# **890.** *Synthetic Applications of Activated Metal Catalysts. Part V.** *The Desulphurisation of Flavophen and of Tetraphenylthiophen.*

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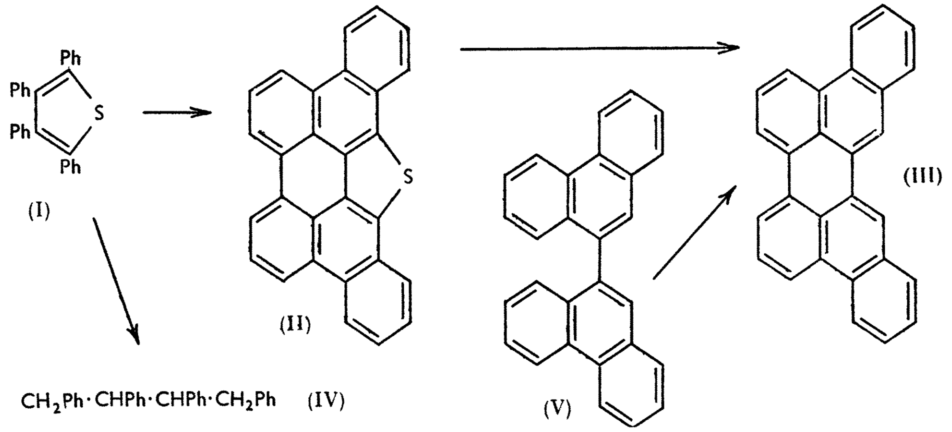
Desulphurisation of flavophen (II) with Raney nickel in boiling mesitylene yields 2 : 3-10 : 11-dibenzoperylene (III), identical with the product obtained from 9 : 9′-diphenanthryl with aluminium chloride. Desulphurisation of 2 : 3 : 4 : 5-tetraphenylthiophen gave 1 : 2 : 3 : 4-tetraphenylbutane and 1 : 2-diphenylethane.

THE desulphurisation of organosulphur compounds with Raney nickel has been widely used for degradative work, but the applications of the method in organic syntheses have been recognised only recently. The desulphurisation of thiophencarboxylic acids, for example, has now been developed as a useful method for the synthesis of a variety of fatty acids.[1, 2] It seemed likely that the reaction could also be applied in the preparation of aromatic hydrocarbons. The present paper reports the preparation of 2 : 3-10 : 11-dibenzoperylene (III) by the desulphurisation of flavophen (II), and the preparation of 1 : 2 : 3 : 4-tetraphenylbutane (IV) from 2 : 3 : 4 : 5-tetraphenylthiophen (I).



When 2 : 3 : 4 : 5-tetraphenylthiophen (I) is heated with aluminium chloride–sodium chloride it is cyclodehydrogenated to flavophen, for which structure (II) was suggested.[3] The sparing solubility of (II) precluded the use of the more usual solvents for the desulphurisation reaction, and a high-boiling solvent was therefore investigated. In pyridine some desulphurisation occurred, but 2 : 2′-dipyridyl was also obtained (this observation led to the development of a general method for the preparation of heterocyclic diaryls [4]). Some desulphurisation of flavophen was effected in xylene and in dimethylformamide but mesitylene was found to give the most satisfactory results. A further problem associated with the desulphurisation of flavophen was a tendency for the product to be partially hydrogenated, rendering final purification extremely difficult. This was avoided by the use of a Raney nickel catalyst containing less hydrogen than usual. A very high nickel : flavophen ratio was also required for complete desulphurisation, this

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* Part IV, *J.*, 1957, 3862.

[1] Badger, Rodda, and Sasse, *J.*, 1954, 4162.

[2] Sy, Buu-Hoï, and Dat Xuong, *Compt. rend.*, 1954, **239**, 1224, 1813; 1955, **240**, 442, 785; *Bull. Soc. chim. France*, 1955, 1583; Sy, *ibid.*, p. 1175.

[3] Steinkopf, *Annalen*, 1935, **519**, 297.

[4] Badger and Sasse, *J.*, 1956, 616.

being much larger than with dibenzothiophen.[5] The high temperature of the reaction (leading to loss of loosely bound hydrogen) may be a factor here; but steric hindrance must also be of importance. The desulphurisation of flavophen was then found to yield 2 : 3-10 : 11-dibenzoperylene (III), identical with the material obtained by heating 9 : 9'-diphenanthryl (V) with aluminium chloride.[6] The desulphurisation therefore satisfactorily establishes the structure of flavophen.

2 : 3 : 4 : 5-Tetraphenylthiophen (I) was also more difficult to desulphurise than dibenzothiophen; but 1 : 2 : 3 : 4-tetraphenylbutane (IV) was obtained with either butanol or xylene as solvent. In the latter some 1 : 2-diphenylethane was obtained and only part of the starting material could be accounted for, suggesting that carbon–carbon hydrogenolysis is important in this case.

## EXPERIMENTAL

*Flavophen.*—The following method was found to be better than that of Steinkopf.[3] Aluminium chloride (8 g.) and sodium chloride (2 g.) were heated at 130°. 2 : 3 : 4 : 5-Tetraphenylthiophen (2 g.; m. p. 182°) was added to the melt, which was maintained at 130°, with stirring by dry air, for 5 hr. After cooling, the mixture was decomposed with dilute hydrochloric acid, and washed with hot ethanol and benzene; the residue was sublimed at 300°/0·05 mm. and finally recrystallised from nitrobenzene or from ethyl benzoate. Flavophen (0·52 g.) was obtained as fine yellow needles, m. p. 378—380° (evacuated tube) (Found: C, 87·5; H, 3·7. Calc. for $C_{28}H_{14}S$: C, 87·9; H, 3·7%). Steinkopf[3] gives m. p. 391—392°. The ultraviolet absorption in benzene gave the following $\lambda_{max.}$ and log $\varepsilon$ values: 280 (4·55); 296 (4·52); 310 (4·44); 324 (4·35); 385 (4·45); 410 mμ (4·49).

2 : 3-10 : 11-*Dibenzoperylene.*—(i) In our hands Zinke and Ziegler's method [6] gave a product which could not be purified; but the following modified method was satisfactory. 9 : 9'-Diphenanthryl (1·2 g.; Bachmann [7]) was added to aluminium chloride (4·8 g.) and sodium chloride (1·2 g.) at 140° in an atmosphere of carbon dioxide. The melt was maintained at this temperature under carbon dioxide for 9 min. (see ref. 6). Longer times led to tars, as did an atmosphere of air. After cooling, the mixture was decomposed with dilute hydrochloric acid, and the product was sublimed at 300°/25 mm. and recrystallised from xylene. 2 : 3-10 : 11-Dibenzoperylene (0·112 g.) had 334—336° (evac. tube) after several crystallisations (lit.,[6] m. p. 315—318°, 329—332°, and 343—345°) (Found: C, 95·2; H, 4·75. Calc. for $C_{28}H_{16}$: C, 95·4; H, 4·6%). Its ultraviolet absorption in benzene was similar to that given by Schauenstein and Burgermeister,[6] the $\lambda_{max.}$ and log $\varepsilon$ values being 291 (4·44); 303 (4·56); 391 (4·18); 411 (4·46); and 439 mμ (4·50).

(ii) Desulphurisation was effected with Raney nickel prepared as described for W-7 catalyst [8] except that the digestion was carried out at 60—65°. Before use the catalyst was heated for ½ hr. at 100° and then washed repeatedly by decantation with methanol.

This Raney nickel (30 c.c.) was added through the condenser to flavophen (0·25 g.) in mesitylene (250 c.c.) at 100°. After the methanol had been distilled off, the mixture was refluxed for 5 hr., cooled to 100°, and filtered. The filtrate was concentrated to 50 c.c. *in vacuo*, and the product allowed to crystallise. 2 : 3-10 : 11-Dibenzoperylene (50 mg.) was obtained as light yellow-brown needles, m. p. 335—338° (evac. tube) not depressed by admixture with a specimen obtained as above. Its ultraviolet and infrared spectra were also identical with those given by the authentic material.

More of the product (35 mg.) was obtained by Soxhlet extraction of the catalyst with mesitylene and with xylene.

*Desulphurisation of* 2 : 3 : 4 : 5-*tetraphenylthiophen.*—(i) Desulphurisation could not be effected in methanol–benzene, but the following method was satisfactory. A mixture of tetraphenylthiophen (1 g.), W-7 Raney nickel [8] (15 c.c.), and butanol (100 c.c.) was refluxed for 5 hr. After separation of the nickel the solution was evaporated and the product dissolved in benzene.

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[5] Badger and Sasse, *J.*, 1957, 3862.

[6] Zinke and Ziegler, *Ber.*, 1941, **74**, 115; Schauenstein and Bürgermeister, *Ber.*, 1943, **76**, 205; Ioffe, quoted by Clar, " Aromatische Kohlenwasserstoffe," Springer, 1952, p. 310.

[7] Bachmann, *J. Amer. Chem. Soc.*, 1934, **56**, 1363.

[8] Billica and Adkins, *Org. Synth.*, 1949, **29**, 24.

Addition of a little light petroleum precipitated some tetraphenylthiophen (0·1 g.). Chromatography of the resulting product, in light petroleum, and recrystallisation from light petroleum (b. p. 40—60°) gave 1 : 2 : 3 : 4-tetraphenylbutane (0·05 g.) as needles, m. p. 180° (Found: C, 93·05; H, 7·3. Calc. for $C_{28}H_{26}$: C, 92·8; H, 7·2%). Lit., m. p. 179—180°.

(ii) A mixture of tetraphenylthiophen (3 g.), W-7 Raney nickel (50 g., washed with methanol), and xylene (100 c.c.) was heated to remove water and methanol (3 hr.) and then refluxed for 7½ hr. The catalyst was washed with boiling xylene four times and the combined filtrates were evaporated. The product was chromatographed in light petroleum, followed by elution with light petroleum and finally with benzene. Evaporation of the first fractions gave a liquid which was twice distilled (0·07 g.; b. p. 67°/0·05 mm.), recrystallised from light petroleum (b. p. <40°), and sublimed (at 50°/0·01 mm.) to give prisms, m. p. 51·5° not depressed by admixture with an authentic specimen of 1 : 2-diphenylethane (Found: C, 92·4; H, 7·7. Calc. for $C_{14}H_{14}$: C, 92·3; H, 7·7%). Its infrared spectrum was also identical with that given by diphenylethane. The middle fractions of the chromatograph gave 1 : 2 : 3 : 4-tetraphenylbutane (0·9 g.) identical with the material described above; and the final fractions yielded traces of a fluorescent substance which could not be identified.

Dissolution of the catalyst with hydrochloric acid, followed by chromatography in light petroleum gave a brown oil (0·3 g.). Repeated chromatography in light petroleum yielded traces of 1 : 2-diphenylethane and a fluorescent substance which could not be identified.

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