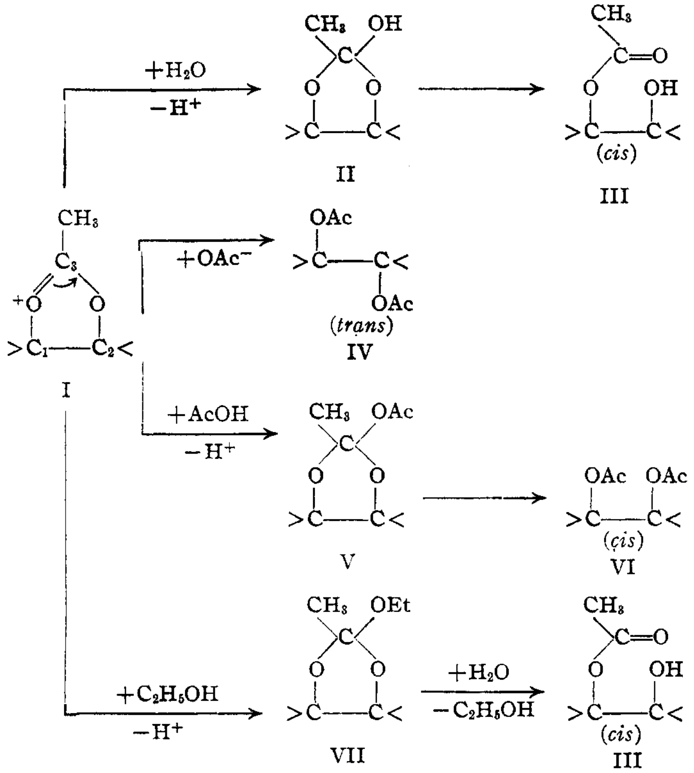
[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

The Role of Neighboring Groups in Replacement Reactions. VI. Cyclohexene Ethyl Orthoacetate

BY S. WINSTEIN AND R. E. BUCKLES

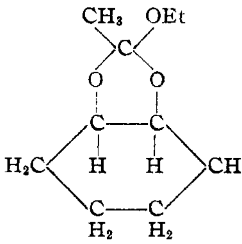
The reaction with silver acetate[1,2] of some acetoxybromides derived from 2-butene and cyclohexene and the solvolysis of *trans*-2-acetoxycyclohexyl *p*-toluenesulfonate[3] are best understood on the basis of participation of the neighboring acetoxy group in the replacement processes.

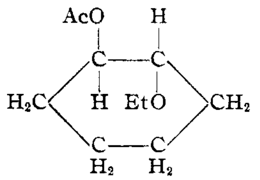


An ion of the type I is then an intermediate. It seems necessary to suppose that I reacts as follows: with water[2,3] in acetic acid rapidly at carbon atom C-3 to give orthomonoacetate II which isomerizes to ordinary monoacetate III; with acetate ion[1,3] in acetic acid, in the absence of water, at carbon atoms C-1 and C-2 to give diacetate IV; with acetic acid,[3] in the absence of water or acetate ion, at carbon atom C-3 to give orthodiacetate V which isomerizes to ordinary diacetate VI; with ethyl alcohol[3] at carbon atom C-3 to give an orthoester VII which, on access of water, hydrolyzes to monoacetate III. The *cis*–*trans*-designations beneath the formulas III, IV and VI refer to the configurations of the cyclohexene derivatives.

The products actually isolated in the previous[1,2,3] work were III IV and VI. Of the unisolated products (II, V and VII) VII is the type substance most easily obtained. In seeking additional support for the previous interpretations we have prepared an orthoester of the type VII. Also we have isolated it from an actual reaction mixture from solvolysis of *trans*-2-acetoxycyclohexyl *p*-toluenesulfonate, and have studied some reactions of the orthoester.

Ethyl *cis*-cyclohexene orthoacetate VIII (VII) is readily prepared by the treatment of *cis*-1,2-cyclohexanediol with an equivalent amount of ethyl orthoacetate in the presence of an acid catalyst.[4] The product has the correct composition and equivalent weight and hydrolyzes to *cis*-glycol (Table I). The molecular refraction of the product shows a depression (0.37) of the order of magnitude to be expected.[5] The orthoester VIII is insoluble in water and alkali and instantly soluble in dilute acid. This is in contrast to the behavior of the isomeric *trans*-1-ethoxy-2-acetoxycyclohexane IX which we prepared for comparison purposes (Table I). Although VIII can theoretically exist in two inactive forms having geometrical isomerism in the five-membered


VIII


IX

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[1] Winstein and Buckles, THIS JOURNAL, **64**, 2780 (1942).

[2] Winstein and Buckles, *ibid.*, **64**, 2787 (1942).

[3] Winstein, Hess and Buckles, *ibid.*, **64**, 2796 (1942).

[4] Mkhitaryan [*J. Gen. Chem.* (U. S. S. R.), **10**, 667 (1940)] has prepared the analogous ethylene glycol derivative [*C. A.*, **34**, 7859 (1940)].

[5] Meerwein and Sönke, *J. prakt. Chem.*, **137**, 295 (1933).

ring, we have not obtained any evidence on this point in the present work.

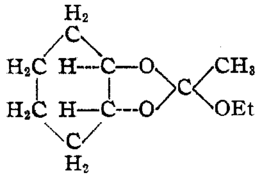
TABLE I

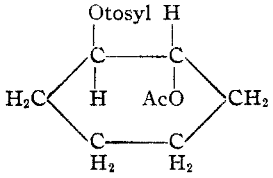
PROPERTIES OF CYCLOHEXENE ETHYL ORTHOACETATE AND *trans*-2-ETHOXYCYCLOHEXYL ACETATE

Isomer	Orthoester *cis* Synthetic	Orthoester *cis* Isolated	Orthoester *trans*	Ether
B. p. (10 mm.), °C.	92–93	91–93	95–96	91–92
n^{25}_D	1.4489	1.4486 1.4479	1.4498	1.4403
d^{25}_4	1.0273	....	1.0244	0.9883
MR_D[a]	48.58	....	48.84	49.65
Equiv. wt.[b]	188	188	190	183
%C[c,d]	64.28	....	64.47	64.32
%H[e]	9.73	....	9.80	9.81
M. p. of glycol[f] from orthoester, °C.	97.5	98	104	....

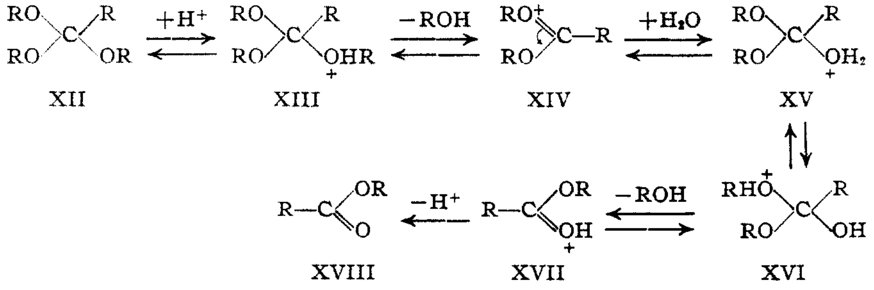
[a] Calculated value: orthoester, 48.95; ether, 49.48. [b] Theoretical value, 186. [c] Calculated value, 64.49. [d] Analyses by Mr. Raymond Clinton. [e] Calculated value, 9.74. [f] M. p. of *cis*-1,2-cyclohexanediol, 98°; *trans*-isomer, 104°.

It is interesting that ethyl *trans*-cyclohexene orthoacetate X may be prepared from *trans*-1,2-cyclohexanediol by the same procedure used for the *cis*-isomer VIII. Again, all the properties of the compound are correct for an orthoester of the *trans*-glycol (Table I).


X


XI

The change in the miscibility temperature[6] of solutions of VIII and water in alcohol toward a paraffin oil gives a qualitative estimate of the rate of hydrolysis of VIII. Ethyl *cis*-cyclohexene orthoacetate VIII hydrolyzes at room temperature in alcohol too slowly to measure in the presence of sodium ethoxide, too fast to measure on addition of *p*-toluenesulfonic acid, and with a half-life of about twenty-five minutes on addition of a little acetic acid. Heating VIII in absolute alcohol at the boiling point for forty hours in the presence of acetic acid causes no consumption of acetic acid as shown by titration. Also, VIII can be recovered after this treatment, if one is careful to exclude water during the experiment.



The orthoester VIII is easily isolated from the solvolysis of *trans*-2-acetoxycyclohexyl *p*-toluenesulfonate XI in absolute alcohol in the presence of potassium acetate.[3] When precautions are taken to dry the alcohol very carefully, to neutralize the generated acetic acid with sodium ethylate in absolute alcohol, and to use dry ether when ether is used during the isolation for decreasing the solubility of salts, the yield of VIII is 51%. When VIII is treated with water in alcohol in the presence of an acid catalyst, there is formed a mixture of 95.5 mole % *cis*-glycol monoacetate III and 4.5 mole % of *cis*-glycol. This experiment together with the isolation of VIII from the solvolysis of XI in absolute alcohol completes the proof for the previously[3] postulated sequence XI → VIII → III. Previously,[3] VIII was allowed to hydrolyze and the small amount of glycol was lost in a large aqueous phase. Thus quite pure III was isolated as the product.

The treatment of an orthoester of the type VII with acid seemed to offer an independent route to the ion I and thus further opportunity to test the previous[1,2,3] formulation of the reactions of I. The most likely mechanism for the hydrogen ion-catalyzed[7] hydrolysis of an orthoester XII appears to us to involve the sequence XII → XIII → XIV → XV → XVI → XVII → XVIII. Some other acid catalyzed reactions of orthoesters (such as exchange of R′O for RO) presumably also proceed by way of XIV as an intermediate. On the basis of the above scheme, an acid-catalyzed reaction of a glycol orthoester of the type VII may proceed by way of either one of the two ions I and XIX. The results

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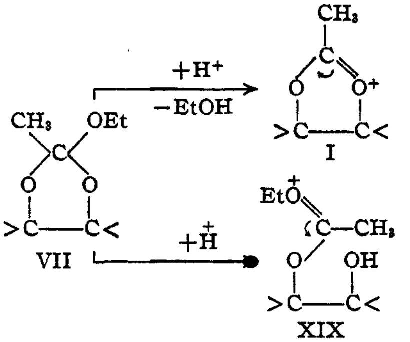
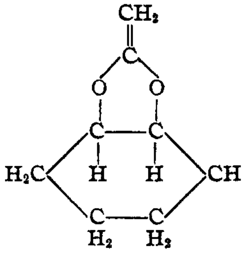
(6) Robertson, "Laboratory Practice of Organic Chemistry," The Macmillan Co., New York, N. Y., 1937, p. 161.

(7) Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, pp. 218–221, 305.

obtained on hydrolysis of the orthoester VIII in alcohol suggest that most but not all of an acid-catalyzed reaction of VIII occurs with the initial removal of the ethoxyl group to yield intermediate I. Thus I is favored over XIX, probably due, in part at least, to the fact that I has a larger resonance energy because of the equivalence of the two resonance forms indicated by the curved arrow. A better independent source for the ion I will be the ketone acetal[8] XX. In the meantime a few conversions of the orthoester VIII have been carried out and, except for one complication, the results were those expected.





XX

The orthoester VIII, dissolved in acetic acid containing a small amount of water, yielded in a short time at room temperature a product which was 92 mole % monoacetate and 8 mole % *cis*-glycol. Presumably most of the reaction is by way of I which reacts with water[2,3] to yield orthomonoacetate II. This then reverts to III.

Heating VIII in a solution of *p*-toluenesulfonic acid and acetic anhydride in acetic acid yields a product which is saponified to *cis*-glycol. This conversion presumably occurs[3] by way of I → V → VI.

One conversion of the orthoester VIII which would be expected to give a change in configuration of the cyclohexane nucleus is the one involving the reaction of I with acetate ion. The attempt to demonstrate the reaction of acetate ion with I derived from VIII (instead of XI) in acetic acid brought to light an interesting and not yet fully investigated reaction between VIII and the acetic anhydride which was added to remove ethyl alcohol as ethyl acetate. The treatment of VIII with an acetic acid solution of acetic anhydride and potassium acetate gave rise to a crude product which yielded quite pure *trans*-glycol on saponification. However, when VIII was heated with acetic anhydride alone in acetic acid the crude unpurified product also yielded mostly *trans*-glycol on saponification. This is in contrast to the results in the presence of *p*-toluenesulfonic acid. Apparently, in the absence of a strong acid catalyst, the reaction by way of I is slower than a direct reaction between VIII and acetic anhydride. Although the addition of acetate ion improved the yield and quality of the *trans*-glycol product this improvement is not necessarily due to reaction of I with acetate ion to give IV. It may be due to the fact that the acetate ion decreases the acidity of the medium so much that the reaction by way of I becomes less important than before.

The direct reaction of acetic anhydride with VIII was studied by heating VIII in pure acetic anhydride. There was obtained a 43% yield of quite pure *trans*-diacetate IV and considerable residue which we could not distil. This residue on saponification yielded *trans*-glycol. The reaction of VIII with acetic anhydride to yield *trans*-diacetate IV involves a Walden inversion and it is interesting in view of Post and Erickson's work[9] on the reaction of orthoesters with acetic anhydride. From ethyl orthoformate these investigators were able to obtain a product of the type V. In this case it is not obvious whether the ethoxyl group is replaced by the acetoxy group by a Walden inversion mechanism or not.

To more nearly duplicate the conditions of Post and Erickson, VIII was left with acetic anhydride six days at room temperature. After this time distillation yielded 47% of unreacted orthoester, a trace of high boiling material and some undistillable residue. The residue yielded predominantly *cis*-glycol on saponification and the intermediate fraction similarly gave rise to *cis*-glycol.

If VIII were to react analogously to ethyl orthoformate,[9] the products would be V, XXI and XXII, depending on the alkoxyl group replaced

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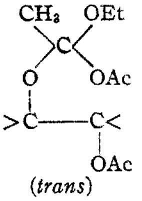
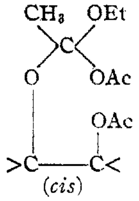
(8) Beyerstedt and McElvain, THIS JOURNAL, **58**, 529 (1936).

(9) Post and Erickson, *J. Org. Chem.*, **2**, 260 (1937).

and whether inversion or retention of configuration of the alkoxyl group obtains. It seems possible that XXI and XXII are present in the



(*trans*)
XXI



(*cis*)
XXII

high-boiling materials obtained under the different conditions.

The failure to demonstrate the reaction of acetate ion with I derived from VIII prompted us to attempt an analogous reaction making use of an ion other than acetate ion. Since the failure was due to the inability to have both acetate ion and strong acid in acetic acid solution, we chose chloride ion to replace acetate ion. Hydrochloric acid was used for the strong acid. When VIII was treated at room temperature with an acetic acid solution of acetic anhydride, lithium chloride and hydrogen chloride, there was isolated a nearly quantitative yield of a mixture of *trans*-1-acetoxy-2-chlorocyclohexane (68 mole %) and *cis*-1,2-diacetoxycyclohexane VI (32 mole %). The acetoxychlorocyclohexane must arise from I by reaction with chloride ion in the way it is thought to react with acetate ion[1,3] to give IV. The indications[3] are that the reaction of an ion such as I with acetate ion and presumably also chloride ion is S_N2 in nature. One would then expect any reaction of XIX with chloride ion to give almost exclusively ethyl chloride and *cis*-glycol monoacetate. The latter would then be converted to diacetate.

Experimental

***trans*-2-Acetoxycyclohexyl *p*-Toluenesulfonate.**—This substance was prepared as before.[3,10] Recrystallization from aqueous methanol instead of ligroin yielded an especially pure product, m. p. 80.5°.

***trans*-2-Ethoxycyclohexanol.**—A mixture of 9.8 g. (0.1 mole) cyclohexene oxide,[11] 50 ml. 99.95% ethyl alcohol, and 5 drops of concd. sulfuric acid was held under reflux four hours. After neutralization of the catalyst with calcium carbonate, distillation through a Weston-type[12] column yielded 11.5 g. (80%) of product, b. p. 86.0–86.5° (15 mm.), $n^{25}\text{D}$ 1.4537.

***trans*-1-Acetoxy-2-ethoxycyclohexane.**—17.0 g. of *trans*-2-ethoxycyclohexanol was acetylated with acetic anhydride in the presence of sulfuric acid in the usual manner.[1] The yield of product was 20.0 g. (91%).

On subjection to the procedure normally employed to hydrolyze glycol mono- or diacetates or orthoesters and to recover the resulting glycol by sublimation, the acetate–ether yields no glycol.

***cis*- and *trans*-1-Acetoxy-2-chlorocyclohexane.**—The acetates of *cis*- and *trans*-cyclohexene chlorohydrin[13] were available in connection with other work.[14]

***cis*- and *trans*-Cyclohexene Ethyl Orthoacetates.**—Equimolar quantities of the proper 1,2-cyclohexanediol[1,2,11] and ethyl orthoacetate were mixed and a few crystals of *p*-toluenesulfonic acid were added. The mixture was heated and ethyl alcohol was removed by fractionation until the theoretical amount was obtained. The residual reaction mixture was subjected to fractionation after neutralization of the catalyst with calcium carbonate. The product (65–70%) distilled at 10 mm. over a 2–3° range near 94°. Some purification of the product was effected by further treatment with a little ethyl orthoacetate and acid to remove any glycol and subsequent distillation through the Weston-type column.

The orthoesters did not dissolve noticeably in water or aqueous alkali but almost instantly in dilute aqueous acid. The ethoxycyclohexyl acetate did not dissolve noticeably in any of the three media.

For hydrolysis to the glycols, small samples of the orthoesters were treated with a solution of 1 drop of 6 *N* hydrochloric acid and several drops of water in alcohol. The mixtures became slightly warm. After they had cooled sodium hydroxide was added and saponification was carried out as usual. The glycols in 90–95% yield were isolated by sublimation (Table I).

The equivalent weights of the orthoesters were determined by treatment first with acid and then with potassium hydroxide in diethylene glycol.[15] Without the preliminary treatment with acid, the orthoesters consumed only a small amount of potassium hydroxide. The orthoester sample was weighed into 5 ml. of diethylene glycol. A drop of standard 0.5 *N* acid and 4 drops of water were added. After several minutes, potassium hydroxide was added and the analysis was continued in the usual manner.[15] In the blank analyses, a drop of acid was also included.

Approximate Rate of Hydrolysis of *cis*-Orthoester in Alcohol.—Enough water was added to 99.95% alcohol to make the miscibility temperature toward a certain paraffin oil[6] 35°. 1.5-ml. samples were used for determination of miscibility temperatures. The *cis*-orthoester (0.56 g.) was added to 10 ml. of the alcohol. The resulting solution displayed a miscibility temperature toward the paraffin oil of approximately 26°, varying slightly with the nature of the trace of catalyst or inhibitor added. With the proper catalyst, the miscibility temperature of the solution left at room temperature dropped approximately 3.0°, the rate of drop varying with the catalyst. There was no measurable reaction in the presence of sodium ethoxide (0.05 ml. of 0.2 *N* absolute alcoholic sodium ethoxide in 10 ml. solution). With *ca.* 0.02 ml. of glacial acetic acid in 10 ml. of

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[10] Criegee and Stanger, *Ber.*, **69B**, 2753 (1936).

[11] Winstein, This Journal, **64**, 2792 (1942).

[12] Weston, *Ind. Eng. Chem., Anal. Ed.*, **5**, 179 (1933).

[13] Bartlett, This Journal, **57**, 224 (1935).

[14] Winstein and Buckles, unpublished work.

[15] Redemann and Lucas, *Ind. Eng. Chem., Anal. Ed.*, **9**, 521 (1937).

solution, the reaction was half over in twenty-five minutes. The addition of a very small crystal of *p*-toluenesulfonic acid to the aqueous-alcoholic solution of the orthoester brought about complete reaction in less than two minutes. The glassware used for these reactions was washed with ammonia solution, rinsed and dried. Otherwise, reaction was often found to occur rapidly in the absence of any added catalyst. This was ascribed to adsorbed strong acid.

Absence of Reaction of *cis*-Orthoester with Acetic Acid in Alcohol.—25 ml. of a solution was prepared by dissolving 0.45 g. (0.008 mole) of glacial acetic acid and 2.0 g. (0.020 mole) of potassium acetate in 99.95% alcohol. To 10 ml. of this solution was added 0.56 g. (0.003 mole) of *cis*-orthoester. One-ml. samples were sealed in tubes and kept in refluxing alcohol. Titration of the contents of the opened tubes with 0.02 *N* base showed no appreciable change in the titration value in forty hours. The same result was obtained when no potassium acetate was added.

Recovery of *cis*-Orthoester from Alcohol.—A mixture of 12.2 g. (0.066 mole) of the orthoester, 20 g. (0.20 mole) potassium acetate, 4.0 g. (0.067 mole) acetic acid and 222 ml. 99.95% ethyl alcohol was heated under reflux thirty-six hours. When the mixture was treated as in the isolation experiments (calcium carbonate was used—see below), 4.0 g. (33%) of the orthoester, b. p. 94–96° (10 mm.), $n^{25}\text{D}$ 1.4498, was recovered. Considerable residue remained in the boiler from the distillation. The residue was partly crystalline, the crystals proving to be *cis*-glycol, m. p. 96–97.5°.

Isolation of *cis*-Orthoester from the Solvolysis of *trans*-2-Acetoxycyclohexyl *p*-Toluenesulfonate.—200 ml. of absolute alcohol was distilled from a mixture of ordinary absolute alcohol, diethyl phthalate, and sodium ethylate into a flask containing 12 g. (0.12 mole) potassium acetate. The flask and potassium acetate were previously stored over phosphorus pentoxide for three days. To the alcohol solution was added 31.2 g. (0.1 mole) acetate–tosylate and the mixture was heated under reflux forty hours with protection against access of moisture.

The reaction mixture was concentrated to a volume of approximately 75 ml. by fractionation of alcohol. 50.8 ml. of 1.98 *N* solution of sodium ethylate in absolute alcohol (dried with sodium ethylate and ethyl phthalate) was added; 200 ml. of absolute ether was also added. The mixture was cooled and filtered. The filtrate was concentrated and 200 ml. of ether again added. Filtration was again resorted to. The filtrate yielded on concentration and fractionation through an eight-inch Vigreux column 9.5 g. (51%) of the *cis*-orthoester (Table I).

The residue from the distillation was saponified by the orthoester procedure, 0.8 g. of quite pure *cis*-glycol, m. p. 95–96.5°, being obtained.

When the isolation of orthoester was carried out as above, except for the use of 99.95% alcohol throughout and the use of calcium carbonate instead of sodium ethylate, poorer results were obtained; 3.0 g. (16%) of orthoester resulted. A small amount of *cis*-glycol was obtained as a higher boiling fraction. The boiler residue yielded *cis*-glycol on saponification.

Reaction of *cis*-Orthoester with Water in Alcohol.—9.0 g. (0.048 mole) of orthoester and 1.5 ml. (0.083 mole) water were mixed with 50 ml. of 99.7% alcohol. The solution became warm to the touch on the addition of a small crystal of *p*-toluenesulfonic acid. After one and one-half hours, the solution was neutralized with calcium carbonate. Distillation through the Vigreux column yielded besides alcohol, b. p. 39° (120 mm.), 6.7 g. (89%) of ester product, b. p. 115.0–115.5° (12 mm.), $n^{25}\text{D}$ 1.4663, equiv. wt.[15] 163.5. The hold-up in the column was 0.6 g. The total yield must have been at least 97%.

Reaction of *cis*-Orthoester with Water in Acetic Acid.—9.0 g. of orthoester and 1.5 ml. of water were dissolved in 50 ml. of acetic acid (m. p. 16.45°). The solution became warm. After several hours, the solvent was removed, b. p. 41° (40 mm.), and the product, 6.4 g. (86%), b. p. 115.0–115.5° (12 mm.) $n^{25}\text{D}$ 1.4670, equiv. wt.[15] 168, was obtained by distillation at reduced pressure through the Vigreux column. The hold-up was 0.7 g. so the total yield must have been at least 95%.

Conversions of *cis*-Orthoester without Isolation of Ester Products.—A solution of the proper reagent in 5 ml. of glacial acetic acid, which contained acetic anhydride more than equivalent to both the water present and the orthoester to be added later, was heated for two hours to destroy water. 0.005 mole of *cis*-orthoester was added and the solution was heated under reflux for an hour. The reaction mixture was diluted with water and extracted with ether. The ether extract was concentrated and alcohol was added. Alkaline hydrolysis and sublimation formed the glycol in approximately 60% yield.

When 0.40 g. *p*-toluenesulfonic acid was used, the crude glycol, mostly *cis*, melted at 85°. When 0.5 g. potassium acetate was used, the crude glycol, *trans*, melted at 101°. In the absence of potassium acetate, the crude glycol, predominantly *trans*, melted at 90°. The melting points of the glycols obtained from crude reaction products without isolation of pure ester mixtures do not indicate very exactly the compositions of the glycols. On recrystallization the glycols were recovered in good yield in nearly pure form.

Treatment of *cis*-Orthoester with Acetic Anhydride at 130°.—9.0 g. of orthoester was heated with 10 ml. 99–100% acetic anhydride at 130° for three hours. Fractionation through the Vigreux column yielded 4.1 g. (43%) of diacetate, b. p. 119–121° (12 mm.), $n^{25}\text{D}$ 1.4478 and 4.7 g. of a viscous residue. Saponification of the diacetate by the method[1] involving extraction with chloroform yielded impure *trans*-glycol; recryst., m. p. 92–97°, mixed m. p. with *cis*-glycol, 78–83°. 1.9 g. of the residue was saponified, 0.55 g. of *trans*-glycol, m. p. 98–100°, being obtained by sublimation.

Treatment of *cis*-Orthoester with Acetic Anhydride at Room Temperature.—9.3 g. of orthoester and 10 ml. of acetic anhydride were kept at room temperature for six days. Distillation through the Vigreux column yielded 4.4 g. (47%) of unreacted orthoester, b. p. 98.5–99.0° (12 mm.), $n^{25}\text{D}$ 1.4485. A viscous residue yielded with difficulty 0.3 g. of an intermediate fraction and 0.47 g. of material, b. p. 130° or higher at 12 mm. This last material yielded on saponification 0.07 g. of recrystallized *cis*-glycol, m. p. 94–95°. 1.9 g. of the residue gave rise to 0.68 g. impure *cis*-glycol, m. p. 85–88°; recryst., 0.50 g., m. p. 92–94°.

Treatment of *cis*-Orthoester with Hydrogen Chloride in Acetic Acid.—Dry hydrogen chloride was absorbed in a solution of 4.3 g. (0.1 mole) lithium chloride and 15.0 ml. of 90–95% acetic anhydride in 100 ml. of acetic acid (m. p. 16.2°) until the gain in weight was 21 g. (0.58 mole). The solution was left for twelve hours and then 16.0 g. (0.086 mole) of orthoester was added. The container was sealed and the mixture was allowed to remain at room temperature for fourteen days. After neutralization of the reaction mixture with bicarbonate and extraction of the reaction products with ether, the ether extract was dried over potassium carbonate. Distillation through the Weston-type column yielded 7.0 g. of nearly pure 1-acetoxy-2-chlorocyclohexane, b. p. 98.5–100.5° (12 mm.), and 3.0 g. of nearly pure 1,2-diacetoxycyclohexane, b. p. 118–120° (12 mm.). An intermediate fraction of 3.5 g., b. p. 100.5–118° (12 mm.), $n^{25}\text{D}$ 1.4592, was obtained. Counting the hold-up the total yield was 92% approximately; *trans*-acetoxy chloride, 63%; *cis*-diacetate, 29%.

Treatment of some of the acetoxy chloride fraction with aqueous-alcoholic sodium hydroxide and sublimation of the resulting glycol gave rise to a 36% yield of *trans*-glycol, m. p. 98–100°. This is essentially the same result obtained with authentic *trans*-1-acetoxy-2-chlorocyclohexane. Analogous treatment of *cis*-1-acetoxy-2-chlorocyclohexane yields no glycol.

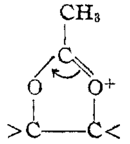
Saponification of the diacetate fraction yielded predominantly *cis*-glycol, m. p. 85–91°; recryst., m. p. 93–95°.

A control experiment showed that, under the conditions used in treating the orthoester with the hydrogen chloride–acetic acid solution, *cis*-diacetate is less than 5% converted to acetoxy chloride.

Summary

The *cis*- and *trans*-cyclohexene ethyl orthoacetates have been prepared and the behavior of the *cis*-isomer toward various conditions has been noted.

The *cis*-orthoester has been isolated in good yield from the solvolysis of *trans*-2-acetoxycyclohexyl *p*-toluenesulfonate in extremely dry alcohol. It yields almost pure *cis*-2-acetoxycyclohexanol on short treatment with water in alcohol. These experiments afford proof of the previously postulated occurrence of the orthoester as an intermediate in the conversion of the acetoxycyclohexyl tosylate to monoacetate. Also, they afford support for the idea that the ion I is an intermediate in such solvolyses.



I

It is believed that certain acid-catalyzed reactions of the *cis*-orthoester proceed largely by way of the ion I. The nature and configuration of the products of several reactions of the *cis*-orthoester in acetic acid as a solvent are those expected on this basis. Water gives rise to nearly pure *cis*-2-acetoxycyclohexanol; *p*-toluenesulfonic acid and acetic anhydride to *cis*-1,2-diacetoxycyclohexane; hydrogen chloride, lithium chloride and acetic anhydride to a mixture of *cis*-1,2-diacetoxycyclohexane and *trans*-1-acetoxy-2-chlorocyclohexane.

A surprising reaction of the *cis*-orthoester takes place with acetic anhydride at 130° to produce *trans*-1,2-diacetoxycyclohexane and a very high-boiling derivative of *trans*-1,2-cyclohexanediol. At room temperature a very high boiling derivative of *cis*-1,2-cyclohexanediol is produced.

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[CONTRIBUTION FROM THE IOWA AGRICULTURAL EXPERIMENT STATION]

Solution Viscosities of the Amylose Components of Starch[1]

BY JOSEPH F. FOSTER AND R. M. HIXON

The development of a potentiometric iodine titration procedure has demonstrated the presence of an unbranched component in starch which differs markedly in character and in quality in the starches from various sources.[2] This component will be called "amylose" in conformity with the nomenclature suggested by Meyer.[3] The titration method indicates that the amylose components from various starches form the iodine complex at characteristic iodine activities which are postulated to be a function of the molecular

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[2] Bates, French and Rundle, THIS JOURNAL, **65**, 142 (1943).

[3] Excellent summaries of the present information regarding the heterogeneity of starch are given by K. H. Meyer in the following texts: "Natural and Synthetic High Polymers," Interscience Publishers, Inc., New York, N. Y., 1942, pp. 391–403; "Advances in Colloid Science," Interscience Publishers, Inc., New York, N. Y., 1942, pp. 143–165.