

Anal. Calcd. for $C_6H_{12}O_2$: C, 62.04; H, 10.41. Found: C, 61.87; H, 10.50.

Infrared Spectra.—Routine spectra were obtained using a Perkin-Elmer Model 21 equipped with sodium chloride prism. Spectra were run in carbon tetrachloride solution or neat in a sandwich cell. The C–H stretching frequencies were studied using a Beckman IR-7 equipped with a grating and capable of resolution to ±1 cm.$^{-1}$ in the 2700–3200-cm.$^{-1}$ range. These spectra were run on 10% solutions in carbon tetrachloride except in those cases where the bands proved too strong in a 0.05-mm. cell and more dilute solutions had to be employed.

Proton Magnetic Resonance Spectra.—Spectra were carried out using a Varian A-60 spectrometer. Samples were run in carbon tetrachloride solution and tetramethylsilane was employed as an internal standard.

Acknowledgment.—The authors are indebted to the Petroleum Research Fund for partial support of this work under Grant 814A. Financial support toward the purchase of the Varian A-60 spectrometer by the National Science Foundation is most gratefully acknowledged.

[22] N. D. Cheronis and J. B. Entrikin, "Semimicro Qualitative Organic Analysis," 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1957, p. 582.

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t-Butyl Hypochlorite Chlorinations of Hydrocarbons. The Role of Chlorinated Solvents[1]

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In the course of a continuing investigation of relationships between reactivity, hyperconjugative stabilization, and activation energies of alkyl radical reactions it became necessary to establish the role of carbon tetrachloride, the usual solvent, in *t*-butyl hypochlorite chlorinations of hydrocarbons.[2] This fairly selective chlorinating agent reacts *via* the chain. Reactions 1–2,

$$(CH_3)_3CO\cdot + RH \longrightarrow (CH_3)_3COH + R\cdot \qquad (1)$$

$$R\cdot + (CH_3)_3COCl \longrightarrow RCl + (CH_3)_3CO\cdot \qquad (2)$$

carried out in nonpolar solvents, proceed cleanly and in high yields. Fluorocarbons, excess hydrocarbon substrate, and carbon tetrachloride have been used as solvents, the last being the most common. Although products and yields are substantially the same in all these solvents, there exists the possibility that in carbon tetrachloride the sequence 3–4 can become a part of the radical chain reaction. The possibility that

$$R\cdot + ClCCl_3 \longrightarrow RCl + \cdot CCl_3 \qquad (3)$$

$$CCl_3 + (CH_3)_3COCl^* \longrightarrow Cl^*CCl_3 + (CH_3)_3CO\cdot \qquad (4)$$

reaction 5 may also occur can be ruled out on the basis of

$$\cdot CCl_3 + RH \longrightarrow HCCl_3 + R\cdot \qquad (5)$$

the report that the relative reactivities of a series of hydrocarbons do not vary significantly with changes in solvent.[3] The absence of any significant amounts of chloroform among the products is inconclusive in view of the considerable selectivity of the trichloromethyl radical.[4] Sequence 3–4 is suggested by the well-known use of polyhalomethanes as chlorinating agents.[5]

The chlorination of toluene, 2,3-dimethylbutane, and 2,2-dimethylpropane (neopentane) in carbon tetrachloride and the possible involvement of the solvent was investigated by the use of *t*-butyl hypochlorite labeled with chlorine-36, a β-emitter. In all cases the activity was found exclusively, within experimental error, in the alkyl chloride product indicating that reactions 3–4 do not occur to any significant extent. Even when the hypochlorite was added dropwise as a dilute solution in carbon tetrachloride to a carbon tetrachloride solution of the hydrocarbon, no activity could be detected in the carbon tetrachloride.

In the case of toluene, the absence of any involvement of the solvent is not unexpected in view of the results of Walling and Padwa who, in a similar reaction with *t*-butyl hypochlorite and toluene in bromotrichloromethane solvent, did not obtain more than a 3% yield of bromotoluene.[6] A reactive alkyl radical (cyclobutyl), however, was reported to react 97% with the solvent to give alkyl bromide, upon dropwise addition of hypochlorite. In our case the failure of even the reactive primary radical neopentyl to react with approximately a 500-fold excess on the average of carbon tetrachloride over hypochlorite indicates a large difference in activation energy for abstraction of bromine *vs.* chlorine from halomethanes. An activation energy of about 13 kcal./mole for abstraction of chlo-

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[1] Research was performed under the auspices of the U. S. Atomic Energy Commission.

[2] (a) C. Walling and A. Padwa, *J. Am. Chem. Soc.*, **85**, 1593 (1963); (b) F. D. Greene, *et al.*, *J. Org. Chem.*, **28**, 55 (1963).

[3] C. Walling and A. A. Zavitsas, *J. Am. Chem. Soc.*, **85**, 2084 (1963).

[4] B. P. McGrath and J. M. Tedder, *Bull. soc. chim. Belges*, **71**, 772 (1962).

[5] (a) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 390; (b) E. S. Huyser, *J. Am. Chem. Soc.*, **82**, 391 (1960).

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