NOTES

dride) react at hydrogen fluoride reflux temperature fast enough for this to be used as a preparative method at atmospheric pressure. The higher homologous acid anhydrides (with the exception of benzoic anhydride) need higher temperatures and, consequently, super-atmospheric pressures. The acyl chlorides, however, react at -10 to $+5^{\circ}$ rapidly and smoothly, thus allowing the halogen exchange to proceed at atmospheric pressure.

Such a preparation of acetyl fluoride is inconvenient, of course, as its boiling point is very similar to that of hydrogen fluoride. It is, therefore, obvious that the two types of starting materials complement one another. It was found possible to apply the reaction of acid anhydrides with anhydrous hydrogen fluoride to mixed anhydrides; this method was found to be extremely useful in the preparation of formyl fluoride.⁶ By carrying out the reaction at atmospheric pressure, with continuous removal of the low boiling formyl fluoride, it was possible to make the reaction go entirely in this direction.



A 61% yield of formyl fluoride was obtained, with a minimum formation of acetyl fluoride.

EXPERIMENTAL

The acyl fluorides were analyzed by gas chromatography and infrared spectroscopy. A Perkin-Elmer Model 154C Vapour Fractometer, having as column material a silicone high vacuum grease and a Perkin Elmer Model 221 infrared spectrograph with sodium chloride optics and silver chloride cells were used. As comparative standards, acyl fluorides described by us but prepared by known methods' were used. The yields, however, as shown in Table I, are those obtained in preparative scale experiments and represent the amount of isolated acyl fluoride and *not* VPC data. All operations were carried out with the usual precautions to exclude moisture.

Reaction of acid anhydrides with anhydrous hydrogen fluoride. Into 2.0 moles of the corresponding acid anhydride, 45 g. (2.25 moles) anhydrous hydrogen fluoride was added. The additon was carried out at approximately -10° with stirring by means of a Teflon covered magnetic stirrer. The mixture was kept at this temperature for an hour. It was then allowed to warm to room temperature and left standing for 2 hr. The mixture was then treated with 15 g. of anhydrous sodium fluoride to remove excess hydrogen fluoride, and distilled. Operations involving anhydrous hydrogen fluoride were performed in fused silica or plastic equipment. Plastic materials used included polyethylene, polypropylene, Teflon, and Kel-F.

Reaction of acyl chlorides with anhydrous hydrogen fluoride. Into 2.0 moles of the corresponding acyl chloride, kept at -5° to 0°, a continuous stream of anhydrous gaseous hydrogen fluoride was introduced at a rate of approximately 1 g./min. for 1 hr. It is also possible to carry out the reaction by adding the required amount of anhydrous liquid hydrogen fluoride to the stirred, cold acyl chloride. The reaction was then allowed to warm to room temperature and was kept there for 2 hr. To remove excess hydrogen fluoride, the reaction mixture was treated with dry sodium fluoride, filtered, and distilled.

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Oxidation of Olefins by Thallium Compounds

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Olefins have long been known to form complexes with various metallic compounds,¹ particularly those of platinum (II), mercury (II), palladium (II), and silver (I). In the case of mercury, a further reaction occurs in which the mercury compound adds across the double bond. For example, in glacial acetic acid, ethylene and mercuric acetate react as follows:²

$$C_2H_4 + Hg(OAc)_2 \longrightarrow AcOC_2H_4HgOAc$$
 (1)

Under certain conditions it is possible to effect an oxidation of the olefin, producing an inorganic mercurous salt and the oxidized carbon compound.³ For example, in moderately strong ($\sim 2M$) nitric acid solution, mercuric nitrate and 2-pentene react as follows:^(3a)

$$CH_{3}CH = CHC_{2}H_{5} + 2Hg^{++} \longrightarrow CH_{3}COC_{3}H_{7} + 2Hg^{+} + 2H^{+} (2)$$

Lead (IV), which is isoelectronic with mercury (II), has also been reported to oxidize olefins, both to carbonyl compounds⁴ and also to glycol derivatives.⁵ This report describes a similar reaction of olefins with a third isoelectronic species, thallium (III). The reaction of thallium (III) solutions with both ethylene and 2-hexene was investigated, and both carbonyl products and glycols or their esters were obtained. The thallium was meanwhile completely reduced to thallium (I).

In nitrate solutions, the highest yield of ethylene glycol obtained was about 32% of the ethylene consumed. The yield of nonvolatile carbonyl com-

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pounds was estimated from the amount of 2,4dinitrophenylhydrazone formed and was about 6% in this case. In the sulfate system the corresponding figures were 45% and 3%. Solutions of thallium (III) chloride reacted only slowly with ethylene, while acetate solutions appeared not to react at all. Acetaldehyde was formed in all cases as evidenced by its odor, but very little was found in the solution. It was suspected that further oxidation of acetaldehyde by thallic ion occurred and a separate experiment was carried out involving thallic sulfate and acetaldehyde. This oxidation proceeded more slowly than that of ethylene, but it was possible to show by means of spot tests and infrared spectra the presence of acetate and glycolate among the products. These same products were also found to occur in the oxidation of ethylene.

In the reaction between 2-hexene and thallium (III) acetate in acetic acid-water media the main products were acetate esters, principally the monoester, of hexane-2,3-diol, yields of which varied with the water content of the medium. With water contents of 2%, 10%, and 25% by volume the yields of esters were roughly 40%, 30%, and 7%, based on the thallium (III). Two per cent water corresponds to about one mole of water per mole of thallium, and in this experiment a trace of 2-hexanone was found. In the other two experiments substantial amounts of 2-hexanone were found.

The stoichiometry of the reaction between olefins and thallium (III) appears to be expressed by the equations

$$RCH = CHR' + Tl^{+++} + 2H_2O \longrightarrow$$

RCHOHCHOHR' + Tl^+ + 2H^+ (3)
$$RCH = CHR' + Tl^{+++} + H_2O \longrightarrow$$

RCOCH₂R' + Tl^+ + 2H^+ (4)

for the formation of glycols and ketones, respectively. It seems reasonable to suppose that the first step in these reactions is the formation of a thallium-olefin complex, similar to that occurring in the mercury-olefin system.² Upon reaction with a base, this complex forms an alkyl-thallium ion which, because of the strong oxidizing properties of thallium (III), decomposes, giving a carbonium ion:

$$\begin{array}{c} \text{RO} & \text{RO} \\ \hline & & & \\ Tl^{++} \\ I, R = H \\ II, R = CH_{*}CO \end{array}$$
(5)

In aqueous media species I (R = H) will exist, and can, among other possibilities, pick up a hydroxyl ion or water molecule at the positive carbon to become a glycol. It can also lose a proton from the carbon bearing the hydroxyl group to become first an enol, then an aldehyde (or ketone):

This mechanism is in accord with the formation of both glycol and acetaldehyde in the oxidation of ethylene. A similar mechanism has been proposed for the reaction of lead (IV) with olefins.⁶

This mechanism can also be applied to the formation of a monoacetate glycol ester in acetic acid media, in which case the product of reaction 5 is II ($\mathbf{R} = CH_3CO$). The reactions of carbonium ions of type II have been studied by Winstein,⁶ who has shown that certain groups, such as acetate, are capable of a "bridging" effect, forming a carbonium ion of somewhat different nature (Equation 7). The C-O bonds of the ultimate glycol are already formed in the intermediate, and attack by a water molecule at the carboxyl carbon produces a monoacetate ester:



The extent to which reaction 5 produces II instead of I presumably depends upon the relative amounts of acetic acid and water in the system. Evidently, at the lowest water concentration reported here, the intermediate is almost entirely II, as judged by the absence of appreciable amounts of carbonyl compounds in the final products.

EXPERIMENTAL

Thallium solutions. c.P. grade thallium salts were obtained from Amend Drug Company, New York. To prepare solutions of thallium (III), a thallous compound (usually thallium chloride) was chlorinated in aqueous solution, and thallium hydroxide was precipitated by addition of sodium hydroxide. The hydroxide was then dissolved in the appropriate acid. For aqueous experiments this solution was used directly, and for experiments in acetic acid media the acetate solution was evaporated to dryness on a steam bath and taken up in glacial acetic acid.

Oxidation of ethylene. The reaction between ethylene and thallium (III) was carried out at ambient temperature in a constant-volume system, in which an atmosphere of ethylene was allowed to react with a stirred solution of a thallic compound, usually about 0.4M in thallium. In the nitrate and sulfate systems, absorption of ethylene occurred readily, 10 mmoles of thallium being completely reduced within a few hours. The reaction appeared to go most rapidly if sodium hydroxide were added to maintain the pH at the point of incipient precipitation of thallium hydroxide.

Oxidation of 2-hexene in glacial acetic acid. The oxidation of 2-hexene by thallium (III) acetate was carried out in glacial acetic acid. These experiments were performed using varying amounts of water in the system. The solutions were warmed gently for a few hours, which was sufficient to reduce the thallium completely.

Separation and determination of products. Thallium was first separated by addition of hydrochloric acid and filtration of insoluble thallium chloride. The determination of

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glycols was carried out by the periodate method' involving oxidation with excess periodate and determination of the residual periodate by addition of potassium iodide and titration with thiosulfate. This procedure also determines glyoxal and glycolaldehyde. In the ethylene experiments, where these compounds appeared to be present, a correction was made, based on the amount of 2,4-dinitrophenylhydrazone obtained. The latter compound was a reddish color, insoluble in most solvents, and melted above 300°. This description fits the glyoxal derivative, which is also obtained from glycolaldehyde. Infrared spectra of the residues obtained by evaporation of the water indicated the presence of glycolate and acetate salts. Oxalate, glyoxylic acid, formaldehyde, and formic acid were shown to be absent by chemical spot tests.⁸ In one experiment the ethylene glycol was isolated by evaporating the aqueous solution to dryness, leaching the residue with propanol to reject inorganic salts, and evaporating the alcohol. The infrared spectrum of the liquid residue was identical with that of ethylene glycol.

The products of oxidation of 2-hexene were isolated by dilution of the system with water and extraction with ether. or by distillation of the solvent followed by partition between ether and water. From the ether was obtained a sweet-smelling liquid, whose infrared spectrum exhibited a strong alcoholic hydroxyl band at 2.88 μ , and another band at 5.75 μ , characteristic of the ester carbonyl group.

This data suggested that the liquid was a monoacetate ester of hexane-2,3-diol, and further evidence of its identity was sought. Monoacetate esters of this type are produced during the reaction of olefins with peroxyacetic acid,⁹ and accordingly 2-hexene was oxidized by the procedure of Swern.¹⁰ The product was purified on a vapor chromatography column, and its infrared spectrum was obtained. It was compatible with designation as a monoacetate ester of hexane 2,3-diol. A product from the thallium oxidation was chromatographed also, and the major product was found to behave identically on the chromatography column with the standard sample. Its infrared spectrum was also identical with that of the standard. In both chromatograms lesser amounts of a second component were observed, whose infrared spectra indicated it to be the diacetate ester. Approximate yields of the total ester product were obtained from the weight of product and the approximate purity as determined from the chromatograms.

A portion of the monoacetate prepared by the peroxidation procedure was hydrolyzed by refluxing 2 hr. in 10% sodium hydroxide solution, and the hexane-2,3-diol was isolated by extracting with ether, drying and evaporating the ether. An ester product from the thallium oxidation procedure was hydrolyzed in the same manner. The infrared spectrum of this hydrolysis product indicated it to be hexane-2,3-diol.

No attempt was made to ascertain whether the monoacetate was the 3-ester or the 2-ester of hexanediol. This point does not appear to have been studied in the peroxidation procedure either, and the question of the identity of the "standard" monoacetate is still open as well.

The carbonyl product obtained in the oxidation of 2hexene in acetic acid was isolated from the distillate as the 2,4-dinitrophenylhydrazone, which was recrystallized from ethanol. It melted at 102-106°, compared to the literature values of 106° for the 2-hexanone derivative and 130° for the 3-hexanone derivative.

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Use of Cation Exchange Resins in Organic Reactions. I. The von Pechmann Reaction

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It has generally been the practice to use large quantities of concentrated sulfuric acid as a condensing agent in the preparation of hydroxycoumarins by the von Pechmann reaction, i.e. the condensation of phenols with malic acid or with β -keto esters.^{1,2} It has, however, been shown by Grieg-Gass¹ and Barris and Israelstam⁴ that such large amounts of acid are unnecessary, since comparable yields of coumarins are obtained by using relatively small quantities of acid. The use of cation exchange resins as condensing agents was therefore investigated and it has now been shown that certain hydroxycoumarins are readily formed in good yield in this reaction using such resins.

In recent years anion exchange resins have been used in organic reactions with some success.⁵⁻⁷ Apart from the use of cation exchange resins as hydrolytic agents, there have been very few applications of such resins in synthetic work.⁷⁻⁹

The cation exchange resins used in this work were Zeokarb 225 and Amberlite IR.120. These resins are resistant to high temperatures and can be used continuously at 100°, or at higher temperatures for short periods. The main advantages of cation exchange resins are that they may be recovered and used again and that they simplify the purification of the final product. Since β keto esters were found to be hydrolyzed by cation exchange resins, it is necessary to limit the weight of resin used, generally between 20 and 40% by

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