vinyl-arsines have been prepared and studied. β-Chlorovinyl-dichloroarsine has been shown to resemble arsenic trichloride in its condensations with diphenylamine and phenyl-α-naphthylamine. The strong tendency of the *tris*-β-chlorovinyl-arsine to form molecular compounds has been demonstrated.

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PREPARATION OF 6-METHYLCOUMARIN AND ITS DERIVATIVES

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The purpose of this investigation was the determination of the most favorable procedure for the preparation of 6-methylcoumarin, and the study of its derivatives.

In 1883 and 1884 von Pechmann[1] and others found that phenols condense with ethyl aceto-acetate and malic acid in the presence of concd. sulfuric acid to form members of the coumarin series. Different phenols were found to condense with various degrees of readiness. Thus, phenol, *o*- and *p*-cresols, quinol and thymol gave extremely poor yields, but resorcinol, orcinol and pyrogallol condensed readily. Later, Fries and Klostermann[2] condensed *m*-cresol with malic acid and ethyl aceto-acetate, and showed that a much better yield was obtainable.

Chuit and Bolsing[3] prepared coumarins by Knoevenagel's reaction. They condensed hydroxy-aldehydes with the appropriate ketonic acid or ester in the presence of an amine (aniline or piperidine). In this way, they prepared acids which on heating lost a molecule of water, forming the coumarin. From 5-methyl-salicylaldehyde and ethyl aceto-acetate, 6-methylcoumarin-carboxylic acid was prepared. This, when heated to 250–300°, yielded a very small amount of 6-methylcoumarin. Still more recently, Bailey and Boettner[4] modified the method of von Pechmann and applied it to the condensation of *m*-cresol and malic acid. They obtained yields of more than 50%. They were not able, however, to condense phenol with maleic acid. Ponndorf[5] in 1921 condensed *p*-cresol with maleic and fumaric acids, using sulfuric acid and zinc chloride as condensing agents. He reports a 50% yield, but his calculation is not based upon the purified product.

We have found that a yield of 80% of purified 6-methylcoumarin is obtained by heating equimolecular quantities of fumaric acid and *p*-cresol

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[1] Von Pechmann, *Ber.*, **16**, 2119 (1883); **17**, 929, 1646 (1884).

[2] Fries and Klostermann, *Ber.*, **39**, 871 (1906).

[3] Chuit and Bolsing, *Bull. soc. chim.*, [III] **36**, 76 (1906).

[4] Bailey and Boettner, *J. Ind. Eng. Chem.*, **13**, 905 (1921).

[5] Ponndorf, Ger. pat. 338,737, **1921.**

with 72% sulfuric acid at 160–180° for two hours (or until the evolution of carbon monoxide ceases). No coumarin was formed when *p*-cresol and fumaric acid were heated together, alone, or with zinc chloride, phosphorus pentoxide, phosphoric acid, acetic anhydride, or aluminum chloride.

As a proof of structure, 6-methylcoumarin was prepared by condensing *m*-homosalicylaldehyde with acetic anhydride. The *m*-homosalicylaldehyde was prepared by the method of Tiemann and Schotten.[6] A small quantity of 6-methylcoumarin was obtained.

In order to substantiate the structure further, the following reaction was carried out. 6-Bromocoumarin, as prepared by Clayton,[7] was treated with methyl iodide in the presence of sodium, thus introducing the methyl group in the 6 position. The products obtained from these two procedures proved to be identical, and were in turn identical with the product obtained from the condensation of *p*-cresol and fumaric acid as determined by the method of mixed melting points.

Other Condensations

***p*-Cresol and Tartaric Acid.**—An attempt was made to condense *p*-cresol with tartaric acid to get a dihydroxy-6-methylcoumarin. The mixture foamed, and could not be heated in an open flask to 180°. The odor of formic acid was noted, but as yet no coumarin has been extracted from the mass that separated when the mixture was poured upon cracked ice.

***p*-Cresol and Succinic Acid.**—Equimolecular quantities of succinic acid and *p*-cresol were heated to 180° with 72% sulfuric acid. When the tarry mass was extracted with ether, crystals were formed which, on recrystallization from boiling water formed reddish-brown needles; m. p., 71–72°. This compound has not yet been identified, but it is not identical with the bihydride of 6-methylcoumarin.

On hydrolysis under suitable conditions, 6-methylcoumarin yields 6-methylcoumaric acid. The coumarin forms a dibromide, and complex salts with mercuric chloride, chloroplatinic acid, and iodine in hydriodic acid and potassium iodide. With sodium amalgam it yields a bihydride; with bromine, a dibromide; and with phosphorus trisulfide it yields 6-methylthiocoumarin.

Experimental Part

The main reaction used in this work for the formation of 6-methylcoumarin consists in the heating of fumaric or maleic acid with *p*-cresol at high temperature in the presence of sulfuric acid. Apparently, an *ortho* hydrogen of the cresol unites with the carboxyl group of the fumaric

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[6] Tiemann and Schotten, *Ber.*, **11**, 767 (1878).

[7] Clayton, *J. Chem. Soc.*, **93**, 2022 (1908).

acid making formic acid. The coumaric acid thus formed splits off water under the influence of the dehydrating agent, and the coumarin is obtained.

In order to determine the best conditions for the formation of 6-methylcoumarin, the procedure of the reaction was as follows. A mixture of various amounts of fumaric or maleic acid (which work equally well) and *p*-cresol was added to sulfuric acid of various concentrations. The mixture was heated on an oil-bath during constant stirring at temperatures ranging from 120° to 190°. The time of heating ranged from 30 minutes to eight hours. The resulting mixtures were allowed to cool, and then poured onto cracked ice. A black, tarry mass separated, and from this the coumarin was extracted with ether, chloroform or alcohol. When the solvent was removed, the impure 6-methylcoumarin remained. This was decolorized with Superfiltchar, and was allowed to crystallize from alcohol. A quicker procedure is to pour the alcoholic solution into ice water, whereupon the coumarin separates as a white, flocculent precipitate. The melting point of the purified product was 73–74°.

Preparation of Derivatives

6-Methylcoumaric Acid.—It was found impossible to prepare 6-methylcoumaric acid by the method of Perkin,[8] as the original coumarin was always reprecipitated on the addition of acid. The acid was formed, however, by applying Ebert's[9] method. 6-Methylcoumaric acid is precipitated as fine, white needles; m. p., 118°.

SODIUM SALT.—The acid was boiled with a sodium carbonate solution, while the acid was kept in excess. After the mixture had stood for several days, light yellow needles formed which were quite soluble in water. They decomposed above 275°.

SILVER SALT.—The silver salt was precipitated from a solution of the sodium salt by silver nitrate. This salt came down as a white, curdy precipitate which rapidly turned black on exposure to light.

Anal. Subs., 0.1027: AgCl, 0.0521. Calcd. for $C_{10}H_9O_3Ag$: AgCl, 0.0518.

POTASSIUM SALT.—This salt was formed from potassium carbonate in the same manner as the sodium salt. It separated as colorless needles.

NICKEL SALT.—The nickel salt was prepared by adding a few drops of the chloride to a concentrated solution of the acid. It formed light green needles.

6-Methylcoumarin Dibromide.—Equimolecular quantities of 6-methylcoumarin and bromine were mixed in carbon disulfide. After 12 hours the solvent was allowed to evaporate spontaneously and the dibromide separated in long, colorless needles; m. p., 65–66°. These may be recrystallized from alcohol as colorless prisms. When they are boiled for a time with water, 6-methylcoumarin is formed.

Anal. Subs., 0.2471: AgBr, 0.1541. Calcd. for $C_{10}H_8O_2Br_2$: AgBr, 0.1452.

6-Methylcoumarin-mercurichloride.—Equimolecular quantities of 6-methylcoumarin and mercuric chloride, each in ether solution, were mixed. A quantitative yield of small, white crystals of 6-methylcoumarin-mercurichloride was obtained; m. p., 189–190°.

Anal. Subs., 0.7971: HgS, 0.4345. Calcd. for $C_{10}H_8O_2HgCl_2$: HgS, 0.4305. Subs., 0.7531: Ag, 0.1232. Calcd. for $C_{10}H_8O_2HgCl_2$: Ag, 0.1245.

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[8] Perkin, *J. Chem. Soc.*, **21**, 472 (1868).

[9] Ebert, *Ann.*, **226**, 347 (1884).

6-Methylcoumarin-platinichloride.—Concentrated solutions of 6-methylcoumarin and chloroplatinic acid, both in concd. hydrochloric acid, were added together. Light yellow crystals were formed which were washed with hydrochloric acid and dried over calcium oxide; m. p., 65°.

6-Methylthiocoumarin.—An intimate mixture of coumarin and phosphorus trisulfide was heated to 120° on a paraffin-bath until the mixture had been molten for seven minutes. The mass, when cooled, was extracted with benzene. The thiocoumarin was recrystallized from alcohol, separating as orange-yellow, seed-like crystals; m. p., 146°. The excess of sulfur which remained was removed by treating the mixture with copper. After purification, the 6-methylthiocoumarin crystallized in yellow plates; m. p., 148°.

6-Methylthiocoumarin-mercurichloride.—Equimolecular quantities of 6-methylthiocoumarin and mercuric chloride, both in ether, were mixed. A canary-yellow precipitate separated which melted, with decomposition, at 225°.

6-Methylcoumarin-hydriodide-periodide.—Concd. hydriodic acid containing free iodine was added to a benzene solution of 6-methylcoumarin, and the mixture was warmed. As it cooled, dark green, irridescent crystals separated. The compound could not be repurified as it decomposes, even on standing, into iodine and 6-methylcoumarin.

6-Methylcoumarin-potassium-iodide-periodide.—To a solution of 5.3 g. of 6-methylcoumarin, 3.1 g. of iodine and 1.5 g. of potassium iodide in 15 cc. of alcohol, warm ether was gradually added until the point of precipitation was reached. As the liquid cooled, beautiful, brown, velvet-like tufts of crystals separated; m. p., 89–90°.

6-Methylcoumarin-bihydride.—Five g. of 6-methylcoumarin was dissolved in 200 cc. of dil. alcohol. In an atmosphere of carbon dioxide, 100 g. of 30% sodium amalgam was added and the mass was warmed on a water-bath. The bihydride that separated was recrystallized from alcohol, forming then a white powder that melted, with partial decomposition, at 225°.

Work is being continued on the preparation of the homologs of 6-methylcoumarin together with the condensation of *o*- and *m*-cresols with fumaric and maleic acids.

Summary

6-Methylcoumarin has been prepared by condensing *p*-cresol with maleic and fumaric acids.

The most favorable conditions for the production of 6-methylcoumarin have been determined.

The following derivatives of 6-methylcoumarin have been prepared: (1) 6-methylcoumaric acid and some of its salts; (2) 6-methylcoumarin-dibromide; (3) 6-methylcoumarin-mercurichloride; (4) 6-methylcoumarin-platinichloride; (5) 6-methylthiocoumarin; (6) 6-methylthiocoumarin-mercurichloride; (7) 6-methylcoumarin-hydriodide-periodide; (8) 6-methylcoumarin-potassium-iodide-periodide; (9) 6-methylcoumarin-bihydride.

The homologs of 6-methylcoumarin are being studied.

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