530. *β-Aroylpropionic Acids. Part XX.* Conversion of β-(2,5-Dimethylbenzoyl)-α- and -β-phenylpropionic Acid into Polynuclear Compounds.*

By F. G. BADDAR, M. F. EL-NEWEIHY, and M. T. EL-ZIMAITY.

The ethoxalyl derivative of ethyl γ-(2,5-dimethylphenyl)-β-phenylbutyrate is cyclised with 80% sulphuric acid, then dehydrogenated to 5,8-dimethyl-3-phenylnaphthalene-1,2-dicarboxylic anhydride. This is cyclised by aluminium chloride in nitrobenzene to 6,9-dimethylbenzo[*b*]fluorenone-10-carboxylic acid. When the ethoxalyl derivative is refluxed with 20% sulphuric acid and then dehydrogenated, it gives rise to 5,8-dimethyl-3-phenyl-1-naphthoic acid. It is decarboxylated to 1,4-dimethyl-6-phenylnaphthalene, identical with the product obtained from γ-(2,5-dimethylphenyl)-α-phenylbutyric acid.

p-XYLENE condensed with phenylsuccinic anhydride in presence of aluminium chloride to give a 2 : 3 mixture of β-(2,5-dimethylbenzoyl)-α- and β-phenylpropionic acid; the higher proportion of the latter acid indicates that non-polar or weakly polar substrates favour the formation of the β-phenyl isomers.[1] The β-phenyl acid was reduced to the butyric acid (Ia), then esterified and condensed with ethyl oxalate in presence of potassium ethoxide,[2] to give the ethoxalyl ester (II) which was cyclised with 80% (v/v) sulphuric acid to the dihydro-anhydride (III). This was dehydrogenated with selenium to the anhydride (IV), then treated with anhydrous aluminium chloride to give 6,9-dimethylbenzo[*b*]fluorenone-10-carboxylic acid (V).

When the crude oxalyl ester (II) was refluxed with 20% (v/v) sulphuric acid,[3] it gave 3,4-dihydro-5,8-dimethyl-3-phenyl-1-naphthoic acid (VI), which was dehydrogenated with selenium to 5,8-dimethyl-3-phenyl-1-naphthoic acid, then decarboxylated to 1,4-dimethyl-6-phenylnaphthalene (VII).

β-(2,5-Dimethylbenzoyl)-α-phenylpropionic acid was reduced by a modified Clemmensen method to γ-(2,5-dimethylphenyl)-α-phenylbutyric acid (VIII), and the crude acid was directly cyclised with phosphorus oxychloride. The product was found to contain 5,8-dimethyl-2-phenyl-1-tetralone (IX), and another ketonic substance, m. p. 89—90°, as the main constituents, with a little 2-phenyl-4-*p*-xylylbut-3-enoic acid lactone. This indicated that the butyric acid was contaminated with unreduced keto-acid. The structure of the tetralone was established by its 2,4-dinitrophenylhydrazone, and its

---

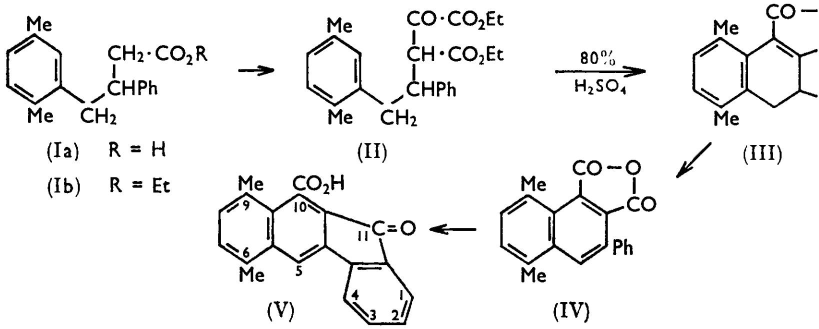
* Part XIX, *J.*, 1961, 1083.

[1] Cf. Baddar, Fleifel, and Sherif, *J. Chem. U.A.R.*, 1960, **3**, No. 1, 47; Wali, Khalil, Bhatia, and Ahmed, *Proc. Indian Acad. Sci.*, 1941, **14**, *A*, 139.

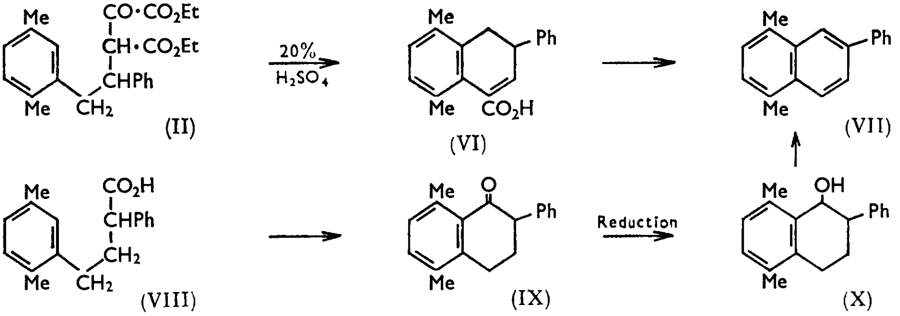
[2] Baddar, Fleifel, and Sherif, *J.*, 1959, 1009.

[3] Baddar and Warren, *J.*, 1939, 944.

infrared spectrum which showed a strong band at 1670 cm.$^{-1}$, characteristic of αβ-unsaturated six-membered cyclic ketones.[4] The structure of the lactone was established by its identity with a specimen prepared by heating β-(2,5-dimethylbenzoyl)-α-phenylpropionic acid with acetic anhydride; its infrared spectrum showed a band at 1750 cm.$^{-1}$ (KBr disc), characteristic of βγ-unsaturated lactones.[5,6]



The ketonic structure of the product, m. p. 89—90°, was inferred from the formation of a dinitrophenylhydrazone, and the appearance in its infrared spectrum of a strong band at 1680 cm.$^{-1}$ (KBr disc), characteristic of aryl ketones.[7] Its analytical data as well as those of its dinitrophenylhydrazone agree with those calculated for β-phenylpropionyl-*p*-xylene, a product that could have resulted from decarboxylation of β-(2,5-dimethylbenzoyl)-α-phenylpropionic acid. However, the exact structure of this product is still under investigation.



The tetralone (IX) was reduced with lithium aluminium hydride to the tetralol (X), whose infrared spectrum showed a band at 3600 cm.$^{-1}$, characteristic of the unbonded hydroxyl group.[8] Dehydrogenation of the crude tetralol with selenium gave 1,4-dimethyl-6-phenylnaphthalene (VII).

EXPERIMENTAL

Infrared spectra were measured on a Perkin-Elmer Infracord spectrophotometer model 137, for Nujol mulls unless otherwise stated.

β-(2,5-*Dimethylbenzoyl*)-β-*phenylpropionic Acid*.—A stirred ice-cold mixture of phenylacetyl chloride (15·5 g., 1 mol.), *p*-xylene (15 g., 1·5 mol.), and *s*-tetrachloroethane (175 ml.)

---

[4] Bellamy, " The Infra-red Spectra of Complex Molecules," Methuen and Co. Ltd., London, 1956, p. 128.

[5] Baddar and Sherif, *J.*, 1960, 2309.

[6] Ref. 4, p. 153.

[7] Ref. 4, p. 114.

[8] Ref. 4, p. 84.

was treated portionwise with finely powdered aluminium chloride (16 g., 1·2 mol.) at such a rate (0·5 hr.) that the temperature was kept at 0—5°. The mixture was then allowed slowly to attain room temperature and left thereat for 48 hr. with occasional stirring, then poured into ice-cold dilute hydrochloric acid, and the solvent was removed in steam. The oily product (20 g.) was distilled to give 2,5-dimethyldeoxybenzoin, b. p. 182°/5·5 mm. (17 g.). Its oxime, crystallised from dilute ethanol, had m. p. 111—113° (Found: C, 80·6; H, 7·4; N, 5·7. Calc. for $C_{16}H_{17}NO$: C, 80·3; H, 7·2; N, 5·85%). Wege[9] gives m. p. 99°.

2,5-Dimethyldeoxybenzoin (9 g., 1 mol.) was gradually added to potassium ethoxide in absolute ethanol (from potassium, 1·9 g., in absolute ethanol, 30 ml.), and the mixture was refluxed for 4 hr. on a boiling-water bath. Ethyl bromoacetate (6·7 g., 1 mol.) was then added, and refluxing was continued for 10 hr. The mixture was filtered while hot from the precipitated potassium bromide, and the filtrate refluxed for 10 hr. with 7% alcoholic sodium hydroxide (70 ml.) and then poured into ice-cold dilute hydrochloric acid. The product which solidified (1·6 g.) on trituration with light petroleum (b. p. 40—60°) crystallised from ethanol to give β-(2,5-*dimethylbenzoyl*)-β-*phenylpropionic acid*, m. p. 171° (Found: C, 76·25; H, 6·35. $C_{18}H_{18}O_3$ requires C, 76·6; H, 6·4%).

Reaction between p-*Xylene and Phenylsuccinic Anhydride*.—A stirred ice-cold mixture of phenylsuccinic anhydride (17·6 g., 1 mol.), *p*-xylene (21·4 g., 2 mol.), and *s*-tetrachloroethane (300 ml.) was treated portionwise with finely powdered aluminium chloride (33·6., 2·5 mol.) at such a rate that the temperature was kept at 0—5° during the addition (½ hr.). Then the mixture was allowed slowly to attain room temperature, left thereat for 48 hr. with occasional stirring, and worked up as usual.[5] The crude acid (27 g.) had m. p. 140—169°, shrinking at 145°, indicating that it was a mixture. On crystallisation from ethanol β-(2,5-dimethylbenzoyl)-β-phenylpropionic acid (15·5 g.), m. p. and mixed m. p. 171°, was obtained (Found: C, 77·1; H, 6·3. Calc. for $C_{18}H_{18}O_3$: C, 76·6; H, 6·4%); its infrared spectrum showed two strong bands at 1724 and 1680 cm.$^{-1}$. The mother-liquor was evaporated to dryness and the residue crystallised from benzene–light petroleum (b. p. 40—60°) to give β-(2,5-*dimethylbenzoyl*)-α-*phenylpropionic acid* (10 g.), m. p. 130° (Found: C, 76·7; H, 6·4%).

γ-(2,5-*Dimethylphenyl*)-β-*phenylbutyric Acid* (Ia).—A solution of β-(2,5-dimethylbenzoyl)-β-phenylpropionic acid (12 g.) in pure sulphur-free toluene (200 ml.) was refluxed with amalgamated zinc (B.D.H.) (150 g.), concentrated hydrochloric acid (200 ml.), and water (50 ml.), for 150 hr., during which further zinc (100 g.), concentrated hydrochloric acid (200 ml.), and water (50 ml.) were added portionwise. The mixture was filtered, and the toluene layer was extracted with 10% sodium hydroxide solution. The oily acid precipitated on acidification crystallised from light petroleum (b. p. 40—60°), to give γ-(2,5-*dimethylphenyl*)-β-*phenylbutyric acid* (8 g.), m. p. 92—93 (Found: C, 80·0; H, 7·3. $C_{18}H_{20}O_2$ requires C, 80·6; H, 7·5%).

The *ethyl ester* (prepared by means of ethyl alcohol–hydrogen chloride) had b. p. 171°/0·1 mm. (Found: C, 81·2; H, 8·1. $C_{20}H_{24}O_2$ requires C, 81·1; H, 8·1%).

3,4-*Dihydro*-5,8-*dimethyl*-3-*phenylnaphthalene*-1,2-*dicarboxylic Anhydride* (III).—Pure powdered potassium (1·6 g., 1 mol.) was covered with dry ether (100 ml.), stirred, and treated portionwise with absolute ethanol (*ca.* 4 ml.). When the evolution of hydrogen ceased, ethyl oxalate (8·8 g.; 1·5 mol.) was added, and the light yellow solution was left for 1 hr. Ethyl γ-(2,5-dimethylphenyl)-β-phenylbutyrate (11·4 g., 1 mol.) was next added and the wine-red solution was left overnight, then gently heated on a boiling-water bath for 7 hr., poured into ice-cold dilute sulphuric acid, and worked up as usual.[2] The crude oxalyl ester (19·2 g.) was directly used in the following experiment.

It was stirred on a boiling-water bath with 80% (v/v) sulphuric acid (150 ml.) for 1 hr. The mixture was poured on ice, and the precipitated viscous brown oil (10 g.) was boiled with sodium carbonate solution, filtered, cooled, and acidified. The precipitated semisolid dibasic acid (7·2 g.) was refluxed with acetyl chloride, which upon evaporation left a solid (3·8 g.). On crystallisation from light petroleum (b. p. 60—80°) greenish-yellow 3,4-*dihydro*-5,8-*dimethyl*-3-*phenylnaphthalene*-1,2-*dicarboxylic anhydride* was obtained having m. p. 130—132° (Found: C, 79·4; H, 5·5. $C_{20}H_{16}O_3$ requires C, 78·95; H, 5·3%).

5,8-*Dimethyl*-3-*phenylnaphthalene*-1,2-*dicarboxylic Anhydride* (IV).—A powdered mixture of the preceding anhydride (1·1 g.) and selenium (0·9 g.) was heated at 290° for 8 hr., cooled, and then extracted with boiling benzene. The product (0·7 g.) that crystallised on cooling

---

[9] Wege, *Ber.*, 1891, **24**, 3540.

recrystallised from benzene–light petroleum (b. p. 40—60°) to give 5,8-*dimethyl*-3-*phenylnaphthalene*-1,2-*dicarboxylic anhydride* in yellow needles, m. p. 210° (Found: C, 79·0; H, 4·5. $C_{20}H_{14}O_3$ requires C, 79·5; H, 4·6%).

6,9-*Dimethylbenzo*[b]*fluorenone*-10-*carboxylic Acid* (V).—Nitrobenzene (10 ml.) was cooled with stirring to 10°, then treated portionwise with a mixture of the preceding anhydride (0·5 g., 1 mol.) and aluminium chloride (*ca.* 1 g., 4 mol.) during 1 hr. The mixture was kept at 10° for 2 hr., then left at 55—60° for 6 hr. and overnight at room temperature, and was worked up as usual.[2] The precipitated *acid* crystallised from acetic acid in yellow needles (0·3 g.), m. p. >300° (Found: C, 78·5; H, 4·6. $C_{20}H_{14}O_3$ requires C, 79·5; H, 4·6%).

3,4-*Dihydro*-5,8-*dimethyl*-3-*phenyl*-1-*naphthoic Acid* (VI).—The crude oxalyl ester (II) (16·7 g.) was refluxed with 20% (v/v) sulphuric acid (170 ml.) for 56 hr., then worked up as usual.[3] The product (6 g.), which partially solidified during 1 month, crystallised from dilute ethanol to give 3,4-*dihydro*-5,8-*dimethyl*-3-*phenyl*-1-*naphthoic acid*, m. p. 165° (Found: C, 82·3; H, 6·7. $C_{19}H_{18}O_2$ requires C, 82·0; H, 6·5%).

5,8-*Dimethyl*-2-*phenyl*-1-*tetralone* (IX).—(i) *Reduction of the α-phenyl-keto-acid.* A mixture of β-(2,5-dimethylbenzoyl)-α-phenylpropionic acid (15 g.), toluene (sulphur-free; 200 ml.), zinc amalgam (250 g.) (B.D.H), concentrated hydrochloric acid (200 ml.), and water (75 ml.) was refluxed for 90 hr., during which further concentrated hydrochloric acid (100 ml.) was added portionwise. The mixture was worked up as in the analogous experiment above. The viscous yellow oil (12·7 g.) was used directly in the following step.

(ii) *Cyclisation of the butyric acid.* Phosphorus oxychloride (30 ml.) was gradually added to a boiling solution of the crude butyric acid (24·5 g.) in dry *s*-tetrachloroethane (350 ml.); the mixture was gently refluxed for 2·5 hr., during which a semisolid product separated. The mixture was poured into ice-cold water, and the solvent removed with steam. The dark brown oily product (19·7 g.) was distilled, to give three fractions. (*a*) A *substance*, b. p. 240°/0·2 mm., solidified (7·6 g.) on trituration with light petroleum (b. p. 40—60°) and had m. p. 89—90° (from dilute ethanol) (Found: C, 85·3; H, 7·3. $C_{17}H_{18}O$ requires C, 85·7; H, 7·6%). Its red 2,4-*dinitrophenylhydrazone* had m. p. 200° (from ethanol) (Found: C, 66·8; H, 5·1; N, 13·1. $C_{23}H_{22}N_4O_4$ requires C, 66·0; H, 5·3; N, 13·4%). (*b*) A second fraction, b. p. 280°/0·2 mm., on treatment with light petroleum (b. p. 40—60°), gave 2-*phenyl*-4-p-*xylylbut*-3-*enoic acid lactone* (0·55 g.) which, crystallised from light petroleum (b. p. 60—80°), had m. p. 127—128° (Found: C, 81·7; H, 6·2. $C_{18}H_{16}O_2$ requires C, 81·8; H, 6·1%); it was identified by mixed m. p. with a specimen, m. p. 127—128°, prepared by heating β-(2,5-dimethylbenzoyl)-α-phenylpropionic acid with acetic anhydride.[10] (*c*) The light-petroleum washings from (*a*) and (*b*) gave on evaporation a viscous oil (7·5 g.), which was identified as 5,8-dimethyl-2-phenyl-1-tetralone through its 2,4-*dinitrophenylhydrazone*, red crystals (from ethyl acetate), m. p. 242° (Found: C, 66·9; H, 5·2; N, 12·9. $C_{24}H_{22}N_4O_4$ requires C, 67·0; H, 5·1; N, 13·0%). The infrared spectrum of the tetralone showed two bands at 1670 and 1750 cm.$^{-1}$; the latter band which is probably due to contamination with the above lactone disappeared in the spectrum of the dinitrophenylhydrazone (KBr disc).

1,4-*Dimethyl*-6-*phenylnaphthalene* (VII).—(i) A solution of the preceding tetralone (2·8 g.) in dry ether (90 ml.) was added during ½ hr. to a suspension of lithium aluminium hydride (1·8 g., excess) in dry ether (90 ml.). The mixture was refluxed for 3 hr., left overnight, and worked up as usual. The product was distilled, to give the tetralol (X), b. p. 250°/0·2 mm. (2·5 g.), $\nu_{\max.}$ 3600 cm.$^{-1}$. It was used directly in the following step.

The tetralol (1 g.) was heated with selenium powder (1 g.) at 230° for 8 hr. The mixture was extracted with ether, and a solution of the product in light petroleum (b. p. 40—60°) was left to evaporate slowly at room temperature. The precipitated solid (0·5 g.) crystallised from methanol (3 days at 0°), to give 1,4-*dimethyl*-6-*phenylnaphthalene*, m. p. 70° (Found: C, 92·3; H, 6·9. $C_{18}H_{16}$ requires C, 93·05; H, 6·95%).

(ii) A mixture of 3,4-dihydro-5,8-dimethyl-3-phenyl-1-naphthoic acid (1·2 g.) and selenium (0·6 g.) was heated at 240° for 8 hr. The product was extracted with boiling benzene, the solvent was then evaporated, and the residue was extracted with boiling sodium carbonate solution. The oily acid (0·7 g.) precipitated on acidification was distilled in a vacuum, to give 5,8-dimethyl-3-phenyl-1-naphthoic acid, b. p. 260°/0·5 mm., which solidified on long storage. To a stirred mixture of this acid (0·5 g.) and quinoline (5 ml.), copper bronze (*ca.* 0·1 g.) was

---

[10] Kugel, *Annalen*, 1898, **299**, 54.

added portionwise while the mixture was gradually heated on a sand-bath. The mixture was refluxed for 1 hr., then worked up as usual. The product crystallised from methanol (2 days at 0°), to give 1,4-dimethyl-6-phenylnaphthalene, m. p. 70°, undepressed on admixture with the specimen prepared by method (i).

A'in Shams University, Faculty of Science,
Cairo, U.A.R.

[*Received, December* 1*st*, 1960.]