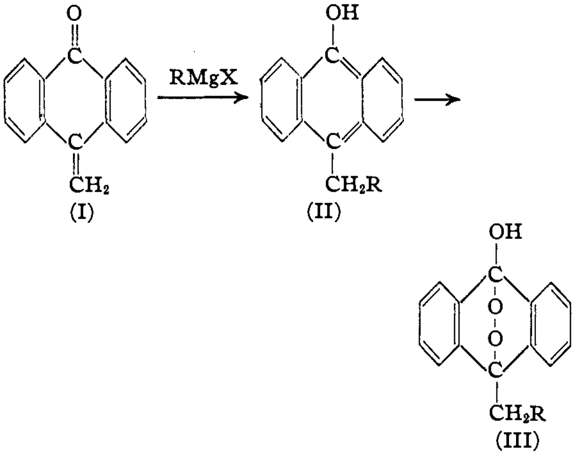
[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE GLIDDEN COMPANY, SOYA PRODUCTS DIVISION]

Conjugated Systems in the Anthracene Series. IV. Transannular Anthranol Peroxides

BY PERCY L. JULIAN, WAYNE COLE AND GERHARD DIEMER

Several years ago, Julian, Magnani and Cole[1] discovered that certain anthranols of the general composition represented by II, rapidly add oxygen across the ring at the active meso-positions to form crystalline anthranol peroxides (III).



R = CH_3, C_2H_5, C_6H_5

These peroxides were all prepared by 1,6-addition of the appropriate Grignard reagent to methyleneanthrone (I) and treatment of the resulting anthranol with atmospheric oxygen. Benzylanthranol peroxide was also prepared by catalytic reduction (1,6-addition of hydrogen) to benzalanthrone in acetone solution, followed by treatment with oxygen. Surprisingly stable crystalline solids at ordinary temperatures, these peroxides undergo thermal decomposition when heated above their melting points, the main products being anthraquinone and the expected alcohol, RCH_2OH. In the earlier papers we reported ethyl, propyl and benzyl anthranol peroxides.

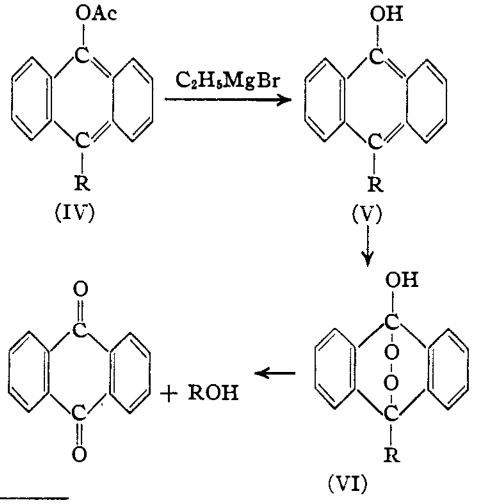
It was recognized immediately that the active meso-positions were responsible for this facile addition of oxygen, a fact which Dufraisse[2] later stated was his working hypothesis in leading him to the discovery of certain photoperoxides in the anthracene series, among them being crystalline anthracene peroxide itself and several meso-substituted anthracene peroxides. It is quite probable that our peroxides and those of Dufraisse belong to the same class and are as closely related as the structural formulas indicate.[3]

In a review of transannular peroxides, Bergmann and McClean[4] express doubt as to the transannular nature of our peroxides. We have considered that the analogies to the open-chain enol peroxides of Kohler,[5] both in method of formation and in thermal decomposition were so striking that one needed only to apply the then-existing knowledge of meso-substituted anthracenes in order to write indisputable formulas for our peroxides.

In this paper, however, we are presenting additional experimental evidence that establishes unequivocally the structure proposed for our anthranol peroxides, and likewise in this and a later paper we are demonstrating that all pure anthranols, with certain understandable exceptions, yield transannular peroxides of the type represented by VI.

Our earlier methods of preparation limited us only to those anthranols obtainable from methyleneanthrone by 1,6-addition. Thus 10-methylanthranol (V, R = CH_3) could not be prepared satisfactorily by catalytic hydrogenation of methyleneanthrone, possibly because of dimolecular reduction.[6] We have found that this anthranol and all other anthranols can be prepared readily in ethereal solution by treatment of the appropriate anthranyl acetate (IV) with ethylmagnesium bromide, followed by acidulation. When oxygen was passed into the resulting ether solution of methylanthranol, the crystalline peroxide (VI, R = CH_3) was secured in good yield. On thermal decomposition it lost methyl alcohol and gave anthraquinone.

Phenylanthranol (V, R = C_6H_5) was likewise prepared from 10-phenylanthranyl acetate (IV,



---

[1] (a) Julian, Magnani and Cole, THIS JOURNAL, **56**, 2174 (1934); (b) **57**, 1607 (1935).

[2] C. Dufraisse, *Bull. soc. chim.*, [5] **6**, 422 (1939).

[3] (a) Dufraisse and Gerard, *Compt. rend.*, **201**, 428 (1935); (b) **202**, 1859 (1936); (c) *Bull. soc. chim.*, [5], **4**, 2052 (1937).

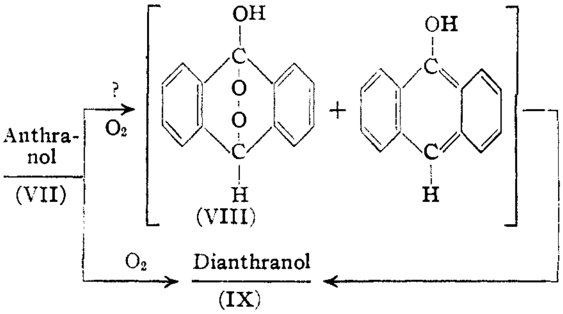
[4] Bergmann and McClean, *Chem. Rev.*, **28**, 391 (1941).

[5] Kohler, *Am. Chem. J.*, **36**, 181 (1906).

[6] *Cf.* Barnett and Matthews, *Ber.*, **59**, 768 (1926).

R = C_6H_5) and the action of oxygen on this anthranol led to pure crystalline phenylanthranol peroxide. On thermal decomposition it yielded phenol and anthraquinone. More strikingly than any other, this reaction demonstrates the general nature of the peroxide decomposition and adds to the evidence for the structures of the peroxides so formed.

Many years ago Bäckström and Beatty[7] expressed the belief that anthranol (VII) formed a peroxide of structure (VIII). We have been unable to confirm this hypothesis by isolation of the peroxide (VIII), but the reason therefore is perfectly understandable. This anthranol unlike the alkyl anthranols and phenyl anthranol contains a reactive hydrogen atom at the 10-position and with atmospheric oxygen yields the bimolecular product (IX).

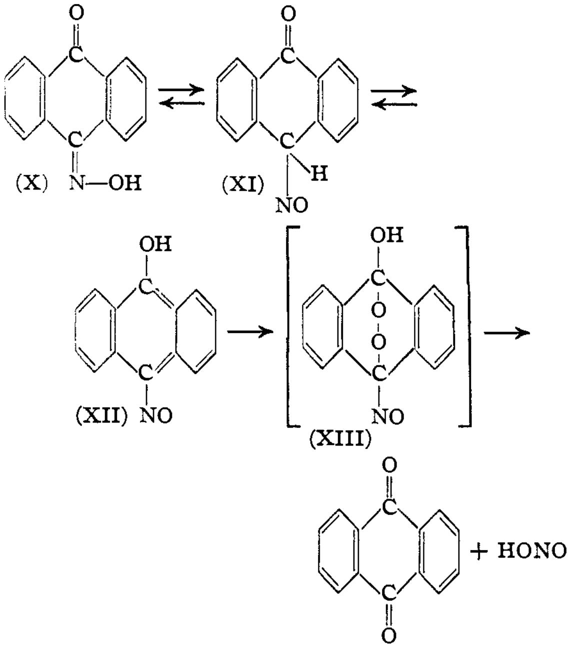


The formation of dianthranol (IX) does not rule out the possibility of formation of peroxide (VIII), for the latter could conceivably oxidize anthranol to IX. At elevated temperatures it has been shown that benzylanthranol peroxide partially oxidizes the eliminated benzyl alcohol to benzaldehyde,[1a] and in paper V of this series it is shown that isopentenylanthranol peroxide oxidizes the eliminated isopropylvinyl alcohol to isobutyraldehyde.[8]

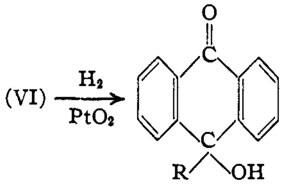
That this type of peroxide formation doubtless represents the mechanism of oxidation of all meso-hydroxy anthracenes is demonstrated strikingly by another reaction. The so-called monoxime of anthraquinone (X) no doubt could exist as nitroso-anthrone (XI) or nitroso-anthranol (XII).

Acid hydrolysis of X in the absence of oxygen leads to hydroxylamine and anthraquinone. When, however, X is dissolved in glacial acetic acid in the presence of oxygen the products are nitrous acid and anthraquinone. In the light of previous work, these reactions are best explained by decomposition of the peroxide (XIII) formed from XII.

As final proof of the "transannular" structure of our anthranol peroxides (VI), we have subjected them to catalytic hydrogenation. Each of these peroxides readily takes up one mole of



hydrogen to yield the expected hydroxyanthrone (XIV).



(XIV)

Experimental

10-Methylanthranol Peroxide (VI, R = CH_3).—Methylanthranyl methyl ether was prepared by the method of Meyer and Schlosser[9] and converted, *via* methylanthrone, into 10-methylanthranyl acetate (yellow needles, m. p. 166–167°) as described by Barnett and Matthews.[10] The over-all yield from anthrone was 20% of the theoretical.

An ether solution of 3 g. of methylanthranyl acetate was added to a Grignard reagent containing 0.08 mole of methylmagnesium bromide in 150 ml. of ether. After five hours stirring and refluxing, the mixture was treated with ice and ammonium chloride and the ether layer was washed. A slow stream of oxygen was then bubbled through the ether solution for two hours. The peroxide crystallized from ether–petroleum ether as 2.5 g. of white powder, m. p. 160–162°, with dec.

Anal. Calcd. for $C_{15}H_{12}O_3$: C, 75.00; H, 5.03. Found: C, 75.06; H, 5.22.

Destructive distillation of the methylanthranol peroxide gave methanol, which was trapped in a benzene solution of 3,5-dinitrobenzoyl chloride and identified as the ester, m. p. 105°. The residue from the pyrolysis contained needles of anthraquinone, m. p. 280°.

10-Methyl-10-hydroxyanthrone (XIV, R = CH_3).—When a solution of 0.3 g. of methylanthranol peroxide in 25 ml. of ethanol was shaken with hydrogen and 0.05 g. of platinum oxide catalyst for fifteen minutes, 0.2 g. of 10-methyl-10-hydroxy-anthrone, m. p. 154°, was formed.

For comparison, the same substance was prepared by the Grignard reaction. A solution containing 0.5 mole of

---

(7) Bäckström and Beatty, *J. Phys. Chem.*, **35**, 2530 (1931).

(8) Julian, Cole and Meyer, THIS JOURNAL, **67**, 1724 (1945).

(9) Meyer and Schlosser, *Ann.*, **420**, 126 (1920).

(10) Barnett and Matthews, *Ber.*, **59**, 767 (1926).

methylmagnesium bromide in 300 ml. of ether was dropped into a stirred suspension of 208 g. of anthraquinone in 750 ml. of benzene during two and one-half hours. The reaction was worked up in the usual way and the product crystallized from ether–petroleum ether, giving 52 g. of 10-methyl-10-hydroxyanthrone, white plates, m. p. 154°.

Anal. Calcd. for $C_{15}H_{12}O_2$: C, 80.34; H, 5.39. Found: C, 80.1; 80.7; H, 5.6; 5.7.

More than 50% of the anthraquinone employed was recovered suitable for re-use.

Ethylanthranyl Acetate (IV, R = C_2H_5).—To a Grignard reagent containing 0.25 mole of methylmagnesium bromide in 250 ml. of ether, 16 g. of powdered methyleneanthrone was added, and the mixture was refluxed for four hours. The fluorescent solution was then cooled in an ice-bath, stirred, and treated dropwise with a solution of 22 g. of acetyl chloride in 100 ml. of benzene during one hour. Ice and dilute acetic acid were added, and the ether layer was separated, washed with water and concentrated *in vacuo* to dryness. The residual yellow oil was crystallized from ether–benzene, giving 16 g. of crude ethylanthranyl acetate. It was recrystallized from ether–methanol, yielding 12 g., m. p. 135–136°.

Anal. Calcd. for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 81.54; H, 6.18.

Dilute solutions of the acetate displayed a strong blue fluorescence.

10-Ethylanthranol Peroxide (VI, R = C_2H_5).—Five grams of ethylanthranyl acetate was added to a Grignard reagent containing 0.2 mole of methylmagnesium bromide in 250 ml. of ether. The mixture was refluxed for four hours, then cooled in an ice-bath, stirred and treated with ice and ammonium chloride solution. The ether layer was separated, washed with water and then oxygen was bubbled through the solution for one hour. The solution was concentrated under partial vacuum, and the peroxide was crystallized by adding pentane and scratching. The ethylanthranol peroxide (3.4 g.) decomposed at 161–164° and was identical with a sample prepared previously.[1b]

When a sample of the peroxide in ethanol was shaken with platinum oxide and hydrogen at slightly above atmospheric pressure, one mole of hydrogen was absorbed quickly. The filtered, concentrated solution yielded only 10-ethyl-10-hydroxyanthrone, m. p. 104–107°, identical with an authentic sample.[1b]

10-Phenylanthranol Peroxide (VI, R = C_6H_5).—Phenylanthranyl acetate (m. p. 165–166°) was prepared in the known manner[11] and also by the action of lead tetraacetate on phenylanthracene in acetic acid solution at 50°.

Five grams of phenylanthranyl acetate was added to an ether solution containing 0.15 mole of methylmagnesium bromide and stirred for three hours. The fluorescent reaction mixture was shaken with ice and ammonium chloride, washed, and then oxygen was bubbled through the ether solution for two hours. The solution was concentrated and the peroxide was crystallized from ether-petroleum ether, yielding 3.5 g. of white powder, m. p. 179–181°.

Anal. Calcd. for $C_{20}H_{14}O_3$: C, 79.45; H, 4.67. Found: C, 79.85; H, 4.89.

Recrystallization from ether did not change the melting point of the peroxide. When a sample was pyrolyzed in a test-tube, the odor of phenol was evolved. The residue was shaken with water, and the solution filtered. The filtrate, upon treatment with bromine water, gave crystals of tribromophenol, m. p. 93°. The residue contained anthraquinone which crystallized from ether as yellow needles, m. p. 285–286°.

When a solution of 0.3 g. of the peroxide in 20 ml. of ethanol was shaken with hydrogen and Raney nickel catalyst, one mole-equivalent of hydrogen was absorbed, and the solution yielded 0.3 g. of 10-phenyl-10-hydroxyanthrone, m. p. 209–210°.

Attempt to Prepare Anthranol Peroxide.—Ten grams of anthranyl acetate was added to an ether solution containing 0.4 mole of methylmagnesium bromide, and the mixture was stirred and refluxed for three hours. Care was taken to avoid contact with air until after the Grignard complex was hydrolyzed. The material was poured into a separatory funnel containing ice, ammonium chloride and nitrogen. After being washed, the ether solution was treated with a stream of oxygen for two hours. Concentration yielded 6 g. of white crystals which melted at 230–240°, and seemed to have all of the properties of bianthrone.[12] Recrystallization from acetone raised the melting point to 250–254°, and acetylation using acetic anhydride–sodium acetate mixture gave bi-anthranyl diacetate, m. p. 276–279°.[12]

Although the crystalline bi-anthrone gave no test for peroxide content, the mother liquors yielded gummy crystals which promptly liberated iodine from acidified sodium iodide solution. These crystals melted at 140–155°, but no pure substance could be separated from the mixture.

10-Nitrosoanthrone (Anthraquinone Monoxime) (IX).—Ten grams of anthrone was added to a solution of sodium ethoxide prepared from 50 ml. of absolute ethanol and 3.5 g. of sodium; then, to the cooled solution, 10 g. of butyl nitrite was added dropwise with stirring. The sodium salt of nitrosoanthrone separated as a red precipitate. The mixture was concentrated *in vacuo* and then treated with 30 ml. of 6 *N* sulfuric acid and ice. Extraction with ether and concentration gave 7.5 g. of nitrosoanthrone as a gray powder, m. p. 224–225°. This material appears to be identical with the anthraquinone monoxime described by Goldschmidt.[13]

Air Oxidation of Nitrosoanthrone.—A suspension of 2 g. of nitrosoanthrone in 30 ml. of glacial acetic acid was swirled and warmed for a few minutes, then let stand in a loosely-stoppered flask for four hours. The odor of nitrous acid fumes became noticeable, and brown fumes were slowly evolved. Fine needles of anthraquinone, m. p. 277–280°, separated from the solution.

Summary

1. The characteristic of 10-alkylanthranols to yield crystalline peroxides on treatment with atmospheric oxygen is shown to be applicable to various meso-substituted anthranols, and we believe such transannular peroxides may be formed from all meso-substituted anthranols.

2. The previously proposed *transannular* nature of these peroxides is evidenced by analogy with open-chain enol peroxides and by catalytic hydrogenation to yield the expected hydroxyanthrone.

CHICAGO, ILLINOIS RECEIVED JULY 26, 1945

---

(11) *Cf.* Bayer, *Ann.*, **202**, 58 (1880); Blicke and Warzynski, THIS JOURNAL, **62**, 3191 (1940).

(12) Barnett and Matthews, *J. Chem. Soc.*, **123**, 387 (1923).

(13) Goldschmidt, *Ber.*, **16**, 2179 (1883).