and 20 cc. of glacial acetic acid. After cooling, phthalic acid was filtered off, and the filtrate was concentrated *in vacuo*, filtered again, and finally taken to dryness in a vacuum desiccator over potassium hydroxide. The crude aminoethyl mercaptan hydrochloride[20] was dissolved in 20 cc. of water, treated with 4.6 cc. of formalin, allowed to stand overnight, and taken to dryness *in vacuo*. The residue was crystallized from alcohol; yield, 6.63 g. (91%) of long needles; m. p. 180° (dec.).

Anal. Calcd. for $C_3H_7NS{\cdot}HCl$: C, 28.66; H, 6.42; S, 25.53; N, 11.15; Cl, 28.24. Found: C, 28.86; H, 6.76; S, 25.77; N, 10.88; Cl, 28.1.

The free base, liberated from the above hydrochloride by potassium carbonate, is readily volatile with steam, miscible in all proportions with water, and can be salted out readily with potassium carbonate. It is a colorless liquid, b. p. 164–165°, d^{25}_4 1.131, n^{30}_D 1.551.

Anal. Calcd. for C_3H_7NS: N, 15.72; C, 40.39; H, 7.92. Found: N, 15.77; C, 40.40; H, 7.80.

Acetylthiazolidine.—An excess (2.5 cc.) of acetic anhydride was added to 1.51 g. of the free base; the acetic acid was removed *in vacuo*, and the residual liquid distilled under reduced pressure; b. p. 83–85° (0.7 mm.); yield 1.96 g. (88%).

Anal. Calcd. for C_5H_9ONS: C, 45.76; H, 6.91; N, 10.68. Found: C, 44.66; H, 6.74; N, 10.24.

Sulfone of Acetylthiazolidine.—To a solution of 0.712 g. of acetylthiazolidine in 10 cc. of glacial acetic acid, 1.5 cc. (2.3 mole) of hydrogen peroxide was added. After a week the solvent was removed *in vacuo* and the residue recrystallized from hot alcohol; stout hexagonal prisms or long plates, m. p. 122°.

Anal. Calcd. for $C_5H_9O_3NS$: C, 36.78; H, 5.56; N, 8.58. Found: C, 36.72; H, 5.33; N, 8.65.

Oxidation of Thiazolidine with Bromine.—*N* Bromine in acetic acid was added to 0.354 g. (4 mml.) of thiazolidine in 5 cc. of water to a faint permanent yellow (5.8 equivalents). The solution was taken to dryness *in vacuo*, and the residue recrystallized by adding alcohol to a concentrated solution in water. The product, taurine, formed fine needles, was neutral in reaction and did not melt below 260°; yield, 0.430 g. (86%).

Anal. Calcd. for $C_2H_7O_3NS$: N, 11.19. Found: N, 10.95.

Oxidation of Thiazolidine with Iodine.—To 0.3358 g. of free thiazolidine (3.77 mml.) in 5 cc. of water was added 37.7 cc. of 0.1 *N* iodine in 2.5% potassium iodide. A white solid appeared which redissolved slowly. After twenty hours the colorless solution was filtered to remove a small red precipitate, and 3.77 cc. of *N* sodium hydroxide was added. A colorless solid which precipitated was filtered off. Formaldehyde was identified in the filtrate. The colorless precipitate, apparently an aldehyde–ammonia, was dissolved in excess hydrochloric acid, when a strong odor of formaldehyde was evolved. The solution was taken to dryness *in vacuo* and the residue recrystallized from ethyl alcohol. The resulting needles, 0.250 g., m. p. 206°, were identified as di-β-aminoethyl disulfide hydrochloride, described by Gabriel.[21]

Anal. Calcd. for $C_4H_{12}N_2S_2{\cdot}2HCl$: N, 12.43. Found: N, 12.33.

Summary

Formaldehyde reacts with cysteine over a wide range of *p*H to form thiazolidine-4-carboxylic acid, the mode of formation, constitution and properties of which are here discussed.

Thiazolidine, similarly prepared from formaldehyde and β-aminoethyl mercaptan, is also described.

NEW YORK, N. Y. RECEIVED OCTOBER 31, 1936

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[20] Gabriel, *Ber.*, **22**, 1137 (1889).

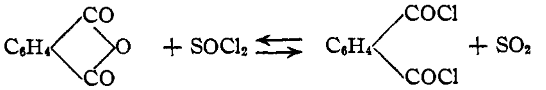
[21] Coblenz and Gabriel, *ibid.*, **24**, 1122 (1891).

[CONTRIBUTION FROM THE RESEARCH LABORATORIES, MONSANTO CHEMICAL CO.]

Phthalyl Chloride

BY L. P. KYRIDES

Phthalyl chloride has been prepared by the interaction of phthalic anhydride and phosphorus pentachloride.[1] Thionyl chloride converts phthalic acid into the anhydride, but is reported to have no action on the latter at refluxing temperatures even in presence of catalysts or pyridine.[2] We found that excellent yields of phthalyl chloride are readily obtained if the reaction is carried out at elevated temperatures in presence of very small amounts of anhydrous zinc chloride.[3] We also observed that the reaction is reversible, since thionyl chloride is obtained when sulfur dioxide and phthalyl chloride react at around 200°, also in presence of zinc chloride. The reaction is, therefore, expressed as



$$C_6H_4\langle(CO)_2\rangle O + SOCl_2 \rightleftarrows C_6H_4\langle(COCl)_2 + SO_2$$

If no zinc chloride is present and thionyl chloride

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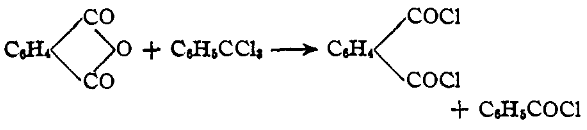
[1] Bruehl, *Ann.*, **235**, 13 (1886).

[2] Meyer, *Monatsh.*, **22**, 437 (1901); McMaster and Ahmann, THIS JOURNAL, **50**, 145 (1928); Carré and Libermann, *Compt. rend.*, **199**, 1422 (1934).

[3] U. S. Patent 1,951,364.

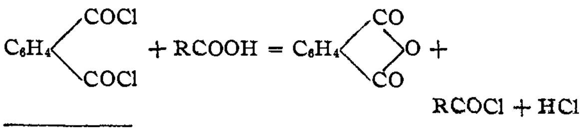
is dropped very slowly into phthalic anhydride at 220° over a period of forty hours, only about 70% of the anhydride is converted into phthalyl chloride. Meyer[2] had observed that thionyl chloride converts maleic and succinic acids into anhydrides but not into chlorides. Fumaryl and succinyl chlorides are obtained in good yields if the reaction is carried out in presence of zinc chloride.

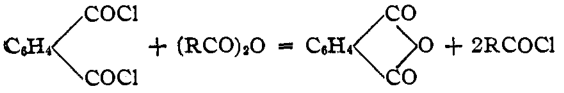
Benzotrichloride has been used in a limited number of cases for the preparation of chlorides from monocarboxylic acids and their anhydrides. Phthalic anhydride and benzotrichloride did not react at 200°; but the addition of a trace of zinc chloride induced a distinct reaction. By increasing the amount of zinc chloride, the conversion proceeded at a fairly rapid rate even as low as 100°.[4] The reaction products were separated easily by simple fractionation. This reaction takes place as follows



The phthalyl chloride obtained by all of the processes contains small amounts of dissolved anhydride, an observation which had also been made by Bruehl[1] in the phosphorus pentachloride reaction. The solubility of the anhydride in phthalyl chloride is of the order of 5–6% at 15°, so that it is easy to free it from an excessive amount of anhydride by filtration after cooling. The phthalyl chloride containing dissolved anhydride is perfectly satisfactory for most reactions.

Van Dorp and Van Dorp[5] found that phthalyl chloride and fumaric acid reacted at 120–160° to give a good yield of fumaryl chloride. We have used phthalyl chloride in many reactions and found it to be an excellent reagent for the nearly quantitative conversion of acids and anhydrides into acid chlorides. If the boiling points of these chlorides are not too close to those of phthalyl chloride and phthalic anhydride, they can be obtained in very pure form by direct fractionation. The reactions take place as follows





Maleic and succinic anhydrides are converted into chlorides with phthalyl chloride only in presence of zinc chloride as is the case with thionyl chloride.

Experimental

1. Phthalyl Chloride from Phthalic Anhydride and Thionyl Chloride.—The apparatus consisted of a three-necked flask, with an efficient reflux condenser, a dropping funnel and an agitator (the latter being used only in case large amounts of materials were to be made).

Three hundred grams of phthalic anhydride and 1.5 g. of technical anhydrous zinc chloride were charged into the flask and the mixture was heated over a wire gauze to 220°. The theoretical amount of thionyl chloride (241 g.) was dropped in over a period of about ten hours, at such a rate that the temperature could be maintained at about 220°. The reaction mass was distilled directly under a vacuum of 4.5 mm. and 380 g. of a liquid distillate was obtained boiling at 119–122°. After standing cold for some time, a small amount of phthalic anhydride separated out, which after isolation weighed 22 g. The filtered phthalyl chloride analyzed 94% by chlorine analysis, so that the conversion amounted to 86% and the yield was practically quantitative on the anhydride consumed.

2. Thionyl Chloride from Phthalyl Chloride and Sulfur Dioxide.—A mixture of 107 g. of phthalyl chloride (94%) and 2 g. of zinc chloride was heated at 200°. A slow current of sulfur dioxide was bubbled through the mixture and the distillate was condensed using running water. After a ten-hour reaction, 44.3 g. of a distillate had collected which upon redistillation gave 39 g. of thionyl chloride, which amounts to 66% of the theoretical yield from phthalyl chloride. No attempt was made to analyze the unreacted sulfur dioxide for its thionyl chloride content. Since, however, the residue from the reaction was practically chlorine free, it is presumed that a considerable portion of the thionyl chloride was lost with the uncondensed gas.

3. Phthalyl Chloride from Phthalic Anhydride and Benzotrichloride.—A mixture of 225 g. of phthalic anhydride, 290 g. of fractionated benzotrichloride (sp. gr. 1.38) and 20 g. of zinc chloride was heated in an oil-bath at 110–120° overnight (reaction time twenty hours) and the reaction mixture was fractionated carefully under a vacuum of about 23 mm. The fractions consisted of 201 g. of benzoyl chloride boiling at 90–95°; 8.8 g. boiling up to 138° and 287 g. of phthalyl chloride boiling mostly at 150–152°.

The phthalyl chloride fraction upon standing cold deposited a few crystals of phthalic anhydride, indicating that it was about 95% pure. The theoretically expected weight yields of phthalyl and benzoyl chlorides were 308 and 208 g., respectively.

The residue from the distillation containing the zinc chloride was found capable of promoting the reaction of fresh quantities of reactants. It was also found that zinc oxide and zinc dust can be used as catalysts in place of zinc chloride. The activity of these is, no doubt, due to their transformation to zinc chloride in the reaction mixture.

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(4) U. S. Patent 1,963,748; 1,963,749.

(5) Van Dorp and Van Dorp, *Rec. trav. chim.*, **25**, 96 (1906).

If the amount of zinc chloride is reduced to one-tenth of that used in this experiment, the temperature has to be raised to about 200° in order that the reaction may proceed at a fairly rapid rate.

When *o*-chlorobenzotrichloride was used in place of benzotrichloride, the reaction products consisted, as was to be expected, of phthalyl and *o*-chlorobenzoyl chlorides.

4. **Butyryl Chloride from Phthalyl Chloride.**—A flask connected to a short fractionating column was charged with 340 g. of phthalyl chloride, heated at about 140° and treated slowly with 132 g. of *n*-butyric acid. Hydrogen chloride was evolved as the acid was added and part of the butyryl chloride distilled over. Finally, vacuum was applied and the remainder of the chloride recovered. Refractionation gave 146.5 g. of butyryl chloride which represents a 91.5% yield of the theoretical on butyric acid.

5. **Fumaryl Chloride from Maleic Anhydride.**—A mixture of 98 g. of maleic anhydride, 231 g. of 94% phthalyl chloride and about 0.5 g. of zinc chloride was heated overnight at about 140°. Vacuum was applied and the fumaryl chloride distilled until phthalic anhydride began to separate in the condenser. The distillate, amounting to 146 g., was found to contain 129 g. of fumaryl chloride and 15 g. of unreacted maleic anhydride. The yield, therefore, of the chloride on the anhydride which was consumed was nearly quantitative.

The writer is indebted to Messrs. M. N. Dvornikoff and O. J. Weinkauff for assistance in the experimental part of the investigation.

Summary

Phthalyl chloride can be made in good yields from thionyl chloride or benzotrichloride and phthalic anhydride at elevated temperatures using zinc chloride as catalyst and, reversibly, thionyl chloride is formed from the interaction of sulfur dioxide with phthalyl chloride under the same conditions.

Acid chlorides can be produced in excellent yields from the interaction of acids or their anhydrides with phthalyl chloride.

In the case of the anhydrides of acids, such as succinic and maleic acids, which do not react directly with phthalyl or thionyl chlorides, the reaction can be catalyzed with traces of zinc chloride to give good yields of the desired acid chlorides.

ST. LOUIS, MO. RECEIVED NOVEMBER 5, 1936

[CONTRIBUTION NO. 45 FROM THE COAL RESEARCH LABORATORY, CARNEGIE INSTITUTE OF TECHNOLOGY]

Mellitic Acid from Coals, Cokes and Graphites

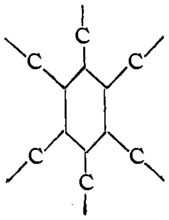
BY BERNARD JUETTNER

Carbonization of coal involves the loss of volatile decomposition products such as gas, tar and water, and the formation of a condensed, nonvolatile residue. The more important factors influencing the degree of condensation of the residue are: the final temperature, the rate of heating and the nature of the coal. Another factor may be the speed at which the decomposition products are removed, which in turn depends largely on the thermal variables mentioned above, on the pressure in the retort during the carbonization, and on the particle size of the coal.[1,2] The ash of the coal may also exert an influence due to catalytic effects.

The purpose of this work is to determine the degree of condensation of various carbonaceous materials, by conversion of these high molecular weight condensed bodies into small identifiable units of structural significance. The development of such a method permits the evaluation of the relative importance of such variables as maximum temperature, heating rate and specific nature of the material.

To accomplish the purpose in view the oxidation reagent employed must be powerful enough to penetrate to the last skeletal nuclei, but should not result in complete breakdown to carbon dioxide.

Mellitic acid, the benzene hexacarboxylic acid, is known as an oxidation product of various carbonaceous materials. It forms a relatively insoluble ammonium salt and hence can be determined nearly quantitatively; it is very resistant to further oxidation, and is of definite structural significance, since it can only be formed from such structures as



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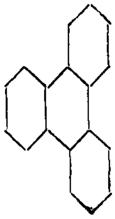

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(1) Lowry, *Ind. Eng. Chem.*, **26**, 321 (1934).

(2) Juettner and Howard, Coal Research Lab., Carnegie Inst. of Tech., Contrib. No. 8; Juettner and Howard, *Ind. Eng. Chem.*, **26**, 1115 (1934).