diene[29] was obtained: 49% yield; b. p. 110.5–110.9°; d^{25}_4 0.7284; $n^{25.1}_D$ 1.4213; *MR* (found) 38.37; *MR* (calcd.) 38.21.

By substituting 4-bromo-2-pentene for allyl bromide in a similar reaction, a 38% yield of 4,5-dimethyl-2,6-octadiene[30] was obtained: b. p. 152.9–153.8°; d^{25}_4 0.7611; $n^{25.1}_D$ 1.4375; *MR* (found) 47.62; *MR* (calcd.) 47.45.

Dehydration of RCH(OH)CH=CHCH$_3$.[31]—The unsaturated alcohols of Table I were dehydrated by adding about one-half their weight of crystalline oxalic acid and slowly distilling them through a long column. The water layer was drawn off from the distillate, the remainder of which was returned to the flask, and the distillation repeated. The resulting hydrocarbon was dried and fractionated. Besides 1,3-pentadiene, b. p. 42.0–42.3°, and 2,4-heptadiene, b. p. 107.5–108.0°, which are already described in the literature,[32] we have prepared 2,4-octadiene[33] in 33% yield: b. p. 133.5–134.0°; d^{25}_4 0.7427; n^{25}_D 1.4542; *MR* (found) 40.19; *MR* (calcd.) 38.21; exaltation, 1.98.

2,2-Dimethyl-4-hexen-3-ol gave 2,2-dimethyl-3,4-hexadiene in 19% yield: b. p. 107.4–108.0°; d^{25}_4 0.7375; n^{25}_D 1.4425; *MR* (found) 39.55; *MR* (calcd.) 38.21; exaltation, 1.34.

Preparation of Alkynes—1-Hexadecyne was prepared in 65% yield, by Bourguel's alkyne synthesis,[34] from cetene dibromide and sodamide: b. p. 156–157° (15 mm.); m. p. 15°.[35] Boiling points of certain other alkynes which we prepared by Bourguel's methods,[34] formerly reported by him and by others, follow: 1-heptyne (from heptaldehyde), b. p. 100.4–100.8°; 2-heptyne (by-product from 3-heptyne), b. p. 111.5–113.0°; 3-heptyne (from 3-heptene), b. p. 105.3–106.7°; 1-octyne (from 2-octyne), b. p. 127.6–128.0°; 2-octyne (from 1-heptyne), b. p. 138.0–138.4°.

Summary

The preparation of alkenes from the Grignard reagent and unsaturated halides has been extended to the use of 4-bromo-2-pentene. A number of new hydrocarbons have been prepared, particularly 2-alkenes and 1,5-alkadienes.

CAMBRIDGE, MASS. RECEIVED NOVEMBER 7, 1934

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(29) Calcd.: C, 87.19; H, 12.81. Found: C, 87.09; H, 13.09.

(30) Calcd.: C, 86.87; H, 13.13. Found: C, 87.28; H, 13.10.

(31) 4-Heptanol, b. p. 154.5–156.0°, was similarly dehydrated to 3-heptene, b. p. 95.8–96.3°; 2,4-dimethyl-3-pentanol, b. p. 138.6–140.1°, to 2,4-dimethyl-2-pentene, b. p. 82.9–83.4°; and 5-nonanol, b. p. 195–197°, to 4-nonene, b. p. 147.5–148.1°. The alcohols were prepared in 60–80% yields from ethyl formate and the corresponding Grignard reagents.

(32) *Cf.*, for example, 1,3-pentadiene: b. p. 43°, von Auwers and Westermann, *Ber.*, **54**, 2993 (1921); b. p. 42°, Hofmann, *Ber.*, **14**, 665 (1881); b. p. 42.4–42.6° (766 mm.), Farmer and Warren, *J. Chem. Soc.* 3221 (1931); 2,4-heptadiene: b. p. 107°, von Auwers and Westermann, *loc. cit.*, etc.

(33) Calcd.: C, 87.19; H, 12.81. Found: C, 87.02; H, 12.67.

(34) Bourguel, *Ann. chim.*, [10] **3**, 191, 325 (1925).

(35) Krafft and Reuter, *Ber.*, **25**, 2245 (1892); m. p. 15°; b. p. 155° (15 mm.).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF DEPAUW UNIVERSITY]

Additions to Conjugated Systems in the Anthracene Series. II. The Behavior of Certain Anthranols

BY PERCY L. JULIAN AND WAYNE COLE[1]

Recently it was shown that methyleneanthrone (I) behaves toward phenylmagnesium bromide like a typical α,β-unsaturated ketone.[2] Since this appears to be the first authentic case on record of 1,6-addition of the Grignard reagent to a conjugated system of multiple linkages,[3] it appeared desirable to add more evidence for such an addition to that already adduced.

The structure of our addition product (II) was proved earlier by conversion with atmospheric oxygen into the peroxide (V) and the constitution of the latter by pyrolysis to anthraquinone and benzyl alcohol. This same peroxide has now been obtained in excellent yield by passing oxygen into the solution secured on catalytic reduction of benzalanthrone (III) in acetone. This proves conclusively the structure of our peroxide (V), especially since catalytic reduction of benzalanthrone in alcoholic solution was shown[2] to yield 10-benzylanthrone (IV), a substance different from the compound described in Beilstein,[4] but the structure of which has now been demonstrated by its conversion with phenylmagnesium bromide into 9-phenyl-10-benzylanthracene (VI), identical with the product secured by Barnett, Cook and Wiltshire[5] from phenylanthrone and benzylmagnesium chloride. Moreover, we have

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(1) Abstracted from the senior research of Wayne Cole at DePauw University, 1934–35.

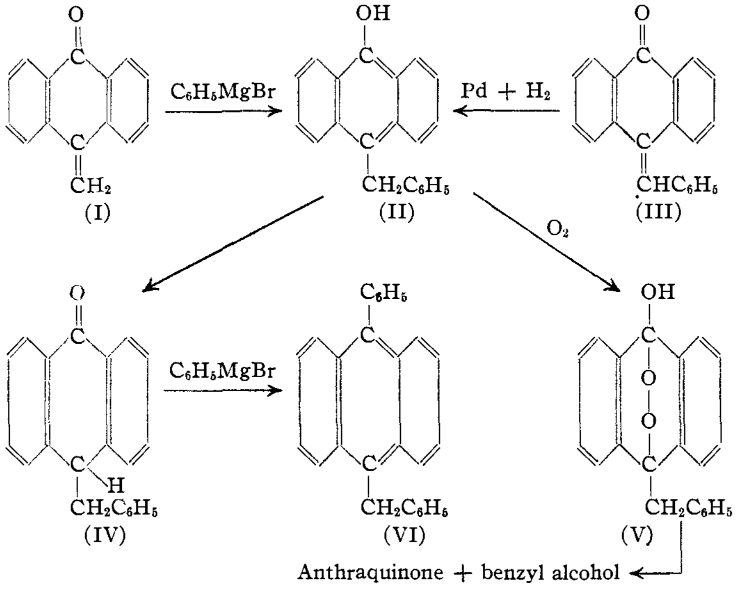
(2) Julian and Magnani, THIS JOURNAL, **56**, 2174 (1934).

(3) Three other cases of 1,6-addition have been reported. Nakanishi [*Proc. Imp. Acad. Tokyo*, **9**, 394–7 (1933)] claimed 1,6-addition of phenylmagnesium bromide to benzanthrone, which findings do not agree with those recently reported by Allen [THIS JOURNAL, **57**, 740 (1935)]. Likewise Nakanishi claims 1,6-addition of phenylmagnesium bromide to benzalanthrone, an observation which the facts recorded in this paper do not support. Baeyer and Villiger [*Ber.*, **36**, 2793 (1903)] report 1,6-addition of methylmagnesium iodide to fuchsone, but give no proof for the structure of their product. This matter is now under investigation in this Laboratory.

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

(5) Barnett, Cook and Wiltshire, *J. Chem. Soc.*, 1730 (1927).

now isolated 10-benzylanthrone from the reaction products secured on adding phenylmagnesium bromide to methyleneanthrone (I).



On pyrolytic decomposition of (V) a considerable portion of the benzyl alcohol is oxidized to benzaldehyde, and we considered isolation of the phenylhydrazone of the latter sufficient proof of our proposed mechanism for this pyrolysis.[2] Certain reactions observed in later work made it necessary to verify benzyl alcohol as a primary product of this reaction. Accordingly the benzaldehyde was removed with bisulfite, the benzyl alcohol obtained pure, and converted into the corresponding 3,5-dinitrobenzoate, a substance which is apparently described for the first time.

Methylmagnesium iodide and ethylmagnesium bromide likewise add 1,6 to methyleneanthrone, the resulting anthranols yielding crystalline peroxides with atmospheric oxygen, and these on pyrolysis furnish ethyl and propyl alcohol, respectively. Thus 1,6-addition of the Grignard reagent to methyleneanthrone is an established fact, and this mode of addition represents the main course of the reaction.

The loss of benzyl, ethyl and propyl alcohols from the peroxides on heating above their melting points is perfectly in harmony with existing knowledge of dihydroanthracene derivatives. Thus dihydroanthranols are known to lose the elements of water, hydrogen halides, alcohols, and addition products of aldehydes by elimination of substituents from the 9,10-positions of the dihydroanthracene nucleus.[6]

Recognition of this tendency toward 1,4-elimination in dihydroanthracene derivatives—representing the inclination of such substances with the dihydride grouping to pass over into anthracene derivatives with the true aromatic structure—as a general characteristic, helps to clarify certain perplexing transformations which these substances undergo. When, for example, benzalanthrone (III) is treated with phenylmagnesium bromide, a very sensitive dihydroanthranol (VII) is secured. Obtained in about 90% yield, it has been found to be the product represented by 1,2-addition of the Grignard reagent, the replacement of a hydrogen atom in methyleneanthrone by phenyl introducing sufficient hindrance to stop practically all 1,6-addition. The colorless product (VII) gives in the Grignard machine one mole of gas, its solutions do not fluoresce, and it suffers oxidation with chromic acid to phenyloxanthranol (IX). Treated with bromine at low temperatures, it absorbs one mole without the slightest evolution of hydrogen bromide, but on warming up to room temperature slowly loses hydrogen bromide and benzaldehyde, passing over into 9-phenyl-10-bromoanthracene (XII), probably by way of the intermediate (X). These reactions, together with its mode of preparation, should establish the structure as (VII).

Nakanishi[3] failed to secure this substance, recording anthrafuchsone as the product of this reaction. Bergmann likewise[7] did not obtain it, reporting anthraquinone (in large yield) as "the only isolable crystalline product of the reaction." Despite repeated efforts we cannot duplicate the results of these workers.

That this compound has escaped detection resides, we believe, in the general characteristic of dihydroanthracene derivatives to which we have referred, namely and more specifically, that 9,10-dihydroanthranols are sensitive substances tending to pass over into anthracene derivatives, either by 1,4-elimination of substituents (from the

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[6] Barnett, *et al.*, *J. Chem. Soc.*, 1730 (1927); *ibid.*, 566 (1928); *Ber.*, **62**, 429 (1929); Cook, *J. Chem. Soc.*, 2803 (1928); Bergmann and Fujise, *Ann.*, **480**, 191 (1930).

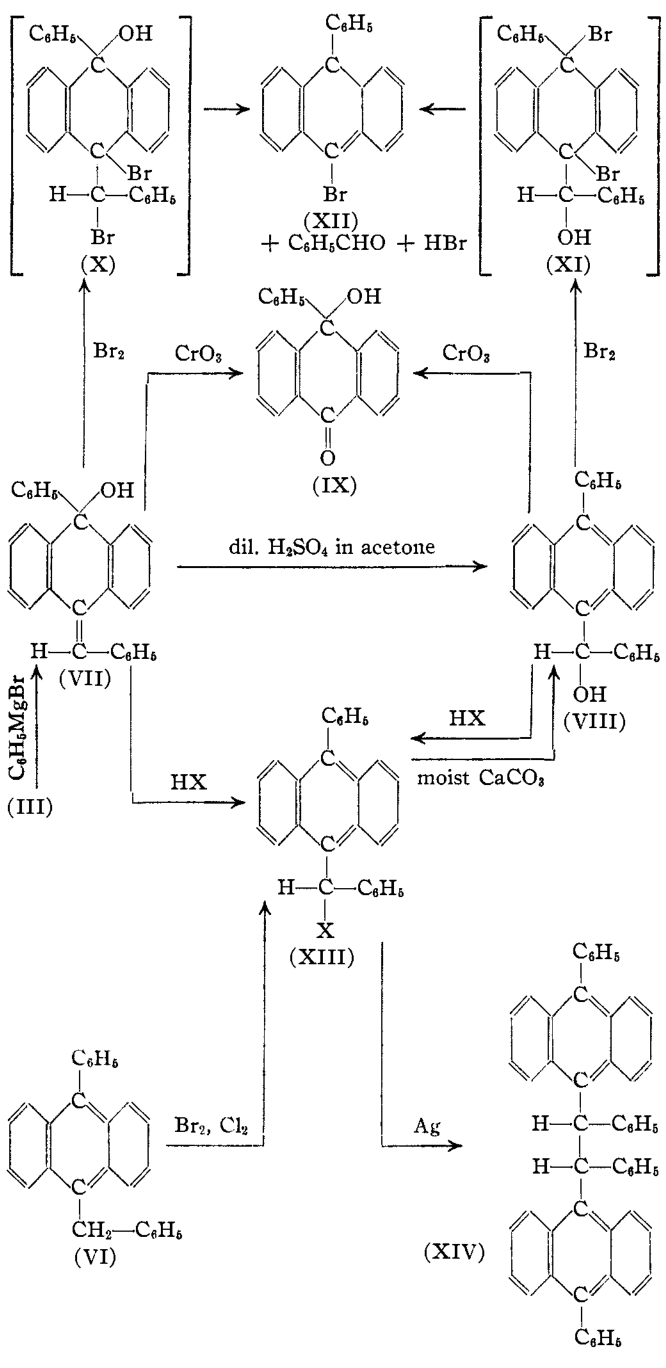
[7] Bergmann, *Ber.*, **63**, 1041 (1930).

9,10-anthracene positions) or, if this be impossible, by rearrangement.[8] Thus our product (VII) might be expected *a priori* to exhibit a five carbon atom isomerism, similar to the well-known three carbon atom isomerism in allyl derivatives, and on least provocation pass over or attempt to pass over into the carbinol (VIII). This is actually the case, and such behavior has been clearly forecasted for this substance in a series of memoirs by Barnett, Cook and their collaborators.[9] Thus mere warming with mineral acids, a procedure suggested by these authors, is sufficient to convert (VII) almost quantitatively into (VIII), and steam distillation of the products of the Grignard reaction often leaves no trace of the dihydroanthranol (VII).[10]

The importance of (VII) for this new isomerism is that it represents the one missing link in the proof. For, despite their numerous researches in elucidation of an isomerism such as is represented by VII ⟶ VIII, Barnett and Cook have not been able to obtain by synthetic means compounds which undoubtedly have the structure represented by (VII).[11] Absence of such proof of the dihydroanthranol structure for their "colorless and non-fluorescent" derivatives led Barnett to propose an endocyclic structure for these instead of the structure represented by (VII).[12]

The dihydroanthranol (VII) is the only derivative we could obtain having that structure, for replacement of its hydroxyl by various groups leads to derivatives of the carbinol (VIII). Even attempts to replace hydroxyl by hydrogen with zinc and acetic acid led to an acetoxy compound corresponding to the structure (XIII).

Proof of the structure of our carbinol (VIII) is to be found in the observations that it is highly fluorescent in contrast to (VII), and is obtained with moist calcium carbonate in acetone from the ω-bromo derivative (XIII), secured on brominating 9-phenyl-10-benzylanthracene (VI). Since no evidence could be obtained for an addition compound between bromine and (VI), the bromo compound can have only the structure (XIII).



There is some evidence for an equilibrium (VII) $\rightleftarrows$ (VIII) in solution. The carbinol (VIII) is a

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(8) It is, of course, conceivable that certain steric influences may contribute to the stability of the dihydro in preference to the simple anthracene structure. *Cf.* Cook, *J. Chem. Soc.*, 2804 (1928).

(9) Barnett, *et al.*, *Ber.*, **59**, 2864 (1926); **60**, 2353 (1927); **62**, 423, 1969, 3063, 3072 (1929); **64**, 49, 1573 (1931); Cook, *ibid.*, **60**, 2366 (1927); *J. Chem. Soc.*, 2798 (1928).

(10) Results of preliminary experiments in the laboratory of Dr. C. F. H. Allen of McGill University (private communication to senior author).

(11) Cook, *Ber.*, **60**, 2369 (1927); *J. Chem. Soc.*, 2801 (1928).

(12) Barnett, *Ber.*, **62**, 423 (1929). Reference there to earlier papers.

secondary alcohol and might be expected to yield phenylbenzoylanthracene on oxidation. Instead it oxidizes smoothly to phenyloxanthrone (IX). This is best explained by assuming an equilibrium between (VII) and (VIII), the former being more easily removed by oxidation from the equilibrium mixture. Moreover, the action of bromine on the carbinol (VIII) is identical with that already described for the dihydroanthranol (VII). We are loathe to accept the intermediate addition compound as (XI) after results with 9-phenyl-10-benzylanthracene show absolutely no 1,4-addition of bromine. An equilibrium in solution would make (X) the intermediate in each case.

The bromo and chloro derivatives react readily with molecular silver, giving an ethane which is believed to have the structure (XIV).

The addition of methylmagnesium iodide to benzalanthrone is by no means so simple a picture, and report of this work will have to be communicated later.

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. Grateful acknowledgment is also made to the Rosenwald Fund for a grant assisting in these and other investigations.

Experimental Part

10-Benzylanthranol Peroxide (V) and its Pyrolysis.—Ten grams of benzalanthrone[2] in 140 cc. of alcohol-free acetone was hydrogenated with a palladium catalyst, the solution filtered and saturated with oxygen; 7.2 g. of peroxide (V), m. p. 143–144°, was obtained. The melting point (133–134°) recorded in the earlier paper is a typographical error.

Fifteen grams of peroxide was decomposed as already described and the residue taken up in ether. The anthraquinone was filtered off, the ethereal solution shaken for some time with bisulfite, separated and distilled. In vacuum about 3 g. (approximately 60% yield) of benzyl alcohol distilled. It was converted in the usual way into benzyl 3,5-dinitrobenzoate, m. p. 114°, recrystallized from ether. A mixed melting point with a sample prepared from an authentic specimen of benzyl alcohol showed no depression.

Anal. Calcd. for $C_{14}H_{10}O_6N_2$: C, 55.63; H, 3.31. Found: C, 55.93; H, 3.65.

9-Phenyl-10-benzylanthracene (VI) from 10-Benzylanthrone (IV).—28.2 grams (0.1 mole) of 10-benzylanthrone (IV)[2] was treated in the usual way with phenylmagnesium bromide from 45 g. of bromobenzene and 7.2 g. of magnesium. The oil secured on working up would not crystallize, and was taken up in 200 cc. of glacial acetic acid. The solution, after boiling for one hour, deposited on cooling 27 g. of fairly pure 9-phenyl-10-benzylanthracene; recrystallized from acetic acid, m. p. 154°.

10-Benzylanthrone (IV) from Methyleneanthrone and Phenylmagnesium Bromide.—Ten grams of methyleneanthrone was treated with phenylmagnesium bromide from 16 g. of bromobenzene and 2.4 g. of magnesium. Alcohol was added to the ether solution on working up to prevent peroxide formation,[13] and after removal of ether the whole residue was taken up in alcohol and set aside for twenty-four hours in a flask filled with carbon dioxide. About 2 g. of anthraquinone separated and was filtered off. Recrystallization of the residue, on removal of alcohol, from ether yielded 1.5 g. of material, m. p. 221–222°. Some of this material is always secured in this reaction. It has not yet been investigated. The mother liquors were distilled in a vacuum. At 205–225° (0.5 mm.) about 3 g. of 10-benzylanthrone came over. Recrystallized from ether–petroleum ether it melted at 92° and was identical with the product obtained on catalytically reducing benzalanthrone.[2] Considerable material which would not distil was left behind.

10-Ethylanthranol Peroxide.—Obtained from methyleneanthrone and methylmagnesium iodide in the same way as was 10-benzylanthranol peroxide, it melted at 164°, recrystallized from ether–petroleum ether.

Anal. Calcd. for $C_{16}H_{14}O_3$: C, 75.59; H, 5.51. Found: C, 75.13; H, 5.45.

The combustion and pyrolysis to yield ethyl alcohol were difficult to carry out because of the loss of alcohol at such high temperature. Nevertheless, under good reflux, nearly all of the alcohol was obtained on pyrolysis and identified by conversion into ethyl 3,5-dinitrobenzoate, m. p. 93°.

10-Propylanthranol Peroxide.—From methyleneanthrone and ethylmagnesium bromide, it melted at 122°, recrystallized from ether–petroleum ether.

Anal. Calcd. for $C_{17}H_{16}O_3$: C, 76.12; H, 5.97. Found: C, 75.90; H, 5.94.

On pyrolysis it yielded propyl alcohol identified by means of the 3,5-dinitrobenzoic ester, m. p. 73°.

9-Phenyl-10-benzylidene-9,10-dihydroanthranol-9 (VII)

Bromination.—The dihydroanthranol (VII), m. p. 147°, described in the earlier paper[2] was brominated in the usual way in chloroform. The product, recrystallized from chloroform and methyl alcohol, melted at 155° and was identical with 9-phenyl-10-bromoanthracene (XII) prepared by brominating 9-phenylanthracene.[14] Benzaldehyde was also isolated and identified as phenylhydrazone.

Oxidation.—With chromic acid in glacial acetic acid at 100°, 1.6 g. of pure phenyloxanthrone, m. p. 215°, was obtained from 3.5 g. of anthranol (VII) and identified by mixed melting point with a sample synthesized from anthraquinone and phenylmagnesium bromide.

Acetylation.—The dihydroanthranol (VII) is very easily acetylated, boiling with acetic acid or with acetic anhydride for two to three hours sufficing to convert it almost completely into 10-ω-acetoxybenzyl-9-phenylanthracene

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

[14] Cook, *J. Chem. Soc.*, 2168 (1926).

(XIII). Almost colorless, yielding solutions with marked blue fluorescence, it melts on recrystallization from acetone and methyl alcohol at 160°.

Anal. Calcd. for $C_{29}H_{22}O_2$: C, 86.52; H, 5.52. Found: C, 86.57; H, 5.68.

Reaction with Hydrogen Halides.—Treatment of (VII) in ether solution with dry hydrogen chloride and hydrogen bromide yields the ω-chloro and bromo derivatives (XIII). Treatment with thionyl chloride in the cold yields the same chloride, m. p. 189°, as yellow needles, highly fluorescent.

Anal. Calcd. for $C_{27}H_{19}Cl$: C, 85.55; H, 5.07. Found: C, 85.35; H, 5.06.

The bromide, m. p. 188°, was obtained as described above, and also by brominating 9-phenyl-10-benzylanthracene in carbon disulfide solution. No bromine was absorbed in the cold in the latter reaction and when reaction began on warming slightly, hydrogen bromide evolution immediately took place. It was recrystallized from carbon disulfide and ether.

Anal. Calcd. for $C_{27}H_{19}Br$: C, 76.56; H, 4.54. Found: C, 76.14; H, 4.81.

9-Phenyl-10-ω-oxybenzylanthracene (VIII).—A solution of 7 g. of the dihydroanthranol (VII) in 40 cc. of acetone and 5 cc. of 10% sulfuric acid was warmed on the water-bath until insoluble and high melting material began to separate (one hour). The solution was then filtered, poured into water and extracted with ether. The residue from evaporation of the washed and dried ether solution was recrystallized, first from alcohol, then from acetone and petroleum ether, m. p. 187°; yield 6.2 g., highly fluorescent in solution.

Anal. Calcd. for $C_{27}H_{20}O$: C, 89.96; H, 5.60. Found: C, 89.65; H, 5.68.

This compound seems to crystallize both with alcohol and acetone of crystallization, the solvent being lost between 70 and 80°. Recrystallization from acetone first, then from hot ethyl alcohol, or *vice versa*, seems to give a solvent-free product. No fluorescence of the original carbinol (VII) in solution could be detected, but on addition of acid and slightest warming, a marked blue fluorescence was noticeable.

On bromination, oxidation, acetylation, and treatment with dry hydrogen halides, this substance behaves exactly like the dihydroanthranol (VII) and yields identically the same products as have already been described.

Molecular Silver on Bromo Compound (XIII).—The bromide (XIII), warmed for a short time in benzene solution with molecular silver, is converted into a yellow, highly fluorescent substance, m. p. 252–253°, recrystallized from benzene–petroleum ether.

Anal. Calcd. for $C_{54}H_{38}$: C, 94.46; H, 5.54; mol. wt. 686. Found: C, 94.06; H, 5.53; mol. wt. (Rast, camphor), 524.

Summary

1. The Grignard reagent adds 1,6- to methyleneanthrone.

2. 10-Alkylanthranols readily yield crystalline peroxides with atmospheric oxygen and these peroxides suffer smooth pyrolysis to anthraquinone and alcohols formed by 1,4-elimination.

3. 10-Alkyl-9,10-dihydroanthranols are readily converted into anthracene derivatives, either by 1,4-elimination of substituents or by migration of groups.

4. A five-carbon atom isomerism in anthracene derivatives similar to the three-carbon atom isomerism in allyl compounds is conclusively demonstrated in the case of 9-phenyl-10-benzylidene-9,10-dihydroanthranol-9.

GREENCASTLE, INDIANA RECEIVED JUNE 17, 1935

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

A Comparison of Heterocyclic Systems with Benzene.[1] IV. Thionaphthenequinones

BY LOUIS F. FIESER AND R. GRICE KENNELLY

This series of investigations was undertaken with the idea that a comparison of the lowering in the reduction potential of a quinone resulting from the fusing of an unsaturated heterocyclic ring to the quinonoid ethylene linkage, with the lowering in potential produced by a benzene ring in the corresponding position, might afford a means of determining the degree of aromaticity of the heterocycle with respect to benzene. Fieser and Ames[1b] studied two quinones containing the thiophene nucleus, but each of these was of a rather special structural type. The purpose of the present work was to prepare and characterize simple ortho and para quinones derived from thionaphthene with the quinone grouping located in the carbocyclic ring.

The problem was largely a preparative one, for few quinones of the desired type have been described previously, and hydroxythionaphthenes suitable for use as starting materials are either unknown or rather inaccessible. The only route to the hydroxy compounds is by synthesis, since

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(1) Previous papers: (a) Fieser, THIS JOURNAL, **48**, 1097 (1926); (b) Fieser and Ames, *ibid.*, **49**, 2604 (1927); (c) Fieser and Peters, *ibid.*, **53**, 4080 (1931).