acid, or ternary azeotropes with formic acid and formamides depending on the particular amine.[2] Appreciable dehydration to formamide required atmospheric distillation over 100°. In contrast, the chloral hydrate reactions were performed at room temperature and the formamides were isolated by extraction with chloroform followed by vacuum distillation.

The hydrolysis of chloral occurs presumably by a mechanism such as that given by Gustafson and Johanson[3]; either hydroxide ion or amine could serve as the base. There is no obvious relationship between amine basicity and degree of either formylation or hydrolysis. However, steric hindrance appears to play an important role. Appreciable hydrolysis only with *t*-butylamine implies that approach of the amine nitrogen to the carbonyl carbon is hindered to such an extent that no formylation was detected. Except for such hindered compounds the reaction of chloral hydrate with amines in water is an acceptable procedure for the preparation of formamides.

Experimental

General Procedure for the Reaction of Chloral Hydrate with Aliphatic Amines in Water.—To a magnetically stirred solution (200 ml.) of the appropriate amine (0.5 mole) in water was added an aqueous solution (150 ml.) of chloral hydrate (82.5 g., 0.5 mole). A liquid or solid separated and the temperature rose to not higher than 45°. The mixture was allowed to stir overnight at room temperature. In all cases two liquid layers remained. The aqueous layer was extracted with chloroform. The chloroform extracts were combined with the organic layer and vacuum distillation gave the appropriate formamide. The aqueous portion was evaporated on a rotating evaporator at 50° under water-aspirator vacuum to give either a solid ammonium formate or a liquid residue. The liquid was distilled to give an ammonium formate azeotrope with formic acid. The various formamides, ammonium formates, and ammonium formate azeotropes were characterized by comparison with authentic samples. Elemental analyses, indices of refraction, infrared absorption curves, boiling points, and melting points were used for this purpose.

Acknowledgment.—The author wishes to acknowledge the technical assistance of Mary D. Pankau. Elemental analyses were performed by the Analytical Research Branch, U. S. Army Chemical Research and Development Laboratories.

(2) E. J. Poziomek and Mary D. Pankau, unpublished results.
(3) C. Gustafson and M. Johanson, *Acta Chem. Scand.*, **2**, 42 (1948).

Complexes of Sugars with Molybdate

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In the course of an investigation of the biological function of molybdenum, complexes of sugars with this metal in aqueous solution have been studied.

Bourne, Hutson, and Weigl have reported the results of paper ionophoresis studies of sugars in acidified molybdate solution.[2] These authors concluded from their results that pyranose sugars possessing three hydroxyl groups in a *cis-cis*-1 (ax), 2 (eq), 3 (ax), arrangement (chair form) complex with molybdate.

(1) Abstracted from the M.S. thesis of S. Kiang, Utah State University, 1962.
(2) E. J. Bourne, D. H. Hutson, and H. Weigl, *J. Chem. Soc.*, 4252 (1960).

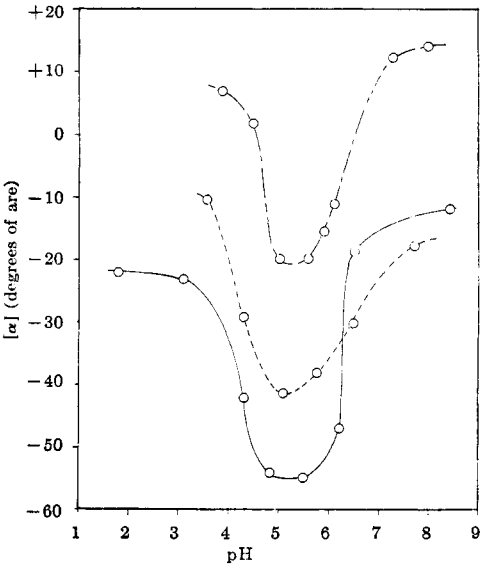

Fig. 1.—Effect of pH on specific rotation ([α]) of sugar–molybdate complexes.
Ratio of sugar to molybdate, 1:1; temp., 25.0 ± 0.5° C.
— — — — D-mannose
---------- D-ribose
—·— D-lyxose

Polarimetric studies of these complexes have verified these conclusions. It was found that when molybdate was added to a solution of a sugar with the correct structure at a pH near 5 a large change in optical rotation due to complex formation occurred, while little or no change occurred with sugars not having this structure. Table I gives the results with various sugars. It can be seen that only those having the necessary 1 (ax), 2 (eq), 3 (ax) arrangement complex. The absence of one of the necessary hydroxyls prevents complexing, as with 2-deoxy-D-ribose and α-methyl-D-mannopyranoside.

TABLE I

Sugars that complex	Sugars that do not complex
D-Mannose	D-Glucose
D-Lyxose	D-Galactose
D-Ribose	D-Arabinose
	D-Xylose
	2-Deoxy-D-ribose
	α-Methyl-D-mannopyranoside

Fig. 1 indicates that the optimum pH for complex formation is about 5.5 and most studies were done in this region.

Continuous variations plots (Fig. 2) show that the ratio of molybdenum:sugar in the complexes is 1:1 in all cases. The plots also show that the complexes are relatively weak. This was confirmed by measuring the optical rotation of a solution of D-mannose in the presence of increasing molybdate concentration. It was found that the optical rotation of the solution did not become constant until a tenfold excess of molybdate had been added.

It is interesting to note that the sign of the rotation for mannose changes upon complex formation. This is undoubtedly due to the fact that the equilibrium mixture of D-mannose consists predominantly of the α-iso-

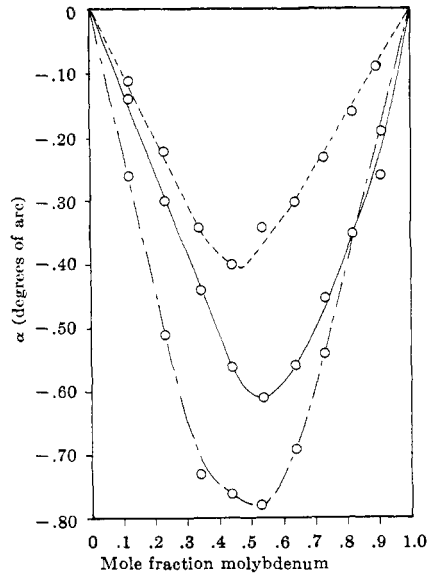

Fig. 2.—Continuous variations plots for sugar–molybdate complexes. The difference in optical rotation (α) between solutions of sugar plus molybdate and solutions containing the same concentration of sugar is plotted *vs.* mole fraction molybdenum.
pH 5.0 in 1.5 *M* acetate buffer; temp., 25.0 ± 0.5 °C.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