Chromatography.—Thin layer chromatography was carried out with silica gel G (Brinkmann Instruments, Inc., Westbury, Long Island, N. Y.) as backing; the developing solvent was *n*-butyl alcohol–acetone–water (4:5:1, v/v/v). After drying, the plates were sprayed with the permanganate–periodate reagent of Lemieux and Bauer.[18] R_f values follow: IIIa, 0.51; IVa, 0.41; VIIa, 0.44; VIIIa, 0.32.

DL-(1,3/2,4)Tetra-O-acetylcyclopentanetetrol (IIIb). A. From DL-(1,3/2,4)Cyclopentanetetrol.—DL-(1,3/2,4)Cyclopentanetetrol[8] (50 mg, 0.37 mmole) was acetylated by adding 3 ml of pyridine and 2 ml of acetic anhydride and allowing the mixture to stand overnight at room temperature. The reagents were evaporated under reduced pressure to give a yellow syrup, 10 ml of water was added, and the mixture was extracted with ether. The ether solution was washed with 2 *N* HCl, 2 *N* NaOH, and water, dried over Na_2SO_4 and evaporated to a colorless syrup, (III, 80 mg, 71%) which crystallized slowly from ethanol, mp 68°.

Anal. Calcd for $C_{13}H_{18}O_8$ (302.27): C, 51.65; H, 6.00. Found: C, 51.47; H, 6.08.

B. From DL-(1,2,3/4)-2,3-Anhydrocyclopentanetetrol (I).—Sulfuric acid (20 ml, 1%) was added to I prepared from II (500 mg, 2.5 mmoles) by hydrolysis with dilute ammonia–methanol solution (10% saturated) and the mixture was refluxed for 1 hr. The solution was cooled and Amberlite IR-4B was added to remove sulfuric acid; the resin was filtered off and washed with water. The combined filtrate was concentrated at reduced pressure to slightly yellow syrup, which was acetylated (5 ml of pyridine and 5 ml of acetic anhydride, heating for 3 hr at 60°). The usual procedures yielded a colorless syrup of III (550 mg, 73%). The infrared spectra of the substances obtained by both methods were identical.

DL-(1,2/3,4)Tetra-O-acetylcyclopentanetetrol (IVb). A. From DL-(1,2/3,4)Cyclopentanetetrol.—DL-(1,2/3,4)Cyclopentanetetrol[8] (20 mg, 0.15 mmoles) was acetylated (pyridine, 3 ml; acetic anhydride, 2 ml) as described above, yielding 30 mg (68%) of colorless syrup (VI).

Anal. Calcd for $C_{13}H_{18}O_8$ (302.27); C, 51.68; H, 6.00. Found: C, 51.92; H, 6.17.

B. From DL-(1,2,3/4)-1,4-Di-O-acetyl-2,3-anhydrocyclopentanetetrol (II).—Compound II (500 mg, 2.50 mmoles) was hydrolyzed in 1% H_2SO_4 and the hydrolysate was worked up and acetylated by the usual procedures, yielding 520 mg (69%) of IV. The infrared spectra of the substances obtained by both methods were identical.

DL-(1,2,4/3)Tetra-O-acetylcyclopentanetetrol (VIIb). A. From DL-(1,2,4/3)Cyclopentanetetrol.—DL-(1,2,4/3)Cyclopentanetetrol[8] (50 mg, 0.37 mmole) was acetylated with pyridine (3 ml) and acetic anhydride (2 ml) according to the procedure described above. There was obtained 80 mg (71%) of white crystals (VIIb). Recrystallization from ethanol gave colorless needles, mp 81–82°.

Anal. Calcd for $C_{13}H_{18}O_8$ (302.27): C, 51.65; H, 6.00. Found: C, 51.39; H, 5.98.

B. From DL-(1,2/3,4)-1,2-Anhydrocyclopentanetetrol (V).—Compound VI (500 mg, 2.50 mmoles) was treated with dilute ammonia–methanol solution (10%). The product was hydrolyzed with 20 ml of 1% H_2SO_4 and the usual procedures then yielded 490 mg (65%) of white crystals. Recrystallization from ethanol gave needles, mp 81–82°; mixture melting point with the authentic sample showed no depression; and the infrared spectra of both products were identical.

DL-(1,2,3/4)Tetra-O-acetylcyclopentanetetrol (VIIIb). A. From DL-(1,2,3/4)Cyclopentanetetrol).—DL-(1,2,3/4)Cyclopentanetetrol[8] (30 mg, 0.22 mmole) was acetylated by the procedure described above, yielding 60 mg (88%) of colorless syrup (VIIIb).

Anal. Calcd for $C_{13}H_{18}O_8$ (302.27): C, 51.65; H, 6.00. Found: C, 51.66; H, 5.94.

B. From DL-(1,2/3,4)-3,4-Di-O-acetyl-1,2-anhydrocyclopentanetetrol (VI).—Compound VI (500 mg, 2.50 mmoles) was hydrolyzed in 1% H_2SO_4 as above. The usual procedures then yielded a colorless syrup (VIIIb, 510 mg, 67%). The infrared spectra of the substances obtained by both methods were identical.

(18) R. U. Lemieux and H. F. Bauer, *Anal. Chem.*, **26**, 920 (1954).

Hydrogen Bonding and Conformational Analysis of 3-Piperidinol Derivatives

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The conformational equilibrium of 1-methyl-3-piperidinol showed that intramolecular hydrogen bonding of the hydroxyl group with the heteronitrogen decreased the apparent steric requirement of the axial hydroxyl. The strength of the hydrogen bond was estimated. Evaluation of several approaches to the conformational analysis of the two isomers of 1-methyl-4-phenyl-3-piperidinol is given.

Conformational analysis, which has proven to be essential for the description of alicyclic chemistry,[2] has only sparingly been applied to similar heterocyclic systems.[3] The similarity of the bond angles and bond lengths of C–C–C in alicyclic rings and the C–N–C in cyclic amines allows some direct applications of the techniques applied to cyclohexane derivatives to be employed in the study of piperidine and piperazine analogs.[3] The obvious difference in the alicyclic and heterocyclic systems is the tercovalent, heteronitrogen atom, and numerous approaches have been employed to evaluate the conformation of substituents on this atom.[4] An all-important feature of the electron pair, the ability to form a hydrogen bond with acidic protons, has not been used in a quantitative treatment of the conformation of nitrogen heterocycles, nor has the role of the hydrogen bond in determining the preferred conformation been established.[5] The formation and detection of such a hydrogen bond have been used to assign nonchair conformations to 1,2,2,6,6-pentamethyl-4-

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(2) (a) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962; (b) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, Inc., New York, N. Y., 1965, p 44; (c) M. Hanack, "Conformational Theory," Academic Press Inc., New York, N. Y., 1965.

(3) (a) Series by A. R. Katritzky and co-workers; see R. J. Bishop, G. Fodor, A. R. Katritzky, F. Soti, L. E. Sutton, and F. J. Swinbourne, *J. Chem. Soc.*, 74 (1966); (b) series by R. J. W. Le Fevre and co-workers; see C. Y. Chen and R. J. W. Le Fevre, *Tetrahedron Letters*, 4057 (1965); M. J. Aroney, C. Y. Chen, R. J. W. Le Fevre, and A. N. Singh, *J. Chem. Soc.*, 98 (1966); (c) series by H. O. House; see H. O. House, B. A. Tefertiller, and C. G. Pitt, *J. Org. Chem.*, **31**, 1073 (1966); (d) series by J. McKenna; see J. McKenna, J. M. McKenna, and J. White, *J. Chem. Soc.*, 1733 (1965).

(4) Reference 2b, pp 244–255, gives a summary of all but the most recent work which is given in ref 3.

(5) See p 471 of ref 2b for illustrations of lack of quantitative data; however, during the preparation of this manuscript the review chapter on the hydrogen bond [M. Tichy, *Advan. Org. Chem.*, **5**, 115 (1965)] appeared. This article contains reference to unpublished work relative to this question on p 155.

phenyl-4-piperidinol[6] and 1,3,5-trimethyl-2,6-diphenyl-4-piperidinol[7] and have been observed with numerous 3-piperidinol derivatives.[8] The importance of such a bond in decreasing the conformational free energy resulting from steric interactions of an axial hydroxyl group has not been demonstrated, however. The determination of the conformational equilibrium, and thus the conformational free energy, of a piperidinol whose hydroxyl was capable of hydrogen-bond formation only in the axial conformation would give an estimate of the energy of such a bond. We wish to report the physical properties of several 3-piperidinols which have allowed such estimates to be made.

The piperidinols chosen for investigation were 3-piperidinol (**1**), 1-methyl-3-piperidinol (**2**), 1-benzyl-3-piperidinol (**3**), and *cis*- and *trans*-1-methyl-4-phenyl-3-piperidinol (**5** and **4**, respectively). The 1-methyl-4-phenyl-3-piperidinols were prepared by routes which led to isomeric homogeneity as confirmed by gas chromatographic analysis. The infrared spectral data for the stretching vibration of the hydroxyl groups are summarized in Table I. Typical curves from which the apparent coupling constants of the carbinol hydrogen with the adjacent hydrogens were obtained are given in Figure 1.

TABLE I

HYDROXYL STRETCHING FREQUENCIES OF 3-PIPERIDINOLS

Substituted 3-piperidinol	OH unbonded, cm^{-1}	OH bonded, cm^{-1}	$\Delta\nu$, cm^{-1}
Unsubstituted (**1**)	3631	3532	99
1-Methyl- (**2**)	3625	3535	90
1-Benzyl- (**3**)	3630	3550	80
1-Methyl-4-phenyl			
trans (**4**)	3612[a]	...	
cis (**5**)	3607[b]	3527	80

[a] This band is probably due to the stretching vibration of a hydroxyl group bonded to the π system of the phenyl group. [b] This band was a shoulder on the major band at 3527 cm^{-1} and resulted from a hydroxyl group bonded to the π system of the phenyl group.

A first-order analysis of the resonance band for the carbinol hydrogen in the nmr spectrum of **1** (a septet at 3.67 ppm) gave 8.1 cps for the weighted average coupling constant with the *trans* hydrogens (J^*)[9] and 4.1 cps for the *cis* hydrogens. A treatment of the band width by the method of Booth[9] gave similar results. The separation of the terminal peaks in the resonance band at 3.69 ppm was 24.4 cps which can be equated to $2(J^* + J_{ae})$. Using the limiting values for the coupling constants of *trans*-diaxial (11.2 cps), *trans*-diequatorial (2.5 cps), and *cis*-axial–equatorial (4.1 cps)[10] the mole fraction of the conformer having *trans*-diaxial hydrogens (**1a**) was estimated as being 0.64,

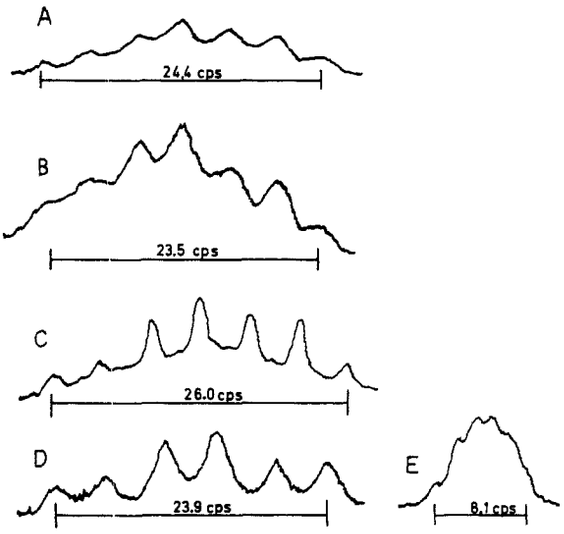
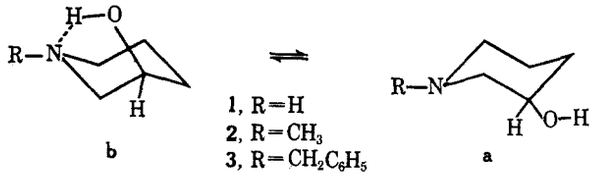


Figure 1.—The 60-Mc/sec proton magnetic resonance signal for the 3 proton of (a) 3-piperidinol (**1**), (b) 1-methyl-3-piperidinol (**2**), (c) 1-methyl-3-acetoxypiperidine, (d) *trans*-1-methyl-4-phenyl-3-piperidinol (**4**), and (e) *cis*-1-methyl-4-phenyl-3-piperidinol (**5**). The magnetic field increases from left to right.

corresponding to a conformational free-energy difference ($-\Delta G°_{OH}$) of approximately 0.37 kcal/mole for the 3-hydroxyl at 35°. This is smaller by at least 0.4 kcal/mole than the $-\Delta G°$ value for 1-methyl-4-piperidinol[3b] or cyclohexanol.[2b] This difference results from a summation of the effects: the enthalpy of the formation of the hydrogen bond, the decrease in steric interference with the axial hydroxyl in conformer **1b** due to the smaller apparent steric requirements of a free pair of electrons than a hydrogen atom,[11] and any entropy effects of the hydrogen-bond formation.



The similar analysis of the nmr spectrum of 1-methyl-3-piperidinol (**2**) a weighted coupling constant for *trans* hydrogen with the carbinol hydrogen (J^*) of 7.7 cps. This value corresponds to about 60% of **2a** in the conformational equilibrium and a conformational free-energy charge ($-\Delta G°$) of about 0.25 kcal/mole. The study of the conformational equilibrium of 1-benzyl-3-piperidinol (**3**) was complicated by the overlap of the resonance band of the benzyl hydrogens with the septet of the carbinol carbon–hydrogen. The spacings of the lines that were unobscured were quite similar to the spacings in the nmr of **2**, however. Thus the conformational free-energy charge for the equilibration of **3** must also be approximately 0.3 kcal/mole.

The importance of the hydrogen bonding of **1**, **2**, and **3** in decreasing the $-\Delta G$ was clearly shown by a study of the nmr spectrum of 1-methyl-3-acetoxypiperidine, which cannot show intramolecular hydrogen bonding. The J^* was measured to be 8.9 cps by analy-

(6) R. E. Lyle, *J. Org. Chem.*, **22**, 1280 (1957).

(7) M. Balasubramanian and N. Padma, *Tetrahedron Letters*, 49 (1963).

(8) (a) G. Hite, E. E. Smissman, and R. West, *J. Am. Chem. Soc.*, **82**, 1207 (1960); (b) M. R. Bell and S. Archer, *ibid.*, **82**, 4642 (1960); (c) J. Sicher and M. Tichy, *Collection Czech. Chem. Commun.*, **23**, 2081 (1958).

(9) H. Booth, *Tetrahedron*, **10**, 2211 (1964).

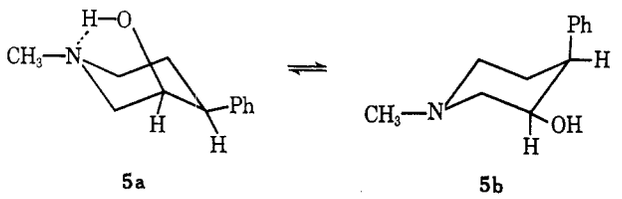
(10) Suitable models were not available for obtaining these constants from 3-piperidinols, so the values obtained from 4-piperidinols were used.[3b] Because of the similarity of the bond angles and bond lengths in cyclohexanol and piperidinol this assumption should be within the limits of the analysis. The spin–spin coupling constants for J_{aa} and J_{ae} obtained from the nmr spectrum of 1,2,2,6,6-pentamethyl-4-piperidinol [C. Y. Chen and R. J. W. Le Fevre, *J. Chem. Soc.*, 3467 (1965)] were reinvestigated in view of the possibility of a typographical error in the name of the compound, for on page 3468 of this paper it is implied that two isomers were anticipated.

(11) A. R. Katritzky, Anniversary Meeting of the Chemical Society, Oxford, March 28–31, 1966; however J. B. Lambert and R. G. Keske [*J. Am. Chem. Soc.*, **88**, 621 (1966)] have presented evidence that the hydrogen may have smaller steric requirements than the electron pair.

sis of the splitting pattern or by the method of Booth. Using the same limiting values for the coupling constants the conformational equilibrium can be estimated as containing 74% of the conformer having an equatorial acetoxy group. This corresponds with a confomational free-energy difference of 0.64 kcal/mole. The difference of about 0.3 kcal/mole must reflect the influence of the hydrogen bond in **1**, **2**, or **3**, for the apparent steric requirements of hydroxyl and acetoxyl are approximately the same as evidenced by the comparable $-\Delta G^\circ$ values obtained for cyclohexane derivatives.[2] The $-\Delta G^\circ$ value of 0.64 kcal/mole found for 1-methyl-3-acetoxypiperidine is comparable with the average value of 0.7 kcal/mole reported for cyclohexylacetate.[2]

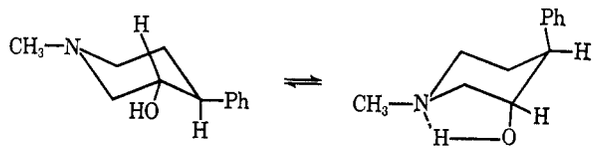
The infrared spectra of 3-piperidinol (**1**) and the methyl (**2**) and benzyl (**3**) derivatives all showed the presence of bonded and unbonded hydroxyl with approximately the same frequency difference between these vibrations. A small but definite trend shows the energy difference to increase as the nitrogen substituent becomes smaller; thus $\Delta\nu$ decreases H > CH_3 > $C_6H_5CH_2$.

Using the $-\Delta G^\circ_{OH}$ value obtained above for the hydroxyl of 3-piperidinols it should be possible to estimate the conformational equilibria for *cis*- and *trans*-1-methyl-4-phenyl-3-piperidinols (**5** and **4**). A value of 3.1 kcal/mole was selected as an average value for the $-\Delta G^\circ$ of a phenyl substituent;[2b] thus the conformational equilibrium for **5** would have a $-\Delta G^\circ$ of about 2.7 kcal/mole corresponding to a composition of about 99% of conformer **5a**. This conclusion was supported by the infrared spectral data which showed only a small shoulder at 3607 cm^{-1} for hydroxyl not bonded to nitrogen, with the major OH stretching vibration at 3527 cm^{-1} due to OH---N. Similarly the resonance band for the hydrogen at the 3 position of **5** showed the coupling characteristic of an equatorial carbinol hydrogen. All of these data are consistent with a conformational equilibrium of **5** containing greater than 99% of **5a**.



5a **5b**

The similar treatment of the conformational equilibrium of *trans*-1-methyl-4-phenyl-3-piperidinol (**4**) gave a $-\Delta G^\circ$ value of about 3.2 kcal/mole requiring about 99.8% of **4a**. The infrared spectral investigation of dilute solutions of **4** showed no OH---N intramolecular bonds. The only band for the hydroxyl stretching vibration was at 3612 cm^{-1} indicating a weak hydrogen bond with the π system of the 4-phenyl substituent. The resonance signal for the 3 proton in the nmr was a sextet which on first-order analysis gave apparent coupling constants of J^*_{aa} = 9.75 cps and J_{ae} = 4.46 cps. Using the same limiting coupling constants applied in the conformational analysis of **1**, the value of J^* = 9.75 cps would lead to an estimation of a conformational equilibrium of 83% **4a** and 17% **4b**. To determine which of these contradictory data were being misinterpreted the nmr spectrum of *trans*-2-phenylcyclohexanol (**6**) was measured for comparison. The resonance band for the carbinol hydrogen in this compound was very similar in shape and spacing with that of **4**. In the absence of the possibility of stabilization by an intramolecular bond of the conformer of **6** having two axial substituents, this identity of the compositions of the conformational equilibria of **4** and **6** seems unlikely. A steric repulsion of the groups in the diequatorial conformation was not probable since the infrared spectra showed hydrogen bonding between the two groups. It is evident from these data that the use of the limiting values for the coupling constants obtained from piperidinols having no α substituents is not correct for the conformational analysis of piperidinols having substituents on carbons adjacent to the hydroxyl.



4a **4b**

Experimental Section

Measurements of Physical Properties.—The infrared spectra were determined using a Perkin-Elmer Model 337 spectrophotometer equipped with diffraction grating and with scale expansion. The spectra were determined using solutions in carbon tetrachloride at dilutions of 5×10^{-3} *M* and a path length of 1.00 cm. The frequencies of the absorption bands were determined by calibration against the absorption of polystyrene at 2850 cm^{-1}.

The nuclear magnetic resonance spectra were determined using a Varian A-60 spectrometer. The compounds were studied in 30% solutions in carbon tetrachloride and deuteriochloroform at 37 ± 2°. The coupling constants were measured from curves determined at 100-cps sweep width. Reproducibility of measured spacings of ±0.05 cps was possible.

3-Piperidinol (**1**) **and 1-methyl-3-piperidinol** (**2**) were obtained from Aldrich Chemical Co. **1-Benzyl-3-piperidinol** (**3**) was prepared by the reduction of 1-benzyl-3-piperidone and **1-methyl-3-acetoxypiperidine** was obtained by the acylation of **2**. All compounds were characterized by infrared and proton magnetic resonance spectroscopy and were shown to be homogenous by gas–liquid partition chromatography. The *cis*-**1-methyl-4-phenyl-3-piperidinol** (**5**) was prepared and purified by the method reported previously.[12]

trans-**1-Methyl-4-phenyl-3-piperidinol** (**4**).—To a solution of 21.65 g (0.125 mole) of 1-methyl-4-phenyl-1,2,5,6-tetrahydropyridine[13] and 7.45 g (0.20 mole) of sodium borohydride in 100 ml of diglyme at 0° under nitrogen was added dropwise a solution of 33.5 ml (about 0.26 mole) of boron trifluoride etherate in 25 ml of diglyme. The mixture was allowed to warm to room temperature and was stirred for 1.5 hr after the addition was completed. The intermediate organoborane was oxidized and hydrolyzed by the addition of 10 ml of water, 30 ml of 6 *N* sodium hydroxide, and 30 ml of 30% hydrogen peroxide. The latter was added over a period of 1 hr while the reaction mixture was warmed to 45–60°. After acidification by the addition of 30 ml of concentrated hydrochloric acid, the reaction mixture was concentrated by evaporation of the solvents under reduced pressure. Water was added to the residue and the evaporation was repeated. The residue was dissolved in water and solid

(12) R. E. Lyle and W. E. Krueger, *J. Org. Chem.*, **30**, 394 (1965).

(13) C. J. Schmidle and R. C. Mansfield, *J. Am. Chem. Soc.*, **78**, 425 (1956).

potassium carbonate was added to neutralize the solution. The basic solution was extracted with ether, and the ether extract was dried over potassium carbonate and fractionally distilled. The fraction boiling at 157–177° (10 mm) crystallized on standing to give 16.0 g (67%) of crude *trans*-1-methyl-4-phenyl-3-piperidinol (4), mp 50–72°. Recrystallization of the solid from *n*-heptane gave an analytical sample, mp 82.0–84.5°.

Anal. Calcd for $C_{12}H_{17}NO$: C, 75.35; H, 8.96. Found: C, 75.63; H, 8.92.

Acknowledgments.—The authors wish to express appreciation to the National Institutes of Health for support of this research in the form of grants CA-04143 and HE-01713. One author (R. E. L.) wishes further to thank Oxford University and Professor E. R. H. Jones and Dr. Sydney Bailey of that university for providing facilities during the writing of this manuscript.

Chlorination of Unsaturated Materials in Nonpolar Media. VII. Butadiene: a Reevaluation[1]

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Interaction of butadiene and chlorine in nonpolar solvents not only produces products by polar addition as generally accepted, but also produces free radicals. In fact, previous investigators of this proposed electrophilic reaction were most likely studying a radical chain reaction. In the present study, the spontaneously initiated radical pathway and the polar pathway have been separated. The former is characterized by addition of chlorine atom to butadiene at a rate *not* particulary accelerated over that of a terminal olefin to produce an allylic radical which reacts with molecular chlorine to produce 3,4-dichloro-1-butene (I) and *trans*-1,4-dichloro-2-butene (II) in a ratio of 22:78. The polar pathway, observable in the presence of radical inhibitors such as oxygen, produces I and II in a ratio of *ca.* 55:45; this polar reaction is *slower* than that of 1-butene. In a normal dark chlorination in the absence of inhibitors, the radical pathway dominates in neat olefin, but is gradually replaced by the polar pathway as nonpolar diluents are added. This gross behavior is analogous to that previously observed for linear olefins.

Chlorination of butadiene in nonpolar solvents such as carbon disulfide, ligroin, or chloroform at *ca.* 0° was first reported by Muskat and Northrup[2] to give a mixture of 3,4-dichloro-1-butene (I) and 1,4-dichloro-2-butene (II) richer in the former. Later workers obtained varying amounts of I and II;[3–6] however, formation of tetrachlorides and polymers[4,5]

$$CH_2{=}CH{-}CH{=}CH_2 + Cl_2 \longrightarrow CH_2{=}CH{-}CHClCH_2Cl + \textit{trans}\text{-}ClCH_2CH{=}CHCH_2Cl$$
I II

accompanied the dichloride products. Products I and II are thermally stable below 130°, and hence the products appear to be kinetically controlled; they can be isomerized by zinc chloride to an equilibrium mixture containing 67–70% of II.[5] Carbonium ion intermediates were invoked by Muskat and Northrup[2] although the concept of allylic resonance was not yet clearly understood. This chlorination has become a standard textbook example[7–10] of electrophilic attack on an unsaturated system followed by kinetic rather than thermodynamic control of product formation. Failure to detect the *cis* isomer of II among the products led Mislow and Hellman[11] to conclude that attack occurred at only one of the double bonds to the exclusion of simultaneous attack at both termini of a cisoid conformation of butadiene.

Our recent finding[12] that interaction of many simple olefins with chlorine in nonpolar solvents leads to production of free radicals and hence to radical rather than polar chlorination prompted us to reinvestigate butadiene, the simplest of conjugated dienes. We wish to report that chlorination of butadiene under conditions comparable to those previously described[2–6] is largely a radical process rather than a polar process as generally assumed.

Results

Treatment of a 2.5 *M* solution of butadiene in carbon tetrachloride with $^1/_3$ equiv of gaseous chlorine diluted with nitrogen in the absence of light at −9° on a preparative scale led to rapid reaction; distillation afforded the expected dichlorides I and II in *ca.* 50% yield along with a liquid residue whose chlorine analysis suggested considerable polychlorination. To obtain quantitative information and avoid secondary reactions, chlorination was run to much lower conversion (always <10%) with slower input rates. Glpc examination of such reaction mixtures revealed I and II as the only significant volatile products (two minor products will be discussed below). However, in several runs under these conditions, small quantities of insoluble material were formed. A study of the effect of butadiene concentration in 1,1,2-trichlorotrifluoroethane as solvent was carried out first. The 1,4-dichloride II makes up 75–80% of the monomeric product at diene concentrations above mole fraction $n = 0.2$; however, below this level, the value of (II)/(I + II) decreases smoothly to *ca.* 0.50 at $n = 0.02$, the lowest concentration studied,

(1) For previous paper, see M. L. Poutsma and J. L. Kartch, *Tetrahedron*, **22**, 2167 (1966).
(2) I. E. Muskat and H. E. Northrup, *J. Am. Chem. Soc.*, **52**, 4043 (1930).
(3) A. A. Petrov and N. P. Sopov, *J. Gen. Chem. USSR*, **15**, 981 (1945); *Chem. Abstr.*, **40**, 6406 (1946).
(4) A. A. Petrov and N. P. Sopov, *J. Gen. Chem. USSR*, **17**, 1105 (1947); *Chem. Abstr.*, **42**, 4518 (1948).
(5) A. N. Pudovik, *J. Gen. Chem. USSR*, **19**, 1179 (1949); *Chem. Abstr.*, **44**, 1005 (1950).
(6) L. N. Owen, *J. Chem. Soc.*, 241 (1949).
(7) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p 673.
(8) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, N. Y., 1959, p 530.
(9) J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 218.
(10) J. D. Roberts and M. C. Caserio, "Basic Principles of Organic Chemistry," W. A. Benjamin, Inc., New York, N. Y., 1964, p 239.
(11) K. Mislow and H. M. Hellman, *J. Am. Chem. Soc.*, **73**, 244 (1951).
(12) M. L. Poutsma, *ibid.*, **87**, 2161, 2172 (1965).