methylaniline, but was not homogeneous, for, on conversion into thiourea with phenylisothiocyanate as in the previous experiment, 1.6 g. of free bases gave about 0.3 g. of *sym.*-diphenylthiourea (corresponding to 0.12 g. of aniline), 1.5 g. of methyldiphenylthiourea (corresponding to 0.7 g. of methylaniline), and 0.2 g. of dimethylaniline was extracted from the residues by hydrochloric acid. The last product was identified by the deep yellow coloration produced by bleaching powder in acid solution.

The benzene mother liquor from the yellow oil left a residue of 2.7 g. on spontaneous evaporation, which consisted of a light yellow syrup containing a few drops of a non-miscible brownish oil, which did not dissolve when treated with water. This was extracted with ether (weight = 0.10 g.); it was not dimethylaniline as shown by color tests, but, on boiling with caustic soda, the white precipitate with barium chloride in acid solution indicated that it was unaltered dimethylsulfate. The water soluble portion of the above residue gave no precipitate with barium chloride until saponified with boiling alkali; the test for sulfate was then strong. Sodium hydroxide liberated 0.15 g. of oil which was identified, by its color reactions and also by conversion into *p*-nitrosodimethylaniline hydrochloride, as dimethylaniline.

The Action of One Molecular Proportion of Dimethylsulfate on Two Molecular Proportions of Aniline at 0°.—Three and five-tenths grams of of dimethylsulfate in 7 cc. of benzene were added to 5.2 g. of aniline (2 molecular proportions), in 21 cc. of benzene and the mixture allowed to stand for 16 hours in a refrigerator. The product, which was not oily, weighed 5.0 g. after standing for one week over concentrated sulfuric acid. This yield corresponds to 88% of the theoretical quantity, calculated from Ullmann's equation. The benzene mother liquor was a light brown color and contained no oil. This was allowed to stand for 8 hours at 0°; no oil deposited. A water extract of a portion of the now deep brown benzene solution gave a strong color test for methylaniline. After standing for several days at room temperature, only a trace of oil separated.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY.]

ACTION OF OXALYL CHLORIDE ON PRIMARY, SECONDARY AND TERTIARY ALCOHOLS.

BY ROGER ADAMS AND L. F. WEEKS.

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Staudinger,[1] who was the first to find a convenient method for the preparation of pure oxalyl chloride, studied several of its reactions. He found that it reacted normally with ethyl alcohol to give ethyl oxalate,

[1] *Ber.*, 41, 3558 (1908); 46, 1426 (1913); *Chem. Zentr.*, 1910, I, 307.

with ammonia and amines to give oxamides. He used it in certain Friedel and Craft's[1] syntheses in the hope of preparing 1,2-diketones, but obtained such compounds in only a few cases. In general, the reaction products were the same as he would have obtained if he had used phosgene. Thus, oxalyl chloride had broken down to phosgene and carbon monoxide before reacting. Staudinger[2] studied the action of oxalyl chloride in Friedel and Craft's reactions more carefully a few years later, and found that the speed of the reaction had much to do with the products which resulted; if a fairly active hydrogen was present in the benzene molecule, as the para hydrogen in anisol, then the reaction took place quickly, and anisil was produced; if unsubstituted benzene were used where there is no active hydrogen, then the oxalyl chloride decomposed first and benzophenone was produced. Liebermann[3] studied the action of oxalyl chloride with and without anhydrous aluminum chloride, on anthracene, ditolyl, indene, etc., and obtained similar results. If he used high temperatures and no aluminum chloride, products the same as those which would form from phosgene were produced, at low temperatures and in the presence of aluminum chloride diketones. In every case, however, the yields of the diketones were small.

The action of oxalyl chloride on mercaptans[4] gave thioesters and on aminoacids,[5] hydrazines,[6] ureas,[7] the normal oxalic acid derivatives in practically all cases, a few exceptions[8] being noted when oxalyl chloride acted like phosgene.

One other interesting and general reaction of oxalyl chloride was discovered by Staudinger[9] who noted the similarity of oxalyl chloride to certain inorganic acid chlorides. Various aldehydes and ketones reacted very readily with it, and gave good yields of products the same as those obtained with phosphorus pentachloride.

Sometime ago it was found in this laboratory,[10] that oxalyl chloride and pyridine reacted at low temperatures with phenols to give quantitative yields of the phenyl or substituted phenyl esters. It was observed, however, during this work, that if the reactions between certain of the phenols and oxalyl chloride were carried out at room or at higher temperatures,

[1] *Ber.*, **41**, 3558 (1908); **42**, 3485 (1909).

[2] *Ibid.*, **45**, 1594 (1912).

[3] *Ibid.*, **44**, 203, 852, 1453 (1911); **45**, 1186 (1912); **46**, 198 (1913).

[4] *J. Chem. Soc.*, **95**, 1904, 1909 (1909).

[5] *Chem. Zentr.*, **1911**, I, 1548; **1912**, II, 910; **1913**, II, 1739; THIS JOURNAL, **32**, 121 (1910).

[6] *Rec. trav. chim.*, **34**, 34 (1914).

[7] *Ber.*, **36**, 1404 (1913).

[8] *Chem. Zentr.*, **1910**, II, 931, 1422.

[9] *Ber.*, **42**, 3966 (1909).

[10] THIS JOURNAL, **37**, 2716 (1915).

dehydration products and not simple esters resulted. It seemed possible, therefore, that if oxalyl chloride were made to react with alcohols under the right conditions, it might act as a dehydrator and ethylene derivatives would results. Oxalyl chloride would be an especially good reagent for such a purpose, since all of the products of the reaction, except the unsaturated compound, would be gaseous. To test this we have taken different types of primary, secondary and tertiary alcohols and tried the action of oxalyl chloride on them. Different alcohols yielded different products, and although we have not yet studied a sufficient number so that a complete generalization may be made as to the exact reaction which will take place, we give below the results already in hand.

As characteristic primary alcohols, we chose *n*-propyl, isobutyl, isoamyl and benzyl alcohols, and allowed oxalyl chloride to act directly on them at room temperatures in the proportion of two molecules of alcohol to one of acid chloride. In each case, immediate reaction took place, and simple esters formed, just as Staudinger found with ethyl alcohol. The esters resulting were very pure and the yields were practically quantitative. For a rapid and convenient method of obtaining small amounts of pure oxalic acid esters of primary alcohols, the above is certainly to be recommended. We tried glycol also, and used the proportion one molecule of diatomic alcohol to one molecule of oxalyl chloride; the cyclic ester, ethylene oxalate, resulted.

For secondary alcohols, we studied benzhydrol, phenyl methyl carbinol and menthol. Benzhydrol in benzene solution gave a small yield of a white solid which proved to be benzhydryl ether. Phenyl methyl carbinol and menthol we treated without a solvent, and obtained in both cases as principal products the corresponding unsaturated compounds styrene and menthene. Small amounts of impure higher boiling products which formed in these last two reactions, we have not worked up, but the boiling points indicated that they were not the corresponding chlorides or oxalates. It was very possible, therefore, that in these instances some carbonates had formed. In general, the purity and yields of the products from the secondary alcohols were not very satisfactory. Possibly a change in conditions, however, might improve them.

For tertiary alcohols, we chose trimethyl carbinol, dimethylethyl carbinol, triphenyl carbinol and pinakone, and treated in each case (except with pinakone) two molecules of alcohol with one of chloride; with pinakone we used one molecule of alcohol to one of chloride. The triphenyl carbinol was dissolved in benzene, but no solvent was used with the others. Instantaneous reaction took place, and the first three yielded chlorides, oxalic acid separating out at the same time. Although the yields and the purity of the chlorides were not so extremely good as the yields and purity of the esters formed by the action of primary alcohols,

still they were very satisfactory. Pinakone reacted differently, as might be expected, since there is a great tendency here for water to split out and for a subsequent rearrangement into pinakoline. We were able to isolate two products, pinakoline and a solid which proved to be the corresponding carbonic acid ester. Here oxalyl chloride reacted like phosgene, and each chlorine atom then combined with a hydrogen atom of a hydroxyl group, yielding a cyclic carbonate.

In conclusion, our work has shown that oxalyl chloride reacts in several ways with alcohols. Primary alcohols go very smoothly to esters, most tertiary alcohols give good yields of chlorides, secondary alcohols and certain tertiary alcohols yield different types of products, dehydration products, such as ethers, or more generally, where such a reaction is possible, unsaturated compounds with small amounts of carbonic acid derivatives as secondary products.

We are now studying the action of oxalyl chloride and pyridine at low temperatures on different kinds of alcohols, and have already obtained oxalates with certain secondary alcohols. We hope this will be general with all alcohols, in which case, on account of the ease of formation at such a low temperature, the quantitative yields produced, and the ease with which the compounds produced, crystallize, we will show oxalyl chloride to be a convenient and valuable reagent for hydroxyl groups.

EXPERIMENTAL PART.

Primary Alcohols.

1. *N*-**Propyl Alcohol, Isoamyl Alcohol, Isobutyl Alcohol.**—In these experiments, a small boiling flask with the side arm attached to a condenser was used. The neck of the flask was fitted with a cork stopper holding a separatory funnel. The pure alcohols (2 mols), *n*-propyl, isobutyl or isoamyl, were placed in the flask and oxalyl chloride (1 mol) was allowed to drop very slowly from the funnel into the alcohol. The contents of the flask immediately heated up and fumes of hydrochloric acid gas were given off. When all the oxalyl chloride had been added, the contents of the flask were simply distilled. The weight of the crude distillate in each case corresponded to practically a quantitative yield of ester. On careful redistillation very pure esters resulted.

n-Propyl oxalate, $(C_3H_7)_2C_2O_4$, b. p. 211–212°.

Isobutyl oxalate, $(C_4H_9)_2C_2O_4$, b. p. 228–229°.

Isoamyl oxalate, $(C_5H_{11})_2C_2O_4$, b. p. 267–268°.

2. **Benzyl Alcohol.**—Benzyl alcohol (2 mols) was heated with oxalyl chloride (1 mol) in the same manner as the above alcohols. After the addition of the chloride, however, the reaction product was allowed to cool and a white crystalline mass formed in the flask. This was crystallized from alcohol, thus yielding practically a quantitative yield of pure benzyl oxalate.

Benzyl oxalate,[1] $(C_6H_5CH_2)_2C_2O_4$, m. p. 80.5–81.5°.

3. **Glycol.**—Oxalyl chloride (1 mol) and glycol (1 mol) were allowed to react and then cooled as in the case of the benzyl oxalate. A pasty mass formed which, crystallized from ethyl oxalate, gave a m. p. 153°, and was undoubtedly the same compound as that which Bischoff[2] obtained from ethyl oxalate and glycol.

Ethylene oxalate, $C_2H_4C_2O_4$, m. p. 153°.

Secondary Alcohols.

1. **Benzhydrol.**—A small flask with the benzhydrol (2 mols) dissolved in warm benzene was fitted with a stopper holding a reflux condenser and a small dropping funnel containing the oxalyl chloride (1 mol). The oxalyl chloride was allowed to run in slowly and the mixture then refluxed for half an hour. On spontaneous evaporation, an oil resulted which, on standing, gradually solidified to a pasty crystalline mass. This was clay-plated, then crystallized from alcohol, and was proved by analysis to be benzhydryl ether. The yield was about 30% of the theory. M. p. 107.5–108°.

Calc. for $[(C_6H_5)_2CH]_2O$: C, 89.14%; H, 6.28%. Found: C, 88.72; H, 6.45.

2. **Phenyl Methyl Carbinol.**—Phenyl methyl carbinol (2 mols) in an apparatus similar to that used for the primary alcohols was treated with oxalyl chloride (1 mol). The reaction mixture was distilled under diminished pressure (about 40 mm.) and yielded a main fraction boiling under 100° and a small fraction boiling at a much higher temperature. Oxalic acid remained behind in the distilling flask. The chief product was treated with bromine until no more was readily absorbed at a low temperature. A white crystalline mass resulted which after one recrystallization proved to be pure styrene bromide, thus showing styrene to be the main compound formed in the reaction. The small portion of higher boiling material was not studied further.

3. **Menthol.**—The reaction was carried out in the same way as for phenyl methyl carbinol, except that here a simple instead of a vacuum distillation was undertaken. Most of the distillate came over below 215° and rapidly absorbed bromine to form menthene bromide, thus proving menthene to be the chief product of the reaction. The material boiling above 215°, as it was so small in amount and so impure, was not studied further, but since it was higher boiling than menthyl chloride and lower boiling than menthyl oxalate, we concluded it was probably impure menthyl carbonate.

Tertiary Alcohols.

1. **Trimethyl Carbinol, Dimethylethyl Carbinol.**—The same apparatus was used as for the primary alcohols. During the addition of the oxalyl

[1] *Ber.*, 35, 3441 (1902).

[2] *Ibid.*, 40, 2806 (1907).

chloride, oxalic acid gradually separated out of the reaction mixture. On distillation trimethyl chloromethane, in one case, and dimethyl ethyl chloromethane in the other, were produced in good yields. On redistillation, the chlorides were readily purified.

Trimethyl chloromethane, $(CH_3)_3CCl$, b. p. 51–52°. Dimethyl ethyl chloromethane, $(CH_3)_2C_2H_5CCl$, b. p. 84–86°.

2. Triphenyl Carbinol.—Triphenyl carbinol (2 mols) was dissolved in benzene in an ordinary flask, the stopper of which was fitted with a reflux condenser and a dropping funnel holding the oxalyl chloride (1 mol). On addition of the chloride, instantaneous reaction took place. After warming gently a short time, the mixture was allowed to evaporate and the resulting solid crystallized from benzene. It proved to be triphenyl chloromethane.

Triphenylchloromethane, $(C_6H_5)_3CCl$, m. p. 100–101°.

3. Pinakone.—Pinakone (1 mol) was treated directly with oxalyl chloride (1 mol) in an apparatus similar to that used with the primary alcohols. On distillation of the reaction mixture, a liquid boiling between 100–128° resulted, which proved to be impure pinakolin. A reddish residue left in the flask solidified on cooling and crystallized from alcohol in long, white needles, which on analysis were found to be the carbonate of pinakone. M. p. 176–177°.

Calc. for $[(CH_3)_2C]_2CO_3$: C, 58.33%; H, 8.33%. Found: C, 58.34; H, 8.28.

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THE CRYSTALLIZATION OF CALCIUM TARTRATE.

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Few salts have been more frequently prepared than calcium tartrate on account of its employment for the recognition of the acid and it is therefore surprising to find that little is known of its behavior when crystallizing from aqueous solution. When a soluble calcium salt is added to a neutral solution of a soluble tartrate the compound which first separates is not the ordinary orthorhombic tetrahydrated salt, $C_4H_4O_6Ca.4H_2O$, but a hexahydrated form, $C_4H_4O_6Ca.6H_2O$, which crystallizes in long, slender needles. This is unstable at the ordinary temperature and transforms with loss of two molecules of water into the well known tetrahydrated salt, small crystals of which quickly make their appearance among the needle-shaped crystals and grow at the expense of the latter, which dissolve and ultimately disappear.

Experimental Part.

When equal volumes of 0.2 *N* solutions of calcium chloride and potassium sodium tartrate are mixed the liquid remains clear for a short time,