[Contribution from the Chemistry Laboratory of Johns Hopkins University]

SOME SUBSTITUTED ORTHO-BENZOYL-BENZOIC ACIDS AND THE CORRESPONDING ANTHRAQUINONES

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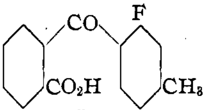
In a recent paper from this Laboratory[2] the condensation of phthalic anhydride with certain aromatic fluorine and iodine derivatives has been described. This investigation has been extended to include condensations with *m*-fluorotoluene, *o*- and *p*-fluoro- and *o*-chloro-ethylbenzenes, *m*-diethyl-, *m*-di-*iso*propyl- and cyclohexylbenzenes. In most cases the corresponding anthraquinones have been obtained.



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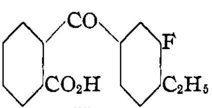

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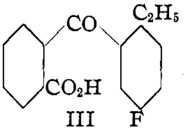

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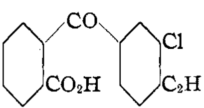

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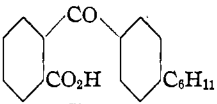

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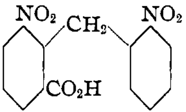

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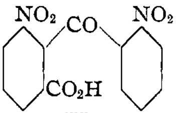

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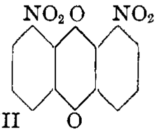

VIII

An attempt has been made to prepare the missing *o*-(*p*-nitrobenzoyl)benzoic acid, but a dinitro was obtained instead.

Results

As new intermediates, *o*- and *p*-fluoro-ethylbenzenes have been made with the usual yields by Holleman's method[3] for the fluorotoluenes.

The condensations with phthalic anhydride have been carried out in the usual way. The benzoyl-benzoic acids were converted into the corresponding substituted anthraquinones[4] by heating with 10 parts of sulfuric acid.

In the case of *m*-fluorotoluene, condensation may take place *para* either to the methyl or to the fluorine. The low melting point of the crude product indicates the presence of isomers, one of which predominates and is readily obtained pure by recrystallization from benzene. Since the influence of the methyl group has been shown by Swarts[5] to be greater than that of fluorine, this acid must be the 4-methyl-2-fluoro isomer, **I**.

From *m*-chloro- and *m*-bromotoluene corresponding acids were similarly prepared. These acids could not be obtained in satisfactory purity as bromine seems to be liberated during the reaction with *m*-bromotoluene.

There are four possible isomeric acids from *o*-fluoro-ethylbenzene but

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[1] From the Doctor's dissertation of Osborne R. Quayle, 1924.

[2] Hahn and Reid, This Journal, **46**, 1645 (1924).

[3] Holleman, *Rec. trav. chim.*, **23**, 233, 238 (1904).

[4] Heller and Schülke, *Ber.*, **41**, 3627 (1908).

[5] Swarts, *Rec. trav. chim.*, **35**, 131 (1915).

the chief product is the 4-ethyl-3-fluoro- acid, II, which is readily obtained pure. This is dehydrated to give 2-ethyl-3-fluoro-anthraquinone. As *o*-chloro-ethylbenzene had not previously been condensed with phthalic anhydride this reaction was tried and the 4-ethyl-3-chloro- acid, IV, obtained, but this acid could not be dehydrated to an anthraquinone. These constitutions are assumed from the reactions of *o*-chlorotoluene[4,6] and *o*-fluorotoluene.[7]

p-Fluoro-ethylbenzene condenses readily with phthalic anhydride. The product is readily purified and must be the 2-ethyl-5-fluoro- acid, III, from which 2-ethyl-4-fluoro-anthraquinone is obtained.

p-Iodotoluene was put through the usual process but the resulting acid contained only a trace of iodine. It had been found previously that the most of the iodine of iodobenzene is liberated when this substance is treated with phthalic anhydride and aluminum chloride. The fact that condensation tends to take place *para* to the methyl group probably aids in the liberation of the iodine of *p*-iodotoluene.

From cyclohexylbenzene, *o*-(*p*-cyclohexyl-benzoyl)benzoic acid was readily obtained, but it was difficult to purify and when purified could not be condensed to the anthraquinone.

From a sample of diethylbenzene, in which the *meta* isomer probably predominated an *o*-(diethylbenzoyl)benzoic acid was obtained which appeared to be a mixture of isomers, as it could not be obtained with a sharp melting point, but this substance yielded an anthraquinone which was probably the 1,3-diethyl isomer. From a similar sample of di-*iso*propylbenzene the acid and the anthraquinone were obtained but both seemed to be mixtures of isomers.

Since in the nitration of *o*-benzoyl-benzoic the nitro group enters the 3′ and 2′ positions only, and since nitrobenzene[8] does not condense with phthalic anhydride, it has never been possible to obtain *o*-(*p*-nitrobenzoyl)-benzoic acid. It was thought that by nitrating *o*-benzylbenzoic acid the nitro group would enter the 4′ position and that this acid could be oxidized to the desired 4′-nitrobenzoyl acid. Accordingly, *o*-benzoylbenzoic acid was reduced by the method of Scholl[9] and the resulting benzyl acid nitrated. The product obtained by recrystallization appears to be the 6,2′-dinitro- acid, VI, which was oxidized to the 6,2′-dinitro-*o*-benzoylbenzoic acid, VII, from which 1,8-dinitro-anthraquinone, VIII, melting at 310°, was obtained. The 1,8 derivative[10] is said to melt at 312°.

[6] Ullmann and Dasgupta, *Ber.*, **47**, 553 (1914).

[7] Ref. 2, p. 1646.

[8] Egerer and Meyer, *Monatsh.*, **34**, 89 (1913). A. Hofmann, *ibid.*, **36**, 806 (1915).

[9] Scholl, *ibid.*, **32**, 687 (1911).

[10] Ger. pat. 167,699 (1904), Meister, Lucius and Brüning Co.: *Chem. Centr.*, **1906**, I, 1070.

In many of its reactions naphthalic anhydride[11] resembles phthalic. This suggested the possibility of condensing it with benzene in the presence of aluminum chloride. Several attempts were made to effect this condensation but without results, the anhydride being recovered unchanged each time.

Experimental Part

***m*-Fluorotoluene and *o*- and *p*-Fluoro-ethylbenzenes.**—These were made according to the general method of Holleman.[3] The amine in 50g. portions is dissolved in 5 parts of water and 1 part of sulfuric acid and diazotized. Several of these solutions may be united for the next step. The cold diazo solution is run slowly through a water-jacketed copper tube into approximately 1.25 times its weight of a hot (90°) commercial, 50% hydrofluoric acid contained in an all-copper vessel, during mechanical agitation and under a copper reflux condenser. By connecting the top of the condenser with a gas wash bottle the progress of the reaction may be judged by the rate of evolution of nitrogen. When the reaction is complete, the temperature of the oil-bath surrounding the reaction vessel is raised until the fluoro compound distils with some of the water. The distillate is collected in a brass vessel. An excess of alkali is added. The oil is steam distilled, separated, dried over calcium chloride and fractionated. The yields, properties and analyses are given in Table I.

TABLE I

PREPARATION OF FLUORO-ETHYLBENZENES

Groups	Amine used G.	Yield G.	Yield %	B. p. °C.	Density d_0^0	Density d_0^{20}	Fluorine, % Calcd.	Fluorine, % Found
o-F-ethyl	100	20	19	136–7	1.002	0.983	15.23	15.16
p-F-ethyl	110	26	24	141	0.994	0.967	15.23	15.55

Benzoylbenzoic Acids and Anthraquinone.—The condensations were carried out in the usual manner using two molecular equivalents of aluminum chloride to one of phthalic anhydride and an excess of the substituted hydrocarbon or carbon disulfide as a diluent. In each case the product was treated with ice and water and steam distilled. The residue was dissolved in alkali. The filtered alkaline solution was poured slowly into concd. hydrochloric acid, since otherwise more or less of an insoluble aluminum salt may be precipitated with the acid. The acid so obtained was redissolved in dil. alkali and cautiously reprecipitated by dil. acid. The acids precipitated as sticky masses which became crystalline on standing. They were recrystallized from acetic acid or benzene. The yields were above 90%.

TABLE II

FLUORO-ALKYL-BENZOYL-*o*-BENZOIC ACIDS

Fluoro-*o*-benzoylbenzoic acid	Phthalic anhydride, g.	Aromatic halide, g.	Aluminum chloride, g.	M. p. °C.	Halogen, % Calcd.	Halogen, % Found
4-Methyl-2-	44	63	86	129	7.36	7.52
4-Ethyl-3-	15	13	30	120	6.98	6.80
2-Ethyl-5-	15	13	30	210–20	6.98	7.23
4-Ethyl-3-	28	26	50	105	12.28	11.86

These acids were condensed to the corresponding anthraquinones by heating them with 10 parts of concd. sulfuric acid. In each case the cooled mixture was poured on ice and the organic material filtered off. The residue was extracted with sodium hy-

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[11] Hahn and Holmes, *J. Ind. Eng. Chem.*, **13**, 822 (1921); **14**, 80 (1922).

droxide solution to remove unchanged benzoyl-benzoic acid. The substituted anthraquinones were purified by crystallization from benzene, dissolved by vatting with zinc dust in alkaline solution and precipitated from the filtered solution by air oxidation. The yields were high except from the 4-ethyl-3-chloro acid from which no anthraquinone was obtained. The time and temperature of heating together with the melting points and analyses are given in Table III.

TABLE III

PREPARATION AND PROPERTIES OF SUBSTITUTED ANTHRAQUINONES

Anthraquinones	Temp. °C.	Time Hours	M. p. °C.	Fluorine, % Calcd.	Found
2-Methyl-4-fluoro-	125	0.5	135.5–7	7.76	7.38
2-Ethyl-3-fluoro-	100	3	110	7.48	7.63
1-Ethyl-4-fluoro-	100	3	80–2	7.48	7.30

From 75 g. of phthalic anhydride and 150 g. of aluminum chloride in 120 g. of diethylbenzene, the diethylbenzoyl-*o*-benzoic acid was obtained. The diethylbenzene had been prepared by the ethylation of benzene and was probably mainly the *meta* isomer. The acid obtained from it was a mixture of isomers as it could not be brought to a constant melting point although the analysis was not far from the calculated value.

Anal. Calcd.: C, 81.20; H, 6.82. Found: C, 81.00; H, 6.69.

It was converted into a diethyl-anthraquinone, m. p. 83–85°, probably the 1,3 isomer.

Anal. Calcd.: C, 87.09; H, 6.50. Found: C, 86.66; H, 6.89.

Similarly a condensation was carried out with di-*iso*propylbenzene but the resulting acid could not be purified. It was converted into an anthraquinone, but this could not be obtained in a satisfactory condition.

From 40 g. of cyclohexylbenzene, 40 g. of phthalic anhydride, 80 g. of aluminum chloride and 200 cc. of carbon disulfide the desired acid was obtained in nearly the calculated amount but was almost black. It proved to be very difficult to purify. The solution of its sodium salt was twice purified with animal charcoal. The precipitated acid was dissolved in hot glacial acetic acid and enough water added to precipitate a large portion of it. This was black and tarry and was discarded. From the mother liquor the remainder of the acid was obtained in better condition and was recrystallized from benzene; m. p., 166–167°.

Anal. Calcd.: C, 77.81; H, 6.54. Found: C, 77.49, 77.54; H, 6.48; 6.27.

The condensation of this acid to cyclohexyl-anthraquinone was tried with 70, 80 and 94% sulfuric acid but was not effected; either a charred mass resulted or there was no action.

***o*-(Dinitrobenzyl)benzoic Acid.**—A solution of 12 g. of benzylbenzoic acid prepared according to Scholl,[9] in 100 g. of 90% nitric acid stood for 26 hours and was then poured into water. The product proved to be a mixture of mono- and dinitro acids from which the dinitro was obtained pure by five crystallizations from acetic acid; m. p., 163–164°.

Anal. Calcd.: C, 55.66; N, 9.26. Found: C, 55.88; N, 9.64.

***o*-(Dinitrobenzoyl)benzoic Acid.**—To a boiling solution of the dinitrobenzyl acid in acetic acid was added a concd. water solution of chromic anhydride until the orange color persisted for half an hour. The *o*-(dinitrobenzoyl)benzoic acid was precipitated by the addition of water and recrystallized from acetic acid. It melted at 201°, softening below this point.

Anal. Calcd.: C, 53.47; H, 2.55; N, 8.86. Found: C, 53.86; H, 2.84; N, 9.16.

1,8-Dinitro-anthraquinone.—The dinitro acid described above was found to be difficult to condense but when it was heated for three hours to 150° with a 23% oleum containing boric acid the dinitro-anthraquinone was obtained; m. p., 310°.

Anal. Calcd.: N, 9.40. Found: 9.60.

Its melting point identifies it as 1,8-dinitro-anthraquinone which is said to melt at 312°. From this it is probable that both the nitro groups enter the benzyl-*o*-benzoic acid *ortho* to the —CH_2— but in separate rings.

Naphthalic Anhydride.—This anhydride was heated with benzene and aluminum chloride but no evidence of any condensation could be found. It was always recovered unchanged. It was heated with hydroquinone and sulfuric acid to 150–180° but no condensation took place.

Summary

Phthalic anhydride has been condensed with *m*-fluorotoluene, *o*- and *p*-fluoro- and *o*-chloro-ethylbenzenes, *m*-diethyl-, *m*-di-*iso*propyl- and cyclohexylbenzenes. The resulting *o*-benzoylbenzoic acids have been condensed to the corresponding substituted anthraquinones. *o*-Benzylbenzoic acid has been nitrated to the 2,2′-dinitro derivative which has been oxidized to *o*-(*o*-nitrobenzoyl)3-nitrobenzoic acid and this condensed to 1,8-dinitro-anthraquinone.

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CHEMISTRY OF THE TRIMETHYLTIN GROUP

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When a carbon atom is joined to three aryl groups, its remaining valence is strongly amphoteric and the group is capable of existing in the positive or negative or the neutral condition. The triphenylmethyl group is the most familiar example of this type of compound. It is known that many other elements, combined with alkyl or aryl groups, form similar compounds. The general group formula is $R_{n-1}M^n$, where R is a hydrocarbon group and M is an element of valence *n*. Groups of the type $R_{n-2}M^n$ are also known. These, however, will be discussed in a subsequent paper.

Groups of the type $R_{n-1}M^n$ often resemble the triphenylmethyl group very closely and exhibit amphoteric properties in a marked degree. While a number of these groups are known to exist,[1] their physical and chemical properties have not been studied extensively. The present investigation is intended to supply further data, particularly with regard to the chemical properties of the trimethyltin group. As has been pointed out elsewhere,[2]

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[1] Rügheimer, *Ann.*, **364**, 53 (1910). E. Krause, *Ber.*, **54**, 2060 (1921); **55**, 888 (1922). Schlenk, Renning and Racky, *Ber.*, **44**, 1178 (1911). Kraus, THIS JOURNAL, **35**, 1732 (1913). Midgley, Hochwalt and Calingaert, *ibid.*, **45**, 1821 (1923). Ladenburg, *Ann. Spl.*, **8**, 65 (1872).

[2] (a) Kraus, *Rec. trav. chim.*, **42**, 588 (1923); (b) THIS JOURNAL, **46**, 2196 (1924). (c) Kraus and Callis, *ibid.*, **45**, 2624 (1923). (d) Kraus and Greer, *ibid.*, **45**, 3078 (1923).