[Contribution from the University of Toronto]

REACTION OF LACTONES AND OF FURFURAN DERIVATIVES WITH AROMATIC HYDROCARBONS AND ALUMINUM CHLORIDE

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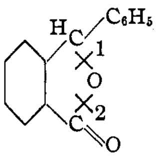
Eijkman[1] used γ-valerolactone with benzene and aluminum chloride and obtained γ-phenylvaleric acid and obtained a similar result when he used toluene instead of benzene. He also found that γ-phenyl-butyrolactone with benzene gave γ-diphenylbutyric acid. Gresly[2] used phenylphthalide and tolylphthalide with benzene and aluminum chloride and obtained triphenylmethane *o*-carbonic acid and tolyl-diphenylmethane *o*-carbonic acid, respectively. In each of these reactions the ring is represented as breaking at the oxygen member and adding one formula weight of the aromatic hydrocarbon, the hydrogen atom attaching itself to the oxygen, forming an acid.



Using the formula for phenylphthalide, it is seen that Gresly represented it as breaking at the 1 position.

If it had broken at the 2 position, a ketone would have resulted. It is also possible that cases might be found where we should have to represent the phenyl group as attaching itself to the oxygen atom.

In the experiments described in this paper, various other cyclic substances containing oxygen as one member of the ring have been used in the Friedel and Crafts reaction, with the object of seeing whether any general rules can be given for the reaction in such cases.

Phthalide was found to react in the same way as phenylphthalide but diphenylphthalide, which for steric hindrance reasons might be expected to behave differently, gave no reaction. Coumarine, a δ-lactone, gave a small yield of α-phenyl-α,β-dihydrocoumarine and the ring was not broken; this corresponds with the finding of Lorriman[3] that naphthalic anhydride, a six-membered ring containing oxygen, did not react with benzene and aluminum chloride and with the finding of Eijkman[4] that various unsaturated acids would react with benzene at the point of unsaturation.

Coumarilic acid with benzene and aluminum chloride gave α-phenyl-α,β-dihydrocoumarilic acid. Pyromucic acid, also, gave no rupture of the ring, but the addition of one formula weight of benzene, and the product is believed to be β-phenyl-α,β-dihydropyromucic acid.

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[1] Eijkman, *Chem. Centr.*, **75** [I], 1416 (1904).

[2] Gresly, *Ann.*, **234**, 241 (1886).

[3] Lorriman, This Journal, **47**, 211 (1925).

[4] Eijkman, *Chem. Centr.*, **78** [II], 2045 (1907).

Phthalimide and phthalimidine were also used in this reaction under various conditions, and although there seemed to be some evidence of reaction nothing but the original substances could be identified in the product.

Experimental Part

Phthalide with Benzene and Aluminum Chloride.—Five g. of phthalide, 18 cc. of benzene and 10 g. of aluminum chloride were used. After 30 minutes, the flask was warmed at 60–70° for 25 hours. The intermediate compound decomposed violently when dil. hydrochloric acid was added and the product, after recrystallization from hot, dil. alcohol, proved to be *o*-benzylbenzoic acid; m. p., 114°; yield, 50%. This acid had previously been prepared by Rotering and Zincke[5] by the reduction of *o*-benzoylbenzoic acid.

Phthalide with Naphthalene and Aluminum Chloride.—Experiments with benzene as solvent showed that the phthalide reacted only with the benzene. Four g. of phthalide and 10 g. of naphthalene were dissolved in 25 cc. of carbon disulfide, and 12 g. of aluminum chloride was added. After heating on the water-bath for two and one half hours, the product gave 1 g. of phthalide and a tar which, on boiling for 18 hours with 10% sodium hydroxide solution, yielded a small amount of a substance; this, after repeated recrystallization from acetic acid, melted at 136–137°. This was identical with the product obtained by the reduction of β-naphthoylbenzoic acid (1,2) and was, therefore, β-naphthylmethylbenzoic acid (1,2), $C_{10}H_7CH_2.C_6H_4.CO_2H$.

Reduction of β-Naphthoylbenzoic Acid (1,2).—One g. of β-naphthoylbenzoic acid and 0.5 g. of copper sulfate were dissolved in 35 cc. of concd. ammonium hydroxide, and 7 g. of zinc dust was gradually added. This was heated for 38 hours, a slow current of ammonia being passed into the flask during that time. The filtrate was acidified and the product recrystallized from acetic acid.

Phenylphthalide with Naphthalene and Aluminum Chloride.—When benzene was used as a solvent the product gave only triphenylmethane *o*-carbonic acid, m. p. 162°, which was further identified by distillation with barium hydroxide at 200°, giving triphenylmethane. Five g. of phenylphthalide and 5 g. of naphthalene were dissolved in 25 cc. of carbon disulfide, and 5 g. of aluminum chloride was added. The reaction was allowed to proceed for 20 hours at room temperature and gave, after removal of the carbon disulfide and excess of naphthalene, a light yellow product which was extracted with 3% sodium carbonate solution; the precipitate, after acidification, was recrystallized from acetic acid and found to be β-naphthyl-phenylmethylbenzoic acid (1,2), $C_{10}H_7.(C_6H_5)CH.C_6H_4.CO_2H$, identical with that prepared by McMullin[6] by the reduction of β-naphthylphenylphthalide.

Diphenylphthalide with Benzene and Aluminum Chloride.—Five g. of diphenylphthalide, 6 g. of aluminum chloride and 25 cc. of benzene were used. There was very little evidence of reaction and after four hours' heating only diphenylphthalide was recovered from the product.

Coumarine with Benzene and Aluminum Chloride.—Three g. of coumarine dissolved in 15 cc. of benzene was treated with 5.5 g. of aluminum chloride. On heating, the aluminum chloride went into solution and a heavy oil settled to the bottom of the flask. The mixture was heated for ten hours and after the addition of dil. hydrochloric acid and removal of the benzene by steam, 1 g. of coumarine was recovered from the aqueous solution. The oily, black tar was heated with 5% sodium hydroxide solution and the liquid, on acidification, gave a fine, grayish-white precipitate which crystallized

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[5] Rotering and Zincke, *Ber.*, **9**, 633 (1876).

[6] McMullin, THIS JOURNAL, **44**, 2060 (1922).

from acetic acid as fine, white needles of β-phenyl-α,β-dihydrocoumarine, m. p. 82°, previously described by Liebermann.[7]

Coumarilic Acid with Benzene and Aluminum Chloride.—Five g. of coumarilic acid, 8.2 g. of aluminum chloride and 40 cc. of benzene were heated for six hours at 60–70°. After acidification and removal of the benzene, the tar was separated from the aqueous solution while still hot. On cooling, 0.4 g. of white crystals was precipitated; m. p., 146–147°. The tar was digested with 10% sodium carbonate solution and a further 2.5 g. of the white crystals obtained which, after recrystallization from benzene, melted at 147–147.5°. This substance is soluble in hot water, alcohol, benzene, acetic acid, ether and chloroform and slightly soluble in carbon tetrachloride. The methyl ester gave white needles; m. p., 68–69°.

Anal. Calcd. for $C_{15}H_{11}O_3Ag$: Ag, 31.1. Found: 31.0.

Bromination of the Acid (m. p., 147–147.5).—One g. of the acid was dissolved in carbon disulfide, and bromine was added. Hydrogen bromide was slowly evolved and after standing for 48 hours at room temperature, the solution was evaporated to a small volume and gave rosets of white needles; m. p., 241°. This product is quite soluble in acetone and moderately soluble in ether, alcohol and carbon disulfide. On oxidation it gave only benzoic acid. Analysis showed that substitution had taken place.

Anal. Calcd. for $C_{15}H_{11}O_3Br$: Br, 25.0. Found: 25.0.

When the acid was brominated in chloroform solution, a product was obtained which melted at 127° after recrystallization from alcohol. Analysis showed that this product contained the same proportion of bromine as that melting at 241°, and boiling the sodium salt in either aqueous or alcoholic solution converted it into the higher-melting compound.

Oxidation of the Acid (m. p., 147–147.5).—Two g. of the acid was dissolved in glacial acetic acid and 15 g. of sodium dichromate added. After heating on the water-bath for 12 hours the solution yielded benzoic acid. In the formation of the acid (m. p., 147–147.5°) if the ring of the coumarilic acid formula had been broken at the oxygen member, two of the possible products are already known and neither melts at 147°, while neither of the other two would give benzoic acid on oxidation. Also, each of these four possible products would be an unsaturated acid and would give an addition compound with bromine. This acid is, therefore, an α,β addition compound of coumarilic acid with benzene and since, if the phenyl group were in the β position, the oxidation would be expected to give benzophenone or a derivative of benzophenone, the acid must be α-phenyl-α,β-dihydrocoumarilic acid. As the oxidation of the acid (m. p., 241°) gave only benzoic acid, these two bromination products are probably different modifications of β-bromo-α-phenyl-α,β-dihydrocoumarilic acid.

Coumarilic Acid with Toluene and Aluminum Chloride.—Four g. of coumarilic acid was added to 30 cc. of toluene, in which it is only slightly soluble. Six g. of aluminum chloride was slowly added and the coumarilic acid gradually went into solution. After one hour the mixture was heated for three and one-half hours. The oily product was crystallized from benzene and recrystallized from carbon disulfide; m. p., 165–165.5°.

Anal. Calcd. for $C_{16}H_{13}O_3Ag$: Ag, 29.9. Found: 30.4.

Bromination of the acid in carbon disulfide solution gave yellowish-white crystals, m. p. 260°, soluble in acetone and less soluble in ether, alcohol and benzene.

Anal. Calcd. for $C_{16}H_{13}O_3Br$: Br, 24.0. Found: 24.2.

Assuming that the reaction with toluene is the same as that with benzene, this

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[7] Liebermann and Hartmann, *Ber.*, **24**, 2582 (1891).

product is α-*p*-tolyl-α,β-dihydrocoumarilic acid. The methyl ester was prepared and melted at 87–88°. The bromine derivative is β-bromo-α-*p*-tolyl-α,β-dihydrocoumarilic acid.

Pyromucic Acid with Benzene and Aluminum Chloride.—Eight g. of the acid was dissolved as far as possible in 200 cc. of benzene, and 19 g. of aluminum chloride was added in small portions. Hydrogen chloride was evolved, the pyromucic acid went into solution and an oily tar was precipitated. The flask was kept cool for two hours and then heated until hydrogen chloride ceased to be evolved. This usually required about six hours. After acidification and removal of the benzene a light brown tar remained. The tar was boiled with concd. hydrochloric acid to remove inorganic matter, and the residue was dissolved in ammonium hydroxide. The ammonia solution was slowly acidified and the first precipitate rejected. Recrystallization from boiling water gave leaflets; m. p., 159°; yield, 5 g. This acid is quite soluble in alcohol, acetone, carbon disulfide and chloroform, and less soluble in benzene and hot water.

Anal. Calcd. for $C_{11}H_9O_3Ag$: Ag, 36.4. Found: 37.0.

Bromination of the Product from Pyromucic Acid.—An excess of bromine was added to a solution of the acid in warm chloroform. Hydrogen bromide was slowly evolved and the flask was kept warm for 12 hours. On cooling, there was a heavy precipitate of small, white needles which, on recrystallization from hot benzene, melted at 251°. This material is soluble in acetone and alcohol and sparingly soluble in chloroform. Boiling with alcoholic potassium hydroxide for 12 hours left it unchanged.

Anal. Calcd. for $C_{11}H_9O_3Br$: Br, 29.7. Found: 29.8.

Oxidation of the Brominated Product.—One g. of the material was boiled for 15 hours with potassium dichromate in glacial acetic acid. This was evaporated to dryness and the residue boiled with water. After removal of the chromium compounds from the solution a silver salt was precipitated by silver nitrate. The silver salt was suspended in water and the silver removed by hydrogen sulfide. The filtrate was evaporated to dryness and the residue dissolved in boiling chloroform, from which the fine needles of phenylsuccinic acid were obtained.

Hill and Sanger[8] oxidized various bromopyromucic acids with bromine and found that δ-bromopyromucic acid was the only one which gave a dibasic acid free from bromine. They also found that the α carbon atom was always completely oxidized. In view of Hill and Sanger's results, our experiments would indicate that the phenyl group was in either the β or the γ position and the bromine in the δ position, and the stability of the bromo compound toward alcoholic potassium hydroxide would indicate that the addition of benzene to pyromucic acid had taken place in the α,β rather than in the γ,δ position. The product before bromination is, therefore, β-phenyl-α,β-dihydropyromucic acid and the brominated product is δ-bromo-β-phenyl-α,β-dihydropyromucic acid.

This research was carried out under the direction of Professor F. B. Allan. The author held a Studentship from the Research Council of Canada.

Summary

1. Phthalide and phenylphthalide, in the Friedel and Crafts reaction, give acids and not ketones. Diphenylphthalide, which, owing to steric

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[8] Hill and Sanger, *Proc. Am. Acad. Arts Sci.*, **21**, 135 (1886).

hindrance, might be expected to give not an acid but a ketone, showed no reaction with benzene and aluminum chloride.

2. When coumarine reacts with benzene and aluminum chloride the ring is not broken but an addition compound with benzene is formed. This corresponds with the results of Lorriman, who found no reaction with naphthalic anhydride, which also has a six-membered ring containing oxygen in the formula.

3. In the reaction with coumarilic acid and with pyromucic acid, addition compounds are formed but the ring is not broken.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WESLEYAN UNIVERSITY]

BROMINE DERIVATIVES OF SOME DELTA KETONIC ESTERS

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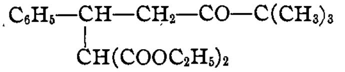
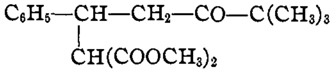
The bromination of certain δ-ketonic esters, such, for example, as dimethyl β-phenyl-γ-benzoyl-ethylmalonate, has already been investigated by Kohler.[1] The esters utilized in this study are closely related to the compound mentioned above, but have a pivalyl group in place of the benzoyl.



$$C_6H_5—\underset{\displaystyle CH(COOC_2H_5)_2}{\underset{|}{CH}}—CH_2—CO—C(CH_3)_3$$



$$C_6H_5—\underset{\displaystyle CH(COOCH_3)_2}{\underset{|}{CH}}—CH_2—CO—C(CH_3)_3$$

The bromine derivatives prepared from them will be used in this Laboratory in a continuation of work in the cyclopropane series.

With benzalpinacolone and sodium ethoxide, ethyl malonate yielded the ethyl ester of β-phenyl-γ-pivalyl-ethylmalonic acid. By brominating this in carbon tetrachloride, only one product, a monobromo compound, was isolated. This substance was quite stable at elevated temperatures, successfully withstanding heating for an hour at 200°.

Because of the generally superior crystallizing power of methyl compounds, work with ethyl esters was temporarily discontinued and methyl derivatives utilized thenceforth. When benzalpinacolone and methyl malonate were treated with sodium methoxide, the methyl ester of β-phenyl-γ-pivalyl-ethylmalonic acid was obtained, and the corresponding ester acid isolated as a by-product. When esterified, the ester acid yielded the dimethyl ester mentioned above.

When the methyl ester obtained by the Michael reaction was brominated in carbon tetrachloride, two crystalline monobromo derivatives melting, respectively, at 83.5° and 85°, were obtained. By gentler bromination of the ester in methyl alcohol, the same products resulted, but in

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[1] Kohler, THIS JOURNAL, **44**, 840 (1922).