

that of a similarly purified authentic specimen. The tosylate II was recovered unchanged after 72 hours at 65° in nitromethane.

The strain energy (about 19 kcal.)⁵ of the norbornyl ring system is almost as great as the calculated standard heat of cyclization of an olefin. The near thermoneutrality of the conversion of I into VI offers in itself no basis for this greatly preferred course of the solvolysis. The drive toward ring closure must be related rather to the favorable electronic structure of the bridge ion V, already well recognized from evidence concerning the behavior of norbornyl sulfonates. We plan to extend this investigation to include the effects of substitution and of structural and stereochemical variations in the starting material.

The present ring closure has been investigated independently by R. G. Lawton⁴ of the University of Wisconsin. This work was supported by the National Science Foundation.

(4) R. G. Lawton, *J. Am. Chem. Soc.*, **83**, 2399 (1961).

(5) The much lower value of 9.49 kcal. has been estimated by Prof. H. J. Dauben, Jr. (private communication).

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RECEIVED APRIL 24, 1961

INTRAMOLECULAR HYDROGEN BONDING IN NON-CHAIR CONFORMATIONS OF CIS-1,4-CYCLOHEXANEDIOLS

Sir:

Examination of models of 1,4-cyclohexanediols suggests that intramolecular hydrogen bonding can occur only when the hydroxyl groups have the *cis* configuration, and then only in certain *non-chair* conformations.¹ Therefore, the observation of strong intramolecular hydrogen bonding in a *cis*-1,4-cyclohexanediol would provide compelling evidence for the presence of non-chair conformations. This communication presents such evidence, obtained by infrared spectroscopy, for a 2,5-di-*t*-butyl-1,4-cyclohexanediol.

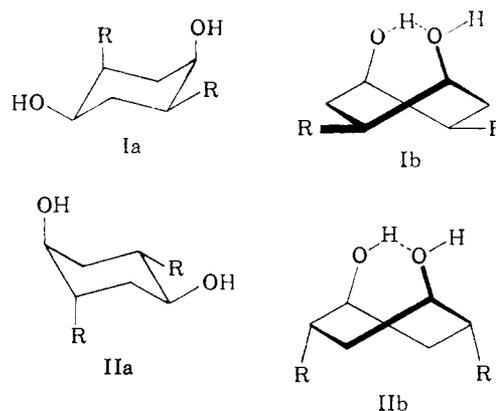
Four racemates and two *meso* stereoisomers are theoretically possible for 2,5-di-*t*-butyl-1,4-cyclohexanediol. Of these, only the two racemates, I and II, in which the hydroxyl groups are *cis* to one another and the *t*-butyl groups are *cis* to one another would be expected to exhibit intramolecular hydrogen bonding. The conformations of I present at equilibrium would include the chair conformation, Ia, destabilized by the crowding together of the axial *t*-butyl group, the abutting axial hydrogen, and the axial hydroxyl group, and the twist² conformation, Ib, in which the *t*-butyl groups can be positioned more comfortably,³ with possible additional stabilization through intramolecular hydrogen bonding.⁴ Similarly, but to a lesser degree, IIa is destabilized by its axial *t*-butyl group, while

(1) G. Hite, E. E. Smisman and R. West, *J. Am. Chem. Soc.*, **82**, 1207 (1960).

(2) W. S. Johnson, V. J. Bauer, J. L. Margrave, M. A. Frisch, L. H. Dreger and W. N. Hubbard, *ibid.*, **83**, 606 (1961).

(3) N. L. Allinger and L. A. Freiberg, *ibid.*, **82**, 2393 (1960).

(4) Partial relief of axial group repulsions in Ia by slight rotation and bond angle bending would be expected to give a distorted chair conformation corresponding to an energy minimum, with a structure intermediate between that drawn for Ia and the transition state leading to Ib.



R is *t*-Bu

IIb may be stabilized by intramolecular hydrogen bonding.

Addition of 3 moles of hydrogen to 2,5-di-*t*-butylhydroquinone in acetic acid solution with platinum oxide catalyst at 25° under 2–3 atm. pressure, yielded a white solid product mixture (from acetic acid–water). Fractional recrystallization effected isolation in 20% yield of a 2,5-di-*t*-butyl-1,4-cyclohexanediol (diol A), m.p. 157.5–158.5°, which exhibited intense absorption at 3480 cm.⁻¹ (C, 73.63; H, 12.11). The maximum amount of diol A present in the total hydrogenation products was about 40% (infrared analysis).

Spectral data for diol A, reproduced in Table I, show that in the concentration range 0.0005 to

TABLE I
CONCENTRATION DEPENDENCE OF INFRARED OH BANDS
FOR DIOL A

| Concn., moles/l. | Relative ^a absorbance at cm. ⁻¹ | | |
|---------------------|---|------|------------------|
| | 3640 | 3619 | 3480 |
| 0.00054 | 1.0 | 1.0 | 1.0 |
| .0011 | 2.0 | 1.9 | 2.0 |
| .0022 | 4.1 | 4.0 | 3.9 ^b |
| .0043 ^c | 7.9 | 7.8 | 7.3 |

^a The values tabulated are relative to the absorbances at the lowest concentration (0.0054 M): 0.036, 0.032 and 0.071 for peaks at 3640, 3619 and 3480 cm.⁻¹, respectively.
^b Band width at half maximum intensity ($\nu_{1/2}$): 71 cm.⁻¹.
^c At 0.0043 M, small but significant absorbance attributable to intermolecular hydrogen bonding is observed.

0.002 M where intermolecular hydrogen bonding is expected to be negligible, the absorption bands at 3640, 3619 and 3480 cm.⁻¹ exhibit the same concentration dependence.⁵ The three peaks were diminished by 2–3% and the frequencies were increased by 1, 3 and 10 cm.⁻¹, respectively, when a 0.002 M solution of diol A in carbon tetrachloride was heated from 20 to 70°. The replacement of the hydroxyl hydrogens by deuterium resulted in the replacement of the absorption bands at 3640, 3619 and 3480 cm.⁻¹ by new bands having similar relative intensities and appearing at 2687, 2672 and 2576 cm.⁻¹.

The slight temperature dependence, the concentration dependence and the results of deuterium

(5) A Perkin-Elmer Model 221G Infrared Spectrophotometer with a sodium chloride prism-grating interchange was employed to record spectra in the region 2500 to 4000 cm.⁻¹. Near-infrared silica cells of 1 cm. path length were used with solutions in carbon tetrachloride (dried "Spectro Grade") at about 30°. The accuracy of the frequencies reported is claimed to be within ± 4 cm.⁻¹.

exchange compel interpretation of the three peaks in terms of absorption by the hydroxyl groups of the monomeric diol. The broad band at 3480 cm^{-1} may be assigned to O-H stretching vibrations of hydroxyl groups, the hydrogen atoms of which are *intramolecularly* hydrogen bonded to oxygen in a seven-membered ring.⁶ The doublet (3640 and 3619 cm^{-1}) may be attributed to O-H stretching vibrations of all of the hydroxyl groups, the hydrogen atoms of which are *not* engaged in hydrogen bonding. If such "free" hydroxyl groups all had the same conformation, a doublet would not be expected.⁷ Therefore, it is highly probable that two or more conformations are significantly populated for diol A, at least one of which is the *intramolecularly hydrogen bonded twist conformation* (Ib or IIb).

The configuration of diol A may be assigned on the basis of the method of synthesis. Diol A most probably has structure I (although structure II cannot be rigorously excluded at this time). Structure I would result from 2,5-di-*t*-butylhydroquinone if a stereospecific addition of all six hydrogen atoms occurred from the same side of the plane of the ring to give an all *cis* configuration. The hydrogenation conditions used, when applied to other aromatic compounds, yield mostly *cis*-substituted cyclohexane derivatives.⁸

The author is indebted to the American Academy of Arts and Sciences for a grant from the Warren Fund, and to Dr. Richard C. Lord for use of equipment which made possible the initiation of this work. Continuing financial support by the National Science Foundation is gratefully acknowledged.

(6) G. C. Pimentel and McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, California, 1960, Chapters 3 and 5; L. P. Kuhn, *J. Am. Chem. Soc.*, **74**, 2492 (1952).

(7) R. Piccolini and S. Winstein, *Tetrahedron Letters*, No. 13, 4 (1959).

(8) R. D. Stolow, *J. Am. Chem. Soc.*, **81**, 5806 (1959), and refs. 29-31 therein.

CONTRIBUTION No. 257

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RECEIVED APRIL 1, 1961

CHEMISTRY OF THE METAL CARBONYLS. X. TETRACARBONYLNITROSYLMANGANESE(O)^{1,2}

Sir:

Treatment of manganese pentacarbonyl iodide with nitric oxide affords carbonyltrinitrosylmanganese.^{3a} Synthesis of this compound significantly extended the "pseudo-nickel tetracarbonyl" series of nitrosyls, previous members of this series being the long established cobalt and iron complexes $\text{Co}(\text{NO})(\text{CO})_3$ and $\text{Fe}(\text{NO})_2(\text{CO})_2$. Barraclough and Lewis^{3a} have pointed out that manganese could conceivably form two monomeric carbonylnitrosyls with inert-gas configurations, *viz.*, Mn-

(1) Part IX R. B. King, T. A. Manuel and F. G. A. Stone, *J. Inorg. Nucl. Chem.*, **16**, 233 (1961). For Part VIII see H. D. Kaesz, R. B. King and F. G. A. Stone, *Z. Naturforsch.*, **15b**, 763 (1960).

(2) We are indebted to the National Science Foundation for support of this work through Grant 14610.

(3) (a) C. G. Barraclough and J. Lewis, *J. Chem. Soc.*, 4842 (1960).

(b) R. F. Lambert and J. D. Johnston, *Chem. and Ind.*, 1267 (1960), have reported a compound $(\text{C}_6\text{H}_5)_2\text{PMn}(\text{CO})_2\text{NO}$ which may be regarded as a derivative of $\text{Mn}(\text{CO})_5\text{NO}$.

$(\text{NO})_3\text{CO}$ and $\text{Mn}(\text{NO})(\text{CO})_4$, and that the latter if it existed would be a member of an entirely new "pseudo-iron pentacarbonyl" nitrosyl series. From arguments based on π -bonding, electronegativity, and stereochemical effects it was concluded that $\text{Mn}(\text{NO})_3\text{CO}$ would be more stable than $\text{Mn}(\text{NO})(\text{CO})_4$, and thus isolation of the former in preference to the latter is understandable.^{3a} We now describe tetracarbonylnitrosylmanganese(O).^{3b}

A 9.2-g. (43 mmoles) sample of N-methyl-N-nitroso-*p*-toluenesulfonamide⁴ was placed in a 1-l. Pyrex reaction bulb fitted with a stopcock. The bulb was attached to the vacuum line and evacuated, Diethyl ether (30 ml.) and manganese carbonyl hydride⁵ (4.0 g., 20.4 mmoles) were distilled into the bulb, which was removed from the vacuum line and stored in the dark at room temperature for 16 hr. During this period the solution changed from pale yellow to deep red. The bulb was re-attached to the vacuum system and its contents fractionated. Dark red crystals of tetracarbonylnitrosylmanganese (2.24 g., 56% yield) collected in a trap cooled to -35° . This compound melts at -1.5 to 0° to a deep-red air-sensitive liquid, forming reddish-brown vapors, resembling bromine in appearance. The new nitrosyl is diamagnetic⁶ and has a vapor pressure of about 8 mm. at 25° . *Anal.* Calcd. for $\text{C}_4\text{NO}_5\text{Mn}$: N, 7.1; Mn, 27.9; CO groups, 4.00; mol. wt., 197. Found: N, 7.2; Mn, 28.2; CO groups,⁷ 4.00, 3.92; mol. wt. (from vapor density), 199, 200.

Tetracarbonylnitrosylmanganese could have either a trigonal bipyramidal or a tetragonal pyramidal structure. Moreover, depending on the position of substitution of the nitric oxide group a trigonal bipyramidal configuration would have C_{3v} or C_{2v} symmetry, and a tetragonal pyramidal arrangement C_{4v} or C_s symmetry. The infrared spectrum of $\text{Mn}(\text{CO})_4\text{NO}$ was examined in an attempt to establish structure. The compound showed three carbonyl stretching bands at 2095 (m), 2019 (s), and 1972 (s) cm^{-1} , and a nitric oxide stretching frequency at 1759 (s) cm^{-1} .⁸ Of the possible structures mentioned above, only the trigonal bipyramidal structure having the NO group at an apex (C_{3v}) would show three infrared active carbonyl stretches. In possessing a trigonal bipyramidal structure tetracarbonylnitrosylmanganese is thus similar to iron pentacarbonyl.⁹

(4) A reagent previously used to prepare the nitrosyl π - $\text{C}_6\text{H}_5\text{Mo}(\text{CO})_2\text{NO}$ (T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **3**, 104 (1956)).

(5) We are indebted to the Ethyl Corporation for a gift of manganese carbonyl from which the hydride may be made; see W. Hieber and G. Wagner, *Z. Naturforsch.*, **13b**, 338 (1958).

(6) Diamagnetism was established by the n.m.r. method described by D. F. Evans, *J. Chem. Soc.*, 2003 (1959).

(7) Determined by heating at 150° weighed samples of the nitrosyl with excess of iodine. No nitric oxide was released, but carbon monoxide was formed and measured with an automatic Sprengel pump (B. Bartocha, W. A. G. Graham and F. G. A. Stone, *J. Inorg. Nucl. Chem.*, **6**, 119 (1958)). Identity of the carbon monoxide was established by quantitative combustion of the gas over copper oxide at 800° to form carbon dioxide, which was identified by its infrared spectrum.

(8) Spectra were taken in tetrachloroethylene solution with a Perkin-Elmer Model 221 Prism-Grating spectrophotometer. We thank Professor M. K. Wilson of Tufts University for making this high-resolution instrument available for our use.

(9) H. Stammreich, Oswaldo Sala and Yara Tavares, *J. Chem. Phys.*, **30**, 856 (1959).