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β — AROYLPROPIONIC ACIDS. PART XXIII. CONVERSION OF β-(4-METHOXY-3-o-METHOXYPHENYL-PHENYL)-, β-(4-METHYL-3-o-TOLYL-PHENYL)-, AND β-6-(1,2,3,4-TETRAHYDRONAPHTHYL) PROPIONIC ACIDS INTO POLYCYCLIC COMPOUNDS.

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Abstract. Ethyl γ-(4-Methoxy-3-o-methoxyphenyl-phenyl)-, γ-4-methyl-3-o-tolyl-phenyl)— and γ-6-(1,2,3,4-tetrahydronaphthyl) butyrates, prepared by the reduction and esterification of the corresponding keto-acids, were condensed with ethyl oxalate in the presence of potassium ethoxide. The formed oxalyl derivatives were cyclised with 70% $H SO_4$ to give dihydronaphthalene-1, 2-dicarboxylic anhydride derivatives and a hexahydrophenanthrene-3,4-dicarboxylic anhydride, respectively.

A) *Conversion of* o, o *-Disubstituted Diphenyl into Phenylnaphthalene derivatives*

1) *Condensation of* 2,2 - *Dimethoxy-and* 2, 2-*Dimethyldiphenyl with Succinic Anhydride.*- When 2,2-dimethoxydiphenyl was condensed with succinic anhydride in the presence of anhydrous aluminium chloride it gave a mixture of β- (4-methoxy-3-o-methoxyphenyl- benzoyl) propionic acid (Ia) (5 parts), and an acid (1 part) to which structure (IIa) was assigned.

The structure of the latter acid was based on the following: (i) Analytical data and molecular weight (710). (ii) Its identity with a specimen prepared by the condensation of the first acid (Ia) (2 mol) with succinyl chloride (1 mol) in the presence of anhydrous $AlCl_3$. A similar reaction is observed when succinyl chloride is allowed to react with aromatic compounds in the presence of aluminium chloride (2).

The formation of (IIa) may be attributed to the high nucleophilicity of positions 5 and 5' in the diphenyl molecule caused by the strong electron-releasing methoxyl group.

2,2-Dimethyldiphenyl gave under similar condition β-(4-Methyl-3-o-tolyl-benzoyl) proprionic acid (Ib) only.

The keto-acids (Ia and b) were reduced by Clemmensen method to the corresponding butyric acids (IIIa and b, respectively). The highest yield was obtained when the reduction of Ia and Ib was carried out with Zn/Hg and concentrated hydrochloric acid without an organic solvent and with xylene, respectively. Both acids were converted into the corresponding esters (IVa and b) in the usual manner.

The infrared data of the above mentioned compounds are reported in Table I. The keto-acids (Ia and b) and (IIa) show one band in the 6 μ region characteristic of overlapped ν c = o of saturated acids (5a) and aromatic ketones (5b). The butyric acids (IIIa and b) also show one band at 1685 and 1690 cm^{-1} , respectively, characteristic of ν c =o of saturated acids.

The butyric ester (IVa) shows a band at 1754 cm^{-1} , characteristic of normal saturated esters (5c).

The infrared spectra of the keto-esters of (Ia and b) show two bands characteristic of ν c = o of aromatic ketones and saturated esters (cf. Table I columns 3 and 4).

TABLE I

Compound	ν C=O cm^{-1}		
	Saturated [5a] acids	Aromatic [5b] ketone	Saturated [5c] esters
Ia	1710		
Ib	1700		
IIa	1715		
IIIa	1685		
IIIb	1690		
IVa			1754
ester of Ia		1680	1740
ester of Ib		1675	1730
ester of XVI		1680	1730

2) *Claisen Condensation.*—The butyric esters (IVa and b) reacted with ethyl oxalate in the

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presence of potassium ethoxide to give the oxalyl-esters (Va and b), which were directly cyclised by heating with 70% (v/v) sulphuric acid at 100°C to give the 3, 4-dihydronaphthalene-1, 2-dicarboxylic anhydrides (VIa and b), respectively.

The failure of the latter anhydrides to isomerise with sulphuric acid, or with aluminium chloride in 1, 1, 2, 2 - tetrachloroethane or in nitrobenzene (1) to a dihydrobenzanthrone derivative (VIII) excluded structure (VII), and favoured structure (VI). The anhydride structure assigned to (VIa and b) was substantiated by their infrared spectra, which show the doublet characteristic of acid anhydrides (5d) (cf. Table II).

TABLE II

Compound	ν -CO-O-CO- cm^{-1}
VIa	1755 , 1835
VIb	1760 , 1845
XIX	1750 , 1818

The electronic spectrum (in acetic acid) of (VIa) shows two maxima at 273nm (ϵ =26,050) and 333nm (ϵ =14,720), which excludes the 2-phenylnaphthalene structure for the compound (6).

Attempts to dehydrogenate the anhydride (VIa) by heating with S, Se or Pd/C-sulphur catalysts were not successful.

The structure of (VIa) was further supported by reaction with benzene in the presence of anhydrous aluminium chloride (3). The product did not isomerise to the dihydrobenzanthrone-carboxylic acid (VIII), but instead it was converted into a keto-acid, which may be 6-o-methoxyphenyl-2-benzoyl-7-methoxy-3,4 - dihydronaphthalene-1-carboxylic acid (IX) or 6-o-methoxyphenyl-1-benzoyl-7 - methoxy - 3,4 - dihydronaphthalene-2-carboxylic acid (X).

However, structure (IX) assigned to the product was inferred from the following observations: It was decarboxylated with copper-bronze and quinoline to give a ketone, which was shown to be 2-benzoyl-7-methoxy-6-o-methoxyphenyl-3,4-dihydronaphthalene (XI), since it was not identical with 1-benzoyl- 7 -methoxy- 6 -o-methoxyphenyl- 3, 4 -dihydronaphthalene (XIV), prepared according to the following scheme.

The oxalyl derivative (Va) was refluxed with 20% sulphuric acid to give 3,4-dihydro-7-methoxy-6-o-methoxyphenyl-naphthalene-1-carboxylic acid (XII) (4). This was converted into its acid chloride (XIII), which was condensed with benzene in the presence of anhydrous aluminium chloride to give 1-benzoyl-3,4-dihydro-7-methoxy-6-o-methoxyphenyl-naphthalene (XIV).

The preferable cyclisation of the oxalyl derivative to give the anhydride (VI) rather than (VII) is attributed to steric factors (cf. carbon atoms a and a' in formula V).

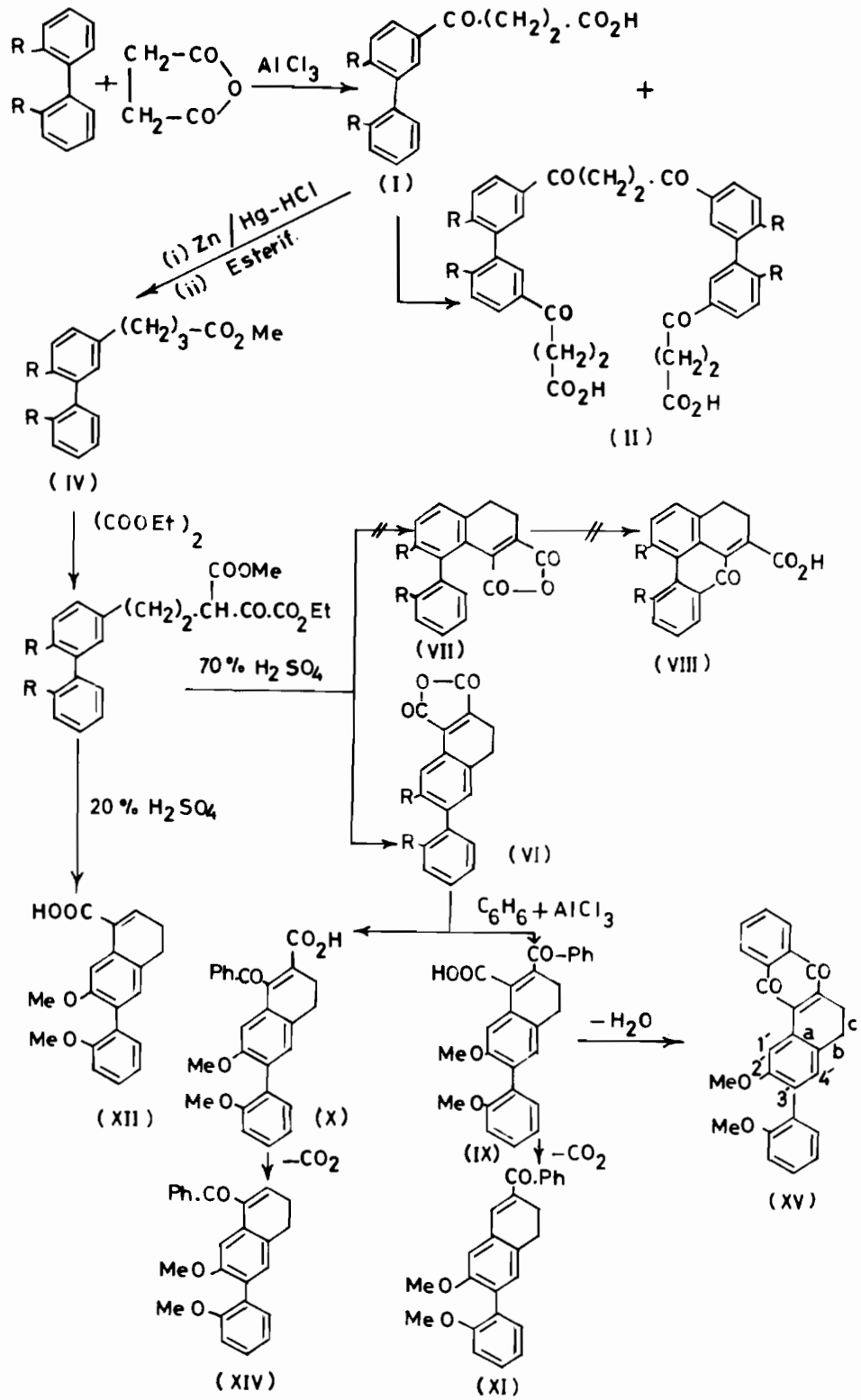
3) *Cyclisation of 2-benzoyl- 7 -methoxy-6-o-methoxyphenyl- 3, 4 -dihydronaphthalene- 1 - carboxylic Acid.* — The Acid (IX) was refluxed with P_2O_5 in dry xylene to give (3-methoxy-2-o-methoxyphenyl- 3, 4-dihydro-1, 2-benzanthraquinone.

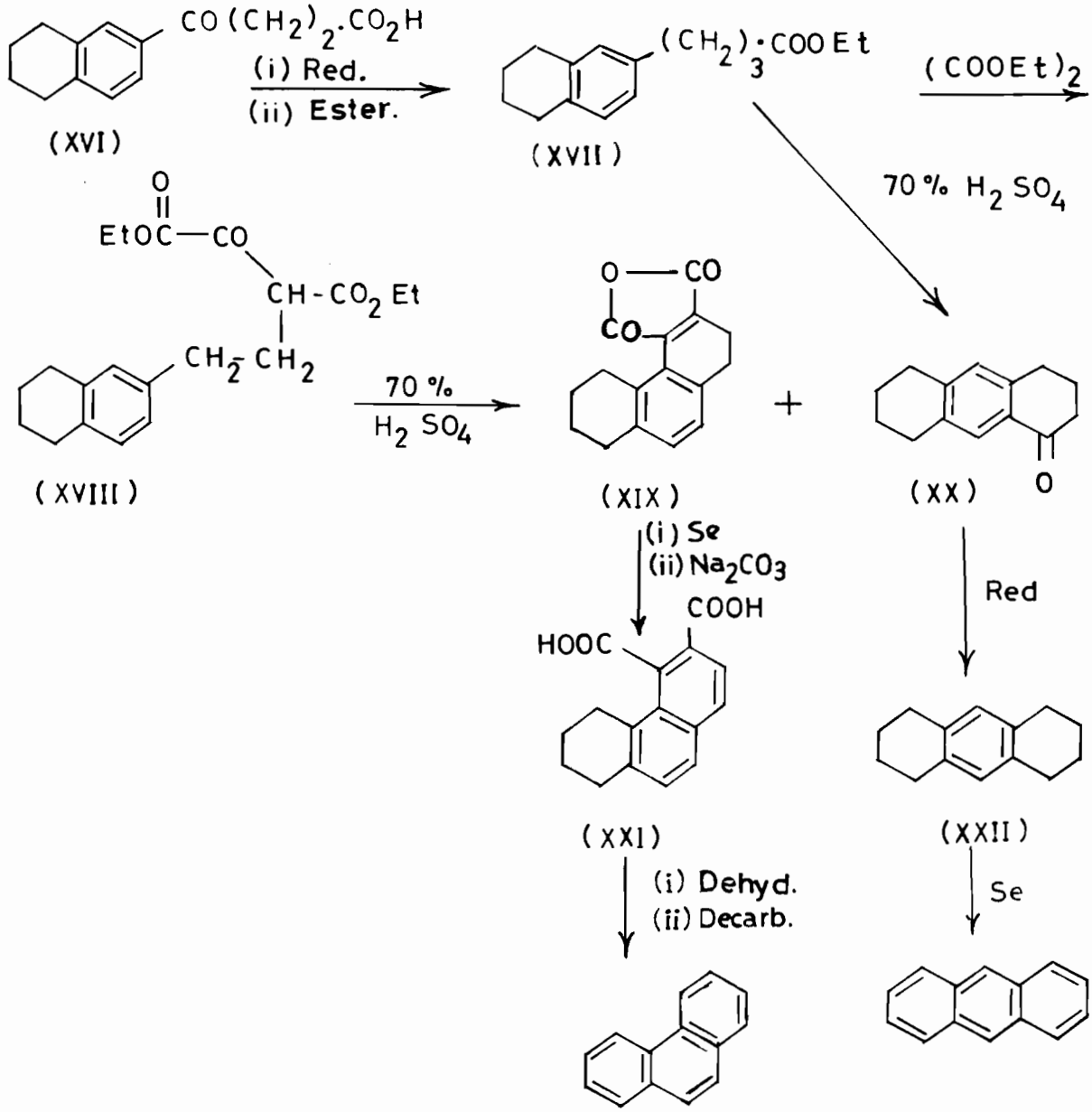
Attempts to dehydrogenate the anhydride (VIb) by heating with S, Se, or Pd/C-sulphur catalysts were not successful.

B) *Conversion of* γ-6-(1,2,3,4-*Tetrahydronaphthyl) butyric Acid into Anthracene and Phenanthrene.*— γ-6-(1,2,3,4-Tetrahydronaphthyl) butyric acid, prepared by Clemmensen reduction of the keto-acid (XVI), was esterified, and the ester (XVII) was condensed with ethyl oxalate in the presence of potassium ethoxide to give the oxalyl derivative (XVIII). This on cyclisation with 70% H_2SO_4 gave 1, 2, 3, 4, 7,8-hexahydro-phenanthrene - 5, 6 - dicarboxylic anhydride (XIX), which crystallised out as yellow crystals from the cold ethereal solution used in the extraction of the product.

The structure of this anhydride (XIX) was substantiated by the appearance of a doublet at 1750 and 1818 cm^{-1} in its infrared spectrum, characteristic of acid anhydrides (5d) (Table II). The ethereal mother liquor, however, contained an oil, which proved to be 1, 2, 3, 4, 5, 6, 7-hepta-hydro-8-oxo-anthracene (XX), since it gave a D.N.P, identical with that of the product obtained by the cyclisation of ethyl γ-6-(1, 2, 5, 4-tetra-hydronaphthyl) butyrate with 80% sulphuric acid. The isolation of the ketone (XX) from the reaction mixture is probably due to the presence of some unchanged butyric ester (XVII), admixed with the oxalyl derivative (XVIII). The anhydride (XIX) was partially dehydrogenated by heating with selenium to give 1, 2, 3, 4-tetra-hydro - phenanthrene-5,6-dicarboxylic anhydride (XXI).

The two hydrogens which are removed are more probably those in the anhydride ring (ring C) (cf. XIX).


AlCl3
(I)
(II)
(i) Zn / Hg-HCl
(ii) Esterif.
(IV)
(COOEt)2
70% H2SO4
20% H2SO4
(VI)
(VII)
(VIII)
C6H6 + AlCl3
(IX)
(X)
(XI)
(XII)
(XIV)
(XV)
-H2O
-CO2


CO(CH2)2.CO2H
(i) Red.
(ii) Ester.
(XVI)
(CH2)3.COOEt
(XVII)
(COOEt)2
70 % H2SO4
EtOC—CO
CH-CO2Et
CH2 CH2
(XVIII)
70 %
H2SO4
(XIX)
(XX)
(i) Se
(ii) Na2CO3
COOH
HOOC
Red
(XXI)
(XXII)
(i) Dehyd.
(ii) Decarb.
Se

The structure of this compound is substantiated by the n.m.r. spectrum of its acid, which shows a multiplet signal lying between 1.5 - 2.3 τ and two other multiplets centred at 6.95 and 8.1 τ , characteristic of aromatic and aliphatic protons, respectively. The ratio of these protons is approximately 1 : 2, i.e. the aliphatic protons are nearly double the aromatic protons, which is the ratio for the hydrogen atoms in the proposed structure. The signal at 6.95 τ stands for the CH_2 groups directly attached to the aromatic ring, whereas that at 8.1 τ stands for the remaining CH_2 groups (8).

When the dibasic acid (XXI), was decarboxylated by heating with copper-bronze and quinoline at 180 - 190 °C, it was converted into phenanthrene (see experimental). This was identified by m.p. and mixed m.p. and by its infrared spectrum, which shows strong bands at 825 and 738 cm^{-1}, characteristic of the out-of - plane bending frequency of 2 and 4 adjacent aromatic hydrogen atoms (5e) which are present in phenanthrene. This shows that dehydrogenation occurred during decarboxylation.

The cyclisation of the oxalyl ester (XVIII) to give a phenanthrene rather than an anthracene derivative is not expected on steric grounds, and can be attributed only to the fixation of the double bonds in the tetralin molecule (7).

However, it was astonishing enough that when ethyl γ-6-(1, 2, 3, 4-tetrahydronaphthyl) butyrate (XVII) was cyclised with 80% sulphuric acid, it gave the ketone (XX), which was identified as its 2: 4-dinitrophenylhydrazone. On reduction of this ketone by Clemmenson's method it gave 1, 2, 3, 4, 5, 6, 7, 8-octahydro-anthracene (XXII). This on dehydrogenation with selenium gave anthracene, identified by m.p. and mixed m.p., and by its infrared spectrum, which shows two strong bands at 890 and 730 cm^{-1}, characteristic of the out-of-plane bending frequencies of 1 and 4 adjacent free aromatic hydrogen atoms (5e), respectively. No reasonable explanation for this abnormal behaviour is available at the present moment.

Experimental

Infrared and electronic spectra were measured on Perkin-Elmer Infracord 137 and spectracord 4000 A spectrophotometers, respectively. M.p.s. are uncorrected.

*β-(4-Methoxy-3-o-methoxyphenyl-benzoyl-*and *β-(4-Methyl-3-o-tolyl-benzoyl)-propionic Acids* (Ia and b).—2,2-Dimethoxydiphenyl (10g;1 mol) was allowed to react with succinic anhydride (5.2 g; 1 mol) and aluminium chloride (13.6g;2 mol) in nitrobenzene (80 ml) as described by Baddar, Fahim and Fleifel (3). The precipitated solid was filtered off, digested with sodium carbonate solution and filtered. The sodium carbonate solution was acidified and the precipitated acid (11 g) was crystallised from glacial acetic acid to give (Ia) in colourless needles, m.p. 229-230°C (Found: C=64.10; H=5.80; OMe=17.1% Calc. for $C_{18}H_{18}O_5 . CH_3CO_2H$: C=64.17; H=5.88; OMe=16.60%). The nitrobenzene mother liquor was extracted with 10% sodium carbonate solution, and the alkaline extract acidified. The precipitated acid (2.0 g) was crystallised from 50% acetic acid to give the *diabasic acid* (IIa) in colourless needles, m.p. 172-3°C, undepressed on admixture with an authentic specimen (see next experiment). Found C=67.34; H=5.60; OMe= 17.52% M.W.= 710. $C_{40}H_{38}O_{12}$ requires: C = 67.34; H=5.60, OMe=17.52%; M.W.=710.43). Its *methyl ester* had m. p. 130-1°C (from methanol) (Found : C=68.37; H=6.00; OMe=25.20. $C_{42}H_{42}O_{12}$ requires: C=68.28; H=5.73; OMe= 25.20%).

When the mixture of 2, 2-dimethyldiphenyl (10 g), succinic anhydride (5.49 g) and aluminium chloride (14.67 g) in nitrobenzene (16.0 ml) was treated in the same manner, it gave a viscous oil which was purified by dissolving in ether or benzene and extraction with sodium carbonate solution. The precipitated oily acid, which solidified on standing, was crystallised from light petroleum (b.p. 60 - 80°C) - benzene mixture to give *β-(4-methyl-3-o-tolyl-benzoyl) propionic acid* (Ib), m. p. 124°C. (Found : C = 76.31; H = 6.38%. $C_{18}H_{18}O_3$ requires: C = 76.57 ; H = 6.43%) ; yield = 39% . Its *methyl ester* was obtained as a pale yellow oil, b.p. 184°C/10 mm (Found: C=77.00 ; H = 6.78; OMe = 10.15%. $C_{19}H_{20}O_3$ requires: 77.00; H = 6.76 ; OMe = 10.47%).

Reaction between *β-(4-Methoxy-2-o-methoxyphenyl-benzoyl)-propionic Acid and Succinyl Chloride.* - The stirred cooled mixture (0-5°C) of the acid (8.0 g ; 2 mol) and succinyl chloride (1.97 g ; 1 mol) in nitrobenzene (64 ml) was treated portionwise with powdered anhydrous aluminium chloride (3.3 g ; 2 mol), keeping the temperature below 5°C. The reaction mixture was kept at room temperature for two days with occasional stirring, and decomposed with ice and dilute hydrochloric acid. The nitrobenzene layer was diluted with benzene or ether then extracted with sodium carbonate solution. The cold alkaline solution was acidified and the precipitated acid was filtered off and crystallised from 50% acetic acid to give (IIa), m.p. 172-

173°C; yield = 96%.

γ-(4-*Methoxy*-3-*o-methoxyphenyl-phenyl*) IIIa-*and* γ-(4-*methyl*-3-*o-tolyl-phenyl*) IIIb-*butyric acid.*-(i) The mixture of the keto-acid (50g) (Ia), zinc amalgam (180g) (B.D.H.) and concentrated hydrochloric acid (260 ml) was refluxed for 24 hrs. The product was filtered off, extracted with sodium carbonate solution, and the alkaline solution filtered and acidified. The precipitated acid was filtered off and crystallised from xylene to give the *butyric acid* (IIIa), m.p. 161°C. (Found: C = 72.00 ; H = 6.65 ; OMe = 20.4%. $C_{18}H_{20}O_4$ requires: C=71.98; H=6.71; OMe=20.6%); yield =96%; (ii) the mixture of the keto-acid (Ib) (50 g) , zinc amalgam (120 g) (B.D.H.), water (75 ml), xylene (100 ml) and concentrated hydrochloric acid (175 ml) was refluxed for 65 hrs. The xylene layer was diluted with ether and extracted with sodium carbonate solution. The oily acid precipitated on acidification was extracted with ether, dried and the solvent evaporated. The acid, which solidified on standing for several days, was crystallised from benzene to give the *butyric acid* (IIIb), m.p. 110°C (Found: C = 80.50 ; H = 7.36. $C_{18}H_{20}O_2$ requires: C=80.56; H=7.51%); yield=99%.

The butyric acids (IIIa and b) were methylated (methyl alcohol + HCl gas) to give the *methyl esters* (IVa and b); yield = 100%. IVa had b.p. 66°C / 10 mm. (Found : C = 72.50; H = 7.00 ; OMe = 29.78%. $C_{19}H_{22}O_4$ requires: C = 72.59 ; H = 7,05 ; OMe = 29.93%). IVb had b.p. 172°C/10 mm (Found: C = 80.85 ; H=7.75; OMe = 11.00%. $C_{19}H_{22}O_2$ requires: C = 80.81; H = 7.85 ; OMe = 10.90%).

Claisen Condensation of *Methyl* γ(4-*Methoxy*-3-*o-methoxyphenyl-phenyl*)- *and* γ(-4-*methyl*-3-*o-tolyl-phenyl*) *butyrate with Diethyl Oxalate.* — The stirred suspension of potassium ethoxide [from potassium (0.051 g-atom) and ethanol (2.5 g)] in a solution of diethyl oxalate (0.089 g-mol) in dry ether (150 ml) was treated portionwise with the solution of the butyric ester (IVa or b) in dry ether (50 ml) during 30 min. The mixture was left for 18 hrs at room temperature with frequent stirring, then poured onto ice and dilute sulphuric acid, and the precipitated oil extracted with ether. Evaporation of the ether left a dark-red oil (20 g) of the oxalyl derivative (Va and b).

Cyclisation of the Oxalyl Derivatives (Va and b): (i) *With* 70% (v/v) *Sulphuric Acid.* - The stirred crude oxalyl derivative (20 g) was heated with 70% sulphuric acid (100 ml) in a boiling water-bath for one hour, then poured onto ice and left over-night. The precipitated solid was filtered off, extracted with 10% cold sodium bicarbonate solution (300 ml), and the insoluble product crystallised from a suitable solvent. 7-*Methoxy*-6-*o-methoxyphenyl*-3,4-*dihydronaphthalene*-1, 2-*dicarboxylic anhydride* (VIa), orange needles from acetic acid, m.p. 348 - 9°C. (Found: C=71.45; H = 4.70; OMe = 18.50%. $C_{20}H_{16}O_5$ requires: C=71.42; H=4.80; OMe=18.45%); yield = 4.5 g. 7-*Methyl*-6-*o-tolyl*-3,4-*dihydronaphthalene*-1, 2-*dicarboxylic anhydride* (VI b), yellow crystals, m.p. 209°C; (Found: C=78.48; H = 5.31%. $C_{20}H_{16}O_3$ requires: C = 78.93; H = 5.30%); yield=5%.

Esterification of the dibasic acid derived from the anhydride (VIa) gave the *dimethyl ester,* m.p. 241-2°C (from methanol) (Found: C=69.23; H=5.36; OMe=33.89%. $C_{22}H_{20}O_6$ requires: C=69.46; H=5.30; OMe=32.68%).

(ii) *With* 20% *Sulphuric Acid.* - The stirred crude oxalyl derivative (Va) (10 g) was heated with 20% (v/v) sulphuric acid (50 ml) on a boiling water-bath for 12 hrs then poured onto ice and left over-night. The product was dissolved in ether and extracted with sodium carbonate solution. The oily acid precipitated on acidification was extracted with ether, and the viscous oil left on the evaporation of the ether, which solidified on standing, was crystallised from light petroleum (b.p. 60-80 °C) to give -7-*methoxy*-6-*o-methoxyphenyl*-3, 4-*dihydronaphthalene*-1-*carboxylic acid* (XII), m.p. 48-9°C. (Found: C=73.33 ; H = 5.78 ; OMe = 19.89%. $C_{19}H_{18}O_4$ requires: C=73.54; H=5.80; OMe= 20.00%).

Attempts to dehydrogenate the anhydrides (VIa and b) with sulphur, selenium or Pd / C - sulphur were unsuccessful.

2-*Benzoyl*-7-*methoxy*-6-*o-methoxyphenyl*-3,4-*dihydro-naphthalene*-1-*carboxylic Acid* (IX). — The stirred mixture of the powdered anhydride (VIa) (0.5 g) and benzene (10 ml) was treated portionwise at room temperature with anhydrous aluminium chloride (2.0 g) during 30 min. The red violet reaction mixture was heated for 4 hrs at 70°C, the benzene evaporated and the remaining deep-orange residue was decomposed with ice and hydrochloric acid. The product was filtered off and crystallised from 1,1,2,2-tetrachloroethane to give the *title acid* (IX) in yellowish-green crystals, m.p. 194-5°C (Found: C=75.07 ; H=5.37 ; OMe=14.40%. $C_{26}H_{22}O_5$ requires: C = 75.35 ; H = 5.35 ; OMe = 14.98%; yield = 100%.

2-*Benzoyl*-7-*methoxy*-6-*o-methoxyphenyl*-3,4-*dihydro-naphthalene* (XI).— The stirred mixture

of the preceding acid (IX) (0.3 g) and copper-bronze (0.1 g) in quinoline (3.0 ml) was refluxed for 2 hrs in an oil-bath at 190°C. The rest of the copper-bronze (0.2 g) was added portionwise during the first hour. The reaction mixture was worked up as usual, and the product extracted from the copper-bronze with hot benzene (charcoaled). The benzene extract was washed with sodium carbonate solution and evaporated. Crystallisation from benzene-light petroleum (b.p. 60-80°C) gave the *title compound* (XI) in pale yellow crystals, m.p. 210°C (Found: C = 81.00; H = 5.92% ; $C_{25}H_{22}O_3$ requires: C = 81.05 ; H = 5.99%); yield = 80%.

1-*Benzoyl*-7-*methoxy*-6-*o*-*methoxyphenyl*-2, 3-*dihydronaphthalene* (XIV). — The 1-naphthoic acid (XII) (2.0 g) was refluxed with thionyl chloride (1.0 g) for 2 hrs. The excess of thionyl chloride was removed and the product was distilled to give 3, 4-dihydro-7-methoxy-6-*o*-methoxyphenyl-1-naphthoyl chloride as a pale yellow oil, b.p. 187°C. The stirred solution of the acid chloride (1.0 g) in benzene (6 ml) was treated portionwise with anhydrous aluminium chloride (1.6 g) during 30 min at room temperature. The reaction mixture was heated for 4 hrs at 70°C, then the benzene was evaporated and the reaction mixture worked up as usual. Distillation of the oily product gave the *title compound,* b.p. 195°C (Found: C = 81.11 ; H = 6.00 ; OMe = 17.00%. $C_{25}H_{22}O_3$ requires: C = 81.01; H = 5.94 ; OMe = 16.75%) ; yield = 98%.

3, 4 - *Dihydro* -2- *methoxy*-3-*o*-*methoxyphenyl*-*benz* [a] *anthraquinone* (XV). — The solution of the keto-acid (IX) (0.6 g) in dry xylene (15.0 ml) was refluxed with P_2O_5 (0.3 g) for 4 hrs and worked up as usual. The product was crystallised from nitrobenzene to give the *title compound* in pale yellow crystals, m.p. 339°C (Found: C = 78.69 ; H = 5.0 ; OMe = 15.0. $C_{26}H_{20}O_4$ requires: C = 78.77; H = 5.09; OMe = 15.6%); yield = 35%.

Ethyl γ - 6 - (1, 2, 3, 4-*Tetrahydronaphthyl*)-*butyrate* (XVII). — The keto-acid (XVI) (50 g) was reduced by refuxing with zinc amalgam (120 g), water (75 ml) and concentrated hydrochloric acid (175 ml) for 5 hours, and worked up as usual (3). The product was crystallised from ethanol to give the *butyric acid* in colourless crystals, m. p. 49.5°C (Found: C = 77.00 H = 8.25% . $C_{14}H_{18}O_2$ requires C = 77.03 ; H = 8.31%) ; yield 96%. The *ethyl ester* (XVII), prepared by refluxing the acid (40 g) with absolute ethanol (80 ml) and concentrated sulphuric acid (3.6 ml), was obtained as a colourless oil, b.p. 155°C/46 mm; (Found: C=78.04; H=8.93% $C_{16}H_{22}O_2$ requires: C=78.01; H=8.90%); yield =100%).

Claisen Condensation. - The solution of the butyric ester (XVII) (12.3 g; 1 mol) in dry ether (50 ml) was added portionwise to the stirred mixture of pot. ethoxide (1.15 mol) [from potassium (2.0 g) and ethanol (2.5 g) in dry ether (100 ml)] and freshly distilled ethyl oxalate (13.0 g; 1.8 mol), and the reaction carried out as mentioned before to give the oxalyl derivative (18 g) (XVIII) as a dark orange-red oil.

Cyclisation of the Oxalyl Derivative (XVIII).— The crude oxalyl derivative (18 g) was stirred with 70% sulphuric acid (100 ml) at 60°C. The product precipitated on addition of water was dissolved in ether, and the ethereal solution washed with sodium bicarbonate solution. The dry ethereal solution was concentrated and left to cool. The product (6.0 g), which crystallised out, was filtered off, and recrystallised from acetic acid to give 1, 2, 3, 4, 7, 8-*hexahydrophenanthrene*-5,6-*dicarboxylic anhydride* (XIX) in canary yellow crystals, m.p. 168 - 169°C (Found: C=75.33; H=5.56%. $C_{16}H_{14}O_3$ requires: C=75.57; H=5.55%).

Removal of the ether from the mother liquor left an oil, b.p. 188°C/45mm, which proved to be 1,2,3,4,5,6,7 - *heptahydro*-8-*oxo*-*anthracene* (XX) (Found: C=83.90, H=8.10%. $C_{14}H_{16}O$ requires: C = 83.96 ; H = 8.05%), identified as its 2, 4-*dinitrophenylhydrazone,* red needles from acetic acid, m. p. 277-278°C (Found: C = 63.03 ; H=5.34 ; N=14.62%. $C_{20}H_{20}O_4N_4$ requires: C = 63.13 ; H = 5.26 ; N = 14.73%). The ketone and its D.N.P. were identical with those obtained by the cyclisation of the butyric ester (XVII) (5 ml) with 80% (v/v) sulphuric acid (30 ml) (heating for 2 hours on a boiling water-bath).

1, 2, 3, 4-*Tetrahydrophenanthrene*-5, 6-*dicarboxylic Acid* (XXI). — The hexahydro-anhydride (XIX) (2.5 g) was heated with selenium (0.3 g) at 260 - 270°C (boiling ethyl cinnamate-bath) for 15 hours. The product was repeatedly extracted with 15% sodium carbonate solution. The acid precipitated on acidification of the alkaline solution was crystallised from glacial acetic acid to give 1,2,3,4-*tetrahydrophenanthrene*-5, 6-*dicarboxylic acid* (XXI) as pale yellow crystals, m.p. 200-1°C (Found: C=70.54; H=5.10%. $C_{16}H_{14}O_4$ requires: C=70.85; H= 5.17%);yield=94%.

Conversion of 1, 2, 3, 4-*Tetrahydrophenanthrene*-5, 6-*dicarboxylic Acid* (XXI) *into Phenanthrene* — The mixture of the dibasic acid (XXI) (1.3 g) and copper-bronze (0.26 g) was heated with quinoline (4 ml) for 2 hours at 180-190°C.

The remaining copper-bronze (0.26 g) was added portionwise during the first hour. The reaction mixture was worked up as usual and the product was purified by sublimation to give phenanthrene (0.7 g), m.p. and mixed m.p. 101°C: (Found: C=93.96; H=5.57%. Calc. for $C_{14}H_{10}$: C=94.34; H=5.66%); yield=86%.

Conversion of 1, 2, 3, 4, 5, 6, 7-*Heptahydro*-8-*oxo-anthacene into Anthracene.*— (i) The ketone (XX) (4.0 g) was reduced with zinc amalgam (10 g) water (4 ml) and concentrated hydrochloric acid (14.5 ml) (10 hours reflux). The product was distilled to give 1, 2, 3, 4, 5, 6, 7, 8-*octahydroanthracene* (XXII) as a colourless oil, b.p. 130°C/45 mm (Found : C = 90.40 ; H = 9.60%. $C_{14}H_{18}$ requires: C=90.26; H=9.74%); yield = 100%. (ii) The above product (XXII) (2.0 g) was dehydrogenated by heating with selenium (0.4 g) at 260-270°C for 10 hours. The product was purified by sublimation to give anthracene, m.p. and mixed m.p. 215-216°C ; yield = 89% (Found : C = 93.96 ; H = 5.75%. Calc. for $C_{14}H_{10}$: C = 94.34 ; H = 5.66%).

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أحماض بيتا ـ آرويل بروبيونيك : الجزء الثالث والعشرون

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خلاصـــة

حضرت أحماض بيتا ـ آرويل ـ بروبيونيك المشار اليها واختزلت الى أحماض جاما ـ آرويل بوتيريك المقابلة ثم حولت الى استراتها . عندما كثفت هذه الاسترات مع اكسالات الايثل في وجود ايثوكسيد البوتاسيوم تحولت الى مشتقات الاكساليل وهذه أعطت مشتقات انهيدريد الاحماض ثنائي ـ هيدرو ـ نفثالين ـ ٢،١ ـ ثنائي كربوكسيليك وانهيدريد حمض سداسي هيدروفينانثرين ـ ٤،٣ـثنائي كربوكسيليك.

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* العنوان الحالي : قسم الكيمياء بكلية البنات بجامعة عين شمس بالقاهرة