# *Synthesis of 3, 6-Dimethyl-2, 3-dihydro-1H-cyclopent[a]anthracene. A Possible Dehydrogenation Product of Anthranoid Rearrangement Product of Steroids**

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(Received February 11, 1959)

A number of works have been accumulated on the dienone-phenol rearrangement of the steroid A ring, and there can be found scrupulous studies on the structures of the products of this rearrangement1), the relation between the products and the reaction conditions2), and the effects of the structures on the rearrangement course3). Stimulated by these studies on steroids, various model compounds were synthesized and the same pattern of reaction was demonstrated4).

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* A preliminary note appeared in *Chem. & Ind.*, **1958**, 43.

1) H. Minlon, *Naturwissenschaften*, **36**, 765 (1938); R. B. Woodward, H. H. Inhoffen, H. O. Larson and K. H. Menzel, *Chem. Ber.*, **86**, 594 (1955); and Inhoffen's preceeding papers, **1940–1953**.

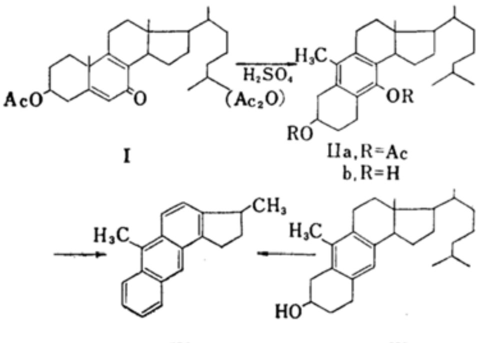
2) A. S. Dreiding and Ann Voltman, *J. Am. Chem. Soc.*, **68**, 1715 (1946); A. S. Dreiding, W. J. Pummer and A. J. Tomosewski, ibid., **75**, 3159 (1953).

3) A. L. Wilds and C. Djerassi., ibid., **68**, 1715 (1946); and numerous studies by Djerassi, ibid., **70**, 1911, 3962 (1948); **72**, 4540 (1950); **73**, 990, 1523 (1951); **76**, 1741 (1954); and *J. Org. Chem.*, **15**, 896 (1950).

4) R. B. Woodward and T. Singh, *J. Am. Chem. Soc.*, **72**, 494 (1950); R. T. Arnold, ibid., **71**, 1781 (1949); **69**, 2322 (1947); **72**, 3153 (1950); F. M. Marbell and E. Magoon, ibid., **77**, 2542 (1955); **76**, 5118 (1954).

But, as to the dienone-phenol rearrangement of the steroid B ring[5], thorough study is still lacking and the structures of the rearrangement products have remained obscure. Tsuda's group[6] was the first to carry out the structural study of a dienone-phenol rearrangement product of the steroid B ring. Namely, 7-keto-5, 8(9)-cholestadien-3β-yl acetate (I)[6,7], prepared by chromic acid oxidation of 5,8(9)-cholestadien-3β-yl acetate in acetic acid, was treated with concentrated sulfuric acid in acetic anhydride to give phenol acetate(IIa). After hydrolysis of IIa with ethanolic potassium hydroxide to a phenol IIb, m. p. 261~265°C, they submitted this phenol to selenium dehydrogenation to obtain, among other products, a hydrocarbon (oil) $C_{19}H_{18}$ in the form of picrate, m. p. 133.5~134°C. The ultraviolet absorption which showed an anthracene type pattern, was attributed by them to the structure IV, and consequently structure IIb was assumed for the phenol, m. p. 261~265°C.

This type of rearrangement is not the only one which can convert the perhydrophenanthrene skeleton of steroids into the perhydroanthracene skeleton, but a smooth "anthrasteroid" rearrangement studied by Mosettig and coworkers[8] can be counted as another type of conversion leading to the anthracene skeleton. Tsuda and coworker[9] also carried out a modification of "anthrasteroid" rearrangement of $\Delta^{5,8}$-cholestadien-3β-ol to the product III, in the presence of mercuric acetate and toluenesulfonic acid in ethanol under the influence of strong irradiation[10]. Dehydrogenation of product III with selenium afforded the same hydrocarbon $C_{19}H_{18}$, which they obtained from II previously. Since 3, 6-dimethyl-2, 3-dihydro-1-*H*-cyclopent[*a*]anthracene (IV) is a dehydrogenation product to be expected from the "anthranoid rearrangement" product and corresponds to Diels' hydrocarbon usually obtained by the dehydrogenation of steroids, the synthesis of this compound IV is considered to be important[11]. In this paper we report the synthesis of compound IV.



IV III

Fig. 1

Whereas the synthetic routes to the phenanthrene type dehydrogenation products of steroids have been well explored[12], there have been few to prepare the anthracene type like IV. Compound VII appears to be the most promising starting material which could be transformed into IX by Johnson's modification of Stobbe condensation[13](Fig. 2). 1-Methyl-2-naphthoic acid (VIa), prepared either

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5) D. H. R. Barton and B. R. Thomas, *J. Chem. Soc.*, **1953**, 1842, converted 7-ketolanosta-5,8-dien-3β-yl acetate into "isomeric phenol" by boiling with acetic acid and zinc dust. P. Bladon, *J. Chem. Soc.*, **1955**, 2176, obtained a phenol from 3β-acetoxylumista-5,8 (9), 20-trien-7-one ($\lambda_{max}$ 246 mμ, ε 11,800) by the action of acetic acid and zinc dust, and discussed the structure. They also pointed out another possible route of dienone-phenol rearrangement by methyl migration.

6) K. Tsuda, K. Arima and R. Hayatsu, *J. Am. Chem. Soc.*, **76**. 2933 (1954). Compound I shows ultraviolet absorption at $\lambda_{max}$ 238 mμ (log ε 4.475), $[\alpha]_D^{22}-67.3°$. m. p. 151~152°C. Semicarbazone: m. p. 210~212°C (decomp.). The same compound prepared by Inhoffen by another route has m. p. 169~170°C $[\alpha]_D^{20}-9°$, $\lambda_{max}$ 248 mμ, ε 12,800 (methanol). H. H. Inhoffen and W. Menzel, *Chem. Ber.*, **87**, 146 (1954).

7) Other steroids possessing 5,8(9)-dien-7-one structure show maxima of ultraviolet absorption as follows: 3β-hydroxy-5,8(9), 20-ergostatrien-7-one, $\lambda_{max}$ 247 mμ (ε 21,000) (D. C. Burke, J. H. Turnbull and W. Wilson, *J. Chem. Soc.*, **1953**, 3237): 3β-acetoxy-5,8(9). 20-ergostatrien-7-one, $\lambda_{max}$ 245 mμ (ε 11,800) (J. Elks, R. M. Evans, A. G. Long and G. H. Thomas, ibid., **1954**, 451); $\lambda_{max}$ 246 mμ (ε 12,800) (J. Elks, R. M. Evans, J. F. Oughton and G. H. Thomas, ibid., **1954**, 463).

8) E. Mosettig and I. Scheer, *J. Org. Chem.*, **17**, 764 (1952); W. R. Nes and E. Mosettig, *J. Am. Chem. Soc.*, **75**, 2787 (1953); **76**, 3182, 3186 (1954); W. R. Nes, ibid., **78**, 193 (1956); I. Scheer, W. R. Nes and P. B. Smeltzer, ibid., **77**, 3300 (1955); W. R. Nes, R. B. Kostic and E. Mosettig, ibid., **78**, 36 (1956). We would like to propose the general term "anthranoid rearrangement" for all rearrangements of steroids to the compounds possessing an anthracene skeleton, and to restrict the term "anthrasteroid rearrangement" to the type of Mosettig's reaction.

9) K. Tsuda and R. Hayatsu, *J. Am. Chem. Soc.*, **77**, 3089 (1955).

10) Being a photochemical reaction accompanied by simultaneous dehydrogenation, the mechanism appears complicated. But the product is in sharp contrast to the product of Mosettig's rearrangement in maintaining the 3-hydroxyl group unattacked.

11) After we completed the synthesis of IV, A. W. Burgstahler, *J. Am. Chem. Soc.*, **79**, 6047 (1957), published a paper in which he described an elegant proof of the structure of anthracholestatetraene proposed by Mosettig et al.

12) L. F. Fieser and M. Fieser, "Natural Products Related to Phenanthrene", 3rd Ed., Reinhold Pub. Corp., New York (1949), p. 148—154.

13) W. S. Johnson and G. H. Daub, "Organic Reactions", Vol. 6, John Wiley & Sons, Inc., New York (1951), p. 1.

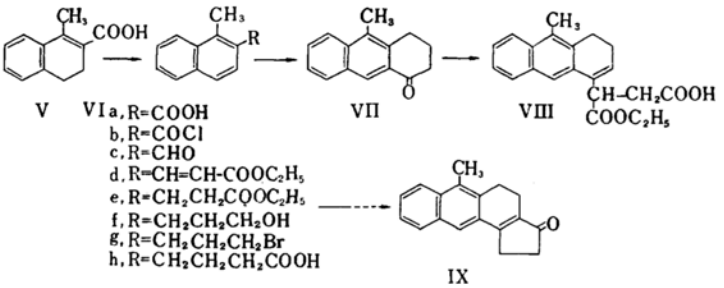

Fig. 2.

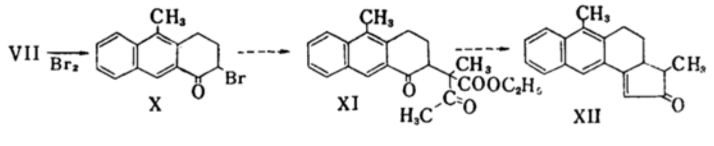

Fig. 3.

by dehydrogenation[14] of V by means of bromine or by the Grignard synthesis from $\alpha$-(chloromethyl)naphthalene, was converted into the aldehyde VIc via the aicd chloride VIb by means of the Rosenmund reduction with Pd-$BaSO_4$. By the Claisen condensation with ethyl acetate, VIc gave the unsaturated ester VId, which in turn was catalytically hydrogenated to VIe. The alcohol VIf, obtained by lithium aluminum hydride reduction of VIe, was treated with phosphorus tribromide to afford the bromide VIg, which gave the acid VIh by the usual nitrile synthesis and hydrolysis.

The Stobbe condensation of the ketone VII, easily accessible from the acid VIh by Wilds' method[15], led to the formation of VIII, but the ring closure to IX by Johnson's method[16] using zinc chloride was unsuccessful, probably owing to the vulnerability of the $\alpha$-position of the naphthalene nucleus to the cationoid attack which would direct the ring closure in an undesired direction. Although the plan to build up the D ring by Johnson's method failed, various synthetic routes which can be carried out in a basic medium so as to avoid the complicated side reaction encountered above, were tried with the ketone VII to secure the D ring.

Condensation of the bromoketone X, provided by the bromination of the ketone VII in ether, with potassium ethyl methylacetoacetate[17] in *tert*-butanol failed to give XI, which was expected to afford XII by ring closure.

Another route tried was an indirect one (Fig. 4). The alcohol XVII which would be prepared following the scheme whereby Johnson achieved his brilliant equilenine synthesis[18], might give IV on dehydrogenation accompanied by the simultaneous migration of the angular methyl group to the position originally occupied by the hydroxyl group.

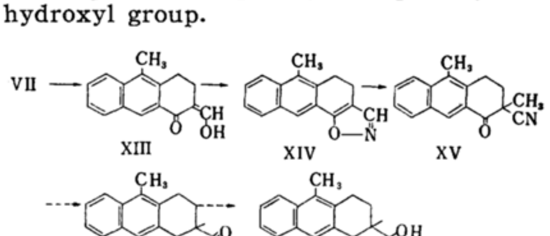

Fig. 4.

The process leading to XV was carried out smoothly, but again the Stobbe condensation of the $\alpha$-cyanomethylketone to afford XVI was fruitless, probably owing to the ready opening of the ketone XV with the base. The sequence of the steps which finally led to IV is shown in Fig. 5.

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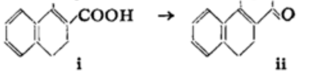
[14] When dehydrogenation was carried out in acetic acid, the bromination product i was the main product, which could be converted into the lactone ii by hydrolysis with methanolic potassium hydroxide followed by acidification.



[15] A. L. Wilds, *J. Am. Chem. Soc.*, **64**, 1424 (1942).

[16] W. S. Johnson and J. W. Peterson, ibid., **67**, 1367 (1945).

[17] Wilds succeeded in the same type of condensation using ethyl acetoacetate, *J. Am. Chem. Soc.*, **64**, 1421 (1949).

[18] W. S. Johnson et al., ibid., **69**, 2942 (1947).

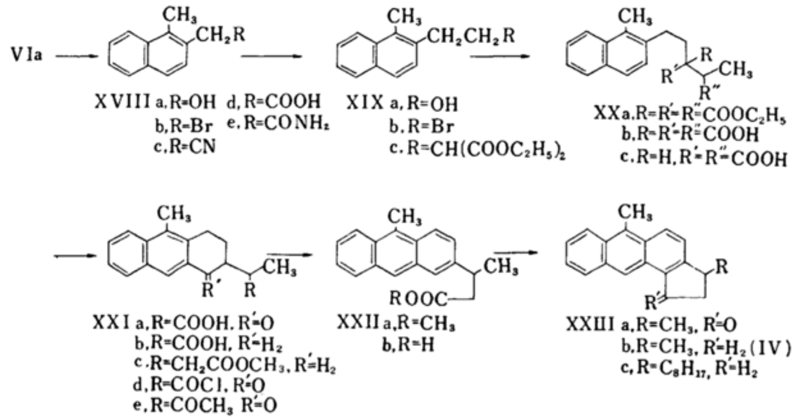


Fig. 5.

1-Methyl-2-naphthoic acid (VIa) was reduced with lithium aluminum hydride to give the alcohol XVIIIa, and its side chain was extended to the homologous alcohol XIXa by the usual sequence of reactions (bromide XVIIIb→cyanide XVIIIc →acid XVIIId→alcohol XIXa). The alcohol XIXa was treated with phosphorus tribromide in benzene to yield the bromide XIXb, which gave the condensation product XIXc with ethyl sodiomalonate.

Condensation of XIXc with ethyl $\alpha$-bromopropionate in the presence of potassium *tert*-butoxide led to the triester XXa. The tricarboxylic acid XXb obtained by the hydrolysis of XXa with methanolic potassium hydroxide was decomposed to the dicarboxylic acid XXc, which was cyclized to the ketocarboxylic acid XXIa by $PCl_5$-$SnCl_4$ method of Wilds[15,19], whereas the ring closure using polyphosphoric acid[20] resulted only in the recovery of the starting material.

After the carbonyl group of XXIa was removed by the Clemensen-Martin reduction, the resulting acid XXIb[21] was transformed into the methyl ester of the homologous acid XXIc by the Arndt-Eistert method. Heating with 30% Pd-C at 290~300°C, followed by hydrolysis, converted the ester XXIc into the anthracene derivative XXIIb, m. p. 160~160.5°C, which showed an ultraviolet absorption spectrum characteristic of an anthracene type (see *Experimental*).

The appearance of new bands in the infrared absorption spectrum (11.90 and 12.30 $\mu$) which can be attributed to the 1, 2, 4-trisubstituted benzene structure[22], together with the characteristic absorption in ultraviolet region, leaves no doubt about the anthracene structure of the compound. The ring closure[23] of the acid XXIIb by $PCl_5$-$SnCl_4$ method accomplished the ketone XXIIIa, which exhibited infrared absorption band at 5.93 $\mu$ (indanone)[24] and 12.2 $\mu$ (two adjacent hydrogens on aromatic hydrocarbon). The ultraviolet absorption spectrum which is very close to $\alpha$-acetylanthracene (see Table I) also confirms the structure of the ketone.

The final stage to IV was the Clemensen-Martin reduction of the ketone XXIIIa. The oily product was purified by chromatography on alumina column to provide colorless crystals, m. p. 78~79.5°C after recrystallization from methanol. The picrate melted at 128~128.5°C (the picrate of Tsuda's hydrocarbon, m. p. 133~134°C), and the 2, 4, 6-trinitrobenzolate at 142~142.5°C. The ultraviolet absorption spectrum of the hydrocarbon XXIIIb (IV) could in almost every detail be overlapped on the spectrum of Mosettig's hydrocarbon XXIIIc (dehydroanthracholesterol), whereas Tsuda's hydrocarbon showed an anomalous absorption in the long wavelength, presumably owing to impurity[25].

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[19] To get the methyl ketone XXIe, which would give a five membered D ring was tried in vain. Cf. A. L. Wilds et al., *J. Am. Chem. Soc.*, **69**, 3079 (1947); **66**, 1688 (1944).

[20] D. D. Gardner and W. J. Horton, ibid., **74**, 4976 (1953).

[21] Two racemates of compound XXIb can be expected, but no attempt was made to separate them.

[22] H. Dannenberg, U. Shiedt and W. Sheidle, *Z. Naturforsh.* **B8**, 269 (1953).

[23] The reactivity to cationoid attack is much greater at $\alpha$-position on anthracene than at $\beta$-position. Cf. L. F. Fieser and H. Heymann, *J. Am. Chem. Soc.*, **63**, 2333 (1941) and W. S. Johnson, "Organic Reactions", Vol. 2, John Wiley & Sons, Inc., New York (1946). p. 114.

[24] H. Dannenberg and D. D. Dannenberg, *Ann.*, **585**, 1 (1954), reported the absorption at 5.92 $\mu$ in the similar system.

[25] The selenium dehydrognation of IIb may lead, although it is highly unlikely, to another structure than IV, but in the case of dehydrogenation of III to IV, there is no reason to expect serious change of the skeleton.

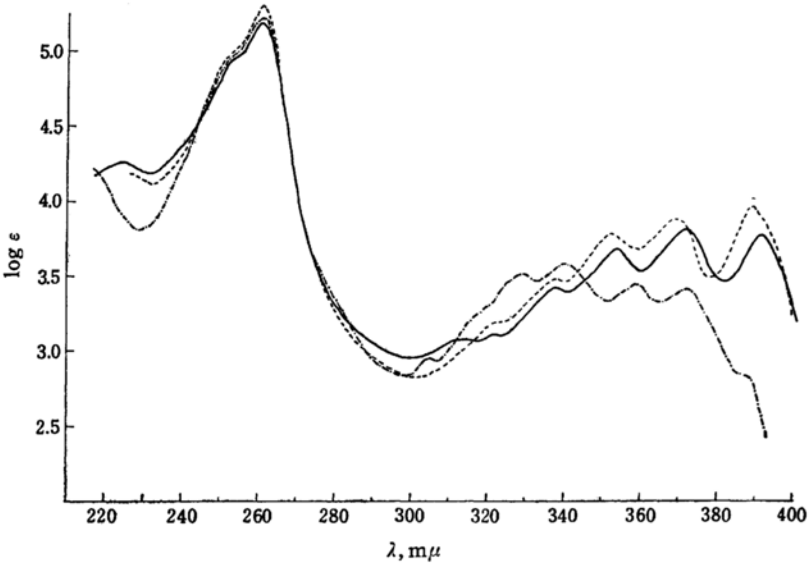

Fig. 6.

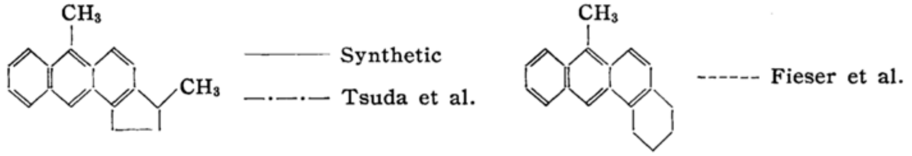

TABLE I.

| XXIIIa[1] | | α-Acetyl anthracene[2] | | IV (synthetic)[3] | | IV (Tsuda)[4] | | XXIIIc (Mosettig)[5] | | 1,2,3,4-Tetra-hydro-10-methyl-beazanthrene[6] | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $\lambda_{max}$ | log ε | $\lambda_{max}$ | log ε | $\lambda_{max}$ | ε | $\lambda_{max}$ | ε | $\lambda_{max}$ | ε | $\lambda_{max}$ | log ε |
| 245 | 4.72 | 241 | 4.76 | 226 | 18,040 | | | 227 | 16,550 | | |
| 263 | 4.73 | 254 | 4.84 | 238 | 21,530 | | | 234 | 17,550 | | |
| 332 | 3.22 | 330 | 3.24 | 255 | 93,750 | | | | | | |
| 346 | 3.49 | 346 | 3.53 | 261 | 145,200 | 262 | 123,600 | 262 | 165,000 | 261 | 5.3 |
| 363 | 3.66 | 366 | 3.71 | 308 | 1,270 | 303 | 790 | | | | |
| 395 | 3.77 | 385 | 3.73 | 323 | 1,317 | 328 | 3,170 | | | | |
| | | | | 338 | 2,650 | 341 | 4,150 | 338 | 2,750 | 336 | 3.5 |
| | | | | 354 | 4,765 | 358 | 4,000 | 354 | 5,000 | 351 | 3.8 |
| | | | | 372 | 6,690 | 372 | 2,980 | 372 | 7,420 | 368 | 3.9 |
| | | | | 393 | 6,260 | 388 | 710 | 391 | 7,520 | 388 | 4.0 |

1) In ethanol.
2) In ethanol: R. N. Jones, *J. Am. Chem. Soc.*, **67**, 2127 (1945). β-Acetylanthracene: see R. N. Jones, *Chem. Revs.*, **41**, 353 (1947).
3) In ethanol.
4) In solvent unspecified: K. Tsuda, K. Arima and R. Hayatsu, *J. Am. Chem. Soc.*, **76**, 2933 (1954); K. Tsuda and R. Hayatsu, ibid., 77, 3089 (1955).
5) In isooctane: W. R. Nes, R. B. Kostic and E. Mosettig, ibid., **78**, 436 (1956).
6) In ethanol: L. F. Fieser and E. B. Hershberg, ibid., **60**, 940, (1938).

## Experimental**

**Ethyl α-Aceto-γ-phenylbutyrate.**—To a stirred and cooled solution of sodium ethoxide prepared from 450 cc. of absolute ethanol and 23 g. of sodium, 143 g. of ethyl acetoacetate was added in an atmosphere of nitrogen, and the reaction mixture was warmed to 60~70°C. After the addition of 197 g. of phenethyl bromide (b. p. 96~98°C/11 mmHg) over a period of 2 hr., the mixture was heated at 70~75°C for 5 hr., 80~85°C

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** All ultraviolet spectra were measured with a Beckmann spectrophotometer DK 2, and infrared spectra with a Perkin Elmer Model 12 C. The anlyses were performed in the Microanalytical Laboratory of the Institute of Polytechnics, Osaka City University, Osaka.

for an additional 5 hr., and refluxed for 6 hr. on a water bath. After the solvent was removed, the residue was poured into water, made sligitly acidic with hydrochloric acid, and extracted with ether. The organic layer was washed with water and dried over anhydrous sodium sulfate, and the ether was removed.

The ester distilled at 124∼127°C/1 mmHg, and weighed 163 g. (Yield, 69.5%).

**1-Methyl-3, 4-dihydro-2-naphthoic Acid.**—Ninety grams of ethyl $\alpha$-aceto-$\gamma$-phenylbutyrate was added dropwise to 375 cc. of concentrated sulfuric acid chilled at $-4$°C with stirring more than 40 min., and the mixture was kept at this temperature for 2 hr. After the reaction mixture was poured on crushed ice, the crystals were collected and washed thoroughly with water. After being dried, they weighed 64.5 g. (yield, 84.2%), and were used in dehydrogenation without further purification. A small portion was recrystallized from petroleum ether, m. p. 127∼130°C. (literature[26]: m. p. 129∼130°C).

**1-Methyl-2-naphthoic Acid (VIa).**—*Dehydrogenation of V.*—To a solution of 58 g. of V in 300 cc. of carbon tetrachloride, 54 g. of bromine was added at 65∼70°C over a period of 2 hr. with stirring. After additional heating (70∼75°C) for 2 hr. with stirring, the mixture was cooled to deposite crystals.

The crude crystalline product (55.6 g.) was dissolved in a solution of 40 g. of sodium hydroxide in 750 cc. of water and the solution was heated on a water bath for 2 hr., and treated with Norit. The alkaline solution was freed from Norit, and made acidic with 1 N hydrochloric acid to afford 34.5 g. of crude VIa (yield, 44.1%), which was recrystallized, m. p. 177.5∼178°C (literature[26]: 177∼178°C).

*Grignard synthesis from $\alpha$-(chloromethyl)naphthalene.*—To a suspension of 35 g. of magnesium in 360 cc. of absolute ether, was added 85 g. of $\alpha$-(chloromethyl)naphthalene in 200 cc. of ether with stirring for more than 5 hr., and the mixture was refluxed for 1 hr.

The Grignard solution was filtered through glass wool to remove excessive magnesium, and added to a chilled solution of 215 g. of ethyl chlorocarbonate in 160 cc. of ether taking more than 40 min. After being kept at room temperature for 30 min., the mixture was decomposed with dilute sulfuric acid and ice, and the organic layer was washed in turn with water and dilute sodium carbonate solution. Romoval of the solvent gave a liquid, which boiled at 140∼143°C/2∼3 mmHg and weighed 46.6 g. Hydrolysis of the ester with 20 g. of potassium hydroxide, 25 cc. of water and 50 cc. of methanol gave 28.6 g. of VIa, m. p. 160∼170°C. Recrystallization from benzene raised the m. p. to 175∼176°C.

**1-Bromomethyl-3, 4-dihydro-2-naphthoic Acid (i).**—To a solution of 15 g. of V (m. p. 127∼130°C) in 60 cc. of glacial acetic acid, a mixture of 13.8 g. of bromine and 20 cc. of acetic acid was added with stirring for more than 1.5 hr. The color of bromine disappeared rather rapidly. The solution was warmed at 55°C for 30 min., and a small amount of sodium sulfite was added to discharge the bromine color.

Crystals, precipitated by the addition of water, were collected and washed with water to give 20 g. of the bromide i, which was recrystallized from benzene to give prismatic crystals, m. p. 177°C (decomp.).

*Anal.* Found: C, 54.44; H, 4.23; Br, 29.96. Calcd. for $C_{12}H_{11}O_2Br$: C, 53.50; H, 4.15; Br, 29.93%.

**The Lactone (ii).**—Five grams of i was dissolved in a solution of 5 g. of potassium hydroxide in 1 cc. of water and 30 cc. of methanol, and the solution was refluxed on a water bath for 40 min. After the addition of 30 cc. of water, the alkaline solution was made acidic to precipitate an oil, which was decanted from superfluous liquid. The viscous oil could be crystallized by trituration with a cold dilute sodium hydroxide solution.

Recrystallization from petroleum ether gave the lactone ii melting at 112∼113°C.

*Anal.* Found C, 77.48; H, 5.68. Calcd. for $C_{12}H_{10}O_2$: C, 77.42; H, 5.38%.

**1-Methyl-2-naphthoyl Chloride (VIb).**—A mixture of 35.0 g. of VIa and 44.5 g. of thionyl chloride was refluxed on a water bath for 2 hr. The excess of thionyl chloride was removed to give an oil, which distilled at 136∼138°C/2 mmHg, m. p. 79∼80.5°C and weighed 36.5 g. The anilide was recrystallized from ethanol m. p. 212∼214°C.

*Anal.* Found: C, 82.75; H, 6.04; N, 5.55. Calcd. for $C_{18}H_{15}ON$: C, 82.73; H, 5.79; N, 5.36%.

**1-Methyl-2-naphthaldehyde (VIc).**—A stream of hydrogen was introduced into a stirred mixture of 36.5 g. of VIb and 3.4 g. of 5% Pd/$BaSO_4$[27] in 330 cc. of xylene at 110°C. When the evolution of hydrogen chloride ceased (in about 2 hr.), the reaction mixture was cooled and freed from the catalyst. Removal of the solvent in vacuo followed by distillation gave 15.4 g. of an oil (yield, 50.6%), which solidified gradually on standing. The semicarbazone was recrystallized from dilute acetic acid, m. p. 227∼231°C (decomp.).

*Anal.* Found: C, 69.16; H, 5.61. Calcd. for $C_{13}H_{13}ON_3$: C, 68.70; H, 5.77%.

**Ethyl $\beta$-(1-Methyl-2-naphthyl)acrylate (VId).**—A mixture of 42 cc. of ethyl acetate and 0.3 cc. of absolute ethanol was added all at once to the cooled powdered sodium[28] provided by vigorous stirring of 2.7 g. of molten sodium under refluxing xylene followed by decantation from the xylene. After stirring for 10 min. at $-5$°C, a solution of 15.2 g. of the aldehyde VIc in 30 cc. of ethyl acetate was added over a period of 1.5 hr. and the mixture was stirred for 1.5 hr. at $-6$°C. The dark red reaction mixture was decomposed by adding 9 cc. of acetic acid and then 200 g. of ice, and the aqueous layer was extracted with ethyl acetate twice. The combined extract was washed

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[26] K. V. Auwers and K. Möller, *J. prakt. Chem.*, **109**, 124 (1925).

[27] R. Mozingo "Organic Syntheses", Vol. 26, John Wiley & Sons, Inc., New York (1946), p. 77.

[28] C. S. Marvel and W. B. King, ibid., Col. Vol. 1, (1948), p. 252.

with water, 5% sodium bicarbonate solution and water. After drying, the solvent was removed to afford a pale yellow liquid, which was distilled to give 10.1 g. of a colorless liquid, b. p. 167~173°C/2 mmHg, (yield, 47%), which solidified on standing and recrystallized from petroleum ether, m. p. 62~63°C.

*Anal.* Found: C, 80.25; H, 6.97. Calcd. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71%.

**Ethyl β-(1-Methyl-2-naphthyl)propionate (VIe).**—Catalytic hydrogenation of 15.3 g. of the unsaturated ester VId with 0.4 g. of 10% Pd/C in 180 cc. of ethanol gave an oil which boiled at 161~162°C/2 mmHg and weighed 11.4 g. (yield, 75%).

*Anal.* Found: C, 79.59; H, 7.71. Calcd. for $C_{15}H_{18}O_2$: C, 79.31; H, 7.49%.

**3-(1-Methyl-2-naphthyl)-1-propanol (VIf).**—To a slurry of 0.95 g. of lithium aluminum hydride in 40 cc. of ether, a solution of 5.4 g. of the ester VIe in 20 cc. of ether was added with stirring. After refluxing for 1 hr., the excess of the reducing reagent was decomposed by adding 4 cc. of ethyl acetate and then 25 cc. of water and 15 cc. of concentrated hydrochloric acid. The organic layer was washed with water, 5% sodium bicarbonate solution and water again. After drying over anhydrous magnesium sulfate, the solvent was removed to give an oil, which was purified by distillation in vacuo, b. p. 173~174°C/3 mmHg. 4.1 g. (yield, 91.9%). The phenylurethane was recrystallized from benzene-petroleum ether, m. p. 113~114°C.

*Anal.* Found; C, 78.96; H, 7.03. Calcd. for $C_{21}H_{21}O_2N$: C, 78.97; H, 6.63%.

**1-Bromo-3-(1-methyl-2-naphthyl)-propane (VIg).**—A solution of 5.0 g. of the alcohol VIf in 19 cc. of benzene was added dropwise to a stirred mixture of 5.0 g. of phosphorus tribromide and 125 cc. of benzene. After heating at 70~75°C for 4 hr., the mixture was poured into ice water and saturated with sodium chloride. The benzene layer was separated, and the aqueous layer was extracted with ether. The combined benzene solution and ether were washed with water and dried over anhydrous magnesium sulfate. The residue freed from the solvent was distilled at 135~136°C/0.002 mmHg, to give the bromide VIg weighing 5.2 g. (yield, 80.4%).

**3-(1-Methyl-2-naphthyl)-1-propanecarboxylic Acid (VIh).**—A mixture of 5.2 g. of the bromide VIg, 89 cc. of ethanol, 5.0 g. of potassium cyanide and 20 cc. of water was refluxed for 26 hr. After removal of the ethanol, the mixture was poured onto ice, acidified with 20 cc. of concentrated hydrochloric aicd, and extracted with ether.

After removal of the ether the residual oil was hydrolyzed by boiling with 59 cc. of acetic acid and 33 cc. of concentrated hydrochloric acid for 7 hr., while 1.2 cc. of concentrated hydrochloric acid was added every hour. The crystals deposited on cooling melted at 123~125°C and weighed 4.3 g. (yield, 94.6%). Recrystallization from benzene-petroleum ether raised the melting point to 126~127°C.

*Anal.* Found: C, 79.62; H, 7.05. Calcd. for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06%.

**1-Oxo-10-methyl-1, 2, 3, 4-tetrahydroanthracene (VII).**—To a solution of 5.1 g. of the carboxylic acid VIh in 44 cc. of dry benzene, 9.2 g. of phosphorus pentachloride was added. After stirring at room temperature for 1 hr., the mixture was heated for 10 min. at 45~50°C, and then a solution of 28.6 g. of stannic chloride in 22 cc. of benzene was added to the chilled solution. The orange-red solution was stirred for 50 min. with cooling in an ice bath, and was decomposed with 200 cc. of water. Addition of 22 cc. of concentrated hydrochloric acid was followed by extraction with ether, and the organic layer was washed with water, 1 N sodium hydroxide solution and water. After drying over anhydrous magnesium sulfate, the solvent was removed to give a solid weighing 4.3 g. (yield, 91.7 g.), which was recrystallized from methanol, m. p. 99.5~100.5°C, 4.0 g. An infrared absorption spectrum indicated a peak at 5.97 μ.

*Anal.* Found: C, 85.95; H, 7.62. Calcd. for $C_{15}H_{14}O$: C, 85.68; H, 6.71%.

**The Stobbe Condensation of VII.**—In a stream of nitrogen, 1.2 g. of potassium was dissolved in 22 cc. of *tert*-butanol. To the solution was added a mixture of 5.4 g. of the ketone VII, 7.2 g. of diethyl succinate and 7.5 g. of *tert*-butanol and the mixture was heated at 110°C for 50 min. To the cooled solution, 8.5 cc. of concentrated hydrochloric acid and 50 cc. of water was added, the separated brown oil was extracted with ether. After being washed with water, the ether layer was extracted with three portions of 160 cc. of 1 N ammonia water to separate the half ester VIII. The turbid solution was cleared with Norit, and was acidified with 4 N hydrochloric acid to precipitate an oil, which was extracted with ether. The ether extract was washed with water and dried over anhydrous magnesium sulfate. To the brown residue (5.3 g.) was added 50 cc. of acetic acid and then a solution of 25 cc. of acetic acid and 1.5 g. of zinc chloride. The solution was heated on a free flame for 5 hr. The reaction mixture turned blue-black in color, and was filled with a voluminous amorphous solid, from which no traceable material was isolated.

**1-Oxo-2-bromo-10-methyl-1, 2, 3, 4-tetrahydroanthracene (X).**—To a chilled suspension of 2.6 g. of the ketone VII in 20 cc. of ether, a solution of 2.0 g. of bromine in 10 cc. of ether was added over a period of 10 min. with stirring. After stirring at room temperature for 2 hr., precipitated crystals were collected and recrystallized from methanol-acetone (3 : 1), m. p. 136~137°C. Yield, 2.7 g.

*Anal.* Found: C, 62.46; H, 4.71. Calcd. for $C_{15}H_{13}OBr$: C, 62.28; H, 4.50%.

**The Condensation of the Bromoketone X with Ethyl Methylacetoacetate.**—To a cold solution of potassium *tert*-butoxide prepared from 0.33 g. of potassium and 11 cc. of *tert*-butanol, 1.35 g. of ethyl methylacetoacetate was added and the mixture was stirred for 5 hr. at room temperature in an atmosphere of nitrogen. After a solution of 2.4 g. of the bromoketone X in 28 cc. of dry benzene was added taking more than 10 min., the reaction mixture was stirred at room temperature for 5 min., and refluxed for 1.5 hr. The solution was acidified with 10 cc. of 1 N hydrochloric acid and ice, and the organic layer was in turn washed with water and 2% sodium hydroxide solution. Removal of the solvent gave a brown oil (3.4 g.) from which no traceable material was isolated by chromatographic adsorption on alumina.

**1-Oxo-2-oxymethylene-10-methyl-1, 2, 3, 4-tetrahydroanthracene** (**XIII**).—To pulverized sodium methoxide prepared from 0.82 g. of sodium and 20 cc. of methanol, a solution of 2.64 g. of ethyl formate in 30 cc. of benzene was added with stirring and cooling in a gentle stream of nitrogen. A mixture of 3.7 g. of the ketone VII and 40 cc. of benzene was added dropwise with stirring for more than 17 min. The color of the solution changed from yellow-green to green-yellow. After heating at 8~20°C for 6 hr., ice water was added to precipitate the sodium salt of the oxymethylene ketone XIII, which was separated and washed with water. A reddish brown oil, separated on addition of hydrochloric acid to the aqueous solution of the sodium salt, was extracted with ether and the extract was washed with water and dried. Removal of the solvent gave 3.9 g. of a viscous oil, which showed a violet color reaction with ferric chloride and was used directly to prepare the isoxazole XIV.

**The Isoxazole XIV.**—To a solution of 3.90 g. of the crude oxymethylene ketone XIII in 144 cc. of acetic acid, was added 1.67 g. hydroxylamine hydrochloride and the mixture was heated at 75~80°C for 7 hr. After the solvent (about 120 cc.) was removed by evaporation in vacuo, 100 cc. of water was added to the mixture to precipitate an oil, which solidified upon standing. The crude isoxazole (3.65 g.) was recrystallized from diluted methanol to give needles melting at 111~112°C.

*Anal.* Found: C, 81.61; H, 5.67; N, 6.46. Calcd. for $C_{16}H_{13}ON$: C, 81.68; H, 5.57; N, 5.94%.

**The Cyanoketone XV.**—To a solution of potassium *tert*-butoxide provided from 1.68 g. of potassium and 47 cc. of *tert*-butanol, was added 3.15 g. of the isoxazole XIV, and the mixture was heated for 10 min. at 70°C. To the orange-red solution, 13.5 cc. of methyl iodide was added taking more than 7 min. at 70~73°C. After heating at 75°C for 25 min. the solvent was removed and water was added to precipitate crystals. They were collected and washed with water, m. p. 141~142°C. Yield, 3.25 g. The melting point was raised by recrystallization from ethanol to 142~143°C.

*Anal.* Found: C, 82.21; H, 6.16; N, 5.93. Calcd. for $C_{17}H_{15}ON$: C, 81.90; H, 6.06; N, 5.62%.

**The Stobbe Condensation of the Cyanoketone XV.**—To a solution of potassium *tert*-butoxide prepared from 0.75 g. of potassium and 30.5 cc. of *tert*-butanol, was added 6.8 cc. of diethyl succinate taking more than 5 min. with stirring and cooling, and then 2.15 g. of the cyanoketone XV. The mixture was stirred for 2 hr. at room temperature, heated at 50°C for 1 hr., and then stirred for 5 hr. at room temperature. After being kept overnight, 20 cc. of 2 N hydrochloric acid solution was added with cooling, when carbon dioxide was evolved. After removal of the solvent in vacuo at 40°C, the aqueous layer was extracted with ether, from which the acidic material was transferred into 5% potassium hydroxide solution. Upon evaporation of the ether, the organic layer gave a small amount of a solid melting at 220~221°C after recrystallization from benzene.

*Anal.* Found: C, 81.22; H, 6.90%.

This was not investigated further because of the small amount available. The alkaline solution which contained the acidic material was acidified with hydrochloric acid to afford a very viscous oil, which was not studied further.

**1-Methyl-2-hydroxymethyl-naphthalene** (**XVIIIa**).—To a slurry of 5.75 g. of lithium aluminum hydride in 120 cc. of ether, a solution of 16 g. of 1-methyl-2-naphthoic acid in 340 cc. of ether was added taking more than 30 min., and the mixture was refluxed for 1 hr. on a water bath. After the excess of the reducing reagent was destroyed with ethyl acetate, the white voluminous precipitate was dissolved in dilute hydrochloric acid, and extracted with ether. The ether extract was washed with water, sodium bicarbonate solution and water. Removal of the solvent gave 14.0 g. of crystals melting at 124~126°C, which were recrystallized from benzene, m. p. 126~126.5°C.

*Anal.* Found: C, 83.88; H, 7.26. Calcd. for $C_{12}H_{12}O$: C, 83,69; H, 7.02%.

**1-Methyl-2-bromomethyl-naphthalene** (**XVIIIb**).—To a solution of 25.3 g. of the alcohol XVIIIa in 90 cc. of acetic acid, 63 g. of acetic acid saturated with hydrobromic acid was added for more than 15 min. After the solution was heated at 50~52°C for 20 min., the precipitate was collected (35.1 g.). Recrystallization from acetic acid afforded crystals melting at 68~69°C, 41.3 g. (yield, 90.6%).

For analysis this was further recrystallized from ligroin to give crystals melting at 69~70°C.

*Anal.* Found: C, 61.37; H, 4.97. Calcd. for $C_{12}H_{11}Br$: C, 61.28; H, 4.68%.

**1-Methyl-2-cyanomethyl-naphthalene** (**XVIIIc**).—A mixture of 10 g. of the bromide XVIIIb, 100cc. of ethanol, 5.0 g. of potassium cyanide and 20 cc. of water was refluxed for 5.5 hr. After the ethanol was removed, 300 cc. of water was added to the solution to precipitate a solid which showed m. p. at 75.5~76.5°C after recrystallization from ligroin, and weighed 7.2 g. (yield, 93.5%).

*Anal.* Found: C, 85.97; H, 6.24; N, 7.98. Calcd. for $C_{13}H_{11}N$: C, 86.16; H, 6.12; N, 7.73%.

**(1-Methyl-2-naphthyl)-acetic Acid** (**XVIIId**) **and its Amide** (**XVIIIe**).—A mixture of 6.8 g. of the cyanide XVIIIc, 10 cc. of acetic acid, 10 cc. of concentrated hydrochloric acid and 10 cc. of water was refluxed for 30 min. After cooling, crystals (m. p. 146~158°C) were collected and washed with 5% sodium hydroxide solution to remove the acid XVIIId. The amide could be further hydrolyzed with concentrated hydrochloric acid and acetic acid to give the acid

XVIIId.

*Anal.* Found: C, 78.36; H, 6.60; N, 7.05. Calcd. for $C_{13}H_{13}ON$: C, 78.36; H, 6.58; N, 7.03%.

The alkaline extract was acidified to precipitate the acid XVIIId which was recrystallized from benzene to afford prisms, m. p. 165~166°C, weighed 5.7 g.

*Anal.* Found: C, 78.00; H, 6.03. Calcd. for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04%.

When an attempt was made to hydrolyze the crude cyanide XVIIIc directly, the overall yield of the acid was 83%.

**2-(1-Methyl-2-naphthyl)-ethanol (XIXa).**—To a slurry of 5.03 g. of lithium aluminum hydride in 120 cc. of ether, was added a solution of 14 g. of the acid XVIIId in 300 cc. of ether with stirring for more than 30 min., and the mixture was refluxed for 3 hr. The excess of the reducing reagent was destroyed with 20 cc. of ethyl acetate, and the mixture was decomposed with dilute hydrochloric acid.

The organic layer was separated and the aqueous layer was extracted with ether. After drying, removal of the ether gave an oil, which was distilled to give a liquid boiling at 140~143°C/1 mmHg and weighing 11.7 g. (yield, 90.0%). For analysis a small sample was recrystallized from ligroin, m. p. 54~55°C.

*Anal.* Found: C, 83.95; H, 7.63. Calcd. for $C_{13}H_{14}O$: C, 83.83; H, 7.58%.

**1-Bromo-2-(1-methyl-2-naphthyl)-ethane (XIXb).**—To a solution of 17.5 g. of the alcohol XIXa in 60 cc. of benzene, 19 g. of phosphorus tribromide in 24 cc. of benzene was added taking more than 25 min., and the mixture was stirred for 3 hr. at 60~70°C. The reaction mixture was poured onto crushed ice, and the bromide was taken into ether. After the ether layer was washed with saturated sodium chloride solution and water, it was dried over anhydrous sodium sulfate. Removal of the solvent gave a liquid, which was distilled to afford the bromide XIXb, boiling at 124~126°C/0.006 mmHg and weighing 14.4 g. (yield, 61.5%).

*Anal.* Found: C, 63.10; H, 5.50. Calcd. for $C_{13}H_{13}Br$: C, 62.60; H, 5.23%.

**Diethyl 1-(1-Methyl-2-naphthyl)-3, 3-propanedicarboxylate (XIXc).**—Under 40 cc. of xylene, 2.52 g. of sodium was pulverized, and the xylene was decanted off and replaced by 18 cc. of benzene. To this mixture, 16.2 cc. of absolute ethanol was added for more than 5 min., and heated for 5 min. After 25.2 cc. of diethyl malonate was added over a period of 10 min., the solution was heated for 10 min. on a water bath, and a solution of 14.3 g. of the bromide XIXb in 118 cc. of benzene was added taking more than 20 min. Then the mixture was heated at 60~63°C for 8 hr. at 70°C for 2 hr., and refluxed for an additional 4 hr. The solution was poured onto ice, acidified with diluted hydrochloric acid, and extracted with ether. The ether extract was washed with water and dried. The residue, obtained by evaporation of the solvent, was distilled to give an oil, b. p. 160~165°C/0.005 mmHg. Yield, 18.1 g. (96.3%).

*Anal.* Found: C, 72.00; H, 7.41. Calcd. for $C_{20}H_{24}O$: C, 73.14; H, 7.37%.

**Triethyl 5-(1-Methyl-2-naphthyl)-2, 3, 3-pentanetricarboxylate (XXa).**—To a solution of potassium *tert*-butoxide in *tert*-butanol, provided from 1.1 g. of potassium and 26 cc. of *tert*-butanol in an atmospher of nitrogen, 8.0 g. of the diethyl ester XIXc was added, the mixture was stirred for 3 min. at room temperature, and 5.4 g. of ethyl $\alpha$-bromopropionate was added for more than 10 min. The solution was stirred for an additional 30 min. After the *tert*-butanol was removed, the residue was poured into ice water and extracted with ether. After washing with water and drying, the solvent was removed to leave an oil, which was distilled at 195~200°C/0.006~0.008 mmHg. Yield, 9.5 g. (91.5%).

*Anal.* Found: C, 70.08; H, 7.59. Calcd. for $C_{25}H_{32}O_6$: C, 70.07; H, 7.53%.

**5-(1-Methyl-2-naphthyl)-2, 3-pentanedicarboxylic Acid (XXc).**—A solution of 11.7 g. of the ester XXa in 40 cc. of methanol was added to a solution of 26.5 g. of potassium hydroxide in 93 cc. of methanol and the mixture was refluxed for 1hr., to precipitate the potassium salt. Water (34 cc.) was added and the mixture was refluxed for 2 hr. After the addition of 30 cc. of water, the methanol was removed and 50 cc. of water was added to the solution. Unsaponified material was removed with ether, and the aqueous layer was acidified with 6 N hydrochloric acid. The tricarboxylic acid was extracted with ether. The ether was removed to give a semisolid which was decarboxylated by heating at 180~185°C. The acid was taken into 10% sodium hydorxide solution, precipitated with 6 N hydrochloric acid, and then extracted with ether. Removal of the ether gave 8.5 g. of tan-yellow semisolid, which was cyclized to XXa without further purification.

**$\alpha$-2-(10-Methyl-1-oxo-1, 2, 3, 4-tetrahydroanthryl)-propionic Acid (XXIa).**—To a solution of 3.8 g. of the dicarboxylic acid XXc in 30 cc. of benzene, 9.7 g. of phosphorus pentachloride was added with stirring, and the mixture was heated at 20°C for 1 hr., and at 45°C for 5 min. To the cold stirred solution, a solution of 37.0 g. of stannic chloride in 15 cc. of benzene was added taking more than 5 min., and the mixture was stirred for 1 hr. at room temperature. The mixture was poured onto a mixture of 200 g. of ice and 30 cc. of concentrated hydrochloric acid, and extracted with ether. The ether extract was washed with water and shaken with 10% sodium hydroxide solution to extract the acid XXIa. The ketoacid (1.15 g., m.p. 179.5~181.5°C) was obtained by acidification followed by extraction with ether, and recrystallized from benzene to give needles melting at 181~182°C.

*Anal.* Found: C, 76.58; H, 6.59. Calcd. for $C_{18}H_{18}O_3$: C, 76.57; H, 6.45%.

The infrared spectrum indicated peaks at 6.00 and 5.90 $\mu$.

**$\alpha$-2-(10-Methyl-1, 2, 3, 4-tetrahydroanthryl)-propionic Acid (XXIb).**—A mixture of 1.0 g. of the ketoacid XXIa, 5 g. of zinc amalgam, 6 cc. of acetic acid and 6 cc. of concentrated hydrochloric acid was covered with a layer of 4 cc. of toluene and the whole was refluxed for 24 hr., while 1 cc. of concentrated hydrochloric acid was added to the solution every four hours (5 cc. in total). The solution, freed from excessive zinc, was diluted with water and extrated with ether. After the ether layer was washed with water and dried over anhydrous sodium sulfate, the solvent was removed to give crystals melting at 133~154°C and weighing 0.48 g. From mother liquor the second crop (0.28 g.) was obtained, m. p. 133~138°C. The combined material was recrystallized from dilute methanol to give a mixture of stereoisomers of the acid XXIb. The infrared spectrum showed peaks at 5.85 $\mu$ and lacked the carbonyl band at 6.00 $\mu$ of the ketocarboxylic acid XXIa.

*Anal.* Found: C, 80.87; H, 7.66. Calcd. for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51%.

**Methyl β-2-(10-Methyl-1, 2, 3, 4-tetrahydroanthryl)-butyrate (XXIc).**—To a solution of 1.58 g. of the carboxylic acid XXIb in 19 cc. of benzene, 5 cc. of thionyl chloride was added and the mixture was heated on a water bath for 1 hr. After removal of the thionyl chloride and benzene in vacuo, 10 cc. of benzene was added and the solvent was evaporated so as to remove the excess of the thionyl chloride completely, and the residue was dissolved in 20 cc. of cold benzene. This solution of the acid chloride was added to a dried etheral solution of diazomethane provided from 6.3 g. of nitrosomethylurea. The reaction mixture was allowed to stand in an ice bath for 50 min., and at room temperature for 3 hr., while vigorous effervescence was observed. After the solvent was evaporated below 25°C, the residue was dissolved in 20 cc. of methanol and the solution was added to a slurry of 0.4 g. of silver oxide in 40 cc. of methanol and the mixture was refluxed for 2 hr.[29] The solution was filtered, and 0.2 g of silver oxide was added. After refluxing for 30 min., again 0.2 g. of silver oxide was added and the mixture was refluxed for an additional 30 min. After filtering off the silver and silver oxide, the solvent was removed to give a viscous liquid weighing 1.38 g., which was directly dehydrogenated to the ester XXIIa.

**β-(10-Methyl-2-anthryl)-butyric Acid (XXIIb).**—A mixture of 1.35 g. of the methyl ester XXIc and 0.2 g. of 30% Pd/C[30] was heated in an atmosphere of nitrogen at 250~280°C for 12 min. at 290~300°C for 1 hr. and at 310°C for 30 min. The reaction mixture was taken into boiling benzene, and freed from the catalyst. Removal of the solvent afforded a viscous orange oil possessing violet-green fluorescence. Beside the carbonyl band at 5.75 $\mu$, the infrared spectrum showed peaks at 12.3 and 11.9 $\mu$ which are characteristic of the 1, 2, 4-trisubstituted benzene nucleus. The methyl ester was directly hydrolyzed. The mixture of 1.11 g. of the ester, 3 cc. of 40% potassium hydroxide solution, 5 cc. of water and 5 cc. of methanol was refluxed for 2 hr. in an atmosphere of nitrogen. After cooling, water was added and the solution was washed with ether to remove unsaponified material. The aqueous layer was acidified with hydrochloric acid, and extracted with ether. The ether extract was washed with water and dried. Removal of the solvent left an oil, which could be brought to crystallization by trituration with a small amount of benzene. The crystals collected weighed 0.60 g. and melted at 148~153°C. These were recrystallized from benzene to yield 0.5 g. of the acid XXIIb, m. p. 154~157°C. From mother liquor, the second crop (0.28 g., m. p. 157~158°C) was obtained by sublimation at 0.5 mmHg. The combined crystals were recrystallized from benzene, m. p. 160~160.5°C. The infrared spectrum showed peaks at 5.90 $\mu$ (carboxyl group) and 12.3 $\mu$ (1, 2, 4-trisubstituted benzen nucleus). The ultraviolet spectrum in ethanol indicated the following maxima: $\lambda_{\max}$ m$\mu$ (log $\varepsilon$): 258 (5.20), 332 (3.41), 347 (3.66), 365 (3.80), 385 (3.75).

*Anal.* Found: C, 82.07; H, 6.74. Calcd. for $C_{19}H_{18}O_2$: C, 81.98; H, 6.52%.

**1-Oxo-3,6-dimethyl-2, 3-dihydro-1*H*-cyclopent[*a*]-anthracene (XXIIIa).**—To a solution of 0.68 g. of the carboxylic acid XXIIb in 20 cc. of benzene, 0.9 g. of phosphorus pentachloride was added and the mixture was stirred for 30 min. at 0°C and 1 hr. at room temperature. To the well chilled and stirred solution, a solution of 0.6 g. of stannic chloride in 2 cc. of benzene was added and the mixture was stirred for 30 min. at 0°C and 1 hr. at room temperature. The reaction mixture was decomposed with a cold solution of 7 cc. of concentrated hydrochloric acid in 30 cc. of water, and extracted with ether. The ether extract was washed with 6 N hydrochloric acid, water, 5% sodium carbonate solution, and water. After drying, the solvent was removed to yield a residue which gave 0.41 g. of crystals, m. p. 135~141.5°C, upon trituration with methanol. For analysis they were recrystallized from methanol to afford needles, m. p. 142~143.5°C. The infrared spectrum indicated peaks at 5.93 $\mu$, and the ultravioled spectrum is shown in Table I.

*Anal.* Found: C, 87.47; H, 6.23. Calcd. for $C_{19}H_{16}O$: C, 87.66; H, 6.17%.

**3, 6-Dimethyl-2, 3-dihydro-1*H*-cyclopent[*a*]-anthracene (IV).**—A mixture of 0.32 g. of the ketone XXIIIa, 5 g. of zinc amalgam, 5 cc. of concentrated hydrochloric acid, 5 cc. of acetic acid and 5 cc. of toluene was refluxed for 22 hr., while 7.5 cc. in total of concentrated hydrochloric acid was added from time to time. After the solution was cooled, the toluene layer was separated and the aqueous layer was extracted with ether. The combined toluene solution and ether were washed with water and dried over anhydrous sodium sulfate. Removal of the solvent yielded 0.265 g. of an orange oil with blue green fluorescence, which was dissolved in 40 cc. of benzene and chromatographed on 15 g. of alumina. Elution with 40 cc. of benzene gave 216 mg. of a pale yellow liquid. This was dissolved in 15 cc. of petroleum ether, and chromatographed again on

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29) W. E. Bachmann and W. S. Struve, "Organic Reactions", Vol. 3, John Wiley & Sons, Inc., New York (1943), p. 38.

30) N. D. Zelinsky and M. B. Turowa Pollak, *Ber.*, **58**, 1298 (1925); H. St. Pfau and Pl. A. Plattner, *Helv. Chim. Acta.*, **23**, 78, (1940).

10 g. of alumina. Elution with 60 cc. of petroleum ether gave first 64 mg. of an almost colorless liquid, which was followed by 134 mg. of a pale yellow liquid eluted with 20 cc. of petroleum ether-benzene (1 : 1) and 30 cc. of benzene. The yellow oil solidified on standing to give crystals, m. p. 64~68°C, which were recrystallized twice from methanol, m. p. 78~79.5°C. The ultraviolet spectrum is given in Fig. 6 and Table I. The molecular weight determination by Rast's method gave the value 236 ($C_{19}H_{18}$: 246.33).

*Anal.* Found: C, 92.06; H, 7.86. Calcd. for $C_{19}H_{18}$: C, 92.63; H, 7.37%.

The picrate was recrystallized from ethanol to give reddish brown needles, m. p. 128~128.5°C.

*Anal.* Found: C, 63.25; H, 4.66; N, 9.13. Calcd. for $C_{25}H_{21}O_7N_3$: C, 63.15; H, 4.45; N, 8.84%.

The 2, 4, 6-trinitrobenzolate was recrystallized from ethanol to afford scarlet needles, m. p. 142~142.5°C.

*Anal.* Found: C, 65.48; H, 4.65; N, 9.12. Calcd. for $C_{25}H_{21}O_6N_3$; C, 65.35; H, 4.61; N, 9.15%.

The authors are indebted to Dr. Takeo Sakan and Dr. Masazumi Nakagawa for many helpful suggestions. The authors wish also to thank Mr. Eiichi Togashi, Shiono Koryo Kaisha, for a generous gift of phenethyl alcohol.

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