The n.m.r. spectrum of the *trans* isomer (72 mg. per 0.25 ml. of carbon tetrachloride) showed the hydrogen alpha to bromine at 2.05 to 2.36 p.p.m. from water, the methyl at 3.56 p.p.m., and the remaining ring protons at 3.78 to 4.10 p.p.m. The n.m.r. spectrum of the *cis* isomer (33 mg. per 0.2 ml. of carbon tetrachloride) contained the same signals at 1.5 to 1.97 p.p.m., 3.5 p.p.m., and 3.62 to 4.39 p.p.m., respectively.

Anal. Calcd. for C_4H_7Br: C, 35.59; H, 5.22; Br, 59.20. Found for *trans* isomer: C, 35.45; H, 5.42. Found for *cis* isomer: C, 35.84; H, 5.50; Br, 58.74.

Hunsdiecker Reaction of Silver *trans*-2-Methylcyclopropanecarboxylate.—To a stirred solution of 1.105 g. (0.0069 mole) of bromine in 30 ml. of anhydrous carbon tetrachloride was added 1.43 g. (0.0069 mole) of silver *trans*-2-methylcyclopropanecarboxylate over a period of 30 min. The mixture was then stirred for an additional 2.5 hr., heated under reflux for 1 hr., and allowed to stand overnight. The silver bromide (1.29 g., 100%) was filtered out, and the filtrate was washed with 10% sodium bisulfite to remove unreacted bromine and with 10% sodium bicarbonate. The carbon tetrachloride solution was then dried over magnesium sulfate and distilled without fractionation. Analysis of the distillate by gas chromatography on didecyl phthalate at 53° (helium flow 92 ml./min.) and measurement of the relative areas of the *cis* (21.4 min.) and *trans* (15.9 min.) peaks showed the product to be 66.0 ± 0.8% *trans*- and 34.0 ± 0.8% *cis*-2-methylcyclopropyl bromide. The total yield was estimated to be 53%. The thermal conductivities of the two isomers were assumed to be equal.

As a control, a reaction of 0.200 g. (0.0012 mole) of silver acetate with 0.08 ml. of bromine in carbon tetrachloride which contained 0.0591 g. of *trans*-2-methylcyclopropyl bromide was run under the same conditions as described above. The silver bromide obtained amounted to 0.229 g. (102%), and the same analysis as used above revealed only *trans*-2-methylcyclopropyl bromide, with none of the *cis* isomer, in the product mixture.

Hunsdiecker Reaction of Silver *cis*-2-Methylcyclopropanecarboxylate.—The same procedure was used as with the *trans* isomer. From 1.62 g. (0.00782 mole) of silver *cis*-2-methylcyclopropanecarboxylate and 1.25 g. (0.00782 mole) of bromine in 25 ml. of carbon tetrachloride was obtained an estimated (from gas chromatography) 50% yield of 2-methylcyclopropyl bromide. The product consisted of 64.7 ± 0.8% *trans*- and 35.3 ± 0.8% *cis*-2-methylcyclopropyl bromide.

URBANA, ILL.

[CONTRIBUTION FROM THE MCPHERSON CHEMISTRY LABORATORY OF THE OHIO STATE UNIVERSITY COLUMBUS, OHIO]

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

BY MELVIN S. NEWMAN, WILLIAM C. SAGAR[1] AND M. V. GEORGE[2]

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The synthesis of pure 1',9-dimethyl-1,2-benzanthracene (VIII) by the steps outlined in the chart is described. It is shown that a previous preparation of VIII consisted of a mixture of VIII and 1'-methyl-1,2-benzanthracene in unknown proportions.

The synthesis of 1',9-dimethyl-1,2-benzanthracene has been reported previously.[3] Because of the small amount of hydrocarbon actually obtained[3] and because of our general interest in syntheses of such intramolecularly overcrowded[4] molecules we continued our efforts in this field. In particular, we thought that if we could obtain larger amounts of VIII and resolve it we might obtain a hydrocarbon which would be lesss easily racemized than 4,5,8-trimethyl-1-phenanthrylacetic acid[5] and 4-(1-methylbenzo[c]phenanthryl)-acetic acid[6] because of the buttressing effect of the fused benzene ring on the methyl group in the 9-position of VIII.

It was also deemed important to prepare enough 1',9-dimethyl-1,2-benzanthracene (VIII) to provide workers in the field of carcinogenesis with ample material for various tests.[7] In this paper we report the successful synthesis of over 20 grams of pure 1',9-dimethyl-1,2-benzanthracene.

When we first obtained supposedly pure VIII we had at hand over one gram which after many recrystallizations yielded colorless crystals which melted sharply at 139.1–139.5°. Because this melting point was higher than that reported (formation of an opalescent melt at 123° with clearing at 131.5–132.0°)[3] we obtained a sample from Dr. Cason.[8] For comparison with our compound we used X-ray powder photographs of the hydrocarbon and of its 2,4,7-trinitrofluorenone (TNF) complex.[8,9] The powder photographs of the hydrocarbons as well as of the TNF complexes showed that the substances were essentially identical.[10] At this point we believed that we had prepared the desired hydrocarbon in somewhat purer form than obtained previously.[3] We attributed the greater purity to the fact that we had prepared a larger quantity and hence could purify the material to a greater degree.[11]

Shortly thereafter, Dr. William Bailey reported to us that the sample of 1',9-dimethyl-1,2-benzanthracene (supposedly) which we had sent to him was not a dimethyl but a monomethyl derivative.[12] By mixed melting point and X-ray powder photographic[10] means we then determined that our supposed 1',9-dimethyl-1,2-benzanthracene, m.p. 139.1–139.5°, was actually 1'-methyl-1,2-benzan-

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[1] National Science Foundation Predoctoral Fellow, 1956–1958.

[2] National Science Foundation Postdoctoral Fellow, 1959–1960.

[3] J. Cason and D. D. Phillips, *J. Org. Chem.*, **17**, 298 (1952).

[4] F. Bell and D. H. Waring, *J. Chem. Soc.*, 2689 (1949), introduced the term "intramolecular overcrowding."

[5] M. S. Newman and A. S. Hussey, THIS JOURNAL, **62**, 2295 (1940).

[6] M. S. Newman and W. B. Wheatley, *ibid.*, **70**, 1913 (1948).

[7] In this connection VIII has long been of interest because of its similarity to 3,4-benzpyrene, one of the most potent carcingenic hydrocarbons; see L. F. Fieser and A. M. Seligman, THIS JOURNAL, **60**, 170 (1938).

[8] We wish to thank Dr. Cason for sending us the material which he and Dr. Phillips obtained.

[9] M. Orchin, L. Reggel and O. Woolfolk, THIS JOURNAL, **69**, 1227 (1947).

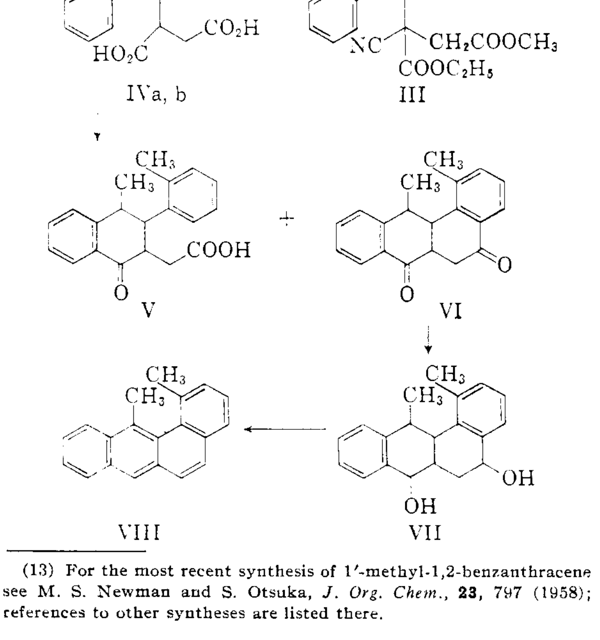
[10] We thank Dr. P. Harris of our department for supervising this part of our work and for the conclusions as to identity.

[11] This work formed the major part of the Ph.D. thesis of W. Sagar, the Ohio State University, 1958.

[12] Dr. Bailey, Shell Development Corp., Houston, Texas, had asked for samples of each of the twelve monomethyl-1,2-benzanthracenes for mass spectrographic studies. We sent a sample of our dimethyl compound along with the rest. Dr. Bailey also kindly determined the molecular weight of other hydrocarbons cited herein.

thracene.[13] However, from the mother liquors of purification of our product, a sample of unsharp melting point was isolated which by mass spectrographic analysis[12] was shown to consist of about 53% of a monomethyl-1,2-benzanthracene and 43% of a dimethyl - 1,2 - benzanthracene. This fact showed that we had undoubtedly prepared some of the desired 1',9-dimethyl-1,2-benzanthracene, but that in the final dehydrogenation step some demethylation had occurred.

These observations forced us to the conclusion that the sample of 1',9-dimethyl-1,2-benzanthracene supplied to us by Dr. Cason contained an unknown proportion of 1'-methyl-1,2-benzanthracene. Judging from the fact that the Cason and Phillips hydrocarbon gave a depression in melting point when mixed with 1'-methyl-1,2-benzanthracene,[3] one would judge that the sample used in that determination was rich in 1',9-dimethyl-1,2-benzanthracene (VIII). Judging from the fact that the X-ray powder photograph of the sample of 1',9-dimethyl-1,2-benzanthracene sent to us was almost identical to that of pure 1'-methyl-1,2-benzanthracene,[10] one would conclude that this sample was mainly the latter compound. Undoubtedly, Cason and Phillips prepared 1',9-dimethyl-1,2-benzanthracene (VIII) for the first time but, because of the small amount of hydrocarbon obtained, did not get it in a pure condition. Since both the previous synthesis[3] and the one reported herein are sound up the last (dehydrogenation) step, it appeared obvious that too high temperatures (>300°) had been used at the end and that partial loss of methyl groups had occurred. This point will be discussed below after our synthesis, outlined below, has been described.



The condensation of hydratropaldehyde with cyanoacetic ester to yield ethyl 2-cyano-4-phenyl-2-pentenoate (I), a liquid, proceeded in 73–76% yield. We do not know whether this substance was a pure substance or a mixture of *cis* and *trans* isomers. However, on treatment with *o*-tolylmagnesium bromide, a mixture of the isomers of ethyl 2-cyano-4-phenyl-3-*o*-tolylpentanoate (II) was obtained[14] which consisted mainly of one isomer. In further work only pure sharp melting II (56% yield) was used. A portion of II was hydrolyzed to the corresponding malonic acid, which was decarboxylated to yield 4-phenyl-3-*o*-tolylpentanoic acid, m.p. 101–102°, identical with a sample previously prepared by homologation of 3-phenyl-2-*o*-tolylbutanoic acid.[15]

Alkylation of II with methyl bromoacetate afforded methyl 3-carbethoxy-3-cyano-5-phenyl-4-*o*-tolylhexanoate (III) in 84% yield. Again the sharp melting point of the crude product indicated that essentially only one isomer was present. Partial hydrolysis of III followed by decarboxylation and further hydrolysis afforded 3-carboxy-5-phenyl-4-*o*-tolylhexanoic acid (IV) in essentially quantitative yield. Two isomers of IV, m.p. 182° and 163°, were isolated from this mixture.

For cyclization to VI various fractions of these acids were used and the results, as far as yields of V and VI obtained, varied considerably. Better yields of the diketone VI were obtained with higher melting acid although not much work has been done on the lower melting acid fractions. Only one pure isomer of VI was isolated although other isomers were present. For further steps, a rather crude diketone mixture could be used with no significant drop in yield. The yield of diketone was never very high. This result is similar to that obtained previously with a similar succinic acid.[16]

Attempts to cyclize the isomeric ketoacids V to yield additional quantities of diketone VI were not promising so that little further work was done with V. One ketoacid, m.p. 199°, of this structure had previously been prepared here[15] by the introduction of an acetic acid side chain in the 2-position of 4-methyl-3-*o*-tolyl-1-tetralone.[17] A mixed melting point determination with the lower melting (199°) isomer of VI obtained in the present study showed that the two were identical.

The final steps of reduction to diol VII, dehydration and dehydrogenation were carried out without isolation of any pure intermediate compounds. Reduction of VI with lithium aluminum hydride afforded in almost quantitative yield a mixture of

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(13) For the most recent synthesis of 1'-methyl-1,2-benzanthracene see M. S. Newman and S. Otsuka, *J. Org. Chem.*, **23**, 797 (1958); references to other syntheses are listed there.

(14) See F. S. Prout, E. P.-Y. Huang, R. V. Hartman and C. J. Korpics, This Journal, **76**, 1911 (1954), for an account of reaction of unsaturated cyanoesters with organometallic reagents.

(15) See Ph.D. thesis of C. C. Cochrane, the Ohio State University, 1951.

(16) M. S. Newman and R. T. Hart, This Journal, **69**, 298 (1947). This synthesis was originally designed for the synthesis of VIII, but in the form originally described had to be abandoned because of the failure of substituted desoxybenzoins to undergo the Stobbe condensation. See M. S. Newman and J. Linsk, *ibid.*, **71**, 936 (1949).

(17) Note compounds Ia and Ib, in M. S. Newman, W. C. Sagar and C. C. Cochrane, *J. Org. Chem.*, **23**, 1832 (1958).

isomeric diols, VII, suitable for further work. The dehydration was effected by heating VII in xylene at reflux after adding a small crystal of iodine.[18] The crude product from this type of dehydration reaction showed the absence of ketonic and hydroxyl absorption on infrared spectrographic analysis.

Attempts at catalytic dehydrogenation of the above mixture did not appear promising since at temperatures above 300° loss of methyl groups occurred and mixtures of mono- and dimethyl-1,2-benzanthracenes were obtained. At lower temperatures, 240–260°, dehydrogenation was incomplete. Trials of the iodine-catalyzed dehydration–aromatization procedure recently used to advantage in the synthesis of 1-bromobenzo[c]phenanthrene[19] afforded only small yields of VIII.

In the best of many attempts at dehydrogenation of the above mixtures, treatment with one equivalent of sulfur (S) at 200° for one hour yielded as much as 69% of almost pure 1′,9-dimethyl-1,2-benzanthracene (VIII), m.p. 134–136°. The purest sample of VIII which we obtained melted at 135.5–136.5°. It was almost colorless with a pale yellowish tint even after rigorous purification. Mass spectrographic analysis[12] indicated a purity of greater than 99.2%. Large melting point depressions were obtained with 1′-methyl- and 9-methyl-1,2-benzanthracenes and X-ray powder photographs also showed significant differences. Thus there remains no doubt that we have prepared pure 1′,9-dimethyl-1,2-benzanthracene (VIII) for the first time.

Experimental[20]

Ethyl 2-Cyano-4-phenyl-2-pentenoate (I).—A mixture of 268 g. of hydratropic aldehyde,[21] 226 g. of ethyl cyanoacetate, 1.4 l. of benzene, 12 g. of piperidine and 10 g. of benzoic acid was refluxed into a column topped with a phase-separating head for 7 hours during which two further additions of small amounts of piperidine and benzoic acid were made. Slightly more than the theoretical quantity of water was collected. Treatment of the products in the usual way yielded 388 g. of liquid, b.p. 70–190° at 5 mm., which on rectification afforded 334 g. (73%) of I, b.p. 136–139° at 2 mm. Redistillation of a portion through a small column yielded the analytical sample, b.p. 141° at 2 mm., n^{20}D 1.5304 (CN, 4.47; C=O, 5.71µ).

Anal. Calcd. for $C_{14}H_{15}NO_2$: C, 73.3; H, 6.6; N, 6.1. Found[22]: C, 73.3; 73.5; H, 6.7, 6.7; N, 6.2, 6.4.

Ethyl 2-Cyano-4-phenyl-3-*o*-tolypentanonate (II).—To a stirred solution of the Grignard reagent prepared from 20.5 g. of *o*-bromotoluene in 120 ml. of ether was added slowly a solution of 21.5 g. of I in 22 ml. of benzene. A yellow gummy complex separated and 30 ml. of benzene was added. After refluxing for 1 hour the reaction mixture was treated with dilute hydrochloric acid and the product worked up in the usual way. The residual oil crystallized from alcohol to yield 19.3 g. (64%) of crude II as a yellowish solid, m.p. 97–102°. Recrystallization from alcohol afforded 16.9 g. (56%) of almost colorless prisms of II, m.p. 108.0–109.5°, which was suitable for further work. In several larger scale runs over 700 g. of II was prepared in similar average yield. The analytical sample, m.p. 108.7–109.3° (CN, 4.52; C=O, 5.77 shoulder 5.89µ), was obtained as colorless crystals by recrystallization from alcohol.

Anal. Calcd. for $C_{21}H_{23}NO_2$: C, 78.5; H, 7.2; N, 4.4. Found: C, 78.7, 78.7; H, 7.2, 7.4; N, 4.6, 4.6.

Hydrolysis of a portion of II by refluxing in a solution of potassium hydroxide in ethylene glycol for 11 hours afforded an oily acid which was decarboxylated by heating at 175° for 15 minutes. Crystallization from low boiling petroleum ether (Skellysolve F) afforded 3-phenyl-2-*o*-tolylbutanoic acid, m.p. 101–102°, undepressed on mixing with a previously prepared[15] sample, in high yield.

Anal. Calcd. for $C_{18}H_{20}O_2$: C, 80.6; H, 7.5. Found[23]: C, 80.8; H, 7.4.

3-Phenyl-2-*o*-tolylbutanoyl chloride, prepared from 40.0 g. of the above acid with phosphorus pentachloride in 280 ml. of benzene was cooled and treated with 89 g. of stannic chloride. After 1 hour at 0–5° and 1 hour at 20–25° the mixture was worked up as usual to yield 33.4 g. (90%) of 1-keto-4-methyl-3-*o*-tolyl-1,2,3,4-tetrahydronaphthalene, m. p. 148–150°. Recrystallization from alcohol afforded pure ketone, m.p. 149–150°, undepressed when mixed with a sample prepared by Cochrane.[15]

Anal. Calcd. for $C_{18}H_{18}O$: C, 86.4; H, 7.3. Found[23]: C, 86.7, 86.6; H, 7.2, 7.0.

Methyl 3-Carbethoxy-3-cyano-5-phenyl-4-*o*-tolylhexanoate (III).—To a well stirred solution of 380 ml. of 0.474 *N* potassium *t*-butoxide in *t*-butyl alcohol was added a solution of 50 g. of II in 250 ml. of benzene followed by 33 g. of methyl bromoacetate. After heating at reflux for 0.5 hour, the cooled mixture was filtered to remove precipitated potassium bromide. The oil remaining after removal of solvent from the filtrate afforded 51.5 g. (84%) of colorless III, m.p. 98.4–99.6°, by crystallization from alcohol. In larger runs the yields averaged 79.6% of similar material. Over 500 g. was prepared. The analytical sample melted at 100.9–101.6° (CN, 4.57; C=O, 5.81µ).

Anal. Calcd. for $C_{24}H_{27}NO_4$: C, 73.3; H, 6.9; N, 3.6. Found: C, 73.2, 73.0; H, 7.1, 7.2; N, 3.8, 3.9.

3-Carboxy-5-phenyl-4-*o*-tolylhexanoic Acids (IVa,b).—A solution of 151 g. of III and 100 g. of sodium hydroxide in 100 ml. of water and 800 ml. of alcohol was refluxed for 30 minutes and cooled. The colorless sodium salt which had precipitated was collected by filtration and dissolved in water. Acidification yielded 124 g. (92%) of acid of m.p. 110–112° w. dec. From the above filtrate more of the same acid was obtained, so that in subsequent runs no attempt was made to separate the sodium salt. The cyanodiacid (102 g.) thus obtained was heated at 160–170° for 45 minutes to complete decarboxylation. The residue was dissolved in ethylene glycol (*ca.* 850 ml.) containing 96 g. of sodium hydroxide. This solution was distilled until the temperature of the solution reached 165°. After refluxing for 7 hours and cooling, the sodium salt was filtered and dissolved in water. Acidification produced an oil which was taken into ether and treated with Darco G-60 (decolorizing carbon, Atlas Powder Co., Wilmington, Del.). Removal of solvent yielded 51 g. (54%) of colorless acid, m.p. 173–176°. A portion was recrystallized several times from chloroform–petroleum ether to yield pure high melting isomer IVa, m.p. 182.0–182.6° (C=O, 5.82 µ).

From the glycol filtrate above there was obtained after a similar procedure 43 g. (46%) of acid, m.p. 152–156°. Recrystallization as for IVa yielded the low melting isomer IVb, m.p. 162.4–163.4° (C=O, 5.80µ).

Anal. Calcd. for $C_{20}H_{22}O_4$: C, 73.6; H, 6.8; neut. equiv., 163. Found: IVa, C, 73.3, 73.5; H, 6.9, 6.7; neut. equiv., 162. IVb, C, 73.4, 73.3; H, 7.1, 7.0; neut. equiv., 162.

In larger runs, the separations of sodium salt after hydrolyses were omitted in some cases because of slowness of filtration. In these cases a mixture of IVa and IVb, m.p. 148–166°, was obtained. This mixture did not yield as

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(18) H. Hibbert, THIS JOURNAL, **37**, 1748 (1915).

(19) M. S. Newman and D. K. Phillips, *ibid.*, **81**, 3667 (1959).

(20) Melting points are uncorrected except those of pure analytical samples which were taken with standardized thermometers. The term "worked up in the usual way" means that an ether–benzene solution of the organic reaction products was washed with alkali and/or acid and saturated sodium chloride solution, and was partly dried by percolating through a filter paper containing powdered anhydrous magnesium sulfate. Numbers in parentheses after analytical samples refer to infrared absorption bands.

(21) We thank the VanAmeringen-Haebler Co., Inc., Union Beach, N. J., for a gift of this aldehyde.

(22) Microanalyses by Galbraith Laboratories, Knoxville, Tenn., unless otherwise noted.

(23) Analyses marked 23 by Clark Microanalytical Laboratory, Urbana, Ill.

much diketone VI on subsequent processing as did purer IVa.

3,10-Diketo-1′,9-dimethyl-3,4,4a,9,9a,10-hexahydro-1,2-benzanthracene (VI).—A stirred mixture of 10.0 g. of IVa, m.p. 177–178°, 13.3 g. of phosphorus pentachloride and 150 ml. of benzene was held near 0° for 1 hour, then at reflux for 2 hours. The solvent and phosphorus oxychloride were removed under reduced pressure. To the residue dissolved in 250 ml. of *o*-dichlorobenzene was added 17.1 g. of aluminum chloride. After 1 hour at 0–5° the mixture was left at 23–25° for 14 hours and it was worked up as usual. From an ether solution of the reaction products there crystallized 3.50 g. of VI, m.p. 114–120°, and a second crop of 2.00 g., m.p. 112–119° (62% in all). Several recrystallizations from methanol afforded colorless prisms of VI, m.p. 140.5–141.5° (C=O, 5.94 μ).

Anal. Calcd. for $C_{20}H_{18}O_2$: C, 82.7; H, 6.3. Found: C, 82.7, 82.6; H, 6.3, 6.2.

For further work crude VI, m.p. in the 112–120° range, was generally used

(1-Keto-4-methyl-3-*o*-tolyl-1,2,3,4-tetrahydro-2-naphthyl)-acetic Acid (V).—From alkaline washes of the above Friedel–Crafts cyclization there was isolated (from the insoluble sodium salt which separated) 2.18 g. (23%) of light tan crude V, m.p. 191–194°. Recrystallization from benzene afforded 1.77 g. (19%) of pure V, m.p. 198.5–199.5°, which gave no melting point depression when mixed with a sample of V, m.p. 198–199°, prepared[15] by introduction of an acetic acid side chain into 1-keto-4-methyl-3-*o*-tolyl-1,2,3,4-tetrahydronaphthalene (see above under II).

Anal. Calcd. for $C_{20}H_{20}O_3$: C, 77.9; H, 6.5. Found[24]: C, 78.2, 78.4; H, 6.9, 6.8.

No appreciable further work was done with V in order to obtain an isomer of VI as sufficient VI was at hand to complete the synthesis of sufficient VIII.

3,10-Dihydroxy-1′,9-dimethyl-3,4,4a,9,9a,10-hexahydro-1,2-benzanthracene (VII).—The above diketone mixture of isomers of VI was reduced by excess lithium aluminum hydride (solution in ether) in almost quantitative yield. The crude diol mixture melted in the 150–164° range and was suitable for the final steps. Recrystallization from acetone–benzene afforded a product, m.p. 170–201° after sintering at 160°, which had no absorption in the 5–6 μ region.

Anal. Calcd. for $C_{20}H_{22}O_2$: C, 81.6; H, 7.5. Found: C, 81.5, 81.6; H, 7.6, 7.7.

1′,9-Dimethyl-1,2-benzanthracene (VIII).—In one of the best runs 9.00 g. of VII, m.p. 160–210°, 15 mg. of iodine and 30 ml. of xylene were refluxed for 60 hours to effect dehydration.[25] The crude dehydrated product, 7.9 g., obtained after the usual workup was heated with 0.99 g. of sulfur at 200° for one hour. A small amount of zinc dust was added and the heating continued for 5 minutes. The crude product was taken into benzene and chromatographed on alumina (Fisher Scientific Co., A-540 alumina), eluted with benzene and crystallized from acetone–methanol to yield 5.45 g. (69%) of VIII, m.p. 134.5–136.0°. Vacuum sublimation, followed by recrystallization from acetone–methanol, yielded pure VIII as dense prisms,[26] m.p. 135.5–136.5°. The crystals had a faint yellow tinge which was not removed (nor was the m.p. raised) by conversion to the trinitrofluorenone (TNF)[9] derivative (see below), recrystallization thereof, further chromatography, and recrystallization from acetone–methanol.

Anal. Calcd. for $C_{20}H_{16}$: C, 93.7; H, 6.3. Found: C, 93.8, 93.8; H, 6.4, 6.4.

A mixture of pure VIII and pure 9-methyl-1,2-benzanthracene,[27] m.p. 138.5–139.5°, melted over the range 105–120° and a mixture of VIII and pure 1′-methyl-1,2-benzanthracene,[13] m.p. 139–140°, melted over the range 108–133°. X-Ray powder photographs[10] of VIII, 9-methyl- and 1′-methyl-1,2-benzanthracenes were all different.

The TNF complex of VIII was readily prepared in good yield in benzene and formed black elongated prisms, m.p. 144.5–145.5°, after one recrystallization from benzene.

Anal. Calcd. for $C_{33}H_{21}N_3O_7$: C, 69.3; H, 3.7; N, 7.4. Found: C, 69.6; H, 3.6; N, 7.4.

The ultraviolet absorption spectrum of VIII in 95% alcohol was characterized by the following maxima in mμ (log *E*): 225 (4.36), 238 (4.19), 263 (4.52), 288 (4.76) and 355 (3.95). Shoulders were observed at 277 (4.60), 298 (4.64), 326 (3.66) and 340 (3.85). In general the spectrum of VIII showed less fine structure than that of either the 1′-methyl- or 9-methyl-1,2-benzanthracenes as is typical for the spectra of intramolecularly overcrowded hydrocarbons.[28]

When 5.29 g. of the diol VII mixture in 18 ml. of xylene containing 10 mg. of iodine was held at reflux for 60 hours, a 4.6% yield of VIII was obtained.[19] By heating the remainder of the reaction products with 0.45 g. of sulfur at 220° for 30 minutes 29% more of VIII was obtained. Hence this over-all procedure was abandoned in favor of a short dehydration period with iodine in xylene (see above) followed by sulfur dehydrogenation.

The relatively large amount of VIII prepared by Dr. M. V. George involved the following amounts of materials (approximate yields in parentheses): hydratropic aldehyde (725 g.) → I (941 g., b.p. 145–150° at 2 mm., 76%); I (920 g.) → II (708 g., m.p. 107–109°, 55%); II (580 g.) → III (564 g., m.p. 96–98°, 80%); III (549 g.) → IVa,b (365 g., m.p. 148–166°, 91%); IV mixture of a and b (340 g.) → V (87 g., m.p. 198–200°, 27%) and VI (62 g., m.p. 126–134°, 21%) and 53 g (17%) of a ketoacid, m.p. 147–152°, isomeric with V with which no further work was done; VI (50 g.) → VII (50 g., m.p. 160–210°, 99%); VII (50 g.) → VIII (24.8 g., m.p. 134–136°, 58%).

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[24] Analysis by Mr. Jack Kraus, the Ohio State University.

[25] This long period of refluxing is surely unnecessary, as after one hour only 12% of diol remained detectable. However, we let the refluxing continue for the longer period because we hoped that more final VIII would be formed as in the case mentioned.[19]

[26] Dr. William Bailey (see ref. 12) reports that this compound is over 99% dimethyl-1,2-benzanthracene.

[27] M. S. Newman and R. Gaertner, This Journal, **72**, 264 (1950).

[28] See spectra of 4,5-dimethylphenanthrene, R. N. Jones, *ibid.*, **63**, 313 (1941), and of 4,5-dimethylchrysene, No. 454, in "Ultraviolet Spectra of Aromatic Compounds," R. A. Friedel and M. Orchin, John Wiley and Sons, Inc., New York, N. Y., 1951.