after they were opened. In the second method (B), samples were prepared by treating the equilibrated mixtures for 30 seconds with 5 ml. of cold concentrated sulfuric acid and then pouring the solution into 25 ml. of water. The samples for vapor phase chromatography were isolated by extracting with ether, washing the extracts with water, drying with anhydrous sodium sulfate, and evaporating the ether. This treatment had the effect of removing alcohols which complicated the analysis. There was no systematic difference in analyses between methods A and B.

Initial experiments with the isomers of 3,5-dimethylcyclohexanone indicated that a good separation could be obtained on a column containing 25% by wt. of the cyanoalkylation product of glycerin on firebrick. However, two of the three isomeric alcohols (prepared for comparison purpose by lithium aluminum hydride reduction of a mixture of *cis*- and *trans*-ketones) had retention times identical to those of the isomeric ketones. Making use of the ability of Tide to separate ketone–alcohol mixtures, a dual column was constructed which contained both stationary phases so that it would separate not only ketone and alcohol but also their isomers. Analysis of a mixture of isomeric ketones and alcohols on Tide alone showed only three peaks, while on the composite column five peaks were observed. The separation while good, was not, however, perfect.

The column used for analysis, a 180 cm. × 7 mm. Pyrex tube bent in a U, contained two different packing materials. The first half of the column contained 40–60 mesh Tide. The second half contained 60–80 mesh firebrick supporting 25% by weight of tris-β-cyanoethyl glyceryl ether as the liquid partitioner. The column was operated at 110° and at an inlet pressure of 8 p.s.i. of helium. The results of equilibration experiments are reported in Table II.

The free energy change, calculated from the data in Table II for the reaction *trans* ⇄ *cis*-3,5-dimethylcyclohexanone, was $\Delta F°_{493} = -0.67 \pm 0.15$ kcal./mole. Recognizing that the *trans* isomer is a *dl*-mixture and the *cis* isomer is a *meso* form ($\Delta S = -1.4$ e.u.), a value of $\Delta H_{493} = -1.36 \pm 0.18$ kcal./mole was calculated. From available data[9,10] for the reaction *trans*-1,3-dimethylcyclohexane ⇄ *cis*-1,3-dimethylcyclohexane, $\Delta H = -1.96 \pm 0.1$ kcal./mole, and the difference in enthalpy for these reactions can be calculated as $(-1.36 \pm 0.18) - (-1.96 \pm 0.1 = 0.60 \pm 0.28)$ kcal./mole. Thus when a keto group replaces a methylene group on a cyclohexane ring, an axial methyl group on the 3-carbon becomes more favorable by 0.6 kcal./mole.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF BOSTON UNIVERSITY, BOSTON 15, MASS.]

Oxymercuration of D-Glucal and Its 3,4,6-Triacetate

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RECEIVED DECEMBER 28, 1961

Crystalline products obtained on addition of methanolic mercuric acetate to D-glucal and to its 3,4,6-triacetate have been shown with the aid of brominolysis and iodide-catalyzed deoxymercuration to be methyl 2-acetoxymercuri-2-deoxy-β-D-mannoside and methyl 2-acetoxymercuri-2-deoxy-3,4,6-tri-O-acetyl-β-D-glucoside, respectively. Oxymercuration thus yields a *cis* product with D-glucal and a *trans* product-with its triacetate. These assignments and related brominolysis data support previously assigned configurations of Fischer's two methyl-2-deoxy-2-bromo-β-D-hexosides. Mechanistic speculations are presented. A small number of related alkoxymercuration products are described.

Results

Relationship between Addition Products.—The reactions of glucal and its 3,4,6-triacetate with methanolic mercuric acetate yield stable crystalline products, which, on the basis of evidence presented below, have been identified, respectively, as methyl 2-acetoxymercuri-2-deoxy-β-D-mannoside (I) and methyl 2-acetoxymercuri-2-deoxy-3,4,6-tri-O-acetyl-β-D-glucoside (III). These appear to be the first reported examples of oxymercuration of glycals. Transformations which establish that III is not the 3,4,6-triacetate of I are summarized in Fig. 1.

Compound I is prepared most efficiently without isolation of glucal; the same product is, however, obtained on treating crystalline glucal with methanolic mercuric acetate. Attempted acetylation of I by acetic anhydride and sodium acetate proceeds with formation of metallic mercury and formation of a solid product, Y, which is not sufficiently soluble in common solvents to permit recrystallization. This product has not yet been identified. However, the fact that its infrared spectrum is devoid of ionic acetate absorption bands (687, 1317, 1607 cm.$^{-1}$) suggests that it may be a dialkyl mercury or a mixture of isomeric compounds of this type. A product with identical infrared spectrum is obtained on subjecting III to the same acetylating conditions. Attempted deacetylation of III by methanolysis catalyzed by sodium methoxide did not yield a pure product even though compound I could be recovered unchanged after exposure to the same conditions. Attempted purification by repeated reprecipitation from diethyl ether of the product of methanolysis of III did not yield a pure substance. Ionic acetate absorption at 687 and 1317 virtually disappeared during this process (but absorption at 1607 did not). Compound III was identified as the triacetate of an isomer of I by comparison of II with V and of I with VI (Fig. 1). The reaction of I with KCl provided only a poor yield of II because of difficulties in freeing the latter of potassium acetate (reaction with NaCl was not attempted), but there is no reason to suspect that I → II involved more than replacement of acetate by chloride. In addition, the infrared spectra of I and II differ largely by the ionic acetate absorption. Similarly III → IV can involve only replacement of ionic acetate by more tightly bound chloride. The reaction of III with aqueous sodium bromide also provides a virtually quantitative yield of D-glucal triacetate·$HgBr{\cdot}OCH_3$, the infrared spectrum of which is almost identical with that of IV. Base-catalyzed methanolysis of IV at room temperature to form V does not displace chlorine from mercury and is very unlikely to cause any change other than removal of acetyl groups with retention of configuration at C-3 and C-5. Although II and V have almost the same melting points, the melting point of their mixture is depressed. Their infrared spectra are strikingly different. Among other differences,

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(1) *Cf.* Abstracts of the 138th Meeting of the American Chemical Society, New York, N. Y., Sept., 1960, p. 36-P for a preliminary report.

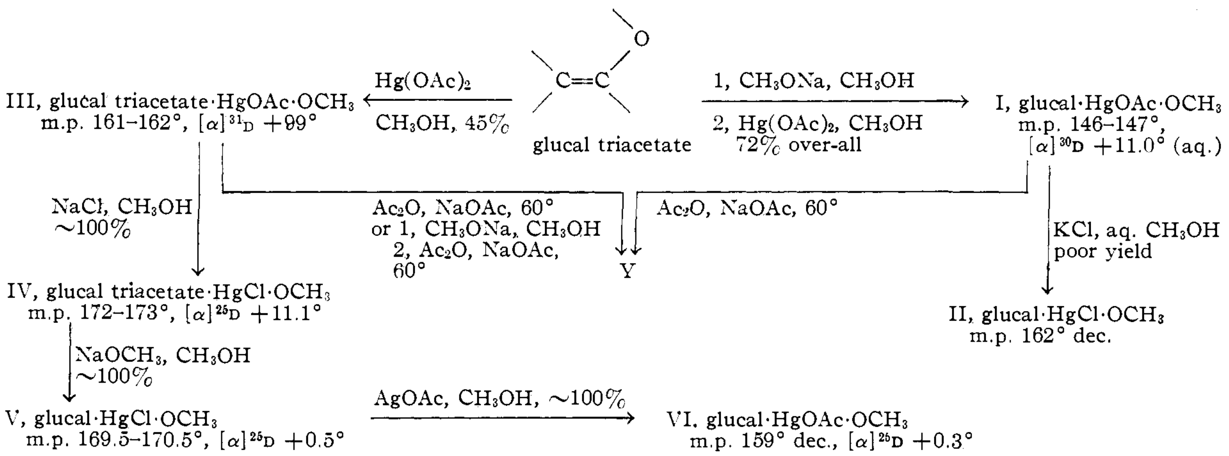

Fig. 1.—Oxymercuration of glucal and its triacetate and attempted interconversion of the products.

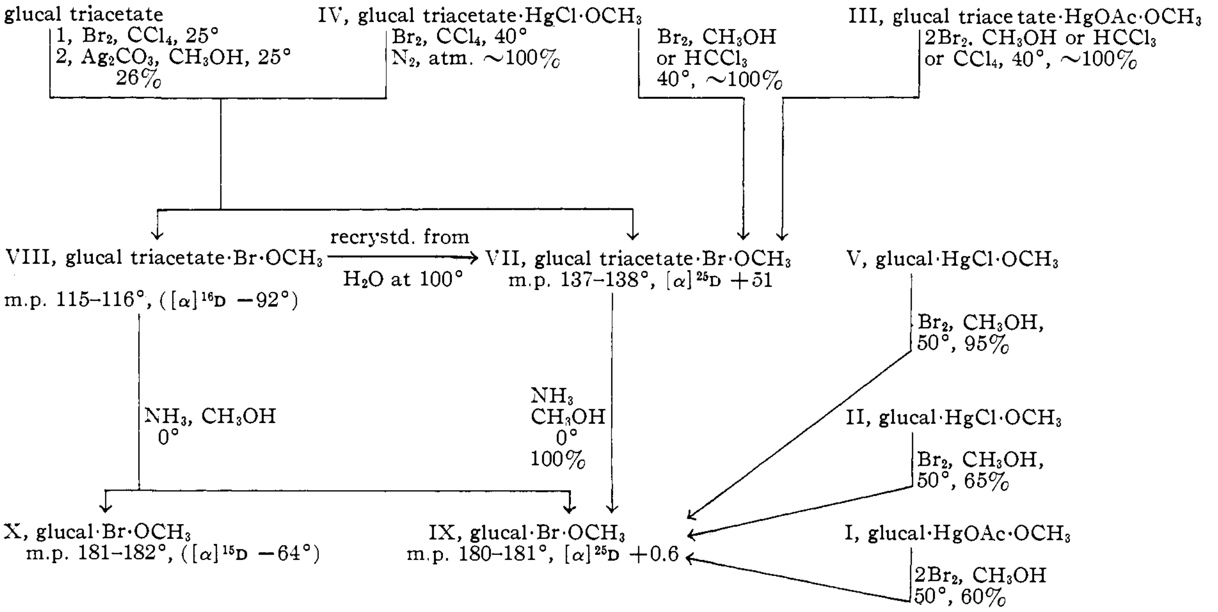

Fig. 2.—Bromination and brominolysis experiments.

important bands of II with maxima at 649, 721, 924, 953, 1114, 1419, 1445 and 1591 cm.$^{-1}$, the last three of which are very strong, are absent for V, while for V there are bands with maxima at 751, 893, 997 and 1152 cm.$^{-1}$ that are absent for II. The replacement of the chloride of V by acetate through reaction of V with methanolic silver acetate at room temperature must also proceed without other alteration of the molecule. The melting point of VI, produced in this way, differs significantly from that of I. The melting point of their mixture is depressed and their infrared spectra are quite different. Since II and V have identical elemental compositions as do I and VI, they must constitute isomeric pairs. It follows that I and II must differ in either structural or configurational orientation of addition of acetoxymercuri methoxide or perhaps in both.

Nature of the Isomerism.—That the isomerism is configurational was demonstrated by brominolysis of I–V to known compounds as shown in Fig. 2. Compounds VII–X were originally reported by Fischer and his co-workers[2] who prepared them by addition of bromine to glucal triacetate, methanolysis of the dibromide in the presence of Ag_2CO_3 to yield the bromomethoxides VII and VIII, and base-catalyzed methanolysis of these products to yield IX and X. Since IX and X yield methyl 2-deoxy-β-D-glucoside[3–5] on reduction with sodium amalgam, their structures as well as those of VII and VIII are fully determined and their configurations are established at all positions save C-2. It can accordingly be concluded[6] from the brominolysis experiments that I–V are methyl 2-deoxy-β-D-glucoside derivatives (and presumably VI is, as well). Compounds I and II must differ from V and VI by their configurations at C-2.

Configuration at C-2.—That the data presented in Fig. 2 are consistent with particular assignments

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(2) E. Fischer, M. Bergmann and H. Schotte, *Ber.*, **53**, 509 (1920).

(3) E. Fischer, M. Bergmann and H. Schotte, *ibid.*, **53**, 543 (1920).

(4) M. Bergmann, H. Schotte and W. Lechinsky, *ibid.*, **55**, 158 (1922).

(5) M. Bergmann, H. Schotte and W. Lechinsky, *ibid.*, **56**, 1052 (1923).

(6) The possibility that anomerization of some or all of the mercury derivatives I–V may accompany brominolysis has not been excluded, but this reaction is very improbable.

of configuration at C-2 is shown below. These data are not conclusive, however. Fortunately, rates of iodide-catalyzed deoxymercuration provide what appears to be an unequivocal basis for assignment. Since the substituents at C-1 and C-3 of the methyl 2-deoxy-β-D-glucoside derivatives are *cis* to each other, the substituent at C-2 is either *cis* to both of them or *trans* to both. It has recently been demonstrated[7,8] that deoxymercuration of vicinal *trans* substituted cyclohexane derivatives is very much faster than is the corresponding reaction of the corresponding *cis* isomers. Thus, regardless of the structural orientation of elimination, compounds I–VI should fall into two classes with respect to their rates of deoxymercuration. The data of Table I show that this is indeed the case. Compounds I and II react much more slowly than do III–V. The latter appear to be more reactive than *trans*-2-chloromercuricyclohexyl methoxide[9] (m.p. 115.5–116°). The somewhat greater reactivity of III and IV is, presumably, a consequence of acetylation of the 3-hydroxyl group. Attempted isolation of the products of deoxymercuration of III and IV did not yield crystalline materials. Oils with essentially identical infrared spectra (Nujol mulls) were obtained. Although these spectra are similar to the spectrum of glucal triacetate, they differ from it sufficiently to prevent any conclusions from being drawn. Whether deoxymercuration involves elimination of the substituent on C-1 or C-3, or whether both reactions occur, is not critical to the argument, however, since, as has already been emphasized, these substituents are *cis* to each other. The mercury atom in I and II must be *cis* to substituents on C-1 and C-3 while that in III–VI must be *trans*. The probable most stable conformations[10] of these compounds are presented in Fig. 3.

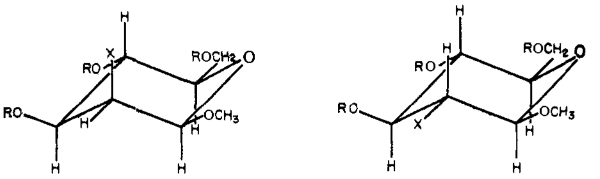
TABLE I

TIMES FOR DEOXYMERCURATION OF 0.1 *M* SUBSTRATES BY 0.4 *M* ETHANOLIC NaI AT 60°

Substrate	Time,[a] min.
I	No reacn.[b]
II	No reacn.[b]
III	2.5
IV	1.5
V	5.5
trans-2-Chloromercuricyclohexyl methoxide[9]	8.5
2-Methoxy-3-acetoxymercuritetrahydropyran	5.5
2-Methoxy-3-chloromercuritetrahydropyran	4.5

[a] Time for first appearance of a precipitate. [b] No reaction in 30 minutes at 60°. Compounds I and II reacted after heating the solutions to boiling.

The deoxymercuration data are sufficient, by themselves, to establish configuration at C-1 and C-2 of compounds I and II, provided structural orientation of addition is known, since only one of the four configurational combinations at C-1 and C-2 has the mercury atom *cis* to hydroxyl at C-3 and to methoxyl at C-1. The three other configurations at C-1 and C-2 would all undergo deoxymercuration relatively rapidly and cannot be distinguished by qualitative deoxymercuration rate data.



I, X = CH_3CO_2Hg,
R = H
II, X = ClHg, R = H
VIII, X = Br, R = CH_3CO
X, X = Br, R = H

III, X = CH_3CO_2Hg,
R = CH_3CO
IV, X = ClHg,
R = CH_3CO
V, X = ClHg, R = H
VI, X = CH_3CO_2Hg,
R = H
VII, X = Br, R = CH_3CO
IX, X = Br, R = H

Fig. 3.—Complete assignments of compounds I–X.

The assignments of configuration shown in Fig. 3 are supported by a number of facts, some of which are presented in Fig. 2. The brominolysis of *cis*- and *trans*-4-methylcyclohexyl mercuric bromides recently has[11] been shown to proceed with nearly complete loss of relative configuration when carried out in CCl_4 under a nitrogen atomosphere and to proceed with predominating or complete retention in a number of polar solvents, including methanol, particularly in the presence of air. Under the former conditions, IV yields both VII and VIII and the amounts of the latter two compounds approach equality when sufficient care is employed to exclude oxygen and moisture. Brominolysis of IV or III in methanol or chloroform solution or of III in CCl_4, all in the presence of air, provides only VII in virtually quantitative yields. This cannot be a result of rearrangement of VIII under the latter conditions since VIII can be recovered unchanged after boiling its solution in methanol in the presence of small amounts of Br_2 and $HgBr_2$. (Compound VIII does isomerize into VII, however, on recrystallization from boiling water; this fact is discussed below.) Although the presence of a vicinal functional group and several additional asymmetric carbon atoms in the molecule weakens the argument by making possible both neighboring group effects and asymmetric chemical transformations that are not possible in Jensen's case, the results can be interpreted on the basis of his data. Reasoning in this fashion, the bromine atom of VII has the same relative configuration as the acetoxymercuri and chloromercuri groups of III and IV. That methanolysis of VII at 0°, catalyzed by dry NH_3, proceeds without stereochemical change follows from the nearly quantitative yield of IX. None of the less stable isomer X (which is formed in admixture with IX by the same reaction of VIII) has been detected in this reaction of VII. Similarities between the infrared spectra of VII and IX and differences between these and the spectra of

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[7] T. G. Traylor and S. Winstein, "Abstracts of the 135th Mtg.," Am. Chem. Soc., Boston, Mass., April, 1959, p. 81-O.

[8] M. M. Kreevoy and F. R. Kowitt, *J. Am. Chem. Soc.*, **82**, 739 (1960).

[9] J. Romeyn and G. F. Wright, *ibid.*, **69**, 597 (1947). The *trans* assignment is that originally made by A. G. Brook and G. F. Wright, *Acta Cryst.*, **4**, 50 (1951), and supported by recent work of Traylor and Winstein[7] and of Kowitt and Kreevoy.[8]

[10] *Cf.* R. J. Ferrier and W. G. Overend, *Quart. Revs.*, **13**, 265 (1959).

[11] F. R. Jensen and L. H. Gale, *J. Am. Chem. Soc.*, **82**, 148 (1960).

VIII and X, particularly in the 1000–1100 cm.$^{-1}$ region, tend to support this conclusion. Although the configurations about C-1 and C-2 of IX were described in 1952 as "still not clarified,"[12] there appears to be excellent evidence in prior literature for the formulation of IX as shown in Fig. 3, namely, as methyl 2-deoxy-2-bromo-β-D-glucoside. Thus,[2,13] IX, but not its isomer X, is converted to methyl 3-amino-3-deoxy-β-D-altroside (XI) by the action of 25% aq. ammonia at 90–100°, a result which can be accommodated *via* initial formation of the 2,3-anhydromannoside by inverting attack of neighboring *trans* alkoxide at C-2 followed by ring opening at C-3 with a second inversion. This interpretation is confirmed by the completely analogous transformation[14] of methyl 2-*p*-toluenesulfonyl-β-D-glucoside (XII) into XI. Completely aside from mechanistic interpretation, the well known similarity of reactions of bromides and *p*-toluenesulfonates serves to establish that the bromine atom of IX and the tosylate group of XII have the same configurational orientations. Since, as rationalized above, the bromine atom of VII and the mercury atom of III and IV are similarly oriented, configurational assignments identical with those based on rates of deoxymercuration are deduced.

The fact that not only V but also its isomer II and the related acetoxy compound I yield only VII on brominolysis in methanol in the presence of air complicates the stereochemical interpretation, however, and demonstrates that caution must be exercised in generalizing Jensen's observations. The present results can be explained if cognizance is taken of the demonstrated instability of VIII with respect to conversion to VII and of X with respect to IX. Not only does VIII yield a mixture of IX and X on treatment with methanolic ammonia at 0° but X undergoes slow isomerization into IX on fractional recrystallization from ethyl acetate. It should be noted that X is considerably less soluble in methanol than IX. Thus, it presumably was not left in mother liquors from the brominolysis of I and II. Apparently inversion at C-2 occurs either during or subsequent to brominolysis of I and II. It should be noted that VIII is not only unstable with respect to conversion to VII but it is also more reactive to aqueous $AgNO_3$ than is VII. The observed stability sequence of VII *vs.* VIII and IX *vs.* X is also consistent with the configurational assignments of Fig. 3. The bromine atoms of VII and IX are presumably equatorial, while those of VIII and X are axial. Eliel[15] has shown that, for cyclohexyl bromide in 85% aqueous ethanol, equatorial bromine is somewhat more stable than axial, the standard free energy difference being given as 0.73 kcal. mole^{-1}. The difference should be of the same sign but larger in the present cases because the angle between the bond moment of the axial C–Br and the resultant of the two C–O bond moments at C-1 is approximately 70°. An electrostatic repulsion, not present in axial cyclohexyl bromide, thus diminishes the stability of axial bromine with respect to equatorial, in the present case, since the angle between the equatorial C–Br bond moment and the resultant of the two C–O bond moments is 145° or thereabouts.[16] This conformational effect seems to be more important in the reaction with aqueous silver nitrate than the possibility of neighboring group participation which is present in VII but not in the more reactive VIII.

Preparation of Related Compounds.—Three compounds homologous to members of the series I–VI were prepared through the reaction of D-glucal triacetate with mercuric acetate in ethanol and isopropyl alcohol and a subsequent transformation. Their preparation and properties are described in the Experimental part. The structural and configurational assignments indicated therein are based on analogy to compounds I–VI and on similarities of infrared spectra with members of the latter series. These examples suggest the generality of the reactions employed.

Discussion

Although vigorous dissent has been offered recently,[17] a substantial weight of evidence[7–9,18] now exists that the normal steric course of oxymercuration is *trans*. This conclusion is supported by very recent proton magnetic resonance data.[19] *cis*-Oxymercuration has been observed in the reaction of 2-norbornene.[18,19] The present cases appear to be the first where both steric modes of addition have been observed in monocyclic molecules.

The deoxymercuration results with the dihydropyran addition products[20] indicate that addition to an unsubstituted ring of this type follows a *trans* course. It is, of course, possible that D-glucal and its triacetate react by completely dissimilar mechanisms, but it seems more plausible to assume that both react by essentially the same type of mechanism, *via* mercurinium ions,[21] and that stereoelectronic differences determine the nature of these ions and their subsequent fate. In this view, D-glucal and its triacetate must undergo initial attack by mercury from opposite directions, at the β- and α-faces, respectively. It is reasonable to assume that the bulky acetate group in β-configuration at C-3 of glucal triacetate tends to shield the double bond from attack from that direction, so that an α-mercurinium ion is formed. This presumably undergoes inverting nucleophilic attack by methanol at C-1 to yield compound III. On the other hand, the more available unshared electrons of smaller hydroxyl oxygen at C-3 of glucal can interact effectively with the mercury atom so that

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[12] B. Helferich *Adv. Carbohydrate Chem.*, **7**, 216 (1952).

[13] N. K. Richtmyer, *ibid.*, **1**, 58 (1945).

[14] E. W. Bodycotte, W. N. Haworth and E. L. Hirst, *J. Chem. Soc.*, 151 (1934).

[15] E. L. Eliel and R. G. Haber, *J. Am. Chem. Soc.*, **81**, 1249 (1959); *cf.* also E. Eliel, *Chemistry & Industry*, 568 (1959).

[16] This corresponds to Reeves' "Δ2 effect"; *cf. Adv. Carbohydrate Chem.*, **6**, 107 (1951).

[17] M. J. Abercrombie, A. Rodgman, K. R. Bharucha and G. F. Wright, *Can. J. Chem.*, **37**, 1328 (1959).

[18] T. G. Traylor and A. W. Baker, *Tetrahedron Letters*, No. **19**, 14 (1959).

[19] M. M. Anderson and P. M. Henry, *Chemistry & Industry*, 2053 (1961).

[20] The structural assignment of this product (*cf.* Table I) is based on the expected structural orientation of addition to a vinylic ether; *cf.* J. Chatt, *Chem. Revs.*, **48**, 15 (1951).

[21] H. J. Lucas, F. R. Hepner and S. Winstein, *J. Am. Chem Soc.*, **61**, 3102 (1939).

initial formation of the mercurinium ion is *cis* to the 3-hydroxyl. This is analogous to an orienting effect of hydroxyl and other electron-donating groups which has been postulated by Henbest and co-workers[22] in the mercuration of several 4-substituted cyclohexenes. This ion may transform more rapidly into a structure where mercury is partially bonded to the oxygen on C-3, and where a positive charge is delocalized over C-1 and the ring oxygen, than it undergoes external inverting nucleophilic attack (which would give methyl 2-deoxy-2-acetoxymercuri-α-D-mannoside). This species may then react with solvent to give the presumably more stable product I.

This discussion is, of source, purely speculative. The major point of interest is the observation of opposite steric courses of addition to two closely related molecules. A delicate balance between orientations of additions is suggested. This balance is also suggested by the low yield of III, 45% and the fact that considerable residual sirupy product has been isolated from the mother liquors of III. Reaction of D-glucal triacetate with mercuric acetate in ethanol and 2-propanol (*cf.* Experimental) yields crystalline products that appear to be homlogs of III, *i.e.*. alkyl 2-deoxy-2-acetoxymercuri-β-D-glucosides, but these also were isolated in relatively low yields, approximately 40%. The reaction of D-glucal is apparently more selective since compound I was obtained in 72% yield. Attempts to isolate other pure products from the various sirupy residues are in progress and should be instructive with respect to stereoselectivity.

The question of whether I and III are primary, *i.e.*, rate controlled, products or whether they are secondary, equilibrium controlled, products can only be dealt with in a tentative way. The fact that the members of each pair I and VI and II and V did not interconvert under any of the conditions under which they were handled suggests that I is a primary product; but, since the two other potentially available stereoisomers (the α-anomers) have not been obtained, this is not conclusive. The available data in no way exclude the possibility that III is an equilibrium-controlled product. The most simple working assumption that can be made is that I and III are primary products.

It is of some interest to note the lack of any obvious relationship between molecular optical rotation in the mercury derivatives I–VI and the bromo-compounds VII–X. Thus, VI and its triacetate III differ in molecular rotation very much less than do the analogous bromides IX and VII, while the difference in rotations of VI and I is actually opposite in sign to that of the analogous pair VII and VIII. Apparently, molecular distortions are sufficiently large and different in these two groups of compounds to render invalid analysis of molecular rotations in terms of group contributions.

Acknowledgment.—This work was supported by Grants 508 of the American Cancer Society (Mass. Div.), Inc., and CY-3826 of the National Cancer Institute of the U. S. Public Health Service.

Experimental

D-Glucal 3,4,6-Triacetate and D-Glucal.—β-D-Glucopyranose pentaacetate (Corn Products Refining Co.) was converted into tetra-O-acetyl-α-D-glucopyranosyl bromide by treatment with hydrogen bromide in glacial acetic acid[23] and recrystallization from a mixture of carbon tetrachloride and 30–60° petroleum ether; m.p. 87–88°. The product was converted into D-glucal 3,4,6-triacetate by shaking with zinc dust (Baker, purified) in 1:1 aqueous acetic acid.[24] The crude sirupy product which remained after vacuum distillation of solvent ether was cooled by Dry Ice while still in the rotating evaporator (Rinco), with continued pumping at 0.1 mm. Solidification occurred within 5–10 min. Recrystallization from absolute ethanol–30–60° petroleum ether afforded a 71% yield of white crystals melting at 53–54°. This product was converted into D-glucal, m.p. 58.5–60°, in 72% yield by catalytic de-O-acetylation with sodium methoxide in absolute methanol (Baker, analyzed reagent, distilled from magnesium methoxide) according to the procedure of Shafizadeh and Stacey.[25]

D-Glucal 3,4,6-Triacetate Acetoxymercurimethoxide (III).—A solution of 3.75 g. (0.0117 mole) of mercuric acetate (Mallinckrodt, analytical reagent) in 50 ml. of anhydrous methanol (Baker, analyzed reagent) was added in one portion to a solution of 3.32 g. (0.0122 mole) of D-glucal 3,4,6-triacetate in 25 ml. of the same solvent. The reaction solution was freed of suspended impurities and allowed to remain at room temperature for about 1 hour. The solvent was removed with a rotating vacuum evaporator and the residue, a white pasty material, was triturated with about 50 ml. of anhydrous ether to give white clustered crystals. The product was collected by suction filtration, washed with a small amount of ice-cold isopropyl alcohol and then ether and finally air-dried. Two or three recrystallizations from isopropyl alcohol afforded a 45% yield of white needles, m.p. 161–162°, $[\alpha]^{31}\mathrm{D}$ +9.9° (0.095 g./cc. in methanol).

Anal.[26] Calcd. for $C_{15}H_{22}O_{10}Hg$: C, 32.00; H, 3.94; Hg, 35.64; CH_3O, 5.51. Found: C, 32.0: H, 4.05; Hg, 34.9; CH_3O, 5.66.

D-Glucal Acetoxymercurimethoxide (I).—D-Glucal acetoxymercurimethoxide was prepared most conveniently directly from a methanolyzed solution of D-glucal 3,4,6-triacetate without prior isolation of D-glucal. A solution of approx. 40 mg. of sodium/100 ml. of anhydr. methanol (Baker, analyzed reagent) was added to a solution of 5.0 g. (0.0184 mole) of D-glucal 3,4,6-triacetate in 100 ml. of the same solvent. After about 1 hour at room temp., 5.8 g. (0.0182 mole) of mercuric acetate (Mallinckrodt, analytical reagent) was added and the reaction mixture was kept at room temp. for an additional hour. The solution was filtered from suspended impurities and then concentrated to about 25–30 ml. An equal volume of 30–60° petroleum ether was added and the solution was allowed to stand, first at room temperature until crystallization began, and then in the refrigerator. The white crystalline product was collected by suction filtration, washed with anhydrous ether and dried in a vacuum desiccator over Drierite. Two or three recrystallizations from methanol (or ethanol)–petroleum ether afforded 5.7 g. 72%, of colorless prisms, m.p. 146–147° with decomposition, $[\alpha]^{28}_{D}$ +11.0° (22 hours after dissolution of 0.203 g. in 2.0 ml. of H_2O). This mercurial decomposes on prolonged storage under dry air into a brown, and eventally black, tarry material. *Anal.*[26] Calcd. for $C_9H_{16}O_7Hg$: C, 24.75; H, 3.69; Hg, 45.93; CH_3O 6.85. Found: C, 24.7; H, 3.55; Hg, 45.7; CH_3O, 6.95.

This compound was also prepared in poor yield by addition of mercuric acetate to a methanolic solution of crystalline D-glucal. The identity of the product with that prepared from glucal generated *in situ* was confirmed by a mixed melting point determination as well as a comparison of infrared spectra.

Acetylation and "Deacetylation" of D-Glucal Acetoxymercurimethoxide (I).—A finely powdered mixture of 2.2 g. (0.005 mole) of I and 2.05 g. (0.025 mole) of anhydrous sodium acetate was heated at 60–65° with 30 ml. of freshly

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(22) H. B. Henbest and B. Nicholls, *J. Chem. Soc.*, 227 (1959); H. B. Henbest and R. S. McElhinney, *ibid.*, 1834 (1959).

(23) "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 14.

(24) E. Fisher, *Ber.*, **47**, 196 (1914).

(25) F. Shafizadeh and M. Stacey, *J. Chem. Soc.*, 3608 (1952).

(26) Analysis by S. Nagy, Mass. Inst. of Technology, Cambridge, Mass.

distilled acetic anhydride for 4 hours in a reflux apparatus with calcium chloride tube. The hot solution was freed of mercury by filtration and poured onto ice, yielding an oil which solidified to a white powder (Y) on stirring. This material was insoluble in common solvents and melted only partially at 158°, with darkening. Compound I was also subjected to deacetylation conditions, *i.e.*, its solution in methanol containing a catalytic amount of sodium methoxide stood at room temperature for 4 hr. Evaporation of the solvent followed by treatment with ether afforded unaltered starting material.

Deacetylation and Acetylation Experiments with D-Glucal 3,4,6-Triacetate Acetoxymercurimethoxide (III).—Compound III was subjected to the same deacetylation conditions as was I. The resulting white solid softened at 75° and turned brown at 135°. No improvement resulted on repeated precipitation of the product from ethanol by addition of ether. The infrared spectrum of this hygroscopic material is devoid of covalent acetate absorption, but extensively different from that of I. Subjection of III or of its deacetylation product to the acetylation procedure employed with I yielded substance Y. When a suspension of Y in methanol containing a catalytic amount of sodium methoxide was stirred at room temperature for 4 hr., it underwent deacetylation (infrared spectrum) without dissolving. The product was identical with neither I nor the deacetylation product of III.

D-Glucal Chloromercurimethoxide (II).—A solution of 2.2 g. (0.005 mole) of I in *ca.* 15 ml. of methanol was allowed to react for 2 hours with 1.0 g. (0.01 mole) of potassium chloride dissolved in 5 ml. of water at room temperature. The solvent was completely removed on the rotating vacuum evaporator and the residue was dried in a vacuum desiccator over P_2O_5. Potassium chloride was first removed by repeated dissolutions in absolute ethanol, filtrations and evaporations of the solvent. When no inorganic matter was apparent in the ethanolic solution, anhydrous ether was added which caused precipitation of a white powder. This product started turning brown at about 150°; most of it melted at *ca.* 170°, while a considerable fraction did not melt at higher temperatures. A positive tartaric acid test for potassium suggested that the non-melting contaminant was potassium acetate which is known to form complexes with certain pyranosides. The potassium acetate was removed by precipitation as the acid tartrate salt from ethanol, filtration and evaporation of the solvent. Finally, after several wasteful recrystallizations from ethanol and petroleum ether (or ether) a small quantity of a pure product was obtained which melted at 162° dec. The infrared spectrum of this compound was very similar to that of the starting material except for the missing ionic acetate absorption bands. *Anal.*[27] Calcd. for $C_7H_{13}O_5HgCl$: C, 20.34; H, 3.17; Hg, 48.54; CH_3O, 7.51. Found: C, 20.57; H, 3.35; Hg. 48.65; CH_3O, 7.42.

D-Glucal 3,4,6-Triacetate Chloromercurimethoxide (IV).—Twenty ml. of 10% aq. sodium chloride was added to a reduced volume (20 ml.) of the reaction mixture produced in synthesizing III or to a solution of 0.0055 mole of isolated III in about 20 ml. of methanol. In either case, crystalline needles precipitated almost instantly. After standing in the refrigerator for 1 hour, the product was collected by suction filtration, washed with a few small portions of distilled water and air-dried. The yield of the crude chloromercurimethoxide compound was almost quantitative. The product was dissolved in a minimum amount of chloroform and recrystallized in colorless needles by adding boiling isopropyl alcohol. After two or more recrystallizations, IV melted at 172–173°, $[\alpha]^{25}_{\mathrm{D}}$ +11.1° (0.004 g./ml. in $CHCl_3$). The infrared spectrum of this compound showed a characteristic split in the carbonyl absorption band with two peaks at 1740 and 1716 cm.$^{-1}$. *Anal.*[27] Calcd. for $C_{13}H_{19}O_8HgCl$: C, 28.95; H, 3.55; Hg, 37.19; CH_3O, 5.75. Found: C, 29.09; H, 3.84; Hg, 37.14; CH_3O, 5.40.

D-Glucal 3,4,6-triacetate bromomercurimethoxide was prepared by treatment of III with aq. sodium bromide in the manner described for the preparation of IV. The product melting at 176–178°, isolated and purified in exactly the same way as for IV, was obtained in 95% yield. Infrared spectrum of this compound was practically identical with that of IV with minor shifts of a few bands toward lower frequencies. *Anal.*[27] Calcd. for $C_{13}H_{19}O_8HgBr$: C, 26.74; H, 3.28; Hg, 34.36; CH_3O, 5.31. Found: C, 26.73; H, 3.54; Hg, 34.13; CH_3O, 5.39.

Catalytic De-O-acetylation of IV; Preparation of V.—Compound IV (5.4 g., 0.01 mole) partially dissolved in 50 ml. of anhydrous methanol (Baker, analyzed reagent) was treated with a solution of *ca.* 60 mg. of sodium in 50 ml. of the same solvent. The mixture was swirled until all the solid had dissolved and left overnight at room temperature. A first crop of a granular white solid was separated by filtration and a second crop obtained by concentration of the filtrate to about one-third its volume and refrigeration. The combined crops were dissolved in methanolic acetone and the filtered warm solution diluted with a small amount of petroleum ether until cloudy. Within a few minutes, massive crystallization took place and, after cooling, the cottonlike product was collected by suction filtration, washed with petroleum ether and air-dried. Two or more recrystallizations from the same solvent gave a product melting at 169.5–170.5°, $[\alpha]^{25}\mathrm{D}$ +0.5° (0.055 g./ml. H_2O). The yield varied in several experiments from 90 to 100%. Comparison of infrared spectra and a mixed melting point determination showed that this compound is different from II. *Anal.*[27] Calcd. for $C_7H_{13}O_5HgCl$: C, 20.34; H, 3.17; Hg, 48.54; CH_3O, 7.51. Found: C, 20.56; H, 3.30; Hg, 48.53; CH_3O, 7.32.

Compound V was also obtained in a different crystalline modification melting at 167–168°. The two forms have infrared spectra in Nujol which are significantly different, particularly with respect to relative intensities of bands. (The spectrum of the higher melting form is described in the Results section.) The infrared spectra of both forms of V lack the very intense bands at 1419, 1445 and 1591 cm.$^{-1}$ which appear in the spectrum of II and, in general, differ much more from the latter spectrum than from each other.

Reaction of V with Silver Acetate; Preparation of VI.—To a solution of 0.826 g. (0.002 mole) of V in about 50 ml. of methanol was added 0.5 g. of silver acetate (0.003 mole) and the mixture was stirred for about 2 hours at room temp. The reaction mixture was filtered free of inorganic salts and the solvent was removed with a rotating vacuum evaporator. The residue, on recrystallization from ethanol–30-60° petroleum ether, gave 0.85 g. (98% yield) of light white needles melting at 159° dec., $[\alpha]^{25}\mathrm{D}$ +0.25 (0.05 g./ml. H_2O). Comparison of infrared spectra and mixed melting point determination showed that this compound is different from I. *Anal.*[27] Calcd. for $C_9H_{16}O_7Hg$: C, 24.75; H, 3.69; Hg, 45.93; CH_3O, 6.85. Found: C, 24.89; H, 3.86; Hg, 45.73; CH_3O, 7.08.

Brominolysis of IV in CCl_4.—To a solution of 5.4 g. (0.01 mole) of compound IV in 40 ml. of carbon tetrachloride (Merck) was added 1.45 g. (0.009 mole) of bromine (Baker, purified) while the mixture was stirred at about 35–40° under a nitrogen atmosphere. After an induction period of about 10 min., a vigorous reaction took place followed by an abrupt decolorization of the solution and deposition of mercury salts. A small amount of bromine was added until the color persisted and the mixture was filtered. Removal of the solvent on the rotating vacuum evaporator afforded a few crystals mixed with semi-solid material. Fractional crystallization yielded two crystalline isomers.

(a) Isolation of VII.—The semi-solid was dissolved in 15 ml. of boiling absolute ethanol and, after dilution with an equal volume of 30–60° petroleum ether, the clear solution remained overnight at room temp. Shiny needles were collected by suction filtration, washed with a small amount of petroleum ether and air-dried. After two recrystallizations from ethanol–petroleum ether (or acetone–petroleum ether or methanol or boiling water), a product (VII) was obtained which melted at 137–138°, $[\alpha]^{25}\mathrm{D}$ +51° (0.05 g./ml. CCl_4). There was no depression of its melting point on admixture with crystals of the same m.p. prepared by the method of Fischer[2] (*cf.* below). Infrared spectra were identical and showed a characteristic split in the carbonyl absorption band with two peaks at 1750 and 1733 cm.$^{-1}$, respectively. Compound VII did not give a precipitate with aq. $AgNO_3$.

(b) Isolation of VIII.—The mother liquor from the separation of the first isomer, diluted with pertroleum ether and cooled overnight at temperatures below 0°, afforded a product (white needles) melting at 98–110°. After several fractional crystallizations from ethanol–petroleum ether, colorless monoclinic prisms of VIII were obtained which melted at 115–116°. This melting point was not depressed on admixture with crystals of the same m.p. prepared by

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[27] Analysis by Schwarzkopf Microanalytical Laboratory.

the method of Fischer[2] (*cf.* below) and the two preparations had identical infrared spectra with a single carbonyl absorption band at 1733 cm.$^{-1}$. On recrystallization of VIII from boiling water it was transformed quantitatively into VII. Treatment of VIII with $AgNO_3$ in boiling water gave a precipitate of AgBr.

The over-all yield of the reaction was on several occasions almost quantitative, with the first isomer representing 60–85%. The ratio of the two products approached unity when moisture and oxygen were most thoroughly excluded during treatment with bromine. *Anal.*[28] Calcd. for $C_{13}H_{19}O_8Br$: C, 40.74; H, 5.00; Br, 20.85. Found for VII: C, 40.8; H, 5.0; Br, 20.7. For VIII: C, 40.9; H, 5.0; Br, 20.7.

Brominolysis of IV in Polar Solvents.—The above reaction was also carried out in chloroform, methanol and pyridine (all Baker analyzed reagent). In some experiments, III was treated with 2 moles of bromine. In all of these cases only VII was isolated. In order to check the possibility of original formation of relatively unstable VIII followed by isomerization to VII in these media, a sample of VIII was treated with boiling methanol containing a small amount of bromine and mercuric bromide. There was no detectable isomerization.

Preparation of VII and VIII by the Method of Fischer.—To a solution of 5.44 g. (0.02 mole) of D-glucal 3,4,6-triacetate in 20 ml. of CCl_4 (distilled from CaH_2) was added a solution of 4.0 g. (0.025 mole) of bromine in an equal volume of the same solvent. Excess bromine was removed along with the solvent on the rotating vacuum evaporator and the residue, a colorless sirup, was dried for 2 hours in a vacuum desiccator over P_2O_5. The crude dibromide was dissolved in 10 times its weight of anhydrous methanol (dried and distilled from magnesium methoxide) and the flask was immediately fitted with a calcium chloride tube. Freshly prepared silver carbonate (11 g., *ca.* 0.04 mole) was added and the mixture stirred for 1.5 hours at room temp. The reaction mixture was then filtered and the filtrate was concentrated to about one-fifth its original volume on the vacuum evaporator. Dilution with 30–60° petroleum ether to cloudiness, followed by overnight standing at room temperature, afforded a first crop of needles. After two recrystallizations from ethanol-petroleum ether, 1.3 g. (17%) of VII, melting at 137–138°, was obtained.

The mother liquor from the separation of VII was evaporated to dryness and the residue, a colorless sirup, was dissolved in a minimum amount of a mixture of equal volumes of ethanol and petroleum ether. Prolonged cooling at temperatures below 0° caused the separation of a second crop of crystals. After several fractional crystallizations, a constant melting point of 115–116° was obtained. The yield of this isomer, VIII, identical with that formed by brominolysis of IV in CCl_4, was 0.52 g. or 8.8%. Purification of VIII is difficult because very little impurity causes a large depression of the melting point.

Brominolysis of I and II.—To a solution of 4.37 g. (0.01 mole) of D-glucal acetoxymercurimethoxide (I) in 40 ml. of methanol (distilled from magnesium methoxide) was added a solution of 2.9 g. (0.018 mole) of bromine in 10 ml. of the same solvent. The mixture was maintained at a temperature of about 50°, with stirring, until all the bromine had reacted (*ca.* 15–20 min.). A small amount of bromine was added until the color persisted and the reaction mixture was cooled to room temperature. The solvent and excess bromine were removed on the rotating vacuum evaporator and the residue, a white paste, was treated with boiling ethyl acetate until most of the organic material had dissolved. The hot solution was filtered from insoluble matter through a funnel with heated walls and allowed to remain at room temperature. Within a few minutes a voluminous precipitate of long white needles appeared. Two recrystallizations from ethyl acetate afforded pure IX, melting at 180–181°, $[\alpha]^{25}_{D}$ $+0.6°$ (0.05 g./ml. H_2O). Yields varied in several experiments from 1.26 to 1.5 g. (50–60%); no other isomer was isolated even when the reaction was carried out at room temp.

The same product was obtained in 65% yield from a reaction of D-glucal chloromercurimethoxide (II) with one equivalent of bromine. *Anal.* Calcd. for $C_7H_{13}O_5Br$: C, 32.70; H, 5.09; Br, 31.09. Found: C, 33.0; H, 5.2; Br, 30.9.

Brominolysis of V.—The product, V, obtained by catalytic de-O-acetylation of D-glucal 3,4,6-triacetate chloromercurimethoxide was treated with bromine according to the procedure employed for II to yield IX, identical with that prepared from I and II. The yield varied from 90 to 95%.

De-O-acetylation of VII.[2]—A solution of 0.385 g. (*ca.* 0.001 mole) of VII in about 5 ml. of anhydr. methanol (distilled from magnesium methoxide) was cooled to 0° and saturated with dry gaseous ammonia and allowed to stand at room temperature for about 3 hr. The solvent and excess ammonia were removed on the rotating vacuum evaporator. The residue was extracted with and recrystallized from boiling ethyl acetate to yield 0.225 g. (almost 100%) of IX, identical with that prepared by brominolysis of I, II and V as proved by mixed melting point, infrared spectra and rotations.

De-O-acetylation of VIII.[2]—The reaction was carried out as in the preceding experiment. On recrystallization of the crude product from ethyl acetate two different kinds of crystals formed which were separated by further fractional crystallizations. One of the products was found to be identical with IX. The other, X, (monoclinic prisms) was less soluble and melted at 181–182°. The melting point of its mixture with IX (143–158) and infrared spectra established that IX and X are different. Like VIII, compound X is unstable with respect to isomerization and was transformed into IX during the fractional crystallization process. *Anal.*[28] Calcd. for $C_7H_{13}O_5Br$: C, 32.70; H, 5.09; Br, 31.09. Found: C, 32.9; H, 5.0; Br, 30.8.

Deoxymercuration.—Rates were compared in a qualitative manner according to a general procedure described by Traylor.[7] One millimole of each compound dissolved in 10 ml. of ethanol was treated with 0.004 mole of sodium iodide and all the solutions were placed in a water-bath at 60–65° simultaneously. The appearance of mercuric iodide precipitate was taken as evidence of reaction. The data are recorded in Table I.

Methoxymercuration of Dihydropyran.—Mercuric acetate (15.9 g., 0.05 mole) was added to a solution of 4.2 g. (0.05 mole) of 2,3-dihydropyran (du Pont, El Chem 880) in 250 ml. of anhydrous methanol (Baker, analyzed reagent) and the solution kept at room temperature for 1 hr. Filtration from impurities followed by evaporation of the solvent on the rotating evaporator afforded a colorless viscous material. Dissolution in 30 ml. of warm isopropyl alcohol followed by dilution with 60 ml. of 30–60° petroleum ether and storage for 3 hr. in the refrigerator afforded a white crystalline material. The crystals (needles) were collected by suction filtration, washed with a small amount of ice-cold petroleum ether and air-dried. The yield of crude product, assumed to be 2-methoxy-3-acetoxymercuritetrahydropyran, which had a melting point of 83–85°, was 14.0 g. (74%). After three recrystallizations from the same combination of solvents the melting point rose to 85–86° and remained constant. On the basis of deoxymercuration data (*cf.* Table I) this appears to be the *trans* isomer. *Anal.*[27] Calcd. for $C_8H_{14}O_4Hg$: C, 25.63; H, 3.76; Hg, 53.52; CH_3O, 8.28. Found: C, 25.78; H, 3.90; Hg, 53.56; CH_3O, 7.83.

Preparation of 2-Methoxy-3-chloromercuritetrahydropyran.—Twenty ml. of saturated aq. sodium chloride was added either to a reduced volume (*ca.* 50 ml.) of the reaction mixture of the previous experiment or to a solution in about 30 ml. of methanol of the crystalline product of a run. In either case, a crystalline material precipitated almost instantly. After allowing the mixture to remain in the refrigerator for 1 hr., the crystals (needles) were collected by suction filtration, washed with a few small portions of ice-cold water and air-dried. The yield of the crude product, melting at 114–116°, was almost quantitative. The product was recrystallized twice from ethanol–petroleum ether to give big rhombic crystals melting at 117–118°. *Anal.*[27] Calcd. for $C_6H_{11}O_2HgCl$: C, 20.52; H, 3.16; Hg, 57.12; CH_3O, 8.83. Found: C, 20.79; H, 3.29; Hg, 57.37; CH_3O, 8.64.

***trans*-2-Chloromercuricyclohexyl Methoxide**[9].—A solution of 7.9 g. (0.025 mole) of mercuric acetate and 2.1 g. (0.025 mole) of cyclohexene in 75 ml. of absolute methanol (Baker, analyzed) was allowed to stand at room temp. overnight and was then evaporated under vac. to 15 ml. Addition of 20 ml. of 10% aq. NaCl and standing at 0° for 30 min. provided crystals which, after washing with 10 ml. of cold water, drying and recrystallization from 95% ethanol, melted at 116–116.5°.

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[28] Analyses by Dr. Carol K. Fitz, 115 Lexington Ave., Needham Heights 94, Mass.

Presumed Ethyl 2-Acetoxymercuri-2-deoxy-3,4,6-tri-O-acetyl-β-D-glucoside (IIIa).—A filtered solution of 6.4 g. (0.02 mole) of mercuric acetate (Mallinckrodt, anal. reag.) in 100 ml. of anhydr. ethanol was added to a solution of 5.45 g. (0.02 mole) of D-glucal 3,4,6-triacetate in the same solvent. Formation of white needles was observed within 5 min. at room temp., after which the reaction mixture was refrigerated for 2 hr. A first crop (4 g.) was collected, washed with cold isopropyl alcohol and then 30–60° petroleum ether. A second crop (1.2 g.) was obtained by concentrating combined filtrate and washings to 50 ml., adding 30 ml. of 30–60° petroleum ether and refrigerating for 1 hr. Three recrystallizations of the combined crops from isopropyl alcohol provided 4.5 g. (39%) of white crystals melting at 172–173.5°. The infrared spectrum of this compound is very similar to that of III. *Anal.*[28] Calcd. for $C_{16}H_{24}O_{10}Hg$: C, 33.30; H, 4.19; Hg, 34.77; EtO, 7.81. Found: C, 33.43; H, 4.41; Hg, 34.65; EtO, 7.70.

Presumed Ethyl 2-Chloromercuri-2-deoxy-3,4,6-tri-O-acetyl-β-D-glucoside (IVa).—A solution of 2.9 g. (0.005 mole) of IIIa in 50 ml. of 95% ethanol was treated with 5 ml. of satd. aq. NaCl. After 2 hr. at rm. temp. and overnight refrigeration, 1.25 g. of white crystals melting at 138–144° was collected. Evaporation to dryness of the filtrate, extraction of the resulting residue with $CHCl_3$, evaporation to dryness of the extract and recrystallization from isopropyl alcohol–30–60° petroleum ether of the remaining solid provided 1.15 g. of crystals melting at 139–145°. The combined crops were recrystallized three times from isopropyl alcohol–petroleum ether to yield 2.0 g. of long, fine, white needles melting at 146–147° and with an infrared spectrum very similar to that of IV. *Anal.*[27] Calcd. for $C_{14}H_{31}O_8$: HgCl: C, 30.38; H, 3.82; Hg, 36.25; EtO, 8.14. Found: C, 30.57; H, 4.02, Hg, 36.40; EtO, 8.21.

Presumed Isopropyl 2-Acetoxymercuri-2-deoxy-3,4,6-tri-O-acetyl-β-D-glucoside IIIb.—The procedure was the same as for the preparation of IIIa except that isopropyl alcohol (Baker, anal. reag.) was used in place of ethanol. Two recrystallizations from isopropyl alcohol–30–60° petroleum ether provided a 40% yield of white needles melting at 190–191°. The infrared spectrum of IIIb is similar to those of III and IIIa. *Anal.*[27] Calcd. for $C_{17}H_{26}O_{10}Hg$: C, 34.55; H, 4.43; Hg, 33.94. Found: C, 34.70; H, 4.63; Hg, 33.76.

Infrared spectra were obtained on Nujol mulls with a model 21C Perkin–Elmer spectrophotometer.

Melting points were determined in a Thomas-Hoover apparatus and are not corrected.

[CONTRIBUTION NO. 658 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO., WILMINGTON 98, DEL.]

Cyanocarbon Chemistry. XIX.[1,2] Tetracyanocyclobutanes from Tetracyanoethylene and Electron-rich Alkenes

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RECEIVED NOVEMBER 13, 1961

1,1,2,2-Tetracyanocyclobutanes are formed in high yield under very mild reaction conditions by the cycloaddition of tetracyanoethylene to electron-rich alkenes such as methyl vinyl ether and *p*-methoxystyrene. 1,1,2-Tricyanocyclobutanes are formed similarly from tricyanoethylene.

The thermal addition of allenes, fluoroalkenes and ketenes to alkenes to give cyclobutanes has been extensively investigated in the last few years and is now one of the most important routes to cyclobutanes, some of which are useful as precursors of alicyclic compounds.[3,4] Tetracyanoethylene, a reactive dienophile in the Diels–Alder reaction,[5] has been observed to form cyclobutane derivatives with a few 1,3-diene systems to which Diels–Alder addition is difficult or impossible.[6]

It has now been found that tetracyanoethylene readily forms 1,1,2,2-tetracyanocyclobutanes (I) with a variety of electron-rich alkenes.[7] Tricyanoethylene behaves similarly. As will be described in a subsequent paper, these polycyanocyclobutanes are good sources of 1,1,2-tricyanobutadienes and other acyclic products *via* ring-opening reactions.

I

X = RO–, RS–, R(R′CO)N–, $C_6H_5SO_2N(\mathbf{R})$–, *p*-ROC_6H_4–

In striking contrast to cycloaddition reactions of allenes, fluoroalkenes and ketenes, which require several hours of heating at 100–225°, the cycloaddition reactions of tetracyanoethylene generally occur rapidly and in high yield at 0–30°. The reactions are easy to follow because tetracyanoethylene forms highly colored π-complexes with alkenes[8]; when the color fades, the cycloaddition reaction is over. Thus, addition of methyl vinyl ether to a tetrahydrofuran solution of tetracyanoethylene at room temperature caused the solution to become deep orange; heat was evolved, the orange color faded to pale green in the course of half an hour, and 1,1,2,2-tetracyano-3-methoxycyclobutane was isolated as a colorless solid in 90% yield.

Vinyl ethers, vinyl sulfides, N-vinylamides and N-vinylsulfonamides all form tetracyanocyclobutanes with tetracyanoethylene as illustrated in Table I. The vinyl group can be substituted; thus, dihydropyran gives a bicyclic adduct (II), as does the 1,2-dialkoxyethylene 2,2-dimethyldioxole, and 4-methylenedioxolane forms a spiro

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(1) Paper XVIII, J. R. Roland and B. C. McKusick, *J. Am. Chem. Soc.*, **83**, 1652 (1961).

(2) Presented at the St. Louis Meeting of the American Chemical Society, March, 1961.

(3) J. D. Roberts and C. M. Sharts, "Cyclobutane Derivatives from Thermal Cycloaddition Reactions" in "Organic Reactions," John Wiley and Sons, Inc., in press.

(4) Recently, the thermal reaction of isobutenylamines with electrophilic olefins such as methyl acrylate and diethyl maleate has been reported to give cyclobutanes; K. C. Brannock, A. Bell, R. D. Burpitt and C. A. Kelly, *J. Org. Chem.*, **26**, 625 (1961).

(5) W. J. Middleton, R. E. Heckert, E. L. Little and C. G. Krespan, *J. Am. Chem. Soc.*, **80**, 2783 (1958).

(6) A. T. Blomquist and Y. C. Meinwald, *ibid.*, **81**, 667 (1959); J. K. Williams, *ibid.*, **81**, 4013 (1959); D. S. Matteson, J. J. Drysdale and W. H. Sharkey, *ibid.*, **82**, 2853 (1960); K. Hafner and J. Schneider, *Ann.*, **624**, 37 (1959).

(7) We are greatly indebted to Prof. Saul Winstein of the University of California at Los Angeles for first suggesting this reaction.

(8) R. E. Merrifield and W. D. Phillips, *J. Am. Chem. Soc.*, **80**, 2778 (1958).