TABLE I

VOLATILE ACIDS FORMED IN RED WINE

Gas	Run 1, g./100 Formic	Run 1, g./100 Acetic	Run 2, g./100 Formic	Run 2, g./100 Acetic
None	0.0226	0.0327	0.0289	0.0292
Air	.0325	.0514	.0489	.0686
Oxygen	.0275	.090	.0273	.132
Nitrogen	....	....	.0162	.0532
Carbon dioxide	.0388	.0186	.0308	.0492

largely in the initial stages of the fermentation when the fermenting medium was protected from oxidation. In the presence of oxygen, volatile acids may be formed or utilized depending on experimental conditions.

3. The formation of volatile acids during the active stage of fermentation corresponds to the stage of decreasing oxidation–reduction potentials.

4. It is impossible to poise the oxidation–reduction potentials of fermenting grape juice by the use of oxygen or air although both reduce the period of time during which the oxidation–reduction level is maintained at the low level characteristic of fermentation and both increase the subsequent rise in oxidation–reduction potential.

5. In grape juice fermented under aeration less volatile acid is formed in the initial stages than in carbon dioxide, nitrogen or plain. Oxygen exerts a similar but not so marked effect and for a shorter period.

6. The changes in volatile acid production are ascribed to the activity of the yeast dehydrogenases in oxidizing aldehydes, alcohol and acetic acid, respectively. It is suggested that there is an association or competitive action on all three substrates. However, these investigations do not exclude the possibility that substances such as fixed acids, tartaric acid, malic acid or N-constituents may not be involved.

7. The role and origin of formic acid found among the volatile acids in fermented juice is yet to be explained.

BERKELEY, CALIF. RECEIVED JANUARY 3, 1938

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE OHIO STATE UNIVERSITY]

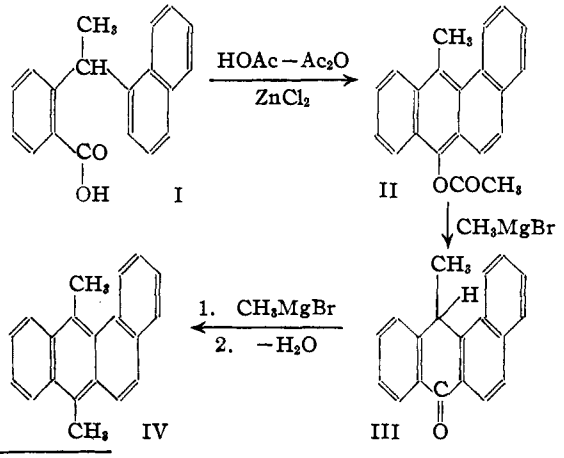
The Synthesis of 9,10-Dimethyl-1,2-benzanthracene

BY MELVIN S. NEWMAN

Because of the high degree of cancer producing activity of 10-methyl-,[1] 5,10-dimethyl-,[1] and 5,9-dimethyl-1,2-benzanthracene,[2] it seemed of interest to synthesize 9,10-dimethyl-1,2-benzanthracene.

Work was commenced upon the most direct approach, namely, the addition of two moles of methylmagnesium bromide to 1,2-benzanthraquinone, but discontinued upon the appearance of the article of Bachmann and Bradbury,[3] who advised us that they were continuing this line of work with the intention of synthesizing 9,10-dimethyl-1,2-benzanthracene. However, as material was desired for biological work, it was deemed worth while to attempt the preparation of this hydrocarbon by a different method.

The starting material for the presently reported synthesis was *o*-(α-methyl-α-1-naphthyl)-toluic acid[2,4] I, which was cyclized to 10-acetoxy-9-methyl-1,2-benzanthracene, II, and the latter compound hydrolyzed to the anthrone, III, by the method of Fieser and Hershberg.[5] The anthrone (or its tautomeric isomer) was not isolated in a pure condition as it could not be crystallized. The final hydrocarbon, IV, obtained by the reaction of III with methylmagnesium bromide followed by dehydration of the resulting carbinol proved identical with the 9,10-dimethyl-1,2-benzanthracene synthesized by



(1) Fieser and Newman, THIS JOURNAL, **58**, 2376 (1936).
(2) Newman, *ibid.*, **59**, 1003 (1937).
(3) Bachmann and Bradbury, *J. Org. Chem.*, **2**, 175 (1937).
(4) Cook, Robinson, and Goulden, *J. Chem. Soc.*, 393 (1937).
(5) Fieser and Hershberg, THIS JOURNAL, **59**, 1028 (1937).

Bachmann and Chemerda.[6] The identity was established by analysis and by a mixed melting point with a sample kindly furnished by Dr. Bachmann.

A report concerning the physiological activity of 9,10-dimethyl-1,2-benzanthracene will be published elsewhere by Dr. M. J. Shear. In a private communication he has indicated that this hydrocarbon has marked biological activity. When 1 mg. per mouse was injected in lard solution severe ulceration was produced in most of the mice in one month, but no tumors had appeared after three months. Doses of 0.1 mg. per mouse did not produce ulceration or tumors after two months.

Experimental[7]

10-Acetoxy-9-methyl-1,2-benzanthracene. II.—To a solution of 2.76 g. of I[2,4] in 10 cc. of acetic acid and 10 cc. of acetic anhydride was added 0.1 g. of anhydrous zinc chloride.[5] After refluxing for two hours, the reaction mixture was cooled and the acetic anhydride decomposed by addition of water. The crystals which separated were collected and recrystallized from acetic acid, coming out as colorless flat needles, m. p. 192.4–193.4°, in a yield of 50%.

Anal. Calcd. for $C_{21}H_{16}O_2$: C, 83.98; H, 5.37. Found: C, 84.16; H, 5.35.

9,10-Dimethyl-1,2-benzanthracene. IV.—To a solution of 1.27 g. of II in 30 cc. of benzene and 20 cc. of ether was added 10 cc. of 0.267 *M* methylmagnesium bromide. The mixture was refluxed for six hours, allowing the ether to distil slowly. The reaction mixture was decomposed with dilute hydrochloric acid and the benzene layer containing the anthrone concentrated and diluted with dry ligroin. As no crystalline material was obtained, the ligroin was removed by distillation and the residual benzene solution treated with 3 cc. of the above methylmagnesium bromide. A vigorous reaction took place with the separation of an orange complex which soon redissolved. After two hours of refluxing the reaction mixture was decomposed with dilute hydrochloric acid and the organic matter remaining after evaporation of all solvent pyrolyzed at 240–250° for fifteen minutes and then distilled at 3 mm. The distillate crystallized immediately and the hydrocarbon was isolated as a red dipicrate melting unsharply at 103–106°.[8] The hydrocarbon was obtained by passage of the dipicrate through a tower of activated alumina. It formed almost colorless plates, m. p. 122.4–122.8°, having an intense blue-violet fluorescence in ultraviolet light. The melting point was not depressed by a sample of 9,10-dimethyl-1,2-benzanthracene supplied by Dr. Bachmann. The over-all yield from acetoxy compound to hydrocarbon was 32%.

Anal. Calcd. for $C_{20}H_{16}$: C, 93.71; H, 6.29. Found: C, 93.58; H, 6.43.

Summary

The synthesis of 9,10-dimethyl-1,2-benzanthracene is described. *o*-(α-Methyl-α-1-naphthyl)-toluic acid was converted into 10-acetoxy-9-methyl-1,2-benzanthracene by a ring closure involving zinc chloride in acetic anhydride. This acetoxy compound was hydrolyzed, and the resulting anthrone was treated with methylmagnesium bromide to yield a carbinol which was dehydrated to yield 9,10-dimethyl-1,2-benzanthracene.

(6) Bachmann and Chemerda, THIS JOURNAL, **60**, 1023 (1938).

(7) All melting points corrected. Analyses by H. S. Clark.

(8) This picrate is the dipicrate of Bachmann and Chemerda[6] who report (in a private communication) the melting range as 102–106° after sintering as low as 95°. This difference in behavior of the dipicrate may be due to the fact that Bachmann and Chemerda used melting point tubes composed of soft glass whereas I used Pyrex melting point tubes. On storing picrates in soft glass there is usually marked decomposition of the picrate due to the alkali in the glass. A similar decomposition is not noticeable when Pyrex containers are used.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Diazo Coupling of Carcinogenic Hydrocarbons

BY LOUIS F. FIESER AND WILLIAM P. CAMPBELL[1]

The coupling of aromatic hydrocarbons with diazotized amines has been observed only in very rare instances, and heretofore only three azo compounds have been obtained in a crystalline condition by utilization of this reaction. In the first published work on the problem K. H. Meyer, Irschick and Schlösser[2] observed that mesitylene, acenaphthene, and anthracene show some indications of coupling with 2,4-dinitrobenzenediazonium chloride in acetic acid solution, but the reactions were slow and incomplete and no azo compounds could be isolated. Meyer and Tochtermann[3] later found that the highly reactive diazonium salt from picramide couples rapidly with mesitylene and gives a crystalline azo compound in good yield. With the other hydrocarbons investigated, including anthracene and α-methylnaphthalene, the reaction was slow and no coupling products could be isolated. In a

(1) Squibb Research Fellow.

(2) Meyer, Irschick and Schlösser, *Ber.*, **47**, 1741 (1914).

(3) Meyer and Tochtermann, *ibid.*, **54**, 2283 (1921).