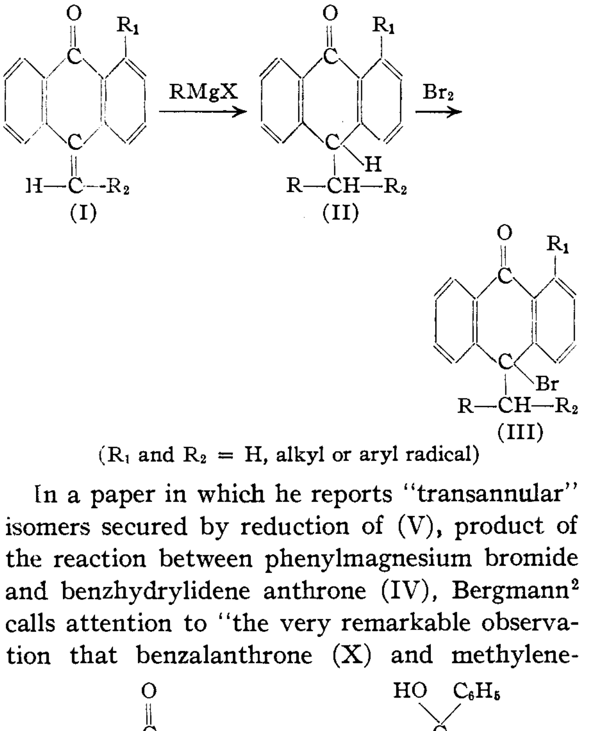
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF DEPAUW UNIVERSITY]

Additions to Conjugated Systems in the Anthracene Series. I. The Action of Phenylmagnesium Bromide on Methyleneanthrone

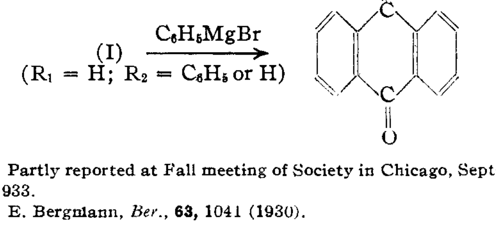
BY PERCY L. JULIAN AND ARTHUR MAGNANI

In connection with an investigation of the reactions of alpha-bromo- and alpha-hydroxy ketones with arylamines, which has been in progress in this Laboratory for some time,[1] we desired halogenated ketones of the type (III). The easiest route to such substances appeared to be by way of ketones of the type (II) which should be available from the reaction between substituted methyleneanthrones and organo-magnesium halides.



(R₁ and R₂ = H, alkyl or aryl radical)

In a paper in which he reports "transannular" isomers secured by reduction of (V), product of the reaction between phenylmagnesium bromide and benzhydrylidene anthrone (IV), Bergmann[2] calls attention to "the very remarkable observation that benzalanthrone (X) and methyleneanthrone (XIII), although wholly similar in constitution to (IV), react indeed readily with phenylmagnesium bromide, but give as only isolable crystalline product, in large quantity, anthraquinone."



The observation called by Bergmann "very remarkable" appears perfectly understandable in view of well-known facts about α,β-unsaturated ketones. Kohler[3] has shown that the enolic compounds, secured on treatment of such ketones with organo-magnesium halides, readily yield monomeric crystalline peroxides, which undergo decomposition on heating, or in solutions of acids or bases, similar to that suffered by ozonides. When one considers the close similarity in structure, for example, between benzaldesoxybenzoin (VII)[3] and benzalanthrone (X), it would not be surprising if the enolic 10-diphenylmethylanthranol (XI), or the 10-benzylanthranol (XIV) formed peroxides, as Kohler found for the analog, tetraphenylpropenol (VIII), from benzaldesoxybenzoin. And one would expect to secure the anthranols (XI) and (XIV) from benzalanthrone and methyleneanthrone, respectively, while in benzohydrylideneanthrone (IV) the hindrance to "transannular" 1,4-addition—or to 1,6-addition, if one prefers to view it from the standpoint of a conjugation that runs continuously around the periphery of the ring—is too great, and the product (V) formed by 1,2-addition is the only one to be expected.

Since it is well known that dihydroanthracene derivatives readily eliminate compounds across the ring, formed by union of the substituents in positions 9 and 10 of the anthracene nucleus, the peroxides (XII) and (XV) would differ from those of Kohler mainly in this regard. Thus (XII) and (XV) would on decomposition yield benzohydrol and benzyl alcohol, respectively, and, in each case, anthraquinone.

We decided, therefore, to repeat Bergmann's experiments with benzalanthrone and methyleneanthrone, both with the hope of securing the desired bromo ketone (III), and explanation of his

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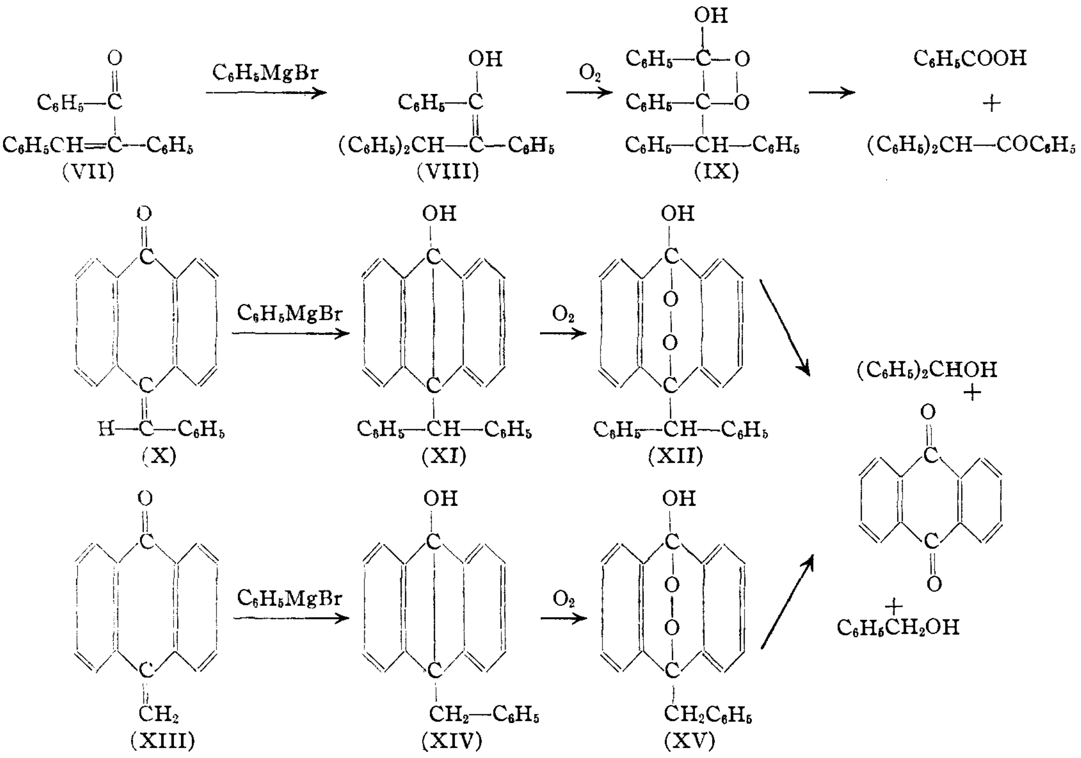
(1) Partly reported at Fall meeting of Society in Chicago, September, 1933.

(2) E. Bergmann, *Ber.*, **63**, 1041 (1930).

(3) E. P. Kohler, *Am. Chem. J.*, **36**, 181 (1906); *cf.* Kohler and Barnes, THIS JOURNAL, **56**, 211 (1934).



observation, through isolation of the peroxides (XII) and (XV).

Our experiments justified in large part the predictions. We first treated benzalanthrone with phenylmagnesium bromide, operating under conditions which Kohler[3] outlined for securing the peroxides. To our surprise, and contrary to the experience of Bergmann, we secured in excellent yield a substance (XVI) analyses of which show that it is formed by addition of one mole of phenylmagnesium bromide to benzalanthrone. This substance is still under investigation.

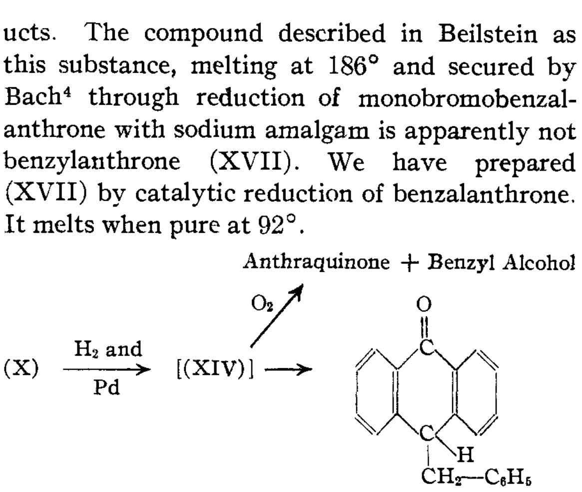
Only after several unsuccessful attempts to duplicate Bergmann's experience with benzalanthrone and phenylmagnesium bromide, were we able to isolate, after removal of the addition product (XVI), a small amount of anthraquinone, which sublimed in high vacuum out of the residues. It was secured in all our earlier experiments, as subsequent investigation showed, in very small quantities, but readily detectable by mixed melting point with an authentic sample. These results, likewise, were understandable and it appeared much more likely that we would be more successful in isolating the peroxide (XV), since it is well known that unsubstituted anthrones far surpass their aryl-substituted derivatives in enolizing power.

$$\text{(X)} \xrightarrow{C_6H_5MgBr} C_{27}H_{20}O \text{ (XVI)}$$

We turned, therefore, to the reaction between methyleneanthrone (XIII) and phenylmagnesium bromide. In this case, as Bergmann stated, the only isolable crystalline product of the reaction is anthraquinone, if the products are worked up in the usual fashion. On passing oxygen into the ethereal solution, however, immediately after decomposition of the Grignard product, it loses its marked fluorescence, characteristic of all solutions of substances having the anthracene structure, and takes on an orange yellow color. On removal of the ether, the residue solidifies almost completely overnight. Taken up again in ether, a quantity of anthraquinone is separated, and from the mother liquors about eight times this quantity of crystalline peroxide (XV).

The peroxide (XV) exhibits all the properties expected of it. On melting it decomposes, with separation of anthraquinone and benzyl alcohol, and the melt does not become completely clear until the melting point of pure anthraquinone is almost reached.

None of the pure 10-benzylanthrone (XVII) was isolated in these reactions, probably due to difficulty of separating it from the various products. The compound described in Beilstein as this substance, melting at 186° and secured by Bach[4] through reduction of monobromobenzalanthrone with sodium amalgam is apparently not benzylanthrone (XVII). We have prepared (XVII) by catalytic reduction of benzalanthrone. It melts when pure at 92°.



(XVII)

As final proof of our mechanism for the reaction between methylene anthrone and phenylmagnesium bromide, we passed oxygen through the deeply fluorescent alcoholic solution obtained on reducing benzalanthrone catalytically. A considerable quantity of anthraquinone was obtained on working up the material and benzyl alcohol was detected in the residues.

Thus the reaction of methyleneanthrone with phenylmagnesium bromide appears entirely analogous to that of an α,β-unsaturated ketone with this reagent, a fact which is in perfect accord with the finding of Barnett and Matthews[5] that hydrogen adds 1,6 to methyleneanthrone—or "transannular" 1,4—producing, when metallic combinations are employed, a dimolecular reduction product.

We hope to report in a later communication certain interesting findings in connection with the addition of the Grignard reagent to benzalanthrone.

The authors are indeed grateful to their first teacher of chemistry, Dean W. M. Blanchard, without whose generous support, constant encouragement, helpful advice and criticisms, this work would have been impossible.

Experimental Part

Preparation of Benzalanthrone (X).—Since the method worked out by Padova[6] and improved by Cook[7] yields a product contaminated with a large quantity of high-melting material, we soon discarded it in favor of the following procedure based upon Kohler's method[8] for securing benzaldesoxybenzoin.

Dry hydrogen chloride was passed for two hours into a mixture of 100 g. of anthrone and 150 cc. of benzaldehyde, contained in a Claisen flask, the latter fitted with a distilling flask to catch the benzaldehyde which distils over and heated on a boiling water-bath. The excess benzaldehyde and water were removed under vacuum, and the residue poured, as far as possible, into alcohol, from which it readily crystallized; yield 138 g., 93% of the theoretical. Recrystallized, it usually melted at 129°, sometimes however at 113°, as Bergmann indicated.[2]

Benzalanthrone and Phenylmagnesium Bromide.—To a Grignard solution prepared from 11.6 g. of magnesium and 75 g. of phenyl bromide in about 1 liter of ether, 45.1 g. of powdered benzalanthrone was added. If the benzalanthrone is added in ether solution, each drop produces a yellow precipitate which rapidly dissolves.[8] The solution finally displayed, as would be expected, a marked yellowish-green fluorescence. Stirred for four hours and worked up in the usual manner, 51 g. of crude product was obtained; recrystallized from ether-petroleum ether, m. p. 147°.

Anal. Calcd. for $C_{27}H_{20}O$: C, 89.96; H, 5.60. Found: C, 89.92; H, 5.63.

The same product is obtained, whether one follows the procedure of Kohler[8] for securing the peroxide. From the residues, distilled in vacuum, 1.4 g. of anthraquinone sublimed.

Reaction of Methyleneanthrone with Phenylmagnesium Bromide.—4.12 grams of powdered methyleneanthrone was added to a Grignard solution from 1.45 g. of magnesium and 9.38 g. of phenyl bromide. The solution had marked fluorescence. The product, decomposed in the usual way, was taken up in ether and let stand in the ice box for several hours, whereupon 2 g. of anthraquinone separated out. The residues, after removal of solid, were distilled, yielding 1.75 g. of low boiling oil which was proved to be largely benzaldehyde (from benzyl alcohol) by converting it into its phenylhydrazone.

10-Benzylanthranol Peroxide (XV).—49.4 grams of methyleneanthrone was treated with 3 moles of phenylmagnesium bromide in the manner described, stirred for three hours, boiled for three hours, let stand overnight, and worked up in the usual way. The moist ethereal solution was divided into two portions and through one oxygen was passed at room temperature for four to five hours. The fluorescence disappears and an orange yellow solution results. On concentrating the ether solution to a small volume and allowing to stand overnight, the contents of the flask were almost completely solid. These were taken up in ether and 3.1 g. of anthraquinone filtered off. The filtrate, concentrated and treated with petroleum ether, deposited 24 g. of peroxide. Recrystallized from ether-petroleum ether, m. p. 133–134° (rapid heating) with decomposition and separation of anthraquinone.

Anal. Calcd. for $C_{21}H_{16}O_3$: C, 79.72; H, 5.10. Found: C, 79.67; H, 4.99.

3.6 grams of peroxide was added through an air condenser to a flask heated to 170–180°. Immediate decomposition resulted with distillation of a colorless liquid. Cooled and taken up in ether, 2.0 g. of anthraquinone was filtered off (theoretical, 2.4 g.). The filtrate gave 0.71 g. of material distilling up to 198° and proved to be a mix-

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(4) Bach, *Ber.*, **23**, 2529 (1890).

(5) Barnett and Matthews, *ibid.*, **59**, 768 (1926).

(6) Padova, *Ann. chim.*, **19**, 353 (1910).

(7) Cook, *J. Chem. Soc.*, 2165 (1926).

(8) Kohler, *Am. Chem. J.*, **36**, 194 (1906).

ture of benzyl alcohol and benzaldehyde; 0.73 g. of resinous material was left.

Attempt to Separate 10-Benzylanthrone (XVII) from Reaction Mixture Above.—From the second half of the ethereal solution of the Grignard product, no crystalline material could be separated except anthraquinone, which was obtained in a yield of 10 g.

Catalytic Reduction of Benzalanthrone

10-Benzylanthrone (XVII).—Twenty grams of benzalanthrone in 225 cc. of absolute alcohol was reduced with hydrogen and a palladium catalyst, absorption being rapid. Allowed to stand in the reaction vessel for thirty-six hours, the fluorescence disappeared. The alcohol was removed under diminished pressure, the residue taken up in ether, warmed on water-bath, and let stand for some hours; 2.0 g. of anthraquinone separated, and on adding petroleum ether to the filtered solution, 9 g. of pure 10-benzylanthrone separated in large colorless prisms; recrystallized from ether–petroleum ether, m. p. 91–92°.

Anal. Calcd. for $C_{21}H_{16}O$: C, 88.7; H, 5.68. Found: C, 88.83; H, 5.67.

When a similar run was made and oxygen passed into the filtered solution immediately upon cessation of absorption of hydrogen, 9.5 g. of anthraquinone was obtained and benzyl alcohol, detected as benzaldehyde, was isolated from the residues.

We attempted to prepare the compound listed in Beilstein as 10-benzylanthrone, according to the method of Bach.[9] On treating benzalanthrone dibromide (for which we find m. p. 138° instead of 148° as Bach gives) as described by him, we secured only anthraquinone and benzalanthrone.[7]

Summary

1. The reactions of arylidene and alkylidene anthrones with phenylmagnesium bromide simulate those of α,β-unsaturated ketones with this reagent.

2. 10-Benzylanthranol, like tetraphenylpropenol, gives a crystalline peroxide with atmospheric oxygen.

3. Benzalanthrone reacts with phenylmagnesium bromide, giving an addition product which is under investigation.

Greencastle, Ind. Received July 27, 1934

(9) Bach, *Ber.*, **23**, 1569 (1890).

[Contribution from the Chemistry Laboratory of the Johns Hopkins University]

Ring Compounds and Polymers from Polymethylene Dihalides and Dimercaptans[1]

By Jacob R. Meadow and E. Emmet Reid

Ring compounds containing two sulfur atoms have been reported from this Laboratory.[2] This study has been extended to include (1) the isolation of the sulfide dimercaptans which are by-products in the preparation of dimercaptans, (2) the preparation of a number of new ring compounds and (3) the decomposition of the polymers.

1. Sulfide Dimercaptans

The high boiling residue when crude ethylene mercaptan is distilled was supposed by Rây[3] to be the disulfide II, but his analyses indicate that his product was impure. By fractionating this residue we have isolated a little II but about ten times as much of the monosulfide mercaptan I. From runs in which a total of 800 g. of ethylene chloride was used we obtained 45 to 55% of ethylene mercaptan, 16% of I and about 1.5% of II along with 5 to 6% of dithiane and 10% of polymers. Besides the usual analyses I was identified by treating it with ethylene chlorohydrin in alkaline solution which converted it into tetraethylene trisulfide glycol, $S(CH_2CH_2SCH_2CH_2OH)_2$, m. p. 91.5°, which had been prepared by Bennett and Whincop[4] from mustard gas and monothioethylene glycol.

The isolation of these sulfide mercaptans is confirmatory evidence for the accepted theory of the building up of sulfide-chain molecules in the reactions of bifunctional compounds. It is probable that even more complicated sulfide mercaptans are present but cannot be isolated on account of their high boiling points and the smallness of the amounts present. As a large excess of sodium hydrosulfide was used all of the products would have —SH terminals which would be less and less evident as the molecular weights increase.

From trimethylene bromide 52% of the calculated amount of trimethylene mercaptan was obtained along with 6% of the sulfide mercaptan III. From dichloroethyl ether and alcoholic potassium hydrosulfide 13% of the oxide mercaptan IV and 5% of the complex mercaptan V were isolated along with 30% of 1,4-thioxane. The

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(1) From Ph.D. dissertation of Jacob R. Meadow, Johns Hopkins University, June, 1933.

(2) Tucker and Reid, This Journal, **55**, 775 (1933).

(3) Râу, *J. Chem. Soc.*, **117**, 1090 (1920).

(4) Bennett and Whincop, *ibid.*, **119**, 1861 (1921).