from 114 grams of glucose he got about 30 g. of hexone acids, largely gluconic acid, that is, one-fourth of the oxidation took this direction. It seems not improbable on the basis of these facts, that gluconic acid may be derived also from some other source than the positive ion.

The products of oxidation of the anion $C_6H_{11}O_6$ are possibly those which have been carefully studied by Nef[1] and the further mechanism of the oxidation he has largely elucidated.

THE ACTION OF NITRIC ACID UPON BENZOYL CHLORIDE IN THE PRESENCE OF ACETIC ANHYDRIDE.

BY W. J. KARSLAKE AND R. C. HUSTON.

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Claus and Schmidt,[1] Orton,[2] Schwalbe,[3] Tingle and Blanck,[4] and many others, have shown that acetic acid and acetic anhydride, when used as solvents and diluents in the nitration of aromatic compounds, exert a more or less marked influence upon the character of the products formed. Pictet and Genequand,[5] and Pictet and Khotinsky[6] have shown that under these conditions the real nitrating agent is probably either diacetylorthonitric acid, or acetyl nitrate, or both. In the general action of these reagents towards aromatic compounds there seems to be, on the whole, a slight tendency to form ortho in preference to para or meta derivatives. Toward aromatic amines they sometimes act as nitrating and sometimes as acylating agents. This behavior is similar to that of benzoyl nitrate.[7] It does not appear, however, that acylation ever takes place in the nucleus, as may nitration, but always in the side chain in connection with hydroxyl, amino, and other similar groups.

In this paper are described a few experiments and the results obtained by the action of mixtures of various proportions (1) of nitric anhydride and acetic anhydride, and (2) of fuming nitric acid and acetic anhydride, upon benzoyl chloride.

In the first set of experiments the conditions are such that the active nitrating agent is acetyl nitrate diluted with more or less acetic anhydride, $(CH_3CO)_2O + N_2O_5 = 2CH_3COONO_2$. When benzoyl chloride, acetic anhydride and nitric anhydride are mixed in a flask at 0° no reaction takes place until they are heated to about 60° when a rather vigorous reaction occurs with evolution of oxides of nitrogen. After the nitrous

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[1] *Ber.*, **19**, 1425.

[2] *J. Chem. Soc.*, **81**, 806. *Ber.*, **40**, 370.

[3] *Ber.*, **35**, 3301.

[4] *Amer. Chem. J.*, **36**, 605.

[5] *Ber.*, **35**, 2526; **36**, 2225.

[6] *Compt. rend.*, **144**, 210.

[7] Francis, *Ber.*, **39**, 3798; Butler, *Ibid.*, **39**, 3804.

fumes are all given off, the contents of the flask, upon cooling, solidifies to a semi-pasty mass which upon examination fails to reveal any products formed by the action of acetyl nitrate upon benzoyl chloride. A semi-pasty mass of the *same* composition may be obtained by treating benzoyl chloride with acetic anhydride alone. The presence of acetyl nitrate is, therefore, unnecessary. The reaction, with evolution of nitrous fumes, which does take place is simply due to the action of acetyl nitrate upon acetic anhydride to form tetranitromethane, as shown by Pictet.[1] No nitro or aceto derivatives of either benzoyl chloride or benzoic acid are formed.

In the second set of experiments the active nitrating agent is probably a mixture of acetyl nitrate and diacetylorthonitric acid diluted with more or less acetic anhydride and, possibly, acetic acid, $2(CH_3CO)_2O + 3HNO_3 = 2CH_3COONO_2 + (CH_3COO)_2N(OH)_3$ and $(CH_3CO)_2O + HNO_3 = CH_3COONO_2 + CH_3COOH$. It is also quite possible that other acetyl derivatives of nitric acid may be present, though they have never been isolated, such as, for example, $(CH_3COO)_2NO.OH$, $(CH_3COO)_3NO$, etc. When various proportions of fuming nitric acid, acetic anhydride and benzoyl chloride are mixed in a flask at 0° no visible reaction takes place, but upon warming to about 35°–40° such a vigorous reaction occurs that the flask and its contents must be cooled in an ice bath. After cooling, and standing some time, the contents of the flask are found to consist chiefly of benzoic acid, metanitrobenzoic acid, and orthoacetobenzoic acid. The relative amount of each present depends upon the proportions of nitric acid, acetic anhydride, and benzoyl chloride taken. One molecular equivalent of nitric acid, in the presence of an equal amount of acetic anhydride, produces only benzoic acid, practically no nitro- or acetobenzoic acids being formed. Any increase over this in the amount of nitric acid produces, at first, both a nitrating and acylating action; but as the proportion of nitric acid still further increases the acylation effect decreases while that of nitration increases. That the presence of the acid-chloride group COCl is not necessary for the introduction of the acetyl group into the nucleus, any more than it is for the nitro group, is seen in the fact that benzoic acid when treated with one molecular equivalent of nitric acid in the presence of acetic anhydride gives both metanitro- and orthoacetobenzoic acids. Acetic anhydride *alone* does not acylate benzoyl chloride or benzoic acid in the nucleus. Hence it is the acetyl nitrate, or the diacetylorthonitric acid, or both, which acts both as the nitrating and acylating agent. Benzoyl chloride, as such, seems to be incapable of being either nitrated or acylated by acetyl nitrate. With diacetylorthonitric acid it seems to be first hydrolyzed to benzoic acid, and then nitrated or acylated.

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[1] *Loc. cit.*

Experimental.—The material used was prepared as follows: The *nitric acid* by distilling the concentrated commercial acid several times from concentrated sulphuric acid. The specific gravity of the final product was 1.515. The *nitric anhydride* by slowly adding 25 grams of nitric acid, sp. gr. 1.515, to 50 grams phosphorus pentoxide in a retort surrounded by an ice bath. After standing 15 hours the nitric anhydride was carefully distilled off and collected in a cooled receiver protected from moisture. The *acetic anhydride* was obtained by boiling 1000 cc. commercial acetic anhydride with 100 cc. acetyl chloride for two hours with a return condenser. The product was then fractionated, using a Hempel still-head. The portion boiling at 135–140° was used. The *benzoyl chloride* was prepared by treating 500 grams benzoic acid with 885 grams phosphorus pentachloride, distilling the resulting liquid with a Hempel still-head to 112°, and then the residue in a common distilling flask. The portion collected between 192–195° was used.

Action of a Mixture of Nitric and Acetic Anhydrides upon Benzoyl Chloride.—Ten grams nitric anhydride in one case, and 20 grams in another, were dissolved in 20 cc. acetic anhydride at 0°, and added to 15 grams benzoyl chloride. No reaction appeared to take place until heated to about 60° when a vigorous reaction set in. After the violence of the reaction had subsided it was warmed to completion, cooled, and the resulting product (oil) extracted with ligroin. The undissolved portion was washed with a little cold water, dissolved in ether, and dried over calcium chloride. After filtering from the calcium chloride, and distilling off the ether, a semi-pasty residue was obtained. Upon examination this residue was found to be slowly soluble in boiling water and to separate upon cooling as benzoic acid. No nitro- or acetobenzoic acid was found. Nor did the ligroin extract contain any. Other experiments gave similar results. The same final products were also obtained by the action of 18 grams acetic anhydride upon 25 grams benzoyl chloride.

Action of a Mixture of Nitric Acid and Acetic Anhydride upon Benzoyl Chloride.—24 grams nitric acid were slowly added to 18 grams acetic anhydride at 0° and this mixture then added to 25 grams benzoyl chloride previously dissolved in 18 grams acetic anhydride. Upon gently heating to about 40° a vigorous reaction set in which was moderated by cooling in an ice bath. After the reaction had subsided it was heated until no more nitrous fumes were given off, and then allowed to stand over night. Benzoic acid separated out, was filtered off, and identified. Upon pouring the filtrate into water, and allowing to stand, metanitrobenzoic acid crystallized out. From the final filtrate and wash water there was obtained, upon evaporation and cooling, some orthoacetobenzoic acid which was identified by its melting point (114–115°), sweet taste, crystal form (small plates), and the preparation and analysis of some of its derivatives. In one experiment where twice as much nitric acid and acetic anhydride were taken, the yield of the nitrobenzoic acid was increased threefold while that of the benzoic and acetobenzoic acids were decreased a corresponding amount. Another experiment where 38 grams *benzoic acid* and 40 grams acetic anhydride were treated with a mixture of 21 grams nitric acid and 30 grams acetic anhydride gave about 45 per cent. *m*-nitrobenzoic acid and 10 per cent. *o*-acetobenzoic acid. Thirty-five to forty per cent. of the benzoic acid remained unacted upon. In some experiments hot ligroin was used to dissolve out the acetobenzoic acid from the nitro-benzoic acid, the latter being quite insoluble in this solvent.

o-Acetobenzoic Acid (Acetophenone-o-carboxylic Acid).—This acid was apparently first obtained by Gabriel and Michael (*Ber.*, **10**, 1554; **11**, 1007; **17**, 2521). They obtained it by heating phthalylacetic acid with water. The properties of the free acid described in this paper as obtained by the action of nitric acid in the presence of acetic anhydride upon either benzoyl chloride or benzoic acid agree with the properties of the free acid described by them. There is a difference, however, in some of the derivatives.

o-Acetobenzoyl Chloride, $CH_3.CO.C_6H_4.COCl$.—This was prepared by the action of the calculated amount of phosphorus pentachloride upon the free acid. It is an oil, soluble in alcohol, ether, and many other organic solvents; insoluble in cold water though quite easily saponified by it to give the free acid, especially if warmed.

o-Acetobenzamide, $CH_3.CO.C_6H_4.CO.NH_2$.—This was prepared by treating the acid chloride with concentrated aqueous ammonia, boiling off the excess of ammonia, and recrystallizing from hot water. It separates in small colorless prisms, melting at 116.5°. Analysis: Nitrogen found, 8.47, 8.52. Calculated, 8.59.

o-Acetobenzanilide, $CH_3.CO.C_6H_4.CO.HN.C_6H_5$.—This was prepared by treating the acid chloride with aniline. It crystallized from 50 per cent. alcohol in small colorless plates, melting at 156–157°. It is insoluble in cold water, rather soluble in cold alcohol, readily so in hot alcohol, ether, chloroform, carbon bisulphide, and benzene. Mertens (*Ber.*, **19**, 2367) obtained this compound by the action of aniline upon phthalylacetic acid and describes it as separating in cubes (from benzene) melting at 189–192°. Analysis: Found, N = 5.87, 5.76. Calculated, N = 5.85.

Barium o-Acetobenzoate, $(CH_3.CO.C_6H_4.COO)_2Ba + 2H_2O$.—This salt was prepared by treating a hot solution of the acid with barium carbonate, filtering hot, and evaporating the filtrate nearly to dryness. Upon long standing (about a week), small crystals separated from the syrupy liquid. Gabriel and Michael failed to obtain crystals. Analysis: Found, Ba = 27.52, 27.48. H_2O (at 170°) = 7.20, 7.18. Calculated, Ba = 27.51, H_2O = 7.21.

Strontium o-Acetobenzoate, $(CH_3.CO.C_6H_4.COO)_2Sr + 2H_2O$.—A hot aqueous solution of the acid was treated with excess strontium carbonate, filtered, and filtrate evaporated nearly to dryness. Like the barium salt, after long standing it separated in small crystals from the syrupy liquid. Analysis: Found, Sr = 19.4, 19.38. H_2O (at 170°) = 7.99, 8.04. Calculated, Sr = 19.45, H_2O = 8.01.

Lead o-Acetobenzoate, $(CH_3.CO.C_6H_4.COO)_2Pb + 2H_2O$.—This was prepared by the action of lead carbonate upon a hot solution of the acid. It separated in small flakes which charred when heated to 130°. Analysis: Found, Pb = 36.25, 36.30. H_2O (at 105°) = 6.30, 6.21. Calculated, Pb = 36.38, H_2O = 6.32.

Silver o-Acetobenzoate, $CH_3.CO.C_6H_4.COOAg + 2H_2O$.—Silver nitrate was added in excess to the hot acid solution, the impurities filtered off, and the filtrate evaporated to small bulk. The salt crystallized out in small prisms. It chars when heated to 120°. Analysis: Found, Ag = 35.09, 35.14. Calculated, Ag = 35.17.

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(CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, No. 161.)

3-AMINO-*o*-PHTHALIC ACID AND CERTAIN OF ITS DERIVATIVES.

BY MARSTON TAYLOR BOGERT AND FAREL LOUIS JOUARD.

Received February 3, 1909.

Early attempts on the part of various chemists to prepare 3-amino-*o*-phthalic acid by reduction of the corresponding nitro acid yielded only *m*-aminobenzoic acid.[1] True, it was shown that the nitro acid was actually reduced and aminophthalic acid formed when tin and hydrochloric acid were used as the reducing agents, but when the aminophthalic solution was de-tinned by hydrogen sulphide and the acid filtrate concentrated, carbon dioxide was lost and only *m*-aminobenzoic acid remained.

In 1901, Onnerz,[2] by evaporating the acid filtrate from the tin sulphide at 50° and 18 mm. pressure, and treating the residue with cold sodium hydroxide solution, obtained what he believed to be the 3-aminophthalic acid as a yellow, indefinitely crystalline meal, beginning to darken at 174°, sintering at 179–81°, and melting at 184–6° to a reddish-brown liquid with evolution of carbon dioxide. In the light of the results reported by us further on, we believe that he did actually have the aminophthalic acid in hand in an impure state. He found it impossible to purify the acid, and analyzed the best product that he could get, supporting the rather unsatisfactory figures obtained in the case of the free acid by much closer ones for certain of its salts. By reducing nitrophthalic acid with ferrous sulphate and barium hydroxide in presence of excess of ammonia, with subsequent careful addition of acetic acid, a white, crystalline precipitate separated, which he assumed to be the same aminophthalic acid, but which Kauffman and Beisswenger[3] showed to be its acid ammonium salt.

Seidel[4] reduced nitrophthalic acid with sodium sulphide and obtained a soft, yellow powder, m. p. 226°, whose analysis gave figures agreeing with those calculated for aminophthalic acid.

Various investigators have reported that 3-aminophthalic acid either decomposes spontaneously in aqueous solution,[5] is destroyed on heating

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[1] Faust, *Ann.*, **160**, 56 (1871). Baeyer, *Ber.*, **10**, 124 (1877). Miller, *Ibid.*, **11**, 992 (1878). *Ann.*, **208**, 223 (1881). Pluss, Inaug. Diss., Geneva, 1901.

[2] *Ber.*, **34**, 3745.

[3] *Ibid.*, **36**, 2494 (1903).

[4] *Ibid.*, **34**, 4351 (1901).

[5] Marignac, *Ann.*, **38**, 1 (1841).