[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

OXALYL CHLORIDE AS A REAGENT IN ORGANIC CHEMISTRY. II. PREPARATION OF AROMATIC ACID ANHYDRIDES; REACTION WITH ALCOHOLS.

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Received November 21, 1917.

In a previous paper[1] the action of oxalyl chloride on phenols in the presence of pyridine and at a very low temperature was shown to give practically quantitative yields of the corresponding oxalic acid esters. This reaction is of particular value in the identification of phenols. During that investigation it was found that oxalyl chloride often had a decided tendency to act as a dehydrating agent and consequently its action[2] on primary, secondary and tertiary alcohols was also studied to see whether it might give a general way of preparing olefines from alcohols. A continuation of the study of oxalyl chloride is described in this paper, the first part dealing with its use as a dehydrating agent to form anhydrides from aromatic acids and the second part with its value as a reagent for the identification of alcohols just as it was for phenols.

Preparation of Aromatic Acid Anhydrides.

When one molecule of oxalyl chloride was allowed to stand with one molecule of benzoic acid for several days, the benzoic acid gradually disappeared, though not completely, and at the same time gases were evolved. On distillation, it was found that the reaction product consisted of benzoyl chloride and a small amount of unchanged benzoic acid. The reaction undoubtedly took place according to the following equation:

$$C_6H_5COOH + (COCl)_2 = C_6H_5COCl + CO + HCl + CO_2$$

In an attempt to hasten the speed of the reaction, a similar mixture of oxalyl chloride and benzoic acid was refluxed for about two hours. On distillation of the product, however, the yield of benzoyl chloride was much smaller than when the reaction ran in the cold and a large amount of another product boiling at 360°, which proved to be benzoic anhydride, formed at the same time. A thorough study was made of the action of oxalyl chloride on aromatic acids with and without various solvents, until ideal conditions were found for producing the corresponding acid anhydrides. Thus when slightly over one molecule of oxalyl chloride was added to a boiling solution or suspension in benzene of two molecules of an aromatic acid, the best results were obtained, and upon evaporation of the benzene very good yields of anhydrides resulted. These anhydrides contained only a small by-product of unchanged acid, which was readily removed with a sodium carbonate solution, and practically no

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[1] THIS JOURNAL, 37, 2716 (1915).

[2] *Ibid.*, 38, 2514 (1916).

by-product of acid chloride. The equation for the above reaction may be represented as follows:

$$2C_6H_5COOH + (COCl)_2 = (C_6H_5CO)_2O + 2HCl + CO + CO_2$$

It seemed probable, however, from a study of certain of the substituted benzoic acids, that the mechanism was not as simple as represented by the above equation, but that two steps were involved, the formation of the mixed anhydride of oxalic acid and the aromatic acid, then decomposition of this to the acid anhydride desired.

$$2C_6H_5COOH + (COCl)_2 = (C_6H_5COOCO)_2 + 2HCl.$$

$$(C_6H_5COOCO)_2 = (C_6H_5CO)_2O + CO + CO_2.$$

The evidence for this mechanism resulted from the isolation of a few of the mixed anhydrides when oxalyl chloride reacted with certain substituted benzoic acids. The *m*-nitrobenzoic acid, the 2,4- and 3,5-dinitrobenzoic acids all formed crystalline mixed anhydrides, which separated out from the benzene during the course of the reaction. These substances were stable to sodium carbonate solution but decomposed quantitatively upon melting to give carbon monoxide, carbon dioxide and the simple acid anhydride. Cold pyridine in the same way effected immediate decomposition of the mixed anhydrides with the evolution of carbon monoxide and carbon dioxide. It was probable, therefore, that in every case these substances were formed primarily, but with many of the acids they were unstable under the conditions of the reaction and broke down into the simple acid anhydrides. The formation of these mixed anhydrides was not dependent upon the presence of a nitro group, for the *o*-nitrobenzoic acid gave the *o*-nitrobenzoic anhydride in one step in the usual way. The relative insolubility of these particular mixed anhydrides in benzene undoubtedly favored their isolation before decomposition had a chance to take place.

The disadvantages of the general methods available at the present time for the preparation of aromatic acid anhydrides and the advantage of the new method described here may be seen at once. Many of the methods described in the literature make use of the aromatic acid or the salt of the aromatic acid with such reagents as phosphorus oxychloride, sulfur chloride, or phosphorus pentachloride. The fact that such strong reagents as those just mentioned must be used, limits the reactions to the preparation of those aromatic acid anhydrides which contain no easily attacked substituting group in the benzene nucleus. Moreover, a by-product of acid chloride, often not easily removed, is invariably obtained. Other methods make use of the aromatic acid chloride in condensation with a large variety of different reagents. Practically none of these processes gives very good yields and most of them give rise to by-products which are none too easily removed. In addition, it may be pointed out that the aromatic acid chlorides themselves are often quite troublesome to prepare. Another method generally mentioned in text-books for the synthesis of aromatic acid anhydrides is to treat the aromatic acid with acetic anhydride. This process seldom gives over 50% yields and often much smaller ones, and as by-products mixed anhydrides of acetic acid and the aromatic acid always form. The method described in this paper is extremely simple, using a reagent most readily obtainable. The yields are very good and no side products form to interfere with the purification of the product. It may, therefore, be recommended as the best and quickest way of securing aromatic acid anhydrides in a pure state.

Experimental Part.

The general process to be followed for the preparation of the anhydrides is as follows: Suspend 5 g. of powdered aromatic acid in about 20 cc. of dry benzene and place in a round-bottom flask attached to a reflux condenser. (It is preferable but not absolutely necessary to have the flask ground to the inside tube of the condenser as oxalyl chloride has a tendency to attack cork stoppers.) Heat the mixture to gentle boiling and allow 1.2 molecules of oxalyl chloride to drop in slowly through the condenser. Each drop causes an immediate evolution of gas and this continues for some time after all the oxalyl chloride has been added. Continue the refluxing for one or two hours to be sure that the reaction is complete. Evaporate off the benzene and wash the solid residue with sodium carbonate solution to take out any small amount of unchanged acid. The product remaining is the acid anhydride and for ordinary work does not need further purification. The yields of the anhydride vary from 70 to 85% of the theory calculated on the amount of acid used, but since some acid is recovered in every case, the yields are actually better than those just mentioned. In working with acids which were very insoluble in benzene, it is advisable to use a slightly larger amount of oxalyl chloride and to reflux the mixture a longer time. Wherever a mixed anhydride forms, the procedure is just the same. It involves an extra step, however, the melting of the reaction product after it has been washed with sodium carbonate solution and dried. The pure anhydride is thus obtained.

By the above procedure, 13 aromatic anhydrides were prepared, some of which had already been made by other methods and some of which had not been synthesized until this time. The following table gives a list of these anhydrides with their melting points.

The benzoic anhydride, the 3 toluic anhydrides, the *p*-chlorobenzoic anhydride, the *o*- and *p*-nitrobenzoic anhydrides and anisic anhydride were all crystallized from the solvents already mentioned in the literature and gave the same crystalline forms which were published. The melting points in one or two cases were slightly different and are shown in the table.

TABLE I.

		This research. Melting point.	In literature. Melting point.	
1	Benzoic anhydride	42°	42°	*Ann.*, **87**, 73 (1853).
2	*o*-Toluic anhydride	36–37°	36–37°	*Ibid.*, **239**, 74 (1887).
3	*m*-Toluic anhydride	70°	71°	*J. Chem. Soc.*, **95**, 1240 (1909).
4	*p*-Toluic anhydride	94°	95°	*Ibid.*, **75**, 344 (1899).
5	*o*-Chlorobenzoic anhydride	78–79°	...	......
6	*m*-Chlorobenzoic anhydride	95°	...	......
7	*p*-Chlorobenzoic anhydride	193–4°	193–4°	*Ber.*, **43**, 2229 (1910).
8	*o*-Nitrobenzoic anhydride	135°	135°	*Ibid.*, **17**, 2789 (1884).
9	*m*-Nitrobenzoic anhydride	162°	...	......
10	*m*-Iodobenzoic anhydride	134°	...	......
11	Anisic anhydride	99°	95–6°	*Ann.*, **102**, 284 (1856).
12	3,5-Dinitrobenzoic anhydride	209°	...	......
13	2,4-Dinitrobenzoic anhydride	160°	...	......

***o*-Chlorobenzoic Anhydride,** $(ClC_6H_4CO)_2O$.—Small, white prismatic needles from alcohol, melting at 78–79°.

0.2346 g. subst.; 0.1161 g. AgCl.
Calc. for $C_{14}H_8O_3Cl_2$: Cl, 24.04. Found: Cl, 23.85.

***m*-Chlorobenzoic Anhydride,** $(ClC_6H_4CO)_2O$.—Short, white needles from alcohol melting at 95°.

0.2160 g. subst.; 0.2076 AgCl.
Calc. for $C_{14}H_8O_3Cl_2$: Cl, 24.04. Found: Cl, 23.99.

***m*-Iodobenzoic Anhydride,** $(IC_6H_4CO)_2O$.—White plates from alcohol melting at 134°.

0.1923 g. subst.; 0.1883 g. AgI.
Calc. for $C_{14}H_8O_3I_2$: I, 53.12. Found: I, 52.91.

***m*-Nitrobenzoicoxalic Anhydride,** $(NO_2C_6H_4COOCO)_2$.—Yellowish crystals decomposing at 157°. Only very slightly soluble in the common organic solvents. For analysis it was washed with dilute sodium carbonate solution, then dried and finally washed several times with hot benzene.

0.1906 g. subst.; 0.2788 g. CO_2; 0.0706 g. H_2O.
0.2419 g. subst.; 19.65 cc. N, 747 mm., 23.0°.
Calc. for $C_{14}H_8O_{10}N_2$: C, 49.5; H, 2.06; N, 7.2. Found: C, 49.30; H, 2.26; N, 7.5.

Upon melting this mixed anhydride, one molecule of carbon monoxide, one molecule of carbon dioxide, and one molecule of *m*-nitrobenzoic anhydride were produced. To show that this decomposition was quantitative, three g. of pure mixed anhydride were placed in a test tube connected with a potash absorption bulb and a tube through which pure air could be forced. The test tube was then heated to 170° and air passed through to sweep the carbon dioxide and carbon monoxide into the absorption bulb. The increase in weight due to the carbon dioxide and the loss in the weight of the mixed anhydride were recorded.

Wt. subst. before heating	3.000 g.
Wt. subst. after heating	2.409 g.
Wt. CO_2 + CO evolved	0.591 g.
Wt. CO_2 collected	0.335 g.

Calc. % loss of CO and CO_2, 19.54. Found: 19.71.
Calc. % of CO_2 evolved, 11.34. Found: 11.16.

***m*-Nitrobenzoic Anhydride,** $(NO_2C_6H_4CO)_2O$, prepared by the decomposition of the mixed anhydride of oxalic acid and *m*-nitrobenzoic acid. White crystals from benzene melting at 163°.

0.1840 g. subst.; 0.3782 g. CO_2; 0.0296 g. H_2O.
0.2675 g. subst.; 20.54 cc. N, 745 mm., 22.0°.
Calc. for $C_{14}H_8O_7N_2$: C, 53.16; H, 2.54; N, 8.86. Found: C, 53.03; H, 2.78; N, 9.50.

m-Nitrobenzoic anhydride was described in the literature by Autenrieth,[1] who made it by the action of acetic anhydride on *m*-nitrobenzoic acid and reported the melting point as 47°. His work was repeated in this laboratory and it was found that provided the reaction was carried out as described, a substance melting at 47° was actually obtained. If, however, the reaction mixture was heated longer and the temperature raised to 175° after the excess of acetic anhydride was distilled off, a good yield of the *m*-nitrobenzoic anhydride melting at 162° resulted. The substance melting at 47° was undoubtedly the mixed anhydride of acetic acid and *m*-nitrobenzoic acid described by Green,[2] who reported the melting point at 45°. This mixed anhydride on high heating decomposed into the *m*-nitrobenzoic anhydride.

3,5-Dinitrobenzoicoxalic Anhydride, $[(NO_2)_2C_6H_3COOCO]_2$, slightly yellowish crystalline powder decomposing at 175°.

0.1625 g. subst.; 0.2382 g. CO_2; 0.0112 g. H_2O.
0.2400 g. subst.; 25.56 cc. N, 741 mm., 23.0°.
Calc. for $C_{16}H_6O_{14}N_4$: C, 40.16; H, 1.25; N, 11.7. Found: C, 39.89; H, 1.41; N, 12.0.

3,5-Dinitrobenzoic Anhydride, $[(NO_2)_2C_6H_3CO]_2O$, short, white crystals from benzene melting at 109°.

0.3319 g. subst.; 23.96 cc. N, 740 mm., 22.0°.
Calc. for $C_{16}H_6O_{11}N_4$: N, 13.79. Found: 14.05.

2,4-Dinitrobenzoicoxalic Anhydride, $[(NO_2)_2C_6H_3COOCO]_2$, slightly yellowish crystalline powder melting with decomposition at 205–209°. This substance was not analyzed but was decomposed directly into the simple anhydride.

2,4-Dintrobenzoic Anhydride, $[(NO_2)_2C_6H_3CO]_2O$, white crystalline powder from benzene, melting at 160°.

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[1] *Ber.*, 34, 184 (1901).

[2] *Ann.*, 11, 415 (1889).

0.2485 g. subst.; 25.9 cc. N, 740 mm., 22.0°.
Calc. for $C_{14}H_6O_{11}N_4$: N, 13.8. Found: 13.1.

Oxalyl Chloride in the Presence of Pyridine with Secondary and Tertiary Alcohols.

Oxalyl chloride[1] reacted instantaneously with primary alcohols to give the corresponding oxalic acid esters. With secondary alcohols, however, either olefines or ethers resulted and with tertiary alcohols, chlorides formed in most cases. It seemed possible that since phenols reacted so readily and quantitatively with oxalyl chloride in the presence of pyridine to give well crystallized oxalic acid esters that oxalyl chloride with pyridine might also give esters of oxalic acid with the various kinds of alcohols and thus might prove to be a convenient way of identifying alcohols in general. As the oxalyl chloride alone reacted in the cold to give quantitative yields of esters with the primary alcohols, this investigation was limited to the study of secondary and tertiary alcohols. The results showed that the secondary alcohols under the above-mentioned conditions gave esters of oxalic acid. Thus benzhydrol, phenyltolylcarbinol, menthol, borneol, benzoin, piperonyolin, iso-propylalcohol, etc., gave the expected derivatives, although with oxalyl chloride alone,[1] no ester formed. The yields averaged about 50%.

The tertiary alcohols with oxalyl chloride and pyridine did not give satisfactory results. The amounts of the products were very small when any ester at all was produced, the tertiary alcohols being recovered unchanged in most cases.

It is evident, therefore, that oxalyl chloride in the presence of pyridine has the same disadvantages as the other alcohol reagents, such as acetyl chloride, benzoyl chloride, phenyl isocyanate, diphenyl chlorourea, etc., in that it does not react satisfactorily with tertiary alcohols. With secondary alcohols, however, it may be recommended, as the reaction can be carried out at low temperatures and the compounds in most cases are well crystallized and easily purified solids. Many other alcohol reagents react with much more difficulty with secondary alcohols than the one mentioned above and the reaction products are often liquids, whereas solids were obtained in this research.

Experimental Part.

The general procedure in this investigation was as follows: Cool 25 cc. of pyridine with ice and add one molecule of oxalyl chloride, drop by drop. A yellow addition product separates out immediately and must be crushed with a spatula. Add to this mixture two molecules of the alcohol dissolved in a little pyridine; allow the mixture to stand two or more hours either in a freezing mixture or at room temperature, then pour into ice and hydrochloric acid. The pyridine goes into solution and the

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[1] This Journal, 38, 2514 (1916).

ester separates out and may be filtered off or separated if it happens to be a liquid.

Benzhydrol Oxalate, $[(C_6H_5)_2CH]_2C_2O_4$, made at 0°. Small white needles from petroleum ether melting at 142–143°.

0.1841 g. subst.; 0.5386 g. CO_2; 0.0906 g. H_2O.
Calc. for $C_{28}H_{22}O_4$: C, 79.62; H, 5.21. Found: C, 79.76; H, 5.46.

Phenyl-tolyl-carbinol Oxalate, $[C_6H_5(CH_3C_6H_4)CH]_2C_2O_4$, made at 0°. White crystals from ligroin melting at 86–87°.

0.1916 g. subst.; 0.5596 g. CO_2; 0.1029 g. H_2O.
Calc. for $C_{30}H_{26}O_4$: C, 80.00; H, 5.77. Found: C, 79.64; H, 5.96.

An attempt was made to prepare phenyl-anisyl carbinol from phenyl-anisyl ketone and sodium amalgam. The carbinol was obtained, but only in small yields, and so was not used in subsequent work. The melting point is considerably higher than 58°, which is reported in the literature.[1] An alcohol solution of 25 g. of phenyl-anisyl ketone was treated with 1 kg. of sodium amalgam. This was allowed to stand overnight, then refluxed on a water bath for two hours. Upon distilling the alcohol, adding water and dilute sulfuric acid to acidify, and finally extracting with ether, a substance was obtained in the ether which crystallized from ligroin in white needles melting at 68° and on analysis proved to be phenyl-anisyl carbinol.

0.2000 g. subst.; 0.5761 g. CO_2; 0.1184 g. H_2O.
Calc. for $C_{14}H_{14}O_2$: C, 78.50; H, 6.54. Found: C, 78.55; H, 6.57.

Dibenzoin Oxalate, $[C_6H_5CO(C_6H_5)CH]_2C_2O_4$, made at room temperature. Fine, white crystals from nitrobenzene, melting at 243–245°.

0.1992 g. subst.; 0.5454 g. CO_2; 0.0852 g. H_2O.
Calc. for $C_{30}H_{22}O_6$: C, 75.31; H, 4.60. Found: C, 74.67; H, 4.75.

Dipiperonyloin Oxalate, $[CH_2O_2C_6H_3CO(CH_2O_2C_6H_3)CH]_2C_2O_4$, made at room temperature. White powder from nitrobenzene melting at 225–226°.

0.2203 g. subst.; 0.4983 g. CO_2; 0.0728 g. H_2O.
Calc. for $C_{34}H_{26}O_8$: C, 62.39; H, 3.36. Found: C, 61.68; H, 3.67.

Borneol Oxalate, $(C_{10}H_{17})_2C_2O_4$, made at room temperature. White crystals from alcohol melting at 108–109°. From oxalic acid and borneol[2] the oxalate is reported as melting at 113°.

0.1898 g. subst.; 0.5091 g. CO_2; 0.1666 g. H_2O.
Calc. for $C_{22}H_{34}O_4$: C, 72.92; H, 9.39. Found: C, 73.15; H, 9.75.

Menthol Oxalate, $(C_{10}H_{19})_2C_2O_4$, white crystals from benzol, melting at 66–67°. Same melting point obtained as when it was prepared from oxalic acid[3] and menthol.

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[1] *J. prakt. Chem.*, [2] **77**, 20 (1908).

[2] C., [1] **998** (1908): D. R. P. 193,301.

[3] *Ber.*, **35**, 2474 (1902).

Isopropyl Oxalate, $[(CH_3)_2CH]_2C_2O_4$, colorless liquid boiling at 189°. Boiling point[1] previously reported is 190°.

Tertiary Alcohols.

Triphenyl carbinol, diethyl-phenyl carbinol and diphenyl-methyl carbinol were studied. In the first two cases no oxalates were obtained, the alcohols being recovered. With the third, however, a small yield of the oxalic acid ester was produced. This was separated from the unchanged carbinol by treatment with cold benzene in which it did not dissolve, then crystallized from hot benzene in colorless pyramids softening at 110° and decomposing gradually between 170–185° with the evolution of gas.

0.2056 g. subst.; 0.6043 g. CO_2; 0.1119 g. H_2O.

Calc. for $C_{30}H_{26}O_4$: C, 80.0; H, 5.77. Found: C, 80.14; H, 6.04.

[CONTRIBUTION FROM THE DIVISION OF AGRICULTURAL BIOCHEMISTRY, MINNESOTA AGRICULTURAL EXPERIMENT STATION.]

THE PRESERVATION OF PLANT JUICES FOR ANALYSIS OF SUGAR CONTENT.[2]

BY D. O. SPRIESTERSBACH.

Received December 12, 1917.

It is desirable at times to preserve samples for future analysis. This was the case recently at the Minnesota Experiment Station while sorghum investigations were in progress; however, certain difficulties are immediately met with when the samples consist of plant juices, *i. e.*, the extreme ease with which sugars are destroyed by microörganisms and the fact that the common disaccharides are rather easily hydrolyzed. The first difficulty can of course be overcome by the use of preservatives which either by virtue of their toxicity can kill microörganisms or are able to inhibit their growth. The second must be overcome by a means which counteracts the hydrolyzing agent, in this case principally acids. At the same time the substances employed must not in any way interfere with the proper determination of the composition of a juice. It is obvious that relatively few of the usual preserving agents meet the above conditions.

Accordingly, at the suggestion of Prof. R. M. West, a few common preservatives were tried in a preliminary way upon sorghum juice. Most of them immediately showed themselves to be unsatisfactory, the exceptions being mercuric iodide dissolved in potassium iodide solution, phenol, and toluene. The former was chosen on account of its high toxicity to microörganisms, and toluene was selected rather than phenol since it appeared to be equally efficient at the same time and was free of certain

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[1] *Ann.*, **139**, 229 (1866).

[2] Published with the approval of the Director as Paper No. 95, Journal Series, Minnesota Agricultural Experiment Station.