The anthrone was prepared also by methylation of compound VII according to the procedure just described.

9,9,10-Tri-(*p*-anisyl)-10-hydroxy-9,10-dihydroanthracene (IX).—Sixteen grams of compound VIII, dissolved in 75 cc. of benzene, was added, gradually, to the Grignard reagent obtained from 18.9 g. of *p*-iodoanisole, 2.0 g. of magnesium and 75 cc. of ether. The mixture was refluxed for five hours, decomposed with ice and ammonium chloride, the ether–benzene layer filtered and the solution steam distilled. The crystalline residue was recrystallized from acetic acid; yield 15 g.; m. p. 226–228°.

Anal. Calcd. for $C_{35}H_{30}O_4$: C, 81.64; H, 5.91. Found: C, 81.42; H, 5.89.

The methyl ether was obtained when a methyl alcohol solution of the anthracene was partially saturated with hydrogen chloride; m. p. 205–206° after recrystallization from acetic acid.

Anal. Calcd. for $C_{36}H_{32}O_4$: C, 81.78; H, 6.11. Found: C, 81.52; H, 6.13.

9,9,10-Tri-(*p*-anisyl)-10-(*p*-hydroxyphenyl)-9,10-dihydroanthracene (X).—A mixture of 5 g. of compound IX, 20 g. of phenol and three drops of sulfuric acid was heated on a steam-bath for three hours, the material washed with hot water and recrystallized from acetic acid; yield 5 g.; m. p. 310–312°.

Anal. Calcd. for $C_{41}H_{34}O_4$: C, 83.35; H, 5.81. Found: C, 83.07; H, 5.84.

9,9,10,10-Tetra-(*p*-hydroxyphenyl)-9,10-dihydroanthracene (XI).—Two grams of compound X, 20 cc. of constant boiling hydrobromic acid and 300 cc. of acetic acid were refluxed for five hours. The mixture was concentrated to a volume of about 75 cc. and poured into 200 cc. of water. The precipitated product was recrystallized from dilute alcohol; m. p. 371–374°.[6] The compound dissolves readily in dilute alkali.

Anal. Calcd. for $C_{38}H_{26}O_4$: C, 83.18; H, 5.15. Found: C, 82.92; H, 5.14.

One gram of the anthracene was heated with 5 g. of *m*-bromobenzoyl chloride for one hour at 190–200°. The material was washed with hot alcohol, then dissolved in hot acetic acid. When the solution cooled a small amount of colored by-product precipitated. The filtered solution was diluted with three volumes of methyl alcohol; the colorless precipitate, which was the tetra-*m*-bromobenzoyl derivative, melted at 163–168°.

Anal. Calcd. for $C_{66}H_{40}O_8Br_4$: Br, 24.99. Found: Br, 25.18.

9,9,10,10-Tetra-(*p*-anisyl)-9,10-dihydroanthracene (XII).—A boiling solution, obtained from 1 g. of compound X, 3 g. of sodium hydroxide and 20 cc. of 50% alcohol, was treated, gradually, with 5 cc. of dimethyl sulfate. The mixture was heated for one hour and the product recrystallized from acetic acid; m. p. 329–331°.[6]

Anal. Calcd. for $C_{42}H_{36}O_4$: C, 83.40; H, 6.01. Found: C, 83.38; H, 6.07.

The same anthracene was obtained when 1 g. of compound IX, 3 g. of anisole and one drop of sulfuric acid were heated for one hour on a steam-bath; mixed m. p. 329–331°.

Summary

A number of 9,9,10-tri- and 9,9,10,10-tetraaryldihydroanthracenes have been prepared in which the aryl groups are phenyl, *p*-hydroxyphenyl and *p*-anisyl.

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(6) Determined in an air-bath with a 250–600° Palo–Myers mercury thermometer.

ANN ARBOR, MICHIGAN RECEIVED AUGUST 15, 1938

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

Hydroxy- and Methoxyphenylanthrones. I.

BY F. F. BLICKE AND R. A. PATELSKI[1]

It is well known that interaction between phthalic anhydride and aromatic hydrocarbons or simple substitution products of the latter yields 2-acylbenzoic acids, diarylphthalides and anthraquinones; other products are formed also but their nature is not known.

It seems to us that in the reaction between phthalic anhydride and phenol, hydroxyphenylanthrones, such as 3,9-dihydroxy-9-(*p*-hydroxyphenyl)-anthrone-10, might be formed and that these anthrones, by further reaction with phenol, might be converted into hydroxy derivatives of diphenylanthrones, tri- and tetraphenyldihydroanthracenes. The hydroxyl groups can occupy either ortho or para positions in the phenyl nuclei and either a 1-, 2-, 3- or 4-position in the anthrone or anthracene nucleus. Since only a few representatives of such compounds have been described in the literature we have synthesized a number of them, often by several different procedures, in order to establish their structure definitely.

In many instances the desired substance has been prepared, with the aid of a Grignard reagent, in the form of its methyl ether; the hydroxy compound was then obtained by demethylation However, this procedure was not always successful since, occasionally, demethylation was accompanied by disruption of the molecule; hence

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[1] Monsanto-Pfizer Research Associate.

it became necessary to search for procedures by means of which the hydroxy compounds could be obtained directly.

Hitherto, we have obtained certain monoarylanthrones by interaction of an anthrone with an arylmagnesium halide,[2,3] by treatment of a diarylphthalin with sulfuric acid[3,4] or thionyl chloride[3] or by the action of phosphorus pentachloride on a diarylphthalide.[4] It should be mentioned that in some cases the action of sulfuric acid on a diarylphthalin yields a diarylbenzofuran or a mixture of a furan and an arylanthrone[2,3,4] (p. 276). In a paper which is to be published soon it will be shown that interaction of a diarylphthalin with zinc chloride yields an arylanthracene; upon oxidation of the latter an arylanthrone is produced.

Diarylanthrones, of the types in which we are interested, have been prepared by oxidation of a diaryldihydroanthracene; the latter were obtained by loss of water from 2-benzyltriphenylcarbinols.[5]

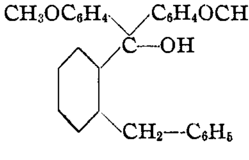
In order to obtain a triaryldihydroanthracene, a diarylanthrone was treated with an arylmagnesium halide.[6]

It was found that a tetra-(*p*-hydroxyphenyl)-dihydroanthracene could be synthesized by demethylation of 9,9,10-tri-(*p*-anisyl)-10-(*p*-hydroxyphenyl)-9,10-dihydroanthracene[6] (p. 2638).

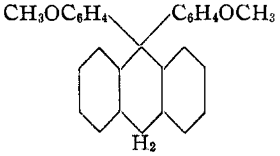
In this paper it has been shown that three different 2-benzyldimethoxytriphenylcarbinols can be converted into 9,9-dianisyl-9,10-dihydroanthracenes by loss of water. Subsequent oxidation and demethylation yielded, in each instance, the desired 9,9-di-(*p*-hydroxyphenyl)-anthrone-10.

It has been found that the ethyl ester of 2-benzylbenzoic acid reacts with two molecular equivalents of 4-anisylmagnesium iodide to yield 2-benzyl-4',4"-dimethoxytriphenylcarbinol (I); the carbinol was prepared also from 2-(4"-methoxybenzoyl)-diphenylmethane and one molecular equivalent of the Grignard reagent.

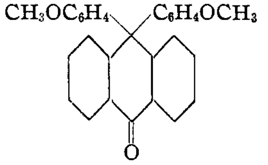
When the carbinol was treated with hydrogen chloride, water was eliminated with the formation of 9,9-di-(*p*-anisyl)-9,10-dihydroanthracene (II). Oxidation of the dihydroanthracene produced 9,9-di-(*p*-anisyl)-anthrone-10 (III) which can be converted into 9,9-di-(*p*-hydroxyphenyl)-anthrone-10 (IV) by demethylation with aluminum chloride. 9,9-Di-(*p*-hydroxyphenyl)-anthrone-10, prepared from anthraquinone, phenol and stannic chloride, according to the method of Scharwin and co-workers,[7] yielded compound III when methylated with dimethyl sulfate.



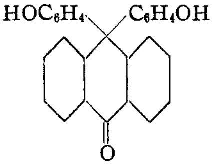
I



II



III



IV

When the ethyl ester of 2-(4'-methoxybenzyl)-benzoic acid was allowed to react with 4-anisylmagnesium iodide there was obtained 2-(4'-methoxybenzyl)-4'',4'''-dimethoxytriphenylcarbinol. This carbinol was converted, by loss of water, into 2-methoxy-9,9-di-(*p*-anisyl)-9,10-dihydroanthracene and the anthracene oxidized to 2-methoxy-9,9-di-(*p*-anisyl)-anthrone-10; upon demethylation 2-hydroxy-9,9-di-(*p*-hydroxyphenyl)-anthrone-10 was formed.

2-(2'-Methoxybenzyl)-4'',4'''-dimethoxytriphenylcarbinol was prepared from the ethyl ester of 2-(2'-methoxybenzyl)-benzoic acid and 4-anisylmagnesium iodide. Ring closure, by elimination of water, produced 4-methoxy-9,9-di-(*p*-anisyl)-9,-10-dihydroanthracene. 4-Methoxy-9,9-di-(*p*-anisyl)-anthrone-10, obtained by oxidation of the anthracene, was demethylated to yield 4-hydroxy-9,9-di-(*p*-hydroxyphenyl)-anthrone-10.

By interaction of ethyl 2-(4'-methoxybenzyl)-benzoate and 2-anisylmagnesium iodide there was obtained 2-(4'-methoxybenzyl)-2'',2'''-dimethoxytriphenylcarbinol which was converted, by ring closure, into 2-methoxy-9,9-di-(*o*-anisyl)-9,10-dihydroanthracene. So far we have been able to obtain the corresponding anthrone only in the form of a gum.

It was thought that 9,9-diarylanthrones might be prepared, easily, by condensation of anisole with a dibromoanthrone such as 3-methoxy-9,9-dibromoanthrone-10. However, we have not been able to effect this condensation. The dibromoanthrone reacts readily with mercury to

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(2) Blicke and Weinkauff, THIS JOURNAL, **54**, 1461 (1932).

(3) Blicke and Swisher, *ibid.*, **56**, 1406 (1934).

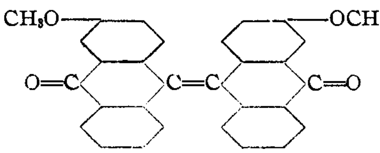
(4) Blicke and Patelski, *ibid.*, **58**, 274 (1936).

(5) Blicke and Patelski, *ibid.*, **58**, 560 (1936).

(6) Blicke and Patelski, *ibid.*, **60**, 2636 (1938).

(7) Scharwin and Kusnezof, *Ber.*, **36**, 2020 (1903); Scharwin, Naumof and Sandurin, *ibid.*, **37**, 3616 (1904).

yield 2,2′(or 2,7′) - dimethoxydianthraquinone (V).[8]



V

Experimental Part

9,9-Di-(*p*-anisyl)-9,10-dihydroanthracene (II).—To the Grignard reagent, prepared from 28.7 g. of 4-iodoanisole, 3.0 g. of magnesium, 50 cc. of ether and 50 cc. of benzene, there was added, gradually, a solution of 6 g. of the ether ester of 2-benzylbenzoic acid,[9] dissolved in 25 cc. of benzene. The mixture was refluxed for three hours, decomposed with ice and ammonium chloride, the solvents removed and the product submitted to steam distillation to remove anisole and other by-products. Since the crude, gummy 2-benzyl-4′,4″-dimethoxytriphenylcarbinol could not be obtained in crystalline form it was prepared by a second method.

Four grams of 2-(4″-methoxybenzoyl)-diphenylmethane,[10] dissolved in 40 cc. of benzene, was added, gradually, to the Grignard reagent prepared from 6.1 g. of 4-iodoanisole, 0.64 g. of magnesium, 30 cc. of ether and 30 cc. of benzene. The mixture was refluxed for three hours and treated as described above. In this instance, too, the carbinol was obtained as a gummy product.

The carbinols, obtained by both procedures, were dissolved in acetic acid or alcohol, the solutions partially saturated with hydrogen chloride and the red mixtures heated for three hours on a steam-bath. Upon dilution with water oils were obtained which crystallized after they had been covered with a small amount of acetic acid for twelve hours. After several recrystallizations from methyl alcohol and then from acetic acid the colorless, crystalline products, obtained from both gummy carbinols, melted at 166–167°. This material was 9,9-di-(*p*-anisyl)-9,10-dihydroanthracene.

Anal. Calcd. for $C_{28}H_{24}O_2$: C, 85.67; H, 6.17. Found: C, 85.52; H, 6.20.

9,9-Di-(*p*-anisyl)-anthrone-10 (III).—A mixture of 0.7 g. of 9,9-di-(*p*-anisyl)-9,10-dihydroanthracene, 1.0 g. of sodium dichromate and 15 cc. of acetic acid was heated on a steam-bath for four hours, diluted with water and the precipitated anthrone recrystallized from alcohol and then from acetic acid; m. p. 208–209°. Mixed with a sample of 9,9-di-(*p*-anisyl)-anthrone-10, obtained by methylation[6] (p. 2637) of 9,9-di-(*p*-hydroxyphenyl)-anthrone-10[11] with dimethyl sulfate, the mixture melted at 208–209°.

2 - (4′-Methoxybenzyl)-4″,4‴-dimethoxytriphenylcarbinol.—A solution of 20.3 g. of the ethyl ester of 2-(4′-methoxybenzyl)-benzoic acid[2] (p. 1464) in 50 cc. of ether was added to the Grignard reagent obtained from 46.8 g. of 4-iodoanisole, 4.8 g. of magnesium and 120 cc. of ether. The mixture was stirred, refluxed for five hours, decomposed with ice and ammonium chloride and a crystalline, ether-insoluble product removed by filtration. After removal of most of the solvent from the filtrate a crystalline material, the desired carbinol, was obtained; yield 17 g.; m. p. 147–148° after recrystallization from a mixture of benzene and petroleum ether (90–100°).

Anal. Calcd. for $C_{29}H_{28}O_4$: C, 79.05; H, 6.41. Found: C, 78.88; H, 6.46.

2 - Methoxy-9,9-di-(*p*-anisyl)-9,10-dihydroanthracene.—A solution of 9.5 g. of the above-mentioned carbinol in 40 cc. of acetic acid was partially saturated with hydrogen chloride and the deep red solution heated on a steam-bath for three hours. The solution then possessed a strong purple fluorescence and, when cooled, deposited the dihydroanthracene in crystalline form; m. p. 167–168° after recrystallization from acetic acid; yield 8.5 g.

Anal. Calcd. for $C_{29}H_{26}O_3$: C, 82.42; H, 6.21. Found: C, 81.92; H, 6.21.

2-Methoxy-9,9-di (*p*-anisyl)-anthrone-10.—A solution of 8 g. of sodium dichromate in 10 cc. of hot water was added to 10 g. of the dihydroanthracene, suspended in 50 cc. of acetic acid, and the mixture heated for three hours on a steam-bath. Upon dilution with water the anthrone was precipitated; yield 8.5 g.; m. p. 183–184°[2] (p. 1464) after recrystallization from acetic acid.

2 - Hydroxy - 9,9 - di - (*p* - hydroxyphenyl) - anthrone-10.—Five grams of anhydrous aluminum chloride was added to a solution of 2 g. of 2-methoxy-9,9-di-(*p*-anisyl)-anthrone-10 in 100 cc. of dry benzene and the mixture refluxed for twenty-four hours on a steam-bath. After treatment with ice and hydrochloric acid the benzene layer was separated, the solvent removed, the residue dissolved in alcohol and the solution decolorized with charcoal. Upon dilution of the solution with water a colorless, crystalline product was obtained which was recrystallized from dilute alcohol; yield 0.9 g.; m. p. 312–314° with decomposition.

Anal. Calcd. for $C_{26}H_{18}O_4$: C, 79.16; H, 4.60. Found: C, 78.98; H, 4.72.

Two grams of the hydroxy-anthrone, dissolved in 50 cc. of hot 10% sodium hydroxide solution was treated gradually with 8 cc. of dimethyl sulfate and the mixture refluxed for three hours. The precipitated material, 2-methoxy-9,9-di-(*p*-anisyl)-anthrone-10, weighed 1.2 g. and melted at 183–184°.

The tri-(3-bromobenzoyl) derivative was obtained when 1.4 g. of the hydroxy-anthrone was heated with 6.5 g. of 3-bromobenzoyl chloride at 140–150° in an oil-bath for two hours. The brown oil was washed thoroughly with 10% sodium hydroxide solution, with water and then with alcohol. The product was covered with ether and, after it had become crystalline, was recrystallized from acetic acid; m. p. 174–176°.

Anal. Calcd. for $C_{47}H_{27}O_7Br_3$: Br, 25.44. Found: Br, 25.12.

Ethyl 2-(2′-Methoxybenzoyl)-benzoate.—A mixture of 90 g. of 2-(2′-methoxybenzoyl)-benzoic acid, 600 cc. of

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[8] 1,1′-Dimethoxydianthraquinone has been described by Attree and Perkin [*J. Chem. Soc.*, 168 (1931)] while 3,3′-dimethoxydianthraquinone was prepared by Barnett, Goodway and Savage [*Ber.*, **64**, 2193 (1931)] and by Perkin and Yode [*J. Chem. Soc.*, **127**, 1884 (1925)].

[9] Barnett, Cook and Nixon, *ibid.*, 508 (1927).

[10] Blicke and Swisher, THIS JOURNAL, **56**, 925 (1934). We found the product melted at 78–79° instead of at 68–70° as reported previously.

[11] See ref. 7. These investigators obtained 9,9-di-(*p*-hydroxyphenyl)-anthrone-10 by demethylation of 9,9-di-(*p*-anisyl)-anthrone-10.

absolute alcohol and 25 cc. of concd. sulfuric acid was refluxed for twenty-four hours, one-third of the alcohol removed by distillation and the residue diluted with two liters of saturated sodium chloride solution. The precipitated oily ester was extracted with ether, the ether extract washed with sodium carbonate solution and then with water. The ether solution was dried with fused sodium sulfate and the solvent removed. The ester boiled at 268–270° under 14 mm. pressure; yield 70 g.

Anal. Calcd. for $C_{17}H_{18}O_3$: C, 75.52; H, 6.72. Found: C, 75.29; H, 6.69.

2 - (2'-Methoxybenzyl)-4'',4'''-dimethoxytriphenylcarbinol.—The Grignard reagent, prepared from 46.8 g. of 4-iodoanisole, 4.8 g. of magnesium and 120 cc. of ether, was stirred and to it there was added, slowly, a solution of 20.3 g. of ethyl 2-(2'-methoxybenzoyl)-benzoate in 50 cc. of ether. The mixture was stirred and refluxed for three hours and then allowed to remain at room temperature for twelve hours. The mixture was decomposed with ice and ammonium chloride. The carbinol was recrystallized from a mixture of benzene and petroleum ether (30–60°); m. p. 139–140°; yield 22.7 g.

Anal. Calcd. for $C_{29}H_{28}O_4$: C, 79.05; H, 6.41. Found: C, 79.11; H, 6.58.

4-Methoxy-9,9-di-(*p*-anisyl)-anthrone-10.—Ten grams of the above mentioned carbinol was dissolved in 50 cc. of acetic acid, the solution partially saturated with hydrogen chloride and the red solution heated for six hours on a steam-bath. The solution, which possessed a strong purple fluorescence, was diluted with water, whereupon a light brown solid, 4-methoxy-9,9-di-(*p*-anisyl)-9,10-dihydroanthracene, precipitated.

A mixture of 10 g. of the dihydroanthracene, 50 cc. of acetic acid, 8 g. of sodium dichromate and 10 cc. of water was heated for three hours on a steam-bath, diluted with four volumes of water and the precipitated, crystalline anthrone recrystallized from acetic acid; m. p. 248–250°.

Anal. Calcd. for $C_{29}H_{24}O_4$: C, 79.78; H, 5.54. Found: C, 79.39; H, 5.52.

4-Hydroxy-9,9-di-(*p*-hydroxyphenyl)-anthrone-10.—Two grams of finely powdered 4-methoxy-9,9-di-(*p*-anisyl)-anthrone-10 and 3 g. of powdered aluminum chloride was heated for one hour at 100–105°, the mixture treated with ice and hydrochloric acid and the gummy product extracted with 10% sodium hydroxide solution. A dark green solid precipitated when the alkaline extract was acidified. The product was dissolved in alcohol and the solution diluted, gradually, with water. A dark brown gum, which precipitated first, was discarded. The light yellow, crystalline precipitate was recrystallized from dilute alcohol; yield 0.8 g.; m. p. 254–256° with decomposition.

Anal. Calcd. for $C_{26}H_{18}O_4$: C, 79.16; H, 4.60. Found: C, 78.89; H, 4.81.

A solution of 0.4 g. of the anthrone in 10 cc. of 10% sodium hydroxide solution was heated to 80° and treated, gradually, with 2 cc. of dimethyl sulfate. The mixture was heated for two hours and the precipitated 4-methoxy-9,9-di-(*p*-anisyl)-anthrone-10 recrystallized from acetic acid; m. p. 247–249°.

A mixture of 0.14 g. of the anthrone and 0.65 g. of 3-bromobenzoyl chloride was heated for two hours at 140–150°, the brown oil washed with 5% sodium hydroxide solution and then with water. The product crystallized when rubbed under ether; m. p. 163–165° after recrystallization from acetic acid.

Anal. Calcd. for $C_{47}H_{27}O_7Br_3$: Br, 25.44. Found: Br, 25.01.

2 - (4'-Methoxybenzyl)-2'',2'''-dimethoxytriphenylcarbinol.—Twenty-three grams of ethyl 2-(4'-methoxybenzyl)-benzoate, dissolved in 50 cc. of ether, was added to 2-anisylmagnesium iodide prepared from 50 g. of 2-iodoanisole, 6.7 g. of magnesium and 150 cc. of ether. The mixture was stirred and refluxed for six hours, the crystalline precipitate removed by filtration and decomposed with ice and ammonium chloride. The crystalline product was recrystallized from petroleum ether (90–100°); yield 26 g.; m. p. 129–130°.

Anal. Calcd. for $C_{29}H_{28}O_4$: C, 79.05; H, 6.41. Found: C, 79.19; H, 6.27.

2 - Methoxy-9,9-di-(*o*-anisyl)-9,10-dihydroanthracene.—A solution of 23 g. of the carbinol described above in 75 cc. of acetic acid was partially saturated with hydrogen chloride and heated for five hours on a steam-bath. The solution, which possessed a high purple fluorescence, was diluted with four parts of water and the oily precipitate, which soon crystallized, was recrystallized from methyl alcohol; m. p. 154–155°.

Anal. Calcd. for $C_{29}H_{26}O_3$: C, 82.42; H, 6.21. Found: C, 82.17; H, 6.27.

3-Methoxy-9,9-dibromoanthrone-10.—Sixteen grams of bromine, dissolved in 100 cc. of carbon disulfide, was added to 11.2 g. of 3-methoxyanthrone-10[12] which was dissolved in 400 cc. of carbon disulfide, cooled to −5° and stirred. The mixture was then allowed to remain at room temperature for one hour, diluted with 500 cc. of petroleum ether (30–60°) and the light yellow crystalline precipitate recrystallized from benzene; yield 12 g.; m. p. 175–177° with decomposition.

Anal. Calcd. for $C_{15}H_{10}O_2Br_2$: Br, 41.88. Found: Br, 42.13.

When 3.0 g. of the brominated anthrone was treated with 20 cc. of water 1.8 g. of 2-methoxyanthraquinone was produced; mixed m. p. 195–196°.

2,2'(or 2,7')-Dimethoxydianthraquinone.—A mixture of 15 g. of the dibromoanthrone, 200 cc. of dry benzene and 5 cc. of mercury was shaken for forty-eight hours, filtered, the benzene removed and the green amorphous solid recrystallized from acetic acid. The yellow crystals melted at 254–256° with decomposition.

Anal. Calcd. for $C_{30}H_{20}O_4$: C, 81.06; H, 4.54; mol. wt., 444. Found: C, 81.14; H, 4.44; mol. wt. (benzene, ebullioscopic procedure), 431.

Summary

A number of new triarylcarbinols, dianisyldihydroanthracenes, dianisylanthrones and di-(*p*-hydroxyphenyl)-anthrones have been described.

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[12] Also called 2-methoxyanthrone-9. See Barnett, Goodway and Savage, *Ber.*, **64**, 2191 (1931); ref. 2, p. 1460.