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

A Synthesis of 1-Keto-1,2,3,4,9,10-hexahydrophenanthrene

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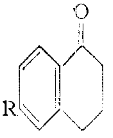
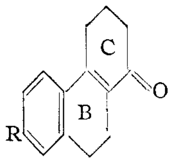
In searching for an improved synthesis of the methoxy ketone IIb,[3] which was desired as an intermediate in a projected synthesis of estrone,[4] we have investigated the synthesis of the unsubstituted ketone IIa. Tetralone-1, Ia, was chosen as a promising starting material, because the 6-methoxy derivative Ib is readily available[5] and presumably could be substituted for tetralone to give IIb. The present communication consists primarily of the announcement of a three-step synthesis of the hitherto unknown 1-keto-1,2,3,4,9,10-hexahydrophenanthrene, IIa, from tetralone-1. Although the over-all yield is as yet low, the new synthesis affords certain advantages, particularly in that it is readily executed.

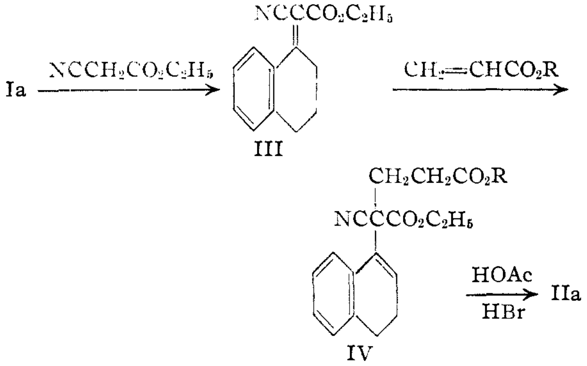


Ia (R = H)
Ib(R = OCH$_3$)



IIa (R = H)
IIb (R = OCH$_3$)

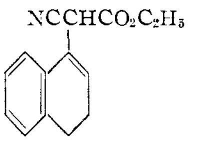
The steps in the synthesis are outlined in the accompanying flow sheet. The condensation of tetralone-1 with ethyl cyanoacetate, which has been previously reported to fail under standard Knoevenagel conditions,[6] was effected by the excellent procedure of Cope and his co-workers,[7] giving ethyl 1,2,3,4-tetrahydro-1-napthylidenecyanoacetate, III, (or possibly the bond isomer V). The yields were about 40% not considering the unreacted ketone which was largely recovered.[8]



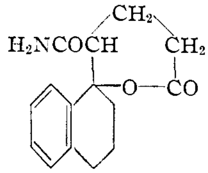
The second step consisted of the reaction of III (as the tautomeric form V) with methyl acrylate by way of a Michael addition. The reaction was conducted in ethanol with sodium ethoxide catalyst, and the oily addition product IV was obtained in 57% yield, together with a crystalline product of unknown structure having an analysis compatible with the formula $C_{17}H_{13}O_3N$ and isolated in 4.5% yield.

When the addition product IV was treated with a refluxing mixture of hydrobromic and acetic acids it was converted directly into 1-keto-1,2,3,4,9,10-hexahydrophenanthrene, IIa, which was isolated as the semicarbazone in 19% yield. Hydrolysis of the semicarbazone afforded the pure crystalline ketone, m. p. 49–50°. The nuclear structure was proved by Wolff–Kishner reduction of the semicarbazone to an oily hydrocarbon which on dehydrogenation over palladium-charcoal afforded phenanthrene. The ultraviolet absorption spectrum of the new ketone, which will be described in the near future by Dr. A. L. Wilds and his collaborators,[9] shows beyond any reasonable doubt that the double bond is conjugated both with the carbonyl group and with the benzene nucleus. This places the unsaturation between rings B and C as indicated in formula IIa.

For the preparation of the ketone IIa it was found unnecessary to isolate the intermediates III and IV. In this way not only was the manipulation simplified, but the over-all yield was raised from 5 to 8% (not considering recovered starting material). Even though the per cent. over-all yield is low, the synthesis affords a fairly easy method of preparing small amounts of the ketone IIa. Thus 15 g. of tetralone-1 yields 2.2 g. of the semicarbazone of IIa.



V



VI

The loss of the cyanide and carbethoxyl groups in the cyclization step is reasonable in view of the lability of similarly located negative groups under

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[3] For previous work on the synthesis of this type of ketone see for example (a) Robinson and Walker, *J. Chem. Soc.*, 192 (1936); (b) Robinson and Schlittler, *ibid.*, 1288 (1935); (c) Bachmann, Kushner, and Stevensen, THIS JOURNAL, **64**, 974 (1942).

[4] *Cf.* Johnson, Petersen and Gutsche, *ibid.*, **67**, 2274 (1945).

[5] Burnop, Elliott and Linstead, *J. Chem. Soc.*, 727 (1940).

[6] Robinson and Walker, *ibid.*, 1530 (1935).

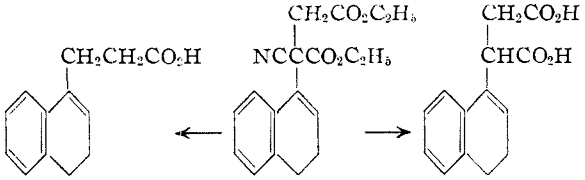
[7] Cope, Hofmann, Wyckoff and Hardenbergh, THIS JOURNAL, **63**, 3452 (1941).

[8] Mowry, *ibid.*, **67**, 1050 (1945), somewhat recently has reported that tetralone-1 condenses with malonitrile giving a crystalline product in 79% yield. This substance could presumably be substituted for III in the synthesis described in the present paper. The over-all yield thus might be correspondingly increased.

[9] Wilds, Beck, Close, Djerassi, J. A. Johnson, T. L. Johnson and Shunk, unpublished results.

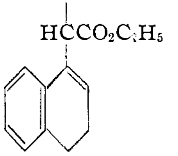
comparable conditions.[10] When hydrochloric acid was substituted for the hydrobromic acid in the cyclization step, instead of IIa there was obtained a high-melting crystalline product, the analysis of which was compatible with the structure VI. The lactonic character was suggested by its insolubility in cold but solubility in warm sodium carbonate solution.

Some investigations were made on other methods of cyclizing the Michael addition product IV. Partial alkaline hydrolysis afforded an oily acid which on treatment with phosphoric anhydride was partly cyclized to neutral material which in turn was converted into IIa by acid hydrolysis. When a zinc chloride–acetic acid–acetic anhydride reagent[10] was substituted for the phosphoric acid, no ketonic material was obtained. Successful cyclization was realized, however, when the product of exhaustive alkaline hydrolysis of IV was treated with the zinc chloride reagent. Neither of these methods of ring closure afforded any advantage over the one-step process, since the yields were all of the same order. In all of the cyclizations acidic material was recovered as well as neutral, non-ketonic material which could not be crystallized. The partial solubility of the latter in warm alkali suggested the presence of lactones.

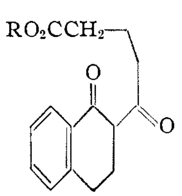


VII VIII IX

Alkylation of the sodio derivative of V with ethyl chloroacetate afforded VIII—the next lower homolog of IV.[11] The structure of VIII was established by conversion to known substances.[10a] Thus alkaline hydrolysis gave (3,4-dihydro-1-naphthyl)-succinic acid (IX), and hydrochloric–acetic acid hydrolysis gave the propionic acid VII.



X



XIa ($R = C_2H_5$)
XIb ($R = H$)

In some further work directed toward another approach to the synthesis of IIa, the condensation of tetralone-1 with diethyl glutarate was examined. It was hoped that the reaction would proceed similarly to the Stobbe condensation with diethyl succinate[10a] to produce a substance X, but instead the diketo ester XIa was the principal product formed by an acetoacetic ester type of condensation. Glutaric ester has been reported to condense with cyclohexanone in a similar fashion.[12] Preliminary attempts to effect cyclodehydration of XIa or XIb to a phenanthrene derivative were unsuccessful.

Experimental Part[13]

Ethyl 1,2,3,4-Tetrahydro-1-naphthylidenecyanoacetate (III).—A mixture of tetralone-1[14] (30.0 g.), ethyl cyanoacetate (23.2 g.), ammonium acetate (3.16 g.) in 9.4 g. of acetic acid and 70 cc. of benzene was refluxed for twenty hours in a system equipped with a continuous water separator (see procedure "B" of Cope, *et al.*[7]). Distillation through a 4-inch modified Widmer column gave 14.1 g. of recovered tetralone-1 of fair purity (boiling range 4°), and 18.5 g. (37% yield) of ethyl 1,2,3,4-tetrahydro-1-naphthylidenecyanoacetate, b. p. 164–169° (2–3 mm.). Accounting for recovered tetralone-1 the yield was 70%. A middle fraction had the following properties: b. p. 166–167° (2–3 mm.), n^{27}D 1.5674.

Anal. Calcd. for $C_{15}H_{15}O_2N$: C, 74.66; H, 6.27. Found: C, 74.77; H, 6.13.

In another experiment the acetic acid and ammonium acetate were replaced by (the relatively non-volatile) benzoic acid and ammonium benzoate, and the amount of cyanoacetic ester was increased. The quantities used were: 26.2 g. of tetralone-1, 30.4 g. of ethyl cyanoacetate, 7.9 g. of ammonium benzoate, 18.6 g. of benzoic acid and 100 cc. of benzene. After seventeen hours of refluxing no more water was separating. An additional 15.2 g. of ethyl cyanoacetate was introduced into the mixture and refluxing resumed until water was no longer separating (five hours). Ammonium benzoate (9.3 g.) was then added, and heating was stopped after an additional five hours. The benzoic acid which crystallized on cooling was filtered. The filtrate was extracted with saturated sodium bicarbonate solution to remove the remaining acid, washed with water and distilled through a 4-inch modified Widmer column. The fractions obtained were: 19.1 g. of ethyl cyanoacetate, b. p. 85–90° (8–10 mm.); 7.6 g. of tetralone-1, b. p. 120–126° (8–10 mm.); 20.6 g. of the condensation product, b. p. 164–168° (2–3 mm.). The conversion was 48% of the theoretical. It should be noted that although the above procedure gave good results with tetralone, it has been found by William P. Schneider to be inferior to the acetic acid method when applied to benzophenone.

Diethyl α-Cyano-α-(3,4-dihydro-1-naphthyl)-glutarate (IV).—To a cooled solution of 0.17 g. of sodium in 100 cc. of ethanol was added a solution of 10.00 g. of ethyl 1,2,3,4-tetrahydro-1-naphthylidenecyanoacetate and 3.82 g. of methyl acrylate in 25 cc. of ethanol. After standing at room temperature for two days the solution was concentrated under reduced pressure. Ether and acetic acid (0.5 cc.) were added, and the solution was washed with water and evaporated. The residue which was partly solid was treated with alcohol which dissolved all but 0.52 g. of reddish crystals, m. p. 197–200°. Recrystallization from benzene gave colorless, hexagonal prisms, m. p. 201–202°. This material was neutral, sparingly soluble in most solvents and gave a red color with ferric chloride.

Anal. Calcd. for $C_{17}H_{13}O_3N$: C, 73.11; H, 4.69; N, 5.02. Found: C, 73.14, 73.16, 73.23; H, 4.81, 4.64, 4.75; N, 5.10.

Distillation of the filtrate yielded a negligible amount of material boiling below 185° (2 mm.). The main fraction which corresponded to IV was collected at 185–200° (1–2 mm.). It was a pale yellow viscous oil, and amounted to 8.0 g. (a 57% yield). A middle fraction was analyzed.

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(10) *Cf.* (a) W. S. Johnson, H. C. E. Johnson and Petersen, THIS JOURNAL, **67**, 1360 (1945), and (b) Johnson and Petersen, *ibid.*, **67**, 1366 (1945).

(11) *Cf.* the alkylation of alkylidenecyanoacetic esters: Cope and Hancock, *ibid.*, **60**, 2903 (1938).

(12) Robinson and Seijo, *J. Chem. Soc.*, 582 (1941).

(13) All melting points are corrected.

(14) Thompson, "Organic Syntheses," **20**, 94 (1939).

Anal. Calcd. for $C_{19}H_{21}O_4N$: C, 69.70; H, 6.47. Calcd. for $C_{20}H_{23}O_4N$: C, 70.36; H, 6.79. Found: C. 71.16, 71.08; H, 6.66, 6.42.

The closer agreement with the higher C_{20} homolog suggests that the methyl group, which originated from the acrylate, may have been largely replaced by the ethyl group. This is reasonable since the conditions used for the Michael reaction are also conditions known to promote ester-exchange.

In one experiment the Michael addition was carried out in the absence of alcohol according to the directions of Koelsch,[15] but the yield was lower.

1-Keto-1,2,3,4,9,10-hexahydrophenanthrene (IIa). (*a*) *Cyclization with Hydrobromic Acid.*—A solution of 1.54 g. of the Michael addition product IV in 15 cc. of glacial acetic acid and 15 cc. of 40% hydrobromic acid was boiled under reflux for thirty hours. Water was added, and the oil which separated was extracted with ether. The ether solution was washed with water, and extracted with saturated sodium bicarbonate solution which removed some nitrogen-containing acidic material. The neutral oil (0.75 g.) which remained on evaporation of the ether was warmed on the steam-bath with 10 cc. of 4% sodium hydroxide solution to cleave lactonic material. The unsaponified portion was separated by ether extraction. The 0.50 g. of oil thus obtained was treated with warm methyl alcohol which dissolved all but a small amount of resin-like material. The solution (100 cc.) was treated with 0.5 g. of semicarbazide hydrochloride and 0.4 cc. of pyridine. After refluxing for one hour the mixture was cooled, and the yellow **semicarbazone** of **1-keto-1,2,3,4,9,10-hexahydrophenanthrene** was filtered. It amounted to 0.22 g. (19% yield), m. p. 252–256° (dec.). Two recrystallizations from alcohol afforded colorless, elongated rectangular prisms, m. p. 257–258° (dec.).

Anal. Calcd. for $C_{15}H_{17}ON_3$: C, 70.56; H, 6.71. Found: C, 70.48; H, 6.66.

The semicarbazone crystallizes nicely from pyridine. It is photosensitive, turning yellow on exposure to sunlight. A portion of the pure derivative was hydrolyzed in a boiling solution of oxalic acid. The ketone IIa was obtained in practically quantitative yield as a yellow oil. After evaporative distillation at 120° (1 mm.) it was obtained as an almost colorless oil which was induced to crystallize by chilling in a Dry Ice-bath. Recrystallization from 40–60° petroleum ether gave almost colorless needles, m. p. 49–50°.

Anal. Calcd. for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 84.63; H, 7.29.

The **oxime** crystallized from ethyl acetate–petroleum ether (60–80°) in the form of colorless needles and prisms; m. p. 141.5–142°.

Anal. Calcd. for $C_{14}H_{15}ON$: C, 78.84; H, 7.09. Found: C, 79.05; H, 7.23.

(*b*) *Phosphoric Anhydride Cyclization of Partially Saponified IV.*—The partial saponification of 5.69 g. of IV was effected with 16.0 cc. of 1.08 *N* sodium hydroxide solution in 100 cc. of alcohol. After refluxing for two hours in an atmosphere of nitrogen, the solution was concentrated and the residue treated with water and extracted with ether. Evaporation of the ether solution left 1.32 g. of neutral unsaponified oil. Acidification of the aqueous solution and extraction with ether afforded 3.90 g. of viscous brown oil.

Cyclization of 3.00 g. of the above acidic material was effected in benzene (90 cc.) solution with 4.5 g. of phosphoric anhydride. Filter-Cel (4.5 g.) was added to prevent coagulation of the anhydride, and the mixture was allowed to reflux with vigorous stirring for three hours. The mixture was worked up by dilution with water followed by alkaline extraction. The neutral material obtained from the organic layer was hydrolyzed with 15 cc. of acetic acid and 10 cc. of concentrated hydrochloric acid. After refluxing for twelve hours the mixture was diluted, and the oil was extracted with ether and washed with saturated sodium bicarbonate solution. The oil obtained on evaporation was treated with 1.4 g. of semicarbazide hydrochloride and 1.0 cc. of pyridine in 20 cc. of methanol. After refluxing for two hours the mixture was cooled, and 0.58 g. of the semicarbazone of IIa, m. p. 256–260° (dec.) was obtained. This corresponds to an 18% yield from IV. A mixed melting point with material prepared in (*a*) showed no depression.

(*c*) *Zinc Chloride-Catalyzed Cyclization of Hydrolyzed IV.*—A mixture of 4.30 g. of the addition product IV and 20 cc. of 10% sodium hydroxide solution was allowed to reflux until ammonia was no longer liberated (twenty hours). The red oil obtained on acidification was isolated by ether extraction, and after drying was dissolved in a mixture of 60 cc. of acetic acid, 40 cc. of acetic anhydride and 0.3 g. of fused zinc chloride. After refluxing for ninety minutes the solution was treated cautiously with enough water to decompose the anhydride, and the mixture was concentrated. Water was added, and the oil was extracted with ether, washed with water and then with saturated sodium bicarbonate solution which yielded 1.6 g. of an oil on acidification. The neutral fraction proved to contain ketonic material as evidenced by the reaction with semicarbazide hydrochloride (0.6 g.) and pyridine (0.5 cc.) in 25 cc. of methanol. After refluxing for one hour the solution was cooled, and 0.70 g. (a 22% yield) of the semicarbazone of IIa, m. p. 252–256° (dec.) crystallized. The melting point was not depressed by the samples from previous preparations (*a*) and (*b*).

When the recovered acidic fraction was treated with hydrobromic and acetic acid according to the procedure (*a*) described above, only a trace of additional ketonic material was obtained. When the reaction time was increased to four hours the yield dropped to 15% and the acidic fraction was larger. After seventeen hours of heating the product was largely acidic and the yield of semicarbazone was negligible.

Preparation of IIa without Isolation of Intermediates.—It seemed desirable to avoid the subjection of the intermediates III and IV to distillation, because of the possibility of promoting disproportionation as in a previous instance (see footnote 10 of ref. 10a).

Fifteen grams of tetralone-1 was condensed with ethyl cyanoacetate (17.2 g.) in the presence of 57.5 cc. of benzene, 10.6 g. of benzoic acid and 4.5 g. of ammonium benzoate (*cf.* the procedure described above). The heating period was twenty hours. Instead of being distilled the crude product was heated on the steam-bath at 0.05 mm. pressure to remove unreacted ketone and ester. The residue (17.5 g.) was treated with a solution of 0.29 g. of sodium in 175 cc. of ethanol, and 6.69 g. of methyl acrylate in 45 cc. of ethanol was added. The procedure was essentially the same as described above except that after the crystalline by-product (0.94 g., m. p. 193–197.5°) was separated, the residue obtained from the filtrate was used without distillation for cyclization. A solution of the crude Michael addition product (24.4 g.) in 250 cc. each of acetic acid and 40% hydrobromic acid was allowed to reflux for thirty hours; a dark oil separated as the reaction progressed. Most of the acetic acid was removed under reduced pressure, and the product was separated with ether and treated with 50 cc. of 10% sodium hydroxide as described above under cyclization (*a*).

The total crude semicarbazone obtained by treating the neutral fraction from the cyclization with excess semicarbazide amounted to 7.08 g. It melted over a wide range below 210°, and obviously contained considerable tetralone semicarbazone which could not be eliminated satisfactorily by recrystallization. The mixture was, therefore, suspended in a solution of 7 g. of oxalic acid in 50 cc. of water and submitted to steam distillation. As the semicarbazone hydrolyzed, tetralone steam-distilled out leaving a dark oily residue which was extracted and again treated with semicarbazide. The crude semicarbazone amounted to 2.21 g. (8% yield) and melted at 237.5–243° (dec.). It was characteristically photosensitive, and on recrystallization from pyridine was obtained as a colorless product, m. p. 254–256° (dec.), undepressed

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[15] Koelsch, THIS JOURNAL, 65, 437 (1943).

on admixture with the specimen of the semicarbazone of IIa described above.

Degradation of IIa to Phenanthrene.—A mixture of 0.200 g. of semicarbazone of IIa and a solution of 0.2 g. of sodium in 20 cc. of alcohol was heated in a sealed tube at 190–200° for sixteen hours. The oil obtained on dilution and extraction with ether was dehydrogenated by heating at 320° with 0.049 g. of 30% palladium–charcoal catalyst.[16] After one hour evolution of hydrogen had ceased, and the cooled product was taken up in ether and filtered. Evaporation of the ether left 0.158 g. of crude phenanthrene, m. p. 80–85°. Recrystallization from dilute alcohol raised the m. p. to 93–95°. When mixed with an authentic specimen of phenanthrene (m. p. 97–98°) the melting point was 96.5–97.5°.

The picrates were also prepared for comparison. That from the dehydrogenated product melted at 139–142°; on mixing with the picrate of phenanthrene (m. p. 143–144°), the melting point was 140–143°.

The Action of Hydrochloric–Acetic Acid on IV.—A solution of 1.69 g. of the addition product IV in 10 cc. of acetic acid and 5 cc. of concentrated hydrochloric acid was allowed to reflux for twelve hours. After dilution with water, the oil was extracted with ether, washed with water and saturated sodium bicarbonate solution. Evaporation of the ether left 0.26 g. (a 20% yield) of colorless prisms, m. p. 175.5–177.5°. After recystallization from benzene it melted at 178–180°. This substance which may be the lactone of **γ-carbamyl-γ-(1-hydroxy-1,2,3,4-tetrahydro-1-naphthyl)-butyric acid (VI)**, dissolved in dilute sodium hydroxide and in warm (but not in cold) dilute sodium carbonate solution. It failed to dissolve in warm sodium bicarbonate solution.

Anal. Calcd. for $C_{15}H_{17}O_3N$: C, 69.47; H, 6.61; N, 5.40. Found: C, 69.15; H, 6.30; N,[17] 5.06.

Diethyl α-Cyano-α-(3,4-dihydro-1-naphthyl)-succinate (VIII).—To alcohol-free sodium methoxide (prepared from 1.0 g. of sodium) was added a solution of 8.1 g. of ethyl 1,2,3,4-tetrahydro-naphthylidenecyanoacetate in 30 cc. of dry benzene. The suspension was warmed until solution was complete; then 5.8 g. of ethyl α-chloroacetate was added. After refluxing for eight hours the solution was cooled, washed with water and dried over anhydrous potassium carbonate. On distillation the portion boiling at 185–210° (2–3 mm.) was collected; the yield was 6.0 g. (55%). Most of this material boiled at 201° (2–3 mm.). A sample of the constant-boiling fraction was collected for analysis.

Anal. Calcd. for $C_{19}H_{21}O_4N$: C, 69.70; H, 6.47. Found: C, 69.84, 69.87; H, 6.07, 6.11.

(3,4-Dihydro-1-naphthyl)-succinic Acid IX.—Saponification of 1.00 g. of the above succinic ester VIII was effected with 10% methanolic potassium hydroxide solution. After ten hours of refluxing in an atmosphere of nitrogen the mixture was acidified, and the precipitate was recrystallized from dilute methanol. The yield of dibasic acid IX was 0.41 g. (55%), m. p. 177–180°. On mixing with an authentic specimen of IX (m. p. 180–182°),[10a] the melting point was 177–180°.

β-(3,4-Dihydro-1-naphthyl)-propionic Acid (VII).—A solution of 1.00 g. of VIII in 15 cc. of acetic acid and 15 cc. of concentrated hydrochloric acid was allowed to reflux for twenty hours. The cooled mixture was diluted with water and extracted with ether. The ether solution was extracted with saturated sodium bicarbonate solution. Acidification of the latter gave a solid acid, which on recrystallization from dilute methanol melted at 107–110°, and had a neutral equivalent of 200 (calcd. for VII, 202); the yield was 0.30 g. (49%). The mixed melting point with β-(3,4-dihydro-1-naphthyl)-propionic acid (m. p. 107–109°)[10a] was 107.5–110°.

γ-(1-Keto-1,2,3,4-tetrahydro-2-naphthoyl)-butyric Acid (XIb).—The condensation between tetralone-1 (2.93 g.) and diethyl glutarate (3.76 g.) was carried out in an ethereal suspension of dry, alcohol-free sodium ethoxide (3.20 g.). The procedure (a) previously described[10a] for the Stobbe condensation was followed. Acidification of the aqueous alkaline extract yielded 1.71 g. of the crude keto acid XIb, m. p. 158–163°, which gave an intense purple color with ferric chloride. The keto acid was obtained rather than the ester XIa, because the latter is easily saponified with cold aqueous alkali in which the enolate is somewhat soluble. Further treatment of the neutral portion of the condensation mixture with dilute alkali afforded an additional 0.36 g. of the keto acid XIb bringing the total yield up to 40%. A pure sample of the acid was obtained by the following steps: reprecipitation from a filtered aqueous solution of its salt, distillation in a two-bulb flask under reduced pressure, recrystallization from ethyl acetate, then from ethanol. This gave yellowish needles, m. p. 171.5–172.5°.

Anal. Calcd. for $C_{15}H_{16}O_4$: C, 69.21; H, 6.20; N. E., 260. Found: C, 69.28; H, 6.23; N. E., 263.

When an alkaline solution of the keto acid XIb was boiled, the odor of tetralone-1 was apparent. The identity of this hydrolytic product was definitely established by conversion to the semicarbazone. No depression of the m. p. was exhibited on admixture with an authentic sample of tetralone-1 semicarbazone.

Ethyl γ-(1-Keto-1,2,3,4-tetrahydro-2-naphthoyl)-butyrate (XIa).—In another condensation 11.7 g. of tetralone-1, 15.0 g. of diethyl glutarate and 5.7 g. of sodium ethoxide were employed. The acid obtained from the aqueous extracts amounted to 5.9 g. The neutral portion in ether solution was distilled at reduced pressure. The keto ester XIa distilled as a yellow oil, b. p. 180–190° (1–2 mm.) which solidified in the receiver; yield 7.3 g. A sample purified by recrystallization from ether–petroleum ether was obtained as colorless plates, m. p. 60.5–61.5°. Like the acid it gave a purple color with ferric chloride.

Anal. Calcd. for $C_{17}H_{20}O_4$: C, 70.81; H, 6.99. Found: C, 70.86; H, 6.83.

Summary

1 - Keto - 1,2,3,4,9,10 - hexahydrophenanthrene has been prepared in a three-step synthesis from tetralone-1. The steps are (1) condensation with cyanoacetic ester to form the tetrahydronapthylidenecyanoacetic ester, followed by (2) the Michael addition of the latter to methyl acrylate, and (3) simultaneous cyclization and hydrolysis of this product with a mixture of hydrobromic and acetic acid. Some other methods of conducting the cyclization also have been investigated.

The tetrahydronapthylidenecyanoacetic ester has been alkylated with chloroacetic ester. The product on alkaline hydrolysis affords (3,4-dihydro-1-naphthyl)-succinic acid, and on acid hydrolysis, β-(3,4-dihydro-1-naphthyl)-propionic acid.

The alkoxide-catalyzed condensation of diethyl glutarate with tetralone-1 has been investigated. The reaction proceeds by way of an acetoacetic ester rather than a Stobbe type of condensation.

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[16] Linstead and Thomas, *J. Chem. Soc.*, 1127 (1940).

[17] Microanalysis by Arlington Laboratories, Fairfax, Virginia.