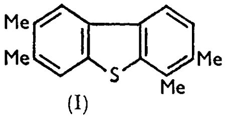
## 565. *The Constituents of High-boiling Petroleum Distillates. Part V.*[1] *Some Condensed Thiophen Derivatives in a Kuwait Oil.*

By W. Carruthers and A. G. Douglas.

1 : 2 : 6 : 7-, 1 : 3 : 6 : 7-, and 1 : 3 : 6 : 8-Tetramethyldibenzothiophen, 3-ethyl-6 : 8-dimethylnaphtho(1 : 2-*b*)thiophen, 9-thia-1 : 2-benzofluorene, and two unidentified alkyldibenzothiophens have been isolated from fractions of a Kuwait oil. The three named dibenzothiophens have been synthesised by Pschorr ring closure of the appropriately substituted 2-aminodiphenyl sulphides.

Very little is known about the sulphur-containing compounds in high-boiling petroleum fractions. Hoog and his colleagues investigated[2] a number of gas-oil fractions boiling in the range 250—350° and concluded that they probably contained considerable amounts of condensed thiophen derivatives, and Thompson, Coleman, Rall, and Smith[3] detected condensed thiophens in a Wasson (North American) crude oil by mass-spectrometry of chromatographic fractions. So far, however, only two compounds of this type have been isolated from petroleum. 1 : 8-Dimethyldibenzothiophen was found in a Middle East oil by one of us,[4] and Richter, Williams, and Meisel[5] isolated thionaphthen from a fraction of a North American oil. We have now obtained the compounds listed in the summary from distillates of a Kuwait oil boiling above 350°.



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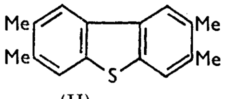

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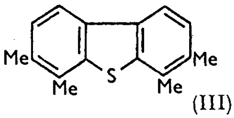

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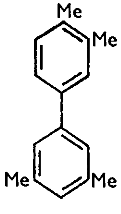

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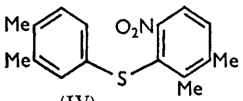

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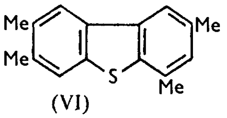

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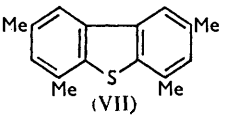

(VII)

The preparation of crystalline picrates from these distillates and the chromatographic separation of material recovered from the picrates into fractions eluted from alumina with light petroleum, benzene, and methanol were described in Part IV.[1] Further chromatography of the benzene and light petroleum eluates afforded a number of crystalline substances, several of which were identified as polycyclic aromatic hydrocarbons.[1] A number of others, however, were found to contain sulphur.

Three of these sulphur compounds were shown by their ultraviolet absorption spectra to be derivatives of dibenzothiophen, and their elementary analyses indicated the molecular formula $C_{16}H_{16}S$. One of them was converted into the known 3 : 4 : 3′ : 4′-tetramethyldiphenyl by desulphurisation with Raney nickel in boiling ethanol[6] and must therefore be represented by one of the three tetramethyldibenzothiophen structures (I), (II), or (III), each of which, of course, would afford 3 : 4 : 3′ : 4′-tetramethyldiphenyl on desulphurisation. It was identified as 1 : 2 : 6 : 7-tetramethyldibenzothiophen (I) by synthesis. 3 : 4-Dimethylthiophenol and 3-chloro-4-nitro-*o*-xylene in hot ethylene glycol solution in presence of sodium hydroxide afforded the expected nitrodiphenyl sulphide (IV) and hence by reduction of the nitro-group and Pschorr cyclisation of the amine the

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[1] Part IV, *J.*, 1957, 278.

[2] Hoog, Reman, and Smithuysen, Proc. Third World Petroleum Congress, 1951, Section IV, p. 282.

[3] Thompson, Coleman, Rall, and Smith, *Analyt. Chem.*, 1955, **27**, 175.

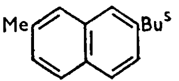
[4] Carruthers, *Nature*, 1955, **176**, 790.

[5] Richter, Williams, and Meisel, *J. Amer. Chem. Soc.*, 1956, **78**, 2166.

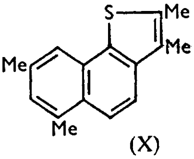
[6] Blicke and Sheets, *ibid.*, 1948, **70**, 3768; 1949, **71**, 4010.

dibenzothiophen (I). The alternative cyclisation product, 1 : 2 : 5 : 6-tetramethyldibenzothiophen, was also formed in small amount. The two products were easily distinguishable since only compound (I) affords 3 : 4 : 3′ : 4′-tetramethyldiphenyl on desulphurisation. 2 : 3 : 6 : 7-Tetramethyldibenzothiophen (II) was also prepared by reaction of 2 : 2′-dihydroxy-4 : 5 : 4′ : 5′-tetramethyldiphenyl and phosphorus pentasulphide. The yield was very poor, however, and a similar approach to the 1 : 2 : 7 : 8-isomer (III) from the corresponding dihydroxydiphenyl did not yield any of the dibenzothiophen.[7] In these experiments it was noted that, whereas nitration of 3-hydroxy-*o*-xylene affords the 4-nitro-compound,[8] which can be converted into its methyl ether with diazomethane, direct nitration of 3-methoxy-*o*-xylene yields an isomer, presumably the 6-nitro-derivative.

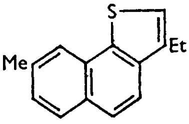
A second dibenzothiophen, $C_{16}H_{16}S$, isolated from Kuwait oil, on desulphurisation with Raney nickel likewise afforded a diphenyl derivative. There was insufficient of this material for analysis but its relative retention volume on vapour-phase chromatography under the conditions described by Beavan, James, and Johnson [9] strongly suggested that it also was a tetramethyldiphenyl. Comparison of the infrared spectrum with those of 3 : 4 : 3′ : 4′- and 3 : 5 : 3′ : 5′-tetramethyldiphenyl suggested that the desulphurisation product might be the unknown 3 : 4 : 3′ : 5′-isomer (V), and this was confirmed by the synthesis of this compound, by Dr. D. A. M. Watkins, from 3 : 4-dimethylphenylmagnesium bromide and 3 : 5-dimethyl*cyclo*hexanone. Two possibilities thus remained for the structure of the dibenzothiophen, and it was identified as the 1 : 3 : 6 : 7-tetramethyl derivative (VI) by comparison with the product of cyclisation of 2-amino-4 : 5 : 2′ : 4′-tetramethyldiphenyl sulphide. An attempt to prepare the other possible compound, 1 : 3 : 7 : 8-tetramethyldibenzothiophen, from 2-amino-2′ : 4′ : 5 : 6-tetramethyldiphenyl sulphide met with unexpected difficulties, and a mixture of products was obtained. The reaction is being further investigated.



(VIII)



(X)



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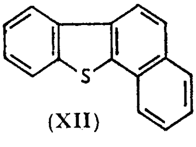

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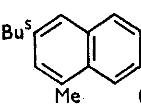

(IX)

$Bu^S{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2{\cdot}CHMe{\cdot}CO_2H$

(XIII)

By a similar method, a third dibenzothiophen was identified as the 1 : 3 : 6 : 8-isomer (VII). This structure followed unequivocally from the desulphurisation of the compound to 3 : 5 : 3′ : 5′-tetramethyldiphenyl, and was confirmed by synthesis from 2 : 4-dimethylthiophenol and 4-chloro-5-nitro-*m*-xylene. We are indebted to Dr. E. A. Johnson of the National Institute for Medical Research, who identified the desulphurisation product from an examination of its infrared spectrum, and by comparison with the authentic hydrocarbon which he has recently synthesised.

Two other pure crystalline alkyldibenzothiophens were isolated from picrate-forming fractions of the Kuwait oil, but because of scarcity of material we have not yet been able to identify them completely. One (m. p. 84—86°) appears to be a tri- or tetra-methyl derivative or its equivalent, and the other (m. p. 196°) a tetramethyl derivative or its equivalent.

Another compound isolated from the Kuwait oil through its crystalline picrate also had the molecular formula $C_{16}H_{16}S$ but its ultraviolet spectrum showed that it was a derivative of naphtho[1 : 2-*b*]thiophen.[10] In agreement, desulphurisation with Raney nickel afforded

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[7] Cf. Gilman and Jacoby, *J. Org. Chem.*, 1938, **3**, 109; Turner and Armarego, *J.*, 1956, 1665.

[8] Holler, Huggett, and Rathmann, *J. Amer. Chem. Soc.*, 1950, **72**, 2034.

[9] Beavan, James, and Johnson, *Nature*, 1957, **179**, 490.

[10] Carruthers and Crowder, *J.*, 1957, 1932.

a naphthalene hydrocarbon $C_{16}H_{20}$ and it appeared probable from the ultraviolet absorption spectrum of this compound that the naphthalene nucleus was trisubstituted.[11] This was supported by the infrared spectrum, which suggested, further, that the substituents occupied the 1-, 3-, and 6-positions: we are very much indebted to Dr. G. Eglinton, of the University of Glasgow, for this information. The mass spectrum of the hydrocarbon, kindly determined for us by Dr. A. Quayle of Thornton Research Centre, Shell Research Ltd., showed a strong peak at mass number 183 and two weaker peaks at mass numbers 197 and 169, and afforded good evidence for the presence of a *sec.*-butyl group in the molecule. Two structures (VIII) and (IX) thus appeared likely for the desulphurisation product, bearing in mind that the *sec.*-butyl group, which must have originated in the thiophen ring of the sulphur compound, occupies a β-position in the nucleus. It was identified as 6-*sec.*-butyl-1 : 3-dimethylnaphthalene (VIII) by synthesis. Friedel–Crafts condensation of *sec.*-butylbenzene and methylsuccinic anhydride in nitrobenzene solution afforded a keto-acid regarded, by analogy,[12] as the α-methyl isomer (XIII), which was converted into the desired naphthalene by standard reactions. It follows that the sulphur compound itself must have one of the two structures (X) and (XI), and of these the latter is favoured by the results of a Kuhn–Roth estimation which indicates the presence of only three *C*-methyl groups.

In connexion with the infrared studies of naphthalene hydrocarbons which led to the recognition of the substitution pattern of the desulphurisation product and will be reported separately by Dr. Eglinton, 1 : 3-dimethyl-6-*n*-propylnaphthalene was required, and a description of its syntheses from *n*-propylbenzene and methylsuccinic anhydride is included in the Experimental section.

In separate experiments with a higher-boiling fraction of Kuwait oil than we have previously employed, chromatography and crystallisation of molecular complexes has led to the isolation of a number of crystalline substances. One of these has been identified as 9-thia-1 : 2-benzofluorene (XII) by ultraviolet absorption measurements, preparation of derivatives, and direct comparison with an authentic specimen.

The isolation of the above crystalline compounds has been facilitated to some extent by the exceptionally high sulphur content of the Kuwait oil used in the investigation. The original distillate fractions[13] of the crude oil with equivalent boiling points in the range 350—390° contained 2—3% of sulphur,[14] and many of the oily fractions obtained by crystallisation of picrates and by chromatography appeared from their ultraviolet absorption spectra to contain high proportions of sulphur compounds; derivatives of dibenzothiophen were particularly abundant. Many other crude oils have a much smaller sulphur content than the Kuwait oil and, although they may contain derivatives of condensed thiophen systems, these are probably present in smaller amounts than in the Kuwait oil and their isolation may, therefore, be correspondingly more difficult.

## EXPERIMENTAL

Ultraviolet absorption spectra were measured in 95% ethanol with a " Unicam " spectrophotometer. M. p.s were determined on a Kofler hot stage.

*Isolations from Kuwait Oil Fractions.*—The particular distillates used as starting materials in this investigation were prepared in the Chemical Engineering Laboratories of the University of Birmingham under the direction of Professor F. Morton. We are very much indebted to Professor Morton for supplying us with these fractions. Their further separation by crystallisation of picrates and chromatography on alumina is described in Parts III[13] and IV.[1]

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[11] Heilbronner, Frohlicher, and Plattner, *Helv. Chim. Acta*, 1949, **32**, 2479; Mosby, *J. Amer. Chem. Soc.*, 1953, **75**, 2348; Dannenberg and Dannenberg-von Dressler, *Chem. Ber.*, 1956, **89**, 1326.

[12] Berliner, " Organic Reactions," John Wiley & Sons, Inc., New York, 1949, Vol. V, p. 229; see also Carruthers and Gray, *J.*, 1958, 1280.

[13] Carruthers, *J.*, 1956, 603.

[14] Carruthers, Cerego, King, Morton, Pell, and Sagarra, Proc. Fourth World Petroleum Congress, Rome, 1955, Section V/A, paper 7.

(a) 1 : 2 : 6 : 7-*Tetramethyldibenzothiophen.* The benzene eluate (22·3 g.) obtained from the picrate of the fraction, b. p. 382·5—385°, as described in Part IV, was rechromatographed on alumina, with light petroleum (b. p. 60—80°) containing increasing proportions of benzene as eluant. Some of the fractions obtained gave crystals at −10°. Further chromatography of these and crystallisation from ethanol–benzene afforded the *dibenzothiophen* as plates, m. p. 188—189° alone or mixed with a specimen synthesised as described below (Found: C, 80·2; H, 6·6; S, 12·8. $C_{16}H_{16}S$ requires C, 80·0; H, 6·7; S, 13·3%), $\lambda_{max.}$ 236, 241, 260, 270 (infl. 283), 294, 312, 324, 352 mμ [log ε 4·72, 4·73, 4·26, 4·30 (3·96), 4·11, 3·44, 3·35, 1·92]. The *sulphone* prepared with hydrogen peroxide in acetic acid formed prisms (in benzene), m. p. 308—309° (Found: C, 70·3; H, 5·7. $C_{16}H_{16}O_2S$ requires C, 70·6; H, 5·9%), $\lambda_{max.}$ 235, 242, 250 (infl. 276), 287, 299, 335 mμ [log ε 4·38, 4·61, 4·73 (4·08), 4·19, 4·17, 3·56]. The s-*trinitrobenzene complex* gave yellow needles, m. p. and mixed m. p. (cf. below) 184—185° (from benzene) (Found: C, 58·4; H, 4·1. $C_{16}H_{16}S,C_6H_3O_6N_3$ requires C, 58·3; H, 4·2%).

The dibenzothiophen (90 mg.) was boiled with W-5 Raney nickel [15] (2 g.) in ethanol for 12 hr., and the crude product converted into the *s*-trinitrobenzene complex. The orange prisms were separated mechanically from the mixture, and by decomposition on alumina afforded 3 : 4 : 3′ : 4′-tetramethyldiphenyl, m. p. and mixed m. p. 73—75°, $\lambda_{max.}$ 256 mμ (log ε 4·37).

(b) 1 : 3 : 6 : 7-*Tetramethyldibenzothiophen.* The light petroleum eluates of refractive index greater than 1·5000 described in Part IV were recombined and fractionally distilled under reduced pressure into 10 c.c. fractions. We thank Professor F. Morton, now of the Department of Chemical Engineering, Manchester College of Science and Technology, for having this distillation carried out, under his supervision, in his former Department at Birmingham. The fractions obtained were converted into their picrates, which were crystallised. Several of these, from fractions of equivalent b. p. 378—383°, on decomposition afforded 1 : 3 : 6 : 7-*tetramethyldibenzothiophen,* forming needles (from benzene–ethanol), m. p. 126—128° alone or mixed with a specimen synthesised as described below (Found: C, 80·2; H, 6·8. $C_{16}H_{16}S$ requires C, 80·0; H, 6·7%), $\lambda_{max.}$ 236, 241, 260, 268, 282, 293, 315, 330, 349 mμ (log ε 4·64, 4·64, 4·31, 4·30, 3·95, 4·13, 3·41, 3·42, 2·40).

Desulphurisation of this compound (25 mg.) with Raney nickel (0·6 g.) in boiling ethanol for 6 hr. afforded an oil (20 mg.), $\lambda_{max.}$ 257—258 mμ (log ε 4·23). The infrared spectrum of distilled material was identical with that of 3 : 4 : 3′ : 5′-tetramethyldiphenyl. On vapour-phase chromatography with Apiezon M grease as stationary phase at 201°, its retention volume relative to diphenyl [9] was 7·1. The synthetic compound had relative retention volume 6·8.

(c) 1 : 3 : 6 : 8-*Tetramethyldibenzothiophen.* Four other fractions, b. p. 364°, obtained by distillation of the light petroleum eluate, gave picrates which, after crystallisation and decomposition on alumina, afforded crystalline material. Purification of this by further chromatography yielded 1 : 3 : 6 : 8-*tetramethyldibenzothiophen* as plates, m. p. 139—141° alone or mixed with an authentic specimen (Found: C, 79·7; H, 6·8. $C_{16}H_{16}S$ requires C, 80·0; H, 6·7%), $\lambda_{max.}$ 235, 242, 258, 268, 279, 290, 320, 333 mμ (log ε 4·64, 4·64, 4·23, 4·04, 3·81, 4·05, 3·44, 3·56).

When this compound (90 mg.) was boiled with Raney nickel (1·5 g.) in ethanol for 5½ hr. an oil (75 mg.), b. p. 110°/0·4 mm. (air-bath), was obtained. It crystallised from methanol as plates, m. p. 43—45° alone or mixed with an authentic specimen of 3 : 5 : 3′ : 5′-tetramethyldiphenyl kindly provided by Dr. E. A. Johnson. It had $\lambda_{max.}$ 256 mμ (log ε 4·17). The infrared spectrum was superposible on that of the synthetic material and the retention volumes [9] relative to diphenyl determined by Dr. E. A. Johnson were 5·48 and 5·40 respectively.

(d) 3-*Ethyl*-6 : 8-*dimethylnaphtho*[1 : 2-b]*thiophen.* The light petroleum eluate ($n_D$ > 1·5000) (93 g.) obtained from the picrate of the fraction of b. p. 377·5—380° (see Part IV) was re-treated with picric acid, and the picrate crystallised from ethanol–benzene and decomposed with alkali. The recovered oil (9·9 g.) partly crystallised when its solution in light petroleum was cooled to −70°. Recrystallisation from benzene–ethanol and purification through the picrate then afforded the *naphthothiophen* as plates, m. p. 150—151° (about 400 mg.) (Found: C, 80·0; H, 6·45; S, 14·0; *C*-Me, 17·65. $C_{16}H_{16}S$ requires C, 80·0; H, 6·7; S, 13·3%), $\lambda_{max.}$ 251, 273 (infl. 290, 302, 312), 334, 350 mμ [log ε 4·44, 4·56, (3·96, 3·84, 3·50), 2·96 2·91]. The s-*trinitrobenzene complex* formed yellow needles (from benzene–ethanol), m. p. 211—213° (Found: N, 9·6. $C_{16}H_{16}S,C_6H_3O_6N_3$ requires N, 9·3%). The picrate gave red needles (from benzene), m. p. 208—209°.

The sulphur compound (100 mg.) and Raney nickel were boiled in ethanol for 6 hr. and the

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[15] Adkins and Billica, *J. Amer. Chem. Soc.*, 1948, **70**, 695.

hydrocarbon obtained was purified through its *s*-trinitrobenzene complex and distilled at 120°/0·2 mm. (air-bath) (Found: C, 90·55; H, 9·25. $C_{16}H_{20}$ requires C, 90·5; H, 9·5%). It had $\lambda_{max.}$ 231, 284, 319 mμ (log ε 4·80, 3·56, 2·28). The infrared spectrum was superposable on that of 6-*sec.*-butyl-1 : 3-dimethylnaphthalene (below). The s-*trinitrobenzene complex* crystallised from benzene–ethanol as yellow needles, m. p. 114—116°, not depressed on admixture with the derivative of 6-*sec.*-butyl-1 : 3-dimethylnaphthalene (Found: C, 62·0; H, 5·4. $C_{16}H_{20},C_6H_3O_6N_3$ requires C, 62·1; H, 5·5%). The 2 : 4 : 7-trinitrofluorenone complex had m. p. 104—107° but dissociated in ethanol. The picrate was unstable.

(e) 9-*Thia*-1 : 2-*benzofluorene*. The residue from the original distillation of the Kuwait oil on the Stedman column (see Part III[13]) was further distilled under reduced pressure on a laboratory scale in the Department of Chemical Engineering, Manchester College of Science and Technology, under the supervision of Dr. P. J. King, and a fraction of corrected b. p. 390—405° was collected. After reaction with maleic anhydride this fraction (630 g.) was treated with picric acid in the usual way[1] and the oil recovered (165 g.) from the crystalline picrate was chromatographed on alumina. Fractions were eluted with light petroleum (b. p. 60—80°), benzene, and methanol. The benzene eluate (41 g.) was reconverted into the picrate which was crystallised several times from benzene–ethanol, and the recovered oil was chromatographed on alumina. Elution with light petroleum containing increasing proportions of benzene afforded a number of crystalline fractions. One of these, after further purification by chromatography gave 9-thia-1 : 2-benzofluorene (20 mg.) as colourless plates, m. p. 186—188° (from benzene–ethanol) not depressed when mixed with a specimen kindly supplied by Professor G. M. Badger (Found: C, 81·9; H, 4·4. Calc. for $C_{16}H_{10}S$: C, 82·0; H, 4·3%), $\lambda_{max.}$ 244, 252, 266, 274, 290, 302, 315, 331 (infl. 340), 347 mμ [log ε 4·58, 4·64, 4·36, 4·54, 4·13, 4·15, 3·71, 3·41 (3·01), 3·45]. The sulphone formed pale yellow needles, m. p. 232—234° (lit., 236°), and its ultraviolet absorption spectrum was identical with that recorded by Badger and Christie.[16] The s-*trinitrobenzene complex* formed yellow needles (from benzene–ethanol), m. p. 174—176° (Found: C, 59·9; H, 3·0. $C_{16}H_{10}S,C_6H_3O_6N_3$ requires C, 59·1; H, 2·9%). The 2 : 4 : 7-trinitrofluorenone complex melted at 244—246°, not 234° as recorded by Badger and Christie.[16]

(f) *Unidentified dibenzothiophen derivatives.* The light petroleum eluate (219 g.) of the picrate-forming part of the Kuwait distillate of b. p. 357·5—360° described in Part IV[1] was fractionally distilled under reduced pressure, and the fractions obtained were converted into their picrates. Two of these, from fractions, b. p. 142°/0·4 mm., by fractional crystallisation from benzene–ethanol and decomposition on alumina afforded oils which partly crystallised. The crystals (200 mg.) were collected and further purified by crystallisation of the *s*-trinitrobenzene complex. The recovered *dibenzothiophen* then formed colourless plates, m. p. 84—86° (from ethanol) (Found: C, 79·9; H, 6·4; S, 14·4. $C_{15}H_{14}S$ requires C, 79·6; H, 6·2; S, 14·2%), $\lambda_{max.}$ 231, 242 (infl. 245), 257, 268, 278, 288, 312, 323 mμ [log ε 4·52, 4·56 (4·44), 4·03, 3·98, 3·79, 3.93, 3·26, 3·38]. The s-*trinitrobenzene complex* crystallised from ethanol in yellow needles, m. p. 177° (Found: C, 57·6; H, 4·4. $C_{15}H_{14}S,C_6H_3O_6N_3$ requires C, 57·4; H, 3·9%), and the *sulphone* formed needles (from benzene), m. p. 282—284° (Found: C, 69·9; H, 5·1. $C_{15}H_{14}O_2S$ requires C, 69·7; H, 5·5%), $\lambda_{max.}$ (infl. 275) 285, 295, 325—335 mμ [log ε (3·90) 3·97, 3·93, 3·52].

The benzene eluate of the picrate-forming part of the distillate fraction of b. p. 380—382·5° (see Part IV) was chromatographed on alumina. Elution with light petroleum afforded a number of crystalline fractions. These were collected and after further purification of the crude material (83 mg.) by crystallisation of the *s*-trinitrobenzene complex, the *dibenzothiophen* derivative was obtained as plates, m. p. 196° (Found: C, 80·0; H, 6·5. $C_{16}H_{16}S$ requires C, 80·0; H, 6·7%), $\lambda_{max.}$ 244 (infl. 260), 270, 282, 292, 311, 324 mμ [log ε 4·86, (4·30), 4·23, 3·98, 4·21, 3·50, 3·59]. The s-*trinitrobenzene complex* formed yellow needles (from ethanol–benzene), m. p. 207—209° (Found: C, 58·1; H, 4·0. $C_{16}H_{16}S,C_6H_3O_6N_3$ requires C, 58·3; H, 4·2%).

3 : 4-*Dimethylthiophenol.*—Zinc dust (34 g.) was added portionwise to a stirred ice-cold suspension of 3 : 4-dimethylbenzenesulphonyl chloride (20 g.) in 5N-sulphuric acid (200 c.c.). After 2 hr. at room temperature the mixture was boiled for 7 hr., and the thiol (11·5 g.) recovered by steam-distillation and distilled at 218°. Reaction with 1-chloro-2 : 4-dinitrobenzene in ethanol afforded the *dimethyldinitrodiphenyl sulphide* as yellow prisms, m. p. 139—140° (Found: C, 55·4; H, 4·0. $C_{14}H_{12}O_4N_2S$ requires C, 55·3; H, 4·0%).

2 : 3 : 3′ : 4′-*Tetramethyl*-6-*nitrodiphenyl Sulphide.*—A solution of 3-chloro-4-nitro-*o*-xylene

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[16] Badger and Christie, *J.*, 1956, 3438.

(12·8 g.) in ethylene glycol (70 c.c.) was added to 3 : 4-dimethylthiophenol (9·5 g.) and sodium hydroxide (2·8 g.) in ethylene glycol (200 c.c.), and the mixture boiled. After ½ hr. water was added and the product extracted with benzene. Chromatography on alumina in benzene furnished the yellow *sulphide*, m. p. 74—75° (from *cyclo*hexane) (Found: C, 66·9; H, 5·95. $C_{16}H_{17}O_2NS$ requires C, 66·9; H, 6·0%).

1 : 2 : 6 : 7-*Tetramethyldibenzothiophen*.—The foregoing nitro-compound (9·0 g.) was reduced with stannous chloride (30 g.) in boiling ethanol (80 c.c.) containing hydrochloric acid (45 c.c.) for 1 hr. The resulting amine (6·0 g., b. p. 210°/5 mm.) in 25% sulphuric acid (450 c.c.) was diazotised with sodium nitrite (3 g.) in water (30 c.c.), then copper powder (10 g.) was added. Next morning the mixture was heated on the water-bath for 6 hr., and extracted with benzene. The crude product, chromatographed on alumina, afforded fractions eluted with light petroleum (b. p. 40—60°) (yield 1 g.) and with benzene (1·4 g.). The latter was recrystallised from benzene–methanol and gave 1 : 2 : 6 : 7-*tetramethyldibenzothiophen*, m. p. 192—194° not depressed when mixed with the specimen isolated from the oil which afforded 3 : 4 : 3′ : 4′-tetramethyldiphenyl on desulphurisation (Found: C, 79·5; H, 7·4. $C_{16}H_{16}S$ requires C, 80·0; H, 6·7%). It had $\lambda_{max.}$ 236 (infl. 242, 260), 268, 292, 312, 325 mμ [log ε 4·76 (4·74, 4·23), 4·23, 4·18, 3·47, 3·49]. The *s*-trinitrobenzene complex had m. p. 178—182°, and the 2 : 4 : 7-*trinitrofluorenone complex* formed orange-red needles, m. p. 204—206° (from ethanol–benzene) (Found: C, 62·4; H, 3·6. $C_{16}H_{16}S,C_{13}H_5O_7N_3$ requires C, 62·7; H, 3·8%).

The light petroleum eluate was rechromatographed on alumina. Elution with light petroleum (b. p. 40—60°) afforded 2 : 3 : 3′ : 4′-*tetramethyldiphenyl sulphide*, m. p. 55—57° (from ethanol) (Found: C, 79·0; H, 7·6. $C_{16}H_{18}S$ requires C, 79·3; H, 7·5%), $\lambda_{max.}$ 252, 272—274 mμ (log ε 4·06, 3·77). Further elution with benzene–light petroleum (b. p. 40—60°) (1 : 10) furnished 1 : 2 : 5 : 6-*tetramethyldibenzothiophen*, m. p. 127—128° (Found: C, 80·2; H, 6·5. $C_{16}H_{16}S$ requires C, 80·0; H, 6·7%), $\lambda_{max.}$ 241, 260, 276, 286, 317, 331 mμ (log ε 4·73, 4·17, 4·02, 4·14, 3·42, 3·58). The *s-trinitrobenzene complex* formed orange yellow needles (from benzene–ethanol), m. p. 176—178° (Found: C, 58·0; H, 4·0. $C_{16}H_{16}S,C_6H_3O_6N_3$ requires C, 58·3; H, 4·2%), and the 2 : 4 : 7-*trinitrofluorenone complex* red needles, m. p. 211—213° (Found: C, 63·1; H, 3·3. $C_{16}H_{16}S,C_{13}H_5O_7N_3$ requires C, 62·7; H, 3·8%).

4-*Methoxy*-5-*nitro*-o-*xylene*.—Concentrated nitric acid (70 c.c.) was added dropwise in ½ hr. to a stirred ice-cold solution of 4-methoxy-*o*-xylene (67 g.) in glacial acetic acid (280 c.c.). After 1 hr. the dark solution was poured into water and extracted with ether. The extract was washed with aqueous sodium hydroxide and evaporated. The crude dark oil crystallised in methanol at −10°. Recrystallisation from *cyclo*hexane afforded the *nitro-compound* (12 g.) as yellow blades, m. p. 76—78° (Found: C 59·9; H, 6·2. $C_9H_{11}O_3N$ requires C, 59·9; H, 6·2%). Further 8 g. of pure material were recovered from the mother-liquors by distillation at 120—130°/2 mm. Hydrolysis of the methoxy-compound gave the nitrophenol,[18] m. p. and mixed m. p. 85—87°.

5-*Iodo*-4-*methoxy*-o-*xylene*.—The foregoing nitro-compound was reduced catalytically with Raney nickel in ethanol. The amine formed plates, m. p. 89—90° (lit.,[17] 91°). It (19·8 g.) in 10% sulphuric acid (180 c.c.) was diazotised at 0° with sodium nitrite (24 g.) in water (50 c.c.), and a solution of potassium iodide (48 g.) in water (50 c.c.) was added. After being heated for 1 hr. on the water-bath the mixture was extracted with ether. The *iodo-compound* (21 g.) distilled at 200°/30 mm. and, crystallised from *cyclo*hexane, had m. p. 57—58° (Found: C, 41·5; H, 4·3. $C_9H_{11}OI$ requires C, 41·4; H, 4·4%). Grewe [17] gives m. p. 37° and no analysis.

2 : 2′-*Dihydroxy*-4 : 5 : 4′ : 5′-*tetramethyldiphenyl*.—Copper bronze (20 g.) was added portionwise in ½ hr. to the preceding iodo-compound (21 g.) at 200—220°, and the temperature was then raised to 260°. After ½ hr. the cooled mass was extracted with acetone. The *dimethoxydiphenyl* had b. p. 160°/0·2 mm. and formed colourless crystals (7·5 g.), m. p. 83—84° (from methanol) (Found: C, 79·8; H, 7·9. $C_{18}H_{22}O_2$ requires C, 79·95; H, 8·2%). Demethylation was effected with hydriodic acid (60 c.c.) in acetic anhydride (30 c.c.) at the b. p. for 4 hr. The *dihydroxy-compound* (6·2 g.), b. p. 200°/0·2 mm., crystallised from benzene–*cyclo*hexane in needles, m. p. 152° (Found: C, 79·1; H, 7·3. $C_{16}H_{18}O_2$ requires C, 79·3; H, 7·5%).

2 : 3 : 6 : 7-*Tetramethyldibenzothiophen*.—A mixture of the foregoing dihydroxydiphenyl derivative (1·5 g.) and phosphorus pentasulphide (0·5 g.) was slowly heated to 300° under reduced pressure (water-pump). The yellow distillate in benzene was washed with sodium

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[17] Grewe, *Ber.*, 1938, **71**, 907.

[18] Diepolder, *Ber.*, 1909, **42**, 2916.

hydroxide, and the neutral gum (1·0 g.) chromatographed on alumina. Benzene–light petroleum (b. p. 60—80°) (1 : 10) eluted 2 : 3 : 6 : 7-*tetramethyldibenzothiophen* (40 mg.), forming rods (from benzene), m. p. 211—212° (Found: C, 80·2; H, 6·4. $C_{16}H_{16}S$ requires C, 80·0; H, 6·7%), $\lambda_{max.}$ 239 (infl. 250), 260, 269, 296 (infl. 307, 315), 326 mμ [log ε 4·94 (4·47), 4·26, 4·21, 4·32, (3·74, 3·55), 3·44]. The *sulphone*, prisms (from benzene), had m. p. 339—340° (Found: C, 70·7; H, 6·1. $C_{16}H_{16}O_2S$ requires C, 70·6; H, 5·9%), $\lambda_{max.}$ 251, 291, 303, 320, 335 mμ (log ε 4·86, 4·03, 4·04, 3·20).

3-*Methoxy*-4- *and* -6-*nitro*-o-*xylene*.—3-*Methoxy*-4-*nitro*-o-*xylene* was obtained from the nitrophenol [8] with diazomethane in ether–methanol as a pale yellow oil, b. p. 80—85°/0·6 mm. (air-bath) (Found: C, 59·4; H, 6·2. $C_9H_{11}O_3N$ requires C, 59·7; H, 6·1%), $\lambda_{max.}$ 270 mμ (log ε 3·68).

Nitration of 3-methoxy-*o*-xylene (7 g.) in acetic acid (30 c.c.) with concentrated nitric acid (7 c.c.) added dropwise at 0° in 1 hr. afforded only the previously unknown 6-*nitro-compound*. After chromatography on alumina in light petroleum (b. p. 60—80°) this formed yellow needles, m. p. 73—74° (from *cyclo*hexane) (Found: C, 59·8; H, 6·2. $C_9H_{11}O_3N$ requires C, 59·7; H, 6·1%), $\lambda_{max.}$ 295 mμ (log ε 3·68). Demethylation with hydriodic acid in acetic anhydride yielded the *nitrophenol*, m. p. 123—125° (Found: C, 57·6; H, 5·2. $C_8H_9O_3N$ requires C, 57·5; H, 5·4%). The sodium salt had $\lambda_{max.}$ 415 mμ (log ε 4·2). (cf. Holler, Huggett, and Rathmann [8]).

2-*Methoxy*-3 : 4-*dimethylaniline*.—This was obtained from the above 4-nitro-compound (20 g.) by hydrogenation with Raney nickel (10 g.) in ethanol for 4 hr., and distilled at 70—75°/0·5 mm. (air-bath) (Found: C, 71·9; H, 8·8. $C_9H_{13}ON$ requires C, 71·5; H, 8·7%). The *acetyl derivative* gave needles, m. p. 115—116°, from aqueous acetic acid (Found: C, 68·8; H, 7·8. $C_{11}H_{15}O_2N$ requires C, 68·4; H, 7·8%).

2 : 2′-*Dihydroxy*-3 : 4 : 3′ : 4′-*tetramethyldiphenyl*.—The foregoing amine (12·7 g.) in 10% sulphuric acid (120 c.c.) was diazotised with sodium nitrite (16 g.) in water (40 c.c.). Potassium iodide (32 g.) in water (40 c.c.) was added at 0°, and reaction completed at 100° for 1 hr. The iodo-compound (13·4 g.), a red oil, b. p. 140—170° (air-bath), was treated with copper bronze (13·4 g.) as described above. The product was distilled, and the *dimethoxydiphenyl* (4·1 g.) collected at 170—200°/0·4 mm. (air-bath). Crystallised from ethanol, it had m. p. 95—96° (Found: C, 79·6; H, 8·5. $C_{18}H_{22}O_2$ requires C, 80·0; H, 8·2%). Demethylation (of 4·9 g.) with hydriodic acid (50 c.c.) in acetic anhydride (25 c.c.) gave the 2 : 2′-*dihydroxy*-3 : 4 : 3′ : 4′-*tetramethyldiphenyl* (2·1 g.) as needles, m. p. 138—140° (from *cyclo*hexane) (Found: C, 79·7; H, 7·5. $C_{16}H_{18}O_2$ requires C, 79·3; H, 7·5%).

2 : 4 : 2′ : 4′-*Tetramethyl*-6-*nitrodiphenyl Sulphide*.—This compound was prepared from 4-chloro-5-nitro-*m*-xylene (2·8 g.), 2 : 4-dimethylthiophenol (2·0 g.), and sodium hydroxide (0·6 g.) in boiling ethanol (15 c.c.) in ¾ hr. After several crystallisations from ethanol–benzene the yellow *sulphide* had m. p. 132—133° (0·5 g.) (Found: C, 66·7; H, 5·7. $C_{16}H_{17}O_2NS$ requires C, 66·9; H, 6·0%).

1 : 3 : 6 : 8-*Tetramethyldibenzothiophen*.—The foregoing nitro-compound (0·59 g.) was reduced with stannous chloride (2·0 g.) and hydrochloric acid (3 c.c.) in boiling ethanol. The crude amine (0·35 g.) in 25% sulphuric acid (25 c.c.) was diazotised with sodium nitrite (0·2 g.) in water (2 c.c.), and copper powder (1 g.) was added. The mixture was boiled for 5 hr. and extracted with benzene. Chromatography on alumina in light petroleum (b. p. 60—80°) afforded 1 : 3 : 6 : 8-*tetramethyldibenzothiophen* as needles, m. p. 142—143° (Found: C, 79·9; H, 6·3. $C_{16}H_{16}S$ requires C, 80·0; H, 6·7%), $\lambda_{max.}$ 235, 242, 268, 279, 289, 320, 333 mμ (log ε 4·65, 4·62, 4·26, 4·00, 3·85, 4·13, 3·51, 3·63).

2 : 4 : 3′ : 4′-*Tetramethyl*-6′-*nitrodiphenyl Sulphide*.—A solution of 4-chloro-5-nitro-*o*-xylene (5·64 g.), 2 : 4-dimethylthiophenol (4·18 g.), and sodium hydroxide (1·25 g.) in ethylene glycol (30 c.c.) was boiled for 15 min. The cooled solution was poured into water, which was extracted with benzene, and the *sulphide* crystallised from light petroleum (b. p. 40—60°) as yellow prisms, m. p. 122—124° (3·97 g.). A further 2·3 g. of pure material were recovered from the mother-liquors by chromatography on alumina and elution with benzene (Found: C, 66·8; H, 5·5. $C_{16}H_{17}O_2NS$ requires C, 66·9; H, 6·0%).

1 : 3 : 6 : 7-*Tetramethyldibenzothiophen*.—The above nitro-sulphide (6·0 g.) in ethanol (140 c.c.) was boiled with stannous chloride (20 g.) and hydrochloric acid (30 c.c.) for 4 hr. The resulting crude amine (4·8 g.) in 25% sulphuric acid (300 ml.) was diazotised with sodium nitrite (3·0 g.) in water (30 c.c.). Copper powder (8·0 g.) was added and after 12 hr. at room temperature the solution was boiled for 2 hr. The product was extracted with benzene and

purified by chromatography on alumina, giving 1 : 3 : 6 : 7-*tetramethyldibenzothiophen* (440 mg.) as needles, m. p. 132·5—134·5° (Found: C, 79·8; H, 6·7%), $\lambda_{max.}$ 235, 261, 269 (infl. 284), 293, 318, 331 mμ [log ε 4·81, 4·21, 4·11 (3·89), 4·14, 3·40, 3·47]. The *sulphone* formed needles, m. p. 272—275° (from ethanol–benzene) (Found: C, 70·7; H, 5·8. $C_{16}H_{16}O_2S$ requires C, 70·6; H, 5·9%).

*Reaction of* sec.-*Butylbenzene with Methylsuccinic Anhydride.*—A solution of *sec.*-butylbenzene (23·8 g.) in nitrobenzene (100 c.c.) was added dropwise to a stirred ice-cold solution of methylsuccinic anhydride (18·4 g.) and aluminium chloride (45·2 g.) in nitrobenzene (200 c.c.). After 4 hr., ice and hydrochloric acid were added and nitrobenzene was removed in steam. The residue was treated with sodium carbonate solution, and the product (25 g.) obtained as an oil on acidification. Crystallisation from benzene–light petroleum (b. p. 60—80°) afforded γ-p-sec.-*butylphenyl-α-methyl-γ-oxobutyric acid* (6 g.) as needles, m. p. 108—109° (Found: C, 72·7; H, 8·2. $C_{15}H_{20}O_3$ requires C, 72·6; H, 8·1%). Oxidation of the acid with 30% nitric acid at 180° gave terephthalic acid (methyl terephthalate, m. p. and mixed m. p. 141—142°).

γ-p-sec.-*Butylphenyl-α-methylvaleric Acid.*—A solution of the methyl ester (prepared with diazomethane) of the preceding keto-acid (5 g.) in benzene (100 c.c.) was added dropwise to a stirred solution prepared from magnesium (0·72 g.) and methyl iodide (4·3 g.) in ether (50 c.c.) under nitrogen. The mixture was boiled for 3 hr., and the complex decomposed with dilute sulphuric acid. Extraction with sodium carbonate afforded 4-p-sec.-*butylphenyl-2-methylpentenoic acid* (2·5 g.), b. p. 130—140°/0·25 mm. (air-bath) (Found: C, 78·3; H, 8·95. $C_{16}H_{22}O_2$ requires C, 78·0; H, 9·0%). This was hydrogenated quantitatively with palladised charcoal in ethanol solution; the *valeric acid* had b. p. 140°/0·15 mm. (air-bath) (Found: C, 77·5; H, 9·8. $C_{16}H_{24}O_2$ requires C, 77·4; H 9·7%).

7-sec.-*Butyl*-1 : 2 : 3 : 4-*tetrahydro*-2 : 4-*dimethyl*-1-*oxonaphthalene.*—Stannic chloride (2·1 c.c.) in benzene (5 c.c.) was added to a cooled (ice-water) solution prepared from the valeric acid described above (2·0 g.) and phosphorus pentachloride (1·9 g.) in benzene. Next morning ice and hydrochloric acid were added and the product was extracted with benzene. The *ketone* (1·6 g.) was distilled at 120°/0·15 mm. (air-bath) (Found: C 83·5; H, 9·8. $C_{16}H_{22}O$ requires C, 83·4; H, 9·6%).

6-sec.-*Butyl*-1 : 3-*dimethylnaphthalene.*—The foregoing ketone (1·5 g.) was reduced with lithium aluminium hydride (1 g.) in ether, and the resulting alcohol (1·5 g.) heated with potassium hydrogen sulphate (0·4 g.) at 150—160° for 30 min. The dihydronaphthalene (1·1 g.) was distilled at 82—87°/0·1 mm., and dehydrogenated with palladised charcoal (0·7 g.) at 260° for 3 hr. in an atmosphere of carbon dioxide. The *naphthalene* was purified through its s-*trinitrobenzene complex* [needles, m. p. 118—119° (Found: C, 62·2; H, 5·7. $C_{16}H_{20},C_6H_3O_6N_3$ requires C, 62·1; H, 5·5%)] and obtained as an oil, b. p. 100°/0·1 mm. (air-bath) (Found: C, 90·6; H, 9·6. $C_{16}H_{20}$ requires C, 90·5; H, 9·5%), $\lambda_{max.}$ 231, 283, 318 mμ (log ε 5·07, 3·79, 2·44).

*Reaction of* n-*Propylbenzene and Methylsuccinic Anhydride.*—This reaction was carried out as described above, with *n*-propylbenzene (21 g.), methylsuccinic anhydride (20 g.), and aluminium chloride (49 g.) in nitrobenzene (300 c.c.). *α-Methyl-γ-oxo-γ*-p-n-*propylphenylbutyric acid* was obtained having m. p. 95—96° (from *cyclo*hexane) (Found: C, 72·2; H, 7·7. $C_{14}H_{18}O_3$ requires C, 71·8; H, 7·7%). The *methyl ester*, prepared from the acid with diazomethane, had b. p. 180°/20 mm. (Found: C, 72·8; H, 8·3. $C_{15}H_{20}O_3$ requires C, 72·6; H, 8·1%). Oxidation of the acid with 40% nitric acid at 180—190° gave terephthalic acid (methyl ester, m. p. and mixed m. p. 138—140°).

*α-Methyl-γ*-p-n-*propylphenylvaleric Acid.*—A solution prepared from magnesium (1 g.) and methyl iodide (6·2 g.) in ether (80 c.c.) was added slowly to a stirred solution in benzene (100 c.c.) of the methyl ester described above (7 g.), under nitrogen. After 2 hr. the complex was decomposed with dilute sulphuric acid, and the organic layer separated and extracted with sodium carbonate. The recovered *pentenoic acid* (4·3 g.) was distilled at 130°/0·25 mm. (Found: C, 77·7; H, 9·0. $C_{15}H_{20}O_2$ requires C, 77·6; H, 8·7%). Hydrogenation of this in ethanol solution with palladised charcoal afforded the *valeric acid*, b. p. 130°/0·08 mm. (air-bath) (Found: C, 77·1; H, 9·5. $C_{15}H_{22}O_2$ requires C, 76·9; H, 9·5%).

1 : 2 : 3 : 4-*Tetrahydro*-2 : 4-*dimethyl*-1-*oxo*-7-n-*propylnaphthalene.*—This (2·1 g.) was obtained, as described for the *sec.*-butyl compound, from the preceding valeric acid (3·5 g.), phosphorus pentachloride (3·4 g.), and stannic chloride (3·5 c.c.) in benzene. It had b. p. 110°/0·1 mm. (air-bath) (Found: C, 83·5; H, 9·5. $C_{15}H_{20}O$ requires C, 83·3; H, 9·3%).

1 : 3-*Dimethyl*-6-n-*propylnaphthalene.*—The foregoing ketone (1·5 g.) was reduced with

lithium aluminium hydride (1 g.) in ether (200 c.c.), and the alcohol (1·5 g.) dehydrated with potassium hydrogen sulphate (0·2 g.) at 150—160° for 20 min. 1 : 2-*Dihydro*-1 : 3-*dimethyl*-6-n-*propylnaphthalene* (0·95 g.) was obtained as an oil, b. p. 80°/0·1 mm. (air-bath) (Found: C, 89·9; H, 10·1. $C_{15}H_{20}$ requires C, 89·9; H, 10·1%). This material was heated with 30% palladised charcoal at 270° for 5 hr. in an atmosphere of carbon dioxide. The *naphthalene* was isolated through its *s*-trinitrobenzene complex and distilled at 100°/0·1 mm. (air-bath) (Found: C, 90·7; H, 9·3. $C_{15}H_{18}$ requires C, 90·8; H, 9·2%). It had $\lambda_{max.}$ 231, 284, 319 mμ (log ε 4·94, 3·72, 2·43). The s-*trinitrobenzene complex* formed yellow needles (from ethanol), m. p. 98° (Found: C, 61·4; H, 5·3. $C_{15}H_{18},C_6H_3O_6N_3$ requires C, 61·3; H, 5·2%). The 2 : 4 : 7-*trinitrofluorenone complex* gave red needles, m. p. 115—116° (Found: C, 65·25; H, 4·5. $C_{15}H_{18},C_{13}H_5O_7N_3$ requires C, 65·5; H, 4·5%).

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