

liquid crystalline solution more concentrated than the equilibrium isotropic phase, the first small additions of lithium chloride lower the soap concentration at which separation occurs. Thus lithium chloride appears to facilitate the formation of the more orderly molecular arrangement of lithium palmitate molecules, represented by superneat soap, regardless of whether the "concentration" of the soap is increased (as along BC) or decreased (as along CD). This result is analogous to the finding that addition of electrolytes to dilute isotropic solutions of detergents increases the proportion of dissolved material present as organized colloidal micelles as judged from solubilization experiments.^{13,14}

Similarly, the isotropic solution from which middle soap separates is progressively more dilute as the salt content is increased. Reference to isothermal diagrams for systems of sodium soaps with sodium chloride and water⁵ or potassium soaps with potassium chloride and water^{7,8} shows that for these systems, the soap concentration at which middle soap separates is increased by the first small additions of salt and subsequently decreased by further additions. If such an effect oc-

(13) J. W. McBain, R. C. Merrill and J. R. Vinograd, *THIS JOURNAL*, **63**, 870 (1941).

(14) G. S. Hartley, *J. Chem. Soc.*, 1968 (1938).

curs with lithium palmitate, the salt content for it must be less than 0.2%.

The other striking effect of small additions of lithium chloride on the phase behavior of lithium palmitate in water is the diminished solubility of the more solid phases in middle soap (Curves HJ). This effect is parallel to the results found for sodium and potassium soaps with salt.

Summary

The phase behavior of lithium palmitate in water has been determined and compared with that of sodium palmitate. Comparison has also been made of available phase diagrams for sodium and potassium soaps. In concentrated soap systems and in dilute ones, the temperatures and compositions of corresponding points vary in a regular manner with the atomic number of the alkali cation, but at intermediate compositions (involving the middle soap phase) no simple general trends are apparent.

The effect of up to 2% of lithium chloride on the phase behavior of lithium palmitate and water has also been determined. The effect of lithium chloride can be regarded as favoring the formation of more highly organized phases over those in which more nearly random molecular distribution occurs.

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[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

The Preparation of Derivatives of Chrysene by Means of the Robinson-Mannich Base Synthesis of Unsaturated Ketones

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Robinson and his co-workers² have developed an ingenious method for converting a cyclic ketone into an unsaturated cyclic ketone containing one additional hydroaromatic ring. The method consists in treating the sodium enolate of the cyclic ketone, or of its carbethoxy derivative, with the methiodide of a Mannich base such as 1-diethylaminobutanone-3. The latter compound acts as a source of methylvinyl ketone for Michael addition, which is followed by cyclization. In this manner, for example, 2-carbethoxycyclohexanone was converted into 2-keto-4a-carbethoxyoctahy-

dronaphthalene, which could be hydrolyzed and decarboxylated to the corresponding octalone.

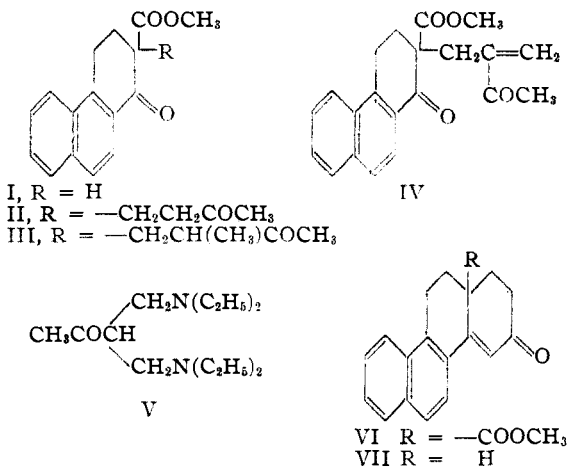
We have now applied this series of reactions to 2-carbomethoxy-1-keto-1,2,3,4-tetrahydropheanthrene (I), leading ultimately to the unsaturated ketone VII and to a number of other new derivatives of chrysene. However, in the application of the method of du Feu, McQuillin and Robinson² to the keto ester I, poor over-all yields of VII resulted and a pure product was obtained only with difficulty. These drawbacks, which are borne out by some of the experiences of Robinson and co-workers² in other examples, constitute a serious limitation in the application of the method to ketones which are not readily available. In the most favorable cases reported by these investiga-

(1) Wisconsin Alumni Research Foundation Research Assistant, 1941-1942.

(2) du Feu, McQuillin and Robinson, *J. Chem. Soc.*, 53 (1937); for a recent paper in this series see McQuillin and Robinson, *ibid.*, 586 (1941).

tors the over-all yields from the cyclic ketone to the higher unsaturated ketone were 38 to 42%, while usually the yields were as low as 12 to 25%.

Therefore a critical examination of this series of reactions was undertaken, employing the keto ester I. Since all of the intermediate compounds were crystalline solids, this case has been particularly suitable for developing favorable conditions for each step, and for determining some of the possible pitfalls of the method.



By using one equivalent of sodium methoxide to prepare the sodium salt of the keto ester I, and treating this with the methiodide from pure 1-diethylaminobutanone-3, it was possible to isolate the diketone ester II in 92% yield. This compound was usually accompanied by varying amounts of a by-product, $\text{C}_{21}\text{H}_{20}\text{O}_4$, later shown to be IV. This by-product was found to arise from 1,1-bis-(diethylaminomethyl)-acetone (V), which resulted from further condensation of 1-diethylaminobutanone-3 with diethylamine hydrochloride and formaldehyde in the preparation of the Mannich base. Therefore, the importance of using carefully purified 1-diethylaminobutanone-3 when preparing compounds similar to II and VII is apparent.

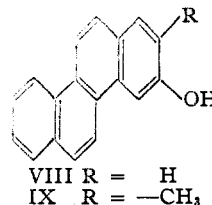
When the diketone ester II was treated with sodium methoxide, the cyclic keto ester VI was obtained, rather than VII. However, when the cyclizing agent was methanolic potassium hydroxide, the unsaturated ketone VII was the product. A yield of 90% for this second step made an 83% yield of unsaturated ketone from the keto ester I, which in turn was prepared in 85% yield from 1-ketotetrahydrophenanthrene.³ Thus the over-all yield for the method in this

(3) Bachmann and Wilds, *THIS JOURNAL*, **62**, 2085 (1940).

case is 70%, considerably higher than any example previously reported. When the intermediate II was not isolated in this series of reactions, the over-all yield was lowered.

Two alternative routes to the ketone VII could be followed. It was found that the angular carbomethoxy group of VI was eliminated by cleavage with alkali, giving VII in 52% yield. This ready cleavage is understandable since VI is the vinylog of a β -keto ester. It was anticipated that heating the diketone ester II with a mixture of acetic and hydrochloric acids would effect hydrolysis and decarboxylation to the corresponding diketone. Actually, however, cyclization also occurred and the unsaturated ketone VII was obtained in 84% yield. This is in contrast to the behavior of 1-keto-1,2,3,4-tetrahydrophenanthrene-2-acetone, which was not cyclized under these conditions to a similar unsaturated ketone containing a five-membered ring.⁴ However, Adamson, *et al.*,⁵ have observed that an analogous diketone could be cyclized by 50% sulfuric acid. The cyclic keto ester VI was not affected by acid under the conditions which converted II into VII.

Evidence confirming the structure of the ketone VII was obtained by dehydrogenation with palladium-charcoal at 300°. Under these conditions a 78% yield of chrysene was obtained. Treatment of the ketone with methylmagnesium iodide, followed by dehydration and dehydrogenation, gave 3-methylchrysene in 76% over-all yield. This hydrocarbon was identical with the compound previously prepared by Bachmann and Struve.^{6a,7} As a by-product in converting the ketone to chrysene there was isolated 18% of the new phenol, 3-hydroxychrysene (VIII). The yield of this phenolic compound could be increased to 83% by carrying out the dehydrogenation in boiling xylene solution for three days.



Attention was next turned to the compound,

- (4) Wilds, *ibid.*, **64**, 1427 (1942).
 (5) Adamson, McQuillan, Robinson and Simonsen, *J. Chem. Soc.*, 1578 (1937).
 (6) (a) Bachmann and Struve, *J. Org. Chem.*, **5**, 427 (1940); (b) **4**, 460 (1939).
 (7) We are indebted to Dr. W. E. Bachmann for sending us samples of 2- and 3-methylchrysene, and their picrates.

$C_{21}H_{20}O_4$, which was a by-product of II when impure 1-diethylaminobutanone-3 was used. The compound was obtained in 72% yield by condensation of the dimethiodide of V with the sodium salt of I. V in turn was the main product (39 to 55% yield) in the reaction of an aqueous solution of diethylamine and formaldehyde with acetone. Although the structure of the bis-diethylamino compound V has not been determined previously, Mannich and Salzmann⁸ have obtained some evidence that the corresponding bis-(dimethylamino-methyl)-acetone has the 1,1-structure. This conclusion was based on the fact that heating the diquatery hydroxide, prepared from the dimethiodide, resulted in loss of only one nitrogen atom, the other remaining as the quaternary base. Assuming that the 1,1-structure is correct for V, a reasonable structure for the compound $C_{21}H_{20}O_4$ would be IV. This would result from the normal elimination of one of the nitrogens of the dimethiodide to give the substituted vinyl methyl ketone, which would undergo Michael addition similar to the formation of II. After the addition, the presence of the new hydrogen atom would now make elimination of the second nitrogen atom possible, with the formation of a double bond. Experimental evidence has been obtained for the correctness of the structure IV. The α,β -unsaturated linkage could be selectively hydrogenated with the formation of a saturated diketone ester (III) and cyclization of this compound by means of methanolic alkali gave the cyclic ketone X. The structure of this last compound was proved by Clemmensen reduction followed by dehydrogenation. The resulting hydrocarbon was found to be identical with 2-methylchrysenene, which has been prepared previously by Bachmann and Struve.^{6b,7} The location of the methyl group proves conclusively that the diamine V actually has the 1,1-structure as shown. If it had the alternative structure 1,5-bis-(diethylamino)-pentanone-3, arising through condensation of diethylamine and formaldehyde with each methyl group of acetone, the methyl

group in the ketone X and in the final methylchrysenene would have appeared in the 4-position, rather than in the 2-position.

Interesting results have been obtained by cyclization of the unsaturated diketone ester IV with alkali, similar to the formation of VII. Under these conditions a 17% yield of the phenolic compound XI was obtained although, as might be expected, most of the material was polymerized. While a ten-fold dilution of the reaction mixture decreased this polymerization and raised the yield of phenol to 43%, the best results were obtained by acid cyclization of IV. In this manner as high as 83% of the dihydrochrysenol XI was obtained, when isolated as the acetate. Quantitative conversion of the acetate to the phenol was accomplished by heating with alcoholic hydrochloric acid.

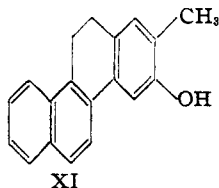
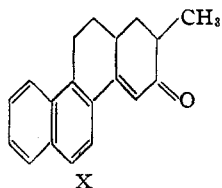
The acetate of XI was readily dehydrogenated to the acetate of 3-hydroxy-2-methylchrysenene (IX), from which the free chrysenol IX could be obtained in good yield by alcoholysis. This same phenol was also obtained in 43% yield by dehydrogenation of the ketone X at 250°.

Experimental

1-Diethylaminobutanone-3.^{8,9,10}—Using the procedure of du Feu, McQuillin and Robinson² our highest yields were 35 to 40%, rather than the 66% yield obtained by these authors. In our experiments considerable high-boiling material containing 1,1-bis-(diethylaminomethyl)-acetone resulted. The amount of this higher condensation product was decreased by using a more dilute solution and a larger excess of acetone.

A mixture of 22 g. (0.2 mole) of diethylamine hydrochloride, 60 cc. (0.82 mole) of acetone, 8.4 g. (0.28 mole) of paraformaldehyde and 40 cc. of alcohol was refluxed on the steam-bath for twenty hours. Longer heating decreased the yield. The cloudy solution was filtered and concentrated under reduced pressure. After adding 50 cc. of water and excess 45% potassium hydroxide, the solution was saturated with potassium carbonate and extracted twice with ether. The extract was washed twice with saturated salt solution and dried first with sodium sulfate and then Drierite. Following removal of the ether, the residue was distilled from a modified Claisen flask and the fraction boiling at 76–78° at 16 mm. was collected; yield 15.7–17.0 g. (55–59%), n_D^{20} 1.4318.

In order to remove a trace of the higher-boiling bis compound V and possibly other impurities,¹¹ it was necessary to refractonate the material twice before it was analytically pure. This purified 1-diethylaminobutanone-3 was



(8) Mannich and Salzmann, *Ber.*, **72**, 506 (1939)

(9) German Patents 266,656 and 267,347 in *Friedlaender*, **11**, 786, 788.

(10) Sohi and Shriner, *This Journal*, **55**, 3833 (1933).

(11) Tsuda, Fukushima and Oguri, *J. Pharm. Soc. Japan*, **61**, 69 *Abstracts* 31 (1941).

a colorless oil which became yellow on standing; b. p. 70–70.5° at 11 mm., n_D^{25} 1.4333, d_4^{25} 0.8630, M_D (found) 43.15, M_D (calcd.) 43.11. While the product of du Feu, McQuillin and Robinson² undoubtedly was this same compound, and the boiling points are in agreement (reported 76–78° at 15 mm.), these authors reported n_D^{16} 1.4628 for their material. Although no analysis was given by them, the nitrogen analysis has been reported by Sohl and Shriner.¹⁰

Anal. Calcd. for $C_8H_{17}ON$: C, 67.1; H, 11.9. Found: C, 67.3; H, 11.9.

The methiodide was prepared by allowing equal weights of the amine and methyl iodide to stand, protected from moisture, for one-half hour at 0° and one hour at room temperature. Although a crystalline methiodide was formed, due to its hygroscopic nature it was not purified before use, other than to wash it twice by decantation with anhydrous ether to remove the excess methyl iodide.

1,1-Bis-(diethylaminomethyl)-acetone (V).—Although we obtained this compound in 10–35% yield as the higher boiling fraction in the preparation of 1-diethylaminobutanone-3 by the method in the literature,² a modification of the method of Mannich and Salzmann⁸ for the corresponding disubstituted product from dimethylamine was more suitable as a means of preparation. To an ice-cold solution of 21 cc. of diethylamine in 40 cc. of water and 30 cc. of acetone was added 18 cc. of 35% formaldehyde solution. The homogeneous mixture was allowed to stand at room temperature. At the end of one hour a small oily layer began to separate. After twenty-four hours a small amount of alkali was added and the aqueous layer was saturated with salt. The product was extracted with two portions of ether, washed twice with salt solution and dried over sodium sulfate and Drierite. Fractional distillation of the residue from a modified Claisen flask gave 4 g. (14%) of crude 1-diethylaminobutanone-3, b. p. 72–80° at 14 mm., n_D^{25} 1.4327, 0.8 g. of an intermediate fraction and 9 g. (39%) of V, b. p. 124–128° at 14 mm., n_D^{25} 1.4459. When the aqueous mixture was allowed to stand longer than one day the yield was sharply reduced and much resinous material resulted which decomposed during the distillation. However, one run in which diethylamine hydrochloride was neutralized with the theoretical amount of potassium hydroxide and the condensation mixture with formaldehyde and acetone was allowed to stand for a week, gave 11% of the mono condensation product and 55% of the bis compound. In this run, due to the salting out action of the potassium chloride, two layers were present throughout the condensation, and this inhibited the formation of the resinous by-products observed above.

Refractionation of the crude product gave colorless material boiling at 92–92.5° at 0.4 mm., n_D^{25} 1.4472, d_4^{25} 0.8758, M_D (found) 69.68, M_D (calcd.) 70.15. Although the molecular refraction was low, the analytical figures were satisfactory. This may indicate the presence of some of the linear isomer as an impurity. The compound has been reported previously in a patent,⁹ although the yield and analysis were not given.

Anal. Calcd. for $C_{13}H_{23}ON_2$: C, 68.4; H, 12.4. Found: C, 68.3; H, 12.2.

2- γ -Ketobutyl-2-carbomethoxy-1-keto-1,2,3,4-tetrahydrophenanthrene (II).—The sodio derivative was pre-

pared from 2.07 g. of 2-carbomethoxy-1-ketotetrahydrophenanthrene,³ by heating for fifteen minutes with a solution of 0.19 g. of sodium in 10 cc. of anhydrous methanol and 10 cc. of dry, thiophene-free benzene. The mixture containing the insoluble sodium salt was then cooled in an ice-bath, and the methiodide from 2.5 g. of redistilled 1-diethylaminobutanone-3 was added in 10 cc. of methanol. The sodium salt slowly dissolved and after four hours at room temperature another crystalline precipitate had separated. The mixture was refluxed for one hour, the clear solution was diluted with water and extracted twice with benzene. After washing with dilute acid and water, the benzene was evaporated and the residue was crystallized from ethyl acetate to give 2.31 g. of cubic prisms, m. p. 141–143°. The second crop (0.18 g., m. p. 130–140°) was a mixture of prisms and needles which could be separated by adding petroleum ether, suspending the lighter needles by swirling and decanting them with the liquid. Recrystallization of the residue gave an additional 0.12 g. of the prisms, m. p. 139–142°, for a total yield of 92%.

For analysis a sample was evaporatively distilled at 0.5 mm. and recrystallized from ethyl acetate, m. p. 145–145.5°. The compound gave an orange-red color with sulfuric acid, but no color with alcoholic ferric chloride solution.

Anal. Calcd. for $C_{20}H_{20}O_4$: C, 74.0; H, 6.2. Found: C, 74.2; H, 6.2.

The needles from the petroleum ether suspension were recrystallized from ethyl acetate and gave 0.02 g. of IV (see below), m. p. 153–155°. When the methiodide was prepared from 1-diethylaminobutanone-3, which had been distilled only once, the amount of this material was increased and purification of the desired compound was difficult.

3-Keto-1,2,3,11,12,12a-hexahydrochrysene (VII). (A) **Alkaline Cyclization.**—A mixture of 50 cc. of methanol, 5 cc. of 45% potassium hydroxide solution and 0.8 g. of II was refluxed under an atmosphere of nitrogen for twenty hours. The solution was then diluted and the product was extracted with three portions of warm benzene. The extract was washed with water and dilute hydrochloric acid, then concentrated. The first crop of 0.40 g. of yellow plates, m. p. 182–185°, and an additional 0.15 g., m. p. 176–183°, made a total yield of 90% of the cyclic ketone.

The analytical sample was evaporatively distilled at 0.5 mm. and recrystallized from benzene as colorless plates, m. p. 188–188.5°. The ketone gave a deep orange color with sulfuric acid.

Anal. Calcd. for $C_{18}H_{16}O$: C, 87.1; H, 6.5. Found: C, 87.1; H, 6.7.

The oxime of VII, prepared in alcohol-pyridine solution, crystallized as colorless leaflets from benzene-alcohol and sintered at 218° before melting at 220–222°, with decomposition.

Anal. Calcd. for $C_{18}H_{17}ON$: C, 82.1; H, 6.5. Found: C, 81.8; H, 6.5.

When the alkaline layer from the cyclization was acidified and the resulting oil was crystallized from benzene-methanol, a trace of acid was obtained, m. p. 232–234° (gas evolution).

(B) **Acid Cyclization.**—When 0.5 g. of the diketo ester II was refluxed with 25 cc. of acetic acid and 5 cc. of hydro-

chloric acid under nitrogen for twenty-three hours, the product obtained by dilution and extraction with benzene was the same ketone VII, weighing 0.32 g. (84%); m. p. 185–187° (mixed m. p. 185–188°).

3-Keto-12a-carbomethoxy-1,2,3,11,12,12a-hexahydrochrysenes (VI).—One gram of the diketo ester II and a solution of 1 g. of sodium in 100 cc. of anhydrous methanol were heated to reflux for two hours under nitrogen. After cooling, water was added and the mixture was extracted twice with benzene. The benzene layer was washed with water, evaporated and the residue was crystallized from ethyl acetate, giving 0.52 g. of yellow needles, m. p. 174–176°. A second crop of 0.23 g. (m. p. 160–175°) brought the total yield to 79%. After another recrystallization from ethyl acetate (Norit) the pale yellow blades had the m. p. 178.5–179.5°. A mixed m. p. with 3-keto-hexahydrochrysenes was depressed to 145–155°. Sulfuric acid gave an orange-red color with VI.

Anal. Calcd. for $C_{20}H_{18}O_2$: C, 78.4; H, 5.9. Found: C, 78.2; H, 6.0.

When VI was refluxed for twenty hours with a mixture of acetic and hydrochloric acids, most of the starting material was recovered unchanged, m. p. and mixed m. p. 173–175°.

However, when 100 mg. of VI was refluxed for two hours with a mixture of 6.5 cc. of 45% potassium hydroxide and 25 cc. of methanol, the ketone VII was obtained in 52% yield by extraction of the alkaline solution; m. p. and mixed m. p. 187–188°. From the alkaline solution there was obtained upon acidification a trace of an acid, which after recrystallization from methanol had the m. p. 146–147° (gas evolution).

Dehydrogenation of VII to Chrysenes.—One-half gram of the ketone VII and 0.1 g. of palladium-charcoal catalyst¹² were heated under nitrogen to 280–300° for one hour. After cooling, dissolving the product in benzene and filtering off the catalyst, the solvent was evaporated and the residue was refluxed with 50 cc. of 5% sodium hydroxide solution, cooled, and filtered. After washing with water and drying at 100° there was obtained 0.36 g. (78%) of chrysenes, m. p. 243–250°. Recrystallization from toluene gave colorless leaflets with the m. p. 252–253°, alone and when mixed with an authentic specimen of chrysenes. When the alkaline filtrate was acidified, 0.09 g. (18%) of 3-hydroxychrysenes (see below) was obtained, m. p. 252–255°. One recrystallization from alcohol raised the m. p. to 263–267°.

3-Hydroxychrysenes (VIII).—The best yields were obtained by carrying out the dehydrogenation of VII according to the method of Mosettig and Duvall for the preparation of 4-phenanthrol.¹³ A mixture of 2.7 g. of the ketone VII, 0.5 g. of palladium-charcoal¹² and 20 cc. of xylene was refluxed under a nitrogen atmosphere for three days. Hydrogen was slowly evolved during the first two days, but had ceased at the end of the period of heating. After cooling the solution, alcohol was added and the catalyst was filtered off. The residue after evaporation of the solvent was recrystallized from alcohol-acetone, giving a total yield of 2.2 g. (83%) of product with the m. p. 262–267°. The phenolic compound was completely dissolved by refluxing with 5% potassium hydroxide in 15% alcohol. No

evidence was obtained for the presence of chrysenes, although on one run there was a small neutral fraction with the m. p. 135–155°.

A sample of 3-hydroxychrysenes was sublimed at 230° and 0.15 mm. and recrystallized from alcohol-benzene, giving colorless plates, m. p. 271–273°. The mixed m. p. with chrysenes was 245–260°. The phenol gave no color with alcoholic ferric chloride solution.

Anal. Calcd. for $C_{18}H_{12}O$: C, 88.5; H, 5.0. Found: C, 88.4; H, 5.2.

The acetate was prepared by refluxing a solution of 0.25 g. of the phenol in 10 cc. of acetic anhydride for four hours. The product obtained by diluting and filtering was evaporatively distilled at 210° and 0.1 mm., and recrystallized from acetone; yield 0.24 g. of colorless plates with the m. p. 201–202°.

Anal. Calcd. for $C_{20}H_{14}O_2$: C, 83.9; H, 4.9. Found: C, 83.9; H, 5.2.

The methyl ether was obtained from 0.25 g. of the phenol by treatment with excess methyl sulfate and sodium hydroxide. After evaporative distillation at 0.1 mm. and recrystallization from acetone, the long, colorless plates of 3-methoxychrysenes (0.15 g.) had the m. p. 147.5–148.5°.

Anal. Calcd. for $C_{19}H_{14}O$: C, 88.3; H, 5.5. Found: C, 88.3; H, 5.8.

3-Methylchrysenes.—To the ice-cold Grignard reagent prepared from 0.8 cc. of methyl iodide and 0.25 g. of magnesium in 20 cc. of dry ether, was added a solution of 0.5 g. of the ketone VII in 6 cc. of dry benzene. The mixture was allowed to stand at room temperature for twelve hours with frequent swirling at first. The mixture was then hydrolyzed with ice-cold ammonium chloride solution, extracted with benzene, washed and evaporated. The crystalline residue (m. p. 75–90°) was dehydrogenated by heating to 300–320° for twenty minutes with 0.1 g. of palladium-charcoal. After isolation of the product with benzene, it was recrystallized from benzene-petroleum ether, m. p. 168–172°; the total yield was 0.37 g. (76%). Evaporative distillation at 220° (0.5 mm.) and recrystallization, first from benzene-petroleum ether and then from alcohol-benzene, gave colorless plates, m. p. 172.5–173.5°. A mixed m. p. with an authentic sample of 3-methylchrysenes prepared by Bachmann and Struve^{6a,7} (m. p. 172.5–173°, with our apparatus) was found to be 172.5–173.5°.

The orange colored picrate of the hydrocarbon was found to have the m. p. 166.5–167.5°. When mixed with the picrate prepared from the sample of Bachmann and Struve (m. p. 166–167°) the m. p. was 166–167°.

2-(β -Methylene- γ -ketobutyl)-2-carbomethoxy-1-keto-1,2,3,4-tetrahydrophenanthrene (IV).—A solution of 0.23 g. (0.01 atom) of sodium in 15 cc. of anhydrous methanol was refluxed for twenty minutes with 2.5 g. (0.01 mole) of the keto ester I and 20 cc. of benzene. The resulting suspension of the sodio derivative was cooled and to it was added a solution of the dimethiodide of V in 25 cc. of anhydrous methanol. (This methiodide was prepared by allowing a mixture of 3 g. of the base and 6 g. of methyl iodide to stand one-half hour at 0° and at least twelve hours at room temperature, before washing twice by stirring with anhydrous ether.) The sodio derivative went into solution and after three hours at room temperature

(12) Zelinsky and Turouva-Pollak, *Ber.*, **58**, 1295 (1925).

(13) Mosettig and Duvall, *THIS JOURNAL*, **59**, 367 (1937).

the mixture was refluxed for one-half hour. Water was added and the product was extracted with warm benzene, then washed with water and dilute acid. After evaporation of the benzene the residue was recrystallized from ethyl acetate, giving 2.1 g. of colorless needles, m. p. 153–155°. A second crop of 0.3 g., m. p. 149–153°, made the total yield 72%. Further recrystallization of the solid from ethyl acetate raised the m. p. to 157.5–158.5°. The compound formed an orange color with sulfuric acid, but none with alcoholic ferric chloride solution.

Anal. Calcd. for $C_{21}H_{24}O_4$: C, 75.0; H, 6.0. Found: C, 74.9; H, 6.0.

The use of two equivalents of sodium in the above condensation, instead of one equivalent as described, resulted in a decrease in yield to 38%.

3-Hydroxy-2-methyl-11,12-dihydrochrysenes (XI). (A) **Alkaline Cyclization.**—One and four-tenths grams of the unsaturated ester IV was cyclized with 100 cc. of methanol and 10 cc. of 45% potassium hydroxide as described above for 3-ketohexahydrochrysenes and after acidification and extraction with benzene the product was isolated by evaporative distillation at 0.2 mm. and recrystallization from methanol. Only 8% of the cyclized phenolic compound could be isolated, m. p. 157–159°. An additional 9% isolated as the acetate, m. p. 166–168°, brought the total yield to 17% for this method. The major product was a high boiling resin. This polymerization could be partially avoided by carrying out the cyclization in a more dilute solution, that is by using ten times the above amount of methanol and alkali. In this manner 17% of the phenol and an additional 26% of its acetate resulted, for a total yield of 43%.

(B) **Acid Cyclization.**—Superior results were obtained with this method. One gram of the unsaturated ester IV was boiled for thirty hours under nitrogen with 40 cc. of acetic acid and 10 cc. of concentrated hydrochloric acid. After dilution with water, the product was extracted with two portions of benzene, the latter was evaporated and the phenol converted to the acetate by refluxing with 10 cc. of acetic anhydride for seven hours. Purification of the product by evaporative distillation at 200–250° (0.2 mm.) and recrystallization from acetone–alcohol gave a total of 0.68–0.75 g. (76–83%) of the acetate of 3-hydroxy-2-methyl-11,12-dihydrochrysenes as thin, colorless leaflets, m. p. 163–166°. Another evaporative distillation and two recrystallizations of the solid from acetone–alcohol raised the m. p. to 167–168°.

Anal. Calcd. for $C_{21}H_{18}O_2$: C, 83.4; H, 6.0. Found: C, 83.3; H, 6.0.

The phenol IX was obtained by refluxing a mixture of 100 mg. of the acetate with 10 cc. of alcohol and 0.5 cc. of concentrated hydrochloric acid for six hours under nitrogen. When the colorless solution was concentrated and diluted slightly with water, a total of 85 mg. (99%) of colorless blades was obtained, m. p. 157–159°. Another recrystallization from methanol raised the m. p. of the product to 159–160°. A mixed m. p. with the same phenol obtained by alkaline cyclization showed no depression. When the phenol was mixed with the unsaturated ester IV, the m. p. was lowered to 135–140°. The compound was only partially extracted from benzene solution by 5% potassium hydroxide. It gave an orange-red color

with concentrated sulfuric acid, but no color with alcoholic ferric chloride solution.

Anal. Calcd. for $C_{19}H_{16}O$: C, 87.7; H, 6.2. Found: C, 87.5; H, 6.4.

3-Hydroxy-2-methylchrysenes (IX).—One-half gram of the acetate of the dihydrochrysenol XI was heated with 0.1 g. of palladium–charcoal under nitrogen. Hydrogen was smoothly evolved at 200–220° and at the end of five minutes the temperature was raised to 250° and maintained there for another ten minutes. After cooling there was a strong odor of acetic acid, indicating partial deacetylation. Therefore, the mixture was refluxed in 1 cc. of acetic anhydride for four hours, alcohol and ethyl acetate were added and the catalyst was removed by filtration. A total of 0.36 g. (72%) of the acetate of 3-hydroxy-2-methylchrysenes crystallized from acetone–alcohol as thin, colorless leaflets, m. p. 184–185°. Another recrystallization gave material which had the m. p. 185–187° when introduced into the bath at 100°. When the sample was placed in the bath at 180°, about one-half of the material melted immediately, and the rest at 185–186°. After cooling slightly, the melt solidified and remelted at 192–193°; cooling again gave a solid which melted completely between 170 and 175°, resolidified quickly and remelted at 186–188°. This same behavior was observed with several different samples, and indicated the existence of at least two and possibly three polymorphic forms.

Anal. Calcd. for $C_{21}H_{16}O_2$: C, 84.0; H, 5.4. Found: C, 84.0; H, 5.3.

3-Hydroxy-2-methylchrysenes was obtained from the acetate in 94% yield exactly as described for the corresponding dihydro derivative. The thin, colorless leaflets obtained by crystallization from alcohol had an indistinct m. p. varying from 270 to 280° (with darkening) when open capillary tubes were used. In an evacuated (to 0.5 mm.), sealed capillary the m. p. was sharp at 287–288° and the colorless melt upon solidification remelted at the same temperature. The phenol gave no color with alcoholic ferric chloride solution.

Anal. Calcd. for $C_{19}H_{14}O$: C, 88.3; H, 5.5. Found: C, 88.1; H, 5.7.

2-(β -Methyl- γ -ketobutyl)-2-carbomethoxy-1-keto-1,2,3,4-tetrahydrophenanthrene (III).—Two grams of the unsaturated ester IV, 0.5 g. of palladium–charcoal catalyst¹² and 50 cc. of pure dioxane were shaken with hydrogen at room temperature and atmospheric pressure. Hydrogenation proceeded readily and 95% of the calculated amount of hydrogen for one mole was absorbed in four hours. There was no tendency for a second mole to react under these conditions. After filtering off the catalyst, the dioxane was evaporated and the residue was crystallized from methanol. This material was a mixture of stereoisomers, containing both colorless prisms and blades, m. p. 103–110°; the total yield was 1.69 g. (84%).

Analytical figures for the mixture agreed satisfactorily with the theoretical values. A pure stereoisomer was obtained after several recrystallizations from methanol–acetone, with seeding and filtering as soon as prisms started to contaminate the blades. In this manner colorless, broad, flat blades were obtained with the m. p. 123.5–124.5°.

Anal. Calcd. for $C_{21}H_{22}O$: C, 74.5; H, 6.6. Found: C, 74.7; H, 6.6.

3-Keto-2-methyl-1,2,3,11,12,12a-hexahydrochrysenes (X).—Cyclization of 2.3 g. of the mixture of stereoisomers was carried out with potassium hydroxide and methanol exactly as described above for 3-ketohexahydrochrysenes. In this manner 1.15 g. of ketone, m. p. 184–187° and an additional 0.09 g., m. p. 177–185° were obtained from benzene. Evaporative distillation of the filtrate at 200–250° (0.2 mm.) and recrystallization from alcohol gave an additional 0.17 g., m. p. 165–185° for a total yield of 79% of the stereoisomeric mixture. One pure form was easily obtained by recrystallization from benzene–alcohol as colorless, needle-like prisms, m. p. 189–190.5°. A mixed m. p. with 3-ketohexahydrochrysenes was depressed to 160–165°. The ketone gave an orange color with sulfuric acid.

Anal. Calcd. for $C_{19}H_{18}O$: C, 87.0; H, 6.9. Found: C, 87.1; H, 7.0.

The oxime, prepared in alcohol–pyridine solution and recrystallized from benzene–alcohol, formed small needles melting unsharply at 252–254°, with decomposition.

Anal. Calcd. for $C_{19}H_{18}ON$: C, 82.3; H, 6.9. Found: C, 82.4; H, 6.7.

Cyclization of 0.15 g. of the pure stereoisomer of the diketo ester III (m. p. 123.5–124.5°) gave 0.07 g. of ketone, m. p. 187–189°, and 0.03 g., m. p. 179–184° (with previous softening), or a total yield of 86%.

Evaporative distillation (at 210° and 0.1 mm.) of a pure sample of ketone melting at 187–189° gave partial epimerization, and about one-half was converted to a mixture of isomers with the m. p. 160–170°. In contrast to this ketone, 3-ketohexahydrochrysenes without the C_2 -methyl group was unchanged after evaporative distillation.

Direct Dehydrogenation of the Ketone X.—A mixture of 0.30 g. of X (m. p. 184–187°) and 0.1 g. of palladium–charcoal was heated at 250–260° for one-half hour. All of the hydrogen was evolved in twenty minutes. After dissolving the product in dioxane and removing the catalyst the material was crystallized from acetone–alcohol. This solid was a mixture, m. p. 247–257°. The filtrate was heated with 1 cc. of acetic anhydride for five hours and crystallized from alcohol. In this manner 0.09 g. of the acetate of 3-hydroxy-2-methylchrysenes was obtained, melting at 180–182°; mixed m. p. 183–186°. The solid mixture (m. p. 247–257°) could be separated by heating with a mixture of 35 cc. of 5% potassium hydroxide and 5 cc. of alcohol for one hour before filtering. From the alkaline layer after acidification was obtained an additional 0.05 g. of the crude phenol IX, m. p. 268–275° (vac.) (which gave the acetate m. p. 183–185°), for a total yield of 43% of phenolic material.

From the neutral fraction after evaporative distillation at 0.1 mm. and recrystallization from alcohol–benzene,

there was obtained 0.08 g. of colorless leaflets with the m. p. 242–245°. A mixed m. p. with chrysenes was depressed to 235–242°. The analysis indicated that this material was impure. Found: C, 93.5; H, 5.9.

2-Methylchrysenes.—Clemmensen reduction of 430 mg. of X was carried out according to the general procedure of Martin.¹⁴ The product after extraction with benzene and evaporative distillation at 200° (0.3 mm.) was nearly all solid, m. p. 100–110°, but was used without further purification. Dehydrogenation was carried out at 300–310° for ten minutes using 0.1 g. of palladium–charcoal. A total of 150 mg. (38%) of 2-methylchrysenes was obtained as thin, colorless leaflets from benzene–alcohol, m. p. 227–229°. Another recrystallization gave material with the m. p. 229.5–230°. When a sample was mixed with authentic 2-methylchrysenes prepared by Bachmann and Struve^{6a,7} (m. p. 227–229°, with our apparatus) the m. p. was 228–230°.

The rather unstable picrate was obtained as orange needles from absolute alcohol, m. p. 145–148°. When mixed with the picrate prepared by Bachmann and Struve (m. p. 146–149°), the sample melted at 146–149°.

The trinitrobenzene complex was found to be a more stable derivative than the picrate, and was prepared from a solution of the hydrocarbon in benzene–alcohol. The canary yellow needles had the m. p. 189–190°; a mixed m. p. with the same derivative prepared from the hydrocarbon of Bachmann and Struve (m. p. 189–190°) showed no depression.

Anal. Calcd. for $C_{18}H_{14} \cdot C_6H_3O_6N_3$: C, 65.9; H, 3.8. Found: C, 65.9; H, 3.6.

Summary

The Robinson–Mannich base synthesis of unsaturated ketones has been applied to 2-carbomethoxy-1-ketotetrahydrophenanthrene, leading to the preparation of 3-ketohexahydrochrysenes. Improved procedures have been developed for carrying out the various steps in this synthesis. Good over-all yields have resulted.

Incompletely purified Mannich base was shown to give rise to an unsaturated diketo ester as a by-product.

This synthesis affords a new route to alkyl derivatives of chrysenes, and the preparation of 2- and 3-methylchrysenes is reported.

3-Hydroxychrysenes and 3-hydroxy-2-methylchrysenes have been synthesized.

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