further use by distilling the diluted acid from the mixture until it begins to "bump." To the residue are added the amounts of acid and alcohol previously used, and the process outlined above is repeated.

The results obtained are given in Table I.

Summary

1. The following alcohols are converted into chlorides when heated in an open vessel with concd. hydrochloric acid and zinc chloride: methyl, ethyl, *n*-propyl, *iso*propyl, *n*-butyl, *sec*-butyl, *iso*amyl, pentanol-2, cetyl, β-phenylethyl, γ-phenylpropyl, *m*-nitrobenzyl, *p*-nitrobenzyl.

2. The best results were obtained when the substances were used in the molecular ratio, 1 of alcohol, 2 of hydrogen chloride as concd. hydrochloric acid and 2 of zinc chloride. The yields varied from 60 to 82%.

3. The lower alkyl halides can be purified from high-boiling polymerization products by refluxing with concd. sulfuric acid.

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[Contribution from the Department of Chemistry, University of Pittsburgh]

DERIVATIVES OF PARA-NITROBENZALDEHYDE. II

By Charles G. King[1] with Alexander Lowy

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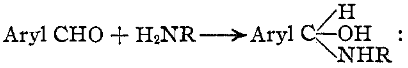
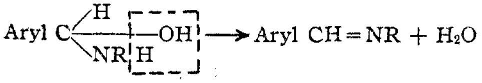
In a previous report[2] the object of the research and references to the literature were given.

The first series of reactions investigated was the preparation of "Schiff bases"[3] according to the following type reactions.



$$\text{Aryl CHO} + \text{H}_2\text{NR} \longrightarrow \text{Aryl C}\begin{cases}\text{H}\\ \text{OH}\\ \text{NHR}\end{cases} : \qquad (1)$$



$$\text{Aryl C}\begin{cases}\text{H}\\ \boxed{\text{OH}}\\ \text{NR}\,\boxed{\text{H}}\end{cases} \longrightarrow \text{Aryl CH}=\text{NR} + \text{H}_2\text{O} \qquad (2)$$

In many cases the reaction is almost instantaneous, the whole mass becoming solid when the two reactants are mixed. It is often necessary, however, to select a suitable condensing medium and solvent, such as alcohol or glacial acetic acid. Heating the reacting materials together for some hours was found necessary to condense *p*-nitrobenzaldehyde with *o*-nitro-aniline, 2,6-dibromo-aniline and 2,4,6-tribromo-aniline. It is often impossible to isolate the intermediate addition compound, due to its instability or the speed of the second reaction. No compounds of the addition product type were isolated during this investigation.

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[1] This report is the abstract of a thesis presented by Charles G. King in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1923.

[2] This Journal, **43,** 625 (1921).

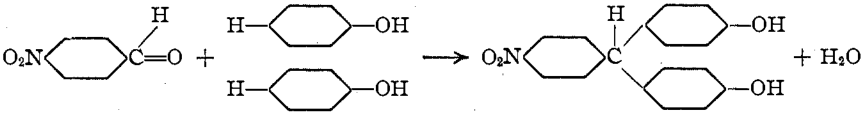
[3] *Ber.*, **35,** 984 (1902).

In a previous study[2] *o*-nitro-aniline and 2,4,6-tribromo-aniline could not be satisfactorily condensed with *p*-nitrobenzaldehyde by refluxing in glacial acetic acid or absolute alcohol. Alway and Gortner[4] were unable to condense *o*-nitro-aniline in a like manner, but stated that *p*-nitrosobenzaldehyde did condense, though with great difficulty. The corresponding *m*- and *p*-nitro-anilines condense readily. Lowy and Downey[5] condensed 2,4-dinitro-benzaldehyde with *o*-nitro-aniline and 2,4,6-tribromo-aniline fairly readily in glacial acetic acid solution. A nitro group in the *ortho* position to the aldehyde group in this case seemed to counteract the "steric hindrance" effect of the *ortho* substituents to the amino group. By heating the reacting materials together in a sealed tube with anhydrous zinc chloride in the opposite cool end, *p*-nitrobenzaldehyde condensed with the amino compounds which had shown a marked "steric hindrance" effect, namely, *o*-nitro-aniline, 2,4,6-tribromo-aniline, and 2,6-dibromo-aniline.

Condensation products were formed by using *p*-nitrobenzaldehyde and the following substituted amines in monomolecular proportions: *o*-bromo-aniline; *m*-bromo-aniline; 2,6-dibromo-aniline; 2,4,6-tribromo-aniline; 3-bromo-4-toluidine; *p*-xylidine and *o*-nitro-aniline.

A second type of condensation studied is that taking place between one molecular equivalent of an aromatic aldehyde or substituted aromatic aldehyde and two of aromatic compounds, such as benzene, phenols, ethers, amines, or substituted phenols and amines. On oxidation the tertiary amine products give rise to dyes of the malachite green series, while the phenolic products give rise to dyes of the aurine type.

This type of reaction may be illustrated by the following equation.



p-Nitrobenzaldehyde was condensed with two moles of the following compounds: phenol, resorcinol, *o*-nitrophenol, thymol and *o*-methylanisole.

The azomethine group characteristic of the "Schiff bases" constitutes a weak chromophore. It was thought that the reduction of the nitro group to an amino group on some of the "Schiff Bases" followed by diazotization, and subsequent coupling with β-naphthol, might furnish a type of dye having a more intense color than that of the corresponding azo dyes. Due to the readiness with which the "Schiff Bases" are hydrolyzed in the presence of acids, alkaline or neutral reducing agents should be used. Sodium hydrogen sulfide was found to be satisfactory. The marked instability of the reduction product which quickly changed to an amorphous, light

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[4] Alway and Gortner, from *C. A.*, 1, 56 (1907).

[5] Lowy and Downey, THIS JOURNAL, **43**, 346 (1921).

yellow, insoluble substance, caused this phase of the work to be discontinued.

Experimental Part

The method used in the preparation of *p*-nitrobenzaldehyde was that described by V. v. Richter.[6]

In the preparation of compounds listed below the ratio of 1 mole of *p*-nitrobenzaldehyde to 1 mole of the substituted amine was used in all cases.

Table I contains the essential results obtained.

TABLE I

RESULTS

No.	Product	M. p. °C.	Condensing medium	Yield %	Time of heating hours	Recrystallizing medium	Analyses Calc.: %	Found: %
1	*p*-nitro-benzal-*o*-bromo-aniline	106	alcohol	80	1	alcohol	Br, 26.20	26.36 26.14
2	*m*-bromo-aniline	102	alcohol	75	1	alcohol	Br, 26.20	26.17 26.42
3	2,6-dibromo-aniline	137	...	65	15	alcohol-toluene 10%	Br, 41.63	41.54 41.47
4	2,4,6-tribromo-aniline	142.5	...	85	48	alcohol-toluene 10%	Br, 51.80	51.85 52.04
5	3-bromo-4-toluidine	112	alcohol	90	½	alcohol	Br, 25.05	25.08 24.84
6	*p*-xylidine	100	alcohol	90	½	alcohol	N, 11.02	11.15 11.05
7	*o*-nitro-aniline	169	...	70	6	alcohol-toluene 10%	N, 15.50	15.64 15.74

In each of the above cases the condensation product was recrystallized from three to six times. The products obtained were golden-yellow needle-like crystals except the last (No. 7) which was obtained in small plates. Numbers 1, 2, 5, 6 were prepared by refluxing on a water-bath. Numbers 3, 4, 7 were prepared by direct fusion in sealed glass tubes containing anhydrous zinc chloride in the cool end. The temperature of fusion was 115° for Nos. 3 and 7 and 140° for No. 4. During the fusion a small amount of *p*-nitrobenzoic acid was formed, which remained after dissolving the condensation product in hot toluene. On hydrolysis with 1:1 hydrochloric acid, the condensation products yield *p*-nitrobenzaldehyde and the respective substituted amines.

[6] V. v. Richter, *Ber.*, 19, 1060 (1886).

The Tetrabromo Derivative of 4,4′-(*p*-Nitrophenylmethylene)-bisphenol, $NO_2C_6H_4.CH:(C_6H_2Br_2OH)_2$.—*p*-Nitrobenzaldehyde was condensed with two molecular equivalents of phenol according to the method of Danckwortt,[7] giving 4,4′-(*p*-nitrophenylmethylene)-bisphenol.

Free phenol and aldehyde remaining were removed by steam distillation. The resulting product was purified by precipitating it twice from alcohol by addition of water, and twice from toluene by cooling to —5°, yielding a light yellow, amorphous solid which slowly softened at room temperature. Danckwortt[7] described the product as a red resin. To 4.0 g. of this product dissolved in 20 cc. of glacial acetic acid was added 4.0 g. of bromine dissolved in 10 cc. of glacial acetic acid. The tetrabromo product was precipitated by addition of water, and purified by recrystallization five times from toluene as yellow platelets; m. p., 215°; yield, 6.8 g. The product was soluble in toluene, alcohol, chloroform and ether, and insoluble in water. It was soluble in an aqueous solution of sodium carbonate or sodium hydroxide, forming an orange-red solution. The alkaline solution of the product before bromination was orange colored. The calcium and barium salts readily precipitated from an alcoholic solution as orange-colored amorphous powders. Bubbling air through the solution or heating the compound in glacial acetic acid solution with potassium dichromate oxidized it to an orange-red product, whose alkaline solution was red.

Analyses. Subs., 0.1166, 0.1522: AgBr, 0.1390, 0.1801. Calc. for $C_{19}H_{11}NO_4Br_4$: Br, 50.20. Found: 50.73, 50.35.

The Diacetyl Derivative of 4,4′-(*p*-Nitrophenylmethylene)-bis-(3,5-di-bromophenol), $NO_2.C_6H_4.CH:(C_6H_2Br_2OCOCH_3)_2$.—Three g. of the tetrabromo product described in the previous experiment was warmed with 5.0 cc. of acetyl chloride for one hour. The product was recrystallized five times from 95% alcohol, giving a pale yellow, amorphous powder; m. p., 168°; yield, 2.8 g. It was soluble in benzene, alcohol, acetone, and chloroform, and insoluble in water. The same product was obtained by brominating the diacetyl derivative of 4,4′-(*p*-nitrophenylmethylene)-bisphenol in glacial acetic acid.

Analyses. Subs., 0.1360, 0.1114: AgBr, 0.1430, 0.1175. Calc. for $C_{23}H_{15}O_6NBr_4$: Br, 44.35. Found: 44.75, 44.89.

The Dibromo Derivative of (*p*-Nitrophenylmethylene)-bisresorcinol, $NO_2.C_6H_4.-CH{=}(C_6H_2(OH)_2Br)_2$.—Five g. of *p*-nitrobenzaldehyde dissolved in 25 cc. of glacial acetic acid was mixed with 8.0 g. of resorcinol dissolved in 50 cc. of the same solvent. To this was added slowly 75 cc. of concd. hydrochloric acid while the mixture was stirred. The solution was then heated on a water-bath for four hours. A precipitate began to form almost immediately which was filtered, washed with glacial acetic acid and dried; yield, 6.8 g. The light yellow, amorphous powder darkened at 245° and slowly charred above 350°. It dissolved readily in potassium and sodium hydroxide solutions, which became orange-red. The calcium and barium salts were readily precipitated as orange-colored amorphous masses from the alkaline solutions. Danckwortt[7] prepared the compound described above, but details of preparation and correct properties are not given. Two g. of the condensation product was suspended in hot glacial acetic acid, and a glacial acetic acid solution of bromine in excess of that required to form the tetrabromo derivative was added drop by drop. The bromine was not taken up readily unless a few drops of water were added. After twelve hours at room temperature and heating on a water-bath for one hour, most of the material had gone into solution. It was filtered, and water was added to the filtrate to precipitate the bromination product which was then filtered off, washed with 80% alcohol, and dried, giving a yellow, amor-

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[7] Danckwortt, *Ber.*, 42, 4163 (1909).

phous powder; yield, 1.8 g. It was purified from hot glacial acetic acid four times, by cooling and adding a small quantity of water. The yellow, amorphous powder became red at 170° and charred above 200°.

Boiling in glacial acetic acid or chloroform with an excess of bromine and a small amount of iodine as a carrier, or heating in a bomb tube at 95° for two hours with an excess of bromine, did not bring about the formation of a tetrabromo product.

Analyses. Subs., 0.2414, 0.1588; AgBr, 0.1760, 0.1180. Calc. for $C_{19}H_{13}O_6NBr_2$: Br, 31.28. Found: 31.03, 31.62.

4,4′-(*p*-Nitrophenylmethylene)-bis-*o*-nitrophenol, $NO_2.C_6H_4.CH{:}(C_6H_3(OH)NO_2)_2$. —A solution of 4.0 g. of *p*-nitrobenzaldehyde and 7.8 g. of *o*-nitrophenol in 50 cc. of glacial acetic acid was cooled, and 25 cc. of cold concd. sulfuric acid added slowly. After 12 hours at room temperature the solution was heated on a water-bath for four hours, cooled, and the product precipitated by addition of ice. *o*-Nitrophenol and *p*-nitrobenzaldehyde were then removed by steam distillation. The residue was dissolved in 95% alcohol and water added until the solution became cloudy. As it cooled, an orange-colored product separated; yield, 3.1 g. It was purified by repeating the above precipitation five times; m. p., 177°. The orange-colored, amorphous powder was soluble in alcohol, benzene, acetone and chloroform, and insoluble in water and petroleum ether. Oxidation by potassium dichromate in glacial acetic acid changed the color of the solution from orange to red. It was soluble in alkali carbonate and hydroxide solution and the solution was red.

Analyses. Subs., 0.1267, 0.2006: 12.0 cc. of N (25.0°, 734.2 mm.), 19.2 cc. (28.0°, 728.0 mm.). Calc. for $C_{19}H_{13}N_3O_8$: N, 10.22. Found: 10.19, 10.00.

One molecular equivalent of *p*-nitro-benzaldehyde was condensed with two equivalents of each of the compounds indicated in Table II.

TABLE II

Product	M. p. °C.	Yield %	Recrystallizing agent	Time of heating hours	Analyses Calc.: %	Found: %
4,4′-(*p*-nitrophenylmethylene)-bis-*o*-methylanisole	52	75	alcohol	10	N, 3.71	4.06 4.10
4,4′-(*p*-nitrophenylmethylene)-bisthymol	143	90	toluene	5	N, 3.23	3.41 3.49

The triphenylmethane derivatives described above were prepared in hot glacial acetic acid and concd. hydrochloric acid (1:1). Both products were colorless and soluble in acetone and glacial acetic acid. On exposure to the air or treating with oxidizing agents, the first became red and the second became violet.

The Dibromo Derivative of 4,4′-(*p*-Nitrophenylmethylene)-bisthymol, $NO_2.C_6H_4.CH{=}(C_6H(CH_3)(C_3H_7)(Br)OH)_2$.—One and a half g. of bromine dissolved in glacial acetic acid was added to 2 g. of 4,4′-(*p*-nitrophenylmethylene)-bisthymol in the same solvent. The bromine reacted readily in the cold solution. Addition of water was necessary for the precipitation of the yellow product. It was filtered, washed with dil. acetic acid, and dried; yield, 2.3 g. It was purified by five recrystallizations from hot 90% alcohol, giving light orange crystals; m. p., 155°. The dibromo product was more soluble in alcohol, benzene, chloroform, acetone, and glacial acetic acid than the original condensation product. It dissolved in alkali hydroxides and carbonates forming an orange-colored solution. Oxidation gave a violet-colored product.

Analyses. Subs., 0.1981, 0.1620: AgBr, 0.1250, 0.1035. Calc. for $C_{27}H_{29}O_4NBr_2$: Br, 27.03. Found: 26.85, 27.19.

The Dibenzoyl Derivative of 4,4'-(*p*-Nitrophenylmethylene)-bis-3-bromothymol, $NO_2.C_6H_4.CH{=}(C_6H(CH_3)(C_3H_7)(Br)C_6H_5COO)_2$.—A solution of 3 g. of 4,4'-(*p*-nitrophenylmethylene)-bisthymol in sodium hydroxide solution was warmed on a water-bath, and benzoyl chloride added drop by drop, while the mixture was constantly stirred, until an acid solution was obtained. The orange-colored, wax-like precipitate was washed with water, dissolved in alcohol, and precipitated by addition of water; yield, 3.2 g. It was recrystallized from 90% alcohol six times, giving a light yellow, amorphous powder; m. p., 60°. This product was dissolved in glacial acetic acid and bromine added. After one hour at room temperature, it was heated on a water-bath for thirty minutes, and then precipitated by addition of water. Recrystallization five times from 90% alcohol gave a light yellow, amorphous powder; m. p., 82°. It was soluble in alcohol, acetone, chloroform and benzene, and insoluble in water.

Analyses. Subs., 0.1250, 0.1821: AgBr, 0.0585, 0.0860. Calc. for $C_{41}H_{37}O_6NBr_2$: Br, 19.99. Found: 19.84, 20.05.

Reduction of *p*-Nitrobenzal-*p*-toluidine.—A solution of 1.5 g. of sodium hydroxide in 5 cc. of water was saturated with hydrogen sulfide. The resulting solution of sodium hydrogen sulfide was added drop by drop to a solution of 6 g. of *p*-nitrobenzal-*p*-toluidine dissolved in 50 cc. of 95% alcohol while the mixture was constantly stirred. Reduction took place slowly, and a red solution formed which was poured into water, whereupon an orange-colored oil separated. The supernatant liquid was decanted, and the residue washed with water; yield, 5.1 g. It was then dissolved in 95% alcohol, forming a yellow solution, and reprecipitated by the addition of water. Attempted purification of separate portions of this product from ether, chloroform, acetone, and petroleum ether gave in each case an amorphous, yellow, insoluble product, apparently due to polymerization.

Reduction was also carried out with glacial acetic acid and various metals, zinc dust and dil. sodium hydroxide, and ferrous sulfate and ammonium hydroxide, and parallel work was done with *p*-nitrobenzal-*o*-toluidine. The reduction products obtained changed to light yellow, amorphous, insoluble products, similar to the above.

Summary

1. Monomolecular condensations were made with *p*-nitrobenzaldehyde and the following substituted amines, and certain properties of the products determined: *p*-bromo-aniline; *m*-bromo-aniline; 2,6-dibromo-aniline; 2,4,6-tribromo-aniline; 3-bromo-4-toluidine; *o*-nitro-aniline; and *p*-xylidine.

2. *p*-Nitrobenzaldehyde was condensed with two molecular equivalents of each of the following compounds: phenol, resorcinol, thymol, *o*-nitrophenol, and *o*-methylanisole. The products obtained from the first three were brominated. The bromination product of the first was acetylated, and the product of the third was brominated before and after benzoylation.

3. (*p*-Nitrophenylmethylene)-bisresorcinol was found to produce only a dibromo substituted product.

4. Reduction of *p*-nitrobenzal-*p*-toluidine and *p*-nitrobenzal-*o*-toluidine yielded unstable compounds.

PITTSBURGH, PENNSYLVANIA