as improvements on previously reported syntheses of the 4-, 5- and 9-isomers. 1,2-Benzanthracene, 10-methyl- and 9,10-dimethyl-1,2-benzanthracene have also been prepared. At least 25 g. of each compound has been made so that these compounds may be made available to cancer research workers.

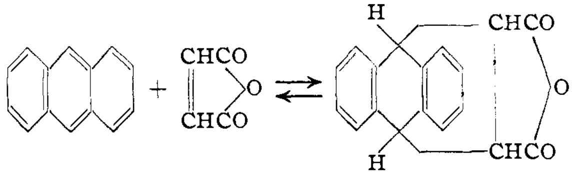
COLUMBUS 10, OHIO RECEIVED SEPTEMBER 6, 1949

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

Polymethyl Aromatic Hydrocarbons. III. The Reaction of 1,2,3,4-Tetramethylnaphthalene with Maleic Anhydride[1]

BY MILTON C. KLOETZEL,* RHODES P. DAYTON AND HERSHEL L. HERZOG[2]

Diels and Alder[3] demonstrated the existence of a dienoid system in the *meso* ring of anthracene by effecting a reaction of this hydrocarbon with maleic anhydride to yield 9,10-dihydroanthracene-9,10-endo-α,β-succinic anhydride (I).



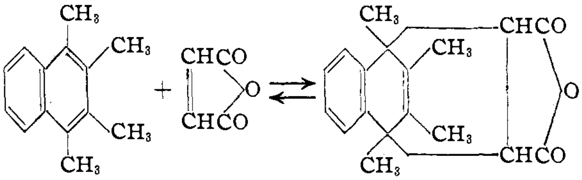
I

Bachmann and Kloetzel[4] later demonstrated the reversible nature of the reaction between maleic anhydride and polycyclic hydrocarbons containing the anthracene nucleus, and also discovered that the presence of methyl groups in the *meso*-positions of anthracene greatly facilitated this reaction. Thus, the reaction of equimolar quantities of maleic anhydride and 9,10-dimethylanthracene in refluxing benzene was 95% complete within five minutes, whereas anthracene itself required seven and seven-tenths hours for 96% reaction under these conditions.

Despite the formal analogy between anthracene and naphthalene, the latter hydrocarbon has been reported[5] not to undergo a reaction with maleic anhydride, even after prolonged refluxing in toluene.[6] Dienoid character in naphthalene is manifested, however, in certain other of its reactions. For example, reduction with sodium and alcohol yields 1,4-dihydronaphthalene.[7] Naphthalene also forms 1,4-organometallic addition products with lithium[8] or sodium[9] in ether.

Consideration of the activating influence of methyl groups upon the anthracene nucleus suggested the possibility that a Diels–Alder type reaction with the naphthalene nucleus might become feasible if enough methyl groups were substituted on one ring of naphthalene to enhance the potential dienoid character of that ring.

Such a reaction now has been effected. A 90% yield of adduct (II) was obtained when 1,2,3,4-tetramethylnaphthalene was treated with a large excess (30 moles) of maleic anhydride in refluxing benzene. To our knowledge, this is the first instance in which a dienoid system wholly within the naphthalene nucleus has been observed to undergo a Diels–Alder reaction. The reaction is remarkable in that a resonance-stabilized aromatic system is disrupted under such mild conditions and illustrates the profound modifying influence which methyl groups can exert upon such a system.



II

The reaction of 1,2,3,4-tetramethylnaphthalene with maleic anhydride was shown to be reversible. The equilibrium yield of adduct, obtained within forty-six hours, from equimolar quantities of hydrocarbon and maleic anhydride in boiling xylene was 4.6–6.4%. Prolonged heating did not increase the yield of adduct. The position of equilibrium was checked by recovering the hydrocarbon produced upon dissociation of the pure adduct in boiling xylene solution. It is evident that equilibrium in boiling xylene is less favorable for the production of adduct from 1,2,3,4-tetramethylnaphthalene than it is from 9,10-diphenylanthracene, which gives the poorest yield (16%) of any anthracene derivative reported by Bachmann and Kloetzel.[4] In spite of this fact, it is possible to obtain an excellent yield (90%)

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* Harvard University Faculty 1938–1941.

[1] Abstracted from the thesis submitted by Rhodes P. Dayton, and a portion of the dissertation submitted by Hershel L. Herzog to the Graduate School of the University of Southern California in partial fulfillment of the requirements for the degrees of Master of Science and Doctor of Philosophy, respectively. Presented before the Division of Organic Chemistry, San Francisco, March, 1949.

[2] Standard Oil Company of California Graduate Fellow in Chemistry.

[3] Diels and Alder, *Ann.*, **486**, 191 (1931).

[4] Bachmann and Kloetzel, THIS JOURNAL, **60**, 481 (1938).

[5] Mameli, Pancotto and Crestani, *Gazz. chim. ital.*, **67**, 669 (1937).

[6] We have found that even when naphthalene is fused with 30 moles of maleic anhydride at 100° for twenty-four hours, reaction occurs to the extent of less than 1%. This reaction will be described in a forthcoming communication.

[7] Bamberger and Lodter, *Ber.*, **26**, 1833 (1893); Straus and Lemmel, *ibid.*, **46**, 232 (1913); Straus, *ibid.*, **46**, 1051 (1913); Straus and Lemmel, *ibid.*, **54**, 25 (1921).

[8] Schlenk and Bergmann, *Ann.*, **463**, 1 (1928).

[9] Hückel and Bretschneider, *ibid.*, **540**, 157 (1939).

of adduct from 1,2,3,4-tetramethylnaphthalene when the reaction is effected with excess maleic anhydride at a lower temperature (boiling benzene solution).

Structure II for the adduct from maleic anhydride and 1,2,3,4-tetramethylnaphthalene is substantiated by its physical and chemical properties. In Fig. 1 is shown the ultraviolet absorption curve from 240–280 mμ for the adduct dipotassium salt in aqueous solution. A close correspondence is evident between the maxima in this curve (at 258, 265 and 272 mμ with ϵ_{max} = 615, 690 and 592, respectively) and the maxima in similar curves for the anthracene–maleic anhydride adduct salt (at 259, 266 and 274 mμ)[10] and for *o*-xylene (at 257, 263 and 271 mμ).[11,12] Moreover, as in the case of the latter two compounds, absorption by the 1,2,3,4-tetramethylnaphthalene adduct rapidly dropped to a relatively small value beyond 280 mμ. Because of the limited solubility of the adduct dipotassium salt in water. and of the anhydride in most other useful solvents, an ethyl acetate solution of the adduct anhydride was employed for determination of absorption in the range 274–320 mμ. Absorption decreased continuously over the entire range, but only a portion of the curve so obtained is shown in Fig. 1. For purposes of comparison, the absorption curve for 1,2,3,4-tetramethylnaphthalene itself, in 95% ethanol, is shown in Fig. 1. This curve was indistinguishable from that obtained for an ethyl acetate solution of the hydrocarbon over the range 274–320 mμ. Strong absorption in the range 280–320 mμ is characteristic of this hydrocarbon as well as other naphthalene derivatives,[13,14] and naphthalene itself[15] shows a series of maxima in this range. Comparison of these curves indicates clearly that the 1,2,3,4-tetramethylnaphthalene–maleic anhydride adduct shows absorption characteristic of an alkylbenzene derivative and no longer contains an intact naphthalene nucleus. It is evident that the adduct cannot be of the type (III) recently reported[16] to be formed by maleic anhydride attack upon a methyl group of *p*-xylene in the presence of a peroxide catalyst.

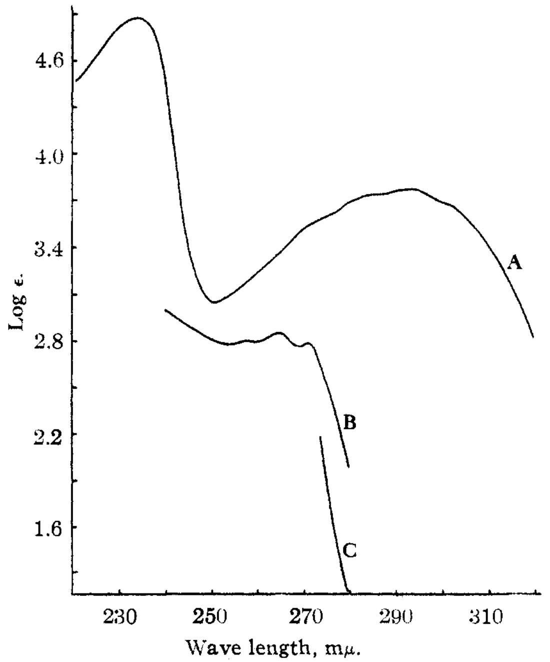
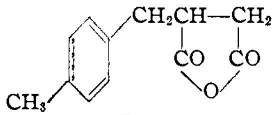
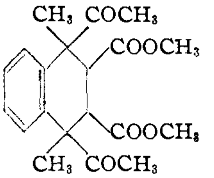


Fig. 1.—Absorption spectra: A, 1,2,3,4-tetramethylnaphthalene; B, dipotassium 1,2,3,4-tetramethyl-1,4-dihydronaphthalene-1,4-*endo*-α,β-succinate; C, 1,2,3,4-tetramethyl-1,4-dihydronaphthalene-1,4-*endo*-α,β-succinic anhydride.

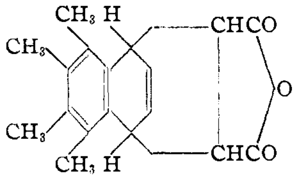


III

Hydrolysis of the adduct (II) was accomplished readily by means of potassium hydroxide and the dicarboxylic acid, precipitated upon acidification of the resulting aqueous solution of the potassium salt, was converted to its dimethyl ester by reaction with diazomethane. Ozonolysis of this ester yielded a compound which showed the proper analysis for IV. That this substance was not an aldehyde was indicated by its failure to reduce Fehling solution or to give a positive Schiff test. This eliminated the possibility that the Diels–Alder reaction had taken place in the unsubstituted ring of 1,2,3,4-tetramethylnaphthalene to yield adduct V, for ozonolysis of the ester from such an adduct would have yielded an aldehyde.



IV



V

1,2,3,4-Tetramethylnaphthalene used in this investigation was synthesized through the sequence illustrated by formulas VI–IX, and proved to be identical with the hydrocarbon previously prepared in a. different manner by Hewett[17] and by Sisido and Nozaki.[18] Succinoylation of prehnitene, prepared from pentamethylbenzene

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[10] Clar, *Ber.*, **65**, 503 (1932). Due to an error in legend, curves for anthracene and its adduct appear interchanged in Clar's paper.

[11] Henri, "International Critical Tables," McGraw-Hill Book Co., Inc., New York, N. Y., 1929, Vol. V, p. 361.

[12] Wolf and Herold, *Z. physik. Chem.*, **B13**, 201 (1931).

[13] Friedel, Orchin and Reggel, THIS JOURNAL, **70**, 199 (1948).

[14] Hirshberg and Jones, *Can. J. Research*, **B27**, 437 (1949).

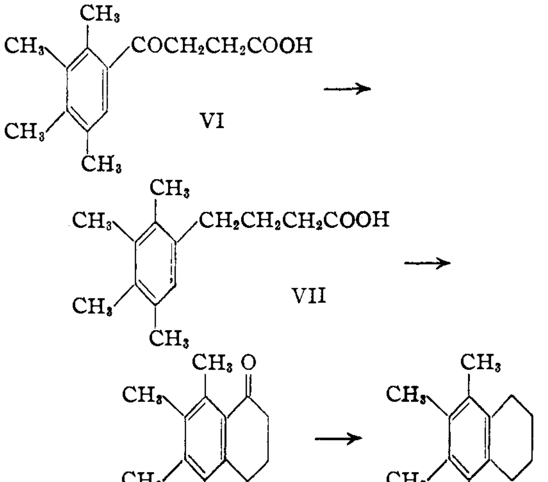
[15] Mayneord and Roe, *Proc. Roy. Soc. (London)*, **A152**, 299 (1935).

[16] Bickford, Fisher, Dollear and Swift, *J. Am. Oil Chemists Soc.*, **25**, 251 (1948).

[17] Hewett, *J. Chem. Soc.*, 293 (1940).

[18] Sisido and Nozaki, THIS JOURNAL, **69**, 961 (1947).

by the method of Smith and Lux[19] was effected in either *sym*-tetrachloroethane or nitrobenzene. Reduction of the resulting keto acid (VI) by the Martin modification[20] of the Clemmensen method proceeded smoothly. Cyclization of the substituted butyric acid (VII) was effected with 80% sulfuric acid, and also by the method employed by Bachmann and Chemerda,[21] in which phosphorus pentachloride and stannic chloride were used for a similar cyclization. The cyclization through the acid chloride was not appreciably affected by the substitution of thionyl chloride for phosphorus pentachloride, or by the use of aluminum chloride in place of stannic chloride. Use of this method gave yields of 70–80%, while with 80% sulfuric acid yields were as high as 95%. Clemmensen reduction of 5,6,7,8-tetramethyl-1-tetralone (VIII) and subsequent dehydrogenation of the resulting tetramethyltetralin (IX) yielded the desired 1,2,3,4-tetramethylnaphthalene. The dehydrogenation was best accomplished with palladium-on-charcoal catalyst,[22] which gave a nearly quantitative yield of colorless product. When sulfur was employed for dehydrogenation, an 82% yield of yellow product resulted. All yields in this sequence were in excess of 94% except reduction of the cyclic ketone VIII, which was accomplished in 84% yield.



VI

VII

VIII

IX

Acknowledgment.—We wish to thank the Standard Oil Company of California for making possible part of this work through the financial aid provided by the Standard Oil Company of California Graduate Fellowship in Chemistry.

Experimental[23]

Synthesis of 1,2,3,4-Tetramethylnaphthalene. (a) β-(2,3,4,5-Tetramethylbenzoyl)-propionic Acid (VI).—Forty grams of prehnitene[19] was succinoylated by the procedure employed by Barnett and Sanders[24] for succinoylation of the xylenes. The acid, 63.7 g. (97%), melting at 114–120°, crystallized from ether–petroleum ether in long, colorless needles, m. p. 124–125°.

Anal. Calcd. for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 72.03; H, 8.00.

(b) **γ-(2,3,4,5-Tetramethylphenyl)-*n*-butyric Acid (VII).**—A mixture of 355 g. of granular zinc, 12 cc. of concentrated hydrochloric acid, 35.5 g. of mercuric chloride and 355 cc. of water was swirled for five minutes and the liquid was decanted. To the residual amalgamated zinc were added in order, 550 cc. of concentrated hydrochloric acid, 12 cc. of ethanol, 24 cc. of toluene and 58 g. of β-(2,3,4,5-tetramethylbenzoyl)-propionic acid. An additional 800 cc. of hydrochloric acid was added during a reflux period of forty hours. The reaction mixture was extracted with benzene and the extract was washed with water. Concentration of the benzene solution and distillation under reduced pressure yielded 51.6 g. (95%) of γ-(2,3,4,5-tetramethylphenyl)-*n*-butyric acid of sufficient purity for direct cyclization. The acid crystallized from ether–petroleum ether in colorless leaflets, m. p. 106.5–107.6°.

Anal. Calcd. for $C_{14}H_{20}O_2$: C, 76.32; H, 9.15. Found: C, 76.51; H, 8.91.

(c) **5,6,7,8-Tetramethyl-1-tetralone (VIII).**—The acid chloride prepared from 6.2 g. of γ-(2,3,4,5-tetramethylphenyl)-*n*-butyric acid with phosphorus pentachloride was cyclized with anhydrous stannic chloride in the manner described by Bachmann and Chemerda[21] for the cyclization of γ-3-phenanthryl-*n*-valeric acid, to yield 4.4 g. (76%) of crude ketone. 5,6,7,8-Tetramethyl-1-tetralone crystallized from 95% ethanol in colorless prisms, m. p. 105–106°.

Anal. Calcd. for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 83.33; H, 9.22.

Thirty-three grams of γ-(2,3,4,5-tetramethylphenyl)-*n*-butyric acid was also cyclized directly, according to the general method employed by Barnett and Sanders[24] for the cyclization of other γ-aryl-*n*-butyric acids, using 185 cc. of 80% sulfuric acid and heating for two hours on the steam-bath. The dark red solution was poured into 600 cc. of water and the mixture was extracted with benzene. After being washed with water and sodium carbonate solution, the benzene solution was concentrated and distilled under reduced pressure; b. p. 156–163° at 1–2 mm. Crystallization as before yielded 28.5 g. (94%) of 5,6,7,8-tetramethyl-1-tetralone.

(d) **5,6,7,8-Tetramethyltetralin (IX).**—To 104 g. of zinc, amalgamated as before, were added in order, 160 cc. of concentrated hydrochloric acid, 6 cc. of ethanol, 18 cc. of toluene and 20.2 g. of 5,6,7,8-tetramethyl-1-tetralone. An additional 125 cc. of hydrochloric acid was added during the reflux period of forty-eight hours. Benzene extraction, followed by distillation, yielded 15.9 g. (84%) of 5,6,7,8-tetramethyltetralin, b. p. 119–122° at 1–1.5 mm. Crystallization from low-boiling petroleum ether yielded colorless leaflets, m. p. 79–79.5°.

Anal. Calcd. for $C_{14}H_{20}$: C, 89.29; H, 10.71. Found: C, 89.35; H, 10.52.

(e) **1,2,3,4-Tetramethylnaphthalene.**—A mixture of 7.52 g. of 5,6,7,8-tetramethyltetralin and 0.75 g. of a 30% palladium-on-charcoal catalyst was placed in a heavy test-tube, air was expelled by the carbon dioxide from a small pellet of Dry Ice, and the tube was heated in a metal-bath for three hours, starting at a temperature of 200° and slowly raising the temperature to 315° at such a rate as to maintain a steady liberation of hydrogen. Evolved hydrogen corresponded roughly to 102% of the theoretical quantity. The reaction product was diluted with benzene, the solution was filtered from catalyst, and the benzene was evaporated. Crystallization from 95% ethanol yielded 7.1 g. (97%) of 1,2,3,4-tetramethylnaphthalene as colorless

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[19] Smith and Lux, THIS JOURNAL, **51**, 2994 (1929).

[20] Martin, *ibid.*, **58**, 1438 (1936).

[21] Bachmann and Chemerda, *J. Org. Chem.*, **6**, 36 (1941).

[22] Zelinsky and Turowa-Pollak, *Ber.*, **58**, 1292 (1925).

[23] All m. p.'s are uncorrected. Analyses are by Dr. G. Oppenheimer, California Institute of Technology.

[24] Barnett and Sanders, *J. Chem. Soc.*, 434 (1933).

prisms, m. p. 106.5–107°; picrate, m. p. 182.5–183°. Hewett[17] reported melting points of 106.5–107.5° and 182–183° for the hydrocarbon and its picrate, respectively, while Sisido and Nozaki[18] reported 106 and 181°.

The absorption curve for 1,2,3,4-tetramethylnaphthalene shown in Fig. 1 was obtained with a Beckman quartz spectrophotometer, model DU, employing 95% ethanol solutions of appropriate hydrocarbon concentration (10^{-4} and 10^{-5} molar). An identical curve was obtained in the range 274–320 mμ employing a 10^{-4} molar solution of the hydrocarbon in ethyl acetate.

Reaction of 1,2,3,4-Tetramethylnaphthalene with Maleic Anhydride.—A mixture of 1.000 g. of 1,2,3,4-tetramethylnaphthalene, 15.95 g. (30 moles) of maleic anhydride and 20 cc. of anhydrous benzene was refluxed for seventy-two hours. After evaporation of the solvent by a current of air, the residue was heated for a few minutes on the steam-bath with 50 cc. of 40% potassium hydroxide solution. The potassium salt of the acid which separated upon cooling was dissolved in hot water and the unreacted hydrocarbon was extracted with benzene. 1,2,3,4-Tetramethyl-1,4-dihydronaphthalene-1,4-*endo*-α,β-succinic acid was precipitated by the addition of hydrochloric acid to the aqueous solution; yield 1.48 g. (90%) of colorless crystals, m. p. 144–147° with decomposition. When this acid was crystallized from ethyl acetate containing a small quantity of acetic anhydride, the adduct anhydride (II) crystallized in colorless hexagonal prisms.

Anal. Calcd. for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43. Found: C, 76.72; H, 6.44.

The m. p. of 1,2,3,4-tetramethyl-1,4-dihydronaphthalene-1,4-*endo*-α,β-succinic anhydride (II) depended upon the temperature at which the sample was introduced into the m. p. bath, and also upon the rate of heating. For this reason, the m. p. was determined as follows: the bath was heated to a temperature near the m. p., a capillary containing the sample was immersed in the bath, and the time required for the sample to melt was determined. The m. p. was taken as the temperature at which an increase in the bath temperature did not decrease the time required to obtain a melt. This temperature was approximately 195°.

When equal quantities of the adduct anhydride and anhydrous picric acid were dissolved in the minimum quantity of hot methanol, no color developed which was more intense than that of picric acid alone, and no characteristic picrate separated upon cooling the solution.

In Fig. 1 is shown a portion of the absorption curve obtained over the range 274–320 mμ with the aforedescribed instrument, employing a 1.098×10^{-2} molar solution of adduct II in ethyl acetate.

A 10^{-3} molar solution of dipotassium 1,2,3,4-tetramethyl-1,4-dihydronaphthalene-1,4-*endo*-α,β-succinate was prepared by dissolving the appropriate quantity of adduct II in the minimum quantity of 5% aqueous potassium hydroxide, with the aid of 5 cc. of methanol, and diluting to 1000 cc. with distilled water. The absorption curve shown in Fig. 1 was then obtained in the usual manner.

Equilibrium Reaction of 1,2,3,4-Tetramethylnaphthalene and Maleic Anhydride in Boiling Xylene.—An equimolecular mixture of hydrocarbon (1.000 g.) and freshly-distilled maleic anhydride (0.533 g.) in 20 cc. of xylene was heated at reflux temperature for an appropriate period of time and the reaction mixture was worked up in a manner similar to that described by Bachmann and Kloetzel[4] for the study of related reactions in the anthracene series. The results of several such experiments are presented in Table I.

TABLE I

EXTENT OF REACTION OF 1,2,3,4-TETRAMETHYLNAPHTHALENE WITH MALEIC ANHYDRIDE IN BOILING XYLENE

Time, hr.	Hydrocarbon recovered, g.	Yield adduct based on hydrocarbon recovered, %	Adduct acid recovered, g.	Yield adduct, %
46	0.936	6.4	0.071	4.33
46	.934	6.6	.081	4.94
72	.940	6.0	.076	4.63
72	.935	6.5	.076	4.63

In order to approach the equilibrium from the opposite direction, 0.307 g. of pure adduct was heated in 4 cc. of boiling xylene for an appropriate period of time, and the amount of 1,2,3,4-tetramethylnaphthalene which was produced by dissociation of the adduct was determined. The results of several such experiments are presented in Table II.

TABLE II

EXTENT OF DISSOCIATION OF 1,2,3,4-TETRAMETHYLNAPHTHALENE–MALEIC ANHYDRIDE ADDUCT IN BOILING XYLENE

Time, hr.	Hydrocarbon, mg.	Recovered, %
48	143	71.5
71	184	92.0
72	187	93.5
95	187	93.5

Dimethyl Ester of Adduct from 1,2,3,4-Tetramethylnaphthalene and Maleic Anhydride.—To a freshly precipitated sample of the adduct dicarboxylic acid dissolved in acetone was added excess diazomethane in ether solution. Following evaporation of the solvents, the residue was crystallized from anhydrous ethyl acetate. Dimethyl 1,2,3,4-tetramethyl-1,4-dihydronaphthalene-1,4-*endo*-α,β-succinate formed colorless, hexagonal prisms, m. p. 157–157.5°.

Anal. Calcd. for $C_{20}H_{24}O_4$: C, 73.15; H, 7.37. Found: C, 73.48; H, 7.47.

Ozonolysis of Adduct Dimethyl Ester.—Adduct dimethyl ester (1.75 g.) was dissolved in 70 cc. of anhydrous ethyl acetate and the solution was exposed to a stream of 3.4% ozone in dry oxygen at 0–5° until ozone began to appear in the exit gas stream (about one hour). The solution was then poured into 25 cc. of water and the mixture was allowed to stand for forty-eight hours. After separation of the layers, the aqueous phase was extracted once with ether, and the ethereal extract was combined with the original ethyl acetate layer and dried over sodium sulfate for several hours. Evaporation of the solvents at room temperature under reduced pressure left a crystalline residue (0.36 g., 19%) of dimethyl 1,4-diacetyl-1,4-dimethyl-1,2,3,4-tetrahydronaphthalene-2,3-decarboxylate (IV). Two crystallizations of this material from methanol containing a drop or two of water yielded colorless rectangular prisms, m. p. 158.5–159.5°.

Anal. Calcd. for $C_{20}H_{24}O_6$: C, 66.65; H, 6.71. Found: C, 66.35; H, 6.89.

This compound did not give a positive Schiff test for an aldehyde, nor did it reduce Fehling solution, even after the mixture was boiled for several minutes and then allowed to stand overnight.

Summary

1,2,3,4-Tetramethylnaphthalene has been shown to react reversibly with maleic anhydride to yield 1,2,3,4-tetramethyl-1,4-dihydronaphthalene-1,4-endo-α,β-succinic anhydride. The equilibrium yield of adduct, obtained within forty-six hours, from equimolar quantities of the reactants in boiling xylene was 4.6–6.4%. However, yields of adduct up to 90% can be obtained by employing a large excess of maleic anhydride and effecting the reaction in boiling benzene.

1,2,3,4-Tetramethylnaphthalene was synthesized by succinoylation of prehnitene, followed by Clemmensen reduction of the resulting keto

acid and subsequent cyclization to yield 5,6,7,8-tetramethyl-1-tetralone. Clemmensen reduction of the cyclic ketone and subsequent dehydrogenation of the tetramethyltetralin then yielded the desired hydrocarbon.

LOS ANGELES, CALIFORNIA RECEIVED SEPTEMBER 12, 1949

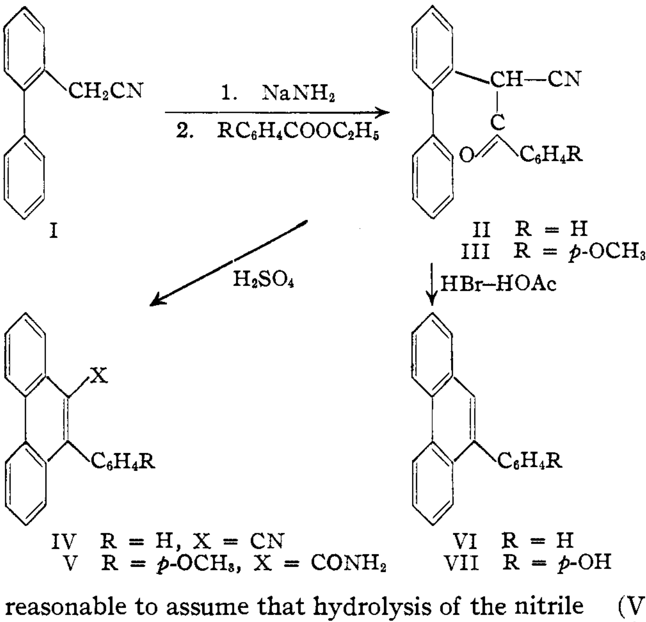
[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF DUKE UNIVERSITY]

Aromatic Cyclodehydration. XXIII.[1] Phenanthrene Derivatives by the Cyclization of Keto Nitriles

BY CHARLES K. BRADSHER* AND RICHARD S. KITTILA[2]

The present work was undertaken to determine whether *o*-phenylbenzyl cyanide (I) could be acylated and whether the resulting ketonitriles (II and III) would undergo typical aromatic cyclodehydration reactions to yield phenanthrene derivatives.[3]

The method which we used in the preparation of *o*-phenylbenzyl cyanide (I) was essentially that of von Braun and Manz,[4] except that the required *o*-phenylbenzyl alcohol was prepared more conveniently from 2-biphenylylmagnesium iodide by the action of paraformaldehyde. Benzoylation of the nitrile was accomplished in 82% yield by treating it first with two moles of sodium amide and then with ethyl benzoate.[5] The resulting keto nitrile (II) when refluxed with a mixture of hydrobromic and acetic acids afforded 9-phenylphenanthrene (VI) in 46% yield. It is reasonable to assume that hydrolysis of the nitrile group, followed by decarboxylation of the resulting keto acid has preceded cyclization.



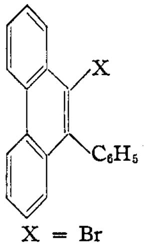
I

II R = H
III R = *p*-OCH$_3$

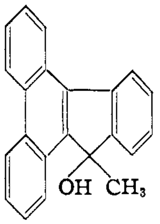
IV R = H, X = CN
V R = *p*-OCH$_3$, X = CONH$_2$

VI R = H
VII R = *p*-OH

When the keto nitrile (II) was treated with cold concentrated sulfuric acid, 9-cyano-10-phenylphenanthrene (IV) was obtained. The structure of IV was established by comparison with the nitrile obtained from 9-bromo-10-phenylphenanthrene[6] (VIII) by the Rosenmund–von Braun method. The nitrile (IV) on treatment with methylmagnesium iodide afforded the expected imine (IX) which, probably as a result of steric hindrance, proved difficult to hydrolyze. With boiling dilute hydrochloric acid, the insoluble imine hydrochloride was recovered, but when the imine was dissolved in boiling dilute acetic acid and refluxed for sixteen hours, a product having the composition expected for 9-aceto-10-phenylphenanthrene (X) was obtained. In view of the failure of the product to undergo reaction with hydroxylamine or phenylhydrazine or to undergo reduction, it may be that the product is the isomeric 9-methyl-1,2,3,4-dibenzofluorenol-9 (XA). The acylation of *o*-phenylbenzyl cyanide (I) with ethyl anisate was accomplished in 55% yield. The product (III), on refluxing with hydrobromic and acetic acids, afforded the new 9-(*p*-hydroxyphenyl)-phenanthrene (VII) in a yield of 96%. The structure of this phenol (VII) was demonstrated by the synthesis of the corresponding methyl ether (XII) by a method studied previously.[7] The addition of *p*-anisylmagnesium bromide to 2-(ω-methoxy)-acetobiphenyl (XI), followed by cyclization of the crude carbinol, afforded a sample of 9-(*p*-methoxy-



VIII X = Br
IX X = (C = NH)CH$_3$
X X = COCH$_3$



XA

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* Harvard University Ph.D. 1937.

[1] For the preceding communication of this series see THIS JOURNAL, **71**, 1434 (1949).

[2] Public Health Service Fellow 1948–1949.

[3] Schönberg and Warren, *J. Chem. Soc.*, 1838 (1939), and Geisman and Tess, THIS JOURNAL, **62**, 514 (1940), have reported the cyclization of a related keto ester.

[4] von Braun and Manz, *Ann.*, **468**, 258 (1929).

[5] Hauser and Levine, THIS JOURNAL, **68**, 760 (1946).

[6] Koelsch, *ibid.*, **56**, 480 (1934).

[7] Bradsher and Schneider, *ibid.*, **60**, 2960 (1938).