Thiophen Derivatives of Biological Interest. Part VI. The Chemistry of* 2-tert.-*Butylthiophen.*

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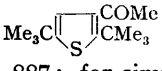
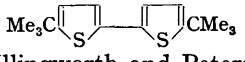
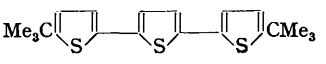
[Reprint Order No. 5070.]

The preparation and properties of 2-*tert.*-butylthiophen have been investigated, and a large number of its derivatives (some with potential pharmacological interest) has been prepared and orientated. One product of the stannic chloride-catalysed alkylation of thiophen with *tert.*-butyl chloride is shown by direct synthesis to be 5 : 5′-di-*tert.*-butyl-2 : 2′-dithienyl, and another is probably 2 : 5-di-(5-*tert.*-butyl-2-thienyl)thiophen.

The *tert.*-butylation of thiophen was first investigated by Kutz and Corson (*J. Amer. Chem. Soc.*, 1946, **68**, 1477) who used *iso*butylene or *tert.*-butyl alcohol as alkylating agent and montmorillonite clays as catalyst; the monoalkylated product thus obtained was later found to be a mixture of 2- and 3-*tert.*-butylthiophen (Appleby, Sartor, Lee, and Kapranos, *ibid.*, 1948, **70**, 1552). The use of *iso*butylene and 75% sulphuric acid has also been advocated (Caesar, *ibid.*, p. 3623); but a most convenient procedure has now been found in the use of *tert.*-butyl chloride and stannic chloride in carbon disulphide. Good yields were thus afforded of a monoalkyl product consisting of 75% of 2-*tert.*-butylthiophen and 25% of the 3-isomer; as earlier methods gave roughly equal quantities of the two isomers, the effect of the catalyst is obvious. This is further demonstrated by the fact that the dialkylated product isolated consisted almost entirely of 2 : 5-di-*tert.*-butylthiophen, also obtained from 2-*tert.*-butylthiophen and *tert.*-butyl chloride by the same method; it was characterised by its crystallised 3-acetyl derivative (I). By contrast, Caesar's method yielded a mixture of di-*tert.*-butylthiophens from which no pure constituent could be isolated, and which gave an impure ketone on acetylation. The 2 : 5-directing influence of stannic chloride is reminiscent of the *para*-orienting effect of ferric chloride in the *tert.*-butylation of toluene (Bialobrzeski, *Ber.*, 1897, **30**, 1773; Buu-Hoï and Cagniant, *Bull. Soc. chim.*, 1942, **9**, 887; for similar cases, see Illingworth and Peters, *J.*, 1951, 1602), a reaction which led to considerable *meta*-alkylation when a stronger catalyst such as aluminium chloride or sulphuric acid was used (Baur, *Ber.*, 1891, **24**, 2833). Another interesting feature of the *tert.*-butylation by means of stannic chloride was the formation of substantial yields of two higher-boiling by-products, one of which was identified as 5 : 5′-di-*tert.*-butyl-2 : 2′-dithienyl (II) by an Ullmann synthesis from 2-*tert.*-butyl-5-iodothiophen, the other being probably 2 : 5-di-(5-*tert.*-butyl-2-thienyl)thiophen (III), on the grounds of composition,

(I) 





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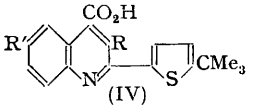

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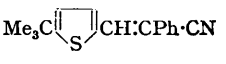

(V)

molecular weight, and physical properties. In these side-reactions, stannic chloride clearly acted as an oxidising agent. The easy formation of a terthienyl derivative is remarkable, in view of the difficulties generally encountered in the synthesis of such compounds.

2-*tert.*-Butylthiophen readily underwent stannic chloride-catalysed Friedel–Crafts acylations to give 5-acetyl, 5-propionyl, and 5-*n*-butyryl derivatives; the site of substitution was determined by sodium hypobromite oxidation of the first-named ketone to 5-*tert.*-butyl-2-thenoic acid (Messina and Brown, *J. Amer. Chem. Soc.*, 1952, **74**, 920); 2-*tert.*-butyl-5-methylthiophen, which these authors synthesised, was also obtained by a Kishner–Wolff–Huang-Minlon reduction of 5-*tert.*-butyl-2-thenaldehyde, prepared from 2-*tert.*-butylthiophen, *N*-methylformanilide, and phosphorus oxychloride (cf. King and

* Part V, Nam, Buu-Hoï, and Xuong, *J.*, 1954, 1690.

Nord, *J. Org. Chem.*, 1948, **13**, 635; Buu-Hoï, Hoán, and Lavit, *J.*, 1950, 2130). 2-*tert.*-Butyl-5-ethyl-, -5-*n*-propyl-, and -5-*n*-butyl-thiophen were similarly prepared. Nitration of 2-*tert.*-butylthiophen afforded the 5-nitro-derivative, and that of 2-acetyl-5-*tert.*-butylthiophen gave 5-acetyl-2-*tert.*-butyl-3-nitrothiophen, both of which had a pleasant odour.

Several derivatives of 2-*tert.*-butylthiophen of potential pharmacodynamic interest were prepared for biological testing. The thiosemicarbazones of 5-*tert.*-butyl-2-thenaldehyde and 2-acetyl-5-*tert.*-butylthiophen had important tuberculostatic activity *in vitro* (cf. Welsch, Buu-Hoï, *et al.*, *Compt. rend.*, 1951, **232**, 1608); condensation with chloroacetic acid gave the corresponding 4-oxo-Δ^2-thiazolin-2-ylhydrazones of very slight activity (cf. Buu-Hoï, Hoán, and Lavit, *J.*, 1952, 4590). 5-*tert.*-Butyl-2-thenoyl chloride gave, with diethylaminoethanol, diethylaminoethyl 5-*tert.*-butyl-2-thenoate, whose hydrochloride showed local anæsthetic properties. The atophan-like 2-(5-*tert.*-butyl-2-thienyl)cinchoninic acid and its 3-methyl and 6-bromo-derivatives [cf. (IV)] were prepared by Pfitzinger reactions from 2-acyl-5-*tert.*-butylthiophens (cf. Buu-Hoï *et al.*, *J. Org. Chem.*, 1953, **18**, 1209).

Condensation of 5-*tert.*-butyl-2-thenaldehyde with benzyl cyanide in the presence of sodium hydroxide yielded β-(5-*tert.*-butyl-2-thienyl)-α-phenylacrylonitrile (V). Hydrogenolysis with Raney nickel of 5-*tert.*-butyl-2-thenoic acid (cf. Papa, Schwenk, and Ginsberg, *J. Org. Chem.*, 1949, **14**, 723; Blicke and Sheets, *J. Amer. Chem. Soc.*, 1948, **70**, 3768) readily gave ω-*tert.*-butyl-*n*-valeric (6 : 6-dimethylheptanoic) acid; the extension of this convenient method to the preparation of further ω-*tert.*-butyl fatty acids of biological interest will be reported later.

Experimental

tert.-*Butylation of Thiophen.*—To an ice-cooled, well-stirred solution of thiophen (168 g.) and *tert.*-butyl chloride (222 g.) in anhydrous carbon disulphide (3000 c.c.), contained in a flask fitted with a calcium chloride tube, stannic chloride (627 g.) was added dropwise (1 hr.). The orange-coloured mixture was kept for 5 hr. at room temperature, and poured into ice-cooled dilute hydrochloric acid. The organic layer was washed with dilute aqueous sodium hydroxide, then with water, and dried ($CaCl_2$). The residue from evaporation of the solvent gave on distillation an 85—88% yield of alkylated products (240 g.). The lower-boiling portions were fractionated by means of a 30-plate Vigreux column, to give 2-*tert.*-butylthiophen (120 g.), b. p. 165°, n_D^{23} 1·5024, 3-*tert.*-butylthiophen (40 g.), b. p. 172°, n_D^{23} 1·5020, and a 15—20% yield of di-*tert.*-butylthiophens (40—50 g.), which consisted mainly of 2 : 5-*di*-tert.-*butylthiophen*, b. p. 219°, n_D^{24} 1·4964 (Found: C, 73·2; H, 10·2. $C_{12}H_{20}S$ requires C, 73·5; H, 10·2%). The higher-boiling portions yielded on vacuum-fractionation: (*a*) 5 : 5′-*di*-(tert.-*butyl*-2 : 2′-*dithienyl*) (15—20 g.), b. p. 200—202°/13 mm., which crystallised as shiny, colourless needles, m. p. 89°, from methanol (Found: C, 68·9; H, 7·9. $C_{16}H_{22}S_2$ requires C, 69·1; H, 7·9%); (*b*) 2 : 5-*di*-(5-tert.-*butyl*-2-*thienyl*)*thiophen*, crystallising as yellow needles (15—20 g.), b. p. 275—285°/13 mm., m. p. 116°, from methanol (Found: C, 66·5; H, 6·6. $C_{20}H_{24}S_3$ requires C, 66·7; H, 6·7%).

Synthesis of 5 : 5′-*Di*-tert.-*butyl*-2 : 2′-*dithienyl* (II).—To an ice-cooled solution of 2-*tert.*-butylthiophen (12 g.) in dry benzene (15 c.c.), iodine (30 g.) and yellow mercuric oxide (20 g.) were alternately added (20 min.); the mixture was kept for 1 hr. at room temperature, then filtered, and the solid washed with ether (25 c.c.). The ether–benzene filtrate was washed with aqueous sodium hydrogen sulphite and dried ($CaCl_2$), and the solvents were removed. The residue gave on vacuum fractionation 2-tert.-*butyl*-5-*iodothiophen* (21 g.), as a yellow liquid, b. p. 123°/13 mm., n_D^{22} 1·5832, darkening on exposure to light (Found: C, 36·0; H, 4·0. $C_8H_{11}SI$ requires C, 36·1; H, 4·1%). A mixture of this compound (20 g.) with copper powder (15 g.) was cautiously refluxed at 190—200° for 30 min., and the product vacuum-fractionated, giving in 80% yield 5 : 5′-di-*tert.*-butyl-2 : 2′-dithienyl, b. p. 200°/13 mm., identical with the by-product from the *tert.*-butylation of thiophen.

5-tert.-*Butyl*-2-*thenaldehyde.*—A mixture of 2-*tert.*-butylthiophen (17·5 g.), *N*-methylformanilide (22·5 g.), and phosphorus oxychloride (24 g.) was refluxed for 2 hr., then cooled; an aqueous solution of sodium acetate was added, and the product worked up in the usual way, giving in 80% yield 5-tert.-*butyl*-2-*thenaldehyde*, as a pale yellow oil, b. p. 246°, n_D^{22} 1·5495 (Found: C, 64·2; H, 7·2. $C_9H_{12}OS$ requires C, 64·3; H, 7·1%); it gave a *semicarbazone*, colourless leaflets, m. p. 249° (from methanol) (Found: C, 53·3; H, 6·5. $C_{10}H_{15}ON_3S$ requires C, 53·3; H, 6·7%), *thiosemicarbazone*, colourless needles, m. p. 197° (from ethanol) (Found: C, 49·5;

H, 6·3. $C_{10}H_{15}N_3S_2$ requires C, 49·8; H, 6·2%), a *4-oxo-Δ²-thiazolin-2-ylhydrazone*, colourless leaflets, m. p. 318° (from ethanol) (Found: C, 51·0; H, 5·2. $C_{12}H_{15}ON_3S_2$ requires C, 51·2; H, 5·3%), and an *oxime*, colourless prisms, m. p. 86° (from aqueous methanol) (Found: C, 59·0; H, 7·3. $C_9H_{13}ONS$ requires C, 59·0; H, 7·1%). A *tert.*-butyl-2-thenaldehyde of unknown constitution prepared by Hartough and Dickert (*J. Amer. Chem. Soc.*, 1949, **71**, 3922) was recorded as boiling at 155—162°/1 mm., and giving a semicarbazone, m. p. 212—214°; Messina and Brown (*loc. cit.*) obtained by a Sommelet reaction with *5-tert.*-butyl-2-thenoyl chloride an aldehyde whose semicarbazone had m. p. 215—216°.

2-tert.-*Butyl-5-methylthiophen.*—A solution of the foregoing aldehyde (8·5 g.) and 85% hydrazine hydrate (14 g.) in diethylene glycol (60 c.c.) was warmed for a few minutes, heated with potassium hydroxide (14 g.) with removal of water, then refluxed for 3 hr. After cooling, water was added, and the product taken up in benzene, washed with dilute hydrochloric acid, and purified by distillation. A 92% yield was obtained of a colourless oil, b. p. 183°, n_D^{23} 1·5031. Messina and Brown (*loc. cit.*), who prepared *2-tert.*-butyl-5-methylthiophen from 6 : 6-dimethylheptane-2 : 5-dione and phosphorus pentasulphide, gave b. p. 74—75°/19 mm.

β-(5-tert.-*Butyl-2-thienyl*)-α-*phenylacrylonitrile* (V).—To a warm solution of equimolecular amounts of *5-tert.*-butyl-2-thenaldehyde and benzyl cyanide in ethanol, a few drops of 40% aqueous sodium hydroxide were added; the solid *nitrile* obtained on cooling formed pale yellow needles, m. p. 100°, from ethanol, giving an orange colour with sulphuric acid (Found: C, 76·3; H, 6·2. $C_{17}H_{17}NS$ requires C, 76·4; H, 6·4%).

2-*Acetyl*-5-tert.-*butylthiophen.*—To an ice-cooled solution of *2-tert.*-butylthiophen (14 g.) and acetyl chloride (8 g.) in carbon disulphide (200 c.c.), stannic chloride was added dropwise with stirring; the mixture was kept for 1 hr. at room temperature, then poured on ice-cooled aqueous hydrochloric acid, the organic layer washed with a dilute solution of sodium hydroxide, then with water, the solvent removed, and the residue vacuum-distilled. The *ketone* (16 g., 88%) was a pale yellow oil, b. p. 255°, 146°/13 mm., n_D^{25} 1·5363 (Found: C, 65·8; H, 7·7. $C_{10}H_{14}OS$ requires C, 65·9; H, 7·7%), and gave a *semicarbazone*, colourless leaflets, m. p. 252° (Found: C, 55·1; H, 7·2. $C_{11}H_{17}ON_3S$ requires C, 55·2; H, 7·1%), a *thiosemicarbazone*, yellowish needles, m. p. 194° (Found: C, 51·5; H, 6·5. $C_{11}H_{17}N_3S_2$ requires C, 51·8; H, 6·7%), and a *4-oxo-Δ²-thiazolin-2-ylhydrazone*, colourless prisms, m. p. 315° (Found: C, 52·6; H, 5·7. $C_{13}H_{17}ON_3S_2$ requires C, 52·9; H, 5·8%), all from ethanol; the *2 : 4-dinitrophenylhydrazone* formed shiny, orange-red needles, m. p. 222°, from acetic acid (Found: N, 15·2. $C_{16}H_{18}O_4N_4S$ requires N, 15·5%); the *oxime* crystallised as colourless prisms, m. p. 118°, from methanol (Found: C, 60·9; H, 7·5. $C_{10}H_{15}ONS$ requires C, 60·9; H, 7·6%). Hartough and Conley (*J. Amer. Chem. Soc.*, 1947, **69**, 3097) obtained from unfractionated *tert.*-butylthiophen an acetyl derivative, b. p. 114°/4 mm., n_D^{20} 1·5343, giving a semicarbazone, m. p. 209—210°.

5-*Acetyl*-2-tert.-*butyl*-3-*nitrothiophen.*—To an ice-cooled solution of nitric acid (8 g.; *d* 1·51) in acetic anhydride (30 c.c.), a solution of the foregoing ketone (18·2 g.) in acetic anhydride (30 c.c.) was added dropwise with stirring; the mixture was kept at room temperature for 2 hr., then poured on ice, and the precipitate washed thoroughly with cold water and recrystallised twice from ligroin; the *nitro-ketone* formed yellow leaflets, m. p. 80° (Found: C, 52·8; H, 5·8. $C_{10}H_{13}O_3NS$ requires C, 52·9; H, 5·7%).

2-tert.-*Butyl-5-nitrothiophen.*—Similarly prepared from *2-tert.*-butylthiophen, this *nitro*-compound formed yellow leaflets, m. p. 74°, from ligroin (Found: C, 51·6; H, 6·2. $C_8H_{11}O_2NS$ requires C, 51·8; H, 5·9%); it could be reduced with tin and hydrochloric acid to the corresponding amine.

2-tert.-*Butyl-5-ethylthiophen.*—Prepared from 2-acetyl-5-*tert.*-butylthiophen and hydrazine hydrate in the usual way, this *thiophen* formed a colourless oil, b. p. 201°, n_D^{23} 1·5010 (Found: C, 71·4; H, 9·5. $C_{10}H_{16}S$ requires C, 71·4; H, 9·4%).

2-tert.-*Butyl-5-propionylthiophen.*—Prepared from *2-tert.*-butylthiophen (14 g.), propionyl chloride (9·5 g.), and stannic chloride (30 g.) in carbon disulphide (200 c.c.), this *propionyl* compound formed a pale yellow oil (16 g.), b. p. 269°, 152°/13 mm., n_D^{22} 1·5313 (Found: C, 67·2; H, 8·2. $C_{11}H_{16}OS$ requires C, 67·3; H, 8·2%). The *semicarbazone* formed colourless leaflets, m. p. 235° (Found: C, 56·6; H, 7·7. $C_{12}H_{19}ON_3S$ requires C, 56·9; H, 7·5%), the *thiosemicarbazone*, yellowish needles, m. p. 187° (Found: C, 53·3; H, 7·0. $C_{12}H_{19}N_3S_2$ requires C, 53·5; H, 7·1%), and the *4-keto-Δ²-thiazolin-2-ylhydrazone*, colourless prisms, m. p. 309° (Found: C, 54·0; H, 6·2. $C_{14}H_{19}ON_3S_2$ requires C, 54·4; H, 6·1%), all from ethanol; the *oxime* formed colourless needles, m. p. 116° (Found: N, 6·5. $C_{11}H_{17}ONS$ requires N, 6·6%).

2-tert.-*Butyl*-5-n-*propylthiophen*, formed by reduction, was a colourless oil, b. p. 222°, n_D^{22} 1·4984 (Found: C, 72·4; H, 10·0. $C_{11}H_{18}S$ requires C, 72·5; H, 9·9%); a by-product was

the *azine* of 2-*tert.*-butyl-5-propionylthiophen, b. p. 255°/13 mm., crystallising from methanol as yellow needles, m. p. 121° (Found : N, 7·0. $C_{22}H_{32}N_2S_2$ requires N, 7·2%).

5-tert.-*Butyl*-2-n-*butyrylthiophen*.—This *ketone* (16 g.), prepared from 2-*tert.*-butylthiophen (14 g.), *n*-butyryl chloride (11 g.), and stannic chloride (30 g.) in carbon disulphide (200 c.c.), was a pale yellow oil, b. p. 159°/13 mm., n_D^{22} 1·5293 (Found : C, 68·5; H, 8·8. $C_{12}H_{18}OS$ requires C, 68·6; H, 8·6%); its *semicarbazone* formed colourless prisms, m. p. 205°, from ethanol (Found : C, 58·2; H, 8·0. $C_{13}H_{21}ON_3S$ requires C, 58·4; H, 7·9%).

2-n-*Butyl*-5-tert.-*butylthiophen* was obtained in the usual way from the foregoing ketone and hydrazine hydrate as a colourless oil, b. p. 116°/13 mm., n_D^{23} 1·4958 (Found : C, 73·5; H, 10·5. $C_{12}H_{20}S$ requires C, 73·5; H, 10·2%), together with a by-product, the *azine* of 5-*tert.*-butyl-2-*n*-butyrylthiophen, b. p. 278°/13 mm., crystallising as long yellow needles, m. p. 119°, from methanol (Found : N, 6·7. $C_{24}H_{36}N_2S_2$ requires N, 6·7%).

3-*Acetyl*-2 : 5-*di*-tert.-*butylthiophen* (I).—This *ketone* (12 g.), obtained from 2 : 5-di-*tert.*-butylthiophen (13 g.), acetyl chloride (6 g.), and stannic chloride (20 g.) in carbon disulphide (150 c.c.), had b. p. 162°/13 mm., and crystallised as colourless prisms, m. p. 78°, from ligroin (Found : C, 70·3; H, 9·4. $C_{14}H_{22}OS$ requires C, 70·6; H, 9·2%); it did not give a semicarbazone, and could not be oxidised to the corresponding acid by sodium hypobromite, or caused to undergo Pfitzinger reactions. Hartough and Conley (*loc. cit.*) obtained from a mixture of di-*tert.*-butylthiophens a ketone, b. p. 105°/3 mm., m. p. 54—55°.

Diethylaminoethyl 5-tert.-*Butyl*-2-*thenoate*.—5-*tert.*-Butyl-2-thenoic acid, prepared in 90% yield from 2-acetyl-5-*tert.*-butylthiophen (19·1 g.) and aqueous sodium hypobromite (from 16 g. of sodium hydroxide and 8·2 c.c. of bromine), formed colourless needles, m. p. 126°, from water; Schick and Hartough (*J. Amer. Chem. Soc.*, 1948, **70**, 1645) gave m. p. 128—128·5°. The corresponding *chloride*, prepared by means of thionyl chloride, was a pale yellow oil, b. p. 120—122°/13 mm., n_D^{23} 1·5522 (Found : C, 53·0; H, 5·3. $C_9H_{11}OSCl$ requires C, 53·3; H, 5·3%); the *amide* formed colourless prisms, m. p. 148°, from methanol (Found : C, 58·8; H, 7·3. $C_9H_{13}ONS$ requires C, 59·0; H, 7·1%). *Diethylaminoethyl* 5-tert.-*butyl*-2-*thenoate*, prepared from the foregoing acid chloride (10 g.) and diethylaminoethanol (14 g.) in benzene, was a thick, pale yellow oil, b. p. 198°/13 mm., n_D^{22} 1·5143 (Found : C, 63·3; H, 8·7. $C_{15}H_{25}O_2NS$ requires C, 63·6; H, 8·8%), which gave a hydrochloride, crystallising as hygroscopic, colourless prisms, m. p. 118°, from methanol.

2-(5-tert.-*Butyl*-2-*thienyl*)*cinchoninic Acid* (IV; R = R′ = H).—A solution of equimolecular amounts of 2-acetyl-5-*tert.*-butylthiophen and isatin in ethanol was refluxed with potassium hydroxide (3 mol.) for 24 hr.; water was added, the neutral impurities were removed by ether-extraction, and the precipitate obtained on acidification with acetic acid was recrystallised from ethanol; the *cinchoninic acid* formed yellowish prisms, m. p. 185° (Found : C, 69·1; H, 5·3. $C_{18}H_{17}O_2NS$ requires C, 69·5; H, 5·5%); 2-(5-tert.-*butyl*-2-*thienyl*)*quinoline*, obtained by heating this acid above its m. p. and vacuum-distillation of the residue, formed colourless prisms, m. p. 65°, from methanol (Found : N, 5·2. $C_{17}H_{17}NS$ requires N, 5·2%), giving a picrate crystallising as deep yellow needles, m. p. 202°, from ethanol.

6-*Bromo*-2-(5-tert.-*butyl*-2-*thienyl*)*cinchoninic acid* (IV; R = H, R′ = Br), prepared with 5-bromoisatin, formed yellow needles, m. p. 237° (decomp.), from ethanol (Found : C, 55·1; H, 4·3. $C_{18}H_{16}O_2NSBr$ requires C, 55·4; H, 4·1%).

2-(5-tert.-*Butyl*-2-*thienyl*)-3-*methylcinchoninic acid* (IV; R = Me, R′ = H), prepared from isatin and 2-*tert.*-butyl-5-propionylthiophen, formed yellowish prisms, m. p. 267° (decomp.) (Found : C, 70·0; H, 6·1. $C_{19}H_{19}O_2NS$ requires C, 70·1; H, 5·8%).

Hydrogenolysis of 5-tert.-*Butyl*-2-*thenoic Acid*.—To a well-stirred solution of this acid (12 g.) in 10% aqueous sodium hydroxide (100 c.c.) heated at 90°, Raney nickel (100 g.) was added in small portions with a few drops of *iso*amyl alcohol to prevent excessive frothing; the mixture was then heated for 2 hr. and filtered hot, and the cooled filtrate acidified with hydrochloric acid; the product was taken up in ether and purified by vacuum-distillation; 6 : 6-*dimethylheptanoic acid*, thus obtained in 70% yield, was a pale yellow oil with an unpleasant rancid smell, b. p. 143°/17 mm., n_D^{22} 1·4375 (Found : C, 68·3; H, 11·5. $C_9H_{18}O_2$ requires C, 68·3; H, 11·4%); the corresponding *chloride* was a pale yellow oil, b. p. 90°/13 mm., n_D^{22} 1·4522 (Found : C, 61·5; H, 9·9. $C_9H_{17}OCl$ requires C, 61·2; H, 9·6%); the *amide* formed colourless needles, m. p. 106°, from benzene (Found : N, 9·0. $C_9H_{19}ON$ requires N, 8·9%); and NN′-*bis*-(6 : 6-*dimethylheptanoyl*)-p-*phenylenediamine*, prepared from the acid chloride with *p*-phenylenediamine in pyridine (cf. Buu-Hoï, *Bull. Soc. chim.*, 1945, **12**, 587), formed colourless needles, m. p. 224°, from methanol (Found : N, 7·0. $C_{34}H_{40}O_2N_2$ requires N, 7·2%).

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