

# A Novel Synthetic Route of 3,6-Dimethyl-2,3-dihydro-1H-cyclopent[*a*]anthracene and 6-Methyl-2,3-dihydro-1H-cyclopent[*a*]anthracene

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Tsuda and coworkers<sup>1)</sup> reported the isolation of a hydrocarbon (C<sub>19</sub>H<sub>18</sub>, oil, melting point of the picrate, 133~134°C) among the products of selenium dehydrogenation of the phenol II which they obtained by the dienone-phenol rearrangement of 7-keto-5,8(9)-cholestadien-3 $\beta$ -yl acetate. The same compound was isolated by them<sup>2)</sup> from the selenium dehydrogenation products of the anthrasteroid III from 5,8(9)-cholestadien-3 $\beta$ -ol.

Starting from 1-methyl-2-naphthoic acid (IV) we<sup>3)</sup> succeeded in preparing 3,6-dimethyl-2,3-dihydro-1H-cyclopent[*a*]anthracene (I). This structure I was assigned by Tsuda and coworkers to their dehydrogenation product, but the comparison of the ultraviolet absorption spectra of synthetic I and the dehydrogenation product indicated that the latter was considerably contaminated with non-anthranoid impurities. Having established the structure of anthracholostatetraene, proposed by Mosettig<sup>4)</sup>, by an excellent method<sup>5)</sup>, Burgstahler and Mosettig<sup>6)</sup> prepared *dl*-5,7,9,14-anthratetraen-17-one (V) to study a possible general synthetic route to anthrasteroids as well as to examine their carcinogenic properties. Sodium borohydride reduction of ketone V afforded alcohol VI, but the dehydrogenation which was expected to be accompanied by the migration of the 18-methyl group to 17-position to give I was found fruitless<sup>7)</sup>.

Since 3,6-dimethyl-2,3-dihydro-1H-cyclopent[*a*]anthracene (I) is an analog of Diel's hydrocarbon usually obtained by the dehydrogenation of steroids, and since we happened to need a considerable amount of it for biological experiments, we explored a simpler route to compound I. In the present paper a new synthetic route to compound I and its nor-compound XIIIb is described.

Our synthesis, shown in Fig. 1, employs the

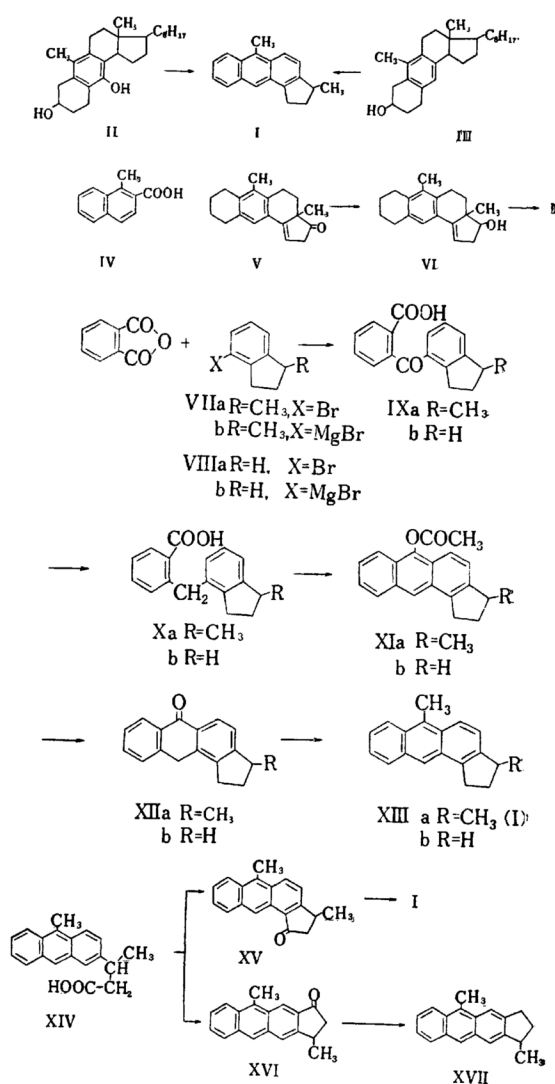


Fig. 1

method developed by Fieser and Hershberg<sup>8)</sup> for the general synthesis of 9-alkylanthracene derivatives. Since the syntheses of I and XIIIb are similar, that of I is described at length. 4-Bromo-1-methylindan (VIIa), our starting substance, had been obtained by Hoyes<sup>9)</sup> by

1) K. Tsuda, K. Arima and R. Hayatsu, *J. Am. Chem. Soc.*, **76**, 2933 (1954).

2) K. Tsuda and R. Hayatsu, *ibid.*, **77**, 3089 (1955).

3) M. Nakazaki and S. Isoe, *Chem. & Ind.*, **1958**, 43; *This Bulletin*, **32**, 1202 (1959).

4) See Ref. 8 in our paper<sup>3)</sup>.

5) A. W. Burgstahler, *J. Am. Chem. Soc.*, **79**, 6047 (1957).

6) A. W. Burgstahler and E. Mosettig, *ibid.*, **81**, 3697 (1959).

7) Private communication from Dr. Mosettig, National Institutes of Health, Bethesda, Maryland, U.S.A.

8) L. F. Fieser and E. B. Hershberg, *J. Am. Chem. Soc.*, **59**, 2331 (1937); **60**, 940 (1938).

9) H. Hoyes, *J. prakt. Chem.*, **139**, 242 (194).

reduction with hydriodic acid and phosphorus of 4-bromo-1-hydroxy-1-methylindan (b. p. 135~136°C/25 mmHg, m. p. 33~34°C), prepared from 4-bromo-1-indanone and methylmagnesium bromide. When we carried out the reaction of methylmagnesium bromide with the bromo-ketone, we obtained unsaturated 7-bromo-3-methylindene (b. p. 137~139°C/19 mmHg) which did not show an OH band in infrared spectrum but could be hydrogenated in a good yield to saturated 4-bromo-1-methylindan (VIIa) (b. p. 75~77°C/1.5 mmHg) in the presence of platinum oxide.

Although Kon and Woolman<sup>10</sup>) observed that 4-bromoindan (VIIIa) could be converted with difficulty into a Grignard complex even under the condition elaborated by Fieser and Hershberg<sup>8</sup>), bromide VIIa could be made to react smoothly with magnesium to afford Grignard compound VIIb, which gave 2-(1-methylindan-4-carbonyl)benzoic acid (IXa) (m. p. 123.5~124.4°C) with phthalic anhydride. The conversion into 2-(1-methylindan-4-yl-methyl)-benzoic acid (Xa) (m. p. 126~127°C) was effected by the high pressure catalytic hydrogenation with a copper chromite catalyst.

Heating with zinc chloride in acetic anhydride and acetic acid accomplished the ring closure of acid Xa to 6-acetoxy-3-methyl-2,3-dihydro-1H-cyclopenta[a]anthracene (XIa) (m. p. 161~161.5°C), which, because of its instability toward acid and alkali, was hydrolyzed indirectly according to Fieser and Hershberg's method<sup>8</sup>).

The reaction of methylmagnesium bromide with acetate XIa provided 3-methyl-6-oxo-2,3,6,11-tetrahydro-1H-cyclopenta[a]anthracene (XIIa) (m. p. 99~100°C), accompanied by a high melting compound (m. p. 221~223°C). The latter, in spite of its sparing solubility in benzene, always appeared in the mother liquor of recrystallization of even the purest sample of anthrone XIIa from benzene. From this behavior, together with other evidences (molecular weight, ultraviolet spectrum and infrared spectrum) it appears that the substance is a condensation product from two anthrone molecules, analogous to the high melting products obtained by Fieser and Hershberg<sup>8</sup>) in their synthesis of 10-isopropyl-1',2',3',4'-tetrahydro-1,2-benzanthracene.

The product from the Grignard reaction of anthrone XIIa with methylmagnesium bromide was decomposed with an acid and extraction with ether gave a highly blue-green fluorescent oil, which was purified by chromatography on alumina to afford pale yellow needles, m. p. 80.5~81°C. The substance was identified with

3,6-dimethyl-2,3-dihydro-1H-cyclopenta[a]anthracene (I) prepared previously<sup>3</sup>) by mixed melting point determination, comparison of infrared and ultraviolet spectra and mixed melting point determination of the trinitrobenzene complex.

In our previous synthesis of I, there remained a question whether the ring closure of acid XIV took place at 1-position to give XV or at 3-position to give XVI. Then, structure XVI was ruled out mainly on account of two observations, i. e. the 1-position of the anthracene nucleus is much more reactive toward electrophilic substitution, and the keto compound (XV) (m. p. 142~143.5°C) obtained showed a markedly similar ultraviolet spectrum with 1-acetylanthracene and exhibited an absorption at 12.2  $\mu$  in infrared spectrum which could be attributed to the presence of two adjacent hydrogen atoms in the anthracene nucleus<sup>11</sup>). The present synthesis with no such ambiguity can be taken as a support to the above view.

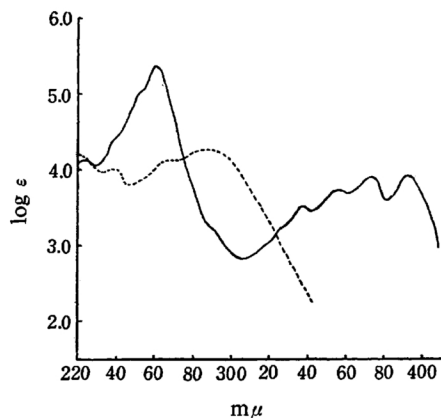
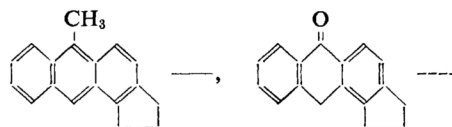


Fig. 2.



Solvent: 95% ethanol

TABLE I. ULTRAVIOLET ABSORPTION SPECTRA (in 95% ethanol)

I		XIIIb		XIa		XIb	
$\lambda_{\max}$	$\log \epsilon$	$\lambda_{\max}$	$\log \epsilon$	$\lambda_{\max}$	$\log \epsilon$	$\lambda_{\max}$	$\log \epsilon$
261	5.33	261	5.22	259	5.30	259	5.29
338	3.46	338	3.53				
354	3.73	354	3.79	353	3.81	356	3.40
372	3.90	372	3.95	371	3.95	375	3.55
392	3.89	392	3.95	391	3.94	396	3.55

11) H. Dannenberg and D. D. Dannenberg, *Ann.*, **585**, 1 (1954), see also W. West, "Chemical Applications of Spectroscopy", Interscience Pub. Inc., New York (1956), pp. 388-406.

10) G. A. Kon and A. M. Woolman *J. Chem. Soc.*, **1939**, 796.

The synthesis of 6-methyl-2,3-dihydro-1*H*-cyclopent[*a*]anthracene (XIIIb) was carried out in a way analogous to that described above, m. p. 127~128°C; melting point of the trinitrobenzene complex, 149.5~150.5°C; melting point of the picrate, 144~145°C, ultraviolet spectrum overlapping that of I (see Fig. 2 and Table I).

### Experimental\*

**Ethyl *o*-Nitrocinnamate**<sup>12</sup>.—Cinnamic acid was nitrated to give a mixture of *o*- and *p*-nitrocinnamic acids, which were esterified with ethanol and hydrogen chloride gas. From the mixture of ethyl *o*- and *p*-nitrocinnamates, the *o*-isomer was separated by virtue of its facile solution in m. p. 42°C, yield, 21.4%.

**Hydrocarbostyryl**.—Ethyl *o*-nitrocinnamate (30 g.) was dissolved in 300 cc. of ethanol and hydrogenated in the presence of 4~5 g. of Raney nickel W-6 at 55~60°C and 47 atms. for 5~7 hr. Hydrocarbostyryl was obtained in a yield of 79%, m. p. 163°C, (literature<sup>13</sup>): m. p. 165~166°C).

**$\beta$ -(2-Bromophenyl)propionic Acid (XVIII)**<sup>14</sup>.—*a*. From Hydrocarbostyryl<sup>15</sup>.—A mixture of 30 g. of hydrocarbostyryl, 97 g. of crystalline barium hydroxide and 400 cc. of water was refluxed for 20 hr. in a stream of nitrogen. The solution was diluted with 500 cc. of water and a stream of carbon dioxide was passed through it to precipitate barium carbonate.

After being freed from barium carbonate, the solution was made just alkaline to phenolphthalein with 10% sodium carbonate solution. The precipitated sodium salt, after being dried and washed with acetone, weighed 64.7 g. (yield, 84%), m. p. 155°C. A solution of 18.7 g. of this sodium salt and 6.9 g. of sodium nitrite in 100 cc. of water was added dropwise into 42 cc. of 48% hydrobromic acid chilled at 0~5°C in an ice bath. Cuprous bromide was precipitated by adding 6.3 g. of sodium sulfite to a mixture of 25 g. of cupric sulfate, 14.6 g. of sodium bromide and 100 cc. of water, and was dissolved by adding 6 cc. of 48% hydrobromic acid, and the solution was kept boiling. Onto this boiling solution, the above-mentioned diazonium bromide solution was added in four portions and the whole was refluxed for 30 min. The precipitated bromo acid was taken into ether, and the ethereal solution was washed with water and dried with anhydrous sodium sulfate. After removal of the solvent, the residue was recrystallized from

aqueous acetic acid, m. p. 91~93°C, 5.6 g. The mother liquor was distilled and the fraction which boiled at 127~128°C/1 mmHg solidified on standing, m. p. 90°C, 1.2 g.

*b*. From *o*-Bromobenzyl Bromide.—*o*-Bromotoluene was brominated according to the procedure of Weizman and Patai<sup>16</sup>, affording *o*-bromobenzyl bromide, m. p. 30°C (yield, 78%). To ethanolic sodium ethoxide prepared from 9.25 g. of sodium and 300 cc. of absolute ethanol, was added 28.5 g. of ethyl malonate and the mixture was heated for 15 min. on a water bath. After a solution of *o*-bromobenzyl bromide in 100 cc. of ethanol was added with stirring during 1 hr., the solution was stirred and refluxed for 3 hr.

The solvent was removed and the residue was diluted with ice water, and then concentrated hydrochloric acid was added to make the solution acidic to Congo red. After extraction with ether, the ether extract was washed with water and dried with anhydrous sodium sulfate. Removal of the solvent afforded a residue which was distilled to give ethyl *o*-bromobenzylmalonate boiling at 165~170°C/3 mmHg, 64.7 g. (yield, 82%)<sup>10,14</sup>. This malonate (64.5 g.) was hydrolyzed by boiling with 150 g. of potassium hydroxide, 175 cc. of ethanol and 300 cc. of water for 1 hr. After the ethanol was removed 250 cc. of concentrated hydrochloric acid was added to precipitate *o*-bromobenzylmalonic acid, which was collected and dried, 87 g. The malonic acid (87 g.) was decarboxylated by boiling with 400 cc. of water for 5 hr.

A heavy red oil which separated was extracted with ether and the ethereal solution was washed with water. After drying with anhydrous sodium sulfate, the solvent was removed to give  $\beta$ -(2-bromophenyl)propionic acid, m. p. 90°C. The yield was about 80% from the malonic ester.

**4-Bromo-1-indanone (XIX)**.—Although Miersch<sup>17</sup> reported the formation of the bromindanone XIX in a yield of 10% by the cyclization with concentrated sulfuric acid, XVIII did not give XIX with polyphosphoric acid<sup>18</sup> either under a rather mild condition (130°C, 20 min., recovery) or under a drastic condition (250°C, 20 min., polymerization). A mixture of 8.9 g. of crude XVIII and 15.6 g. of thionyl chloride was refluxed for 3 hr. After the excess of the thionyl chloride was removed, the residue,  $\beta$ -(2-bromophenyl)propionyl chloride, b. p. 120~123°C/2 mmHg, was dissolved in 240 cc. of carbon disulfide, and the solution was chilled at 5°C. To the stirred solution, 7.6 g. of aluminum chloride was added during 1.5 hr. After being allowed to stand at room temperature for 1.5 hr., the reaction mixture was refluxed for 15 min., and then a mixture of 100 cc. of concentrated hydrochloric acid and 300 cc. of water was added to decompose the reaction complex. The bromindanone was steam-distilled and recrystallized from ethanol, colorless needles, m. p. 95~96°C, (literature<sup>19</sup>), m. p. 98~99°C, 6.2 g. (yield, 85%).

\* All melting points are uncorrected. All ultraviolet spectra were measured with an EPS-2 Hitachi autorecording spectrophotometer and infrared spectra with a Perkin Elmer Model 12 C. The analyses were performed in the microanalytical laboratory of the Institute of Polytechnics, Osaka City University.

12) L. Müller, *Ann.*, **212**, 124 (1882); L. Vanino, "Handbuch der Präparativen Chemie", Band II, Ferdinand Enke, Stuttgart (1937), p. 599.

13) E. R. Blout and D. C. Silverman, *J. Am. Chem. Soc.*, **66**, 1442 (1944).

14) For detailed discussion on the preparation of XVIII, see L. F. Fieser and A. M. Seligman, *ibid.*, **57**, 2175 (1935).

15) F. Mayer, H. Phillips, F. W. Ruppert and A. T. Schmidt, *Ber.*, **61**, 1966 (1928).

16) M. Weizman and S. Patai, *J. Am. Chem. Soc.*, **68**, 151 (1946).

17) W. Miersch, *Ber.*, **25**, 2109 (1892).

18) F. D. Popp and W. E. Ewen, *Chem. Revs.*, **58**, 321 (1958).

**4-Bromoindan (VIIIa)**<sup>10,14</sup>.—To a solution of 11.0 g. of XIX and 110 cc. of ethanol, 99 g. of amalgamated zinc was added with 70 cc. of concentrated hydrochloric acid. While the mixture was refluxed for 3 hr., 60 cc. of concentrated hydrochloric acid was added in three portions, and refluxing was further continued for 2 hr. The reaction mixture was diluted with water and, after the excess of zinc was removed, was extracted with ether. After drying with anhydrous sodium sulfate, the solvent was removed to give a liquid, which was distilled in vacuo, b. p. 75~77°C/2 mmHg, 8.7 g. (yield 85%), (literature, b. p. 118°C/18 mmHg<sup>14</sup>, 100°C/1.5 mmHg<sup>10</sup>).

**7-Bromo-3-methylindene (XX)**<sup>9</sup>.—Methyl bromide-gas was introduced into a stirred mixture of 6.1 g. of magnesium and 200 cc. of ether until the magnesium disappeared. To the Grignard reagent, a solution of 2.5 g. of XIX in 500 cc. of ether was added during 1 hr., and the mixture was refluxed for 2 hr. While the solution was cooled in an ice bath, a mixture of 100 cc. of concentrated hydrochloric acid and 500 cc. of ice water was added, and the solution was extracted with ether. After the extract was washed with water and dried with anhydrous sodium sulfate, the solvent was removed to give an oil, which was distilled in vacuo, b. p. 137~139°C/19 mmHg, 11.1 g. (yield, 45%).

**4-Bromo-1-methylindan (VIIa)**.—To a solution of 11.1 g. of XX in 50 cc. of ethanol, 0.2 g. of platinum oxide was added and the mixture was shaken in an atmosphere of hydrogen. Hydrogen was absorbed rapidly, and after 2 hr. the solution was freed from the catalyst. Removal of the solvent gave an oil, which was distilled in vacuo, b. p. 75~77°C/1.5 mmHg, 9.4 g. (yield, 84%), (literature<sup>9</sup>, b. p. 245°C).

**2-(1-Methylindan-4-carbonyl)benzoic Acid (IXa)**.—When a mixture of 5 drops of ethyl iodide and 10 drops of VIIa was added to a stirred mixture of 2.16 g. of magnesium and 5 cc. of ether, ebullition of ether was observed to indicate the start of the Grignard reaction. With stirring and heating on a water bath, a solution of 9.4 g. of VIIa in 80 cc. of ether was added during 3 hr., and the mixture was refluxed for 15 hr. in an atmosphere of nitrogen.

The Grignard solution was transferred into a dropping funnel with the aid of the pressure of nitrogen from a tank; then the reaction flask was washed with 100 cc. of ether, and the washing was transferred again into the funnel.

To a solution of 11.4 g. of phthalic anhydride in 200 cc. of benzene, the above Grignard solution was added during 1.5 hr. with stirring and refluxing, and the mixture was stirred and refluxed for 2 hr. in an atmosphere of nitrogen. Dilute hydrochloric acid was added to decompose the Grignard complex, and the solution was steam-distilled. The precipitate which separated from the distilled was dissolved in 10% sodium carbonate solution, and the resulting solution was again steam-distilled. The turbid solution was filtered through a layer of Hyflo and was made acidic with dilute hydrochloric acid to precipitate IXa, which was recrystallized from benzene, m. p. 114~120°C. Recrystallization from benzene-ligroin yielded pure carboxylic acid, m. p.

123.5~124.5°C, 4.5 g. (yield, 36%). IR spectrum: 5.95 and 6.0  $\mu$ .

Found: C, 77.15; H, 5.89. Calcd. for C<sub>18</sub>H<sub>16</sub>O<sub>3</sub>: C, 77.12; H, 5.75%.

**2-(1-Methylindan-4-ylmethyl)benzoic Acid (Xa)**.—A mixture of 3.5 g. of IXa and 140 cc. of ethanol was refluxed with a small amount of Raney nickel. The Raney nickel was filtered off, and the solution was hydrogenated with 0.5 g. of a copper chromite catalyst in a steel bomb at 149~155 atms. and 210~220°C for 4 hr. After the bluish green solution was freed from the catalyst, hydrogen sulfide was introduced to remove copper and chromium ions, and precipitated sulfides were filtered off through a layer of Hyflo. Removal of the solvent from the filtrate gave crystals, which were recrystallized from ethanol, m. p. 126~127°C, 3.2 g. IR spectrum: 5.9  $\mu$ .

**6-Acetoxy-3-methyl-2,3-dihydro-1H-cyclopent[ $\alpha$ ]anthracene (XIa)**.—To a mixture of 3.2 g. of Xa, 30 cc. of acetic anhydride and 20 cc. of acetic acid, was added 0.27 g. of fused zinc chloride. After the brown mixture was refluxed for 1 hr., 50 cc. of water was added and the precipitated crystals were recrystallized from ethanol, m. p. 137~138°C, 2.5 g. (yield, 72%). IR spectrum: 5.7  $\mu$ . UV spectrum: see Table I.

Found: C, 82.87; H, 6.64. Calcd. for C<sub>20</sub>H<sub>18</sub>O<sub>2</sub>: C, 82.73; H, 6.25%.

**3-Methyl-6-oxo-2,3,6,11-tetrahydro-1H-cyclopent[ $\alpha$ ]anthracene (XIIa)**.—To a Grignard reagent, prepared from 0.755 g. of magnesium, 30 cc. of ether and methyl bromide gas, 2.3 g. of XIa was added with 90 cc. of benzene. After the ether was removed, 90 cc. of benzene was added and the mixture was refluxed for 30 min. To the yellow solution, 100 cc. of diluted hydrochloric acid was added and the product was extracted with ether. After the ether extract was washed with water and dried with anhydrous sodium sulfate, the solvent was removed and the crystals were recrystallized from ethanol-ligroin, m. p. 86~93°C. For the preparation of an analytical sample, the product was recrystallized from methanol, m. p. 99~100°C.

Found: C, 86.11; H, 6.26. Calcd. for C<sub>18</sub>H<sub>16</sub>O: C, 87.06; H, 6.50%.

The mother liquor gave sparingly soluble crystals which were recrystallized from benzene-ethanol, m. p. 221~223°C.

**3,6-Dimethyl-2,3-dihydro-1H-cyclopent[ $\alpha$ ]anthracene (I)**.—To the Grignard reagent, prepared from 0.252 g. of magnesium, 30 cc. of ether and methyl bromide, 427 mg. of XIIa was added with 50 cc. of benzene. After the ether was removed, the reaction mixture was refluxed on a water bath for 30 min. While the solution was chilled in an ice bath, 50 cc. of 2N hydrochloric acid was added and the product was extracted with ether. The greenish blue fluorescent ether extract was washed with water and dried with anhydrous sodium sulfate. Removal of the solvent gave an oil which was chromatographed on 10 g. of alumina. Elution with benzene-benzene gave crystals which were recrystallized from methanol, pale yellow crystals, m. p. 80.5~81°C, 177 mg. (yield, 42%). The substance was found identical with I previously



prepared<sup>3</sup>) by the comparison of the infrared spectra and the mixed melting point determination. UV spectrum: see Table I.

Found: C, 92.14; H, 7.60. Calcd. for  $C_{19}H_{18}$ : C, 92.63; H, 7.37%.

The trinitrobenzene complex was prepared from 35 mg. of I and 30 mg. of trinitrobenzene in benzene, and recrystallized twice from ethanol, reddish scarlet needles, m. p. 141.5~142°C. The mixed melting point determination (m. p. 140.5~142.5°C) confirmed the identity with the trinitrobenzene complex previously prepared<sup>3</sup>) (m. p. 142~142.5°C).

Found: C, 65.37; H, 4.60; N, 9.15. Calcd. for  $C_{28}H_{21}O_6N_3$ : C, 65.35; H, 4.61; N, 9.15%.

**2-(4-Indancarbonyl)benzoic Acid (IXb).**—To a suspension of 2.05 g. of magnesium in 5 cc. of ether, was added a mixture of 2 drops of ethyl iodide and 10 drops of VIIIa to start the Grignard reaction. When ebullition of ether was observed, a mixture of 8.7 g. of VIIIa and 60 cc. of ether was added dropwise during 4 hr. After the solution was refluxed and stirred for 20 hr., the solution was transferred into a dropping funnel by means of the pressure of nitrogen from a tank, then the flask was washed with 100 cc. of ether and the washing was also transferred into the dropping funnel. To a solution of 11.3 g. of phthalic anhydride in 120 cc. of benzene, was added the above Grignard solution during 1.5 hr., and the mixture was refluxed for 30 min. A mixture of concentrated hydrochloric acid and 300 cc. of ice water was added to the reaction mixture and the whole was steam-distilled to remove volatile by-products. Ketoacid IXb was separated and dissolved in 150 cc. of a 10% sodium carbonate solution and the solution was steam-distilled for 2 hr. Fifty cubic centimeters of concentrated hydrochloric acid was added to the solution to give IXb, which was collected and recrystallized from benzene, m. p. 174~175°C. For the preparation of an analytical sample, the substance was recrystallized from benzene, m. p. 175~176°C, 6.8 g. (yield, 58%). IR spectrum: 6.01 and 5.94  $\mu$ .

Found: C, 76.29; H, 5.54. Calcd. for  $C_{17}H_{14}O_3$ : C, 76.67; H, 5.30%.

**2-(4-Indanylmethyl)benzoic Acid (Xb).**—A solution of 6.2 g. of IXb in 125 cc. of ethanol was refluxed with a small amount of Raney nickel. The solution, after the catalyst was filtered off, was hydrogenated in a steel bomb with 0.3 g. of a copper chromite catalyst at 199~202 atm. and 215°C for 4 hr. The solution was separated from the catalyst and treated with hydrogen sulfide to remove copper and chromium ions as the sulfides. The solution was filtered through a layer of Hyflo and the filtrate was concentrated under reduced pressure to afford crystals, which were recrystallized from benzene, m. p. 146~146.5°C, 5.42 g. (yield, 72%). IR spectrum: 6.01  $\mu$ .

Found: C, 81.00; H, 6.24. Calcd. for  $C_{17}H_{16}O_2$ : C, 80.92; H, 6.39%.

**6-Acetoxy-2, 3-dihydro-1*H*-cyclopent[*a*]anthracene (XIb).**—To a mixture of 4.2 g. of Xb, 30 cc. of acetic acid and 20 cc. of acetic anhydride, was added 0.35 g. of zinc chloride and the solution was refluxed for 1 hr. To the brown solution, 200 cc. of water was added to precipitate a dark brown

solid mass, which was continuously extracted with benzene to remove a brown insoluble by-product. The benzene extract was concentrated to afford yellow crystals, which were recrystallized from benzene, yellow prisms, m. p. 161~161.5°C, 3.4 g. (yield, 74%). IR spectrum: 5.70 and 12.35  $\mu$ . UV spectrum: see Fig. 1 and Table I.

Found: C, 82.69; H, 6.12. Calcd. for  $C_{19}H_{18}O_2$ : C, 82.58; H, 5.84%.

**6-Oxo-2,3,6,11-tetrahydro-1*H*-cyclopent[*a*]anthracene (XIb).**—To the Grignard reagent, prepared from 1.15 g. of magnesium, 60 cc. of ether and methyl bromide, was added 3.4 g. of XIb in three portions, which was followed by 40 cc. of benzene and then the ether was distilled off. The yellow reaction complex was decomposed with 100 cc. of water, while the solution was chilled in an ice bath, and the product was extracted with ether. After the ether extract was washed with water and dried with anhydrous sodium sulfate, the solvent was removed to give crystals, m. p. 115~140°C, which were recrystallized from benzene, m. p. 160~163°C. For the preparation of an analytical sample, the substance was recrystallized from benzene, m. p. 165~166°C, 0.981 g. (yield, 34%). IR spectrum: 6.10  $\mu$ . UV spectrum: see Fig. 1.

Found: C, 86.68; H, 6.25. Calcd. for  $C_{17}H_{14}O$ : C, 87.15; H, 6.02%.

The mother liquor gave pale yellow needles, which were sparingly soluble in benzene, m. p. 222~223.5°C.

Found: C, 86.40; H, 5.63%.

**6-Methyl-2,3-dihydro-1*H*-cyclopent[*a*]anthracene (XIIb).**—To the Grignard solution, prepared from 0.488 g. of magnesium, 30 cc. of ether and methyl bromide, was added 0.98 g. of XIIb, which was followed by 50 cc. of benzene. After the ether was distilled off, the benzene solution was refluxed for 30 min. After diluted hydrochloric acid was added to decompose the Grignard complex, the solution was extracted with ether. The bluish green fluorescent ether extract was washed with water and dried with anhydrous sodium sulfate. Removal of the solvent gave orange yellow needles, which were recrystallized from benzene to give pale yellow needles, m. p. 127~128°C. The mother liquor was concentrated and the residue was chromatographed on 10 g. of alumina affording an additional crop, with made the total yield of XIIb 434 mg. (yield, 56%). UV spectrum: see Fig. 1 and Table I.

Found: C, 92.83; H, 6.85. Calcd. for  $C_{18}H_{16}$ : C, 93.06; H, 6.94%.

The trinitrobenzene complex was prepared from 20 mg. of XIIb and 20 mg. of trinitrobenzene, and was recrystallized from ethanol, reddish scarlet needles, m. p. 149.5~150.5°C.

Found: C, 64.92; H, 4.35; N, 9.59. Calcd. for  $C_{24}H_{19}O_6N_3$ : C, 64.71; H, 4.30; N, 9.34%.

The picrate was recrystallized from benzene, brownish black needles, m. p. 144~145°C.

Found: C, 62.87; H, 4.19; N, 8.88. Calcd. for  $C_{24}H_{19}O_7N_3$ : C, 62.47; H, 4.15; N, 9.11%.

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