in four stages over anhydrous magnesium sulfate. The ether was distilled until the temperature rose to 50°, and then the residue was pumped under reduced pressure to remove the last traces of solvent. Distillation through a 10-cm. Vigreux column gave 29.6 g. (82%) of methylstyrylcarbinol as a colorless liquid, b.p. 73–81° (less than 1 mm.), $n^{25}D$ 1.5594; lit.[26] b.p. 106° (18 mm.). The infrared spectrum showed no carbonyl absorption. There was a broad band at 3.0 μ characteristic of O–H stretch. There were three bands at 3.30, 3.39, and 3.51 μ assigned to the various C–H stretching vibrations. The bands at 6.25, 6.34, 6.69, and 6.90 μ were assigned to aromatic C=C stretch, and the weak band at 6.03 μ was assigned to C=C stretch. A broad band at 7.1 μ could be due to C–H deformation.

The 4-nitrobenzoate was prepared by the pyridine method. Recrystallization of this ester from a number of solvent systems gave only oils which crystallized after standing in the refrigerator for several days to several weeks. Five "recrystallizations" (the material oiled out) from pentane gave a white powder, m.p. 61–65°; lit.[27] m.p. 60°.

Anal. Calcd. for $C_{17}H_{15}O_4N$: C, 68.67; H, 5.09. Found: C, 68.84; H, 5.15.

4-Nitrobenzoate of Cinnamyl Alcohol.—The ester was prepared from the alcohol and acid chloride in pyridine[24] and after three recrystallizations from pentane had m.p. 76.5–77.0°; lit.[24] m.p. 78°.

Anal. Calcd. for $C_{16}H_{13}O_4N$: C, 67.84; H, 4.63. Found: C, 67.62; H, 4.72.

Hydrolysis Rate Measurements.—The rates were measured by a procedure similar to that described by Goering and Silversmith.[19] In all but one case, stock solutions of the esters were made up and aliquots sealed in ampoules. The 4-nitrobenzoate of 2-chloro-3-phenyl-2-cyclobutenol was so insoluble at room temperature that individual samples (20–30 mg.) were weighed out and transferred to ampoules to which the measured volumes of the purified solvent was added. The solvent was prepared by mixing 80% by volume of acetone[28] with 20% by volume of boiled, distilled water. The acidic solvent was made similarly, except that a solution of reagent grade perchloric acid in boiled, distilled water was mixed with the acetone. Titrations were carried out under nitrogen with 0.01 *N* carbonate-free sodium hydroxide solution to an end point of pH 7.50. A Leeds and Northrup direct-reading pH meter was employed. Preliminary titrations using indicators gave poor results. The rate data are summarized in Table I. Most of the kinetic runs were 50% complete after 20 hr. Initial rate constants were obtained graphically from plots $[(\chi_0 - \chi)/\chi_0]$ *vs.* time where χ_0 is the initial concentration of ester present and χ is the concentration of acid produced at time t.

(26) A. Klages, *Ber.*, **35**, 2649 (1902).
(27) H. Burton, *J. Chem. Soc.*, 455 (1929).
(28) J. K. Kochi and G. S. Hammond, *J. Am. Chem. Soc.*, **75**, 3452 (1953).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY, AMES, IOWA]

The Chemistry of Cyclopropanols. I. The Hydrolysis of Cyclopropyl Acetate and the Synthesis of Cyclopropanol

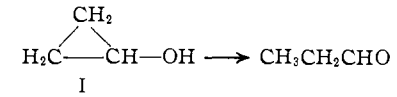
BY C. H. DEPUY[1a] AND L. R. MAHONEY[1b]

RECEIVED DECEMBER 19, 1963

A kinetic study of the alkaline hydrolysis in pure water of cyclopropyl acetate, *n*-butyl acetate, and cyclopentyl acetate as well as several enol acetates has been carried out. Examination of the activation parameters indicated no abnormality for any of these esters, and suggested that there was no ring opening of cyclopropyl acetate in the transition state for the hydrolysis. The ultimate product from the treatment of cyclopropyl acetate with base is the aldol condensation product of propionaldehyde, 2-methyl-2-pentenal. Under conditions where cyclopropyl acetate is rapidly and completely hydrolyzed, the rate of appearance of this aldol product is 100–200 times more rapid from propionaldehyde than it is from the ester. From these data it was deduced that cyclopropanol has a reasonable lifetime in basic solution, and in agreement with this deduction it was isolated from aqueous solution. A more satisfactory synthetic method is hydride reduction of the ester in ether solution and purification by preparative gas chromatography.

Despite much recent interest in the chemistry of small ring compounds, the intriguing and potentially useful molecule cyclopropanol (I) has apparently excited little attention since its original, inadvertent synthesis by Magrane and Cottle in 1942.[2] Part of the reason for this neglect may be traced to the fact that, as prepared by the method of Magrane and Cottle, the alcohol was contaminated and could not be obtained in greater than 87% purity. In addition, cyclopropanol readily rearranges to its isomer, propionaldehyde (eq. 1), especially in basic solution.[3] Indeed, an attempt to dry a solution of the alcohol over anhydrous potassium carbonate sufficed to destroy it. A small sample of cyclopropanol, again impure, was prepared by Roberts and Chambers[4] by the air oxidation of cyclopropylmagnesium chloride. No other simple cyclopropanols have been reported in the literature.

The method of Magrane and Cottle for the preparation of cyclopropanol involved the reaction of epichlorohydrin with magnesium bromide, ferric chloride, and ethylmagnesium bromide in ether solution. Neither



(1)

this method, nor the Grignard synthesis of Roberts and Chambers, appeared to be well adapted to the preparation of substituted cyclopropanols of known structure.[5] It was felt that other methods for the synthesis of these interesting compounds should be explored, and to that end a study of the hydrolysis of cyclopropyl acetate was undertaken and is reported herein.

The preparation of cyclopropanols by the hydrolysis of the corresponding esters appeared worthy of investigation because two recent synthetic advances have made cyclopropyl esters easily available. The first of these advances was the observation of Emmons and Lucas[6] that peroxytrifluoroacetic acid converts

(1) (a) Alfred P. Sloan Fellow, 1960–1964; (b) National Science Foundation Cooperative Fellow, 1959–1960.
(2) J. K. Magrane and D. L. Cottle, *J. Am. Chem. Soc.*, **64**, 484 (1942).
(3) C. W. Stahl and D. L. Cottle, *ibid.*, **65**, 1782 (1943).
(4) J. D. Roberts and V. C. Chambers, *ibid.*, **73**, 3176 (1951).
(5) See, however, C. H. DePuy, L. R. Mahoney, and K. L. Eilers, *J. Org. Chem.*, **26**, 3616 (1961).
(6) W. D. Emmons and G. B. Lucas, *J. Am. Chem. Soc.*, **77**, 2287 (1955).

methyl cyclopropyl ketone into cyclopropyl acetate. Since the ketone is commercially available, the acetate can be obtained in one step. It had previously been shown that perbenzoic acid was not effective in this conversion.[7] In a second method, iodomethylzinc iodide[8] was allowed to react with vinyl acetate to furnish the desired cyclopropyl ester in one step (eq. 2). If this reaction should prove to be general for enol esters, a variety of cyclopropyl esters of known

$$CH_2{=}CH{-}OOCCH_3 + ICH_2ZnI \longrightarrow \underset{\diagdown\,\diagup}{CH_2{-}{-}CHOCOCH_3}\ \ (2)$$
$$CH_2$$

structure and stereochemistry could be prepared. A method for the conversion of these esters into the corresponding cyclopropanols seemed of possible synthetic utility, and at the same time the hydrolysis has some interesting features in its own right.[9]

A difficulty anticipated in the conversion of the ester to the alcohol was the isomerization of the alcohol to propionaldehyde. This presumably proceeds by way of the alkoxide anion and is closely related to the acyclic alcohol cleavages investigated by Cram and coworkers.[10] Since the driving force for the reaction is the relief of strain, it appeared that the hydrolysis might proceed with simultaneous ring opening so that cyclopropanol would not be an intermediate in the hydrolysis at all. Alternatively, a cyclopropanol, if it were produced, might undergo isomerization at a faster rate than the ester hydrolysis and so not accumulate.

We turned our attention first to a study of the rate of hydrolyses of cyclopropyl acetate in aqueous base. Preliminary experiments showed that this rate was rapid, even at 0°, and ordinary titrimetric methods for following the reaction could not be used. Consideration of other available techniques led to the adoption of conductometry as the most convenient; all subsequent kinetic studies of ester hydrolyses were performed in this way (see Experimental). If an accurate and useful comparison of activation parameters with other esters were to be made, it was obvious that the rates had to be measured under identical conditions of solvent and base. Since few data were available on the rates of ester hydrolysis in aqueous solution, we measured these rates for a number of esters. In addition to some normal esters, a variety of enol esters were studied because no data on their hydrolysis had been published previously with the exception of one study on the hydrolysis of vinyl acetate in buffered solution,[11] and it was felt that they might somehow differ from normal esters in their mechanism of hydrolysis. These rate data are collected in Table I, and the activation energies and entropies are listed in Table II.

It is obvious from the data in Table II that cyclopropyl acetate does not differ appreciably in its activation parameters from other esters, nor do enol esters differ appreciably from alkyl esters. The comparison may be put on a more quantitative basis by constructing a plot of enthalpy *vs.* entropy after the method of Leffler.[12] Both the enol acetates and the alkyl formates give good straight lines in such a plot, with cyclopropyl and the other alkyl acetates falling close to the enol line. The lines for the formates and enol acetates are parallel, with similar intercepts.[13] It seems reasonable to conclude that all these hydrolyses proceed by similar mechanisms.

TABLE I

RATES OF ALKALINE HYDROLYSIS OF A VARIETY OF ACETATES IN PURE WATER

Acetate	t, °C.	Concn. × 10^3, moles/l.	NaOH concn. × 10^3, moles/l.	k_2, l./mole-sec.	k
Cyclopropyl	20.0	4.818	1.531	0.169	
		4.080	2.130	.183	0.178 ± 0.006
		6.100	1.347	.183	
	40.0	3.115	1.515	.723	.717 ± .007
		3.758	1.368	.710	
Vinyl	0.20	0.999	0.817	.625	
		1.358	0.907	.643	.61 ± .03
		1.795	1.415	.568	
	20.0	1.245	1.027	3.13	
		1.172	1.066	3.50	3.28 ± .13
		1.038	0.865	3.22	
Isopropenyl	0.20	1.571	0.754	0.059	0.065 ± .002
		1.853	1.173	.070	
		2.275	1.328	.065	
		2.513	1.558	.065	
	20.0	3.817	1.313	.318	.301 ± .015
		2.405	2.055	.300	
		4.665	1.962	.286	
Cyclopentenyl	20.0	3.408	1.975	.796	.855 ± .038
		3.468	1.475	.888	
		2.856	1.255	.882	
	40.0	1.409	1.245	2.78	2.86 ± .012
		1.972	1.085	2.75	
		2.055	1.570	3.06	
Cyclohexyl	20.0	2.832	1.854	0.175	0.178 ± .003
		3.295	1.712	.181	
	40.0	3.62	5.64	.564	
Cyclopentyl	20.9	2.84	1.51	.025	.026 ± .001
		2.86	1.93	.027	
	40.0	4.00	2.09	.089	.089 ± .001
		4.55	2.61	.089	
n-Butyl	20.0	4.70	2.72	.064	.065 ± .001
		2.89	1.93	.066	

TABLE II

ACTIVATION PARAMETERS FOR THE ALKALINE HYDROLYSIS OF A VARIETY OF ESTERS IN WATER

Acetates	$\Delta H^{\ddagger}$, kcal.	$\Delta S^{\ddagger}$, e.u.
Cyclopropyl	12.1	−20.8
Ethyl	(11.0)	−31.0
n-Butyl	10.6	−27.7
Cyclopentyl	11.9	−25.2
Vinyl	12.8	−12.7
Isopropenyl	11.6	−21.2
1-Cyclopentenyl	10.5	−24.8
1-Cyclohexenyl	10.5	−26.5
Formates[11]		
Methyl	9.0	−20.1
Ethyl	8.3	−24.2
n-Propyl	7.9	−25.6
n-Butyl	7.4	−28.0

(7) S. L. Friess, *J. Am. Chem. Soc.*, **71**, 14 (1949); S. L. Friess and R. Pinson, Jr., *ibid.*, **74**, 1302 (1952).

(8) H. E. Simmons and R. D. Smith, *ibid.*, **81**, 4256 (1959).

(9) Since the completion of this work a third extremely convenient method for the synthesis of cyclopropyl acetates has been developed: J. P. Freeman, *J. Org. Chem.*, **28**, 8815 (1963).

(10) D. J. Cram, A. Langemann, J. Allinger, and K. R. Kopecky, *J. Am. Chem. Soc.*, **81**, 5740 (1959), and subsequent papers.

(11) R. Leimu, R. Korte, E. Laaksonen, and J. Lehmuskoski, *Suomen Kemi.*, **19b**, 93 (1946).

(12) J. E. Leffler, *J. Org. Chem.*, **20**, 1202 (1955).

(13) For a more detailed discussion see the Ph.D. dissertation of L. J. Mahoney, Iowa State University, 1960.

Concurrently with the rate studies discussed above, we had been examining the products of the hydrolysis of cyclopropyl acetate. Cottle has reported that cyclopropanol itself in the presence of base is converted to 2-methyl-2-pentenal (the aldol product of propionaldehyde) and we isolated this aldehyde from cyclopropyl acetate. We were also able to demonstrate that propionaldehyde itself is formed in the reaction by carrying out the hydrolysis in a specially designed apparatus which swept the aldehyde, as formed, into a dimedone solution before it condensed with itself. The dimedone derivative of propionaldehyde was isolated, although the yield was only 15%. When vinyl acetate was hydrolyzed in the same apparatus the dimedone derivative of acetaldehyde was formed in 85% yield.

At this point, then, we knew that cyclopropyl acetate was hydrolyzed normally by base, and, from kinetic indications, that the ring opening was not simultaneous with hydrolysis. The aldol product of propionaldehyde was the ultimate product of the reaction, but evidently not much was present as propionaldehyde since only 15% could be isolated in that form.

The next question to be answered was whether the ring opening of cyclopropanol was more or less rapid than the hydrolysis of the acetate. Since cyclopropanol is very soluble in water and boils at 101°, it was not thought practical at that time to attempt to isolate the alcohol. Instead, a further kinetic investigation was made of the rate of formation of 2-methyl-2-pentenal from propionaldehyde and from cyclopropyl acetate. From this study it was possible to deduce that the hydrolysis of cyclopropyl acetate leads directly to cyclopropanol, and that this alcohol is relatively stable to base, undergoing ring opening to propionaldehyde only slowly.

A number of investigators[14-15] have studied the aldol condensation of acetaldehyde with base, and have found that the rate is a complex function of the concentration of aldehyde. In concentrated solutions the rate of disappearance of acetaldehyde is first order in both aldehyde and base. On the other hand, in more dilute solutions (*ca.* 0.1 *M* in aldehyde) the reaction becomes second order in aldehyde while remaining first order in base. These experimental observations are rationalized by assuming that in concentrated solutions the rate-determining step is the formation of the enolate anion, while in dilute solutions the slow step is the subsequent condensation of this anion with a second molecule of acetaldehyde. There have been no studies reported on the aldol condensation of propionaldehyde.

With these facts in mind it was realized at the start of this portion of the study that it was improbable that a complete kinetic description of the transformation of cyclopropyl acetate to 2-methyl-2-pentenal could be obtained without a very involved study. Fortunately, a much simpler study was sufficient for our purposes.

The main complications in the study of the aldol condensation were circumvented by studies of the initial rates of formation of product before reversible reactions and polycondensations become of kinetic importance. By following the formation of product to the first few per cent reaction, a plot of a function of the concentration of 2-methyl-2-pentenal *vs.* time yielded a straight line whose slope m is the initial rate of formation of the product at a very nearly constant concentration of aldehyde and base. Since 2-methyl-2-pentenal shows strong absorption in the ultraviolet, and none of the starting materials have appreciable absorption, the rate was followed spectrophotometrically.

Although the kinetics of the aldol condensation are probably of mixed order (since good agreement over the entire range of concentrations studied was not obtained assuming either first- or second-order dependence in aldehyde), it is probable that the over-all process is first order in base, as is the case with acetaldehyde. *On this assumption*, the ratio of the initial rate of formation of aldol product (m) and the concentration of base is a function only of the propionaldehyde concentration. Thus, the quantity $m/[OH^-]$ in Tables III and IV is a direct measure of the rate of formation of 2-methyl-2-pentenal at a given propionaldehyde concentration or from cyclopropyl acetate.

TABLE III

RATE OF FORMATION OF 2-METHYL-2-PENTENAL FROM PROPIONALDEHYDE AND SODIUM HYDROXIDE

Aldehyde, moles/l. × 10^3	Base, moles/l. × 10^3	$m/[OH^-]$, sec.$^{-1}$ × 10^9
2.85	1.93	4300
1.43	3.98	2950
1.29	5.70	1750
0.86	7.60	770
1.62	174.0	1900

TABLE IV

RATE OF FORMATION OF 2-METHYL-2-PENTENAL FROM CYCLOPROPYL ACETATE AND SODIUM HYDROXIDE

Acetate, moles/l. × 10^3	Base, moles/l. × 10^3	$m/[OH^-]$, sec.$^{-1}$ × 10^9
1.85	180	21
0.88	22	8.2
0.44	44	3.8

It is immediately obvious from these tables that *the aldol product, 2-methyl-2-pentenal, is consistently formed 100 to 200 times more rapidly from propionaldehyde than it is from cyclopropyl acetate*, under conditions in which the acetate is extremely rapidly hydrolyzed. Consider the first entry in Table IV. From the concentrations and rate constant involved, it may be calculated that only 200 sec. is required for 99% of the acetate to be hydrolyzed. If the isomerization of cyclopropyl alcohol were simultaneous with, or a very fast reaction immediately after, hydrolysis of the acetate, the concentration of propionaldehyde would be, within a very short period, approximately 1.8×10^{-3} *M*. However, as can be seen from a comparison of Table III and IV, the rate of formation of aldol product is 100 to 200 times too slow for a solution of propionaldehyde of this concentration. Consequently, some intermediate must intervene between the ester and the aldehyde. This intermediate could only be cyclopropanol, and it is clear that this alcohol must have an appreciable lifetime in basic solution.

These kinetic results made it obvious that cyclopropanol was present in appreciable concentrations in these solutions, and that an isolation was practical.

(14) B. P. Bell and P. T. McTigue, *J. Chem. Soc.*, 2983 (1960).
(15) A. Brocke and R. Coelbert, *Bull. soc. chim. France*, 131 (1955).

Once it was known that the alcohol was quite stable, rather conventional schemes for its preparation were considered. The separation of the alcohol from water proved possible, but the great solubility and similarity in boiling point made this method a poor one. The use of lithium aluminum hydride in ether proved to be more feasible. The yield of cyclopropanol obtained by gas chromatography was 53% (see Experimental).

Cyclopropanol is a reactive colorless liquid, b.p. 100.5–101.0° with decomposition and odor of propionaldehyde. It is very hydroscopic and soluble in all organic solvents and in water. It readily forms alcohol derivatives and appears to be quite stable in the absence of acids and bases. When heated in carbon tetrachloride or chloroform at 80° in the presence of air it is rapidly converted to propionaldehyde.[16]

As a check on our previous kinetic experiments, pure cyclopropanol was dissolved in base and the rate of appearance of the aldol product was measured. This rate was the same as that observed from cyclopropyl acetate, demonstrating that the alcohol was indeed an intermediate in the hydrolysis of the ester. Other reactions of this alcohol will be reported in due course.

Experimental

Gas Chromatography.—All gas chromatographic analyses were performed on a Perkin–Elmer vapor fractometer Model 154C on a 2 m. × 15 mm. column of 30% Ucon LB550X on 60/80 firebrick.

Cyclopropyl Acetate.—Cyclopropyl acetate was prepared by the method of Emmons and Lucas.[6] An alternative synthesis by the method of Simmons and Smith[8] was unsuccessful. The ester was carefully purified by distillation and its purity checked by gas chromatography; b.p. 110.5–111.0° (740 mm.), n^{20}D 1.4084.

Cyclopropanol.—Lithium aluminum hydride (1.1 *M*, 35 ml., 0.0385 mole) in ether was added to a solution of 6.20 g. (0.0620 mole) of cyclopropyl acetate in 35 ml. of anhydrous ether at a rate to keep a gentle reflux. About 5 g. of sodium sulfate saturated with water was added to the mixture immediately after complete addition of the hydride. The ether solution was filtered and dried over anhydrous sodium sulfate. Solvent was removed by distillation through a 12-in. packed column. The residual liquid was shown by comparative retention times to contain ether, ethyl alcohol, and cyclopropanol. The retention time of cyclopropanol was longer and completely different from that of *n*-propyl, isopropyl, and allyl alcohol. Isolation as affected by preparative scale gas phase chromatography (g.p.c.) at 50° to give 1.9 g. (53%) of cyclopropanol, b.p. 100.5–102.0°, m.p. phenylurethan (CCl_4) 101.5–102.5°, reported[4] b.p. 100–103°, phenylurethan 101.5–102.0°.

Anal. Calcd. for C_3H_6O: C, 62.03; H, 10.41. Found: C, 61.60; H, 10.76.

Vinyl Acetate.—Eastman (practical grade) vinyl acetate was distilled just prior to use. The constant boiling center fraction had b.p. 72.5° (750 mm.), n^{20}D 1.3944.

Isopropenyl Acetate.—Matheson Coleman and Bell (practical grade) isopropenyl acetate was fractionally distilled. The constant boiling center fraction was used; b.p. 95.8° (740 mm.), n^{20}D 1.3993.

1-Cyclopentenyl Acetate.—1-Cyclopentenyl acetate was prepared by treating isopropenyl acetate and cyclopentanone using a catalytic amount of *p*-toluenesulfonic acid according to the method of Hagemeyer and Hull.[17] The center fraction from a reduced pressure fractional distillation was used; b.p. 77.5–78.0° (50 mm.), n^{20}D 1.4456.

1-Cyclohexenyl Acetate.—1-Cyclohexenyl acetate was prepared by treating cyclohexanone and acetic anhydride using a catalytic amount of sulfuric acid. Repeated fractional distillations at reduced pressure gave the acetate containing a 3% impurity (g.p.c.) of cyclohexanone, b.p. 68.5–69.0° (12 mm.), n^{20}D 1.4532.

Cyclopentyl Acetate.—Cyclopentanol (Eastman Kodak White Label) was esterified with acetic anhydride in pyridine. Fractionation at reduced pressure gave a constant boiling middle fraction, b.p. 50.0° (13 mm.), n^{20}D 1.4305.

***n*-Butyl Acetate.**—Matheson Coleman and Bell commercial *n*-butyl acetate was fractionated and a constant boiling middle fraction was taken; b.p. 125° (740 mm.), n^{20}D 1.3955.

Preparation of 2-Methyl-2-pentenal.—2-Methyl-2-pentenal was prepared according to the procedure of Doebner and Weissenborn.[18] A fractional distillation gave the pure product in 37% yield, b.p. 134.0–135.5°, n^{20}D 1.4487.

Isolation of a Crystalline Derivative of Propionaldehyde, an Intermediate in the Hydrolysis of Cyclopropyl Acetate.—Propionaldehyde released during the alkaline hydrolysis of cyclopropyl acetate was captured by condensation with 5,5-dimethylcyclohexa-1,3-dione (dimedone) in a special apparatus. The apparatus consists of a glass cylinder (2 × 10 cm.) with a disk base constructed of sintered glass, through which purified nitrogen could be passed at a rapid rate. Two side arms were provided near the top of the cylinder through which solutions could be injected by means of a syringe. The top of the cylinder was connected to two gas wash bottles. The glass cylinder reaction vessel was thermostated at 48° in a constant temperature bath containing 0.2% aqueous dimedone solutions. With a syringe, 0.010 ml. of cyclopropyl acetate was injected into 5 ml. of 0.15 *N* sodium hydroxide in the glass cylinder at 15-min. intervals until 0.050 ml. had been added; 1 ml. of 0.75 *M* sodium hydroxide was then added and five more injections of 0.010 ml. of the ester were then made at 15-min. intervals. During the injections and for an additional 8 hr. afterward, nitrogen was bubbled through the glass cylinder and wash bottles at a rate of 50 ml./min. The gas bottles were stoppered and allowed to stand 2 days. The white crystals that precipitated were filtered to give 0.035 g. (15%) of the dimedone derivative of propionaldehyde, m.p. 154.5–155.0°, reported[19] m.p. 154–156°.

This experiment was repeated using vinyl acetate instead of cyclopropyl acetate. An 85% yield of the dimedone derivative of acetaldehyde was obtained.

Rates of Hydrolysis of Acetates by Conductometry. Conductivity Water.—Conductivity water with a specific conductance less than 2.5×10^{-6} mho as measured in the c nductivity cell was prepared by passing distilled water through a column of mixed anion–cation resin (Amberlite MB-300).

Conductance Apparatus.—A cell of the type described by Jones and Ballinger[20] was used with two modifications; only one opening was provided for filling, and a capillary gas inlet in the base was added in order to flush the cell with purified nitrogen. The cell was cleaned with hot concentrated sulfuric–nitric acid mixture before each run. The conductivity bridge was of commercial design manufactured by Industrial Instruments, Inc., Model RClB 60 cycle.

Sodium Hydroxide Solutions.—Since the sodium hydroxide solutions used in this study were very dilute, absorption of carbon dioxide became a serious problem. The base solution was freshly prepared before each kinetic run using the following technique. A capillary tube was filled with sodium by forcing the tube into a freshly cut piece of the metal. The tube was then dropped, under a nitrogen atmosphere, into a volumetric flask filled with conductivity water. The base was standardized by transferring an aliquot into excess standard hydrochloric acid and back titrating the excess with dilute sodium hydroxide, all titrations being carried out under an atmosphere of purified nitrogen.

Kinetic Measurements.—Two flasks containing the sodium hydroxide solution and conductivity water were equilibrated in a constant temperature bath. The bath was equipped with an NBS thermometer and a refrigeration unit with a built-in thermoregulator manufactured by Wilken–Anderson Co. Ester solutions of definite concentration were prepared by weighing the ester into S-shaped capillary tubes. The tube was dropped into the flask containing the equilibrated conductivity water and crushed by a glass rod extending through a rubber stopper. The contents of the flask were shaken until dissolution of the ester and the flask was returned to the bath. The conductance cell

(16) C. H. DePuy, G. M. Dappen, and J. W. Hausser, *J. Am. Chem. Soc.*, **83**, 3156 (1961).

(17) H. S. Hagemeyer and D. C. Hull, *Ind. Eng. Chem.*, **41**, 2920 (1949).

(18) O. Von Doebner and A. Weissenborn, *Ber.*, **35**, 1144 (1902).

(19) "Tables for Identification of Organic Compounds," supplement to Handbook of Chemistry and Physics, Chemical Rubber Publishing Co., Cleveland, Ohio, 1960.

(20) G. Jones and G. M. Ballinger, *J. Am. Chem. Soc.*, **53**, 411 (1931).

was then flushed with purified nitrogen and 4.94 ml. of ester solution was transferred to the conductivity cell with a calibrated pipet. Timing was started when one-half of the base was added from a 2.42-ml. fast delivery pipet. Zero-time resistance values, obtained before each run, were determined by carrying out the above procedure with the exclusion of ester. Infinity-time resistance values were obtained from independent measurements of standard solutions of sodium acetate. These values agreed within 2% for those reactions carried to infinite time.

Treatment of Kinetic Data.—The integrated second-order rate equation was used in calculating the rate constant

$$k_2 t = \frac{2.303}{C^0_{\text{ester}} - C^0_{\text{NaOH}}} \log \frac{C^0_{\text{NaOH}} C^t_{\text{ester}}}{C^0_{\text{ester}} C^t_{\text{NaOH}}} \quad (3)$$

where C^0_{ester} and C^t_{ester} are the concentrations of the ester at zero and time t, respectively; C^0_{NaOH} and C^t_{NaOH} are the concentration of sodium hydroxide at zero and time t, respectively. Term C^t_{NaOH} is calculated from the resistance [$C^t_{\text{ester}} = C^0_{\text{ester}} - (C^0_{\text{NaOH}} - C^t_{\text{NaOH}})$]. It is assumed that the reciprocal of the resistance is proportional to the concentration of dissolved electrolyte, where δ is a proportionality constant.

$$1/R = \delta_x C_x \quad (4)$$

In a solution containing sodium acetate and sodium hydroxide at any time, t

$$\frac{1}{R} = \delta_b C^t_{\text{NaOAc}} + \delta_a C^t_{\text{NaOH}} \quad (5)$$

where δ_b and δ_a are the proportionality constants calculated from the slope obtained from a plot of $1/R$ *vs.* concentration of sodium acetate and sodium hydroxide, respectively. Substituting the equality, $C^0_{\text{NaOH}} = C^t_{\text{NaOH}} + C^t_{\text{NaOAc}}$, in eq. 5, and after rearranging terms, eq. 6 was obtained.

$$C^t_{\text{NaOH}} = \frac{1}{ab}\left(\frac{1}{R} - \delta_b C^0_{\text{NaOH}}\right) \quad (6)$$

Thus the concentration of sodium hydroxide at any time during the run was calculated from the resistance.

Rates of Formation of 2-Methyl-2-pentenal by Treatment of Propionaldehyde, Cyclopropyl Acetate, and Cyclopropanol with Sodium Hydroxide Solution.—Standard solutions of propionaldehyde (cyclopropyl acetate, cyclopropanol) in water were prepared by weighing the material into S-shaped capillary tubes which were then dropped into volumetric flasks, filled to the mark with conductivity water, and crushed with a glass rod. After equilibration in an air-conditioned room at 20 + 2°, aliquots of base and aldehyde (cyclopropyl acetate and cyclopropanol) were mixed, the timer was started, and a solution of the reaction mixture was transferred to a stoppered quartz Beckman cell. Absorbance of the solution from 3000 to 2000 Å. was recorded at various intervals on a Cary Model 14 recording spectrophotometer. The absorption maximum at 2355 (ϵ 17,700) was used to calculate the amount of 2-methyl-2-pentenal formed. Rate constants were subsequently calculated from this.

Reaction solutions containing high hydroxide concentration (*ca.* 0.1 *M*) were diluted before obtaining the spectrum.

Infinity points were obtained by sealing aliquots of base and propionaldehyde (cyclopropyl acetate and cyclopropanol) in tubes and placing them in an 80° bath for 2 days. At the end of this period the tubes were opened, contents diluted, and spectra obtained. Approximately 80–85% of the theoretical yield of 2-methyl-2-pentenal was obtained as calculated from the absorption maximum at 2355 Å. 2-Methyl-2-pentenal was shown to be stable in 0.2 *M* sodium hydroxide under the above conditions.

[CONTRIBUTION FROM COATES CHEMICAL LABORATORIES, LOUISIANA STATE UNIVERSITY, BATON ROUGE, LA.]

Acid-Catalyzed Rearrangements of Medium Ring Cycloalkene Glycols[1]

BY JAMES G. TRAYNHAM AND PEGGY M. GREENE

RECEIVED FEBRUARY 14, 1964

Acid-catalyzed rearrangements of some medium ring cycloalkene glycols have been investigated with the intent of assessing the carbonium ion nature of intermediates formed in these reactions. Complex mixtures of products, resembling those formed in acid-catalyzed hydrolyses of cyclooctene oxides and strongly suggestive of a carbonium ion mechanism, are obtained from *cis*- and *trans*-cyclooctene glycols. Unlike cyclononene oxide and cyclodecene oxide, however, *cis*-cyclononene glycol and *cis*-cyclodecene glycol rearrange predominantly to the corresponding cycloalkanone (40 and 51% yields, respectively). Because nine- and ten-membered rings usually exhibit maximum tendencies for transannular processes in carbonium ion reactions, carbonium ion mechanisms are not believed to be of major importance in the pinacolic transformations of these glycols. The suggestion is made that (at least to the extent that ketone formation occurs) neighboring hydrogen migration coincides with departure of a water molecule from the protonated glycols, and substantial carbonium ion character never develops at the migration terminus.

Medium ring compounds exhibit a number of features which set them apart from other cyclic and acyclic compounds,[2] and we have found them useful in studies designed to unveil details of reaction mechanisms. Different kinds of intermediates (or transition states) can lead to different kinds of products to an extent seldom matched in other systems.[3] Reaction courses seem to be particularly sensitive to carbonium ion character in intermediates.[3] We have undertaken an extensive investigation of rearrangement reactions of 2-substituted cycloalkanols, which presumably could react through 2-hydroxycycloalkyl cations, and report here initial investigations of acid-catalyzed rearrangements (pinacolic transformations) of some cycloalkene glycols.

Pinacol (2,3-dimethyl-2,3-butanediol) undergoes acid-catalyzed rearrangement to pinacolone by a carbonium ion process,[4] and tertiary glycols in general appear to react in this fashion. Rearrangements of pinacols, olefin oxides, and amino alcohols of corresponding structure are presumed to be closely related processes.[5] In fact, the oxide, glycol, halohydrin, and amino alcohol derivatives of tetramethylethylene all give equivalent

(1) (a) We gratefully acknowledge the partial support of this research by Grant G14461 from the National Science Foundation. (b) Presented in part at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963. (c) Taken in part from the M.S. thesis submitted by P. M. G., Jan., 1964.

(2) For two recent reviews, see: (a) V. Prelog and J. G. Traynham in "Molecular Rearrangements," P. de Mayo, Ed., John Wiley and Sons, Inc.–Interscience Publishers, New York, N. Y., 1963, Chapter 9; (b) J. Sicher in "Progress in Stereochemistry," Vol. 3, P. B. D. de la Mare and W. Klyne, Ed., Butterworths, London, 1962, Chapter 6.

(3) For example, see J. G. Traynham and W. C. Baird, Jr., *J. Org. Chem.*, **27**, 3189 (1962).

(4) C. A. Bunton, T. Hadwick, D. R. Llewellyn, and Y. Pocker, *Chem. Ind.* (London), 547 (1956); *J. Chem. Soc.*, 403 (1958).

(5) Y. Pocker, ref. 2a, Chapter 1.