[CONTRIBUTION FROM THE COLLEGE OF PHARMACY, UNIVERSITY OF MICHIGAN]

# Hydroxy- and Methoxyphenylanthrones. III[1]

BY F. F. BLICKE AND R. J. WARZYNSKI[2]

It was shown by Baeyer[3] that diphenylphthalin (triphenylmethane-2-carboxylic acid) is converted rapidly, by concentrated sulfuric acid, into 9-phenylanthrone-10 (or 9-phenyl-10-hydroxyanthracene) and that oxidation of the latter yields 9-hydroxy-9-phenylanthrone-10.

It has been found that substituted diphenylphthalins, such as 4′-methoxy-,[4] 2′,4″-dimethoxy-,[5] 4′,4″-dihydroxy-,[6] 4′,4″-dimethoxy-,[4,6] 4′,4″-dichloro-,[7] and 3′,3″,5′,5″-tetrabromo-4′,4″-dihydroxydiphenylphthalin[5] react, in some instances, with sulfuric acid or thionyl chloride in an analogous manner to form a substituted 9-arylanthrone-10 (or the tautomeric 9-aryl-10-hydroxyanthracene).[8] However, in other cases, a substituted 2,5-diaryl-3,4-benzofuran is produced; the furan is converted, by oxidation, into a substituted 2-benzoylbenzophenone.

Recently, it was discovered[9] that in the case of phenolphthalin (4′,4″-dihydroxytriphenylmethane-2-carboxylic acid) the nature of the reaction product can be changed by the use of zinc chloride and acetic anhydride instead of sulfuric acid. Thus, treatment of this phthalin with zinc chloride and acetic anhydride yields the triacetyl derivative of 3,10-dihydroxy-9-(4′-hydroxyphenyl)-anthracene,[10] whereas interaction with sulfuric acid converts the phthalin into 2,5-di-(*p*-hydroxyphenyl)-3,4-benzofuran.[6]

In this paper we have described the effect of zinc chloride, in the presence of acetic anhydride, on a number of diarylphthalins.

Diphenylphthalin was converted by these reagents into the acetyl derivative of 9-phenyl-10-hydroxyanthracene and this, when oxidized, produced 9-hydroxy-9-phenylanthrone-10. The hydroxy anthrone reacted readily with phenol to yield 9-phenyl-9-(4′-hydroxyphenyl)-anthrone-10[11] and with anisole to produce 9-phenyl-9-(4′-methoxyphenyl)-anthrone-10. Methylation of 9-phenyl-9-(4′-hydroxyphenyl)-anthrone-10 with dimethyl sulfate converted it into 9-phenyl-9-(4′-methoxyphenyl)-anthrone-10. The structure of the latter anthrone was proved definitely in the following manner: 2-benzoylbenzoic acid → 2-benzylbenzoic acid[12] → 2-cyanodiphenylmethane[13] → 2-benzylbenzophenone[14] → 2-benzyl-4′-methoxytriphenylcarbinol → 9-phenyl-9-(4′-methoxyphenyl)-9,10-dihydroanthracene → 9-phenyl-9-(4′-methoxyphenyl)-anthrone-10.

9-Hydroxy-9-phenylanthrone-10 reacted with acetyl chloride to yield 9-chloro-9-phenylanthrone-10 and silver acetate converted the latter into the 9-acetoxy derivative.

4′-Hydroxydiphenylphthalin (I), as well as 4′-acetoxydiphenylphthalin, when treated with zinc chloride and acetic anhydride, yielded 9-(4′-acetoxyphenyl)-10-acetoxyanthracene (II), a substance which, in solution, exhibits the characteristic blue anthracene fluorescence. It was converted into 9-hydroxy-9-(4′-acetoxyphenyl)-anthrone-10 (III) by oxidation. In accordance with its structure this anthrone forms a carbinol chloride, 9-chloro-9-(4′-acetoxyphenyl)-anthrone-10, which reacts with silver acetate to form 9-acetoxy-9-(4′-acetoxyphenyl)-anthrone-10, and with molecular silver to yield the free radical 9-(4′-acetoxyphenyl)-anthronyl-10 (IV). A benzene solution

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[1] We wish to express our indebtedness to the Monsanto Chemical Company and to Charles Pfizer and Company for their assistance which made this investigation possible.

[2] This paper represents part of a dissertation to be submitted to the Horace H. Rackham School of Graduate Studies by R. J. Warzynski in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the University of Michigan.

[3] Baeyer, *Ann.*, **202**, 52, 58 (1880).

[4] Blicke and Swisher, THIS JOURNAL, **56**, 1407 (1934).

[5] Blicke and Patelski, *ibid.*, **58**, 277 (1936).

[6] Blicke and Weinkauff, *ibid.*, **54**, 1458 (1932).

[7] Blicke and Patelski, *ibid.*, **58**, 274 (1936).

[8] In several cases diarylphthalides have been converted into anthrones by the action of phosphorus pentachloride. Thus diphenylphthalide yielded 9-chloro-9-phenylanthrone-10 (Haller and Guyot (*Bull. soc. chim.*, [3] **17**, 877 (1897)); Schlenk and Bergmann (*Ann.*, **463**, 150 (1928)) and from phenolphthalein there was produced 3,9-dichloro-9-(4′-chlorophenyl)-anthrone-10 (ref. 7, p. 273).

[9] Blicke and Patelski, THIS JOURNAL, **60**, 2642 (1938).

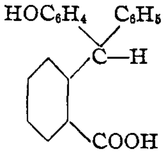
[10] Fieser and Hershberg, (THIS JOURNAL, **59**, 1030 (1937)) used this reaction to convert a diarylmethane-2-carboxylic acid into a 10-acetoxyanthracene; see also Fieser and Kilmer, *ibid.*, **61**, 863 (1939).

[11] Liebermann and Lindenbaum (*Ber.*, **38**, 1801, 1802 (1905)) carried out this same reaction and also condensed 9-chloro-9-phenylanthrone-10 with phenol. In each instance the same reaction product was obtained which they stated was 9-phenyl-10-hydroxy-9,10-diphenoxy-9,10-dihydroanthracene (9,10-Diphenoxy-9-phenylanthranoldihydrür). Although Liebermann and Lindenbaum wrote the incorrect name as well as the incorrect formula and seem to have been the only other investigators who studied these reactions, the correct name for the reaction product—9-phenyl-9-(4′-hydroxyphenyl)-anthrone-10—is recorded in "Beilstein," Vol. VIII, p. 223. The nature of the reaction which took place between the 9-chloro-9-phenylanthrone and *o*-cresol was also interpreted incorrectly by Liebermann and Lindenbaum.

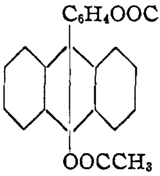
[12] Barnett, Cook and Nixon, *J. Chem. Soc.*, 508 (1927).

[13] Blicke and Swisher, THIS JOURNAL, **56**, 923 (1934).

[14] Seidel, *Ber.*, **61**, 2275 (1928).



I



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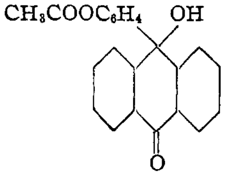

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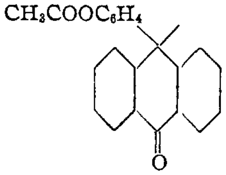

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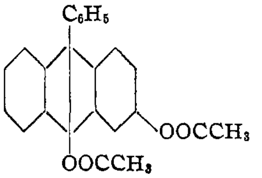

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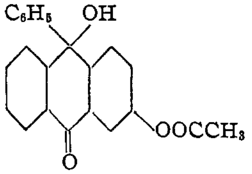

VI

of the radical is deep red and the solution is decolorized immediately upon contact with air. The peroxide of the radical seems to be quite unstable.

In order to prove that the anthracene II and the anthrone III were produced and not the isomeric compounds V and VI, compound III was hydrolyzed to 9-hydroxy-9-(4′-hydroxyphenyl)-anthrone-10 (VII). Methylation of the latter with dimethyl sulfate yielded 9-hydroxy-9-(4′-methoxyphenyl)-anthrone-10 and upon condensation of VII with phenol 9,9-di-(*p*-hydroxyphenyl)-anthrone was obtained. The last-mentioned compound was converted into 9,9-di-(*p*-methoxyphenyl)-anthrone-10 by dimethyl sulfate.

From 4′-methoxydiphenylphthalin, zinc chloride and acetic anhydride there were obtained, after oxidation of the mixture of anthracenes produced as the initial reaction product, 9-hydroxy-9-(4′-methoxyphenyl)-anthrone-10 and 3-methoxy-9-hydroxy-9-phenylanthrone-10.

By the same procedure mentioned above, 4′,4″-dimethoxydiphenylphthalin was converted into 2,5-di-(*p*-methoxyphenyl)-3,4-benzofuran and the latter, by oxidation, into 2-(4″-methoxybenzoyl)-4′-methoxybenzophenone.

4′,4″-Dichlorodiphenylphthalin yielded 3-chloro-9-(4′-chlorophenyl)-10-acetoxyanthracene which was oxidized to 3-chloro-9-hydroxy-9-(4′-chlorophenyl)-anthrone-10.

## Experimental Part

**Diphenylphthalin and Zinc Chloride.**—Five grams of diphenylphthalin was added to 2 g. of fused zinc chloride, dissolved in 10 cc. of acetic anhydride with the aid of heat. The mixture was heated on a steam-bath for fifteen minutes, poured into water which contained a small amount of hydrochloric acid, the 9-phenyl-10-acetoxyanthracene filtered, digested with hot alcohol and recrystallized from acetic acid; yield 4.8 g.; m. p. 165–166°.[15]

To 1.5 g. of the acetyl derivative, dissolved in 20 cc. of hot acetic acid, there was added 1 g. of sodium dichromate, dissolved in a small amount of hot water. The mixture was heated on a steam-bath for one hour, poured into water, the 9-hydroxy-9-phenylanthrone-10 filtered and recrystallized from acetic acid; yield 0.9 g.; m. p. 211–212°.[16]

**9 - Phenyl - 9 - (4′ - methoxyphenyl) - anthrone - 10.**—(a) Three drops of concd. sulfuric acid were added to 2 g. of 9-hydroxy-9-phenylanthrone-10 dissolved in 10 g. of warm phenol and the mixture heated for three hours on a steam-bath. The crude 9-phenyl-9-(4′-hydroxyphenyl)-anthrone-10 was treated with warm water until free from phenol and recrystallized from acetic acid; yield 2.5 g.; m. p. 253–254°.[17]

One gram of the anthrone was dissolved in 5 cc. of alcohol and 25 cc. of 10% sodium hydroxide solution, stirred and heated on a steam-bath and 5 cc. of dimethyl sulfate added gradually. After one hour the precipitated 9-phenyl-9-(4′-methoxyphenyl)-anthrone-10 was filtered, dried and recrystallized from acetic acid; yield 0.9 g.; m. p. 182–183°.[18]

(b) Two grams of 9-hydroxy-9-phenylanthrone-10, dissolved in 15 g. of warm anisole, was heated with three drops of concd. sulfuric acid on a steam-bath for eight hours, the excess anisole removed by steam distillation and the anthrone recrystallized from acetic acid; yield 2.2 g.; m. p. 182–183°.

(c) In order to obtain 2-benzyl-4′-methoxytriphenylcarbinol, the Grignard reagent prepared from 31.7 g. of 4-iodoanisole, 3.3 g. of magnesium and 125 cc. of ether there was added 22 g. of 2-benzylbenzophenone, dissolved in 60 cc. of the same solvent. The mixture was heated for four hours, decomposed with ice and ammonium chloride, the solvent removed from the ether layer and the residue steam distilled for some time to remove by-products. The carbinol was recrystallized from petroleum ether (90–100°); yield 13 g.; m. p. 92–93°.

*Anal.* Calcd. for $C_{27}H_{24}O_2$: C, 85.22; H, 6.36. Found: C, 85.24; H, 6.45.

Hydrogen chloride was passed into a hot solution of 11 g. of the carbinol in 50 cc. of acetic acid until it became red-brown; about ten minutes were required. The solution was then heated on a steam-bath for twelve hours, the crystalline, precipitated 9-phenyl-9-(4′-methoxyphenyl)-9,10-dihydroanthracene filtered and recrystallized from acetic acid; yield 7 g.; m. p. 192°.

*Anal.* Calcd. for $C_{27}H_{22}O$: C, 89.46; H, 6.12. Found: C, 89.46; H, 6.15.

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[15] Baeyer (ref. 3, p. 58), who acetylated 9-phenyl-10-hydroxyanthracene, reported the same melting point.

[16] Baeyer (ref. 3, p. 59) found 208°. Haller and Guyot (*Compt. rend.*, **138**, 1251 (1904)), who allowed anthraquinone to react with phenylmagnesium bromide, reported 207°.

[17] Liebermann and Lindenbaum (ref. 11) found 251–252°.

[18] Tetry (*Compt. rend.*, **128**, 1406 (1899)), who obtained the anthrone from 9-chloro-9-phenylanthrone-10, anisole and aluminum chloride, reported 180–181°.

To 5 g. of the dihydroanthracene, dissolved in 75 cc. of hot acetic acid, there was added 3.5 g. of sodium dichromate, dissolved in 3 cc. of warm water. The mixture was heated on a steam-bath for twelve hours, poured into warm water, the precipitated 9-phenyl-9-(4′-methoxyphenyl)-anthrone-10 filtered and recrystallized from acetic acid; yield 3.5 g.; m. p. 183–184°.

**9-Chloro- and 9-Acetoxy-9-phenylanthrone-10.**—When a suspension of 2 g. of 9-hydroxy-9-phenylanthrone-10 in 30 cc. of dry benzene and 10 cc. of acetyl chloride was refluxed the anthrone dissolved gradually. After twenty hours the mixture was reduced to a very small volume under diminished pressure, low boiling petroleum ether added and the crystalline 9-chloro-9-phenylanthrone-10 recrystallized from a small amount of benzene; yield 1.6 g.; m. p. 165–167°.[19]

A solution of 1 g. of the chloro compound in 20 cc. of benzene was refluxed with 1.6 g. of silver acetate for three hours, filtered, the filtrate concentrated and the product precipitated by the addition of low boiling petroleum ether. The 9-acetoxy-9-phenylanthrone-10 melted at 196–198°[20] after it had been recrystallized from a mixture of benzene and petroleum ether; yield 0.7 g.

**4′-Hydroxydiphenylphthalin and Zinc Chloride.**—Fifty grams of the phthalin (I), 15 g. of fused zinc chloride and 100 cc. of acetic anhydride were treated in the manner described above. There was obtained 57.5 g. of 9-(4′-acetoxyphenyl)-10-acetoxyanthracene (II); m. p. 195–196° after recrystallization from acetic acid.

*Anal.* Calcd. for $C_{24}H_{18}O_4$: C, 77.82; H, 4.90. Found: C, 77.62; H, 4.97.

The compound exhibits an intense purple fluorescence when dissolved in organic solvents and becomes deep green when moistened with concd. sulfuric acid; the color changes successively to blue, purple and finally red-brown when the mixture is warmed.

In order to obtain 4′-acetoxydiphenylphthalin, a mixture of 10 g. of 4′-hydroxydiphenylphthalin and 30 cc. of acetic anhydride was refluxed for one hour, poured into water, the oily precipitate separated and washed with water. After several days the oil became crystalline. It was dissolved in hot acetic acid and an equal volume of water added; the oily product soon solidified; yield 9 g.; m. p. 149–151°.

*Anal.* Calcd. for $C_{22}H_{18}O_4$: C, 76.28; H, 5.24. Found: C, 76.12; H, 5.34.

Two grams of the phthalin and 0.6 g. of fused zinc chloride, dissolved in 4 cc. of warm acetic anhydride, were heated on a steam-bath for fifteen minutes, the solution cooled and the crystalline 9-(4′-acetoxyphenyl)-10-acetoxyanthracene filtered, washed with acetic acid and then recrystallized from this solvent; yield 1.6 g.; m. p. 195–196°.

To 41 g. of the anthracene, dissolved in 700 cc. of hot acetic acid, there was added 20.5 g. of sodium dichromate dissolved in a small amount of hot water. The mixture was heated on a steam-bath for thirty minutes, cooled, the crystalline 9-hydroxy-9-(4′-acetoxyphenyl)-anthrone-10 (III) washed with a small amount of acetic acid and recrystallized from dioxane; yield 34 g.; m. p. 281–282° with decomposition.

*Anal.* Calcd. for $C_{22}H_{16}O_4$: C, 76.73; H, 4.68. Found: C, 76.68; H, 4.81.

Solutions of the anthrone do not fluoresce. When moistened with concd. sulfuric acid the compound becomes deep green and the color changes to purple and finally red-brown when the mixture is warmed.

**9-Chloro- and 9-Acetoxy-9-(4′-acetoxyphenyl)-anthrone-10.**—Hydrogen chloride was passed into a hot suspension of 10.5 g. of 9-hydroxy-9-(4′-acetoxyphenyl)-anthrone-10 in 70 cc. of benzene and 9 cc. of acetyl chloride until a clear solution was obtained. The solvent was removed under diminished pressure, the residue dissolved in benzene and precipitated by petroleum ether (90–100°). The 9-chloro compound melted at 187–189°; yield 8.1 g.

*Anal.* Calcd. for $C_{22}H_{15}O_3Cl$: Cl, 9.77. Found: Cl, 9.54.

To obtain the 9-acetoxy derivative a mixture of 1.0 g. of the carbinol chloride, 1.4 g. of silver acetate and 20 cc. of dry benzene was heated for three hours on a steam-bath, filtered, the solvent removed under reduced pressure and the residue recrystallized from a mixture of benzene and petroleum ether; yield 0.8 g.; m. p. 205–206°.

*Anal.* Calcd. for $C_{24}H_{18}O_5$: C, 74.60; H, 4.70. Found: C, 74.43; H, 4.75.

**9-(4′-Acetoxyphenyl)-anthronyl-10 (IV).**—When 1.00 g. of the colorless carbinol chloride, dissolved in 20 cc. of benzene, was shaken with 3.5 g. of molecular silver in a sealed tube color developed at once. After twelve hours the deep red solution was filtered; 0.40 g. of silver chloride was formed; calcd. amount 0.43 g. Low boiling petroleum ether was added to the filtrate, which became light yellow upon exposure to air, and the precipitated, amorphous peroxide filtered. The latter was placed in a desiccator but after some time it became gummy hence was not analyzed.

**9-Hydroxy-9-(4′-hydroxyphenyl)- and 9-Hydroxy-9-(4′-methoxyphenyl)-anthrone-10.**—A mixture of 15 g. of 9-hydroxy-9-(4′-acetoxyphenyl)-anthrone-10, 75 cc. of 10% sodium hydroxide solution and 75 cc. of alcohol was heated on a steam-bath for fifteen minutes, cooled, filtered, diluted with 150 cc. of water and then treated with 300 cc. of saturated ammonium chloride solution. The colorless, crystalline precipitate of 9-hydroxy-9-(4′-hydroxyphenyl)-anthrone-10 was recrystallized from a mixture of dioxane and petroleum ether (30–60°) and then from ether; yield 13 g.; m. p. 208–210° with decomp.

*Anal.* Calcd. for $C_{20}H_{14}O_3$: C, 79.45; H, 4.66. Found: C, 79.63; H, 4.60.

The anthrone melts with the formation of a deep red liquid; concd. sulfuric acid turns the anthrone deep green, a color which becomes an intense purple when the mixture is warmed.

One gram of the anthrone, dissolved in 20 cc. of 10% sodium hydroxide solution, was heated on a steam-bath, stirred and 5 cc. of dimethyl sulfate added, gradually, during the course of an hour. The precipitated methoxy

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(19) Obtained by different procedures Haller and Guyot (*Compt. rend.*, **121**, 105 (1895); *Bull. soc. chim.*, [3] **17**, 877 (1897)) reported 164° and Liebermann, Glawe and Lindenbaum (*Ber.*, **37**, 3338 (1904)) found 168–169°.

(20) Baeyer (ref. 3, p. 61) reported 194–196°.

compound was recrystallized from alcohol; yield 0.85 g.; m. p. 205–206°.[21]

**9,9-Di-(*p*-hydroxyphenyl)-anthrone-10.**—To a solution of 2.0 g. of 9-hydroxy-9-(4′-hydroxyphenyl)-anthrone-10 in 10 cc. of hot phenol there was added three drops of concd. sulfuric acid. The mixture was heated for four hours on a steam-bath, the crystalline precipitate filtered through a warm funnel, recrystallized twice from dilute alcohol and then from acetic acid; yield 1.9 g.; m. p. 305–306°[22] with decompn.

**9,9-Di-(*p*-methoxyphenyl)-anthrone-10.**—After 1.0 g. of 9,9-di-(*p*-hydroxyphenyl)-anthrone-10, 50 cc. of 10% sodium hydroxide and 4 cc. of dimethyl sulfate had been stirred and heated for one hour on a steam-bath, the dimethoxy compound was obtained upon acidification; yield 0.9 g.; m. p. 206–207°[23] after recrystallization from alcohol.

**4′-Methoxydiphenylphthalin and Zinc Chloride.**—A mixture of 18.0 g. of the phthalin,[24] 5.4 g. of fused zinc chloride and 35 cc. of acetic anhydride was heated for five minutes on a steam-bath and poured into water which contained a small amount of hydrochloric acid. The gummy precipitate became solid when digested with water on a steam-bath. It was dissolved in 50 cc. of acetic acid, 9 g. of sodium dichromate added and heated for one-half hour on a steam-bath; 8.6 g. of crystalline product precipitated which was separated with the aid of acetic acid into 9-hydroxy-9-(4′methoxyphenyl)-anthrone-10 (4.1 g.) which melted at 205–206°[25] and 3-methoxy-9-hydroxy-9-phenylanthrone-10 (0.5 g.) which was found to melt at 177–178°.[26] Each product was purified by three recrystallizations from acetic acid.

**4′,4″-Dimethoxydiphenylphthalin and Zinc Chloride.**—From 1 g. of the phthalin[27] there was obtained 0.65 g. of yellow, crystalline 2,5-di-(*p*-methoxyphenyl)-3,4-benzofuran[6]; 0.5 g. of the furan yielded, upon oxidation, 0.4 g. of 2-(4″-methoxybenzoyl)-4′-methoxybenzophenone which melted at 157–158°.[28]

**4′,4″-Dichlorodiphenylphthalin and Zinc Chloride.**—From 2 g. of the phthalin[7] we obtained 1.6 g. of 3-chloro-9-(4′-chlorophenyl)-10-acetoxy-anthracene; m. p. 155–156° after recrystallization from acetic acid.

*Anal.* Calcd. for $C_{22}H_{14}O_2Cl_2$: Cl, 18.60. Found: Cl, 18.54.

Upon oxidation of 1.1 g. of the product there was produced 0.9 g. of 3-chloro-9-hydroxy-9-(4′-chlorophenyl)-anthrone-10; m. p. 222°.[29]

## Summary

The action of zinc chloride and acetic anhydride on diphenyl-, 4′-hydroxydiphenyl-, 4′-methoxydiphenyl-, 4′,4″-dimethoxydiphenyl- and 4′,4″-dichlorodiphenylphthalin was studied. Oxidation of the initial reaction products yielded in one instance a 2-benzoylbenzophenone, in others hydroxy- or methoxyphenylanthrones.

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[21] Blicke and Weinkauff (THIS JOURNAL, **54**, 1462 (1932)) found 206–207°; ref. 4, m. p. 205–206°.

[22] Scharwin and Kusnezof (*Ber.*, **36**, 2020 (1903)) reported 308–309°.

[23] Scharwin, Naumof and Sandurin (*ibid.*, **37**, 3618 (1904)) found 208°.

[24] Ref. 13, p. 924.

[25] The same melting point is reported in the literature (ref. 4).

[26] Ref. 4, m. p. 177–178°.

[27] Grande, *Gazz. chim. ital.*, **26**, I, 228 (1896).

[28] Ref. 6, p. 1459, m. p. 157–159°.

[29] Ref. 7, p. 275, m. p. 223–224°.

ANN ARBOR, MICHIGAN RECEIVED SEPTEMBER 16, 1940

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 228]

# The Preparation of Fibrous Iodo-cellulose Nitrates and the Probable Distribution of Nitrate Groups in Partly Nitrated Celluloses[1]

BY G. E. MURRAY AND C. B. PURVES[2]

Although the average degree of substitution in partly nitrated celluloses can be calculated easily from the nitrogen content, no methods have been developed to determine the distribution of nitrate groups along the cellulosic chain or between the second, third and sixth positions of the individual glucose residues. This article is concerned with the latter aspect of the distribution and originated from a consideration of the work of others in the methylglucoside series. The 2,3-dimethyl-4,6-dinitrate derivative of the latter gave a 70% yield of crude 2,3-dimethyl-6-iodomethylglucoside-4-nitrate when heated at 100° with sodium iodide in acetone.[3] On the other hand, the 2,3,4-trinitrate gave a small amount of halogen-free product in the same conditions[4a] while recrystallized 4,6-ethylidene methylglucoside 3-mononitrate was produced in 70% yield from the corresponding 2,3 dinitrate.[4b] Although side reactions were obvious, it was clear that only nitrate groups in

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[1] Presented at the Boston meeting of the American Chemical Society, September, 1939.

[2] This article is based on a thesis submitted by G. E. Murray to the Faculty of the Massachusetts Institute of Technology in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1939.

[3] Irvine and Rutherford, THIS JOURNAL, **54**, 1491 (1932); Oldham, *J. Chem. Soc.*, 2840 (1925).

[4] Bell and Synge, *ibid.*, (a) 1711 (1937); (b) 833 (1938).