Three additional recrystallizations from 60–90° ligroin gave an analytical sample of pure *cis*-α-**phenylcrotonic acid**, m.p. 98.5–100°.

Anal. Calcd. for $C_{10}H_{10}O_2$: C, 74.05; H, 6.22. Found: C, 74.25; H, 6.55.

Fractions 10–13 were treated as indicated above for fractions 2–7. Evaporation of the ether gave 0.17 g. (10.5%) of cream colored solid, m.p. 120–131°. Recrystallization from 60–90° ligroin gave 0.13 g. (8.03%) of tiny cream-white crystals, m.p. 134–136.5° (lit.[25] m.p. 135°). The infrared spectrum was identical with that of an authentic sample of *trans*-α-phenylcrotonic acid and showed no significant contamination by the *cis* isomer by the absence of strong bands at 12.80 μ (781.3 cm.$^{-1}$) and 11.70 μ (854.7 cm.$^{-1}$). Fractions 8 and 9 were mixtures containing mainly the *cis*- and *trans*- acids, respectively.

In the present work we tentatively assign structure Va to the compound m.p. 98.5–100° on the basis of method of synthesis (*cf.* the other cases examined here wherein both labile and stable acids have long been known), greater acidity and lesser rate of esterification (see below) compared with its isomer, m.p. 134–136.5°.

Separation of the *cis*-acid was also possible by a modification of the method of Sudborough and Lloyd.[16] A solution of 0.58 g. (78%) of a crude mixture of the *cis* and *trans* isomers obtained from 0.96 g. of IIIa in 5 ml. of a 3% solution of hydrogen chloride gas in commercial absolute methanol was allowed to stand at room temperature for 1.75 hours and then poured into water. Extraction of the precipitated material into ether followed by extraction of the ether solution with several portions of 1 *M* sodium bicarbonate solution served to remove the *cis*- acid from the majority of the *trans*-methyl ester. After acidification and isolation of the crude *cis*-acid (0.45 g., m.p. 88–92°) by means of ether the crude solid was again added to 5 ml. of 3% hydrogen chloride in methanol and allowed to stand for one hour at room temperature. Working up as before gave 0.4 g. (53.9%) of the *cis*-acid, m.p. 92–96° (softening at 88°). Recrystallization from 90–120° ligroin gave 0.26 g. (35%) of snow-white flakes, m.p. 94–98°.

Conversion of 3,4-Diphenyl-4-chloro-2-pyrazolin-5-one (IIIc) to *cis*- and *trans*-α-Phenylcinnamic Acids.—The initial reaction was carried out essentially as indicated above for the corresponding 3-methyl-4-phenyl derivative using 0.01 mole of the pyrazolone. However when fractions 12–14 were reached it appeared that the calculated amount of acid was no longer being extracted. Since the separation point had been passed, the extraction was completed with three 10-ml. portions of 1 *M* bicarbonate. Evaporation of the ether extracts of fractions 2–8 gave 1.0 g. (44.6%) of cream-white crystals, m.p. 123–131° (softening at 100°). Recrystallization from nitromethane gave 0.8 g. (35.7%) of yellow-cream crystals, m.p. 137–139° (lit.[26] m.p. 136–137°).

Fraction 10 and the following were combined and worked up as usual giving 0.39 g. (17.4%) of cream-white crystals, m.p. 160–167° (softening at 155°). Recrystallization from nitromethane gave 0.33 g. (14.7%) of cream colored needles, m.p. 173.5–175° (lit.[26] m.p. 170–172°).

Conversion of 3-Phenyl-4-methyl-4-chloro-2-pyrazolin-5-one to *cis*- and *trans*-α-Methylcinnamic Acids.—The initial reaction of 0.01 mole of the halopyrazolone with alkali was carried out essentially as indicated for the 3-methyl-4-phenyl derivative except that after acidification of the reaction mixture and extraction into ether the mixed acids were then extracted together from the ether solution into about six 20-ml. portions of 1 *M* sodium bicarbonate solution. The bicarbonate extracts were then acidified and the mixed acids again taken into ether and the ether solution then fractionally extracted as: 1–5, 0.05 *M* sodium bicarbonate; 6–10, 0.10 *M* sodium bicarbonate; 11–15, 0.05 *M* sodium bicarbonate; 16–19, 0.10 *M* sodium bicarbonate.

Finally the extraction was completed with four 10-ml. portions of 1 *M* sodium bicarbonate solution. Evaporation of the ether extracts of fractions 5–10 left a slightly oily solid which was dried on a clay plate; 0.45 g. (27.8%) of m.p. 60–85°. Recrystallization from ligroin (60–90°) gave 0.35 g. (21.6%) of well-formed cream-colored crystals, m.p. 86–91°. A second recrystallization gave 0.3 g., m.p. 90–92° (lit.[10] m.p. 91–92°). Evaporation of the ether extracts of fractions 12–20 gave a cream-colored solid which was dried on a clay plate; amount 0.18 g. (11.1%), m.p. 76–79.5° (softening at 74°). Recrystallization from ligroin (60–90°) gave 0.14 g. (8.6%) of tiny cream-colored crystals, m.p. 79–80.5° (lit.[10] m.p. 81–82°).

AMHERST, MASS.

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[25] H. Gilman and S. A. Harris, THIS JOURNAL, **53**, 3541 (1931).

[26] M. Bakunin, *Gazz. chim. ital.*, **27**, II, 48 (1897).

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY]

A Novel Elimination of Acetyl Chloride

BY R. K. SUMMERBELL AND HANS E. LUNK

RECEIVED AUGUST 29, 1957

At temperatures below 200°, 2-chloro-3-acyl-*p*-dioxanes (I) decompose to form acid chlorides and *p*-dioxanone. A mechanism is proposed for this reaction. The reaction of 2,3-dichloro-*p*-dioxane with anhydrous formic acid at 170° serves as a convenient laboratory synthesis for *p*-dioxanone. 2-Acetoxy-3-chlorotetrahydropyran does not pyrolyze in a manner similar to the 2-chloro-3-acyl-*p*-dioxanes, but eliminates acetic acid at about 200°.

Discussion

In the course of an investigation concerned with the stereochemistry of 2,3-disubstituted *p*-dioxanes, we were interested in obtaining examples of isomeric pairs of esters of *p*-dioxane-2,3-diol. Several methods of preparation of individual isomers of these compounds are described in the literature. Boeseken and co-workers[1] treated *trans*-2,3-dichloro-*p*-dioxane[2] with potassium acetate or lead acetate in acetic acid and obtained a 2,3-diacetoxy-*p*-dioxane, m.p. 104–105°, of unknown configuration. Another method of preparation is described by Slagh,[3] who treated various acids with *trans*-2,3-dichloro-*p*-dioxane in inert solvents such as toluene and xylene at reflux temperature to prepare the corresponding esters, and claims to have obtained a diacetate having a m.p. of 79°. Hoping that this compound would prove to be the second isomer of 2,3-diacetoxy-*p*-dioxane, we have repeated the work. However, the only compound obtained in several runs was the 2,3-diacetoxy-*p*-dioxane, m.p. 104–105°, identical with that obtained by the method of Boeseken.[1] The treatment of *p*-dioxene with hydrogen peroxide in *t*-butyl alcohol, followed by acetylation of the dihydroxy compound with acetic anhydride and pyridine, resulted likewise in

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[1] J. Boeseken, F. Tellegen and P. Cohen Henriquez, THIS JOURNAL, **55**, 1284 (1933).

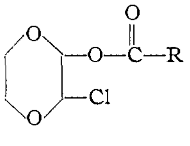
[2] R. K. Summerbell and Hans E. Lunk, *ibid.*, **79**, 4802 (1957).

[3] Harold R. Slagh, U. S. Patent 2,164,355.

the formation of the known 2,3-diacetoxy-*p*-dioxane, m.p. 104–105°.

When *trans*-2,3-dichloro-*p*-dioxane was treated with *p*-chlorobenzoic acid in xylene solution according to the method described by Slagh,[3] there was obtained a considerable amount of *p*-chlorobenzoic anhydride. We decided to investigate this unanticipated reaction.

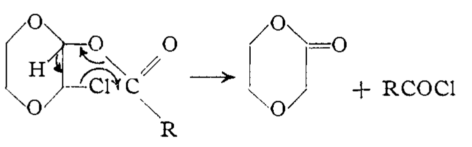
Esters of *p*-dioxane-2,3-diol are relatively stable, distillable compounds, and their decomposition to give an anhydride seemed improbable. For example, 2,3-diacetoxy-*p*-dioxane was recovered unchanged after heating to 160° for five hours. It was suspected that the intermediate 2-chloro-3-*p*-chlorobenzoöxy-*p*-dioxane (Ia) could be responsible for the formation of the anhydride.



Ia, R = *p*-C_6H_4Cl
Ib, R = CH_3
Ic, R = H

On the assumption that this reaction might be general for compounds of structure I, the simpler 2-chloro-3-acetoxy-*p*-dioxane (Ib) was chosen for further investigations. This compound, a colorless liquid, was prepared from acetic acid and an excess of *trans*-2,3-dichloro-*p*-dioxane. When Ib was heated to 150°, a reaction started which at 180–200° became fast enough to cause a slow, continuous distillation of acetyl chloride, identified by its reaction with aniline to give acetanilide. The residue of the pyrolysis reaction was distilled under vacuum, yielding a colorless liquid which solidified in the cold room. The solid melted originally at 27°, but during the next few weeks the melting point gradually rose to about 80°. This peculiar behavior became understandable when the product was identified as *p*-dioxanone by its reaction with phenyl magnesium bromide to give the known α,α-diphenyldiethylene glycol,[4] followed by ring closure to give 2,2-diphenyl-*p*-dioxane.[4] The melting point of *p*-dioxanone varies widely depending on the previous history of the sample and the resulting degree of polymerization.

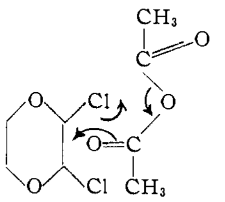
The products of the reaction thus being established as acetyl chloride and *p*-dioxanone, the reaction may be pictured as proceeding by a concerted mechanism



The interaction of the acid chloride with unreacted acid from the starting material would explain the formation of the anhydride observed in the case of *p*-chlorobenzoic acid. Indeed, we were able to isolate *p*-dioxanone from the products of the reaction of *p*-chlorobenzoic acid with *trans*-2,3-dichloro-*p*-dioxane.

An extension of this new reaction is a convenient laboratory synthesis of *p*-dioxanone, namely, the treatment of *trans*-2,3-dichloro-*p*-dioxane with anhydrous formic acid at 170°. At this temperature, the intermediate 2-chloro-3-formoxy-*p*-dioxane (Ic) should be unstable and decompose immediately to give *p*-dioxanone, carbon monoxide and hydrogen chloride. A 75% yield of *p*-dioxanone was obtained, and the reaction is probably the method of choice for laboratory scale preparations of *p*-dioxanone.

The reactions are presumably initiated by the attraction of the halogen atom by the partial positive charge on the carbonyl carbon. Intramolecular reactions as above have the advantage of the two reacting groups continuously being in a favorable position, but under proper conditions similar reactions of intermolecular nature might be expected. We have treated *trans*-2,3-dichloro-*p*-dioxane with acetic anhydride at reflux temperature and obtained acetyl chloride and 2,3-diacetoxy-*p*-dioxane, m.p. 104–105°. The crude product is of higher purity than that obtained by us from other preparations. A possible mechanism for the reaction is



It appears that the elimination of acid chloride requires a halogen activated as in α-chloroethers. When 2-acetoxy-3-chlorotetrahydropyran, prepared from 2,3-dichlorotetrahydropyran and acetic acid, was heated to 190°, the products of the reaction were acetic acid and 3-chlorodihydropyran rather than acetyl chloride and δ-valerolactone. The configuration of the 2-acetoxy-3-chlorotetrahydropyran is not known, but the question is of little importance as far as this reaction is concerned, since at the pyrolysis temperature the compound should be easily isomerized to the more stable form. The surprisingly low elimination temperature apparently is the result of the electron-donating abilities of the α-ether oxygen. A similar case can be found in the pyrolysis of α-alkyl substituted acetates, where the ease of elimination is in the order tertiary > secondary > primary.[5]

Acknowledgment.—We wish to thank the Hercules Powder Co. for a fellowship held by H. E. L.

Experimental

Hydroxylation of *p*-Dioxene with Hydrogen Peroxide.—The method was adapted from a procedure described by Hurd and Kelso[6] for the hydroxylation of dihydropyran. *p*-Dioxene (17.2 g., 0.2 mole) and 1 ml. of osmium tetroxide catalyst[7] were placed in a three-necked flask. Under stirring, 130 ml. of an approximately 6% solution of hydrogen peroxide in *t*-butyl alcohol[7] was added while the temperature was kept below 20° by outside cooling with ice. The mixture was allowed to stand overnight at room temperature. Then the solvent was evaporated under reduced pressure, the bath temperature being kept below 60°. After addition of 50 ml. of pyridine, 75 ml. of acetic anhydride was added dropwise under stirring and cooling. The temperature was maintained at 10–15° by adjusting the rate

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[4] I. P. Settle, M.S. Thesis, Northwestern University, 1950.

[5] C. D. Hurd and F. H. Blunck, THIS JOURNAL, **60**, 2419 (1938).

[6] C. D. Hurd and C. D. Kelso, *ibid.*, **70**, 1484 (1948).

[7] N. A. Milas and S. Sussman, *ibid.*, **58**, 1302 (1936).

of addition. Then 30 ml. of 75% ethyl alcohol was added to the reaction product, and the mixture was allowed to stand at room temperature for several hours. Solvent and excess reagent were evaporated, and the residue was distilled at 1 mm. pressure. There was obtained 8.1 g. (20%) of material, b.p. 105–107° (1 mm.), m.p. after recrystallization from ethyl ether 104–105°. The infrared spectrum was identical with that of 2,3-diacetoxy-*p*-dioxane.

Formation of *p*-Chlorobenzoic Anhydride in the Reaction of *p*-Chlorobenzoic Acid with *trans*-2,3-Dichloro-*p*-dioxane.—A mixture of 25 g. (0.16 mole) of *p*-chlorobenzoic acid, 25 g. (0.16 mole) of *trans*-2,3-dichloro-*p*-dioxane and 60 ml. of xylene was refluxed for 14 hours. The 16 g. of solid material which separated on cooling to −10° was dissolved in ether, washed with sodium bicarbonate, and dried with calcium chloride. After evaporation of the solvent, the residue was recrystallized several times from ethyl acetate with use of Norite. The product was identified by its melting point (194°) and combustion analysis as *p*-chlorobenzoic anhydride.

In another run, 50 g. of *p*-chlorobenzoic acid, 50 g. of *trans*-2,3-dichloro-*p*-dioxane and 120 ml. of xylene were heated to 142–144° for 20 hours. After cooling, the precipitate was filtered, and the filtrate was distilled *in vacuo*. The highest boiling fraction, b.p. 87–88° (12 mm.), gave 0.8 g. of a colorless solid material after standing in the cold room. It was identified as *p*-dioxanone by comparison of its infrared spectrum with that of an authentic sample.

Preparation of 2-Chloro-3-acetoxy-*p*-dioxane.—A solution of 320 g. (2.05 moles) of *trans*-2,3-dichloro-*p*-dioxane, 90 g. (1.5 moles) of acetic acid and 400 g. of toluene was gently refluxed for eight hours. The solvent was then evaporated under reduced pressure. A careful fractionation through a 20-inch glass packed column yielded 142 g. (53% based on acetic acid) of a colorless liquid, b.p. 78–80° (0.1 mm.).

Anal. Calcd. for $C_6H_9O_4Cl$: C, 39.91; H, 5.02. Found: C, 39.96; H, 5.06.

The possibility of the compound being an equimolar mixture of 2,3-dichloro-*p*-dioxane and 2,3-diacetoxy-*p*-dioxane was excluded by examination of the three infrared spectra. After hydrolysis, 2-chloro-3-acetoxy-*p*-dioxane gave a precipitate with 2,4-dinitrophenylhydrazine, which decomposed at approximately 325° (2,4-dinitrophenyl osazone of glyoxal). Furthermore, a mixture of 8.8 g. (0.049 mole) of 2-chloro-3-acetoxy-*p*-dioxane, 10 g. of finely powdered silver acetate and 150 ml. of toluene was shaken for 20 hours. The precipitate of silver chloride was filtered and the volume of the filtrate was reduced to 30 ml. Cooling in ice caused the precipitation of 7.2 g. (74%) of a solid which melted at 104° and was identified by its infrared spectrum as 2,3-diacetoxy-*p*-dioxane.

Pyrolysis of 2-Chloro-3-acetoxy-*p*-dioxane.—In a distilling flask fitted with a Vigreux column, 50 g. (0.28 mole) of 2-chloro-3-acetoxy-*p*-dioxane was heated to 190°. Within 1.5 hours, a colorless liquid distilled, with a b.p. rising slowly from 50 to 100°. On redistillation, 15.2 g. of material, b.p. 50–51°, was obtained. The distillation of the residue of the pyrolysis reaction through an alkali-rinsed column yielded 22 g. (71%) of a colorless liquid, b.p. 104–107° (16 mm.), which solidified in the cold room. It is important that the distilling apparatus be free from acid as otherwise a polymer is obtained.

Identification of the Pyrolysis Products.—The lower boiling product of the pyrolysis reaction (b.p. 50–51°) was identified as acetyl chloride by its reaction with aniline to give a compound, m.p. 114°, which was not depressed on admixture of an authentic sample of acetanilide.

The higher boiling product in its monomeric form was treated with a phenylmagnesium bromide solution according to the procedure of Settle.[4] There was obtained a 69% yield of α,α-diphenyldiethylene glycol, m.p. 108–109°, which was converted to 2,2-diphenyl-*p*-dioxane, m.p. 120°, by treatment with hydrogen chloride in benzene solution according to the method described by Settle.[4] The melting point of this derivative was low until it had been recrystallized from aqueous methyl alcohol containing a large amount of Norite. The latter probably absorbed unreacted starting material.

A New Method of Preparation for *p*-Dioxanone.—In a reaction flask equipped with stirrer, dropping funnel, condenser and thermometer. 100 g. (0.64 mole) of *trans*-2,3-dichloro-*p*-dioxane was heated to 170°. Over a period of two hours, 25 ml. of anhydrous formic acid (95%) was added. The mixture was kept at 170° for another hour until no more hydrogen chloride developed, and finally heated to 200° for 10 minutes. Distillation of the product through an alkali-rinsed Vigreux column yielded 48 g. (75%) of material, b.p. 55–56° (0.3 mm.). The infrared spectrum was identical with that of *p*-dioxanone from other preparations.

Reaction of 2,3-Dichloro-*p*-dioxane with Acetic Anhydride.—*trans*-2,3-Dichloro-*p*-dioxane (15.7 g., 0.1 mole) and acetic anhydride (20 ml., 0.2 mole) were refluxed for 20 hours. Distillation of the reaction product gave 9 g. of material, b.p. 50–75° (mainly acetyl chloride) and about 4 ml. of material, b.p. 40–50° (15 mm.) (unreacted acetic anhydride). When the residue was seeded with 2,3-diacetoxy-*p*-dioxane, crystallization occurred, yielding 9.8 g. (48%) of relatively pure compound, m.p. 104°, after one recrystallization.

In another experiment, 7.8 g. (0.05 mole) of *cis*-2,3-dichloro-*p*-dioxane 2 and 20 ml. (0.2 mole) of acetic anhydride were heated to 100° for 20 hours. After working up, there was obtained 3.8 g. (37%) of 2,3-diacetoxy-*p*-dioxane, m.p. 104°, identical with the product isolated from the above experiment.

Preparation of 2-Acetoxy-3-chlorotetrahydropyran.—2,3-Dichlorotetrahydropyran was prepared by addition of chlorine to dihydropyran according to the procedure of Paul.[8] A solution of 86 g. of 2,3-dichlorotetrahydropyran (0.52 mole) and 31 g. (0.52 mole) of glacial acetic acid in 100 ml. of toluene was refluxed for 24 hours. After removal of the solvent under reduced pressure, the main fraction distilled at 60–61° (0.3 mm.), yield 49 g. (51%), $n^{20}D$ 1.4797.

Anal. Calcd. for $C_7H_{11}O_3Cl$: C, 47.07; H, 6.21. Found: C, 47.31; H, 6.11.

Pyrolysis of 2-Acetoxy-3-chlorotetrahydropyran.—2-Acetoxy-3-chlorotetrahydropyran (9.6 g., 0.054 mole) was placed in a small flask fitted with a short Vigreux column and condenser. The flask was heated to 190° until a colorless liquid distilled. The temperature of the oil-bath slowly was raised to 210° to maintain a continuous slow distillation yielding 8.3 g. of material, b.p. 115–150°. It was dissolved in ether, extracted several times with sodium carbonate solution, and dried with calcium chloride. The residue after evaporation of the solvent gave 4.2 g. of a liquid, b.p. 140–142° (760 mm.), $n^{20}D$ 1.4756; b.p. and refractive index were in agreement with the literature values for 3-chlorodihydropyran.[8] The infrared spectrum was identical with that of a sample prepared by the procedure of Paul.[8]

In another experiment the distillate was redistilled and collected in two fractions: 1. 110–124°, mostly acetic acid; 2. 124–143°, mostly 3-chlorodihydropyran.

Fraction 1 was neutralized and treated with an ethanolic solution of *p*-nitrobenzyl chloride. The precipitate melted at 78° as reported for *p*-nitrobenzyl acetate.

EVANSTON, ILLINOIS

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(8) R. Paul, *Compt. rend.*, **218**, 122 (1944).