[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA, LOS ANGELES]

The Role of Neighboring Groups in Replacement Reactions. XXIV.[1] The Acetoxy Group. Preparation and Reactions of the Ketene Acetal of *cis*-1,2-Cyclohexanediol (2-Methylene-*cis*-4,5-tetramethylenedioxolane)[2,3]

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As previously anticipated, the ketene acetal of *cis*-1,2-cyclohexanediol (2-methylene-*cis*-4,5-tetramethylenedioxolane) is a source of the *cis*-cyclohexeneacetoxonium ion. Therefore, knowledge about the behavior of this ketene acetal in solvolytic media contributes to the understanding of the mechanisms of transformations involving neighboring acetoxy group participation. In ethanol the ketene acetal is transformed smoothly to *cis*-cyclohexene ethyl orthoacetate, while in moist acetic acid the product is the monoacetate of *cis*-1,2-cyclohexanediol. In hot anhydrous acetic acid the ketene acetal is converted to *trans*-1,2-diacetoxycyclohexane. This is true whether the acetic acid is rendered anhydrous by drying with triacetyl borate, or whether it contains excess acetic anhydride. Also, the stereochemical outcome is the same whether or not the acetic acid solvent contains potassium acetate. In anhydrous acetic acid containing toluenesulfonic acid the ketene acetal is converted partly to *cis*-1,2-diacetoxycyclohexane and partly to *trans*-2-acetoxycyclohexyl *p*-toluenesulfonate. The latter substance has been isolated in *ca.* 70% yield. It seems likely that the reactions of the ketene acetal in acetic acid solvent commence with proton addition. The cyclohexene acetoxonium ion intermediate is presumed to react with nucleophilic agents uniformly more rapidly at C-3 than at C-1 or C-2. Thus, an orthodiacetate is the product of kinetic control of the reaction of the acetoxonium ion intermediate in neutral or basic anhydrous acetic acid solution. Under these conditions the orthodiacetate is converted to *trans*-1,2-diacetoxycyclohexane by ionization and eventual attack of acetate ion on C-1 or C-2. An acid-catalyzed path from orthodiacetate to *cis*-1,2-diacetoxycyclohexane is available, and possible mechanisms involving glycol oxygen ionization are suggested. The orthodiacetate reacts with toluenesulfonic acid to give *trans*-2-acetoxycyclohexyl *p*-toluenesulfonate, this product arising from attack of toluenesulfonate ion on C-1 or C-2 of the cyclohexene acetoxonium ion. The formation of acetoxy-toluenesulfonate in the present work fits in with the previously observed downward drift in the first-order rate constant for acetolysis of the acetoxy-toluenesulfonate as toluenesulfonic acid accumulates. Ion pair considerations explain the decrease of acetolysis rate by toluenesulfonic acid and not by diphenylguanidinium toluenesulfonate.

Previous work[2,4-8] on participation of the neighboring acetoxy group in nucleophilic substitution has shown that solvolysis of *trans*-2-acetoxycyclohexyl *p*-toluenesulfonate (I) proceeds by way of the *cis*-cyclohexeneacetoxonium ion V in solvents such as acetic acid or ethanol. As mentioned in connection with the previous work,[6] another likely source of the bridged ion V appears to be II, the ketene acetal of *cis*-1,2-cyclohexanediol (2-methylene-*cis*-4,5-tetramethylenedioxolane). Therefore, knowledge about the behavior of this ketene acetal in solvolytic media can contribute to our understanding of the mechanisms of transformations involving neighboring acetoxy group participation. In this paper are reported the results of a study of the preparation and behavior of the ketene acetal II. Preliminary results of the study of the analogous acetal of dichloroketene are also reported.

Ketene Acetal of *cis*-1,2-Cyclohexanediol.—The bromoacetal of *cis*-1,2-cyclohexanediol (X) was prepared by acid-catalyzed exchange between the *cis*-glycol and diethyl bromoacetal, the reaction being driven to completion by distillation of the ethanol produced. Incidentally, the bromoacetal of *trans*-1,2-cyclohexanediol also was prepared, but no further work was carried out with it.

Elimination of hydrogen bromide from the *cis*-bromoacetal X was achieved readily by the use of potassium *t*-butoxide in McElvain's customary method of preparation of ketene acetals.[9] Like other ketene acetals,[9] the ketene acetal II proved to be an extremely reactive substance, difficult to work with. It polymerized readily at room temperature to a white solid, the polymerization being considerably accelerated by minute traces of acid. Distillation at reduced pressure caused spontaneous polymerization unless the entire distillation apparatus was previously treated to ensure a dry, neutral surface.

Behavior of Ketene Acetal in Ethanol and Moist Acetic Acid.—In absolute ethanol at room temperature the ketene acetal II was converted smoothly to *cis*-cyclohexene ethyl orthoacetate (III), while in moist acetic acid the product was a mixture of predominantly monoacetate IX with some diacetate VII of pure *cis*-1,2-cyclohexanediol. These results parallel the observation that the cyclohexeneacetoxonium ion V is diverted to isolable orthoester III by ethanol[6] and to the partially hydrolyzed orthoester VI by water in moist acetic acid during solvolysis of *trans*-2-acetoxycyclohexyl toluenesulfonate[5] (I) or in analogous reactions.[4] Tautomerization[4-6] of the partially hydrolyzed orthoester VI gives rise to *cis*-monoacetate IX, which is in turn partially acetylated to yield diacetate VII.

The diversion of cyclic acetoxonium ions such as V by even small amounts of water in acetic acid has been observed generally, and brief reviews of available examples were included in previous

(1) Paper XXIII, F. L. Scott, R. E. Glick and S. Winstein, *Experientia*, **13**, 183 (1957).

(2) Most of the material of this paper was reported in summary: (a) before the Organic Division of the American Chemical Society, St. Louis, Mo., Sept., 1948; (b) at the Eleventh National Organic Symposium, Madison, Wis., June 21, 1949, p. 65 of Abstracts; (c) at Montpellier, France, April 26, 1950 [*Bull. soc. chim.*, [5] **18**, 55C (1951)].

(3) The research reported in this manuscript was kindly supported by the Research Corporation and by the Eli Lilly Co.

(4) (a) S. Winstein and R. E. Buckles, THIS JOURNAL, **64**, 2780, 2787 (1942); (b) S. Winstein and D. Seymour, *ibid.*, **68**, 119 (1946); (c) S. Winstein and R. M. Roberts, *ibid.*, **75**, 2297 (1953).

(5) S. Winstein, H. V. Hess and R. E. Buckles, *ibid.*, **64**, 2796 (1942).

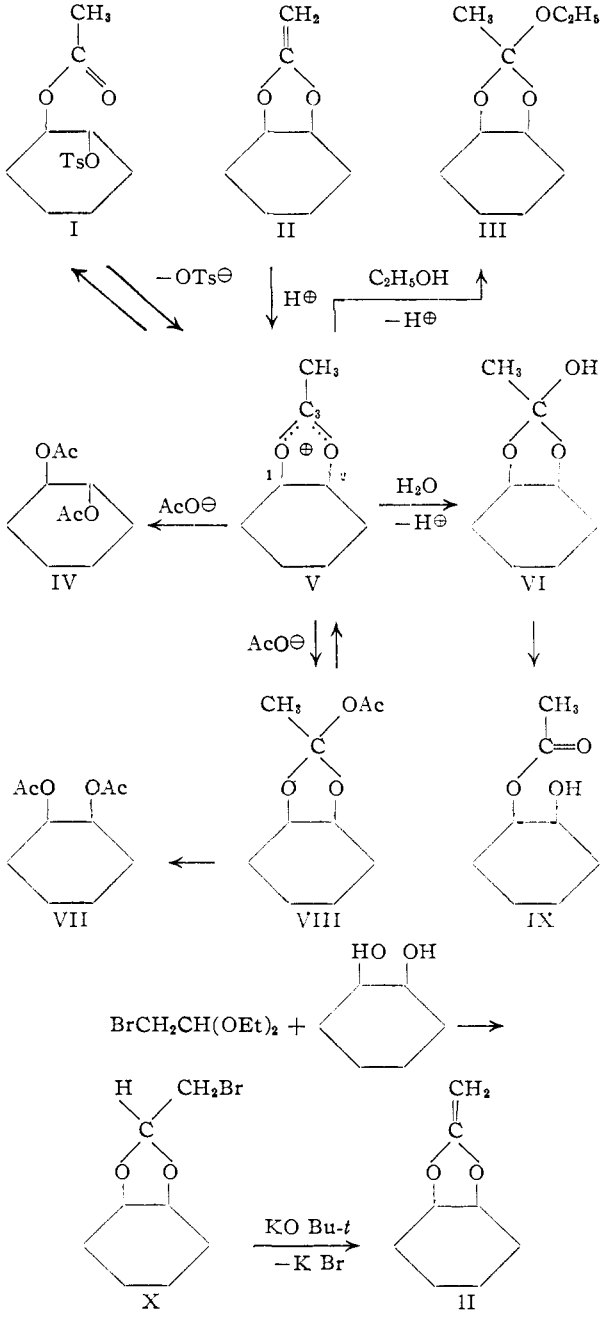
(6) S. Winstein and R. E. Buckles, *ibid.*, **65**, 613 (1943).

(7) (a) S. Winstein, C. Hanson and E. Grunwald, *ibid.*, **70**, 812 (1948); (b) S. Winstein and R. Heck, *ibid.*, **74**, 5584 (1952).

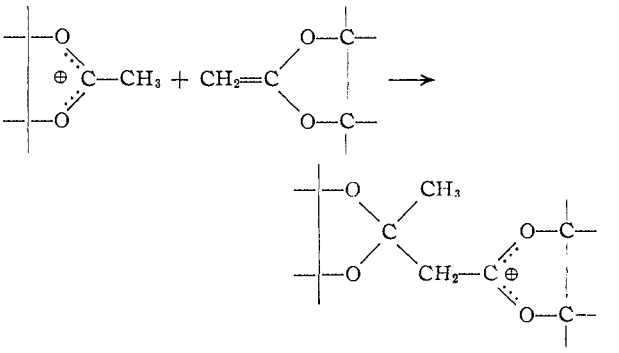
(8) (a) S. Winstein, E. Grunwald and L. L. Ingraham, *ibid.*, **70**, 821 (1948); (b) S. Winstein, E. Grunwald, R. E. Buckles and C. Hanson, *ibid.*, **70**, 816 (1948).

(9) F. Beyerstedt and S. M. McElvain, *ibid.*, **58**, 529 (1936).

papers.[4a,c] An interesting example recently reported by Brutcher and Vara[10] involves the cyclopentadieneacetoxonium ion produced by the action of lead tetraacetate on cyclopentadiene in acetic acid solvent.



Behavior of Ketene Acetal in Anhydrous Acetic Acid.—The reaction of ketene acetal with anhydrous acetic acid was complicated by formation of higher molecular weight products unless the ketene acetal was added dropwise slowly to hot stirred acetic acid. A plausible explanation of the formation of higher molecular weight products involves electrophilic attack of the cyclohexene acetoxonium ion intermediate V on ketene acetal II as



The proportion of such reaction is minimized by the slow addition of ketene acetal to hot acetic acid, each increment of ketene acetal tending to proceed to final stable product before the next increment is added.

The diacetoxycyclohexane product, whether obtained in poor yield or in high yield under the different reaction conditions employed, was quite pure *trans*-IV. This was true whether the acetic acid was rendered anhydrous by treatment with triacetyl borate, or whether it contained excess acetic anhydride. Also, the stereochemical outcome was the same whether the acetic acid solvent contained potassium acetate or not.

Anhydrous Acetic Acid Containing Toluenesulfonic Acid.—A somewhat surprising observation was that the addition of ketene acetal II to hot anhydrous acetic acid containing 0.1 of an equivalent of toluenesulfonic acid (0.1 *N*) gave rise to a diacetate product in 71% yield, evidently a *cis–trans* mixture, but quite predominantly *trans*-IV. Diacetate, again predominantly *trans*-IV, was obtained in lower yield, along with higher molecular weight material, when the ketene acetal was added to 0.1 equivalent of toluenesulfonic acid in anhydrous acetic acid at room temperature, and then the reaction mixture was heated.

When the ketene acetal II was added over a period of 45 minutes to hot anhydrous acetic acid containing *ca.* 0.5 equivalent of toluenesulfonic acid (*ca.* 0.45 *N*), and then the reaction mixture was held at 100° three hours longer, the diacetate produced was now predominantly *cis*-VII rather than *trans*-IV.

An important feature of the reactions of ketene acetal II with anhydrous acetic acid containing toluenesulfonic acid is that considerable ketene acetal II may be first converted to *trans*-2-acetoxycyclohexyl *p*-toluenesulfonate (I). Then this material solvolyzes under the conditions employed. The formation of the *trans*-acetoxy-toluenesulfonate I was proved by its isolation in 69% yield from an aliquot of the reaction mixture from addition of ketene acetal II to 0.5 equivalent of toluenesulfonic acid just after the addition was complete.

At 100°, the formation of acetoxy-toluenesulfonate I from ketene acetal II is rapid. According to titrations of the toluenesulfonic acid, this reaction is complete within several minutes. On the other hand, the solvolysis of the acetoxy-toluenesulfonate I is relatively slow.[7] Therefore, it was possible to determine by titration how much toluene-

(10) F. V. Brutcher, Jr., and F. J. Vara, THIS JOURNAL, **78**, 5695 (1956).

sulfonic acid was consumed by ketene acetal II in the initial phase of the reaction. Also, it was possible to isolate the diacetate which was formed simultaneously with the acetoxy-toluenesulfonate before it became intermingled with diacetate produced in solvolysis of acetoxy-toluenesulfonate. In this way it was determined that 60% of the toluenesulfonic acid was consumed by the addition of ketene acetal II at 100° to 1 equivalent of 0.15 *N* toluenesulfonic acid. Also, the diacetate formed simultaneously with the acetoxy-toluenesulfonate was relatively pure *cis*-VII. When ketene acetal II was added at 100° to half an equivalent of 0.075 *N* toluenesulfonic acid, nearly quantitative consumption of the acid occurred.

Since the final *cis*- and *trans*-1,2-diacetoxycyclohexanes were stable toward toluenesulfonic acid at 100°, the ability of ketene acetal or derived intermediates to consume toluenesulfonic acid could be put to use in following reaction progress during treatment of ketene acetal in anhydrous acetic acid. In this way it was ascertained that no ketene acetal or toluenesulfonic acid-consuming intermediate survived by the end of the addition of ketene acetal at 100° to anhydrous acetic acid over a 3-minute period.

When ketene acetal II was added at room temperature over a 6-minute period to 0.07 equivalent of 0.01 *N* toluenesulfonic acid, there was visible evidence of reaction, the mixture tending to warm up. Treatment of aliquots of this solution kept at room temperature with aliquots of standard 0.1 *N* toluenesulfonic acid for a few minutes at 100° and back titration showed that the reaction solution contained more than 46% of toluenesulfonic acid-consuming material initially. Further, the concentration of acid-consuming material decreased with time, being negligible after *ca.* 800 minutes.

cis-Cyclohexene Ethyl Orthoacetate in Anhydrous Acetic Acid Containing Toluenesulfonic Acid.—The behavior of *cis*-cyclohexene ethyl orthoacetate (III) toward toluenesulfonic acid in anhydrous acetic acid also was examined for comparison with that of the ketene acetal II. Thus, from addition of orthoester III at 110° to 0.4 equivalent of 0.35 *N* toluenesulfonic acid was isolated a 56% yield of *trans*-2-acetoxycyclohexyl *p*-toluenesulfonate (I).

The orthoester III was added at room temperature to 1 equivalent of 0.098 *N* toluenesulfonic acid in acetic acid containing excess acetic anhydride, and the consumption of toluenesulfonic acid was followed by titration. There was consumed 63% of the equivalent amount of toluenesulfonic acid, this reaction being half complete after *ca.* 300 minutes.

Mechanistic Interpretation of the Reactions in Anhydrous Acetic Acid.—It seems likely that the reactions of the ketene acetal II in anhydrous acetic acid commence with proton addition. This gives rise to the cyclohexeneacetoxonium ion V. This intermediate may react with nucleophilic species at C-3 or at C-1 and C-2; the assumption that the rate of reaction is uniformly much greater at C-3 than at C-1 or C-2 leads to the most satisfactory interpretation of all of the various observations.

By reaction with either acetate ion or acetic acid, cyclohexeneacetoxonium ion V leads to orthodiacetate[5,7a] VIII. While this is the product from kinetic control of reaction product in dry, neutral or basic, acetic acid solution, the orthodiacetate VIII has only a short life at 100°. Under such conditions, the orthodiacetate VIII is quickly converted to *trans*-diacetate IV. For the mechanism of this conversion one may visualize reionization to the cyclohexeneacetoxonium ion V, which eventually undergoes nucleophilic attack at C-1 or C-2 to yield the *trans*-diacetate IV. Thus thermodynamic control of reaction product involves reaction at C-1 or C-2, in contrast with kinetic control which involves C-3.

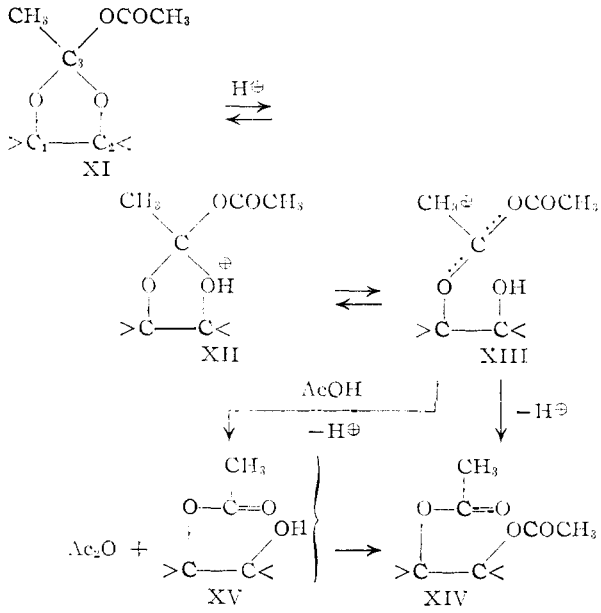
According to the present interpretation, the orthodiacetate VIII is involved also in the acetolysis of *trans*-2-acetoxycyclohexyl toluenesulfonate[5,7,8] (I) and in the treatments of the corresponding bromide[4a] with silver acetate in glacial acetic acid. It is now clear that no extra acetate salt need be added in order to achieve an over-all stereochemical result leading to *trans*-diacetate IV since orthodiacetate VIII gives rise to *trans*-diacetate IV even in neutral anhydrous glacial acetic acid solution. Thus, it is not necessary to comment, as we did previously,[5] on the unusual effectiveness of acetate ion in the reaction mixtures using silver acetate and a bromide compared to that of acetate ion in reaction mixtures employing potassium acetate and the acetoxy-toluenesulfonate I.

The present results have a bearing on the interpretation of the reaction of orthoester III in acetic acid containing acetic anhydride.[6] It was previously[6] reported that *trans*-diacetate IV was obtained in the absence or presence of added potassium acetate. A possible role of acetic anhydride in causing the inversion reaction leading to *trans*-diacetate IV was visualized,[6] but this is no longer necessary. The results are explicable now on the basis of formation of orthodiacetate VIII from the orthoester III followed by its conversion to *trans*-diacetate IV.

Since *cis*-diacetate VII is obtained under acidic conditions in glacial acetic acid from reactions proceeding by way of the cyclohexeneacetoxonium ion V[5], it seems clear that there exists[5] an acid-catalyzed route from orthodiacetate VIII to *cis*-diacetate VII. The acid-catalyzed conversion of orthodiacetate VIII to *cis*-diacetate VII may be depicted as follows. Whereas ionization of the neutral orthodiacetate species XI involves essentially only the acetate group at C-3, ionization of the conjugate acid of XI may be visualized to involve also ionization of a glycol oxygen atom. This would give rise to the ionic species XIII. The latter may be expected to be a powerful acetylating agent, and *cis*-diacetate XIV may conceivably be formed by intramolecular acetylation of the free hydroxyl group

An alternative route from the ionic species XIII to *cis*-diacetate XIV may involve formation of acetic anhydride and the monoacetate of the *cis*-glycol XV, followed by acetylation of the monoacetate by the acetic anhydride to give *cis*-diacetate XIV. The envisioned possible reaction of XIII

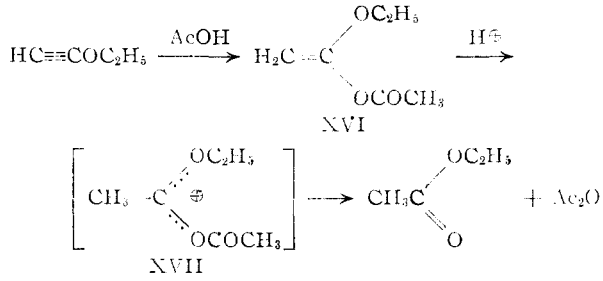
giving rise to acetic anhydride recalls the formation of acetic anhydride observed by Arens and Modderman[11] in the treatment of ethoxyacetylene with acetic acid. This reaction may be visualized to involve the addition product XVI and later the ion XVII, an analog of ion XIII.



It is apparent, when toluenesulfonic acid is the acid with which the glacial acetic acid is acidified, that the orthodiacetate VIII produces substantial amounts of *trans*-2-acetoxycyclohexyl toluenesulfonate (I). This product may be visualized to arise from attack of toluenesulfonate ion on C-1 or C-2 of the acetoxonium ion V, akin to the attack of chloride ion[6] or acetate ion.[4,5] Because this reaction competes with the acid-catalyzed conversion of orthodiacetate VIII to *cis*-diacetate VII, it is clear why treatment of ketene acetal II with glacial acetic acid containing toluenesulfonic acid gives rise to a mixture of *cis*-diacetate VII and *trans*-2-acetoxycyclohexyl toluenesulfonate (I). In runs in which the latter material is allowed to solvolyze subsequent to its formation, the final diacetate includes the diacetate from solvolysis of the initially formed acetoxy-toluenesulfonate I.

The peculiar results obtained when ketene acetal II is added to 0.1 equivalent of toluenesulfonic acid in anhydrous acetic acid now become understandable. Because of the large excess of ketene acetal, the toluenesulfonic acid concentration is reduced to such a low figure while the bulk of the ketene acetal is being added, that it is proceeding to *trans*-diacetate IV by the mechanism which does not involve strong acid catalysis. Eventually, the acetoxy-toluenesulfonate I does solvolyze to give mainly *cis*-diacetate VII, and a mixed diacetate which is mainly *trans* is finally obtained.

The situation that prevails in the treatment of orthoester III with toluenesulfonic acid in anhydrous acetic acid is similar to that which obtains for the ketene acetal II. Considerable acetoxy-toluenesulfonate I is obtained, presumably by way of the orthodiacetate VIII. In the previous work in which orthoester III was treated with toluenesulfonic acid in acetic acid, the acetoxy-toluenesulfonate I was allowed to solvolyze.[6]



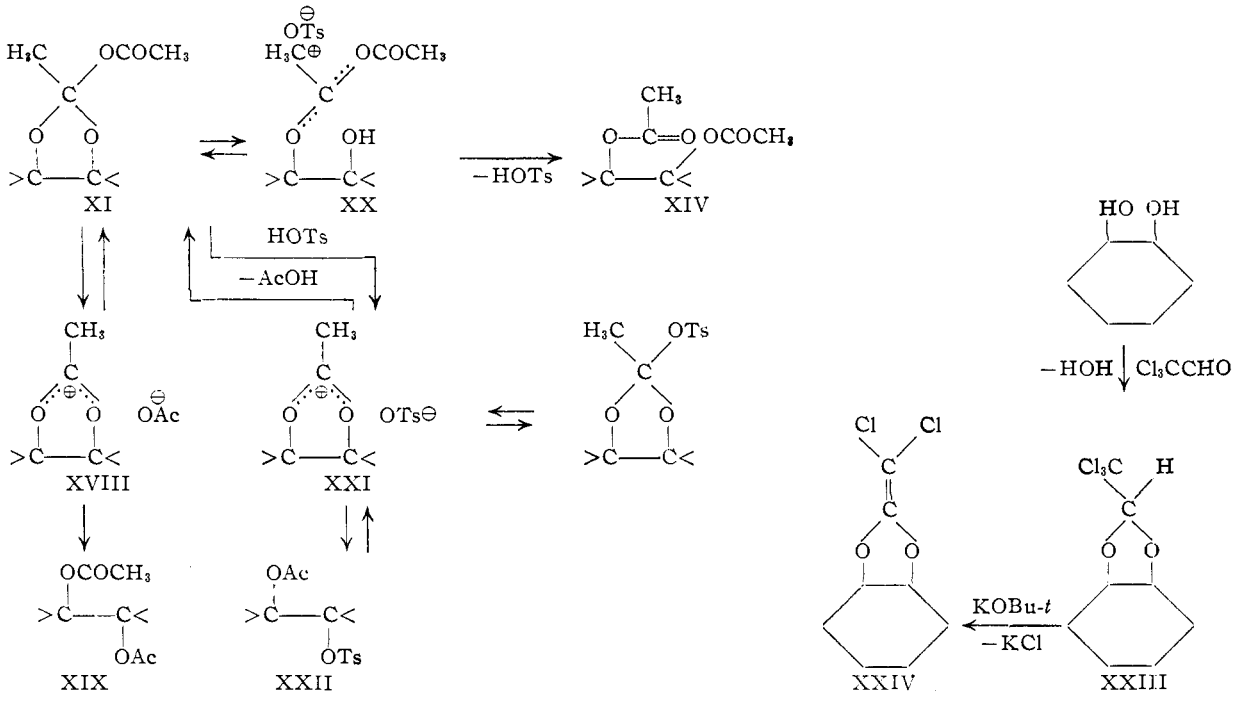
The observed formation of acetoxy-toluenesulfonate I in the present work fits in with the previous kinetic work[7a] on the acetolysis of the acetoxy-toluenesulfonate I. In solvolysis of this material in the absence of potassium acetate, first-order acetolysis rate constants drifted down to approximately one-third the initial value as toluenesulfonic acid accumulated.[7a] This was visualized as due to a reaction between some intermediate and toluenesulfonic acid which regenerated acetoxy-toluenesulfonate I. While we have now actually observed this reaction which regenerates the acetoxy-toluenesulfonate I, one feature of the observed kinetics still requires explanation. This feature is that diphenylguanidinium toluenesulfonate was not effective in reducing the first-order rate of solvolysis of the acetoxy-toluenesulfonate I, while toluenesulfonic acid was. If *trans*-diacetate formation involves the acetoxonium ion V, which also gives rise to the acetoxy-toluenesulfonate I, it is still not clear why toluenesulfonate ion is more effective in competition for the acetoxonium ion V when it is supplied as toluenesulfonic acid rather than as a toluenesulfonate salt. It seems likely that the difficulty here is that the reactions being observed are chiefly those of ion pairs rather than dissociated ions.[12]

Even though the matter needs actual study, we can sketch the manner in which the competition between toluenesulfonate ion and acetate ion (or acetic acid) for the acetoxonium ion V may be controlled by ion pair considerations. In view of the evidence[12] on the nature of the intermediates in acetolysis of other systems, it seems logical that most of the conversion of orthodiacetate XI to *trans*-diacetate XIX occurs by way of an acetoxonium acetate ion pair XVIII. Such an intermediate can return to orthodiacetate XI or, after some reorientation of the two component ions, it can also give rise to *trans*-diacetate XIX.

In the reaction between orthodiacetate XI with toluenesulfonic acid, the ionic species XIII produced by glycol oxygen ionization is better described as the ion pair XX, while the acetoxonium ion V produced by acetate ionization is better described as the acetoxonium toluenesulfonate ion pair XXI. The latter, after attaining the proper

(11) *Proc. Koninklijke Nederlandse Akademie van Wetenschappen*, **53**, No. 8, 1 (1950).

(12) See, *e.g.*, (a) S. Winstein, E. Clippinger, A. H. Fainberg and G. C. Robinson, THIS JOURNAL, **76**, 2597 (1954); *Chemistry & Industry*, 664 (1954); (b) S. Winstein, E. Clippinger, A. H. Fainberg, R. Heck and G. C. Robinson, THIS JOURNAL, **78**, 328 (1956); (c) S. Winstein and G. C. Robinson, *ibid.*, **80**, 169 (1958).



orientation of the component ions, can give rise to *trans*-acetoxy-toluenesulfonate XXII.

On the above basis, the acetoxonium ion V is produced from orthodiacetate XI as the acetate ion pair XVIII in neutral or basic acetic acid solution, but as a toluenesulfonate ion pair XXI under conditions where toluenesulfonic acid-promoted reactions of orthodiacetate XI have become predominant. If conversion of acetate ion pair XVIII to toluenesulfonate ion pair XXI by exchange,[12] followed by its conversion to acetoxy-toluenesulfonate XXII, does not compete with formation of *trans*-diacetate XIX from acetate ion pair XVIII, the ineffectiveness of added toluenesulfonate salt compared to acid in producing kinetic disturbances[7a] in acetolysis of acetoxy-toluenesulfonate I is understandable.

Dichloroketene Acetal of *cis*-1,2-Cyclohexanediol.—The dichloroketene acetal of cyclohexanediol (2-dichloromethylene-*cis*-4,5-tetramethylene-1,3-dioxolane, XXIV) was anticipated to be more favorable for actual isolation of derivatives akin to the orthodiacetate VIII. Therefore, the dichloroketene acetal XXIV was prepared. Preliminary work with this material was promising, but the work has remained interrupted for some time.

Acid-catalyzed reaction of chloral with *cis*-1,2-cyclohexanediol gave rise to the chloral acetal XXIII, just as in the analogous reaction between chloral and ethylene glycol.[13] Dehydrochlorination of the chloral acetal XXIII with potassium *t*-butoxide yielded the desired dichloroketene acetal[14] XXIV. This material, a crystalline solid, was sensitive to acids, but in carefully treated glassware it kept better than the unchlorinated ketene acetal II. For the ethylene glycol derivatives, McElvain and Curry[13] have reported greater stability of the dichloroketene acetal.

Experimental

***trans*-2-Hydroxycyclohexyl *p*-toluenesulfonate** was prepared from cyclohexene by a modification of the method previously used by Criegee and Stanger.[15] A 90-g. (0.88 mole) quantity of acetic anhydride was added to a solution of 40 g. (0.21 mole) of *p*-toluenesulfonic acid monohydrate in 24.0 g. of 30% hydrogen peroxide solution. During the addition of the acetic anhydride the temperature was kept below 40° with the aid of an ice-bath. After addition of the acetic anhydride, 16.8 g. (0.205 mole) of cyclohexene was added, the temperature still being kept under 40°. After the addition of cyclohexene was complete, the reaction mixture was stirred for three hours at room temperature, and then it was poured into *ca.* 300 ml. of cold water. The oil which originally formed crystallized readily. The crystals were filtered to yield 33 g. (57%) of product, m.p. 93–95°.

***trans*-2-Acetoxycyclohexyl-*p*-toluenesulfonate** was prepared by acetylation of *trans*-2-hydroxycyclohexyl toluenesulfonate.[5]

***cis*- and *trans*-1,2-Cyclohexanediols.**—Some of the *cis*-glycol was prepared by solvolysis of *trans*-2-acetoxycyclohexyl *p*-toluenesulfonate in moist acetic acid containing potassium acetate.[5] Some of the *trans*-glycol was prepared by acid-catalyzed opening of cyclohexene oxide with water.[16] Large amounts of the glycols were prepared by separation of the glycol mixture obtained by hydrogenation of catechol over Raney nickel catalyst at 1800 lb. pressure and 175°. The separation of the glycols was achieved by a procedure very similar to that of Derx,[17] the *cis*-glycol being converted to the acetonide. Steam distillation of the ketal and subsequent hydrolysis gave rise to *cis*-glycol, m.p. 97°. From the residue remaining after steam distillation of the ketal was obtained the *trans*-glycol by chloroform extraction, m.p. 104° after recrystallization.

2-Bromomethyl-*cis*-4,5-tetramethylene-1,3-dioxolane.—A 32.8-g. (0.282 mole) quantity of *cis*-1,2-cyclohexandiol, 60.0 g. (0.305 mole) of diethyl bromoacetal and a crystal of *p*-toluenesulfonic acid monohydrate were heated in a bath at 100–110° (173 mm.) with two Dry Ice–ethanol traps to collect the distillate. During 2.5 hours, 32.5 cc. (99%) of ethanol was collected in the first trap. The reaction mix-

(13) S. M. McElvain and M. J. Curry, THIS JOURNAL, **70**, 3781 (1948).

(14) This material has also been prepared by A. Scattergood and W. Marcy (private communication from A. Scattergood, Sept., 1949).

(15) R. Criegee and H. Stanger, *Ber.*, **69B**, 2753 (1936).

(16) S. Winstein, THIS JOURNAL, **64**, 2792 (1942).

(17) H. G. Derx, *Rec. trav. chim.*, **41**, 312 (1922).

ture was allowed to cool; then it was shaken with *ca.* 0.5 g. of calcium carbonate for 20–30 minutes and allowed to stand overnight. The calcium carbonate was filtered off, and the filtrate was fractionally distilled. Besides 2.7 g. of forerun, b.p. 25–90° (7 mm.), there was collected 61.1 g. (98%) of main fraction, b.p. 93° (3.2 mm.) –87° (2.0 mm.), $n^{25}D$ 1.5012, $n^{20}D$ 1.5032, d^{25}_4 1.4343, d^{20}_4 1.4405, MR_D 45.80 (calcd.), 45.43 (25°), 45.41 (20°).

Anal. Calcd. for $C_8H_{13}O_2Br$: C, 43.46; H, 5.92. Found: C, 43.55; H, 5.92.

2-Bromomethyl-*trans*-4,5-tetramethylene-1,3-dioxolane.—A solution of 38.5 g. (0.33 mole) of *trans*-1,2-cyclohexanediol and 67 g. of bromoacetal was heated with a small crystal of *p*-toluenesulfonic acid at 172 mm. in an oil-bath at 108° for 2.5 hours. There was recovered 29 ml. of ethanol in a Dry Ice trap (theory 38 ml.). The residue in the reaction flask was poured into cold potassium carbonate solution and extracted with ether. There was obtained 48.6 g. of product, b.p. 108–113° (3–5 mm.). Redistillation gave rise to 45.6 g. (61.9%) of material, b.p. 107–108° (6 mm.), d^{25}_4 1.434, $n^{25}D$ 1.5056, MR_D 45.78 (calcd. 45.80).

***cis*-2-Methylene-4,5-tetramethylenedioxolane.**—In a 200-cc. round-bottomed flask was placed 105 g. (133 cc.) of dry *t*-butyl alcohol and 6 g. (0.154 g. atom) of clean potassium metal. The mixture was refluxed for two hours to dissolve the potassium and allowed to stand overnight. To this solution was added 27.8 g. (0.126 mole) of the bromoacetal of *cis*-1,2-cyclohexanediol and several boiling chips. An 8-cm. Vigreux column, insulated with glass wool, was connected, and the reaction mixture was heated in an oil-bath at 120°. Potassium bromide began to precipitate in *ca.* 3 minutes, and after 10 minutes the solvent began to distil at 82–85°. After 50 minutes the bulk of the *t*-butyl alcohol had distilled, and the distillation rate was very slow. The pressure was gradually lowered to 29.5 mm. and the main fraction of ketene acetal, 15.6 g. (88.5%), was collected, b.p. 99° (29.5 mm.), d^{25}_4 1.0226, $n^{25}D$ 1.4720, MR_D 38.39 (calcd. 37.57). The material polymerized rapidly on the refractometer plates, the index increasing. The above $n^{25}D$ is the lowest of several observed.

Anal. Calcd. for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 67.99; H, 8.95.

In order to prevent polymerization of the ketene acetal during its isolation, all the apparatus used in this preparation was soaked in ammonium hydroxide solution for an hour or more, rinsed with water, and dried thoroughly before use. The ketene acetal tended to polymerize on standing, but it could be kept for periods of several weeks at Dry Ice temperatures in carefully treated glassware. Usually, the material was prepared immediately before use.

Reaction of Ketene Acetal with Anhydrous Ethanol.—In test-tube experiments on the addition of ketene acetal to absolute ethanol, a white precipitate, presumably polymeric material, was observed. Therefore, the ketene acetal was added dropwise to a large volume of stirred ethanol in order to minimize polymerization.

To 200 cc. of high-grade absolute ethanol in a 500-cc. round-bottomed flask at room temperature was added 13.8 g. (0.099 mole) of ketene acetal dropwise with stirring over a period of 25 minutes. Stirring was continued for an hour more, and the mixture was distilled through an efficient column. After the ethanol was removed at atmospheric pressure, the residue was distilled at 10 mm. to yield 15.2 g. (83%) of a colorless liquid; b.p. 94° (10 mm.), $n^{25}D$ 1.4470 (reported[6] for cyclohexene ethyl orthoacetate, b.p. 92–93° (10 mm.), $n^{25}D$ 1.4479–1.4489).

Reaction of Ketene Acetal with Moist Acetic Acid.—A 15.7-g. (0.112 mole) quantity of ketene acetal was added dropwise with stirring over a period of 22 minutes to 100 ml. of acetic acid, m.p. 16.1°, to which 3.1 ml. of water had been added (1.5 moles of water per mole of ketene acetal). The solution became quite warm during the addition of the ketene acetal. After the addition was complete, the solution was allowed to stand at room temperature for 2 hours. Then the reaction mixture was filtered from a small amount of polymer and distilled through a 20-cm. Vigreux column until 85 cc. of acetic acid had been collected. The concentrated reaction mixture was then neutralized with 32 cc. of nearly saturated potassium carbonate solution. An oily layer separated which was extracted with three portions of ether (total 250 cc.). The ether extract was dried over potassium carbonate overnight, and the ether was removed through a Vigreux column on a steam-bath. The residue was transferred to a small flask and distilled through a 40-cm. glass-sleeve column, 13.4 g. of distillate, b.p. 116–118° (12.5 mm.), $n^{25}D$ 1.4624, being obtained. On the basis of reported refractive indices of the pure and mixed diacetate and monoacetate of *cis*-1,2-cyclohexanediol,[4a,6] the above product corresponds to more than 84 mole % monoacetate. On this basis, the calculated yield is 72.5%.

Saponification of 1 cc. of the ester product yielded 0.67 g. (*ca.* 95%) of *cis*-cyclohexanediol, m.p. 94–98°, m.p. after recrystallization from carbon tetrachloride 94–96.5°, m.p. 94.5–97° after a second recrystallization. The mixed m.p. taken with an authentic sample of *cis*-1,2-cyclohexanediol was 94–97°; the mixed m.p. taken with a sample of *trans*-1,2-cyclohexanediol was 69–75°.

Reaction of Ketene Acetal with Anhydrous Acetic Acid.—The addition of a few drops of ketene acetal to dry acetic acid at room temperature caused formation of some white precipitate, presumably polymeric material. The addition of ketene acetal dropwise to hot acetic acid gave much less of undesired side reaction. At 100°, the over-all reaction of ketene acetal with dry acetic acid to yield diacetate was quite rapid. An 0.0148-mole quantity of ketene acetal was added over a period of 3 minutes at 100° to 100 ml. of acetic acid dried with triacetyl borate[18] or containing excess acetic anhydride. Then the mixture was cooled and aliquots were added to standard toluenesulfonic acid in glacial acetic acid and heated 5 minutes at 100°. Back titration of the toluenesulfonic acid showed no consumption of acid by the ketene acetal reaction mixture.

In a 500-cc. 3-necked round-bottomed flask equipped with a stirrer and reflux condenser was placed 100 cc. of anhydrous acetic acid which was dried over triacetyl borate. The acetic acid was heated to 100° by an oil-bath kept at 105–110°, and 14.4 g. (0.103 mole) of ketene acetal was added dropwise to the stirred solution so that the drops fell freely into the stirred acetic acid. After the addition of ketene acetal, which required 40 minutes, the mixture was kept at 105–110° in the oil-bath for 2.5 hours and allowed to stand overnight. Distillation through a 40-cm. glass-sleeve column gave rise to 14.4 g. (70%) of diacetate, b.p. 120–121° (12 mm.), $n^{25}D$ 1.4456 (reported[4a] for *trans* 1,2-diacetoxycyclohexane, b.p. 120° (12 mm.), $n^{25}D$ 1.4457).

A one-ml. sample of the diacetate was saponified to yield 0.7 g. of crude glycol, m.p. 84–94°, m.p. 90–99° when mixed with *trans*-glycol, m.p. 62–78° when mixed with *cis*-glycol. One recrystallization from carbon tetrachloride yielded 0.50 g. of white crystals, m.p. 102–104°, m.p. 101–104° when mixed with *trans*-glycol, m.p. 71–79° when mixed with *cis*-glycol.

Similar results were obtained when acetic acid dried with excess acetic anhydride was employed instead of the material dried with triacetyl borate.

When the addition of ketene acetal to anhydrous acetic acid was performed in 10 minutes at room temperature, and then the reaction mixture was refluxed for 2 hours, only an 18.5% yield of *trans*-diacetate was obtained. A large non-volatile residue remained after the distillation. When the ketene acetal was added in 25 minutes at room temperature to the anhydrous acetic acid *ca.* 1.5 *M* in potassium acetate, and then the reaction mixture was refluxed 2 hours, a 26% yield of *trans*-diacetate was obtained.

Reaction of Ketene Acetal with Anhydrous Acetic Acid Containing Toluenesulfonic Acid.—To 100 cc. of acetic acid (m.p. 16.2°) was added 1.9 g. (0.01 mole) of *p*-toluenesulfonic acid monohydrate and 6 cc. of acetic anhydride (calcd. 2.0 cc. required), and the solution was refluxed for 2 hours and allowed to cool. The solution was heated in an oil-bath at 110° with stirring while 14.7 g. (0.105 mole) of ketene acetal was added dropwise over a period of 45 minutes. The solution was kept at 100° for 5 hours after the addition and allowed to stand overnight. Then 1.96 g. (0.02 mole) of anhydrous potassium acetate was added and the mixture was refluxed for 2 hours and allowed to cool. The solution was added to 500 cc. of water and worked up in the usual way. Distillation gave rise to 14.8 g. (71%) of diacetate, b.p. 118° (12.2 mm.), $n^{25}D$ 1.4460.

Saponification of 1 cc. of the ester product yielded 0.55 g. of crude glycol, m.p. 70–90°, mixed m.p. with *cis*-glycol 62–73°, mixed m.p. with *trans*-glycol 75–97°. One recrys-

(18) W. C. Bichelberger and V. K. LaMer, THIS JOURNAL, **55**, 3633 (1933).

tallization from carbon tetrachloride yielded 0.43 g. of white crystals, m.p. 92–100°, mixed m.p. with *cis*-glycol 73–76°, mixed m.p. with *trans*-glycol 92–102°.

When the above addition of ketene acetal to 0.1 equivalent of toluenesulfonic acid in anhydrous acetic acid was repeated with initially 0.045 *N* toluenesulfonic acid instead of 0.1 *N*, and with the addition carried out at room temperature, after which the mixture was held 3 hours at *ca.* 105°, a 42% yield of diacetate was obtained. Considerable non-volatile residue also was observed. The diacetate was again predominantly *trans*.

A 9.5-g. (0.05 mole) quantity of toluenesulfonic acid monohydrate was added to 100 cc. of acetic acid (m.p. 16.2°). To this solution was added 10.0 ml. of acetic anhydride, and the mixture was refluxed for 2 hours. A 15.6-g. (0.11 mole) quantity of ketene acetal was added dropwise to the acetic acid solution at 100° over a period of 45 minutes. A 10-ml. sample of the mixture was removed and added to 100 cc. of water. The remainder of the reaction mixture was kept at 100° for *ca.* 3 hours longer; then it was poured into 500 cc. of water and worked up in the usual way. Distillation through a 40-cm. glass-sleeve column gave 0.5 g. of forerun, 6.3 g. of diacetate, b.p. 118–119° (12 mm.), $n^{25}D$ 1.4480, and 3.3 g. more, $n^{25}D$ 1.4450, collected after some decomposition of pot residue set in. The combined yield of diacetate, 9.6 g., was 48%.

Saponification of 1 cc. of the main fraction of diacetate gave rise to an oil which crystallized slowly when seeded with a tiny crystal of *cis*-1,2-cyclohexanediol. This yielded 0.65 g. of crystals, m.p. 50–68°. After one recrystallization from 10 cc. of carbon tetrachloride, there was obtained 0.3 g. of white crystals, m.p. 83–87°, mixed m.p. with *cis*-glycol 86–93°, mixed m.p. with *trans*-glycol 71–74°. One more recrystallization from 8 cc. of carbon tetrachloride yielded *ca.* 0.2 g. of crystals, m.p. 90–92°, mixed m.p. with *cis*-glycol 93–96°, mixed m.p. with *trans*-glycol 70–74°.

The 10-ml. sample which was removed after the ketene acetal was added to the acetic acid and poured into 100 cc. of water was extracted with ether. The ether extract was washed with potassium carbonate solution, then with water, and dried over anhydrous potassium carbonate. The ether was removed and 15 cc. of petroleum ether (b.p. 30–60°) was added. This gave rise to 0.80 g. (69%) of yellow crystals, m.p. 69–74°. One recrystallization yielded 0.6 g. of light yellow crystals, m.p. 76–77.5°, mixed m.p. (with authentic *trans*-2-acetoxycyclohexyl *p*-toluenesulfonate) 76–78.5°.

In a run similar to the one described above, 0.126 mole of ketene acetal was added over 65 minutes at 80° to a solution of 0.06 mole of toluenesulfonic acid in 132 ml. of anhydrous acetic acid (*ca.* 0.45 *N* acid). This solution was maintained 20 more minutes at 80°, and then it was worked up to yield 8.66 g. (46%) of *trans*-2-acetoxycyclohexyl *p*-toluenesulfonate and 5.36 g. (21%) of predominantly *cis*-diacetate.

A 0.0148-mole quantity of ketene acetal was added to 100 ml. of 0.149 *N* toluenesulfonic acid in dry acetic acid at 100° over a period of 5 minutes. The reaction mixture was heated and stirred an additional 3 minutes and cooled. Titration of 5-ml. aliquots of this solution with 0.1000 *N* sodium acetate in acetic acid showed that 0.0090 equivalent (60%) of *p*-toluenesulfonic acid was consumed.

The rest of the above reaction mixture was poured into excess potassium bicarbonate solution and extracted with ether. Evaporation of the ether from the dried ether extract and addition of petroleum ether gave a crystalline product. After recrystallization there was obtained 2.65 g. (31%) of *trans*-2-acetoxycyclohexyl *p*-toluenesulfonate, m.p. 76–78°, mixed m.p. 76–77°.

By distillation of the mother liquors from the crystallization of the acetoxycyclohexyl toluenesulfonate there was obtained 0.53 g. of diacetate, b.p. 97–107° (5–6 mm.), as well as an 0.85 g. of non-volatile residue (probably acetoxycyclohexyl toluenesulfonate). Saponification of the diacetate gave rise to 0.21 g. of sublimed glycol, recrystallization of which yielded 0.14 g. of *cis*-glycol, m.p. 92.5–93°, mixed m.p. with *cis*-glycol 94.8–95.2°, mixed m.p. with *trans*-glycol 74.5–75.8°.

An 0.0148-mole quantity of ketene acetal was added over a 3.3-minute period to 100 ml. of 0.0752 *N* *p*-toluenesulfonic acid in dry acetic acid at 100°. Titration of 5-ml. aliquots of the reaction mixture indicated that at least 98% of the toluenesulfonic acid had been consumed. When the ketene acetal was added to 0.297 *N* toluenesulfonic acid solution over a period of 4.5 minutes at 100°, 22% of the acid was consumed, 44% of the ketene acetal reacting with acid.

A 0.0148 mole quantity of ketene acetal was added at room temperature over a 6-minute period to 100 ml. of anhydrous acetic acid 0.01 *N* in toluenesulfonic acid. The reaction mixture warmed up perceptibly during the addition. From time to time, 5-ml. aliquots were added to 5 ml. of 0.1 *N* toluenesulfonic acid and heated 6–7 minutes at 100° to allow toluenesulfonic acid to be consumed. Back titration with standard diphenylguanidinium acetate solution showed that 46% of the equivalent amount of acid was consumed by an aliquot 3 minutes after the addition of ketene acetal was completed. However, less and less acid was consumed by aliquots of the ketene acetal solution as it stood at room temperature. The half-life of reactive species was roughly 150 minutes. The concentration of reactive species was inappreciable at 829 minutes.

Reaction of *cis*-Cyclohexene Ethyl Orthoacetate with Anhydrous Acetic Acid Containing Toluenesulfonic Acid.—To 25 cc. of acetic acid (m.p. 16.2°) was added 5 cc. of acetic anhydride and 2.0 g. (0.0105 mole) of *p*-toluenesulfonic acid monohydrate. The mixture was refluxed for two hours and allowed to stand overnight. To this solution, heated in an oil-bath at 110°, was added 4.65 g. (0.0250 mole) of cyclohexene ethyl orthoacetate in several portions with swirling. The solution was kept in the bath at 110° for 20 minutes, then cooled and poured into 250 cc. of water. This aqueous solution was extracted with two 200-cc. portions of ether. The ether solution was washed with potassium carbonate solution and dried over anhydrous potassium carbonate. The ether was removed on the steam-bath and 50 cc. of petroleum ether, b.p. 60–72°, was added. From this mixture there was obtained 1.83 g. (56%) of crystals, m.p. 75–77°, m.p. 75–78° when mixed with an authentic sample of *trans*-2-acetoxycyclohexyl *p*-toluenesulfonate.

A 1.81-g. (0.00971 mole) quantity of orthoester was added at room temperature to 100 ml. of 0.0978 *N* toluenesulfonic acid in anhydrous acetic acid. Aliquots (5 ml.) of this solution were titrated with 0.0996 *N* diphenylguanidinium acetate. The titration data showed that 63% of the equivalent amount of toluenesulfonic acid was consumed, the half-time for the reaction being roughly 300 minutes.

Stability of Diacetoxycyclohexanes.—Samples of *cis*- and *trans*-1,2-diacetoxycyclohexane were held at 100–105° for 100 hours in solution with 0.5 *N* toluenesulfonic acid in dry acetic acid. The diacetates were then recovered in 91–97% yields. Saponification of the diacetates gave rise to essentially pure glycols. Solutions of the diacetates with 0.1 *N* toluenesulfonic acid in dry acetic acid at 75° were followed for acid consumption up to elapsed times of 147 hours. No detectable acid consumption was observed.

2-Trichloromethyl-*cis*-4,5-tetramethylene-1,3-dioxolane.—To a solution of 10.0 g. (0.0863 mole) of *cis*-1,2-cyclohexanediol and 25.0 g. (0.170 mole) of freshly distilled chloral in 75 cc. of anhydrous benzene was added three drops of concd. sulfuric acid. The mixture was refluxed for four days with an attached water trap, 3.33 g. of an aqueous fraction being collected. The benzene solution was poured into 300 cc. of saturated sodium bicarbonate solution and extracted with four portions of ether (*ca.* 300 cc.). The dried ether extract was distilled, the last traces of solvent being removed on an aspirator. There remained 19.14 g. of a yellow liquid, to which 10 cc. of petroleum ether, b.p. 30–60°, was added, and the solution was cooled in Dry Ice. A 3.91-g. quantity of white crystals, m.p. 33.5–35.0°, was filtered off. An additional 5.20 g. of crystals were obtained in a similar fashion from the mother liquor to bring the total yield of acetal to 43%. After another recrystallization the analytical sample melted at 34.5–35.0°.

Anal. Calcd. for $C_8H_{11}O_2Cl_3$: C, 39.12; H, 4.52. Found: C, 38.94; H, 4.65.

A liquid remained after evaporation of solvent from the filtrate, which yielded 3.7 g. of colorless liquid, b.p. 95° (2 mm.), on distillation.

Anal. Calcd. for $C_8H_{11}O_2Cl_3$: C, 39.12; H, 4.52. Found: C, 41.57; H, 5.05.

The liquid is probably acetal contaminated with *cis*-cyclohexanediol, so, including this liquid, the total yield of acetal is 60%.

2-Dichloromethylene-*cis*-4,5-tetramethylene-1,3-dioxolane.—To a solution of 1.2 g. (0.031 g. atom) of freshly trimmed potassium metal in *ca.* 40 cc. of anhydrous *t*-butyl alcohol was added 2.96 g. (0.012 mole) of the acetal described above, and the mixture was refluxed for 80 minutes. Part of the *t*-butyl alcohol was removed by reduced pressure distillation, but the brown suspension bumped badly. The solution was diluted with anhydrous ether, but it could not be filtered through a sintered glass funnel. After the solution was distilled to dryness at reduced pressure and more ether was added, the brown suspension could be filtered through a fine sintered glass filter. The ether was removed from the clear filtrate by distillation, and *ca.* 10 cc. of petroleum ether was added to the residue. The mixture was cooled in Dry Ice and filtered to yield 1.20 g. (48%) of white crystals, m.p. 55.5–56.0°, m.p. 56.5–57.0° after two recrystallizations from petroleum ether. The sample was dried in a vacuum desiccator over paraffin and 85% potassium hydroxide.

Anal. Calcd. for $C_8H_{10}O_2Cl_2$: C, 45.96; H, 4.82. Found: C, 45.95; H, 4.87.

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[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

The Reaction of Aromatic Aldehydes with *n*-Butylamine. Acid Catalysis and Substituent Effects[1]

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General acid catalysis has been demonstrated for the reaction of substituted benzaldehydes with *n*-butylamine by employing acetic acid–lithium acetate buffers in methanol. The plot of log *k vs.* Hammett's σ-function, for the uncatalyzed reaction, is not linear but has a maximum near the point corresponding to benzaldehyde. Apparent energies and entropies of activation are given.

Recent studies of the kinetics of Schiff base formation[2] have been concerned with the second-order reaction which takes place in the absence of any acid catalyst other than the solvent.

$$RCHO + R'NH_2 \longrightarrow RCH{=}NR' + H_2O \quad (1)$$

The reaction of an aliphatic amine with an aromatic aldehyde, however, should be no exception to the rule that carbonyl addition reactions can be acid catalyzed; this paper describes the detection of acid catalysis and the effect of ring substituents on the rate.

The difficulties expected in determining the rate constant for an acid-catalyzed reaction of a base were described by Conant and Bartlett in their classical investigation of semicarbazone formation in aqueous solution.[3] Our acid-catalyzed reactions were run in methanol at 25°. For a thorough interpretation of the rate of reaction 1 in the presence of an acid, the dissociation constants of the acid (acetic) and *n*-butylamine (the only amine used in this investigation) must be known. The value of Kilpatrick and Eanes[4] for K_{HAc} in methanol containing 0.1 *M* lithium chloride is 2.19×10^{-9}. The dissociation constant, K_{HB^+}, of butylammonium ion in methanol is reported by Schaefgen, Newman and Verhoek[5] to be 1.78×10^{-12}. By their method we determined the value 2.57×10^{-12} in 0.1 *M* methanolic lithium chloride.

Experimental

Materials.—*p*-Chlorobenzaldehyde, benzaldehyde, *p*-methylbenzaldehyde and *p*-methoxybenzaldehyde were distilled at atmospheric pressure. The last three were handled in nitrogen. Piperonal was recrystallized from ethanol-water, the remaining aldehydes from water. Glacial acetic acid was dried by azeotropic distillation from benzene.

The following Schiff bases were prepared according to Campbell and co-workers[6]: *p*-methoxybenzal-*n*-butylamine, b.p. 164–165° (20 mm.); *p*-methylbenzal-*n*-butylamine, b.p. 138° (19 mm.); benzal-*n*-butylamine, b.p. 129–131° (25 mm.); *m*-nitrobenzal-*n*-butylamine, b.p. 193–194° (25 mm.).

Baker and Adamson reagent lithium chloride was treated with hydrochloric acid and heated until dry; assay 99.8% of theoretical chloride. Lithium acetate was prepared by dissolving Eimer and Amend C.P. lithium carbonate in acetic acid and evaporating. The fused mass was pulverized, dried at 160°, and thereafter handled in a dry-box.

The solvent for the kinetic runs and spectral measurements was reagent grade methanol. This solvent was distilled from magnesium methoxide for the determination of K_{HB^+}.

Procedure.—The kinetic runs were made as previously described.[7] Samples were withdrawn and diluted with methanolic hydrochloric acid to convert the Schiff base to its conjugate acid and any unreacted aldehyde to the acetal. The Schiff base concentration then was obtained easily from the optical density at the ultraviolet absorption peak, using the last two columns of Table I. The measured absorption of the acetal at the wave length of the Schiff base conjugate acid was usually negligible (for example, ϵ_{320} 0.02×10^4 for an acidified solution of *p*-methoxybenzaldehyde). In the

TABLE I

SPECTRA OF ALDEHYDES AND SCHIFF BASES IN METHANOL

	λ_{max}, mμ			
RCHO[a]	RCHO	RCH=NBu	RCH=NBu·HCl	$\epsilon_{max} \times 10^{-4}$
p-$(CH_3)_2N$	340	329[b]	393[b]	4.92
p-CH_3O	275	268	320	2.89
3,4-CH_2O_2	310	305[c]	348[c]	1.73
p-CH_3	256	254	288	2.14
m-OH	254	250[b]	283[b]	1.52
H	246	246	275	1.71
p-Cl	255	253[b]	286	1.82
m-NO_2	257	235	250	1.31
p-NO_2	265	281[b]	261[b]	1.14

[a] Substituted benzaldehydes. [b] Observed in a solution of aldehyde and *n*-butylamine after complete reaction. [c] Ref. 7.

(1) Presented before the Division of Organic Chemistry of the American Chemical Society, Miami, Fla., April 9, 1957. Taken in part from the dissertation of Georges M. Santerre, University of Virginia, 1956.

(2) R. L. Hill and T. I. Crowell, THIS JOURNAL, **78**, 2284, 6425 (1956).

(3) J. B. Conant and P. D. Bartlett, *ibid.*, **54**, 2881 (1932).

(4) M. Kilpatrick and R. D. Eanes, *ibid.*, **75**, 586 (1953).

(5) J. R. Schaefgen, M. S. Newman and F. H. Verhoek, *ibid.*, **66**, 1847 (1944).

(6) K. N. Campbell, *et al.*, *ibid.*, **70**, 3868 (1948).

(7) T. I. Crowell and D. W. Peck, *ibid.*, **75**, 1075 (1953).