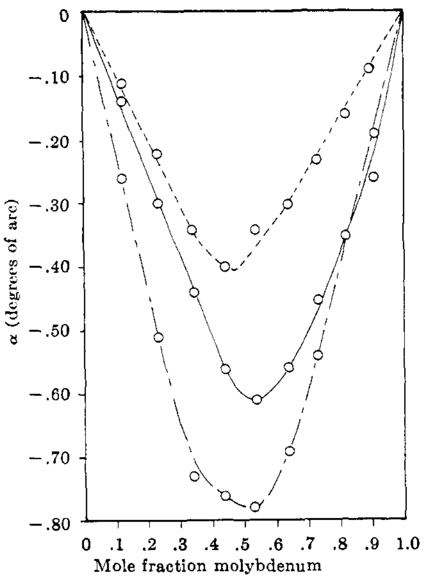

Fig. 2.—Continuous variations plots for sugar–molybdate complexes. The difference in optical rotation (α) between solutions of sugar plus molybdate and solutions containing the same concentration of sugar is plotted *vs.* mole fraction molybdenum. pH 5.0 in 1.5 *M* acetate buffer; temp., 25.0 ± 0.5 °C. Sum of sugar plus molybdate concentration, 0.1000 *M*

— — — — D-mannose
------------ D-ribose
— · — · D-lyxose

mer[3] and has a positive rotation. However, only the β-isomer can complex and the inversion of the rotation is due to the transformation to this form upon complex formation. D-Lyxose is similar to D-mannose, except that the equilibrium mixture has a negative rotation and complex formation with the β-isomer makes the rotation more negative. D-Ribose is a somewhat different case. There are two possibilities for the ax-eq-ax hydroxyl arrangement. The first involves hydroxyls 1, 2, and 3 and the second, hydroxyls 2, 3, and 4. In the first case, only the α-isomer can complex. Therefore, since the α-isomer is more dextrorotatory, the addition of molybdate should cause the rotation of the solution to become more positive. However, the rotation becomes more negative. This indicates that the complexing must occur with hydroxyls 2, 3, and 4, and does not involve hydroxyl 1.

It is clear that complexing with molybdate provides a simple method to detect the presence of a *cis-cis*-1 (ax), 2 (eq), 3 (ax) triol system in a pyranose. A large change in the optical rotation upon addition of molybdate at a pH near 5 indicates this arrangement. Furthermore, complexing with molybdate suggests a method for determining the configuration of the anomeric carbon for sugars having the necessary 2 (eq), 3 (ax) structure, similar to the use of borate, which would not suffer from the ambiguities of the borate method.[4]

### Experimental

Sodium molybdate (Baker certified reagent) was dried at 105° for 24 hr. Its purity was determined to be 99.7% by the α-benzoinoxime method.[5] D-Mannose, D-ribose, D-lyxose, D-xylose, D-arabinose, α-methyl-D-mannopyanoside, and 2-deoxy-D-ribose were purchased from Nutritional Biochemicals Corp. D-Glucose and D-galactose were Eastman Kodak Co. products. These compounds were used without further purification since their melting points checked the literature values.

Polarimetric measurements were made with a Schmidt and Haensch polarimeter, reading to ± 0.01° of arc. Temperature was controlled to 25.0 ± .2° by use of a jacketed polarimetric tube. All measurements were made at the sodium D line (5890 Å.). Sufficient time was allowed for each solution to reach a constant rotation before measurements were made.

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## The Effect of Ether Oxygen on the Methylene Stretching Absorptions

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In all types of aliphatic hydrocarbons the methylene group, —$CH_2$—, gives rise to an asymmetrical stretching vibration near 2926 cm.$^{-1}$ and a symmetrical stretching vibration near 2853 cm.$^{-1}$.[1] The positions of the absorption bands are fairly constant. Ordinarily the intensity of the band at 2926 cm.$^{-1}$ is stronger than the one at 2853 cm.$^{-1}$, but when carbonyl or ester groups are attached to the methylene group the intensity of both bands is diminished.[2] It has also been reported that in oxygen-containing materials, generally, the extinction coefficient of the methylene group is affected.[3]

We have accumulated some data which show that the oxygen of an ether linkage can affect the methylene group in two ways, by shifting the asymmetrical stretching absorption to a higher frequency, and sometimes by enhancing the intensity of the symmetrical stretching absorption.

In the course of examining some rather complex compounds containing ether oxygen adjacent to methylene groups, a very sharp, intense absorption band was always found near 2856 cm.$^{-1}$. Because of the complexity of some of the materials, simpler and better known compounds were selected for investigation. These are listed in Table I.

The first example in the table is 1,4-dioxane, in which each methylene group is attached to oxygen without intervening functional groups. Four absorption bands are found in this region of the spectrum of 1,4-dioxane. The high frequency band is near 2967 cm.$^{-1}$, the low frequency band near 2858 cm.$^{-1}$, 109 cm.$^{-1}$ apart. The origin of the bands between the two has not been assigned and will not be discussed here. The work of Pozefsky and Coggeshall[3] in a study of sulfurized and oxygenated compounds, lends considerable weight to the assignment of the other two bands to the asymmetrical $CH_2$ stretching vibration at

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[3] W. Pigman, "The Carbohydrates," Academic Press, Inc., New York, N. Y., 1957, p. 52.

[4] J. Boeseken, *Advan. Carbohydrate Chem.*, **4**, 189 (1949).

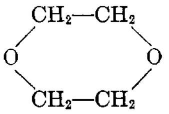
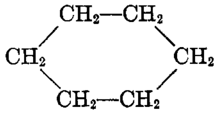
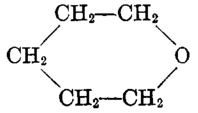
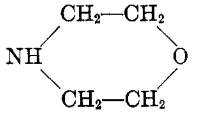
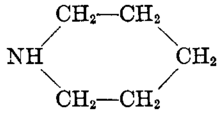
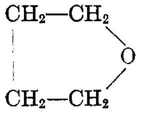
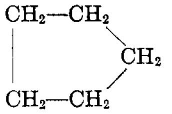
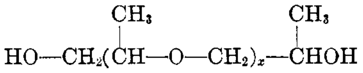
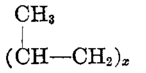
[5] H. B. Knowles, *J. Res. Natl. Bur. Stand.*, **9**, 1 (1932).

[1] R. N. Jones and C. Sandorfy, "Technique of Organic Chemistry, Vol. IX, Chemical Applications of Spectroscopy," Interscience Publishing Co., New York, N. Y., 1956, p. 338.

[2] S. A. Francis, *J. Chem. Phys.*, **19**, 942 (1951).

[3] A. Pozefsky and N. D. Coggeshall, *Anal. Chem.*, **23**, 1611 (1951).

TABLE I

| Compound | Formula | —$CH_2$— stretching frequency, cm.$^{-1}$ | | |
|---|---|---|---|---|
| | | Asymmetric frequency | Intensity[a] | Symmetric frequency |
| 1,4-Dioxane |  | 2967 | w | 2858 |
| Cyclohexane |  | 2941 | s | 2858 |
| Tetrahydropyran |  | 2946 | s | 2856 |
| Morpholine |  | 2959 | w | 2841 |
| Piperidine |  | 2926 | s | 2857 |
| Tetrahydrofuran |  | 2976 | s | 2857 |
| Cyclopentane[b] |  | 2959 (?) | s | 2874 (?) |
| Polypropylene glycol |  $HO{-}CH_2(\overset{CH_3}{CH}{-}O{-}CH_2)_x{-}\overset{CH_3}{CH}OH$ | 2976 | s | 2874 |
| Polypropylene |  $(\overset{CH_3}{CH}{-}CH_2)_x$ | 2958 | s | 2841 |
| Polyethylene glycol | $HO{-}CH_2({-}CH_2{-}OCH_2)_xCH_2OH$ | 2941 | w | 2856 |
| Polyethylene | ${-}(CH_2{-}CH_2)_x{-}$ | 2907 | s | 2849 |
| Ether | $CH_3CH_2{-}O{-}CH_2CH_3$ | 2985 | Equal | 2865 |
| Pentane | $CH_3CH_2CH_2CH_2CH_3$ | 2958 | s | 2874 |

[a] Intensity relative to that of the symmetrical stretching band. w = weaker; s = stronger. [b] From Sadtler standard spectra no. 680. The frequencies cannot be located exactly from the printed spectra.

2967 cm.$^{-1}$ and to the symmetrical stretching vibration at 2858 cm.$^{-1}$.

The shifting of frequency and enhancement of intensity of the bands under discussion can best be illustrated by comparing the spectrum of 1,4-dioxane with that of cyclohexane. In both compounds the symmetrical stretching frequency of the methylene group occurs near 2858 cm.$^{-1}$, but the asymmetrical stretching frequency occurs 26 cm.$^{-1}$ higher in the spectrum of 1,4-dioxane than it does in that of cyclohexane. Thus it is evident that this shift to higher frequency is caused by the presence of oxygen in the molecule.

In the straight chain compounds, polyethylene and polyethylene glycol, listed in Table I, the symmetrical methylene absorption shift from polyethylene to polyethylene glycol is only 7 cm.$^{-1}$ higher while the asymmetrical methylene absorption shift is 34 cm.$^{-1}$ higher.

In a slightly more complicated situation, in which a methyl group enters the picture, a comparison of the spectra of ethyl ether and pentane may be made. In this situation it is difficult to assign bands to individual methyl or methylene groups. However, the absorption band of highest frequency occurs in ethyl ether at 2985 cm.$^{-1}$ as compared to 2958 cm.$^{-1}$ in pentane. Because in ethyl ether the methyl group is not attached directly to oxygen, the effect of oxygen on this group would be limited and it seems more likely that the band at 2985 cm.$^{-1}$ is attributable to the asymmetrical stretching vibration of the methylene group. Therefore, a shift of 27 cm.$^{-1}$ higher from pentane to ether is observed. The —$CH_2$— symmetrical stretching vibration of ether shifts only 9 cm.$^{-1}$ higher when compared with that of pentane.

Other materials in the table show the same stability of position for the symmetrical stretching absorption and the shift to higher frequency for the asymmetrical stretching absorption. In general, when ethers are compared with corresponding hydrocarbons, the preceding behavior is noted.

Another feature noted is the enhancement of the intensity of the symmetrical methylene stretching vibration when ether oxygen is present. In the spectra of 1,4-dioxane, polyethylene glycol, and ethyl ether, the intensity of the symmetrical absorption is equal to or stronger than the asymmetrical, while in the spectra of cyclohexane, polyethylene, and pentane the situation is reversed. The intensity of the symmetrical methylene stretching absorption seems to be related to the number of —CH$_2$O groups present in the molecule, as can be seen by comparing the spectra of tetrahydropyran, tetrahydrofuran, and 1,4-dioxane. However, in the more complex molecule, polypropylene glycol, this correlation cannot be applied.

The effect of ether oxygen on the methyl stretching vibration has been reported.[4,5] A similar effect appears to apply to the methylene group. It is believed that the C—H force constants are greater in the presence of the more electronegative oxygen, which causes the asymmetrical methylene stretching vibration to shift to higher frequencies. It may be concluded that a greater net dipole moment change occurs with the symmetrical methylene vibration than with the asymmetrical when oxygen of ether type is present and that, therefore, the intensity of the asymmetrical absorption band is enhanced.

All the samples were examined by Perkin-Elmer, Model 21 spectrophotometer with a calcium fluoride prism. Most of the samples were obtained from Eastman Kodak Co. and were used without further purification. Carbon tetrachloride was used as a solvent. The thickness of the cell was 0.2 mm.

(4) H. B. Henbest, G. D. Meakins, B. Nicholls, and A. A. Wagland, *J. Chem. Soc.*, 1462 (1957).

(5) F. Dalton, R. D. Mill, and G. D. Meakins, *ibid.*, 2927 (1960).

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# Quantitative Study of the Interconversion of Hydrindane Isomers by Aluminum Bromide

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*Received August 13, 1962*

In connection with investigations of aluminum halide isomerization of polycyclic hydrocarbons,[3] the development of quantitative techniques for studying the relative stabilities of isomers was desired.[4] The interconversion of *cis-* and *trans-* hydrindane was chosen as a model system, since the present study should complement nicely two recent investigations which employed different methods to obtain the same thermodynamic information. Allinger and Coke[5] equilibrated the two isomers at high temperatures by means of the hydrogenation–dehydrogenation action of a palladium-on-charcoal catalyst and studied the variation of the relative equilibrium concentrations with temperature. Browne and Rossini[6] determined the heats of combustion, isomerization, and formation of the pure isomers in both the liquid and gaseous states.

In the present investigation equilibration was carried out by aluminum bromide, which offers the advantage over aluminum chloride of being somewhat soluble in organic liquids. The catalyst, a powerful Lewis acid, effects equilibration by an ionic chain process[4]; abstraction of a hydride ion produces a carbonium ion which can react further by several paths, *e.g.*, fragmentation and rearrangement, in addition to reverting to one of the hydrindane isomers.[7] It was found that these undesired side reactions could be suppressed by the addition of small amounts of indane, which was more effective than benzene for this purpose.[4]

The relative equilibrium concentrations were determined at four different temperatures ranging from 251–320.3° K.[8] By gas chromatographic analysis identical compositions wereo btained approaching equilibrium from both the *cis* and *trans* sides. The results are shown in Table I.

TABLE I

EQUILIBRIUM COMPOSITION OF HYDRINDANE ISOMERS

| $T$, °K. | $K$[a] | % *trans* |
|---|---|---|
| 251 | 1.926 | 65.8 |
| 277 | 1.728 | 63.3 |
| 300.0 | 1.586 | 61.3 |
| 320.3 | 1.482 | 59.7 |

[a] See ref. 8.

From these data a plot of ln $K$ *vs.* $1/T$ was made and a straight line of best fit was calculated by the method of least squares; the slope of this line gave $-\Delta H/R$. The value of ln $K$ at 298° from the graph was used to calculate $-\Delta F^{298}$ and $-\Delta S^{298}$ was estimated from the equation, $\Delta F = \Delta H - T\Delta S$. The thermodynamic values obtained are summarized in Table II, along with literature values.

TABLE II

THERMODYNAMIC VALUES FOR HYDRINDANE ISOMERIZATION

| State | $T$, °K. | $-\Delta H$, kcal./mole | $-\Delta S$, e.u. | $-\Delta F$, kcal./mole | Ref. |
|---|---|---|---|---|---|
| Liquid | 298 | 0.74 ± 0.52 | 1.68 ± 0.10 | 0.24 ± 0.52 | 6 |
| Gas | 298 | 1.04 [illegible] 0.53 | | | 6 |
| Liquid (?) | 552 | 1.07 ± 0.09 | 2.30 ± 0.10 | [a] | 5 |
| Liquid | 298 | 0.58 ± 0.05 | 1.00 ± 0.06 | 0.28 ± 0.06 | This work |

[a] Extrapolation of Allinger and Coke's data[5] to 298° gives ln $K = 0.642$; $-\Delta F$ (298°) = 0.38 kcal./mole.

Agreement between our results and those of Browne and Rossini[6] is very good; however, if the relative heat capacities of the hydrindane isomers can be considered nearly constant over the range from 552–298° K., there is a small but significant difference between our values and those of Allinger and Coke.[5] The data of the latter authors correspond closely to that

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(1) National Science Foundation Predoctoral Fellow, 1962–1963.

(2) Alfred P. Sloan Research Fellow.

(3) P. von R. Schleyer and M. M. Donaldson, *J. Am. Chem. Soc.*, **82**, 4645 (1960); P. von R. Schleyer and R. D. Nicholas, *Tetrahedron Letters*, No. **9**, 305 (1961).

(4) For a review, see H. Pines and J. M. Mavity, "The Chemistry of Petroleum Hydrocarbons," Vol. 3, B. T. Brooks, *et al.*, eds., Reinhold Publishing Corp., New York, N. Y., 1955, chap. 39, pp. 9-58.

(5) N. L. Allinger and J. L. Coke, *J. Am. Chem. Soc.*, **82**, 2553 (1960).

(6) C. C. Browne and F. D. Rossini, *J. Phys. Chem.*, **64**, 927 (1960).

(7) N. D. Zelinsky and M. B. Turowa-Pollak, *Ber.*, **62**, 1658 (1929), reported the treatment of hydrindane (mostly *cis* isomer from hydrogenation) with aluminum bromide at steam-bath temperature. They claimed that the product was *trans*-hydrindane, but it is clear from the properties of the material they reported and from our experience with this reaction that fragmentation, disproportionation, etc., are the main reactions under these conditions, rather than isomerization.

(8) In keeping with the convention used previously[5,6] the isomerization is regarded to proceed from *cis-* to *trans*-hydrindane; $K$ (equil.) = (*trans*/*cis*).