specific conductivity, *k*, for the acetonitrile so prepared was found to be $3.95 \cdot 10^{-7}$ ohm$^{-1}$ cm.$^{-1}$. Walden[8] reported $k = 3.98 \times 10^{-7}$.

The solutions for measurement were in all cases prepared by weight and different concentrations obtained by weight dilution. The conductivity cells were maintained in a thermostat at $25 \pm 0.05°$.

**Absorption Spectra.**—Solutions of the perchlorates were made up in dry redistilled ethylene chloride and the absorption at various wave lengths determined by use of the Beckman spectrophotometer. The data are shown in Figs. 2 and 3.

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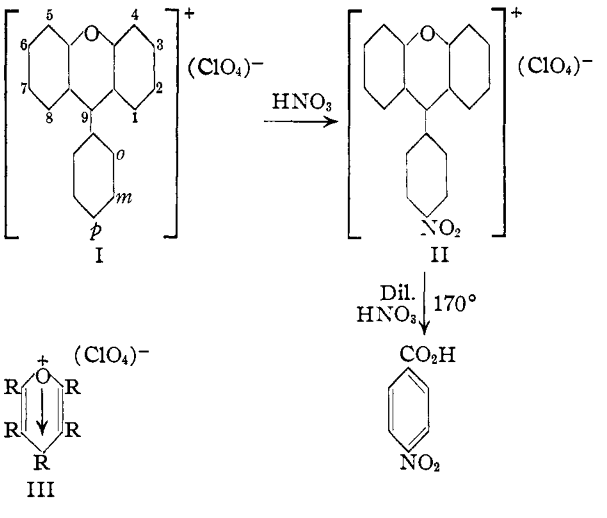
[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE STATE UNIVERSITY OF IOWA]

# The Structure of the Nitration Products of 9-Phenylxanthylium Salts[1]

BY R. L. SHRINER AND CALVIN N. WOLF[2a,b]

The nitration of 9-phenylxanthylium perchlorate has been shown to yield 91% of 9-(*m*-nitrophenyl)-xanthylium perchlorate as shown by hydrolysis to the carbinol and reduction to 9-(*m*-nitrophenyl)-xanthene. The structure of the latter compound was established by condensation of xanthydrol with *o*-nitraniline to 9-(*p*-amino-*m*-nitrophenyl)-xanthene from which the amino group was removed by diazotization and treatment with hypophosphorus acid. The results show that these cationic salts orient the entering nitro group predominately to the meta-position.

Le Fevre and Pearson[3] reported that 9-phenylxanthylium perchlorate (I) gave a mononitro derivative which, upon oxidation with dilute nitric acid, gave *p*-nitrobenzoic acid (yield not given). The nitration product was, therefore, considered to be 9-(*p*-nitrophenyl)-xanthylium perchlorate (II) and the authors assigned the general structure (III) for the pyrylium salt nucleus in which the arrow represented a special case of "long bond."



Nitration studies of substituted benzopyrylium salts and isobenzopyrylium salts showed that the entering nitro group was oriented to the meta-position[4,5] The para nitration reported by Le Fevre for the compound I, was a very disturbing exception to this behavior.

The question of orientation of the nitro group in the nitration of 9-phenylxanthylium salts has been reinvestigated (see Chart I). The nitration of 9-phenylxanthylium salts proceeded readily and was performed either by addition of 9-phenylxanthylium perchlorate (IV) to the nitration mixture or by addition of nitric acid to 9-phenylxanthylium sulfate obtained by dissolving 9-phenylxanthenol in sulfuric acid. Both methods gave identical results. The nitration product was isolated in nearly quantitative yield as the carbinol (VI), by pouring the reaction mixture into water and neutralizing with ammonia. This crude carbinol (VI) was a mixture and could not be fractionally crystallized but the perchlorate, ferrichloride, methoxy and ethoxy derivatives were obtained as pure crystalline compounds whose analyses and yields indicated at least a 91% yield of a pure mononitro derivative. Furthermore, reduction of VI, using the formic acid method of Kovache,[6] gave a crude nitrophenylxanthene in nearly quantitative yield. Repeated recrystallization of this crude reduction product gave pure 9-(*m*-nitrophenyl)-xanthene (VII) in 91.6% yield.

Catalytic reduction of VII gave 9-(*m*-aminophenyl)-xanthene (VIII). This compound (VIII) was different from the condensation product of xanthydrol (IX) and aniline, which was postulated by Adriani[7] to be 9-(*p*-aminophenyl)-xanthene (X) Chart II. Proof that xanthydrol actually does condense with aromatic amines at the para-position in the presence of hydrochloric acid was provided by diazotization of X and conversion of the diazonium salt to 9-(*p*-methoxyphenyl)-xanthene (XI). This compound (XI) was identical with an authentic sample of XI obtained by the addition of *p*-anisylmagnesium bromide to xanthone followed by formic acid reduction of the carbinol (XII). This was further evidence of the fact that the principal nitration product of IV was not the para derivative (II).

Conclusive evidence for the structure of V by independent synthesis of the formic acid reduction product (VII) was obtained by condensation of xanthydrol (IX) with *o*-nitroaniline in presence of hydrochloric acid to give 9-(*p*-amino-*m*-nitrophenyl)-xanthene (XIII) followed by replacement of the amino group of XIII by hydrogen (see

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(2) (a) From a thesis submitted to the Graduate College of the State University of Iowa in partial fulfillment of the requirements of the degree, Doctor of Philosophy. (b) Ethyl Corporation, Detroit, Michigan.

(3) Le Fevre and Pearson, *J. Chem. Soc.*, 482 (1933).

(4) Le Fevre, *ibid.*, 2771 (1929).

(5) Shriner and Moffett, THIS JOURNAL, **66**, 301 (1944); Shriner, Johnson and Kaslow, *J. Org. Chem.*, **14**, 205 (1949).

(6) Kovache, *Ann. chim. phys.*, [9] **10**, 223 (1918).

(7) Adriani, *Rec. trav. chim.*, **35**, 188 (1915).

Chart I.

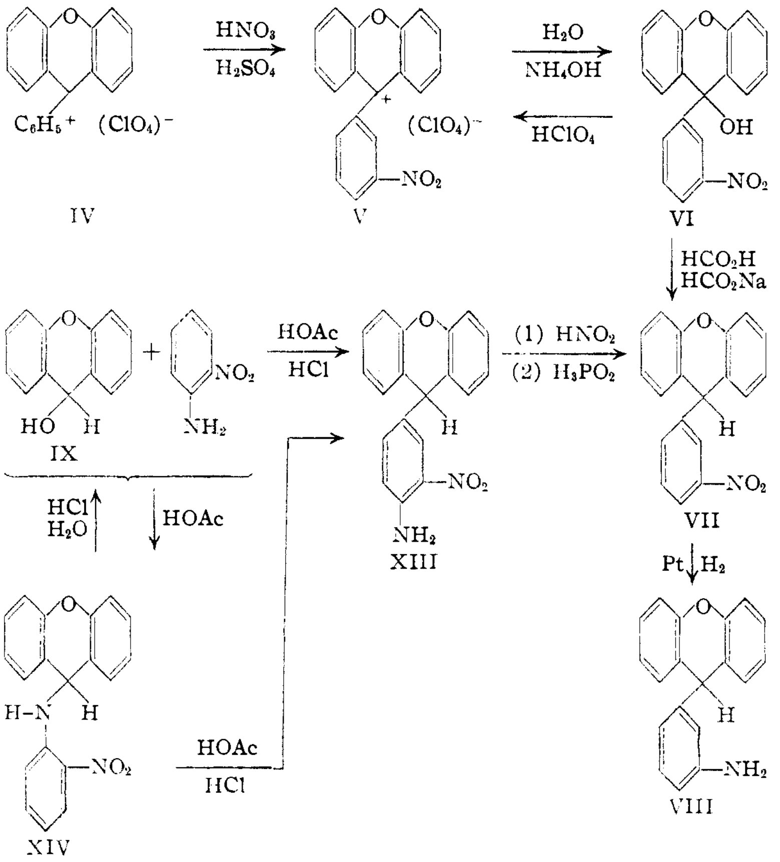


Chart I). Since the product of this sequence of reactions was identical with VII, this establishes the fact that the meta-nitro derivative (V) is the principal mononitration product of 9-phenylxanthylium perchlorate (IV).

The reaction between xanthydrol (IX) and *o*-nitroaniline in a solution of ethanol and acetic acid at 25° readily gives the secondary amine (XIV) in high yield. This compound (XIV) could be hydrolyzed back to the starting materials and, upon refluxing in acetic acid–hydrochloric acid solution, rearranged to give XIII. Similar rearrangements in the triphenylcarbinol series have been reported.[8]

Since the above syntheses establish the structure of the chief nitration product as the meta-derivative (V), the oxidative degradation was reinvestigated. Permanganate oxidation of the crude carbinol (VI) gave only 3.8% of *p*-nitrobenzoic acid. However, when acid dichromate was used as the oxidizing agent, the crude carbinol VI gave 49.5% of *m*-nitrobenzoic acid and 4.2% *p*-nitrobenzoic acid.

The results of this investigation establish the predominant meta-nitration of 9-phenylxanthylium salts and are in entire agreement with all the other nitration studies of substituted benzopyrylium and isobenzopyrylium salts and, indeed parallel the numerous nitration studies of aromatic compounds containing a positively charged atom attached to the ring.[9,10]

## Experimental

**9-Phenylxanthenol.**—An 86% yield of this compound, m.p. 158–159°, was obtained from xanthone[11] by the reaction with phenylmagnesium bromide.[12]

**9-Phenylxanthylium Perchlorate (IV).**—To a solution of 10 g. (0.0368 mole) of 9-phenylxanthenol in a mixture of 50 ml. of benzene and 25 ml. of acetone was added with stirring 5.85 g. (0.059 mole) of 70% perchloric acid. After being chilled in the refrigerator, the product was isolated by filtration and washed with dry ether. The yield of yellow crystals was 13.4 g. (97.5%), melting at 280–281°. Since these perchlorates explode during attempted combustion, analyses were made for the perchlorate anion using tetraphenylarsonium chloride.[13]

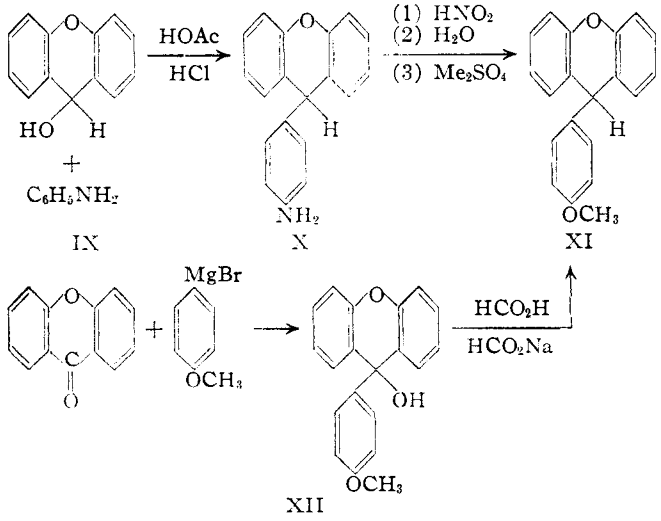
*Anal.* Calcd. for $C_{19}H_{13}OClO_4$: $ClO_4$, 27.9. Found: $ClO_4$, 27.9.

**9-Phenylxanthylium Ferrichloride.**—To a solution of 2 g. of 9-phenylxanthenol in 100 ml. of hydrochloric acid was added an excess of a hydrochloric acid solution of ferric chloride. The yellow precipitate was collected on a glass filter, dried and recrystallized from glacial acetic acid. The yield of yellow crystals was 3.14 g. (70%), melting at 170°.

*Anal.* Calcd. for $C_{19}H_{13}OFeCl_4$: Fe, 12.3. Found: Fe, 12.4.

**Nitration of 9-Phenylxanthylium Sulfate.**—A solution of 10 g. of 9-phenylxanthenol in 50 ml. of concentrated sulfuric acid was cooled in an ice-bath to 5–10°, and 30 ml. of cold concentrated ntric acid was added dropwise, with stirring, over a period of 5–10 minutes. The mixture was then poured onto 500 g. of cracked ice and neutralized with ammonium hydroxide. The cream-colored solid was isolated by filtration and thoroughly washed with water. After being dried in a

Chart II.



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[8] van Alphen, *Rec. trav. chim.*, **46**, 502 (1927); Iddles and Hussey, This Journal, **63**, 2769 (1941).

[9] Gilman, "Organic Chemistry," Vol. I, John Wiley and Sons Inc., New York, N. Y., 1943, p. 203; Price, "Reactions at Carbon-Carbon Double Bonds," Interscience Publishers Inc., New York, N. Y., 1946, p. 25; Price, *Chem. Revs.*, **29**, 32 (1941).

[10] Wolf and Shriner, *J. Org. Chem.*, **15**, 367 (1950).

[11] Holleman, "Organic Syntheses," Coll. Vol. I, 1941, p. 552.

[12] Gomberg and Cone, *Ann.*, **370**, 142 (1909); **376**, 183 (1910).

[13] Shriner, Johnson and Kaslow, *J. Org. Chem.*, **14**, 205 (1949).

vacuum desiccator, the crude nitro-9-phenylxanthenol (VI) weighed 12 g. (99.2%) and melted at 55–59°. All attempts at crystallization were unsuccessful.

*Anal.* Calcd. for $C_{19}H_{13}NO_4$: N, 4.40. Found: N, 4.57.

**9-(*m*-Nitrophenyl)-xanthylium Perchlorate (V)**.—A 10-g. portion of the crude nitration carbinol (VI) was dissolved in 30 ml. of a 50% benzene–acetone mixture, and 5 ml. of 70% perchloric acid was added, with stirring. After standing in the cold for 24 hours, the product was isolated by filtration and washed with dry ether. The yield of yellow crystals was 12.2 g. (97%), melting at 250–255° (cor.). After two recrystallizations from glacial acetic acid the yield was 11.3 g. (90%), melting at 255–257° (cor.). Further recrystallizations did not raise the melting point.

*Anal.* Calcd. for $C_{19}H_{12}O_3NClO_4$: $ClO_4$, 19.8. Found: $ClO_4$, 19.8.

**9-(*m*-Nitrophenyl)-xanthylium Ferrichloride**.—A 10-g. portion of crude 9-(*m*-nitrophenyl)-xanthenol (VI) was dissolved in the minimum amount of concentrated hydrochloric acid, and an excess of a solution of ferric chloride in concentrated hydrochloric acid was added, with efficient stirring. After being chilled at 5° for 24 hours, the product was isolated by filtration. The yield of orange crystals was 14.7 g. (94%), melting at 234–239° (cor.) with decomposition. Two recrystallizations from acetic acid reduced the yield to 13.6 g. (86%), melting at 242–243° (cor.).

*Anal.* Calcd. for $C_{19}H_{12}O_3NFeCl_4$: N, 2.80; Fe, 11.18. Found: N, 3.04; Fe, 11.10.

**Methoxy Derivative of 9-(*m*-Nitrophenyl)-xanthenol**.—A solution of 2 g. of crude 9-(*m*-nitrophenyl)-xanthenol in 5 ml. of concentrated sulfuric acid was added to 100 ml. of methanol and allowed to stand at 20° for 30 minutes. The solution was poured onto 500 g. of cracked ice, and the solid was collected on a filter. Crystallization from methanol gave 1.7 g. (82%) of white crystals which melted at 134–135°.

*Anal.* Calcd. for $C_{20}H_{15}O_4N$: N, 4.21. Found: N, 4.14.

**Ethoxy Derivative of 9-(*m*-Nitrophenyl)-xanthenol**.—The procedure described above for the methoxy derivative was followed, using absolute ethanol. The yield of white prisms, after crystallization from ethanol, was 1.8 g. (83%), melting at 118–119°.

*Anal.* Calcd. for $C_{21}H_{17}O_4N$: N, 4.03. Found: N, 4.17.

**9-(*m*-Nitrophenyl)-xanthene (VII)**.—To a solution of 50 g. (0.157 mole) of crude 9-(*m*-nitrophenyl)-xanthenol in 600 ml. of 90% formic acid was added 10 g. of sodium carbonate. The solution was boiled with reflux for 1–1.5 hours and then cooled at 5–10° for 4 hours. The product was isolated by filtration and washed with water. The yield of tan crystals was 47 g. (99%), melting at 146–150°. A series of crystallizations from ethanol gave 43.5 g. (91.6%) of pale tan crystals which melted at 155–156°, and which showed no rise in melting point upon further recrystallization. The procedure described is similar to that of Kovache.[6]

*Anal.* Calcd. for $C_{19}H_{13}O_3N$: C, 75.23; H, 4.32; N, 4.62. Found: C, 74.98; H, 4.35; N, 4.76.

**Nitration of 9-Phenylxanthylium Perchlorate**.—Ten grams of 9-phenylxanthylium perchlorate (V) was dissolved in 40 ml. of concentrated sulfuric acid, cooled to 5–10°, and 30 ml. of cold concentrated nitric acid was added over a period of 5–10 minutes, with stirring. The solution was poured onto an ice–water mixture and neutralized with ammonium hydroxide. The solid was isolated by filtration, washed thoroughly with water and dried. The yield of crude nitrated carbinol was 11.2 g. (99%). This product was shown to be identical with the crude 9-(*m*-nitrophenyl)-xanthenol (VI) obtained by nitration of 9-phenylxanthylium sulfate, since it gave identical yields of 9-(*m*-nitrophenyl)-xanthylium perchlorate (V) and 9-(*m*-nitrophenyl)-xanthene (VII).

**Permanganate Oxidation of Crude 9-(*m*-Nitrophenyl)-xanthenol**.—A solution of 3 g. (0.0094 mole) of the crude nitration product (VI), in a mixture of 60 ml. of concentrated sulfuric acid and 300 ml. of water was treated with 50 g. (0.316 mole) of potassium permanganate in small portions over a period of 2–3 hours, with stirring and heating on the steam-bath. The mixture was saturated with sulfur dioxide and then extracted with ether. The ether extract was evaporated to dryness, leaving 0.06 g. (3.8%) of brown crystals which melted at 222–237° (cor.). After two recrystallizations from water (Norite) the yield of pale yellow crystals was 0.03 g. (1.9%), melting at 238–239° (cor.). When mixed with an authentic sample of *p*-nitrobenzoic acid (m.p. 241°), the mixture melted at 240° (cor.).

A sample of the oxidation product obtained above was converted to methyl *p*-nitrobenzoate by treatment with methanol saturated with dry hydrogen chloride. Pale yellow crystals were obtained which melted at 96° after recrystallization from methanol and which showed no depression in melting point when mixed with an authentic sample of methyl *p*-nitrobenzoate (m.p. 96°).

**Dichromate Oxidation of Crude 9-(*m*-Nitrophenyl)-xanthenol**.—In a 1-l. flask fitted with a stirrer were placed 10 g. (0.0314 mole) of the crude nitration product (VI), 300 ml. of water and 143 g. (0.48 mole) of sodium dichromate. To this was added 140 ml. of concentrated sulfuric acid, with stirring. Spontaneous boiling began, and an additional 55 ml. of sulfuric acid was added dropwise over a period of one-half hour. The mixture was then gently refluxed, with stirring, for 2 hours, cooled to 20° and the solid collected on a glass filter. After washing with 20 ml. of ice-cold water and drying, the tan solid weighed 3.1 g. (59%). This was dissolved in 10% sodium hydroxide solution, stirred with Darco, filtered and acidified with concentrated hydrochloric acid. The yield of white crystals was 2.8 g. (53.4%), melting at 115–160°. The mixture of nitrobenzoic acids was dissolved in 120 ml. of hot water, cooled to 25° and allowed to stand for 14 hours. The white crystals which separated weighed 0.70 g. (13.3%) and melted at 130–205°. Recrystallization from 120 ml. of water gave 0.30 g. (5.7%) of crystals, melting at 225–234°. This was dissolved in the minimum amount of boiling water, cooled at 0–5° for 24 hours, and the crystals isolated by filtration. The product weighed 0.22 g. (4.2%), melted at 239–241° (cor.), and showed no depression in melting point upon mixture with an authentic sample of *m*-nitrobenzoic acid.

The methyl ester was prepared by treatment with methanol saturated with hydrogen chloride; it melted at 96° and showed no depression in melting point when mixed with an authentic sample of methyl *p*-nitrobenzoate.

The combined mother liquors from which *p*-nitrobenzoic acid was isolated by the above procedure were reduced to a volume of 10 ml. and chilled at 0° for 24 hours. The white crystals which separated were removed by filtration. The yield of crystals was 2.6 g. (49.5%), melting at 137–139°; when mixed with an authentic sample of *m*-nitrobenzoic acid (m.p. 141°), the mixture melted at 139–140°.

A sample of the acid was converted to the methyl ester, by boiling with methanol saturated with hydrochloric acid. Pale yellow crystals were obtained which melted at 78° after recrystallization from methanol and which showed no depression in melting point when mixed with an authentic sample of methyl *m*-nitrobenzoate (m.p. 78°).

**9-(*m*-Aminophenyl)-xanthene (VIII)**.—A solution of 2 g. of 9-(*m*-nitrophenyl)-xanthene (VII) in 200 ml. of absolute ethanol was catalytically reduced, using platinum oxide catalyst. The reduction was complete in 5–10 minutes at 25° and 20 lb. pressure of hydrogen. The alcohol solution was evaporated to a volume of 35 ml. and chilled to 0°. The product was isolated by filtration. The yield of white crystals was 1.8 g. (98%), melting at 154–155°.

*Anal.* Calcd. for $C_{19}H_{15}ON$: N, 5.12. Found: N, 4.94.

The amine (VIII) was also obtained by chemical reduction of 1 g. of the nitro compound (VII) by refluxing for 8 hours with a mixture of 10 ml. of concentrated hydrochloric acid, 15 ml. of water, 15 ml. of acetic acid and 2 g. of zinc. The mixture was made alkaline with sodium hydroxide and extracted with benzene. Evaporation of the benzene gave 0.2 g. (22%) of nearly white crystals which melted at 153–155° after crystallization from alcohol.

**9-(*p*-Aminophenyl)-xanthene (X)**.—A solution of 24 g. (0.12 mole) of xanthydrol (IX), 22 g. (0.24 mole) of aniline, 6 ml. of concentrated hydrochloric acid and 120 ml. of glacial acetic acid was refluxed for 4 hours, cooled to 25°, and stirred into 2 l. of cold water, containing 20 g. of sodium carbonate. The mixture was stirred and heated on the steam-bath for one-half hour and then filtered while hot. The white solid was washed with water and dried; the yield was 34.5 g., consisting of a mixture of the amine, LI, and its acetyl derivative. The solid was refluxed with a mixture of 70 ml. of concentrated hydrochloric acid and 500 ml. of 80% ethanol for 6 hours, cooled, poured into 2 l. of cold water, neutralized with sodium carbonate and warmed on the steam-bath for 15–20 minutes. The white crystals were collected on a filter and washed with water; the yield was 31.3 g. (95.5%), melting at 175–180°. After two recrystallizations from ethanol the yield of white prisms was 20 g. (61%), melting at 185°. Adriani[7] reported the melting point as 185.5–187°. When mixed with the 9-*m*-aminophenylxanthene (VIII) derived from the nitration product of 9-phenylxanthylium salts, the melting point was depressed to 126–138°, showing that the two amines are different.

*Anal.* Calcd. for $C_{19}H_{15}ON$: C, 83.49; H, 5.53; N, 5.12. Found: C, 83.21; H, 5.42; N, 5.29.

**9-(*p*-Acetylaminophenyl)-xanthene.**—A solution of 3 g. of the amine, (X) in 25 ml. of glacial acetic acid was refluxed for 6 hours, poured into water and the solid collected on a filter, washed and dried. After crystallization from ethanol the white crystals weighed 2 g. (58%) and melted at 186–187°. The product was shown by mixed melting points to be different from the starting material (m.p. 185°).

*Anal.* Calcd. for $C_{21}H_{17}O_2N$: C, 79.98; H, 5.43; N, 4.45. Found: C, 79.77; H, 5.43; N, 4.38.

**9-(*p*-Methoxyphenyl)-xanthenol (XII).**—To a solution of *p*-anisylmagnesium bromide prepared from 1.2 g. (0.049 mole) of magnesium, 9.2 g. (0.049 mole) of *p*-bromoanisole, and 50 ml. of dry ether was added 6.5 g. of xanthone in 30 ml. of hot benzene. The mixture was stirred and refluxed for 4 hours and hydrolyzed with ammonium chloride solution. After crystallization from acetone the white prisms[14] weighed 6 g. (60%) and melted at 120–121°.

**9-(*p*-Methoxyphenyl)-xanthene (XI).**—A solution of 5 g. (0.0165 mole) of 9-(*p*-methoxyphenyl)-xanthenol (XII) in 100 ml. of 90% formic acid, to which 2 g. of sodium carbonate was added, was refluxed 1 hour and cooled to 20°. The crystals were collected on a filter, washed, dried and recrystallized from ethanol. The yield of white prisms was 4.3 g. (93%), melting at 113–114° which checked the literature value.[14]

**Conversion of 9-(*p*-Aminophenyl)-xanthene (X) to 9-(*p*-Methoxyphenyl)-xanthene (XI).**—A solution of 10 g. (0.0366 mole) of the amine (X) in 30 ml. of acetic acid and 10 ml. of concentrated sulfuric acid was diazotized at 5–10° by treatment with 2.55 g. (0.037 mole) of sodium nitrite, with stirring over a period of 2 hours. The mixture was then poured slowly into a boiling solution of 50 ml. of concentrated sulfuric acid and 50 ml. of water. After boiling for 15 minutes, the mixture was poured into ice-water, and the solid was isolated by filtration and washed with water. The yield of red solid was 6 g., melting at 130–140°. This crude product was methylated by refluxing with 0.8 g. of sodium hydroxide, 3 ml. of methyl sulfate and 20 ml. of water for 20 hours. The mixture was cooled to 20° and poured into cold water. The dark solid was collected on a filter, washed, dried and recrystallized three times from methanol. The yield of white prisms was 2.1 g. (20%) which melted at 113–114°, and which did not depress the melting point of the sample of 9-(*p*-methoxyphenyl)-xanthene (XI) synthesized as described above from xanthone.

**9-(*p*-Amino-*m*-nitrophenyl)-xanthene (XIII).**—A solution of 24 g. (0.12 mole) of xanthydrol, 20 g. (0.15 mole) of *o*-nitroaniline, 10 ml. of concentrated hydrochloric acid and 120 ml. of glacial acetic acid was refluxed for 4 hours, cooled to 25°, poured into 1 l. of water, containing 20 g. of sodium carbonate, and then warmed and stirred on the steam-bath for 30 minutes. The solid was collected on a filter, washed with water, and dried. The yellow solid weighed 28 g. This was refluxed with 400 ml. of 80% ethanol and 100 ml. of concentrated hydrochloric acid for 8 hours, cooled and poured into 1 l. of water. The mixture was then treated with sodium carbonate to neutralize the acid. The yellow solid was isolated by filtration, washed with water, and dried at 70–80°. The yield of crude product was 22.5 g. (59%), melting at 130–140°. After crystallization from 500 ml. of absolute ethanol the yellow crystals weighed 17.8 g. (46.6%) and melted at 158–160°. A second recrystallization from ethanol raised the melting point to 160–161°; further recrystallizations did not affect the melting point.

*Anal.* Calcd. for $C_{19}H_{14}O_3N_2$: C, 71.68; H, 4.43; N, 8.80. Found: C, 71.55; H, 4.40; N, 8.97.

**9-(*o*-Nitrophenylamino)-xanthene (XIV).**—To a solution of 24 g. (0.12 mole) of xanthydrol in 450 ml. of 95% ethanol was added 20 g. (0.15 mole) of *o*-nitroaniline. The mixture was stirred for a few minutes until solution was complete, and then 20 ml. of glacial acetic acid was added, with stirring. Yellow crystals began to separate within a few minutes. Stirring was continued at 25° for 2 hours, and the mixture was then cooled at 0–5° for 2 hours. The solid was collected on a filter, washed with 50 ml. of 80% ethanol and dried. The yield of yellow crystals was 36.5 g. (94.6%), melting at 192–197°. Upon recrystallization from pyridine orange crystals were obtained which melted at 197–199° (uncor.).

*Anal.* Calcd. for $C_{19}H_{14}O_3N_2$: C, 71.68; H, 4.43; N, 8.80. Found: C, 71.54; H, 4.30; N, 8.84.

**Hydrolysis of 9-(*o*-Nitrophenylamino)-xanthene (XIV).**—A suspension of 2 g. (0.0063 mole) of the secondary amine, XIV, in 50 ml. of 15% hydrochloric acid was refluxed for 4 hours and then allowed to cool to room temperature. The solid was isolated by filtration and, after being dried, weighed 1.2 g. and melted at 116–120°; this represented 96% the theoretical yield of xanthydrol. The filtrate was made basic by the addition of sodium hydroxide solution, and the orange solid which separated was collected on a filter and dried. After crystallization from 80% ethanol the orange needles weighed 0.5 g. (57%) and melted at 70–71°; there was no depression in melting point upon admixture with an authentic sample of *o*-nitroaniline.

A portion of the crude xanthydrol obtained above was converted to N-xanthylacetamide by treatment with acetamide in acetic acid solution, according to the procedure of Phillips and Pitt.[15] White crystals were obtained which melted at 237–239° and which showed no depression in melting point when mixed with an authentic sample of N-xanthylacetamide.[15]

**Rearrangement of 9-(*o*-Nitrophenylamino)-xanthene (XIV) to 9-(*p*-Amino-*m*-nitrophenyl)-xanthene (XIII).**—A solution of 10 g. of the secondary amine (XIV) in 50 ml. of glacial acetic acid, containing 2 ml. of concentrated sulfuric acid, was refluxed for 4 hours, cooled to 25°, and poured into 500 ml. of water. The mixture was then treated with 5 g. of sodium carbonate and warmed and stirred on the steam-bath for 30 minutes. The yellow solid was collected on a filter, washed with water and dried. The crude product weighed 9.6 g. (96%) and melted at 145–152°. After crystallization from ethanol the yield of XIII was 8.4 g. (84%), melting at 159–161°.

**9-(*m*-Nitrophenyl)-xanthene (VII); Replacement of the Amino Group of 9-(*p*-Amino-*m*-nitrophenyl)-xanthene (XIII) by Hydrogen.**—A solution of 10 g. (0.031 mole) of the amino compound, XIII, in 30 ml. of glacial acetic acid and 5 ml. of concentrated sulfuric acid was cooled to 5°, and a solution of 2.15 g. (0.032 mole) of sodium nitrite in 10 ml. of cold water was added dropwise over a period of 15 minutes, with stirring. Stirring was continued at 5–10° for one hour, and then 15 ml. of cold 50% hypophosphorous acid was added. Nitrogen was evolved slowly. Stirring in the cold was continued for 1 hour, and the loosely stoppered solution was kept at 0–5° for 16 hours. At the end of this period an additional 10 ml. of 50% hypophosphorous acid was added, and the mixture was then diluted with 25 ml. of water and extracted with three 100-ml. portions of benzene. The combined benzene extract was washed with water, 20% aqueous sodium hydroxide, and again with water. The benzene solution was dried over calcium chloride, and the benzene was removed by distillation on the steam-bath. The residue consisted of 8.1 g. of red crystals which melted at 120–130°. This was dissolved in 125 ml. of 95% ethanol and allowed to stand at 25° for 8 hours. The yellow crystals which separated were isolated by filtration; the yield was 2 g., melting at 129–135°. When mixed with the nitrophenylxanthene derived from the nitration product of 9-phenylxanthylium sulfate, the melting point was 140–148°. After three recrystallizations from ethanol the yield of pale yellow crystals was 0.5 g. (5.3%), melting at 155–156°. There was no change in the melting point upon further recrystallization. Mixed melting points with the nitrophenylxanthene derived from the nitration product of 9-phenylxanthylium sulfate, in which the ratios of the two constituents were varied, showed no depression.

*Anal.* Calcd. for $C_{19}H_{13}O_3N$: C, 75.23; H, 4.32; N, 4.62. Found: C, 75.03; H, 4.33; N, 4.76.

IOWA CITY, IOWA

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[14] Gomberg and West, This Journal, **34**, 1529 (1912).

[15] Phillips and Pitt, *ibid.*, **65**, 1355 (1943.)