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

A New Synthesis of Benzo(c)phenanthrene: 1,12-Dimethylbenzo(c)phenanthrene[1]

BY MELVIN S. NEWMAN AND MILTON WOLF[2]

A new method for the elaboration of the benzo(c)phenanthrene ring system is described and illustrated by the synthesis of 1-methyl, 1,12-dimethyl- and 1,5,8,12-tetramethylbenzo(c)phenanthrenes. The reactions are outlined in Fig. 1.

In 1940, the theory leading to the prediction of optical activity in molecules having the 4,5-dimethylphenanthrene nucleus was outlined.[3] Since this time the prediction has been verified by the partial resolution of three compounds: 4,5,8-trimethyl-1-phenanthrylacetic acid,[4] 4-(1-methylbenzo(c)phenanthryl)-acetic acid[5] and 4',4'',6',6''-tetramethyl-3,4,5,6-dibenzphenanthrene-9,10-dicarboxylic acid.[6] In each case the optically active forms exhibited great instability, complete racemization resulting in several hours.[7]

In order to prepare compounds whose optically active forms should possess more stability we have developed a new synthesis for the benzo(c)phenanthrene nucleus which has proved adaptable to the synthesis of 1-methylbenzo(c)phenanthrene,[5] and the 1,12-dimethyl- and 1,5,8,12-tetramethyl derivatives. It is hoped that derivatives adapted for optical resolution can be prepared by suitable variations in the scheme. This phase is now being studied in this Laboratory.

The synthesis is outlined in Fig. 1. Two steps are noteworthy: the 1,4-addition of *o*-tolylmagnesium bromide to ethyl *o*-methylbenzalmalonate (I) which went in over 70% yield; and the double homologation of the substituted malonic acid, III, to the substituted glutaric acid, IV, which went in 40% yield. Only a single attempt was made to homologate the malonic ester *via* the alcohol, V, the di-*p*-nitrobenzenesulfonate, VI, and the dicyanide (not isolated). Although the over-all yield in this variation was poor it is felt that considerable improvement is possible. The last few steps went well except for the final aromatization which gave about 19% of VIII in the best experiment. The yield was better (45%) in the final step to IX from VII.

By adding *o*-tolylmagnesium bromide to benzalmalonic ester *o*-methylbenzhydrylmalonic ester was obtained from which 1-methylbenzo(c)phenanthrene (X) was similarly elaborated. The melting point of the X produced this way was not depressed by mixing with a sample of X prepared previously[5] nor was the X-ray diffraction pattern different.[8] The ultraviolet spectra of benzo(c)phenanthrene, the 1-methyl, 1,12-dimethyl and 1,5,7,12-tetramethyl derivatives are given in Fig. 2. We wish to thank Dr. Henry Hemmendinger of General Aniline and Film Corporation for these determinations. The most notable feature of these curves lies in the region 310 to 370 mμ where there is considerable loss of fine structure in the methyl derivatives. This loss of fine structure is comparable to that observed for 4,5-dimethylchrysene[9] and may be a general feature in compounds characterized by intramolecular overcrowding.[10]

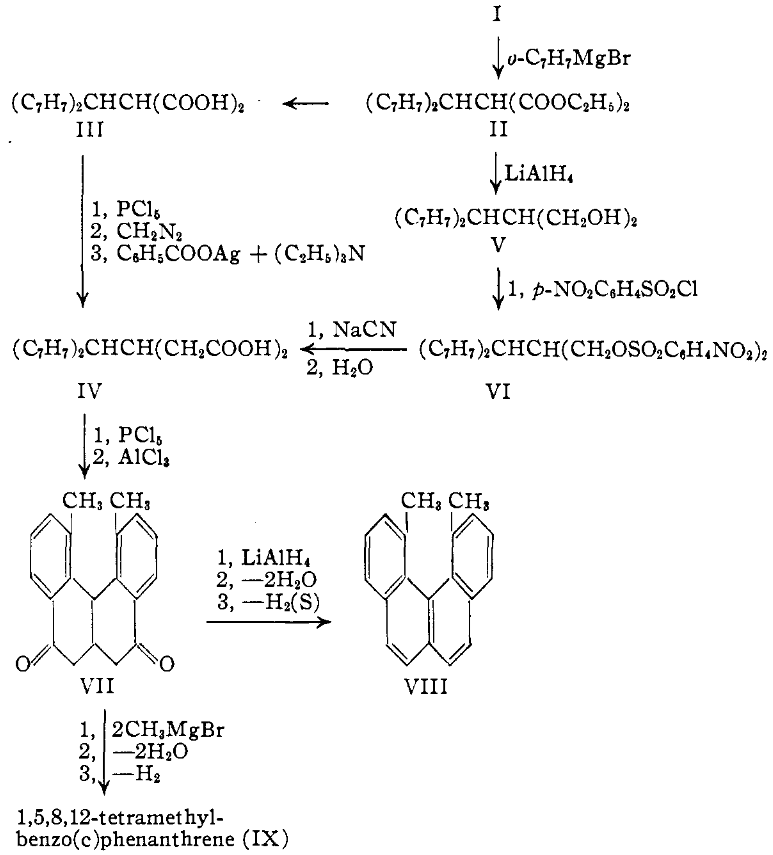

Fig. 1.—Synthesis of methylbenzo(c)phenanthrenes.

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[1] Presented before the Twelfth International Congress of Pure and Applied Chemistry, New York, 1951.

[2] Taken from The Ohio State University Ph.D. thesis of Milton Wolf.

[3] M. S. Newman, THIS JOURNAL, **62**, 2295 (1940).

[4] M. S. Newman and A. S. Hussey, *ibid.*, **69**, 978 (1947); *ibid.*, **69**, 3023 (1947).

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

[6] F. Bell and D. H. Waring, *J. Chem. Soc.*, 2689 (1949).

[7] We have previously (ref. 4) termed this type of optical activity as "optical activity of the 4,5-phenanthrene type." However the title suggested (ref. 6) "optical activity due to intramolecular overcrowding" seems preferable and we will adopt this nomenclature.

[8] We are indebted to Dr. S. Gross of the General Aniline and Film Corporation, Easton, Pa., for these X-ray powder diffraction pattern analyses.

[9] R. N. Jones, THIS JOURNAL, **63**, 313 (1941).

[10] See also M. S. Newman and H. S. Whitehouse, *ibid.*, **71**, 3664 (1949); G. M. Badger, J. W. Cook, *et al.*, *J. Chem. Soc.*, 2326 (1950), and ref. 4.

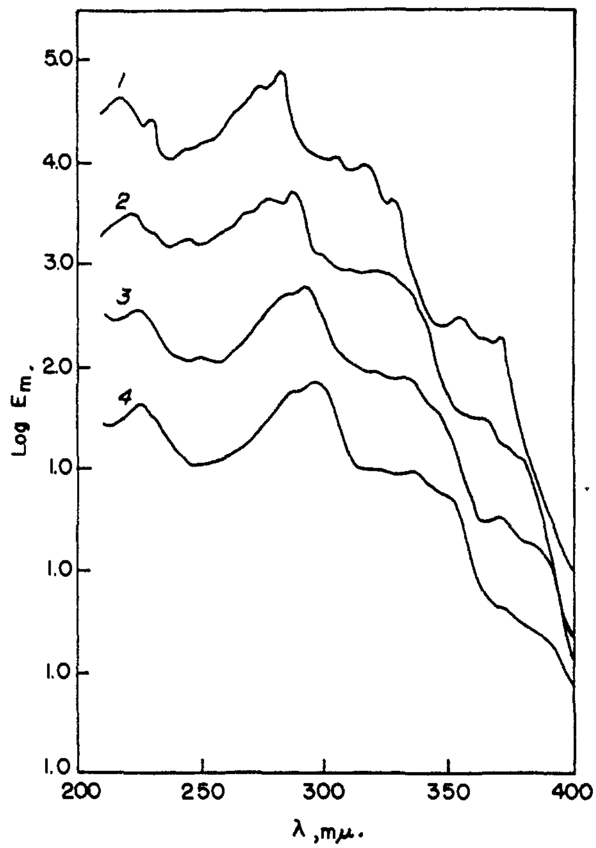

Fig. 2.—Ultraviolet absorption spectra: 1, benzo(c)phenanthrene; 2, 1-methylbenzo(c)phenanthrene; 3, 1, 12-dimethylbenzo(c)phenanthrene; 4, 1,5,8,12-tetramethylbenzo(c)phenanthrene. Curves 2,3 and 4 are dropped one, two and 3 log E_m units, respectively, to avoid overlapping with curve 1.

Experimental[11]

Ethyl 2-Methylbenzalmalonate (I).—A mixture of 284 g. of *o*-tolualdehyde,[12] 445 g. of ethyl malonate, 750 cc. of benzene, 7.5 g. of benzoic acid and 9 cc. of piperidine was refluxed into a 60-cm. packed column (glass helices) topped by a phase-separating head until no more water was being collected (about 20 hours). In all 30 cc. (about 70% of theory) of water was obtained. After suitable treatment 454 g. (73.5%) of I, b.p. 126–129° at 0.6–0.8 mm., was obtained after a forerun of 231 g. which contained unreacted aldehyde and ester. This fraction was processed again as above to yield an additional 15.8% of I (total yield—89.3%). A sample, b.p. 128° at 0.6–0.7 mm., $n^{25}D$ 1.5266, was taken for analysis.

Anal. Calcd. for $C_{15}H_{18}O_4$: C, 68.7; H, 6.9. Found: C, 68.7, 68.7; H, 6.9, 6.9.

Ethyl 2,2′-Dimethylbenzhydrylmalonate (II).—To a well stirred solution of the Grignard reagent from 18.0 g. of *o*-bromotoluene, 3 g. of magnesium and 100 cc. of ether was added dropwise a solution of 25 g. of I in 25 cc. of ether, the temperature being held at 0–5° during the addition (one hour). After stirring for two hours at room temperature the mixture was hydrolyzed and the desired ester obtained as a viscous almost colorless oil, b.p. 175–190° at 0.7–0.8 mm., in 72% yield. On standing the oil crystallized, the analytical sample, recrystallized from low boiling petroleum ether, melting at 52.8–53.8°.

Anal. Calcd. for $C_{22}H_{26}O_4$: C, 74.6; H, 7.4. Found: C, 74.4, 74.1; H, 7.3, 7.5.

In other runs in which the above procedure was varied by adding Grignard reagent to ester at temperatures of 0 and −80°, the yields were 72.6 and 73.3%, respectively.

The malonic acid, III, was obtained from II in 92.7% yield by alkaline saponification followed by crystallization of the free acid from benzene. The analytical sample melted at about 194°, dec.

Anal. Calcd. for $C_{18}H_{18}O_4$: C, 72.5; H, 6.1. Found: C, 72.7, 72.9; H, 6.0, 6.0.

2-Methylbenzhydrylmalonic Acid.[13]—In a similar way a solution of 860 g. (3.47 moles) of ethyl benzalmalonate[14] in 900 cc. of ether was added dropwise to the Grignard reagent prepared from 675 g. (3.95 moles) of *o*-bromotoluene, 96 g. of magnesium and 750 cc. of ether. The addition took seven hours and the temperature was maintained at 0–5° by an ice–salt cooling bath. After warming to room temperature and standing for 12 hours the homogeneous mixture was treated with an excess of dilute hydrochloric acid. On rectification there was obtained 980 g. (83% calculated on benzal ester) of ethyl 2-methylbenzhydrylmalonate, b.p. 182–186° at 0.9–1.5 mm. After alkaline saponification the corresponding acid, m.p. 178.2–180.0° dec., was obtained in 92% yield. The analytical sample, recrystallized from acetic acid–water, melted at 182.4–182.8° dec.

Anal. Calcd. for $C_{17}H_{16}O_4$: C, 71.9; H, 5.7. Found: C, 72.0; H, 5.5.

β-(2,2′-Dimethylbenzhydryl)-glutaric Acid (IV) (a) From III.—To a hot well stirred suspension of 38.6 g. of phosphorus pentachloride in 100 cc. of dry benzene was added portionwise 27.0 g. of III. After refluxing, followed by removal of the benzene and phosphorous oxychloride under reduced pressure, the viscous acid chloride was taken up in 100 cc. of dry ether and this solution added dropwise to 700 cc. of a stirred ethereal solution at 0° of an excess of diazomethane. The crystalline bisdiazomethyl ketone which separated was collected, made into a slurry with 100 cc. of pure dry acetone and added rapidly to a stirred solution of 500 cc. of methanol containing 10 cc. of a saturated solution of silver benzoate in triethylamine.[15] The evolution of nitrogen began immediately, the solution turned dark, and a silver mirror was gradually formed. Five or six additions of solid silver benzoate were necessary to maintain a brisk evolution of nitrogen. After four hours, 2600 cc. (64%) of nitrogen had been collected and a further addition of silver benzoate caused no further action. The ester produced was distilled and then saponified with potassium hydroxide in 80% alcohol. On cooling some potassium salt separated which, on acidification, yielded 7.73 g. of IV, m.p. 205.0–207.0°. From the remaining reaction mixture there was obtained an additional 4.2 g. of good acid, making a total of 11.93 g. (40.4%). The analytical sample, thrice recrystallized from acetone–benzene, melted at 207.5–208.0°.

Anal. Calcd. for $C_{20}H_{22}O_4$: C, 73.6; H, 6.8; neut. equiv., 163. Found: C, 73.5, 73.8; H, 6.7, 6.9; neut. equiv., 163.

(b) From II.—The malonic ester was reduced by treating 20.0 g. of II with 4.3 g. of lithium aluminum hydride in 300 cc. of ether at reflux for one hour. The desired 2-(2,2′-dimethylbenzhydryl)-1,3-propanediol (V) was obtained in 95.5% yield as a viscous oil, b.p. 196–200° at 0.5–0.6 mm. On trituration with petroleum ether, b.p. 65–70° (Skellysolve B), the oil crystallized completely to solid V, m.p. 79.3–80.4.° The analytical sample, crystallized from benzene–Skellysolve B, melted at 79.4–80.4°.

Anal. Calcd. for $C_{18}H_{22}O_2$: C, 80.0; H, 8.2. Found: C, 79.9, 80.0; H, 7.9, 7.7.

The bis-*p*-nitrobenzenesulfonate, VI, m.p. 197.5–198.5° dec. when pure, was formed in about 74% yield in a single experiment.

Anal. Calcd. for $C_{30}H_{28}O_{10}N_2S_2$: C, 56.2; H, 4.4. Found: C, 56.5, 56.5; H, 4.7, 4.4.

In a single try 5.0 g. of VI in 150 cc. of acetone was refluxed with a solution of 0.1 g. of sodium iodide and 3.3 g. of potas-

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[11] All melting points were taken in Pyrex tubes and were corrected. Analyses by the Clark Microanalytical Laboratory, Urbana, Illinois.

[12] L. I. Smith and M. Bayliss, *J. Org. Chem.*, **6**, 437 (1941). We used the ethyl orthoformate procedure.

[13] This acid was first prepared by Dr. Hugh Anderson and the acid used in the later work was that prepared by him. Recently Dr. K. Takemura has improved the yield and this procedure is that described herein.

[14] C. F. H. Allen and F. W. Spangler, *Org. Syntheses*, **25**, 42 (1945).

[15] M. S. Newman and P. F. Beal, THIS JOURNAL, **72**, 5163 (1950).

sium cyanide in 100 cc. of water. The non-homogeneous reaction mixture was stirred at room temperature for 20 hours and at reflux for 4 hours. The crude product thus obtained was hydrolyzed by refluxing with 100 cc. of concentrated hydrochloric acid and 25 cc. of acetic acid for one day. The acid fraction of the hydrolysis products yielded 0.60 g. (22%) of acid, m.p. 205.6–206.8°, which gave no depression when mixed with IV. This procedure can undoubtedly be improved.

5,6,6a,7,8,12b-Hexahydro-1,12-dimethylbenzo(c)phenanthrene-5,8-dione (VII).—The acid chloride from 7.0 g. of IV prepared in the usual way using phosphorus pentachloride was dissolved in 100 cc. of pure *s*-tetrachloroethane, cooled to 0°, and treated portionwise with 6.3 g. of aluminum chloride. The mixture turned tan then deep red. After 5 minutes the cooling bath was removed and the mixture allowed to stand with stirring for 29 hours at room temperature. After 17 hours the color had changed to chocolate brown and a yellow complex had separated. After hydrolysis with ice and acid the solvent was steamed off and the product taken up in benzene–ether and washed with alkali. By crystallization a total of 3.91 g. (62%) of diketone, VII, m.p. 218–222°, was obtained.

The analytical sample, crystallized from absolute alcohol, formed colorless needles, m.p. 222.2–222.8° with darkening.

Anal. Calcd. for $C_{20}H_{18}O_2$: C, 82.7; H, 6.3. Found: C, 82.9, 82.9; H, 6.1, 6.2.

The solution containing the acid chloride prepared from 1.5 g. of IV and 2.1 g. of phosphorus pentachloride in 12 cc. of benzene was cooled to −5° and treated with 5.3 g. of anhydrous stannic chloride, a yellow complex forming immediately. After 5 minutes the mixture was allowed to stand at 20° for 45 minutes and was then poured on ice. Extraction of a benzene–ether solution of the product with alkali followed by acidification afforded 1.40 g. (98.5%) of a colorless solid, m.p. 165.4–167.4°. This was the ketoacid, 1,2,3,4-tetrahydro-4-keto-8-methyl-1-*o*-tolyl-2-naphthaleneacetic acid. The analytical sample, crystallized from benzene, formed small colorless needles, m.p. 167.6–168.6°.

Anal. Calcd. for $C_{20}H_{20}O_3$: C, 77.9; H, 6.5. Found: C, 77.5, 77.5; H, 6.4, 6.4.

The 2,4-dinitrophenylhydrazone, m.p. 278.5–279.6° dec. when inserted in a copper block at 260° and heated rapidly, crystallized in orange-red plates from aqueous dioxane.

Anal. Calcd. for $C_{26}H_{24}O_6N_4$: C, 63.9; H, 5.0. Found: C, 64.0, 64.3; H, 5.1, 5.2.

The same ketoacid was formed in 90% yield by cyclization of acid IV in anhydrous hydrogen fluoride.

1,12-Dimethylbenzo(c)phenanthrene (VIII).—The diketone, VII, was reduced by lithium aluminum hydride in ether to the corresponding diol, 5,6,6a,7,8,12b-hexahydro-1,12-dimethylbenzo(c)phenanthrene-5,8-diol, in quantitative yield. The analytical sample of the diol, crystallized from benzene, formed colorless fine needles, m.p. 213.0–214.0°.

Anal. Calcd. for $C_{20}H_{22}O_2$: C, 81.6; H, 7.5. Found: C, 81.8, 81.5; H, 7.6, 7.5.

A mixture of 3.25 g. of diol and 0.352 g. of sulfur was heated to 195° in a small distilling flask whereupon dehydration started. After 20 minutes at 205–210° the dehydration was ended and the flask was heated at 225° for 75 minutes. Vacuum distillation at 0.06–0.07 mm. yielded two fractions: I, 1.16 g., bath *T* at 200–240°; and II, 0.70 g., bath *T* at 240–280°. Chromatographic separation over alumina using benzene afforded material from the first two 50-cc. portions of eluate which when crystallized from alcohol yielded a total of 0.545 g. (18.9%) of crude VIII, m.p. 95–102°. Recrystallization yielded a purer sample, m.p. 105.8–107.2°, as elongated prisms having a yellow tinge.

Anal. Calcd. for $C_{20}H_{16}$: C, 93.7; H, 6.3. Found: C, 93.7, 93.8; H, 6.2, 6.1.

We were unable to prepare a pure picrate or 2,4,7-trinitrofluorenone (TNF) derivative[16] from VIII.

1,5,8,12-Tetramethylbenzo(c)phenanthrene (IX).—A solution of 0.95 g. of VII in 25 cc. of benzene was treated at reflux for 30 minutes with the Grignard reagent prepared from 2.8 g. of methyl iodide. The crude product obtained after hydrolysis with ammonium chloride solution was heated with 0.105 g. of sulfur first to 180° at which temperature dehydration occurred and then at 220–225° for 75 minutes for dehydrogenation. The vacuum distillate yielded a red oil which partly crystallized. After chromatographic purification in benzene over alumina there was obtained 0.30 g. (32%) of glistening platelets having a yellow tinge, m.p. 175–176.5° and 0.125 g. (13%) of more yellow material, m.p. 167–171°. A pure sample of IX recrystallized from benzene–alcohol for analysis melted at 176.2–177.0°.

Anal. Calcd. for $C_{22}H_{20}$: C, 92.9; H, 7.1. Found: C, 93.0, 93.0; H, 6.8, 7.0.

The TNB derivative formed dense transparent red prisms, m.p. 139.6–141.2°, from alcohol. Analysis indicated that this complex had two molecules of hydrocarbon to one of TNB.

Anal. Calcd. for $C_{50}H_{43}O_6N_3$: C, 76.8; H, 5.5; N, 5.4. Found: C, 76.8, 77.0; H, 6.2, 5.9; N, 5.5, 5.4.

β-**(2-Methylbenzhydryl)-glutaric Acid.**—The diacid chloride was prepared by adding 62.4 g. (0.300 mole) of phosphorus pentachloride with swirling to a suspension of 42.6 g. (0.150 mole) of *o*-methylbenzhydrylmalonic acid in 300 ml. of dry benzene. After several hours at room temperature the acid and phosphorus pentachloride all went into solution, and the evolution of hydrogen chloride ceased. The benzene and phosphorus oxychloride were removed under reduced pressure at 35–40°.

The acid chloride dissolved in 250 cc. of dry ether was added dropwise with stirring to a solution of diazomethane prepared from 113 g. of *n*-nitrosomethylurea in 1150 ml. of ether at 0–5°. After all of the acid chloride had been added, the reaction mixture was stirred for one hour at 0–5°, and was then allowed to stand at room temperature for 16 hours. The mixture was then concentrated under reduced pressure at room temperature to a volume of about 250 cc. The dark red supernatant liquid was decanted from the white crystalline diazoketone. The diazoketone was washed once with ether by decantation, the washing being combined with the above decantate. The crystalline diazoketone was dissolved in 450 cc. of methanol and about 25 cc. of a saturated solution of silver benzoate in triethylamine was quickly added.[15] About 48% of the theoretical amount of nitrogen was collected in 1–2 hours. After no further gas was being evolved, the mixture was refluxed for two hours and filtered. The solvent was removed and the brown oily residue was dissolved in benzene and washed successively with dilute hydrochloric acid, water, and carbonate. The benzene was then removed and the residue was refluxed on a steam-bath for 16 hours with a solution of 10 g. of potassium hydroxide in 20 cc. of water and 50 cc. of alcohol. From this hydrolysis 18.0 g. (38.5%) of pale orange acid, m.p. 186–195°, was isolated. This was recrystallized from acetone–benzene to give 14.1 g. (30%) of colorless acid, m.p. 198.0–200.4° dec.

A sample[13] for analysis melted at 200.2–200.6°. Calcd. for $C_{19}H_{18}O_2$: C, 73.1; H, 6.4. Found: C, 72.9; H, 6.5.

The red solution decanted from the crystalline diazoketone (see above) was concentrated further under reduced pressure to a volume of about 150 cc., diluted with 200 cc. of methanol, and treated with silver benzoate in triethylamine.[15] About 12% of the theoretical amount of gas was collected during one hour. This reaction mixture was worked up in a similar manner to that above to give 1.2 g. (2.5%) of good acid, m.p. 194.0–196.0°.

5,6,6a,7,8,12b-Hexahydro-1-methylbenzo(c)phenanthrene 5,8-dione.—The diacid chloride from 5.0 g. of *β*-(2-methylbenzhydryl)-glutaric acid, prepared as in the case of the preparation of VII, was dissolved in 60 cc. of *s*-tetrachloroethane and the solution was cooled to 0°. A total of 4.68 g. of anhydrous aluminum chloride was added in several portions during ten minutes, the color turning orange-red and then red. After a further 31 hours at 20° the red brown solution was decomposed with ice and acid and solvent removed by steaming. From the neutral portion there was obtained 1.85 g. (42%) of tan needles, m.p. 180.6–181.6°. The colorless analytical sample, recrystallized from benzene–Skellysolve B, melted at 181.0–182.0°.

Anal. Calcd. for $C_{19}H_{16}O_2$: C, 82.6; H, 5.8. Found: C, 82.7, 82.9; H, 5.9, 5.6.

1-Methylbenzo(c)phenanthrene.—A solution of 1.25 g. of the above diketone was reduced with an excess of ethereal lithium aluminum hydride as in the preparation of VIII.

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(16) M. Orchin and E. O. Woolfolk, THIS JOURNAL, **68**, 1727 (1946).

The mixture of diols thus produced, 1.18 g. in all, was placed in a small distilling flask with 0.135 g. of sulfur and heated first to 180° when dehydration occurred and then to 225–230° for one hour for dehydrogenation. After adding a little zinc dust the material was vacuum distilled to yield 0.62 g. (60.5%) of a light yellow oil which soon crystallized. Repeated crystallization from Skellysolve B afforded a total of 0.35 g. (34%) of good 1-methylbenzo(c)phenanthrene, m.p. 136.8–141.0°. A pure sample, m.p. 139.6–141.0°, was compared with a sample of the same hydrocarbon previously synthesized by a different method[6] and found to be identical by mixed m.p. and by X-ray powder diffraction analysis.[8]

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, DUKE UNIVERSITY]

Proportions of Isomeric Ketone Enol Acetates from O-Acetylations of Methyl-methylene Ketones with Isopropenyl Acetate[1]

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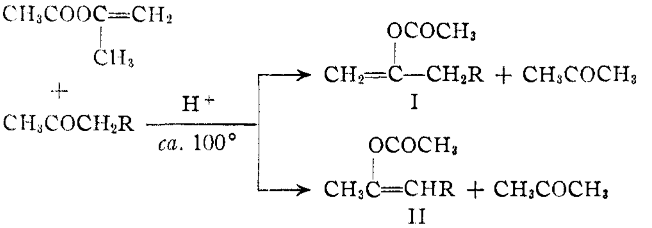
The structures of ketone enol acetates produced by the O-acetylation of methyl-methylene ketones by the isopropenyl acetate method were determined. Methyl *n*-hexyl ketone gave entirely the methylene derivative, whereas methyl neopentyl ketone formed entirely the methyl derivative. Other methyl-methylene ketones produced mixtures of the two isomers. These structures were based on those of corresponding β-diketones produced on C-acetylation with acetic anhydride by boron trifluoride. The alkali extraction method for separating isomeric β-diketones was refined and developed. Syntheses of a new ketone and of several new ketone enol acetates and β-diketones are described.

The O-acetylation of ketones to form ketone enol acetates may be effected with acetic anhydride,[4] ketene[5] or isopropenyl acetate[5,6] in the presence of a catalytic amount of strong acid. The reaction involves presumably the acid-catalyzed enolization of the ketone, and the acetylation of the resulting enol. The O-acetylation of methyl-methylene ketones may form the methyl derivative (I) or the methylene derivative (II), depending on whether a methyl or methylene hydrogen is enolized. The isopropenyl acetate method is particularly convenient and generally produces good yields of the ketone enol acetates; it involves an acetate–ketone exchange and the volatilization of the by-product acetone (equation 1).



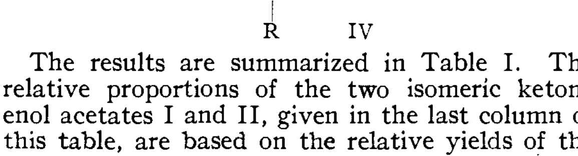
$$\underset{\displaystyle CH_3}{CH_3COOC{=}CH_2} + CH_3COCH_2R \xrightarrow[ca.\ 100°]{H^+} \begin{cases} \underset{\text{I}}{CH_2{=}\overset{\displaystyle OCOCH_3}{C}{-}CH_2R} + CH_3COCH_3 \\ \underset{\text{II}}{CH_3\overset{\displaystyle OCOCH_3}{C}{=}CHR} + CH_3COCH_3 \end{cases} \quad (1)$$

This method has previously been employed to prepare the ketone enol acetates of several methyl-methylene ketones[6]; but apparently the structure of the product was established only for the acetate from methyl *n*-amyl ketone which gave exclusively the methylene isomer (II, R = C_4H_9).[5]

In the present investigation, the relative proportions of methyl and methylene derivatives produced from various methyl–methylene ketones by the isopropenyl acetate method were determined. These proportions were established by effecting the C-acetylations of the ketone enol acetates with acetic anhydride by boron trifluoride to form corresponding β-diketones (equations 2 and 3). It has previously been shown[5] that ketone enol acetates having structures I and II, as determined by ozonolysis, give β-diketones having structures III and IV, respectively. This conversion of the O-acetyl derivatives to the C-acetyl derivatives with the retention of the methyl or methylene structure is to be expected on the basis of the mechanism.[7]

The isomeric β-diketones III and IV were readily separated by the preferential extraction of the relatively more acidic methyl derivative (III) from an ether solution of the two by means of dilute alkali, according to the general method described previously.[8] This alkali extraction method, which has now been refined and developed, gave relative yields of isomeric β-diketones that were reproducible to within ±3% with mixtures of isomers containing 10% or less of the methyl derivative, and to within ±6% with mixtures containing 50% or more of the methyl derivative.

$$(CH_3CO)_2O + \text{I} \xrightarrow{BF_3} \xrightarrow{NaOAc} \underset{\text{III}}{CH_3COCH_2COCH_2R} + CH_3COOH \quad (2)$$



$$(CH_3CO)_2O + \text{II} \xrightarrow{BF_3} \xrightarrow{NaOAc} \underset{\text{IV}}{CH_3CO\underset{\displaystyle R}{C}HCOCH_3} + CH_3COOH \quad (3)$$

The results are summarized in Table I. The relative proportions of the two isomeric ketone enol acetates I and II, given in the last column of this table, are based on the relative yields of the two isomeric β-diketones III and IV. Results with dibenzyl ketone, which can form only a methylene derivative, are also given in Table I.

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[1] This work was supported in part by a grant from the Duke University Research Council.

[2] E. I. du Pont de Nemours and Co. Fellow, 1950–1951.

[3] Carbide and Carbon Chemicals Co. Fellow, 1949–1950.

[4] P. Z. Bedoukian, THIS JOURNAL, **67**, 1430 (1945).

[5] F. G. Young, F. C. Frostick, Jr., J. J. Sanderson and C. R. Hauser, *ibid.*, **72**, 3635 (1950).

[6] W. M. Quattlebaum, Jr., and C. A. Noffsinger, U. S. Patent 2,466,737 (1949); *C. A.*, **43**, 7037 (1949); see also H. J. Hagemeyer, Jr., and D. C. Hull, *Ind. Eng. Chem.*, **41**, 2920 (1949).

[7] C. R. Hauser, F. C. Frostick, Jr., and E. H. Man, THIS JOURNAL, **74**, 3231 (1952).

[8] C. R. Hauser and J. T. Adams, *ibid.*, **66**, 345 (1944).