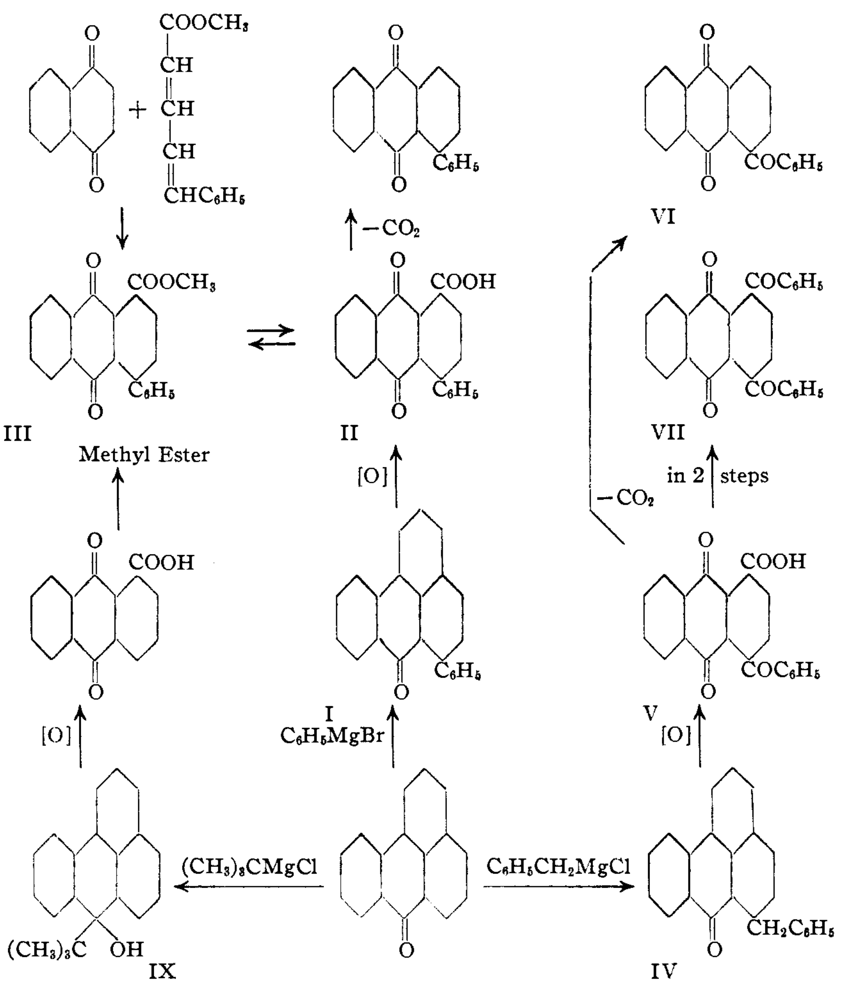
[Contribution from the Chemical Laboratory of McGill University]

# The Use of the Grignard Reagent for Locating Certain Double Bonds in Polynuclear Ring Systems. I. Benzanthrone

By C. F. H. Allen and S. C. Overbaugh

4-Phenylbenzanthrone (I) is obtained when benzanthrone is allowed to react with phenylmagnesium bromide. The structure of this substance was determined by degradation and synthesis. The ketone was oxidized by permanganate to a phenylanthraquinone-α-carboxylic acid (II), which on decarboxylation gave α-phenylanthraquinone; therefore the phenyl group was on one of the carbon atoms in the alpha position of the anthracene residue of benzanthrone. Upon esterification, the acid gave a methyl ester (III) which proved to be identical with the product obtained by the diene synthesis from α-naphthoquinone and cinnamylidene acetic ester; therefore, the phenyl group must be on the 4-carbon atom, and the ketone is 4-phenylbenzanthrone (I).



4-Benzylbenzanthrone (IV) was obtained by a similar procedure when benzylmagnesium chloride was used. Upon oxidation it gave 4-benzoylanthraquinone-1-carboxylic acid (V), which on decarboxylation formed α-benzoylanthraquinone (VI), identical with an authentic specimen; the acid was also converted by the Friedel–Crafts reaction into 1,4-dibenzoylanthraquinone (VII), the properties of which agreed with those described for that substance in the literature.[1] The results are summarized in the flow-sheet.

Ketones were also formed when *n*-heptylmagnesium bromide and cyclohexylmagnesium chloride were used, but *t*-butylmagnesium chloride gave an alcohol. The nature of the products was easily shown by the results obtained in the Grignard machine,[2] the ketones adding one mole of reagent but evolving no gas, whereas the alcohol did just the opposite.

The addition of the Grignard reagent to conjugated systems involving an aromatic ring has been described previously by Gilman[3] and Kohler.[4] The product is always a benzene derivative; there have been no indications of any partially reduced (dihydro) intermediate products. Similarly, in the benzanthrone series the ketones obtained seem to have an aromatic structure. It is probable that the dihy-

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[1] Scholl and K. Meyer, *Ann.*, **512**, 119 (1934).

[2] Kohler and Richtmyer, This Journal, **52**, 3736 (1930).

[3] Gilman, *ibid.*, **51**, 2252 (1929).

[4] Kohler and Nygaard, *ibid.*, **52**, 4128 (1930).

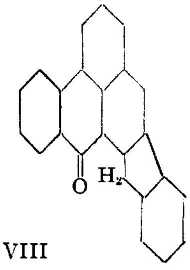
dro ketones, which would be expected to be formed first, undergo simultaneous oxidation and reduction, since (1) the yield is seldom over 50%, and (2) there is a large amount of untractable tarry material which may well contain some reduction product, for treatment with quinone brings about a vigorous reaction and yields a further amount of the substituted benzanthrone. The simultaneous formation of a 1,2-addition product is not excluded, since it may be a component of the tar; with *t*-butylmagnesium chloride, the reaction proceeded much more slowly and gave 20% yields of carbinol. The isolation of the carbinol may have been possible in this case on account of its more favorable physical properties.

Although these new ketones showed one addition in the Grignard machine, all efforts to isolate a pure substance from the untractable oils obtained by the use of a variety of Grignard reagents were unsuccessful; thus it cannot be demonstrated whether 1,2 or 1,4-addition has occurred.

Four phenylbenzanthrones have been described in the literature. Scholl[5] secured the 7-phenyl homolog by ring closure of xenyl $\alpha$-naphthyl ketone. The Bz-1,2- and 3-derivatives are mentioned in numerous patents.[6] Clar[7] and Nakanishi[8] both claimed to have prepared the Bz-3-phenyl homolog by the action of phenylmagnesium bromide on benzanthrone; they placed the phenyl group in the Bz ring because on oxidation they obtained anthraquinone-$\alpha$-carboxylic acid. This was represented as a case of 1,6-addition. Neither gave any further data. They overlooked the fact that the three possible Bz-phenyl derivatives were known and different from their substance. Charrier and Ghigi,[9] on repeating the work and oxidizing the product, obtained an acid, which showed a similar behavior on heating, but an analysis of the sodium salt did not give the expected result; instead, the percentage of sodium found corresponded to a larger molecule, for which they wrote a structure and concluded that Clar had been mistaken in his identification. All these investigators used chromic acid in the oxidation.

In the writers' work, the use of permanganate gave the phenyl acid (II), the structure of which was determined as previously outlined. On comparison of the acid (II), anthraquinone-$\alpha$-carboxylic acid, and the acid obtained by chromic acid oxidation, it was noted that all melted with decomposition over practically the same range; therefore, methyl esters, having sharp melting points, were prepared. Each acid gave a different ester, showing their non-identity, and all admixtures gave depressions of the melting point. Charrier and Ghigi suggested a possible structure for the acid obtained by chromic acid oxidation; the authors of this paper have not concerned themselves with this substance other than to check its properties.

Since the oxidation product is not anthraquinone $\alpha$-carboxylic acid, the apparent discrepancies are cleared up, and the assumed 1,6-addition of the Grignard reagent to benzanthrone is disproved. Clar also claimed to have established an instance of 1,6-addition of benzylmagnesium chloride in which 2-benzylbenzanthrone was produced. The structure of the latter was assumed, since on heating with platinized charcoal it gave a polynuclear ketone, presumably identical with one obtained by Dziewoński and Moszew[10] in an independent manner. However, as shown above, the substance is actually 4-benzylbenzanthrone, so Clar's polynuclear hydrocarbon cannot have the structure assigned unless there has been a molecular rearrangement. It is probably 3,4 (3,2)-indenobenzanthrone (VIII).



VIII

Charrier and Ghigi[9] found that methylmagnesium iodide gave both 1,2- and 1,4-addition with benzanthrone, and proved conclusively the structure of the 4-methylbenzanthrone. They obtained only a ketone with ethylmagnesium bromide. Nakanishi, assuming 1,6-addition as mentioned above, secured a ketone with *n*-butylmagnesium bromide.

Thus there are three instances[11] in which the

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(5) Scholl and Seer, *Ann.*, **394**, 150 (1912).

(6) Bz-1-$C_6H_5$: English Patent 268,830; *Chem. Abs.*, **22**, 1366 (1928); English Patent 297,129; *Chem. Abs.*, **23**, 2579 (1929); Swiss Patent 127,033; *Chem. Zentr.*, **100**, I, 146 (1929); Swiss Patent 133,994; *Chem. Zentr.*, **101**, I, 1373 (1930); U. S. Patent 1,713,590; *Chem. Zentr.*, **100**, II. 1073 (1929); U. S. Patent 1,713,571; *Chem. Abs.*, **23**, 3479 (1929); U. S. Patent 1,736,061; *Chem. Abs.*, **24**, 628 (1930); German Patent 488,607; *Chem. Abs.*, **24**, 2148 (1930); German Patent 488,608; *Chem. Zentr.*, **101**, II, 3860 (1930). Bz-2-$C_6H_5$: U. S. Patent 1,713,591; *Chem. Zentr.*, **100**, II, 1074 (1929); also English Patent 297,129 above. Bz-3-$C_6H_5$: German Patent 552,269; *Chem. Zentr.*, **103**, II, 2736 (1932).

(7) Clar, *Ber.*, **65B**, 846 (1932).

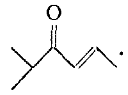
(8) Nakanishi, *Proc. Imp. Acad.* (*Tokyo*), **9**, 394 (1933).

(9) Charrier and Ghigi. *Gazz. chim. ital.*, **62**, 928 (1932).

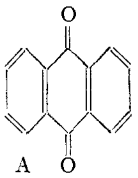
(10) Dziewoński and Moszew, *Roczniki Chem.*, **11**, 169 (1931); *Chem. Abs.*, **26**, 131 (1932).

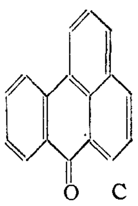
(11) In a subsequent paper, the authors will describe five more examples of authentic 1,4-addition of the Grignard reagent to a homolog of benzanthrone.

structures of the ketones obtained by the action of the Grignard reagent on benzanthrone have been determined; in every case, the entering group is on position 4 (*i. e.*, 1,4-addition). By analogy, in the other reactions in which a ketone was found, the product is probably a 4-substituted benzanthrone. 1,2-Addition to give a carbinol is also a possibility, but there is no evidence of the formation of any substance requiring the assumption of 1,6-addition.

The striking feature of the results described in this paper is the occurrence of 1,4-addition. The special feature required for 1,4-addition is the bond structure . The products may come from only one component of a tautomeric mixture, but this must be present to the extent of at least 60% (heptyl). The contrast with other compounds such as anthrones, anthraquinone and fluorenone is quite significant in demonstrating a real difference in the bond structures.[12]

Simple anthrones[13] and anthraquinones[13] have been treated with diversified Grignard reagents in numerous instances, but in every case only carbinols (1,2-addition products) have been obtained. This would indicate that, at least in ether solution, anthraquinone must have the bond structure (A), otherwise 1,4-addition would have been possible and probably detected. This is in agreement with the conclusion reached by Anderson[14] from a study of the ultraviolet absorption spectra.


A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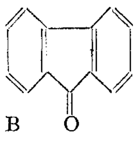
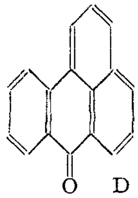
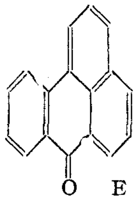

B

There are three bond arrangements possible in fluorenone; since it gives only alcohols (1,2-addition) with various Grignard reagents[15] structure B is indicated. This, however, is a dibenzocyclopentadienone and would be expected to add maleic anhydride.[16] The structure cannot be excluded for the reasons mentioned above, even though the authors have been unable to bring about the addition, for the diene synthesis is only of diagnostic value when positive.

In a lengthy paper dealing with the "finer structure" of polynuclear compounds, Clar[7] concludes, from a study of absorption spectra and non-addition of maleic anhydride, that benzanthrone must have one of the systems of linkages shown in formula C or D. The formation of the 4-substituted benzanthrones by the action of the Grignard reagent, as described above, would be impossible with structure D and therefore favors C. However, non-addition of maleic anhydride to benzanthrone does not necessarily rule out structure E, which contains the normal naphthalene nucleus, for the reason mentioned above.


D


E

Investigations, dealing with the action of Grignard reagents on other polynuclear ketones, are in progress.

## Experimental

**A. Products Resulting from the Action of the Grignard Reagent.**—In the reaction between benzanthrone and the various Grignard reagents, three times the calculated amount of the latter was used; the actual procedure may be illustrated by a typical run. Twenty grams of powdered benzanthrone[17] was added to phenylmagnesium bromide, prepared in the usual manner (from 6 g. of magnesium, 39 g. of bromobenzene, and 125 cc. of ether) and the mixture refluxed for an hour. The ether was then replaced by benzene and after an additional hour of refluxing, the complex was decomposed by the gradual addition of 100 cc. of 30% acetic acid. The mixture was steam distilled, the aqueous solution decanted, and the residual tar, that usually hardened, dried in the air and extracted with suitable solvents. Ether or acetone proved the most useful; the ketone usually remained largely undissolved, and was filtered. Since the crude ketone, though sparingly soluble in the reagent, dissolved readily when impurities were present, the total yield was only obtained by several re-workings of the filtrate. The addition of 1–2 g. of quinone to the tars in solution was distinctly beneficial; a great deal of heat was generated, and more ketone separated in a short time. In the case of the *n*-heptyl compound, no solid could be separated until

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[12] Coffman and Carothers, This Journal, **55**, 2043 (1933).

[13] Barnett, "Anthracene and Anthraquinone," Baillière, Tindall and Cox, London, 1921, pp. 85–90.

[14] Anderson, This Journal, **55**, 2094 (1933).

[15] Everest, "The Higher Coal Tar Hydrocarbons," Longmans, Green and Co., Ltd., London, 1927, Chap. 2.

[16] Allen and Sheps, *Can. J. Res.*, **11**, 171 (1934).

[17] "Organic Syntheses," Vol. XIV, p. 4. The 1060 cc. of sulfuric acid specified should read 1060 g. Some technical benzanthrone was also supplied by the National Aniline and Chemical Co., whose kindness is gratefully acknowledged. It was further purified as directed in "Organic Syntheses."

quinone had been added. The results are summarized in Tables I and II.

TABLE I

DATA ON PRODUCTS FROM ACTION OF GRIGNARD REAGENT

| No. | RMgX | Yield, % | Solvent for purification | M. p., °C. | Crystal form |
|---|---|---|---|---|---|
| I | Phenyl | 42 | Acetic acid | 186 | Prisms |
| IV | Benzyl | 22 | Acetic acid | 135 | Needles |
| X | *n*-Heptyl | 61 | Alcohol | 77–78 | Needles |
| XI | Cyclohexyl | 15 | Alcohol | 138 | Needles |
| IX | *t*-Butyl | 20 | Alcohol | 140 | Square plates |

The heptyl and cyclohexyl ketones gave orange solutions with concentrated sulfuric acid, but the other substances gave deep red colors.

In the runs with cyclohexylmagnesium chloride, an unstable product (m. p. 240° dec.) was often isolated, but on attempted recrystallization the ketone (XI) always resulted.

Since benzene and anhydrous aluminum chloride often give the same product as phenylmagnesium bromide with $\alpha,\beta$-unsaturated ketones, these reagents were applied to benzanthrone. Other than the formation of a halochromic salt, from which the ketone was recovered unchanged, there was no action, even at the boiling point of benzene for several hours.

TABLE II

ANALYTICAL DATA

| No. | Formula | Calcd., % | | Found, % | | Quantitative $CH_3MgI$ Addition |
|---|---|---|---|---|---|---|
| | | C | H | C | H | |
| I | $C_{23}H_{14}O$ | 90.2 | 4.6 | 90.4 | 5.0 | 1.0 |
| IV | $C_{24}H_{16}O$ | 90.0 | 5.0 | 90.2 | 4.8 | 0.9 |
| X | $C_{24}H_{24}O$ | 87.8 | 7.3 | 87.4<br>87.8 | 7.0<br>7.7 | 1.0 |
| XI | $C_{23}H_{20}O$ | 88.4 | 6.4 | 88.1 | 6.3 | 1.1 |
| IX | $C_{21}H_{20}O$ | 87.5 | 6.9 | 87.8 | 7.2 | 1.0 (active H) |

The further action of various Grignard reagents on the ketones gave orange solutions, that left varnishes on attempted recrystallization, and turned black when exposed to the air.

### B. Determination of Structures

(1) **4-Phenylbenzanthrone.**—(a) Oxidation by permanganate to 4-phenylanthraquinone-1-carboxylic acid (II). A mixture of 6 g. of potassium permanganate, 3 g. of sodium hydroxide, 3 g. of 4-phenylbenzanthrone, and 500 cc. of water was refluxed with stirring for twenty hours. After filtering, acidification of the colorless filtrate precipitated 0.1 g. of acid, m. p. 288–290° with dec.; 2.1 g. of the unoxidized ketone was recovered unchanged from the manganese dioxide. The acid (II) was converted into a bright yellow silver salt in the usual manner, and the latter refluxed on the steam-bath for five hours with 4 cc. of methyl iodide. The silver iodide was filtered, the filtrate evaporated to dryness, and the residue recrystallized from dilute acetone. Rosets of bright yellow needles separated identical with the synthetic ester; a mixed melting point showed no depression.

**Synthesis of the Methyl Ester, III.**—A mixture of 2.3 g. of methyl cinnamylideneacetate[18] and 2.1 g. of $\alpha$-naphthoquinone was heated in an oil-bath at 180–190° for twenty minutes. The dark, viscous mass was removed by hot acetone, and the crystals that separated on cooling filtered and washed with methanol. On recrystallization from acetone, 0.6 g. of rosets of yellow needles separated, m. p. 197–198°.

*Anal.* Calcd. for $C_{22}H_{14}O_4$: C, 77.2; H, 4.1. Found: C, 77.0; H, 4.2.

On further standing, 0.3 g. of a second ester was deposited, mixed with ester (III); it crystallized in bronzy plates from acetic acid, m. p. 164–165°. The analysis indicated it was the tetrahydro ester, the primary addition product.

*Anal.* Calcd. for $C_{22}H_{18}O_4$: C, 76.3; H, 5.1. Found: C, 76.4; H, 5.2.

The ester (III) was readily hydrolyzed by boiling for fifteen minutes with a 1% solution of sodium hydroxide in 50% methanol; on acidifying, the acid obtained was collected; m. p. 288–290° with dec. It gave a red solution with alkaline sodium hydrosulfite, which was decolorized on shaking in the air. On account of its extremely slight solubility it was analyzed without recrystallization.

*Anal.* Calcd. for $C_{21}H_{12}O_4$: C, 76.8; H, 3.6. Found: C, 76.6; H, 4.0.

For decarboxylation, 0.3 g. of the acid was heated with 2 cc. of quinoline and a trace of copper powder at 140–160° for fifteen minutes, when gas evolution ceased. The mixture was extracted with dilute hydrochloric acid and filtered; the solid was washed with sodium hydroxide solution, filtered, and the residue recrystallized from acetic acid. The $\alpha$-phenylanthraquinone formed sheaves of yellow needles, m. p. 176–178°, and gave a red vat, as recorded in the literature.[19]

(b) **Chromic Acid Oxidation.**—A suspension of 25 g. of chromic acid in 50 cc. of hot acetic acid was added during three-quarters of an hour to 5 g. of 4-phenylbenzanthrone in 50 cc. of acetic acid, the last portion of solid being rinsed in with 10–5 cc. of water. After three hours of refluxing, four volumes of water were added; on cooling, the solid that had separated was filtered, and a further amount obtained from the filtrate by adding 37 g. of concentrated sulfuric acid, evaporating to a sirup, and diluting. The combined solid was warmed with dilute ammonia, containing a little ammonium chloride to coagulate the insoluble material, and filtered. On acidification, a light brown amorphous acid was precipitated; it was very insoluble in the usual organic solvents and purified through the sparingly soluble sodium salt.[9] On acidification, a nearly white acid resulted, m. p. 286–288° with gas evolution.

*Anal.* Calcd. for $C_{21}H_{12}O_4$: C, 76.8; H, 3.6. Found: C, 76.7; H, 3.3.

It did not give a colored vat with either alkaline sodium hydrosulfite or zinc dust and alkali, and is probably not an anthraquinone derivative.

The methyl ester separated in colorless needles on cooling a mixture of 0.35 g. of the acid and 15 cc. of methanol containing one-fourth its weight of hydrogen chloride that had been refluxed one and one-half hours. It was

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(18) Hinrichsen and Triepel, *Ann.*, **336**, 196 (1904).

(19) Diels and Alder, *Ber.*, **62**, 2361 (1929).

recrystallized from a mixture of chloroform and methanol, from which it separated in white needles, m. p. 216–217°.

*Anal.* Calcd. for $C_{22}H_{14}O_4$: C, 77.2; H, 4.1. Found: C, 77.4; H, 4.0.

In Table III are given the melting points of the acids and esters for comparison with anthraquinone α-carboxylic acid.

TABLE III

MELTING POINTS OF ACIDS AND ESTERS

| | |
|---|---|
| Anthraquinone α-COOH | 286–288 dec. |
| Methyl ester | 188–190 |
| Acid II | 288–290 dec. |
| Methyl ester III | 197–198 |
| Chromic oxide acid | 286–288 dec. |
| Methyl ester | 216–217 |

(2) **4-Benzylbenzanthrone.**—This substance was easily oxidized by chromic acid, essentially as described above. The combined yield of 4-benzoylanthraquinone-1-carboxylic acid (V) was 75%. It was purified through the sparingly soluble sodium salt. The amorphous acid was practically insoluble in the usual organic solvents, but on boiling in acetone or acetic acid became crystalline (needles); m. p. 275–278° dec. It gave a yellow solution in concentrated sulfuric acid, which turned green on the addition of copper powder; a flocculent, violet-blue precipitate was obtained on dilution. A yellow silver salt was prepared in the usual manner.

*Anal.* Calcd. for $C_{22}H_{12}O_5$: C, 74.2; H, 3.4. For $C_{22}H_{11}O_5Ag$: Ag, 23.3. Found: C, 74.3; H, 3.6; Ag, 23.5.

The methyl ester was obtained by the use of methyl sulfate and 20% aqueous potassium hydroxide; it was recrystallized from a chloroform–methanol mixture, from which it separated in pale yellow plates, m. p. 184–185°.

*Anal.* Calcd. for $C_{23}H_{14}O_5$: C, 74.6; H, 3.8. Found: C, 74.5; H, 4.2.

α-Benzoylanthraquinone (VI) (m. p. 224–227°) resulted on decarboxylation by the procedure previously outlined. A mixed melting point with some authentic ketone (m. p. 225–227°) showed no depression.

**1,4-Dibenzoylanthraquinone, (VII).**—The acid chloride of (V) separated in fine needles when a mixture of 3 g. of the acid in 26 g. of thionyl chloride was refluxed for one and three-fourths hours. After filtering and washing with dry ether, 2.6 g. of a light gray product remained. A mixture of 2 g. of the latter, 0.2 g. of anhydrous ferric chloride and 25 cc. of dry benzene was refluxed for three hours, the solvent steam-distilled, and the residual dark green solid pulverized, and washed with dilute ammonia and water. A large part dissolved when boiled with 2 g. of potassium hydroxide in 25 cc. of methanol for an hour. The insoluble material was dark gray; m. p. 224–226°. It formed light yellow needles on recrystallization from acetic acid. A mixed melting point with an authentic specimen (m. p. 225–227°) was 225–226° (Scholl gives m. p. 225°).

**Ethyl Ether of the Carbinol (IX); 10-Ethoxy-10-*t*-butylbenzanthrenol-10.**—A solution of 0.3 g. of the carbinol in 6 cc. of absolute ethanol containing 1 drop of concentrated hydrochloric acid was refluxed for twenty minutes; on cooling, the white needles that separated were collected and recrystallized from alcohol; m. p. 159–160°.

*Anal.* Calcd. for $C_{23}H_{24}O$: C, 87.6; H, 7.3. Found: C, 87.4; H, 7.7.

Chromic acid oxidation of the carbinol, by the procedure above, gave anthraquinone α-carboxylic acid, m. p. 286–288° with dec. It was converted into the methyl ester by the use of alcoholic hydrogen chloride, forming needles, m. p. 183–185°. A mixed melting point with a specimen of pure ester (m. p. 188–189°) was 184–186°.

This work has been assisted by a generous grant from the Cyrus M. Warren Fund of the American Academy of Arts and Sciences.

## Summary

4-Substituted benzanthrones are obtained by the action of phenyl, benzyl, cyclohexyl and *n*-heptylmagnesium halides on benzanthrone, but *t*-butylmagnesium chloride gives a carbinol. The formation of the ketones is an additional example of 1,4-addition to a conjugated system involving a benzene ring.

This reaction affords a new method for determining the location of certain double bonds in polynuclear ring systems.

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