The results of a more quantitative study using phosphorus pentoxide and *p*-toluenesulfonic acid as catalysts are summarized in Table I.

2-Methoxy-*p*-oxathiane (V) was prepared by a modification of the procedure previously described.[2] Dimethyl-(2-hydroxyethylthio)-acetal (prepared from 7.5 moles of monothioglycol) was not distilled but treated directly with 105 ml. of methanolic hydrogen chloride. The acidified reaction product was protected from moisture and allowed to stand overnight. The product was then neutralized with anhydrous potassium carbonate. There was obtained 734 g. (72.3%) of V; b.p. 57° (5 mm.) or 85° (20 mm.), n^{23}_D 1.4911.

Anal. Calcd. for $C_5H_{10}O_2S$: C, 44.75; H, 7.51. Found: C, 44.85; H, 7.48.

***p*-Oxathiene** (I).—In a distilling flask fitted with a 5-inch column packed with glass helices was placed 102 g. (0.76 mole) of 2-methoxy-*p*-oxathiane and one gram of P_2O_5. The mixture was heated slowly to 160° and held at this temperature as long as methanol distilled (about five hours). The residue was then distilled at reduced pressure to give 58.6 g. (76%) of *p*-oxathiene, b.p. 54° (20 mm.), $n^{20.7}_D$ 1.5357, and 18.6 g. of unchanged starting material, b.p. 81° (20 mm.).

Anal. Calcd. for C_4H_6OS: C, 47.03; H, 5.92. Found: C, 47.18; H, 6.25.

Reaction of *p*-Oxathiene with Methanol.—A solution of 16.05 g. of *p*-oxathiene in 25 ml. of anhydrous methanol was cooled to 0° and 3 drops of 7 *N* methanolic hydrogen chloride was added. The mixture was allowed to warm to room temperature, and was maintained at this temperature for 20 hours. During this time the reaction mixture was protected from all sources of moisture. The mixture was then heated at the reflux temperature for five minutes, cooled and made alkaline with methanolic sodium methoxide. Distillation of the product gave 18.33 g. (87%) of product boiling at 85° (20 mm.), n^{23}_D 1.4915–1.4910.

This product had an infrared absorption spectrum identical to that shown for V; furthermore, it was easily converted[1] to 2-hydroxyethylthioacetaldehyde 2,4-dinitrophenylhydrazone (m.p. and mixed m.p. with that obtained from V[1] was 74–75°).

The Hydrolysis of *p*-Oxathiene.—A solution containing 0.80 g. (0.0097 mole) of 2,4-dinitrophenylhydrazine, 4 ml. of concd. sulfuric acid, 6 ml. of water and 20 ml. of ethanol was added to a solution containing 1.0 g. (0.0097 mole) of *p*-oxathiene in 41 ml. of ethanol. The resulting solution was allowed to stand for 24 hours, 7 ml. of water was added and the resulting solution was allowed to stand at 0° for 70 hours. The crude hydrazone was filtered, washed with water and allowed to dry (wt. 0.96 g., m.p. 65–71°). An additional 0.19 g. (m.p. 67–71°) was obtained from the filtrate by the addition of 25 ml. of water. The hydrazone was purified by several recrystallizations from ethanol–water, m.p. 74–75°.

An identical experiment using 0.0097 mole of V gave 1.29 g. of crude hydrazone (m.p. 65–71°). The pure hydrazone (m.p. 74–75°) obtained from V did not depress the melting point of the hydrazone obtained from I.

The reaction of I with hydrogen peroxide was carried out in the usual manner using acetone as the solvent. When the reaction mixture was added to ice, no precipitate was formed. The resulting mixture was extracted with methylene chloride, and a small quantity of white solid was obtained from the organic layer. The solid was purified by sublimation (m.p. 91°); however, it did not have the composition calculated for the sulfone or sulfoxide of I. The structure of this product is undetermined.

Anal. Found: C, 48.48; H, 8.21.

The Reaction of I with 2,4-Dinitrobenzenesulfenyl Chloride.—A solution of 1.4 g. (0.006 mole) of the sulfenyl chloride and 1.44 g. (0.014 mole) of I in 30 ml. of glacial acetic acid, was heated for 20 minutes on a steam-bath. The reaction mixture was cooled, poured upon 100 g. of ice and the yellow precipitate was collected. The precipitate turned to a gum which gave orange needles (m.p. 144–148°, 75% yield) from 95% ethanol. The product melted at 148–149° after recrystallization from 95% ethanol.

Anal. Calcd. for $C_{12}H_{12}O_7N_2S_2$: C, 40.00; H, 3.36. Found: C, 40.20; H, 2.91.

MINNEAPOLIS 14, MINN. RECEIVED OCTOBER 19, 1951

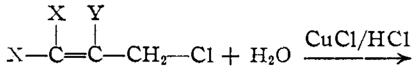
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS]

Allylic Chlorides. XVI. Copper(I) Chloride Catalyzed Acid Hydrolysis of the 1,3-Dichloropropenes Containing Cl^{36} [1]

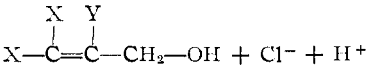
BY LEWIS F. HATCH, LEON O. MORGAN AND VIRGIL L. TWEEDIE[2]

Both *cis*- and *trans*-1,3-dichloropropene containing radioactive chlorine have been prepared and shown to be labeled exclusively in the allylic position. The rate of copper(I) chloride catalyzed acid hydrolysis has been determined with each isomer at 40° and also with the *cis* isomer at 60°. Complete hydrolysis of either isomer gave chloride ion in solution corresponding to 100% removal of one chlorine atom from the 1,3-dichloropropene molecule. From the *trans* isomer approximately 10% of the vinylic chlorine was removed during the reaction; from the *cis* isomer 17% of the vinylic chlorine appeared as chloride ion in solution. A rapid exchange reaction occurred between the labeled allylic chlorine atom and the inactive chloride ion of the hydrolytic medium. It was shown that the vinylic chlorine of the dichloride became partially labeled during the hydrolysis reaction. A reaction mechanism is presented.

In studies concerning the relative reactivities and geometrical configuration of certain allylic chlorides the copper(I) chloride acid hydrolysis has been a useful and interesting reaction.[3] With monochloro compounds unambiguous results were obtained in following the extent of hydrolysis by titration of the chloride ion produced in solution during the course of the reaction.



$$X-\overset{X}{\overset{|}{C}}=\overset{Y}{\overset{|}{C}}-CH_2-Cl + H_2O \xrightarrow{CuCl/HCl}$$



$$X-\overset{X}{\overset{|}{C}}=\overset{Y}{\overset{|}{C}}-CH_2-OH + Cl^- + H^+$$

However, when the allylic compounds under study contained both allylic and vinylic chlorine atoms (X or Y was chlorine), there arose a question as to the source of chloride ion being titrated.[4] In the present investigation this difficulty has been resolved for the copper(I) chloride acid hydrolysis of the 1,3-dichloropropenes through the use of radioactive chlorine to label the allylic position.

Both *cis*- and *trans*-1,3-dichloropropene containing Cl^{36} in the allylic position ($CHCl{=}CH{-}CH_2Cl^{36}$) were prepared by treatment of the corresponding 3-chloro-2-propen-1-ols with radioactive

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(1) Presented in part at the 118th Meeting of the American Chemical Society, Chicago, Ill., September, 1950.

(2) Research Corporation Fellow 1949–1950.

(3) L. F. Hatch, A. N. Brown and H. P. Bailey, THIS JOURNAL, **72**, 3198 (1950).

(4) L. F. Hatch and S. G. Ballin, *ibid.*, **71**, 1041 (1949).

hydrogen chloride in the presence of zinc ion. A 35–65% mole excess of chloroalcohol was used to force the reaction toward completion; it also served as solvent. The 3-chloro-2-propen-1-ol recovered from this reaction was found to be non-radioactive, indicating that no exchange had taken place between the vinylic chlorine of the chloroalcohol and the radioactive chlorine.

The labeled 1,3-dichloropropenes were shown to contain radioactive chlorine exclusively in the allylic position by the preparation of non-radioactive 3-chloro-2-propenyl 3,5-dinitrobenzoates from these dichlorides and silver 3,5-dinitrobenzoate. The silver chloride recovered from these preparations exhibited all the radioactivity originally possessed by the labeled 1,3-dichloropropenes.

Initially in the copper(I) chloride catalyzed acid hydrolyses of the labeled 1,3-dichloropropenes the concentration of labeled chloride ion in solution rose rapidly at the expense of unlabeled chloride ion. As the hydrolysis proceeded the appearance of labeled chloride ion in solution approached a maximum of 80–90% of that originally present in the 1,3-dichloropropenes (based upon one chlorine atom). The total formation of chloride ion in solution did not exceed, beyond the limits of probable experimental error, a value corresponding to 100% removal of one chlorine atom from the 1,3-dichloropropene molecule. The difference in the concentrations of total chloride ion and of labeled chloride ion represented the extent of removal of inactive vinylic chlorine from the 1,3-dichloropropenes. The results of the hydrolysis of labeled *cis*-1,3-dichloropropene at 60° and at 40° are presented in Fig. 1.

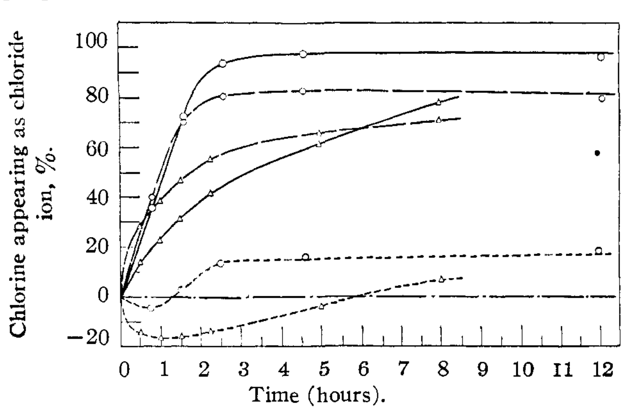

Fig. 1.—Copper(I) chloride catalyzed acid hydrolysis of *cis* $CHCl{=}CHCH_2Cl^{36}$: ○, 60°; △, 40°; —, total chloride ion; — —, labeled chloride ion; inactive chloride ion.

Hydrolysis of labeled *trans*-1,3-dichloropropene at 40° gave data similar to those for the *cis* isomer at 60°. The over-all hydrolysis data are in agreement with those obtained for unlabeled 1,3-dichloropropenes at 40° and at other temperatures.[3,5] Attempts to hydrolyze the vinylic chlorine from unlabeled 3-chloro-2-propen-1-ols under similar conditions at 40° showed that less than 1% appeared as chloride ion in solution.

Portions of the chloroalcohols produced during the hydrolysis of labeled 1,3-dichloropropenes were isolated and found to obtain some radioactive chlorine. Thus, the vinylic chlorine of the 3-chloro-2-propen-1-ols was found to have been partially labeled during the hydrolytic reaction.

As a possible explanation of these results there is shown in Fig. 2 a mechanism which is in agreement with the experimental observations.

It has been postulated that the catalytic effect of the copper(I) chloride on this hydrolytic reaction results from an enhancement of the ionization of the 1,3-dichloropropene by the formation of an association complex involving the copper(I) chloride–chloride ion complex and the carbon–carbon double bond of the allylic chloride system.[6,7] Resonance would contribute to the ease of formation and the stability of the carbonium ion (II and III). The principal product of the hydrolytic reaction is known to be 3-chloro-2-propen-1-ol.

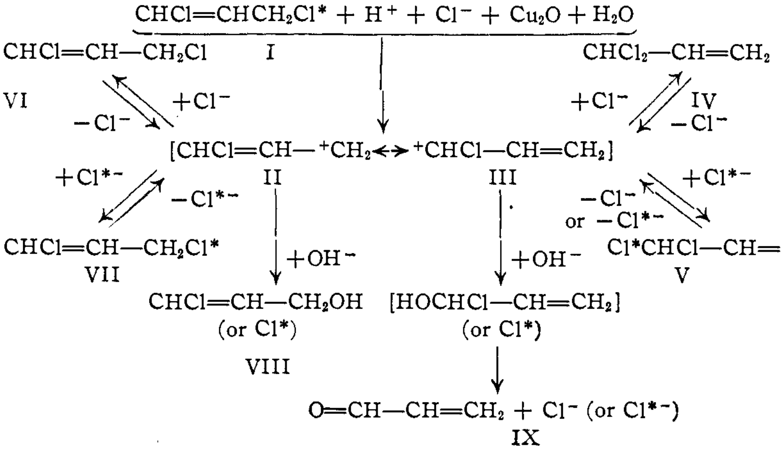

Fig. 2.—Proposed mechanism of hydrolysis and exchange reactions.

The rapid increase of labeled chloride ion in solution during the early stages of the reaction is believed attributable to exchange between inactive chloride ion from the hydrochloric acid hydrolysis medium and the radioactive allylic chlorine atom of I through II to form VI. Were not the hydrolytic reaction in competition with the exchange reaction, it would be expected that under these conditions, which initially involved approximately equal molar quantities of labeled 1,3-dichloropropene and inactive chloride ion, the exchange reaction would yield 1,3-dichloropropene having half its original radioactivity and chloride ion in solution of like activity.

As the reaction proceeds and the concentration of labeled chloride ion increases with respect to that of unlabeled chloride ion in solution, the probability of exchange to produce VI and VII (or I) becomes approximately equal as does the probability of formation of IV and V. IV and VI are synionic

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[5] L. F. Hatch and G. B. Roberts, THIS JOURNAL, **68**, 1196 (1946).

[6] L. F. Hatch and R. R. Estes, *ibid.*, **67**, 1730 (1945).

[7] R. M. Keefer and L. J. Andrews, *ibid.*, **71**, 1723 (1949).

mesomers, as are V and VII. Kirrmann, Pacaud and Dosque[8] have observed that in metathetical reactions, such as those with sodium acetate, with diethylamine or with sodium ethoxide, IV forms the same derivatives as VI only at a slower rate. Thus, the exchange reactions involving II, III and V, which are probably rapid with respect to the rate of hydrolysis to form VIII, account for the appearance of unlabeled chloride ion in solution and the production of partially labeled VIII. Formation of IX probably occurs to a slight extent but this cannot account for any appreciable amount of the inactive chloride ion in solution since the total hydrolysis would be substantially above 100% on the basis of removal of one chlorine atom from the molecule of 1,3-dichloropropene.

Acknowledgment.—The authors wish to express appreciation to both the Research Corporation, New York, and the Defense Research Laboratory, The University of Texas, for their financial assistance in support of this investigation.

Experimentation

Radioactive Chlorine.—Chlorine isotope, Cl^{36}, (Isotopes Division, U. S. Atomic Energy Commission, Oak Ridge, Tenn.) was used as a tracer. This isotope is reported[9] to have a half-life of 4.5×10^5 years and to decay by beta radiation having a maximum energy of 0.64–0.66 Mev. For this investigation the labeled chlorine was diluted with carrier chlorine to an approximate specific activity of 150 counts per minute per milligram of chlorine (c./min./mg. Cl) with the counting arrangement employed. It was prepared as dry potassium chloride for the generation of radioactive hydrogen chloride.

Preparation of the Labeled 1,3-Dichloropropenes.—The apparatus for the preparation of the labeled 1,3-dichloropropenes from the corresponding chloroalcohols was constructed entirely of glass and consisted essentially of a hydrogen chloride generator, a 100 ml.-reaction vessel equipped with a stirrer, thermometer, gas inlet tube, condenser, and a trap system for recovery of unreacted hydrogen chloride.

The *cis*- and *trans*-3-chloro-2-propen-1-ols used in the preparation of the labeled 1,3-dichloropropenes were obtained by sodium carbonate hydrolysis[10] of *cis*- and *trans*-1,3-dichloropropene (Shell Chemical Corp.).

In a typical experiment 8.86 g. (0.24 mole) of labeled hydrogen chloride, generated slowly over an 11-hour period by dropping sulfuric acid onto dry potassium chloride of known specific activity, was passed into a stirred mixture of 31.7 g. (0.34 mole) of 3-chloro-2-propen-1-ol and 0.40 g. (0.0047 mole) of zinc oxide at 70 ± 5°. Unreacted hydrogen chloride was swept from the system with a stream of dry nitrogen into a water trap for recovery. The reaction mixture was poured into 25 ml. of water and extracted several times with small portions (3–5 ml.) of ether. The extract, after drying over sodium sulfate, was fractionated on a 15-inch Vigreux column under reduced pressure. Based on hydrogen chloride the conversion was 73% and the yield 71% of labeled *cis*-1,3-dichloropropene, $n^{25}D$ 1.4651 (lit.[11] $n^{25}D$ 1.4652). In a similar manner the labeled *trans*-1,3-dichloropropene, $n^{25}D$ 1.4710 (lit.[11] $n^{25}D$ 1.4712), was prepared; conversion based on hydrogen chloride was 76%, yield 68%.

For the purpose of radioactivity assays and chlorine analyses, the labeled 1,3-dichloropropenes and recovered 3-chloro-2-propen-1-ols were decomposed by the Chablay[12] method.

Characterization of the Labeled 1,3-Dichloropropenes.—A solution of 1.6 g. (0.005 mole) of silver 3,5-dinitrobenzoate in 6 ml. of dry pyridine was prepared by adding the dry salt slowly with stirring to the pyridine at room temperature. To this solution 0.56 g. (0.005 mole) of the 1,3-dichloropropene was added and the mixture maintained at 60° for 30 minutes. The reaction mixture was poured into 25 ml. of water, ether extracted, and centrifuged to remove the silver chloride which was then taken up in ammonia water for radioactivity assay. The ether extract was washed successively with dilute acid, dilute potassium carbonate solution and finally with water. The ether was evaporated and the derivative crystallized from ethanol–water. Repeated recrystallizations of the benzoate from ethanol–water produced white crystals, plates melting at 80.5–81° from the *trans* isomer and needles melting at 66.0–66.5° from the *cis* isomer.

Compound	Chlorine, % Calcd.	Chlorine, % Found	Specific activity, Calcd. (from KCl)	c./min./mg. Cl Found
cis-$CHCl{=}CHCH_2Cl$	63.90	64.0	92	85.3
trans-$CHCl{=}CHCH_2Cl$	63.90	64.1	60	57.8
cis-$CHCl{=}CHCH_2OH$	38.32	37.8	..	0.2
trans-$CHCl{=}CHCH_2OH$	38.32	38.4	..	0.05

The crystalline benzoates and the silver chloride recovered from their preparation were assayed for radioactivity. The benzoates were decomposed by the Chablay method.

SPECIFIC ACTIVITY, C./MIN./MG. CL

	cis isomer	*trans* isomer
Calcd., of allylic chlorine of 1,3-dichloropropene	171	116
Found, of AgCl	173	111
Found, of benzoate	0.03	0.2

Copper(I) Chloride Catalyzed Acid Hydrolyses.—The apparatus and procedure previously described for similar studies[4] were used with only slight modifications. Because of the limited amounts of labeled dichlorides, it was necessary to use half the usual quantities in the hydrolytic reactions; the size of the reaction vessel was reduced accordingly. The materials used in each hydrolysis run were: 0.1250 g. (0.00175 mole) of copper(I) oxide (Baker C.P. Analyzed, 98.8%); 50 ml. of 1.5% hydrochloric acid (0.0195 mole) (standardized against sodium carbonate); 2.220 g. (0.020 mole) of labeled 1,3-dichloropropene. To retard oxidation of copper(I) ion an atmosphere of nitrogen was maintained over the hydrolytic solution.

At the end of a predetermined time the entire amount of reaction mixture, without cooling, was transferred quantitatively into a liter volumetric flask containing 70 ml. of 10% sodium carbonate solution and diluted to volume. Aliquots of this diluted reaction mixture were used for total chloride ion determination by the Mohr procedure and for radioactivity assay. The results of the hydrolysis of labeled *trans*-1,3-dichloropropene at 40° are shown in Table I; those of the labeled *cis*-isomer at 40° and at 60° in Fig. 1.

TABLE I

PER CENT. REMOVAL WITH TIME OF LABELED AND INACTIVE CHLORINES FROM *trans*-1,3-DICHLOROPROPENE DURING COPPER(I) CHLORIDE HYDROLYSIS

Time, hr.	Total chlorine, %	Labeled chlorine, %	Inactive chlorine (total less labeled), %
0.5	36	48	−12
1.0	55	54	1
2.5	89	86	3
3.5	98	89	9
4.5	101	90	11
12.0	99	90	9

Radioactivity of 3-Chloro-2-propen-1-ols from Labeled 1,3-Dichloropropenes.—The chloroalcohols produced in the hydrolyses of labeled 1,3-dichloropropenes were recovered by azeotropic distillation from the diluted reaction mixture and ether extraction of the distillate. The alcohols were then converted to benzoate derivatives by warming with 3,5-dinitrobenzoyl chloride. The recrystallized benzoates

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[8] A. Kirrmann, Pacaud and H. Dosque, *Bull. soc. chim.*, [5] **1**, 860 (1934).

[9] C. S. Wu, C. H. Townes and L. Feldman, *Phys. Rev.*, **76**, 692 (1949).

[10] L. F. Hatch and A. C. Moore, THIS JOURNAL, **66**, 285 (1944).

[11] L. F. Hatch and R. H. Perry, Jr., *ibid.*, **71**, 3262 (1949).

[12] E. Chablay, *Ann. chim.*, (Ser. 9), **1**, 510 (1914).

were decomposed by the Umhoefer[13] method to obtain the vinylic chlorine atom as chloride ion for radioactivity assay.

1,3-Dichloropropene isomer hydrolyzed and conditions	*cis* isomer 5 hr., 40°	*cis* isomer 8 hr., 40°	*trans* isomer 10.5 hr., 40°
Calcd. specific activity of allylic chlorine of 1,3-dichloropropene	120	120	116
Specific activity of chlorine in 3-chloro-2-propenyl 3,5-dinitrobenzoates	4.7	9.8	7.5

Radioactivity Assays.—The radiochemical assays of the various materials containing chlorine were made by determination of the amount of radiation from silver chloride spread on 25.0-mm. watch glasses of uniform curvature. The silver chloride counting plates were prepared in the following manner. A quantity of chloride ion solution, calculated from titration data to contain 6.3 mg. of chlorine, was measured accurately into a 15-ml. graduated centrifuge tube, acidified with 6 *N* nitric acid, and the chloride ion precipitated by addition of 2–3 ml. of 1 *N* silver nitrate solution. The mixture was centrifuged, the supernatant liquid removed, the precipitate washed with water, centrifuged and the washings discarded. The silver chloride was then peptized in 3 ml. of 0.02% gelatin solution using a motor driven platinum wire stirrer. The peptized silver chloride was transferred quantitatively in small portions to a 25.0 mm. watch glass, previously brought to constant weight, and dried in an oven at 100–105°. After cooling, the spread of silver chloride was covered with a collodion film, weighed, and stored in darkness until counted.

This technique of plate preparation has given reproducible results within 1–2%. Losses in radioactivity resulting from deterioration of the sample by light over a period of several days were negligible. The distribution of silver chloride on the plate appeared to be the primary factor influencing the precision of counting. The specific activities of various samples as determined from counting rates were found to vary directly, within the limits of experimental error, with the isotopic composition of the sample and were not influenced by variation of 20% in the total weight of the sample.

A Tracerlab TGC-2 Geiger tube with a mica end-window of less than 2 mg./cm.^{2} thickness, mounted in a lead shield, was used with a Tracerlab "64" Scaler (Tracerlab, Inc., Boston, Mass.) for all radioactivity measurements. The relative counting rates of all samples were determined in exactly the same position with respect to the Geiger tube, which gave a counting geometry of approximately 9%. The expected instrumental and standard statistical error under these conditions was less than 1%.

AUSTIN, TEXAS RECEIVED AUGUST 9, 1951

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[13] R. R. Umhoefer, *Ind. Eng. Chem., Anal. Ed.*, **15**, 383 (1943).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF WASHINGTON]

The Aromatic Elimination Reaction. II. The Mechanism of the Acid-catalyzed Deacylation of Aromatic Ketones[1]

BY W. M. SCHUBERT AND H. K. LATOURETTE[2]

The rate-determining step in the reaction of 2,6-dimethylacetophenone and acetomesitylene with strong sulfuric acid to yield the aromatic hydrocarbon and acetic acid was found to be a first order decomposition of the conjugate acid of the ketone. Taking into account the appreciable ionization of the ketone, the expression, $\log k + H_0 - \log([B]/([B] + [BH^+])) =$ const., was derived and found to hold over a wide range of acid concentration. The *p*Ka of 2,6-dimethylacetophenone was found to be −7.8. The deacylation step for acetomesitylene was 66 times as fast as that for 2,6-dimethylacetophenone.

The aromatic elimination reaction, which can be looked upon as an example of electrophilic aromatic substitution, may be represented crudely by the equation

$$ArX + Y^+ \longrightarrow ArY + X^+$$

A common example of the aromatic elimination reaction is aromatic deacylation, in which X is an acyl group and Y^+ is a proton. The deacylation reaction was discovered by Louise,[3] who found that benzoylmesitylene upon treatment with hot phosphoric acid yielded mesitylene and benzoic acid. In a more extensive study, Klages and Lickroth[4] found that acylbenzenes having at least one ortho alkyl substituent were cleaved in boiling sirupy phosphoric acid to the aromatic hydrocarbon and the fatty acid. If no bulky ortho alkyl substituent were present, cleavage of the acylbenzene did not occur. More recently, Arnold and Rondestvedt[5] were able to bring about deacetylation of 9-acetyloctahydroanthracene and 4-acetylhydrindacene in boiling sirupy phosphoric acid.

In order to elucidate the mechanism of deacylation and gain further insight into electrophilic aromatic elimination and substitution, the deacylation was quantitatively studied. The ketones used were 2,6-dimethylacetophenone and acetomesitylene (2,4,6-trimethylacetophenone). They were found to deacetylate readily in strong sulfuric acid at or near room temperature. The formation of acetic acid in the deacylation afforded a ready means of measuring the rate of reaction, since a method of determining concentration of acetic acid in the presence of a large excess of sulfuric acid had already been reported.[6]

Experimental

Preparation of Materials.—Acetomesitylene prepared by the method of Adams and Noller[7] was purified by fractional distillation, b.p. 100–102° (7 mm.), n^{20}D 1.5155. The method of De Jong[8] was used to convert 2,6-dimethylbenzoyl chloride to 2,6-dimethylacetophenone, b.p. 117–118° (26 mm.), n^{28}D 1.5120.

Solutions of 72.5 to 96% sulfuric acid were prepared by dilution of C.P. concentrated sulfuric acid. The 100% sulfuric acid was prepared by mixing appropriate amounts of concentrated and fuming sulfuric acid. The strength of each acid solution was determined by titration against standard alkali of an aliquot portion of a diluted sample of the acid.

Technical grade methanesulfonic acid was dried by continuous azeotropic distillation with a mixture of equal parts

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[1] For paper I in this series see THIS JOURNAL, **71**, 2639 (1949).

[2] Abstracted in part from the Ph.D. thesis of H. K. Latourette, University of Washington, 1951.

[3] E. Louise, *Ann. chim. phys.*, [6] **6**, 206 (1885).

[4] A. Klages and G. Lickroth, *Ber.*, **32**, 1549 (1899).

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[6] D. N. Craig, *Bur. Standards J. Research*, **6**, 169 (1931).

[7] R. Adams and C. R. Noller, THIS JOURNAL, **46**, 1892 (1924).

[8] P. De Jong, *Rec. trav. chim.*, **61**, 539 (1942).