

**204.** *β-Aroylpropionic Acids. Part X.\* Conversion of γ-Aryl-β-phenylbutyrates into Polynuclear Compounds.*

By F. G. BADDAR, ABDALLAH M. FLEIFEL, and SAYED SHERIF.

Reduced β-benzoyl-β-phenyl- and β-phenyl-β-*p*-toluoyl-propionic acids are converted into 2:3-benzofluorenones. These are converted, by alkali fusion and recyclisation of the resulting acids, into the corresponding 1:2-benzofluorenones.

THE crude ester (I; R = H), prepared by condensing ethyl βγ-diphenylbutyrate with ethyl oxalate in presence of potassium ethoxide,<sup>1</sup> was cyclised in 80% sulphuric acid to the 3:4-dihydro-anhydride (II; R = H). This was dehydrogenated with sulphur to the anhydride (III; R = H), then treated with anhydrous aluminium chloride to give 2:3-benzofluorenone-1-carboxylic acid (IV; R = H). This acid was decarboxylated with copper and quinoline to 2:3-benzofluorenone (V; R = H), which was reduced with lithium aluminium hydride to give 2:3-benzofluorenone (VI; R = H).

Attempts to convert 2:3-benzofluorenone-1-carboxylic acid into 1:2-benzofluorenone-3-carboxylic acid (VIII; R = H) by aluminium chloride-sodium chloride at 150° or 210° were unsuccessful. The conversion was, therefore, effected as follows:

The acid (IV; R = H) was fused with potassium hydroxide at 250° to give 3-*o*-carboxyphenyl-1-naphthoic acid (VII; R = H), which on cyclisation with concentrated sulphuric acid, gave 1:2-benzofluorenone-3-carboxylic acid (VIII; R = H). This was decarboxylated to 1:2-benzofluorenone (IX; R = H), then reduced with lithium aluminium hydride to 1:2-benzofluorenone (X; R = H).

When 2:3-benzofluorenone (V; R = H) was similarly fused with potassium hydroxide, it gave a 1:2-mixture of the acids (XI and XII; R = H). Cyclisation of these two acids with concentrated sulphuric acid gave 2:3- and 1:2-benzofluorenone, respectively.

When the crude ethoxalyl derivative (I; R = H) was refluxed with 20% (v/v) sulphuric acid,<sup>1</sup> it gave 3:4-dihydro-3-phenyl-1-naphthoic acid, which was dehydrogenated with sulphur to 3-phenyl-1-naphthoic acid, then decarboxylated to 2-phenylnaphthalene.

A similar series of reactions with the ethoxalyl ester (I; R = Me) gave 2'-methyl-2:3-benzofluorenone-1- (IV; R = Me) and 3'-methyl-1:2-benzofluorenone-3-carboxylic acid (V; R = Me) and 2-methyl-6-phenylnaphthalene.

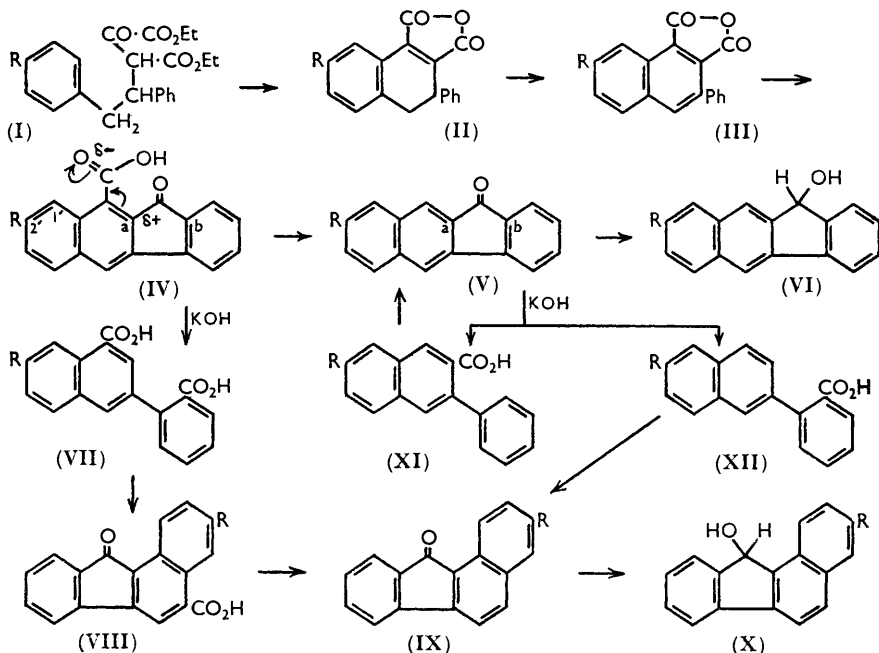
Alkali fission of 2:3-benzofluorenone-1-carboxylic acid and 2:3-benzofluorenone to

\* Part IX, preceding paper.

<sup>1</sup> Baddar and Warren, *J.*, 1939, 944.

give 3-*o*-carboxyphenyl-1-naphthoic acid, and a mixture of *o*- $\beta$ -naphthylbenzoic acid and 3-phenyl-2-naphthoic acid, respectively, indicates that the mode of fission is governed by the electron density on carbon atoms a and b.<sup>2,3</sup>

Cyclisation of the dicarboxylic acids (VII) to give only the 1:2-benzofluorenone-3-carboxylic acids (VIII) cannot be attributed to the steric effect of the bulky carboxyl



group, since even *o*- $\beta$ -naphthylbenzoic acid (XII; R = H) gave only 1:2-benzofluorenone on cyclisation. It appears, therefore, that this is due to the fact that position 1 in the naphthalene nucleus is more susceptible to electrophilic attack than position 3.

#### EXPERIMENTAL

*Ethyl  $\beta\gamma$ -diphenylbutyrate* was obtained from  $\beta\gamma$ -diphenylbutyric acid<sup>4</sup> as an oil (87%), b. p. 190—195°/3 mm.,  $n_D^{21.5}$  1.5460 (Found: C, 80.9; H, 7.45.  $C_{18}H_{20}O_2$  requires C, 80.6; H, 7.5%).

**3:4-Dihydro-3-phenylnaphthalene-1:2-dicarboxylic Anhydride.**—Finely powdered potassium (1.9 g., 1 g.-equiv.) was covered with dry ether (100 ml.), allowed to react with absolute ethanol (3.5 ml.), then treated with freshly distilled ethyl oxalate (10.9 g., 1.5 mol.), followed by ethyl  $\beta\gamma$ -diphenylbutyrate (13.5 g., 1 mol.). The mixture was left overnight, then refluxed for 7 hr. and worked up as usual.<sup>1</sup> The crude ester (I) (20 g.) was heated on the water-bath with 80% (v/v) sulphuric acid (200 ml.) for 0.5 hr. The whole was poured on ice and the product filtered off (10.5 g.). Crystallisation from benzene-light petroleum (b. p. 40—60°) gave 3:4-dihydro-3-phenylnaphthalene-1:2-dicarboxylic anhydride, m. p. 144—145° (Found: C, 78.3; H, 4.5.  $C_{18}H_{12}O_3$  requires C, 78.25; H, 4.4%). The dimethyl ester, obtained in 70% yield by the action of diazomethane on the freshly precipitated acid, crystallised from benzene-light petroleum (b. p. 40—60°) in needles, m. p. 97—98° (Found: C, 75.0; H, 5.5; OMe, 19.1.  $C_{20}H_{18}O_4$  requires C, 74.5; H, 5.6; 2OMe, 19.2%).

**3-Phenylnaphthalene-1:2-dicarboxylic Anhydride.**—The above dihydro-anhydride (1 g., 1 mol.) and sulphur (0.14 g., 1.2 g.-equiv.) were heated together at 205—210° for 10 hr. The product (0.8 g., 81%) crystallised from benzene to give 3-phenylnaphthalene-1:2-dicarboxylic

<sup>2</sup> Lea and Robinson, *J.*, 1926, 2351; Baddar and Gindy, *J.*, 1948, 1231.

<sup>3</sup> Olifson, *J. Gen. Chem. (U.S.S.R.)*, 1939, 9, 36; preceding paper.

<sup>4</sup> Ali, Desai, Hunter, and Mohammed, *J.*, 1937, 1013.

anhydride in yellow needles, m. p. 201—202° (Found: C, 79.05; H, 3.8.  $C_{18}H_{10}O_3$  requires C, 78.8; H, 3.7%). The dimethyl ester had m. p. 84—85° (from methanol) (70%) (Found: C, 75.0; H, 5.05; OMe, 19.1.  $C_{20}H_{16}O_4$  requires C, 75.0; H, 5.0; 2OMe, 19.4%).

2 : 3-Benzofluorenone-1-carboxylic Acid.—(i) A powdered mixture of the anhydride (2.2 g., 1 mol.) and aluminium chloride (5 g.) was added portionwise to cooled nitrobenzene (36 ml.) at <10°. The mixture was heated at 55—60° for 6 hr., then worked up as usual. The acid produced (1.7 g., 77%) was digested with hot benzene, then crystallised from xylene to give 2 : 3-benzofluorenone-1-carboxylic acid in orange-yellow needles, m. p. 244—245° (Found: C, 78.8; H, 3.5.  $C_{18}H_{10}O_3$  requires C, 78.8; H, 3.7%). It gave a green colour with concentrated sulphuric acid. (ii) The same acid was obtained in 50% yield by heating the anhydride (0.5 g.) with aluminium chloride (5 g.) and sodium chloride (1 g.) at 150—155° for 90 min. 2 : 3-Benzofluorenone-1-carboxylic acid 2 : 4-dinitrophenylhydrazone crystallised from dioxan or acetic acid in orange-red crystals, m. p. 315—316° (Found: C, 63.4; H, 2.9; N, 11.7.  $C_{24}H_{14}O_6N_4$  requires C, 63.4; H, 3.1; N, 12.3%). The methyl ester was obtained in yellow needles (86%) (from methanol), m. p. 152—153° (Found: C, 79.0; H, 4.2; OMe, 11.4.  $C_{19}H_{12}O_3$  requires C, 79.15; H, 4.2; OMe, 10.8%).

2 : 3-Benzofluorenone.—2 : 3-Benzofluorenone-1-carboxylic acid was decarboxylated in 74% yield by copper-bronze and quinoline (1 hr.) in the usual manner. 2 : 3-Benzofluorenone had m. p. 152—153° (from ethanol), undepressed when admixed with an authentic specimen<sup>5</sup> (Found: C, 88.4; H, 4.35. Calc. for  $C_{17}H_{10}O$ : C, 88.7; H, 4.4%).

2 : 3-Benzofluorenone.—A solution of 2 : 3-benzofluorenone (0.5 g.) in dry thiophen-free benzene (20 ml.) was reduced with lithium aluminium hydride (0.4 g.) in dry ether (10 ml.) (5 hr. on water-bath), and worked up as usual.<sup>6</sup> The product (0.4 g., 79%), crystallised from benzene, gave 2 : 3-benzofluorenone, m. p. 185°, undepressed on admixture with an authentic specimen.<sup>7</sup>

Alkali Fission of 2 : 3-Benzofluorenone-1-carboxylic Acid.—The fluorenone (0.6 g., 1 mol.) was heated with fused potassium hydroxide (0.9 g.) at 240—250° for 1 hr. The acid product (0.4 g., 63%), crystallised from ethanol-benzene, gave 3-*o*-carboxyphenyl-1-naphthoic acid, m. p. 266—267° (Found: C, 73.6; H, 4.2. Calc. for  $C_{18}H_{12}O_4$ : C, 74.0; H, 4.1%). Baumgarten and Olshausen<sup>8a</sup> and Potts<sup>8b</sup> give m. p.s 267—268° and 261—262°, respectively.

Methyl 1 : 2-Benzofluorenone-3-carboxylate.—3-*o*-Carboxyphenyl-1-naphthoic acid (0.2 g.) was dissolved in concentrated sulphuric acid (2 ml.), left overnight, then worked up as usual. The acid was directly esterified to give the methyl ester (0.17 g., 86%) in orange needles [from benzene-light petroleum (b. p. 40—60°)], m. p. 163—164°, depressed to 135—140° when admixed with methyl 2 : 3-benzofluorenone-1-carboxylate (Found: C, 79.6; H, 4.3; OMe, 10.6.  $C_{19}H_{12}O_3$  requires C, 79.15; H, 4.2; OMe, 10.8%).

1 : 2-Benzofluorenone.—1 : 2-Benzofluorenone-3-carboxylic acid was decarboxylated with copper-bronze and quinoline in the usual manner (74%). It crystallised from ethanol in orange needles, m. p. 132—133°, undepressed when admixed with an authentic specimen<sup>9</sup> (Found: C, 88.6; H, 4.45. Calc. for  $C_{17}H_{10}O$ : C, 88.7; H, 4.4%).

1 : 2-Benzofluorenone.—1 : 2-Benzofluorenone was reduced in 79% yield with lithium aluminium hydride in benzene-ether as previously mentioned for 2 : 3-benzofluorenone. It had m. p. 166—167° (from ethanol), not depressed when mixed with an authentic specimen.<sup>10</sup>

Alkali Fission of 2 : 3-Benzofluorenone.—The fluorenone (1 g.) was heated with potassium hydroxide (1.5 g.) at 205—210° for 1 hr. The product (0.9 g.), m. p. 140—155°, was fractionally crystallised from acetic acid, to give *o*-β-naphthylbenzoic acid (0.6 g.), m. p. 190°, undepressed on admixture with an authentic specimen.<sup>11</sup> Ring closure of this acid with concentrated sulphuric acid at room temperature gave 1 : 2-benzofluorenone.<sup>9</sup>

The acetic acid mother-liquor was diluted with water; the precipitated acid crystallised from ether-light petroleum (b. p. 40—60°) to give 3-phenyl-2-naphthoic acid (0.3 g.), m. p. 173—174°, depressed to 150—155° when admixed with its isomer (Found: C, 82.2; H, 5.0.  $C_{17}H_{12}O_2$  requires C, 82.2; H, 4.9%). Cyclisation of this acid with concentrated sulphuric acid at room temperature afforded 2 : 3-benzofluorenone<sup>5</sup> (m. p. and mixed m. p.).

<sup>5</sup> Koelsch, *J. Amer. Chem. Soc.*, 1933, **55**, 3885.

<sup>6</sup> Baddar, Fahim, and Fleifel, *J.*, 1955, 2199.

<sup>7</sup> Thiele and Wanscheidt, *Annalen*, 1910, **376**, 269.

<sup>8</sup> (a) Baumgarten and Olshausen, *Ber.*, 1931, **64**, 925; (b) Potts, *J.*, 1956, 1269.

<sup>9</sup> Graebe, *Ber.*, 1896, **29**, 826.

<sup>10</sup> Bamberger and Kranzfeld, *Ber.*, 1885, **18**, 1934.

<sup>11</sup> Graebe, *Annalen*, 1904, **335**, 129.

**3 : 4-Dihydro-3-phenyl-1-naphthoic Acid.**—This acid was obtained by refluxing the crude ester (I) (4 g.) with 20% (v/v) sulphuric acid (40 ml.) for 48 hr. It (2 g.) had m. p. 150—151° [from ether—light petroleum (b. p. 40—60°)] (Found: C, 81·3; H, 5·7.  $C_{17}H_{14}O_2$  requires C, 81·6; H, 5·6%).

**3-Phenyl-1-naphthoic Acid.**—The above dihydro-acid (1 g.) and sulphur (0·15 g.) were heated at 205—210° for 5 hr., then worked up as usual. The acid product (0·8 g., 81%) crystallised from toluene to give **3-phenyl-1-naphthoic acid**, m. p. 221—222° (Found: C, 81·7; H, 4·8.  $C_{17}H_{12}O_2$  requires C, 82·2; H, 4·9%).

**2-Phenylnaphthalene.**—**3-Phenyl-1-naphthoic acid** was decarboxylated in 97% yield with copper-bronze and quinoline in the usual manner. **2-Phenylnaphthalene** had m. p. 103—104° (from ethanol), not depressed when admixed with an authentic specimen.<sup>12</sup>

**Ethyl β-Phenyl-γ-p-tolylbutyrate.**—This ester had b. p. 190—192°/25 mm. (85% yield),  $n_D^{21.5}$  1·5410 (Found: C, 80·7; H, 7·9.  $C_{19}H_{22}O_2$  requires C, 80·8; H, 7·85%).

**3 : 4-Dihydro-7-methyl-3-phenylnaphthalene-1 : 2-dicarboxylic Anhydride.**—Ethyl β-phenyl-γ-p-tolylbutyrate was converted into ethyl β-ethoxycarbonyl-α-oxo-γ-phenyl-δ-p-tolylvalerate in the usual manner. This was heated with 80% (v/v) sulphuric acid at 45—50° for 2 hr. The product (96%) crystallised from benzene—light petroleum (b. p. 50—70°) to give **3 : 4-dihydro-7-methyl-3-phenylnaphthalene-1 : 2-dicarboxylic anhydride** in pale yellow needles, m. p. 141—142° (Found: C, 78·1; H, 5·15.  $C_{19}H_{14}O_3$  requires C, 78·6; H, 4·85%).

**7-Methyl-3-phenylnaphthalene-1 : 2-dicarboxylic Anhydride.**—Prepared by dehydrogenation of the above dihydro-anhydride with selenium at 205—210° for 8 hr., this anhydride (40%) crystallised from benzene in yellow needles, m. p. 241—242° (Found: C, 79·3; H, 4·3.  $C_{19}H_{12}O_3$  requires C, 79·15; H, 4·2%).

**2'-Methyl-2 : 3-benzofluorenone-1-carboxylic Acid.**—Obtained in 86% yield by the action of aluminium chloride on **7-methyl-3-phenylnaphthalene-1 : 2-dicarboxylic anhydride** as described above and crystallised from ethanol, **2'-methyl-2 : 3-benzofluorenone-1-carboxylic acid** formed orange needles, m. p. 253—254° (Found: C, 79·2; H, 4·3.  $C_{19}H_{12}O_3$  requires C, 79·15; H, 4·2%).

**2'-Methyl-2 : 3-benzofluorenone.**—The preceding acid was decarboxylated in 70% yield with quinoline and copper-bronze. **2'-Methyl-2 : 3-benzofluorenone** was obtained in orange-yellow needles (from ethanol), m. p. 155—156° (Found: C, 88·5; H, 4·8.  $C_{18}H_{12}O$  requires C, 88·5; H, 4·95%).

**Alkali Fission of 2'-Methyl-2 : 3-benzofluorenone-1-carboxylic Acid.**—The fluorenone was heated with fused potassium hydroxide at 205—210° for 10 min. **3-o-Carboxyphenyl-7-methyl-1-naphthoic acid** had m. p. 275—276° (from ethanol—benzene) (47% yield) (Found: C, 74·5; H, 4·5.  $C_{19}H_{14}O_4$  requires C, 74·45; H, 4·6%).

**3'-Methyl-1 : 2-benzofluorenone-3-carboxylic Acid.**—**3-o-Carboxyphenyl-7-methyl-1-naphthoic acid** was cyclised with concentrated sulphuric acid. **3'-Methyl-1 : 2-benzofluorenone-3-carboxylic acid** crystallised from ethanol in orange crystals, m. p. 320—321°, depressed to 240—250° when admixed with **2'-methyl-2 : 3-benzofluorenone-1-carboxylic acid** (Found: C, 79·0; H, 4·2%).

**3'-Methyl-1 : 2-benzofluorenone.**—This ketone was obtained (70%) by decarboxylation of the preceding acid and from ethanol formed orange-yellow crystals, m. p. 137—138° (Found: C, 88·5; H, 5·0%).

**3 : 4-Dihydro-7-methyl-3-phenyl-1-naphthoic Acid.**—The crude ethoxalyl derivative was refluxed with 20% (v/v) sulphuric acid as mentioned for the unsubstituted derivative. **3 : 4-Dihydro-7-methyl-3-phenyl-1-naphthoic acid**, crystallised from benzene—light petroleum (b. p. 40—60°), had m. p. 234—235° (Found: C, 81·7; H, 6·0.  $C_{18}H_{16}O_2$  requires C, 81·8; H, 6·1%).

**7-Methyl-3-phenyl-1-naphthoic Acid.**—This acid was obtained in 70% yield by dehydrogenating the dihydro-acid with selenium; it had m. p. 237—238° (from benzene), depressed to 220—225° on admixture with the dihydro-derivative (Found: C, 82·4; H, 5·4.  $C_{18}H_{14}O_2$  requires C, 82·4; H, 5·4%).

**2-Methyl-6-phenylnaphthalene.**—The above acid was decarboxylated in 80% yield by the usual method. **2-Methyl-6-phenylnaphthalene** had m. p. 110—111° [from light petroleum (b. p. 50—70°)] (Found: C, 93·5; H, 6·5.  $C_{17}H_{14}$  requires C, 93·5; H, 6·5%).