moved from the center. Slides 5 and 6 show statistically straight lines, in good agreement with the work of Hughes.

If slides had been taken exhibiting the usual fine rhythm of extremely constant spacing over wide areas in large arcs such that the theoretical center of crystallization would be situated off the slide, no distances from the center could have been measured. If the first period formed had been used as a center of crystallization, and measurements made from it, however, a regular series like those in slides 2, 3 and 5 would have been found in those numerous cases in which the periods are of equal width over large areas. These cases would give perfect agreement with the work of Jablczynski and good agreement with the work of Hughes and of Dippy.

For suggestion of the subject of research, acknowledgment and thanks are due to Professor Cecil H. Desch, George Fisher Baker lecturer in Chemistry at Cornell University, October, 1931, to January, 1932.

Summary

Distinction has been made between *coarse rhythm* and *fine rhythm* produced by crystallization of potassium dichromate from aqueous solutions. Fine rhythm has been shown to be the true criterion of periodicity. A method has been described by which very regular fine rhythm can be obtained over large areas.

It has been shown that differences in temperature and in concentration do not, within wide limits, materially affect the rhythmic crystallization of potassium dichromate from aqueous solution.

The rhythmic crystallization of ammonium dichromate and of sodium dichromate from their aqueous solutions has been reported.

The specific influence of a foreign anion in inhibiting the formation of fine rhythm of potassium dichromate has been shown. It has been determined that the nitrate ion is more effective than the sulfate ion, while the sulfate ion is more effective than the chloride ion. The molar ratio of each of these ions to dichromate ion necessary completely to inhibit formation of rhythm has been reported.

It has been shown that the spacing of periods from the center of crystallization, in rhythmic crystallization of potassium dichromate from aqueous solution, agrees, roughly, with the spacing of Liesegang rings reported by Jablczynski, and with the spacing of rhythmic banding resulting from crystallization from the melt, as reported by Hughes and substantiated by Dippy. This would indicate that there may be a common cause underlying the formation of Liesegang rings, rhythmic banding from the melt and rhythmic crystallization from solution.

Amherst, Mass. Received June 27, 1935

[Contribution from the Chemical Laboratory of DePauw University]

Additions to Conjugated Systems in the Anthracene Series. III. Factors Influencing the Mode and Extent of Reaction of the Grignard Reagent with Ketones

By Percy L. Julian, Wayne Cole and Thomas F. Wood[1]

When benzalanthrone (I) is treated with methylmagnesium iodide, the main product (II) isolated is the one formed by 1,2-addition. The reaction was puzzling for a long time, first of all because it is difficult to duplicate results unless the proper concentration of reactants is consistently maintained. Secondly, the behavior of our product (II) toward bromine, as well as behavior on attempted rearrangement into the isomer with the anthracene structure,[2] were not what we had expected. All these results appear, however, to find satisfactory explanation in the ease with which (II) loses water, possessing as it does a very reactive hydroxyl group.

The product secured on treatment of (II) with one mole of bromine in the cold indicates addition of two atoms of bromine and elimination of a molecule of water. It is highly fluorescent in solution, and both bromine atoms are very reactive, as is shown by the ease with which the dibromide is converted into a diacetate. We are suggesting structure (V) for it, and (III) and (IV) as logical intermediates. The diacetate would then have the structure (VI). On further treat-

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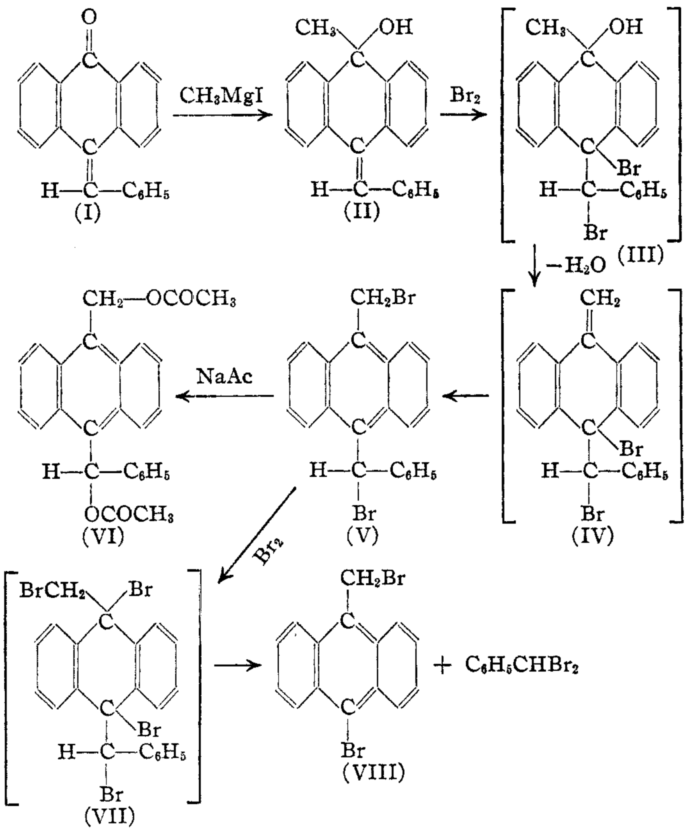
[1] Abstracted from the senior researches of Messrs. Cole and Wood at DePauw University, 1934–1935.

[2] *Cf.* Julian and Cole, This Journal, **57**, 1607 (1935).

ment with bromine in the cold (V) absorbs, somewhat more slowly than (II), a second molecule of bromine, the compound (VIII) being deposited, a substance identical with one of the products secured by Barnett and Matthews[3] on brominating 9-methylanthracene and assigned this structure. The residue on evaporation of the mother liquor is hydrolyzed on warming with water into benzaldehyde and hydrogen bromide. Compound (VII) is suggested as the intermediate in the formation of (VIII) from (V).



With the behavior of (II) satisfactorily explained, our attention was directed to the original object of these investigations, namely, a study of the factors influencing different types of addition of the Grignard reagent to ketones of the anthracene series. It was conceivable that, in view of the fact that a small quantity of anthraquinone is always secured on working up the product from the reaction between phenylmagnesium bromide and benzalanthrone (indicating in all probability formation of a small amount of 1,6-addition product), the action of methylmagnesium iodide might result in a larger percentage of 1,6-addition.[4]

Actually on working up the reaction products on treatment of benzalanthrone with methylmagnesium iodide, an appreciable quantity of anthraquinone was always obtained. Accordingly we employed the usual procedure[2,5] for isolation of peroxides and obtained a very small quantity of a highly insoluble crystalline substance, which decomposed violently at 74° without melting, and yielded anthraquinone. Since its isolation in workable quantities was difficult and no criterion of its purity was available, we decided to undertake the preparation of this same compound by the action of phenylmagnesium bromide on ethylidene anthrone (IX).

The only reference to ethylidene anthrone in the literature is that of Liebermann.[6] Employment of his procedure as well as several other methods which should lead to a compound of this structure yielded invariably anthraquinone. The conclusion was inevitable that ethylidene anthrone (IX) is easily oxidized by atmospheric oxygen to anthraquinone. That atmospheric oxygen should cleave a carbon–carbon double linkage of this type is hardly conceivable in view of the stability of methylene anthrone and benzalanthrone. Since it has been shown[2,5b] that atmospheric oxygen readily converts anthranols into peroxides, it seemed reasonable, proceeding from the principle of vinylogy,[7] to expect that the fundamental difference in behavior between ethylidene anthrone (IX) and methylene and benzalanthrone resides in the ability of the former to exist in the anthranol modification (X), which would be expected to undergo oxidation by atmospheric oxygen to anthraquinone and vinyl alcohol *via* the peroxide (XI).

To test out this hypothesis we undertook the identification of vinyl alcohol as acetaldehyde. A sample of ethyloxanthrone (XII) was dissolved in glacial acetic acid, a few drops of sulfuric acid added and the solution allowed to stand under

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[3] Barnett and Matthews, *Ber.*, **59**, 1434 (1926).

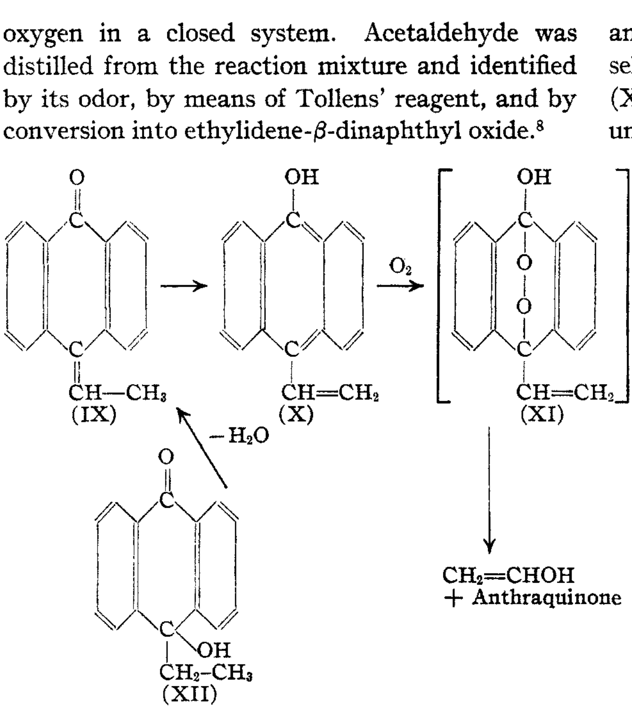
[4] *Cf.* Julian and Gist, THIS JOURNAL, **57**, 2030 (1935); Kohler and Nygaard, *ibid.*, **52**, 4132 (1930).

[5] (a) Kohler, *Am. Chem. J.*, **36**, 189, 192; (b) Julian and Magnani, THIS JOURNAL, **56**, 2174 (1934).

[6] Liebermann, *Ber.*, **13**, 1598 (1880).

[7] Fuson, *Chem. Rev.*, **16**, 1 (1935).

oxygen in a closed system. Acetaldehyde was distilled from the reaction mixture and identified by its odor, by means of Tollens' reagent, and by conversion into ethylidene-β-dinaphthyl oxide.[8]

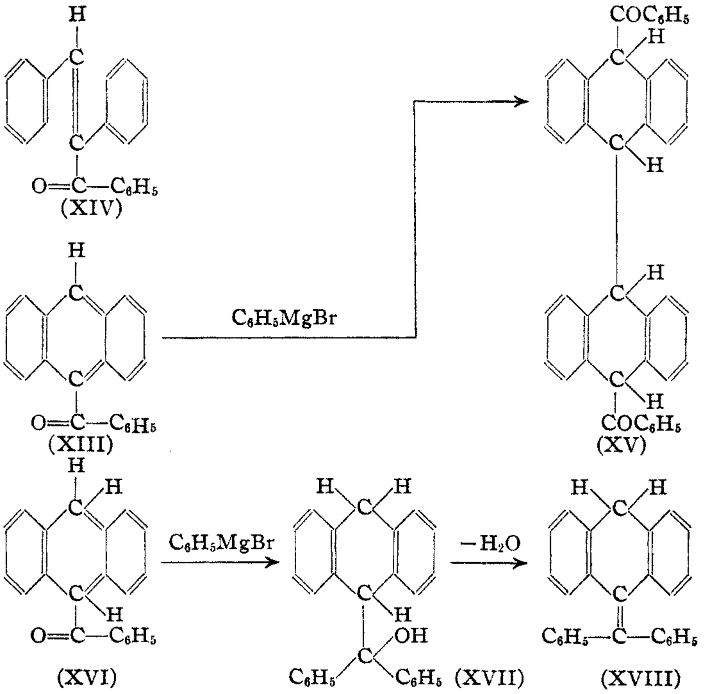


Ethylidene anthrone was obtained as a red oil by destructive distillation of ethyloxanthrone in an atmosphere of nitrogen at ordinary pressure. On redistillation in vacuum this oil boiled constantly at 245–247° at 20 mm.; on attempting to distil this material under atmospheric conditions, however, considerable decomposition took place, yielding anthraquinone and a combustible gas which was collected over water and identified as acetylene. The formation of acetylene is further proof of the proposed oxidation mechanism, since vinyl alcohol formed in this manner at high temperature would be expected to lose water rather than rearrange to acetaldehyde.

The properties of ethylidene anthrone and related anthrones are being further investigated in these laboratories, and our studies of the influence on the mode of reaction with the Grignard reagent, occasioned by substitution of the hydrogen atoms in the methylene group of methylene anthrone, must await the results of these investigations.

We, therefore, turned our attention to the other side of the problem, namely, the influence of the anthracene nucleus on the mode of reaction, selecting as starting material anthraphenone (XIII). Viewed from the standpoint of meso-unsaturation this substance resembles benzaldesoxybenzoin (XIV) and phenylbenzaldesoxybenzoin. Since 1,2-addition of phenylmagnesium bromide seemed highly improbable in view of the sluggish character of the carbonyl group (anthraphenone gives none of the typical ketone reactions),[9] it was expected that either 1,4-addition into the phenyl ring might occur, or what was less probable 1,6-addition to the conjugated system extending to the 9-carbon atom of the anthracene nucleus, yielding a dihydroanthracene derivative. In fact neither of these reactions occurred, instead dimolecular 1,6-reduction took place yielding 10,10′-dibenzoyl-9,9′,10,10′-tetrahydro-9,9′-dianthranyl (XV), a compound already described by Cook and secured by reducing anthraphenone with zinc and acetic acid.[10]

In the case of dihydroanthraphenone (XVI) in which the meso-unsaturation is removed, all hindrance to 1,2-addition disappears and phenylmagnesium bromide gives the expected carbinol (XVII) in practically quantitative yield. The in-



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[8] Mulliken, "Identification of Pure Organic Compounds," 1st edition, 1904, Vol. I, p. 23.

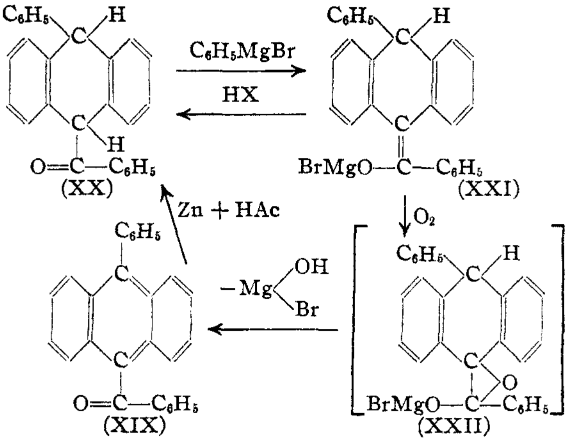
[9] Cook, *J. Chem. Soc.*, **129**, 1282, 1677, 2170 (1926).

[10] Cook, *ibid.*, 1680 (1926).

fluence of this meso-unsaturation upon the additive powers of the carbonyl group is in striking analogy to the difference in behavior, reported by Kohler, between phenylbenzaldesoxybenzoin and its saturated derivative, α,β,β-triphenylpropiophenone.[11] The structure of the carbinol (XVII) was proved by elimination of water to form the hydrocarbon (XVIII), the latter oxidized with chromic acid to one mole of anthraquinone and one mole of benzophenone.

Following up the analogy between these meso-unsaturated anthracene ketones and α,β-unsaturated ketones, we next investigated 9-phenylanthraphenone (XIX). Despite numerous attempts we have been unable to isolate any pure products from the reaction between this substance and phenylmagnesium bromide. Most of the material is recovered unchanged. A quantity of gum was always obtained and this is still under investigation. We are therefore not prepared to state with certainty that no reaction takes place in view of the difficulty often experienced in the isolation of pure products from Grignard reactions involving highly phenylated unsaturated compounds.

Here again the situation is quite different when the meso-unsaturation is removed by hydrogen. The dihydro derivative (XX) reacts readily with phenylmagnesium bromide in ether solution, but on working up in the usual manner the products consisted of unchanged material (XX) and phenylanthraphenone (XIX). The reaction was carefully checked, perfectly pure dihydro compound (XX) containing no phenylanthraphenone being employed. The results were consistent, (XX) and (XIX) representing the products. To explain this peculiar oxidation of (XX) during the course of the Grignard reaction, we again call attention to Kohler's experience with an analog of (XX), namely, α,β,β-triphenylpropiophenone.[12] The reactions are entirely analogous, especially in view of the fact that Cook[9,10] has called attention to the similarity in enolizing power between (XX) and diphenylacetophenone. This enolizing power of our compound (XX) constitutes the main difference between our substance (XX) and α,β,β-triphenylpropiophenone of Kohler, enabling the substance (XX) to form a magnesium derivative (XXI) directly on treatment with phenylmagnesium bromide.



It is understood in the abbreviated flow sheet that the oxide (XXII) has been formed from the action of a peroxide of (XXI) on (XXI) itself, something as Kohler has indicated for his highly phenylated ketones. We are at present engaged in attempts to isolate compounds of the type represented by (XXII), a feat involving difficulty because of the ease with which dihydroanthracene derivatives lose constituents across the ring, passing over into anthracene derivatives with the true aromatic structure.

Our present inadequate understanding of "steric" influences does not allow an explanation of the influence of unsaturation upon the additive power of a carbonyl group; such as is revealed in these results. Taken together with those recorded by Kohler and Nygaard[11] they show this influence to be a definitely indisputable factor in determining both extent and mode of reaction with the Grignard reagent.

The authors acknowledge gratefully a generous grant to one of them from the Rosenwald Fund, and likewise their indebtedness to their first teacher of Chemistry, Dean W. M. Blanchard, Head of the Department, whose untiring efforts have made possible this research program.

Experimental Part

Action of Methylmagnesium Iodide on Benzalanthrone.—The procedure described herewith is that found satisfactory for isolation of the maximum quantity of the carbinol (II). Fourteen grams of powdered benzalanthrone was added gradually to a Grignard reagent prepared from 3.6 g. of magnesium and 22 g. of methyl iodide in 700 cc. of ether. The ketone dissolved to yield a clear, green-yellow fluorescent solution. The solution was stirred cold for three hours, decomposed with ammonium chloride and oxygen passed into the washed ethereal solution; 0.3 gram of colorless, compact crystals separated and was filtered. They decomposed at 74° with separation

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(11) Kohler and Nygaard, THIS JOURNAL, **52**, 4129 (1930).

(12) Kohler and Mydans, *ibid.*, **54**, 4667 (1932).

of anthraquinone, and were insoluble in any solvents boiling lower than this temperature. Analysis of the crude material giving results which could not be interpreted, further investigation of this substance was postponed, pending our results with ethylidene anthrone. From the ethereal solution on concentration and addition of petroleum ether, 13 g. of crude carbinol (II) was obtained. Recrystallized from ether–petroleum ether, 12 g. of material melting at 148° was secured.

Anal. Calcd. for $C_{22}H_{18}O$: C, 88.59; H, 6.09. Found: C, 88.75; H, 6.25.

In the Grignard machine it gave 1 mole of gas and consumed one mole of reagent. On oxidation with chromic acid it gave anthraquinone and benzoic acid.

Behavior of Carbinol (II) toward Bromine.—To a well-cooled solution of 3 g. of carbinol (II) in 20 cc. of chloroform, a solution of 1.6 g. of bromine in 10 cc. of chloroform was added dropwise. The bromine was momentarily absorbed without evolution of hydrogen bromide. Allowed to stand in the cold for one hour, the solvent was removed under diminished pressure, ether added to the residue, which on stirring crystallized. Recrystallized from chloroform–ether, the substance (V) weighed 4 g. and melted at 168° with decomposition.

Anal. Calcd. for $C_{22}H_{16}Br_2$: C, 60.00; H, 3.64. Found: C, 59.57; H, 3.75.

Bromination of 1 g. of (V) in exactly the same manner with 0.5 g. of bromine yielded 0.6 g. of hard yellow crystals, m. p. 200° (VIII).

Anal. Calcd. for $C_{15}H_{10}Br_2$: C, 51.43; H, 2.86. Found: C, 51.11; H, 3.00.

A mixture of 2.5 g. of the dibromide (V), 2.5 g. of fused sodium acetate and 25 cc. of glacial acetic acid was refluxed for forty minutes. The warm acetic solution was filtered and 2 cc. of water was added (no turbidity). On cooling and scratching 1.6 g. of light yellow crystalline material separated, m. p. 188°, recrystallized from chloroform–methyl alcohol, which solutions displayed strong blue fluorescence. It gave no test for halogen.

Anal. Calcd. for $C_{26}H_{22}O_4$: C, 78.39; H, 5.60. Found: C, 77.90; H, 5.60.

Attempts to Prepare Ethylidene Anthrone

(a) Adapted from Procedure for Preparation of Methylene Anthrone.[13]—Twenty cc. of a 40% solution of acetaldehyde in water was added portionwise to a warm mixture of 10 g. of anthrone, 50 cc. of methyl alcohol and 5 drops of piperidine. After a small quantity of the acetaldehyde had been added the anthrone dissolved to yield a clear yellow solution. Obtaining no crystalline material on cooling the solution, 10 cc. of water was added, precipitating a yellow oil which solidified on standing. Attempts to recrystallize it gave only anthraquinone in large quantity.

(b) From Ethyl Oxanthrone.—The preparation of ethyl oxanthrone in workable quantities is best achieved as follows. To a stirred suspension of 140 g. of anthraquinone in 800 cc. of dry benzene, a Grignard reagent prepared from 13 g. of magnesium and 65 g. of ethyl bromide in 300 cc. of ether was added from a dropping funnel in the course of two and one-half hours. After addition was complete the mixture was stirred at room temperature for one hour, poured onto ice and hydrochloric acid and filtered through glass wool to remove anthraquinone. The filtrate was separated, and the washed and dried benzene layer was concentrated to about 200 cc. Petroleum ether was added and 65 g. of crude ethyl oxanthrone precipitated. Recrystallized from ether–petroleum ether it gave colorless prisms, m. p. 107°.

Attempt was first made to eliminate water by passing dry hydrogen chloride into a benzene solution of ethyl oxanthrone. On concentrating and adding petroleum ether, the tertiary chloride crystallized out, 1.6 g. out of 2 g. of the oxanthrone, m. p. 85°. On heating to about 120–130° this chloride lost hydrogen chloride and left behind a yellow oil which could not be crystallized and on standing deposited crystals of anthraquinone.

Two grams of ethyl oxanthrone was dissolved in 6 cc. of glacial acetic acid and 6 drops of sulfuric acid added. On standing for fifteen hours at room temperature, approximately 1 g. of anthraquinone was deposited, and on attempting to work up the mother liquors only more anthraquinone could be obtained.

Eight grams of ethyloxanthrone was dissolved in 15 cc. of glacial acetic acid, 1 cc. of concentrated sulfuric acid added, the flask filled with oxygen under pressure and carefully stoppered. After standing overnight, it was warmed gently and volatile material collected in a receiver cooled in a freezing mixture. Various tests already referred to were made on the distillate to demonstrate the presence of acetaldehyde, the most convincing one being its conversion into ethylidene-β-dinaphthyl oxide, m. p. 173°, which compound gave no depression with a sample prepared from an authentic specimen of acetaldehyde.

The formation of acetylene by distillation of ethylidene anthrone in the presence of atmospheric oxygen has been described in foregoing paragraphs. The acetylene was identified by its odor and by conversion into cuprous acetylide.

Action of Phenylmagnesium Bromide on Anthraphenone.—When the ketone was added to 4 moles of reagent in ether solution, allowed to stand overnight and worked up in the usual way, the solid material from 5 g. of ketone consisted of 1.1 g. of reduction product (XV) and 3.5 g. of unchanged anthraphenone. The latter was removed from the mixture by continued extraction with warm ether. The reduction product was recrystallized from benzene, m. p. 265°. With a specimen prepared by the method of Cook[9,10] it gave no depression. When benzene was substituted for the ether and the substance heated with the Grignard reagent in this solvent, the proportions of the products were unaltered. Phenylmagnesium iodide gave the same results. With methylmagnesium iodide, the original ketone was recovered quantitatively, no reaction taking place.

Action of Phenylmagnesium Bromide on Dihydroanthraphenone.—Five grams of the dihydro product (XVI) —prepared according to the method of Cook[10]—dissolved in ether was added to the Grignard reagent prepared from 1.4 g. of magnesium and 9.5 g. of bromobenzene in 200 cc. of ether. A noticeable warming of the reaction mixture accompanied the addition. Worked up in the usual way

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

the ethereal solution on concentration and addition of petroleum ether gave 4 g. of pure material (XVII), m. p. 173°, recrystallized from ether–petroleum ether or from methyl alcohol.

Anal. Calcd. for $C_{27}H_{22}O$: C, 89.50; H, 6.08. Found: C, 89.30; H, 6.19.

The product (XVII) examined in the Grignard machine gave one mole of gas and consumed one mole of reagent.

Elimination of Water from (XVII) to Give (XVIII).—Eight drops of concentrated sulfuric acid was added to a solution of 2 g. of carbinol (XVII) in 35 cc. of glacial acetic acid. On allowing to stand for three days 1.5 g. of material (XVIII) was deposited. Recrystallized from chloroform–methyl alcohol it gave colorless, glistening flakes, m. p. 258°.

Anal. Calcd. for $C_{27}H_{20}$: C, 94.13; H, 5.87. Found: C, 94.10; H, 5.79.

Half a gram of the hydrocarbon on oxidation with 0.5 g. of chromic acid in glacial acetic acid solution yielded 0.3 g. of anthraquinone and 0.2 g. of benzophenone.

Action of Phenylmagnesium Bromide on Dihydrophenylanthraphenone (XX).—Three and one-half grams of (XX) dissolved in ether was added to a Grignard solution from 0.72 g. of magnesium and 5.7 g. of bromobenzene. On first addition the solution was deep violet in color, gradually changing to red and on continued stirring to pale yellow. Worked up in the usual manner 2.0 g. of crystalline product was obtained, which was separated by fractional crystallization from ether into 1.2 g. of starting material and 0.7 g. of phenylanthraphenone.

Summary

1. Benzalanthrone gives mainly 1,2-addition with methylmagnesium iodide.

2. Ethylidene anthrone exists in an enolic modification involving a 1,7-shift of hydrogen, the anthranol suffering oxidation to a peroxide, which cleaves spontaneously to anthraquinone and vinyl alcohol.

3. Anthraphenone undergoes 1,6-dimolecular reduction on treatment with phenylmagnesium bromide or iodide, and no reaction with methylmagnesium iodide. Dihydroanthraphenone gives normal 1,2-addition.

4. No clean products could be isolated from the reaction between phenylanthraphenone and phenylmagnesium bromide. Dihydrophenylanthraphenone yielded with phenylmagnesium bromide phenylanthraphenone and unchanged material.

5. Striking analogies have been brought forward between meso-unsaturated anthracene ketones and α,β-unsaturated ketones. The analogies are likewise maintained when the unsaturation is removed in both types of ketones.

GREENCASTLE, INDIANA RECEIVED AUGUST 19, 1935

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY]

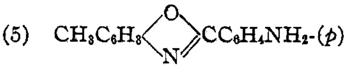
The Preparation and Tinctorial Properties of Certain Benzoxazole Dyes[1]

BY VLADIMIR J. MIKESKA AND MARSTON TAYLOR BOGERT

In a previous article,[2] we have pointed out certain of the similarities and dissimilarities which appear on comparing the chemical properties of the structurally related series of oxazoles, thiazoles and imidazoles.

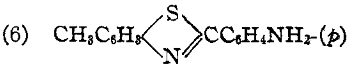
Having been interested for several years in the connection between chemical constitution and tinctorial properties in the thiazole series,[3] we have conducted some experiments also in the oxazole field and the present communication records the results. Our prior paper[2] described the syntheses of the necessary intermediates.

From the standpoint of the dye chemist, the thiazole derivatives of most interest are the intermediates dehydrothio-*p*-toluidine (II) and primuline (III), from which are manufactured dyes of the Thioflavine (IV) (Colour Index No. 815) or Chloramine Yellow (V) (Colour Index No. 814) types; or azo derivatives like the so-called "Ingrain colors" (Colour Index No. 812), prepared by diazotizing (II) or (III), or their sulfonates, and combining with suitable couplers.



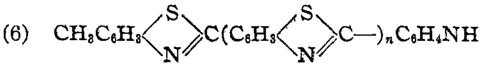
$$(5)\ \mathrm{CH_3C_6H_3}\langle{}^{\mathrm{O}}_{\mathrm{N}}\rangle\mathrm{CC_6H_4NH_2}\text{-}(p)$$

(I)



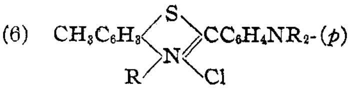
$$(6)\ \mathrm{CH_3C_6H_3}\langle{}^{\mathrm{S}}_{\mathrm{N}}\rangle\mathrm{CC_6H_4NH_2}\text{-}(p)$$

(II)



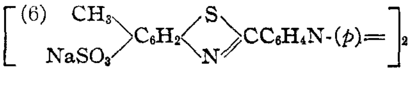
$$(6)\ \mathrm{CH_3C_6H_3}\langle{}^{\mathrm{S}}_{\mathrm{N}}\rangle\mathrm{C(C_6H_3}\langle{}^{\mathrm{S}}_{\mathrm{N}}\rangle\mathrm{C{-})_nC_6H_4NH_2}\text{-}(p)$$

(III)



$$(6)\ \mathrm{CH_3C_6H_3}\langle{}^{\mathrm{S}}_{\mathrm{N(R)Cl}}\rangle\mathrm{CC_6H_4NR_2}\text{-}(p)$$

(IV)



$$\left[(6)\ {}^{\mathrm{CH_3}}_{\mathrm{NaSO_3}}\rangle\mathrm{C_6H_2}\langle{}^{\mathrm{S}}_{\mathrm{N}}\rangle\mathrm{CC_6H_4N}\text{-}(p)=\right]_2$$

(V)

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[1] Based upon the dissertation submitted by V. J. Mikeska, June, 1934, for the Ph.D. degree under the Faculty of Pure Science, Columbia University, New York, N. Y., to which dissertation the reader is referred for further experimental details and literature citations.—M. T. B.

[2] Mikeska and Bogert, THIS JOURNAL, **57**, 2121 (1935).

[3] Bogert and Allen, *ibid.*, **49**, 1315 (1927).