This "apparent reduction potential" is in every case, except one, essentially the same in the two solvents.

3. A theory of irreversible reductions has been put forward which connects the "apparent reduction potential" with a true oxidation-reduction potential of the substance in question.

4. A series of unsaturated carbonyl compounds has been studied. The results show that the potential at which the substance is irreversibly reduced is approximately proportional to the reactivity of the carbonyl group.

5. The reduction of nitroso-benzene to phenyl-hydroxylamine has been shown to be reversible and the potential has been measured.

6. A series of nitrogen compounds, which are irreversibly reduced, has been studied and preliminary values for their "apparent reduction potential" established.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

DERIVATIVES OF 2,4-DINITRO-BENZALDEHYDE. III

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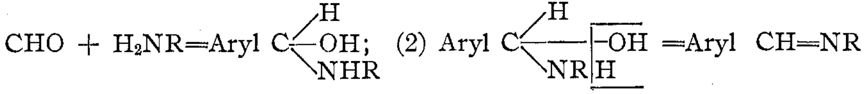
In the two previous reports,[2] the object of the research and references to the literature were given.

In the present study of 2,4-dinitro-benzaldehyde, two types of condensation reactions were investigated. The first type was the reaction between 2,4-dinitro-benzaldehyde and different aromatic amines producing the class of compounds known as "Schiff bases."[3] The reaction proceeds in two steps as represented by the following general equations: (1) Aryl



$$\text{CHO} + \text{H}_2\text{NR} = \text{Aryl C}\begin{cases}\text{H}\\ \text{OH};\\ \text{NHR}\end{cases} \quad (2)\ \text{Aryl C}\begin{cases}\text{H}\\ \boxed{\text{OH}}\\ \text{NR}\,\boxed{\text{H}}\end{cases} = \text{Aryl CH{=}NR}$$

$+\text{H}_2\text{O}$. In most cases, it was not found possible to isolate the intermediate addition product due to its tendency to eliminate water, as shown by Equation 2. However, the addition product of 2,4-dinitro-benzaldehyde and *o*-tolidine was isolated from a 95% alcoholic solution. The addition reaction takes place slowly even in an aqueous solution, while in the presence of acetic acid the condensation product is formed. Condensation products were formed by using 2,4-dinitro-benzaldehyde and the following substituted amines in unimolecular proportions: *o*-chloro-aniline, *p*-chloro-aniline, 2,4-dichloro-aniline, *p*-amino-azobenzene and *o*-tolidine.

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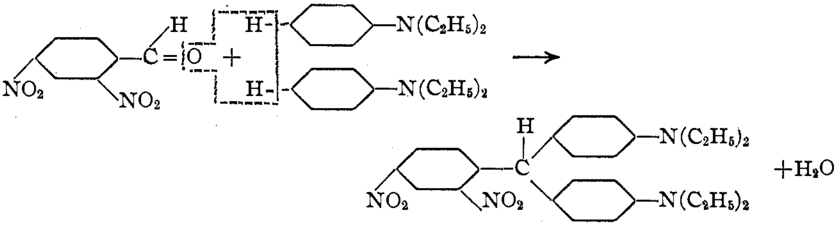
[1] This report is the abstract of a thesis presented by Thomas B. Downey, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] THIS JOURNAL, (a) **42,** 849 (1920); (b) **43,** 346 (1921).

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

The second type of condensation is that taking place in the reaction of 1 mole of 2,4-dinitro-benzaldehyde and 2 moles of tertiary alkylated aromatic amines or substituted aromatic amines and phenolic bodies. This type may be illustrated by the following equation.



Condensations were effected with the following compounds: phenol, *o*-cresol, guaiacol, *o*-chlorophenol, resorcinol, salicylic acid, dimethylaniline, diethylaniline and benzylethylaniline. The leuco bases obtained by the condensation with the 3 last-named compounds were oxidized to their respective dyes.

Experimental Part

Preparation of 2,4-Dinitro-benzaldehyde.—The method used in the preparation of the base compound of these derivatives, 2,4-dinitro-benzaldehyde, is essentially that described by F. Sachs and R. Kempf.[4] Certain modifications of this method worked out in these Laboratories were used.[5]

The Addition Compound of 2,4-Dinitro-benzaldehyde and *o*-Tolidine, $C_6H_3(NO_2)_2CHO.NH_2(CH_3)C_6H_3.C_6H_3(CH_3)NH_2$.—A solution of 10 g. of 2,4-dinitro-benzaldehyde in 30 cc. of alcohol was added gradually to a warm solution of 11.4 g. of *o*-tolidine in 60 cc. of 95% ethyl alcohol. The mixture was then maintained at a temperature of 65–75° for 30 minutes. The solution first turned a deep red and finally gave a purple crystalline precipitate. The mixture was allowed to cool and the product filtered off, washed and dried; yield 19.2 g. The product was purified by recrystallizing thrice from acetone, forming deep purple plates; m. p., 232°. The compound is soluble in alcohol, chloroform or benzene, and insoluble in water. It was hydrolyzed easily by dil. hydrochloric acid to 2,4-dinitro-benzaldehyde and *o*-tolidine. The products of hydrolysis were identified by their melting points. The addition product was also formed in a 5% ethyl alcohol solution.

The addition product was dissolved in acetone and to this solution was added a small amount of glacial acetic acid to give approximately a 1% solution. After the solution had stood for some time a yellow precipitate separated in hard, crystalline, lumpy masses. This was later shown to be the condensation product. The finely ground addition product when warmed with acetic anhydride rapidly passed over into the acetyl derivative of the condensation product.

Analyses. (Addition product.) Subs., 0.2363, 0.2563: 31.1 cc. of N (30°, 741.5 mm.), 32.9 cc. (24°, 742.5 mm.). Calc. for $C_{21}H_{20}O_5N_4$: N, 13.72. Found: 13.84, 13.97.

2,4-Dinitro-benzal-2,4-dichloro-aniline, $C_6H_3(NO_2)_2CH:NC_6H_3Cl_2$.—To a hot solution of 2 g. of 2,4-dinitro-benzaldehyde in 20 cc. of alcohol was added 1.6 g. of 2,4-

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[4] Sachs and Kempf, *Ber.*, **35**, 2704 (1902).

[5] Lowy and Wescott, Ref. 2a, p. 850.

dichloro-aniline dissolved in 10 cc. of alcohol. The mixture was heated on a water-bath for 1 hour, then cooled and the resulting yellow crystalline mass separated by filtration and dried at 100°; yield, 3.3 g. The product was purified by crystallizations from acetone and from alcohol, yielding bright orange plates; m. p., 185°. The compound is insoluble in water, soluble in alcohol and very soluble in acetone, benzene or chloroform. 2,4-Dinitro-benzaldehyde was formed upon hydrolysis with 1:1 hydrochloric acid.

Analyses. Subs., 0.2865, 0.2504: 16.7 cc., 14.8 cc. of 0.1 *N* $AgNO_3$. Calc. for $C_{13}H_7O_4N_3Cl_2$: Cl, 20.84. Found: 20.7, 20.92.

In the preparation of the condensation products listed below, the same general method was used as described above. The mixtures were heated on a water-bath for from 30 to 60 minutes to complete the reactions. The yields obtained were approximately 90%.

Product 2,4-Dinitro-benzal-	M. p. ° C.	Color and crystalline form	Condensing medium	Analyses Calc. %	Found %
o-chloro-aniline....	167.5	yellow needles	alc.	Cl, 11.60	11.51 11.37
p-chloro-aniline...	161.5	yellow needles	alc.	Cl, 11.60	11.78 11.45
p-aminoazobenzene	229	red prisms	alc.	N, 18.67	18.46 18.75
o-tolidine.........	282 with decomp.	yellowish-red	acetic acid	N, 14.36	14.23 14.54
aceto-*o*-tolidine....	231.5	orange-yellow needles	acetic anhydride	N, 12.96	12.79 12.96

The last compound given in the above table was prepared by heating the addition product of 2,4-dinitro-benzaldehyde and *o*-tolidine with acetic anhydride. It was purified by recrystallization from benzene.

In the preparation of compounds listed above, the ratio of 1 mole of 2,4-dinitrobenzaldehyde to 1 mole of the substituted amine was used. The condensation products were recrystallized several times from alcohol, acetone or benzene. They are insoluble in water, and on hydrolysis with 1:1 hydrochloric acid yield 2,4-dinitro-benzaldehyde and the respective substituted amines.

4,4′-(2,4-Dinitrophenylmethylene)-bisphenol, $C_6H_3(NO_2)_2CH:(C_6H_4OH)_2$.—To a hot solution of 6.3 g. of 2,4-dinitro-benzaldehyde and 6 g. of phenol (in the proportion of 1 mole to 2 moles) in 60 cc. of glacial acetic acid was added 100 cc. of conc. hydrochloric acid and the whole refluxed on a water-bath for 2 hours. The solution became red, and as the heating continued a heavy, reddish-yellow precipitate gradually formed. The mixture was allowed to cool and the condensation product filtered off, washed with water and dried at 115°. A further amount was secured by evaporating a portion of the mother liquor; total yield, 10 g. The compound was purified by repeated solution in alcohol and precipitation with water. It was then crystallized from alcohol as a light yellow, finely divided precipitate; m. p., 204°. It is very soluble in alcohol, acetone or hot glacial acetic acid, soluble in chloroform or benzene and slightly soluble in water. It is oxidized in the air to an orange-colored product.

The sodium salt can be precipitated from its alcoholic solution as brick-red leaflets by the addition of sodium hydroxide or sodium carbonate. The potassium salt is more soluble in alcohol while the calcium salt is more insoluble.

The compound acts as an indicator for the normal carbonates and hydroxides of the alkali metals and acids, giving a color change of red for alkalies to a pale yellow in acid solutions.

Analyses. Subs., 0.1518, 0.2164: 11.05 cc. of N (25°, 743 mm.), 15.4 cc. (27°, 740.5 mm.). Calc. for $C_{19}H_{14}O_6N_2$: N, 7.65. Found: 7.89, 7.61.

In the preparation of the following triphenylmethane derivatives the same general method was used as described above.

Product 4,4'-(2,4-Dinitrophenylmethylene)-	M. p. ° C.	Color	Yield %	Analyses Calc. %	Analyses Found %
bis-*o*-chloro-phenol	190.5	yellow	80	Cl, 16.30	16.20 16.08
bis-*o*-cresol	200.5	yellow	75	N, 7.10	6.86 6.90
bis-guaiacol	221	yellow	65	N, 6.57	6.42 6.77
bis-salicylic acid	268.5	yellow	40	N, 5.34	5.44 5.56

No. 1 was purified by recrystallizing repeatedly from alcohol; No. 2 by adding hot water to a hot alcoholic solution to faint cloudiness; No. 3 from benzene; No. 4 from acetic acid and finally from ethyl acetate. The above compounds form bright red sodium, potassium, ammonium and calcium salts which are soluble in water.

The Tetrabromo Derivative of 4,4'-(2,4-Dinitro-phenylmethylene)-bisphenol, $C_6H_3(NO_2)_2CH{:}(C_6H_2Br_2OH)_2$.—This compound was prepared by adding the calculated amount of bromine dissolved in acetic acid to a warm glacial acetic acid solution of 4,4'-(2,4-dinitrophenylmethylene)-bisphenol. A yellow precipitate began to separate after 30 minutes' heating. The product was purified by recrystallizations from alcohol giving yellow, needle-like crystals; m. p., 234°; yield, 70%.

Analyses. Subs., 0.2200, 0.2537; AgBr, 0.2417, 0.2797. Calc. for $C_{19}H_{10}N_2O_6Br_4$: Br, 46.88. Found: 46.75, 46.91.

(2,4-Dinitrophenylmethylene)-bisresorcinol, and its Calcium Salt, $C_6H_3(NO_2)_2$-$CH{:}(C_6H_3(OH)_2)_2$.—To a hot solution of 6 g. of 2,4-dinitro-benzaldehyde and 7 g. of resorcinol in 150 cc. of glacial acetic acid, was added 100 cc. of conc. hydrochloric acid and the mixture was refluxed at 90–115° for 2 hours. A yellow product began to separate after 30 minutes. The mixture was cooled and the precipitate filtered off, washed with water until free from acids and dried to constant weight at 120°; yield, 4 g. The mother liquor was retained for further treatment, as it was shown later to consist of the xanthene derivative. The bright yellow condensation product was purified by dissolving in hot alcohol and gradually removing the solvent by warming at 40–50° in a vacuum. A bright yellow, amorphous product resulted. When the compound was heated it changed from a yellow to a red color at 210–215° and then gradually charred above 280°. This change of color indicated its transformation into the corresponding xanthene derivative described later.

The calcium salt was prepared by dissolving the yellow, amorphous condensation product in a dil. solution of potassium hydroxide. The solution was filtered and heated to 90–100°, stirred, and a saturated solution of calcium chloride added drop by drop until precipitation was complete. The dark red, finely divided precipitate was filtered, washed with water and dried to constant weight by heating at 125–150° for 6 days. The analysis for calcium shows that there are 4 hydroxyl groups in the compound.

Analyses. Subs., 0.3861, 0.3202: $CaSO_4$, 0.2166, 0.1817. Calc. for $C_6H_3(NO_2)_2$-$CH{:}(C_6H_3O_2Ca)_2$: Ca, 16.87. Found: 16.51, 16.70.

9-(2,4-Dinitrophenyl)-3,6-dihydroxy-xanthene and its Calcium Salt, $C_6H_3(NO_2)_2$-$CH{:}(C_6H_3OH)_2O$.—The mother liquor obtained in the preparation of (2,4-dinitrophenylmethylene)-bisresorcinol was evaporated to 150 cc., and 200 cc. of water was added to the cold solution. A deep red, amorphous product, contaminated with a tarry material, was precipitated. The mass was filtered, washed with water and then extracted with an aqueous solution of sodium carbonate which formed a deep red solution. This was acidified with hydrochloric acid and the resulting precipitate filtered, washed with water and dried. It was then dissolved in hot alcohol and treated with boneblack. The boneblack was removed and to the hot alcoholic solution hot water was added until a faint cloudiness was produced. On cooling the mixture a yellowish-red, amorphous mass separated. It was dried at 115°; yield, 2 g. When heated above 280° it slowly chars without melting. The potassium, sodium and ammonium salts are very soluble in water and are deep red. The calcium salt is insoluble in water.

Analyses. Subs., 0.2825, 0.1270: 19.2 cc. of N (27°, 738.6 mm.), 8.4 cc. (27°, 738.5 mm.). Calc. for $C_{19}H_{12}N_2O_7$: N, 7.37. Found: 7.24, 7.05.

The above xanthene derivative was also prepared by heating 2,4-dinitro-benzaldehyde and resorcinol with zinc chloride for 6 hours at 95–130°. It was also formed by dissolving 2,4-dinitro-benzaldehyde and resorcinol in conc. sulfuric acid and heating the solution at 60° for 5 hours. The xanthene derivative separated as a red flocculent precipitate when the mixture was poured into ice water.

The calcium salt of this xanthene derivative was prepared according to the directions given for the calcium salt of (2,4-dinitrophenylmethylene)-bisresorcinol. The analysis showed that there are two hydroxyl groups in the compound.

Analyses. Subs., 0.4895, 0.3362: $CaSO_4$, 0.1537, 0.1060. Calc. for $C_{19}H_{10}N_2O_7Ca$: Ca, 9.58. Found: 9.24, 9.28.

The Tetrabromo Derivative of 9-(2,4-Dinitrophenyl)-3,6-dihydroxy-xanthene, $C_6H_3(NO_2)_2CH{:}(C_6HBr_2OH)_2O$.—This compound was prepared by the same general method outlined under the tetrabromo derivative of 4,4′-(2,4-dinitrophenylmethylene)-bisphenol. The product is more soluble in glacial acetic acid and consequently a considerable amount of the solvent had to be evaporated before the product crystallized. It was purified by recrystallizing from chloroform, forming red prisms. It charred when heated above 290°. The sodium and potassium salts are soluble in water with a deep red color.

Analyses. Subs., 0.2303, 0.2645: AgBr, 0.2482, 0.2845. Calc. for $C_{19}H_8N_2O_7Br_4$: Br, 45.94. Found: 45.86, 45.76.

4,4′- (2,4 - Dinitrophenylmethylene)bis-dimethylaniline, $C_6H_3(NO_2)_2CH{:}(C_6H_4N(CH_3)_2)_2$; **Leuco base of 2,4-Dinitro-malachite Green; the Color Base and Dye.**—2,4-Dinitro-benzaldehyde was condensed with dimethylaniline by the zinc chloride fusion method commonly employed for the preparation of malachite green. This condensation was also effected by means of conc. hydrochloric acid; yield, 80%. The compound was recrystallized thrice from alcohol, giving yellow, needle-like crystals; m. p., 151.5°.

Analyses. Subs., 0.1800, 0.1900: 22.8 cc. of N (28°, 735 mm.), 23.3 cc. (23.5°, 737 mm.). Calc. for $C_{23}H_{24}O_4N_4$: N, 13.33. Found: 13.35, 13.29.

The leuco base was oxidized to the color base and dye by the usual method.[6] Both the zinc chloride and the oxalate salts were prepared. Dyeings made from either salt give a blue-green color on silk and wool without mordanting, a characteristic property of malachite green dyes.

4,4′ - (2,4 - Dinitrophenylmethylene)bis-diethylaniline, $C_6H_3(NO_2)_2CH{:}(C_6H_4N(C_2H_5)_2)_2$; **Leuco base of 2,4-Dinitro-brilliant Green; the Color Base and Dye.**—The leuco base, color base and dye were prepared in a manner analogous to that for the pre-

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[6] Gatterman, "Practical Methods of Organic Chemistry," The Macmillan Co., **1921,** pp. 354–357.

viously described products. This leuco base was purified by extractions with benzene and subsequent precipitation by the addition of petroleum ether. The compound is very susceptible to oxidation and consequently was obtained as a dirty green product.

Analyses. Subs., 0.2605, 0.2340: 28.6 cc. of N (29°, 738 mm.), 25.5 cc. (29°, 738 mm.). Calc. for $C_{27}H_{32}O_4N_4$: N, 11.76. Found: 11.56, 11.47.

The color shade produced from this dye is more towards the blue than that shown by the previously described dyes.

4,4′-(2,4-Dinitrophenylmethylene)bisbenzylethylaniline, $C_6H_3(NO_2)_2CH{:}(C_6H_4N\text{-}(CH_5)(CH_2.C_6H_5))_2$; **the Color base and Dye.**—The method described for the preparation of the above dyes was used. The leuco base obtained was a brownish-yellow, finely divided product; yield, 32%.

Analyses. Subs., 0.3094, 0.2885: 27.0 cc. of N (28°, 738 mm.), 24.6 cc. (27°, 738 mm.). Calc. for $C_{37}H_{36}N_4O_4$: N, 9.33. Found: 9.24, 9.10.

The dye obtained from this leuco base is only slightly soluble in water. Its solution is bluish-green. In order to produce a water-soluble dye, the leuco base was treated with fuming sulfuric acid at room temperature for 48 hours. The sulfonated product was then oxidized and produced a water-soluble dye analogous to Light Green SF.

Summary

1. The intermediate compound in the condensation of 2,4-dinitrobenzaldehyde and *o*-tolidine was isolated.

2. 2,4-Dinitro-benzaldehyde was condensed with *o*-chloro-aniline, *p*-chloro-aniline, 2,4-dichloro-aniline, *p*-amino-azobenzene and *o*-tolidine, in the proportions of 1 mole to 1 mole, yielding modified Schiff bases.

3. 2,4-Dinitro-benzaldehyde was condensed with phenol, *o*-cresol, guaiacol, *o*-chloro-phenol, and salicylic acid in proportions of 1 mole to 2 moles, yielding the corresponding triphenylmethane derivatives. The first-named product was brominated.

4. 2,4-Dinitro-benzaldehyde was condensed with resorcinol in the proportions of 1 mole to 2 moles to give the triphenylmethane and the xanthene derivatives. The latter product was brominated.

5. Three new dyes of the triphenylmethane series were isolated and their properties noted. Dyeings were made on cotton, silk and wool.

PITTSBURGH, PENNSYLVANIA