

**332. 2-2'-Naphthylbenzo[b]thiophen. Part I. Structure, Bromination, and Nitration.**

By ALEX. H. LAMBERTON and P. T. MCGRAIL.

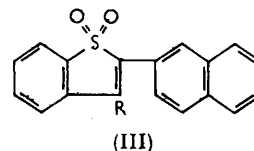
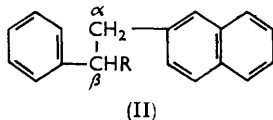
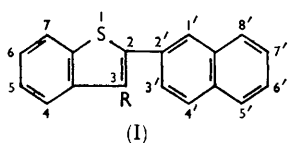
2-2'-Naphthylbenzo[b]thiophen can readily be isolated as a by-product of the purification of coal-tar naphthalene and is thus potentially available on a tonnage scale. Its structure (I; R = H) has been determined, and various derivatives, of which the most noteworthy, to date, are of the formulæ (I; R = Br, CO<sub>2</sub>H, NO<sub>2</sub>, or NH<sub>2</sub>), have been characterised.

JUST as benzene derived from coal contains thiophen, so crude naphthalene can contain some 5% by weight of benzo[b]thiophen ("thionaphthen"). Purification of crude naphthalene by heating it with fuller's earth has given, at the Rotherwood Laboratories of the United Coke and Chemicals Company, a residue from which 2-2'-naphthylbenzo[b]thiophen (I; R = H) was isolated by vacuum-distillation and subsequent crystallisation alternately from benzene and carbon tetrachloride.<sup>1</sup>

Elemental analyses suggested a simple linkage between the naphthalene and "thionaphthen" ring systems, though with some uncertainty in respect of the hydrogen content. The molecular weight, measured by mass spectroscopy, agreed with that required for

<sup>1</sup> Lamberton and McGrail, *Chem. and Ind.*, 1961, 986.

structure (I; R = H), and not with that of a dihydro-derivative; confirmation was provided by the absence of any indication of aliphatic protons from the nuclear magnetic resonance spectrum in pyridine. The molecular weight and lack of aliphatic hydrogen also excluded unlikely formulations containing five fused rings, which could not all be of aromatic character.



The position of linkage was determined by reduction with Raney nickel in ethanol to give 2-phenethylnaphthalene (II; R = H) in 80% yield. Cyclisation through sulphur must have been from the  $\alpha$ -carbon atom to the benzene ring, since the  $\beta$ -carbon atom has been shown (see next paragraph) to carry a replaceable hydrogen atom in the initial compound. It may be noted that restricted rotation around the 2,2'-bond would give rise to optical isomerism, and hence some of the compounds now reported may eventually be found to be racemates.

Bromination of 2-2'-naphthylbenzo[b]thiophen in carbon tetrachloride gave the 3-monobromo-derivative (I; R = Br). The structure of this compound was determined by preparation of the Grignard reagent, carboxylation to form the acid (I; R = CO<sub>2</sub>H), and removal of sulphur by means of Raney nickel in aqueous sodium hydroxide to yield the carboxylic acid (II; R = CO<sub>2</sub>H), identical with material synthesised from benzyl cyanide and 2-naphthaldehyde. This route, though satisfactory as a proof of structure, afforded the heterocyclic acid (I; R = CO<sub>2</sub>H) only in poor yield. We therefore sought an alternative method of preparation, and have found that the monobromo-derivative can be converted into the corresponding cyanide (I; R = CN) by treatment with cuprous cyanide in dimethylformamide. As the cyanide is effectively di-*ortho*-substituted, ordinary methods of hydrolysis converted it only into the amide (I; R = CO·NH<sub>2</sub>), but treatment with sodium hydroxide in glycerol at 190° led smoothly to the 3-carboxylic acid (I; R = CO<sub>2</sub>H) in an overall yield of 75% from 2-2'-naphthylbenzo[b]thiophen. Decarboxylation of this in quinoline (I; R = CO<sub>2</sub>H → H; 75% yield) showed that skeletal changes did not vitiate this proof of the constitution of 2-2'-naphthylbenzo[b]thiophen.

Nitration with one molecular proportion of nitric acid in acetic acid gave a mononitro-compound, in which substitution has been shown to be again in the 3-position (I; R = NO<sub>2</sub>). Reduction of the nitro-compound, catalytically or with tin and hydrochloric acid, gave the corresponding amine (I; R = NH<sub>2</sub>): this is stable and has also been characterised as its hydrochloride and as its benzoyl, toluene-*p*-sulphonyl, and methoxy-carbonyl derivatives (I; R = NH<sub>3</sub><sup>+</sup>Cl<sup>-</sup>, NHBz, NH·SO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>Me, and NH·CO<sub>2</sub>Me, respectively).

Structural proof of the position of nitration was first attempted by way of diazotisation of the monoamine, but this did not proceed smoothly. Under normal conditions of diazotisation a red precipitate appeared concurrently with the addition of nitrous acid and, though the filtrate would couple with alkaline  $\beta$ -naphthol, we have not yet been able to establish conditions suitable for preparative work. A link with the bromination series has, however, been made by working in the opposite direction: the 3-carboxamide has been converted, by a Hofmann type reaction, into the methyl carbamate, and this, in turn, into the amine (I; R = CO·NH<sub>2</sub> → NH·CO<sub>2</sub>Me → NH<sub>2</sub>).

In contrast with the valuable information obtained by reductive desulphurisation, degradative oxidation has not been successful. Mild oxidation with hydrogen peroxide in acetic acid has given good yields of the SS-dioxides (*e.g.*, III; R = H, Br, or NO<sub>2</sub>), though not (for R = Br or NO<sub>2</sub>) in an analytically pure condition. By analogy, these

sulphones should show the localisation of a double bond in the 2,3-position; but we have been unable to induce 2-2'-naphthylbenzo[*b*]thiophen SS-dioxide (III; R = H) to add hydrogen iodide, ethanol, or piperidine by methods<sup>2</sup> applicable to the dioxide of benzo[*b*]thiophen.

#### EXPERIMENTAL

*2-2'-Naphthylbenzo[*b*]thiophen, and its Reduction to 2-Phenethylnaphthalene.*—The initial material (I; R = H), plates of m. p. 209°, or 213—214° (corr.), has already been characterised.<sup>1</sup> It is slightly soluble in the common organic solvents, and moderately soluble in pyridine or dimethyl sulphoxide; pure samples lack colour, and show no fluorescence in ultraviolet light.

A solution of 2-2'-naphthylbenzo[*b*]thiophen (2 g.) in ethanol (250 ml.) was refluxed for 24 hr. with Raney nickel (25 g. of type<sup>3</sup> W-2). The hot solution was filtered to remove nickel, and the filtrate concentrated to ca. 50 ml.; on cooling, 2-phenethylnaphthalene (1.36 g.; m. p. 98°) separated. The compound was identified by m. p. (99° after recrystallisation from ethanol), analysis (Found: C, 93.0; H, 7.1. Calc. for C<sub>18</sub>H<sub>16</sub>: C, 93.1; H, 6.9%), and mixed m. p. with an authentic specimen.

*Synthesis, for Comparison, of 2-Phenethylnaphthalene.*—2-Cyanonaphthalene (6.4 g.; prepared from 2-naphthylamine) in toluene (60 ml.) was added dropwise in 1 hr. to a stirred solution of benzylmagnesium chloride (prepared from 1.3 g. of magnesium and 5.75 ml. of benzyl chloride) in ether (30 ml.). The ether was removed by distillation, and the residual solution in toluene heated to reflux for 6 hr.; then, after cooling, saturated ammonium chloride solution (20 ml.) and a little ice were added. The toluene layer was separated, and the aqueous layer extracted with ether; the combined ether and toluene extracts were washed with water, and the imine then taken up in 2N-sulphuric acid (2 × 20 ml.). Hydrolysis to the ketone was carried out by boiling the solution in dilute sulphuric acid for 2 hr. Extraction with ether-benzene, followed by washing with sodium hydrogen carbonate solution, drying (Na<sub>2</sub>SO<sub>4</sub>), and evaporation yielded benzyl 2-naphthyl ketone, m. p. 97° (lit.,<sup>4</sup> 99—100°). The crude ketone was converted into the semicarbazone (m. p. 204°, from ethanol; yield from 2-cyanonaphthalene ca. 20%) by treatment with semicarbazide hydrochloride in moist pyridine.

The semicarbazone (1.65 g.) was heated to 190° for 6 hr. with sodium (1.65 g.) dissolved in diethylene glycol (20 ml.). Water (300 ml.) was added and the precipitate of 2-phenethylnaphthalene (0.8 g.) collected; it had m. p. 99° after crystallisation from ethanol (charcoal).

2-Phenethylnaphthalene has been prepared by Cook and Hewett,<sup>5</sup> using naphthalene and phenylacetyl chloride as initial materials. Our method avoided the mixture of 1- and 2-naphthyl ketones produced by the Friedel-Crafts reaction but, if uncorroborated, could be criticised for its dependence on benzylmagnesium chloride. The identity of our m. p.s with those of Cook and Hewett (for the ketone, the semicarbazone, and the final hydrocarbon) shows that the addition of benzylmagnesium chloride to 2-cyanonaphthalene must have proceeded in the "normal" fashion.

*3-Bromo-2-2'-naphthylbenzo[*b*]thiophen.*—2-2'-Naphthylbenzo[*b*]thiophen (10 g.) was added portionwise, with stirring, to a solution of bromine (3.5 ml.) in carbon tetrachloride (250 ml.). Dissolution was complete after 1 hr. at room temperature; and, after a further 1 hr., the carbon tetrachloride was removed by distillation. The residue yielded 3-bromo-2-2'-naphthylbenzo[*b*]thiophen (12 g.) as needles of m. p. 95° (from ethanol) (analyses have been reported<sup>1</sup>).

*2-2'-Naphthylbenzo[*b*]thiophen-3-carboxylic Acid.*—(a) *Preparation by way of the Grignard reagent.* A solution of 3-bromo-2-2'-naphthylbenzo[*b*]thiophen (5 g.) in freshly distilled tetrahydrofuran (30 ml.) was added dropwise in 1 hr. to a stirred suspension of magnesium (0.35 g.) in ether (10 ml.), in which Grignard formation had been initiated by prior addition of a few drops of methyl iodide. The mixture was then refluxed for 1 hr., cooled, and poured, with stirring, on to solid carbon dioxide (30 g.) suspended in tetrahydrofuran (10 ml.). After evaporation of the carbon dioxide, the residue was heated to reflux for 15 min., treated with 5N-hydrochloric acid (ca. 50 ml.), and boiled to remove the volatile organic solvents. The yellow solid which separated was collected and warmed with 2N-sodium hydroxide; insoluble material was

<sup>2</sup> Challenger and Clapham, *J.*, 1949, 1615; Bordwell and McKellin, *J. Amer. Chem. Soc.*, 1950, **72**, 1985.

<sup>3</sup> Mozingo, *Org. Synth.*, Coll. Vol. III, p. 181.

<sup>4</sup> Cook, *J.*, 1931, 2015.

<sup>5</sup> Cook and Hewett, *J.*, 1934, 376.

removed, and acidification of the filtrate yielded 2-2'-naphthylbenzo[b]thiophen-3-carboxylic acid (1.2 g.), needles, m. p. 214° (from ethanol) (Found: C, 74.9; H, 4.0; S, 10.4. C<sub>19</sub>H<sub>12</sub>O<sub>2</sub>S requires C, 75.0; H, 4.0; S, 10.5%). For no obvious reason, even the small yield reported could not be achieved with regularity, and carboxylation with solid carbon dioxide in an autoclave<sup>6</sup> did not give improved results.

(b) *Preparation by way of the cyanide.*<sup>7</sup> A mixture of 3-bromo-2-2'-naphthylbenzo[b]thiophen (10 g.), cuprous cyanide (6 g.), and dimethylformamide (6 ml.) was heated under reflux for 3 hr. and poured, whilst hot, into a solution of ethylenediamine (10 ml.) in water (20 ml.). The resultant mixture was refluxed for 15 min. and extracted with hot toluene (3 × 100 ml.). The combined extracts were washed with 10% sodium cyanide solution and with water, dried (Na<sub>2</sub>SO<sub>4</sub>), and evaporated to yield 3-cyano-2-2'-naphthylbenzo[b]thiophen (8 g.; m. p. 123°) which formed needles, m. p. 130°, from toluene-ligroin (b. p. 40–60°) (Found: C, 79.7; H, 4.1. C<sub>19</sub>H<sub>11</sub>NS requires C, 80.0; H, 3.9%).

The crude cyanide (1 g.) was heated to 190° for 12 hr. with sodium hydroxide (1.2 g.) in glycerol (20 ml.). The solution was then cooled, poured into water (150 ml.), and filtered. On acidification with concentrated hydrochloric acid, the filtrate yielded 2-2'-naphthylbenzo[b]thiophen-3-carboxylic acid (1 g.; m. p. 210°), found, after one crystallisation from ethanol, to be identical (m. p. and mixed m. p.) with material prepared by route (a).

2-2'-Naphthylbenzo[b]thiophen-3-carboxamide.—(a) *By alkaline hydrolysis.* 3-Cyano-2-2'-naphthylbenzo[b]thiophen (1 g.) and potassium hydroxide (1.2 g.) in ethanol (10 ml.) were heated at the b. p. for 24 hr. On cooling, 2-2'-naphthylbenzo[b]thiophen-3-carboxamide separated as needles (1 g.), m. p. 242° unchanged on recrystallisation from ethanol (Found: C, 74.9; H, 4.1. C<sub>19</sub>H<sub>13</sub>NOS requires C, 75.3; H, 4.3%).

(b) *By acid hydrolysis.* The cyanide (1 g.) in 3 : 1 : 1 v/v acetic acid-sulphuric acid-water (16 ml.) was heated at the b. p. for 12 hr., and the product poured into water (ca. 150 ml.). The precipitate of amide crystallised from ethanol to yield material (0.9 g.) identical with that obtained by route (a).

*Decarboxylation of 2-2'-Naphthylbenzo[b]thiophen-3-carboxylic Acid.*—A solution of the acid (100 mg.) in quinoline (5 ml.) was boiled for 4 hr., cooled, and acidified with 2N-hydrochloric acid, to yield 2-2'-naphthylbenzo[b]thiophen (70 mg.), whose identity was established by m. p. (208° from ethanol) and mixed m. p.

*Reduction of 2-2'-Naphthylbenzo[b]thiophen-3-carboxylic Acid to β-2-Naphthyl-α-phenylpropionic Acid.*—A solution of the heterocyclic acid (1 g.) in 0.2N-sodium hydroxide (25 ml.) was refluxed for 15 min. with a suspension of Raney nickel (ca. 5 g. of type<sup>3</sup> W-2). After cooling and filtration of the mixture, the product was precipitated by hydrochloric acid and extracted with ether (2 × 100 ml.). The extract was washed with water, dried (Na<sub>2</sub>SO<sub>4</sub>), and evaporated to yield the propionic acid (II; R = CO<sub>2</sub>H), obtained in a pure condition (500 mg. of needles, m. p. 152°) by crystallisation, first from ethanol and then from ligroin (b. p. 40–60°) (Found: C, 82.8; H, 6.0. C<sub>19</sub>H<sub>16</sub>O<sub>2</sub> requires C, 82.6; H, 5.8%).

*Independent Synthesis of β-2-Naphthyl-α-phenylpropionic Acid.*<sup>8</sup>—Aqueous sodium hydroxide (40%; 2 ml.) was added dropwise, with stirring, to a mixture of 2-naphthaldehyde (5 g.) and benzyl cyanide (3.75 g.) in absolute ethanol (65 ml.), and, after cooling in ice, the resultant precipitate was removed. The filtrate was concentrated and cooled to yield 2-β-cyanostyryl-naphthalene (5.3 g.), needles, m. p. 121° (Found: C, 89.0; H, 5.2. C<sub>19</sub>H<sub>13</sub>N requires C, 89.4; H, 5.1%).

Benzyl alcohol (110 ml.) and potassium hydroxide (4 g.) were heated to distil off water and 10 ml. of the alcohol. 2-β-Cyanostyrylnaphthalene (5 g.) was added to the resultant solution of potassium benzyl oxide, and the whole refluxed 20 min., cooled to < 100°, treated with water (1 ml.), and refluxed again for 1 hr. The acid products were isolated, and benzoic acid was removed by steam-distillation to leave the propionic acid which, on crystallisation from ligroin (b. p. 40–60°), was identical (m. p., mixed m. p., and infrared spectrum) with the material prepared as above (yield, 2.2 g.) (Found: C, 82.5; H, 5.9%).

*Nitration of 2-2'-Naphthylbenzo[b]thiophen.*—A stirred suspension of finely powdered 2-2'-naphthylbenzo[b]thiophen (10 g.) in acetic acid (150 ml.) was heated to the b. p., and fuming nitric acid (2 ml.) in acetic acid (5 ml.) added dropwise in ½ hr. The resultant dark brown

<sup>6</sup> Cf. Haynes and Jones, *J.*, 1946, 503.

<sup>7</sup> Cf. Friedman and Shechter, *J. Org. Chem.*, 1961, 26, 2522.

<sup>8</sup> Cf. Avramoff and Sprinzak, *J. Amer. Chem. Soc.*, 1958, 80, 493.

solution was refluxed for 1 hr., then cooled to yield solid material (8 g.; m. p. 136°). Crystallisation from acetic acid and then from carbon tetrachloride gave 3-nitro-2-2'-naphthylbenzo[b]thiophen (5.5 g.) as a pale yellow powder of m. p. 145° (Found: C, 70.2; H, 3.8; M, 279. C<sub>18</sub>H<sub>11</sub>NO<sub>2</sub>S requires C, 70.8; H, 3.6; M, 305). The 3-nitro-compound crystallised from ethanol as yellow felted needles, and from ligroin as yellow cubes; both forms had m. p. 144°, and there was no m. p. depression on mixture with the microcrystalline powder from carbon tetrachloride. The use of more nitric acid gave dinitro-compounds, which have not yet been characterised.

*3-Amino-2-2'-naphthylbenzo[b]thiophen.*—(a) *By catalytic reduction.* 3-Nitro-2-2'-naphthylbenzo[b]thiophen (2 g.) in acetic acid (100 ml.) was reduced by hydrogen at room temperature and atmospheric pressure, in the presence of palladium-charcoal, some 500 ml. being taken up smoothly in 3 hr. The suspension was filtered after removal of most of the acetic acid by evaporation *in vacuo*, and the filtrate was made alkaline with aqueous sodium hydroxide to give a yellow precipitate. This yielded 3-amino-2-2'-naphthylbenzo[b]thiophen (1.6 g.) as light brown plates, m. p. 169° (from ethanol) (Found: C, 78.7; H, 4.9. C<sub>18</sub>H<sub>13</sub>NS requires C, 78.6; H, 4.8%).

(b) *By reduction with tin and hydrochloric acid.* Concentrated hydrochloric acid (20 ml.) was added portionwise to a mixture of 3-nitro-2-2'-naphthylbenzo[b]thiophen (1 g.), ethanol (10 ml.), and granulated tin (2 g.). The mixture was refluxed for 5 hr. and made alkaline, with cooling, by addition of 10N-sodium hydroxide. The amine was extracted with chloroform (4 × 50 ml.), and the extracts were washed repeatedly with water, solid impurities being discarded with the water layers. After drying (Na<sub>2</sub>SO<sub>4</sub>), the solvent was removed by evaporation under reduced pressure to yield a white residue, which rapidly became yellow in the air; 3-amino-2-2'-naphthylbenzo[b]thiophen (0.7 g.) was obtained, after crystallisation from ethanol, with a slightly higher m. p. (171°) than that of material prepared by route (a), but clearly identical by the tests of mixed m. p. and analysis (Found: C, 78.9; H, 5.1%). In spite of superficial atmospheric oxidation, the amine is reasonably stable on storage; after 6 months a specimen still had m. p. 169—170°.

*Derivatives of 3-Amino-2-2'-naphthylbenzo[b]thiophen.*—Hydrogen chloride in ether yielded the *hydrochloride*, needles, m. p. 228° (from ethanol) (Found: C, 69.8; H, 5.0; N, 4.7. C<sub>18</sub>H<sub>14</sub>CINS requires C, 69.4; H, 4.5; N, 4.5%). Benzoyl chloride, and toluene-*p*-sulphonyl chloride, each in pyridine, yielded, respectively, 3-*benzamido*-, felted needles, m. p. 213° (from ethanol) (Found: C, 79.2; H, 4.9; N, 3.6. C<sub>25</sub>H<sub>17</sub>NOS requires C, 79.2; H, 4.5; N, 3.7%), and 3-*toluene-p-sulphonamido-2-2'-naphthylbenzo[b]thiophen*, plates, m. p. 145° (from ethanol) (Found: C, 69.9; H, 4.6; N, 3.4. C<sub>25</sub>H<sub>19</sub>NO<sub>2</sub>S<sub>2</sub> requires C, 69.9; H, 4.3; N, 3.3%). Treatment with methyl chloroformate in a mixture of acetone and dilute sodium hydroxide, followed by ether-extraction and evaporation of the extract, yielded *methyl N-(2-2'-naphthylbenzo[b]thienyl)-carbamate* (I; R = NH·CO<sub>2</sub>Me), needles, m. p. 156° [from ligroin (b. p. 40—60°)] (Found: C, 72.3; H, 4.8. C<sub>20</sub>H<sub>15</sub>NO<sub>2</sub>S requires C, 72.1; H, 4.5%).

*Proof of the Position of Nitration: Preparation of 3-Amino-2-2'-naphthylbenzo[b]thiophen from the 3-Carboxyamide.*—Sodium (46 mg.) was added to a suspension of 2-2'-naphthylbenzo[b]thiophen-3-carboxyamide (300 mg.) in boiling methanol (150 ml.), and, when the amide had dissolved (2 hr.), the solution was cooled in ice. Bromine (160 mg.) in methanol (10 ml.) was then added, and the solution heated again for 24 hr. After cooling, the solution was made just acid with acetic acid, and evaporated *in vacuo* to yield a residue which was partitioned between water and ether. The ether layer was re-washed with water, dried (Na<sub>2</sub>SO<sub>4</sub>), and evaporated to give a gum which, on crystallisation successively from moist ethanol and ligroin (b. p. 80—120°) (charcoal), yielded needles of methyl *N-(2-2'-naphthylbenzo[b]thienyl)carbamate* (150 mg.), m. p. 156—158°, identical with material prepared directly from the amine as in the preceding paragraph (Found: C, 72.0; H, 4.8%).

A mixture of the carbamate (100 mg.), calcium oxide (500 mg.), and a few drops of water was heated at 300° for 1 hr., cooled, and extracted with ether (3 × 25 ml.). Treatment of the extract with hydrogen chloride gave 3-amino-2-2'-naphthylbenzo[b]thiophen hydrochloride (30 mg.), m. p. 228°. The identity of this material with the product previously prepared by nitration and reduction was confirmed by mixed m. p., and by further mixed m. p.s after conversion into the amine and the benzoyl derivative.

*Preparation of SS-Dioxides.*—(a) A mixture of 2-2'-naphthylbenzo[b]thiophen (10 g.), acetic acid (120 ml.), and 30% hydrogen peroxide (22.5 ml.) was refluxed for 30 min. and cooled,

to yield 2-2'-naphthylbenzo[*b*]thiophen SS-dioxide (9.5 g.), m. p. 188°. Crystallisation from ethanol gave yellow plates of m. p. 190° (analyses for material of m. p. 188° have been reported <sup>1</sup>).

(*b*) A mixture of 30% hydrogen peroxide (5 ml.) and acetic anhydride (5 ml.) was added dropwise to a solution of 3-bromo-2-2'-naphthylbenzo[*b*]thiophen (2 g.) in hot acetic acid (20 ml.), and the whole was refluxed for 1 hr. The solid which separated in cooling was crystallised repeatedly from ethanol, to yield 3-bromo-2-2'-naphthylbenzo[*b*]thiophen SS-dioxide, yellow needles, m. p. 169° (Found: C, 57.5; H, 3.5.  $C_{18}H_{11}BrO_2S$  requires C, 58.2; H, 3.0%). Passage of a solution of the product in chloroform down a column of alumina gave 1.1 g. of material of m. p. 170°, but did not improve the carbon analyses (Found: C, 57.2, 57.3; H, 3.0, 3.1%).

(*c*) Crude 3-nitro-2-2'-naphthylbenzo[*b*]thiophen SS-dioxide was prepared in the same manner as the bromo-compound (*b*, above); it formed orange needles, m. p. 161°, from ethanol (Found: C, 65.2, 65.7; H, 3.5, 3.8.  $C_{18}H_{11}NO_4S$  requires C, 64.1; H, 3.3%). Passage of a solution of the product in chloroform down a column of alumina gave 1 g. of material of m. p. 165°, but did not improve the analysis (Found: C, 66.2; H, 3.6%).

*Infrared Spectra.*—These, measured by an "Infracord" instrument, showed marked family likenesses in the range 1800—700  $cm^{-1}$ , whilst unresolved absorption at  $>1800 cm^{-1}$  did not permit useful assignments in this region. The aliphatic carboxyl group (in II; R = CO<sub>2</sub>H) shows clearly at 1700  $cm^{-1}$ ; but other assignments, though in some cases plausible, cannot be made with certainty owing to the predominating influence of the aromatic ring systems.

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THE UNIVERSITY, SHEFFIELD, 10.

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