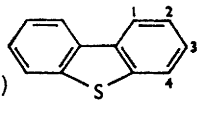
1010. *Derivatives of Dibenzofuran and Dibenzothiophen. Part II.*[1] *Free-radical Phenylation of Dibenzothiophen.*

By E. B. McCall, A. J. Neale, and T. J. Rawlings.

The free-radical phenylation of dibenzothiophen has been studied with benzoyl peroxide and benzenesulphonyl chloride as sources of phenyl radicals. In contrast to results for phenanthrene, substitution takes place at all four available positions, with preference for the hindered positions 1 and 4.

Although electrophilic substitution in dibenzothiophen (I) has been given some consideration,[2,3] there have been no previous attempts to examine its free-radical substitution. In Part I,[1] we reported the syntheses of the isomeric phenyl derivatives of dibenzothiophen and are thus able to assess the distribution of isomers produced in free-radical phenylation. Benzoyl peroxide and benzenesulphonyl chloride[4] have been used as sources of phenyl radicals.

(I)



Phenylations with the former were carried out at 110° essentially according to the procedure of Beckwith and Thompson[5] except that the isomer mixture, after isolation by distillation, was analysed directly by infrared spectroscopy.

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[1] Part I, *J.*, 1962, 4900.

[2] Baker and Eaborn, *J.*, 1961, 5077.

[3] Eaborn and Sperry, *J.*, 1961, 4921.

[4] Bain, Blackman, Cummings, Hughes, Lynch, McCall, and Roberts, *Proc. Chem. Soc.*, 1962, 186.

[5] Beckwith and Thompson, *J.*, 1961, 73.

Phenylations with benzenesulphonyl chloride were carried out at 240—270° and followed by the evolution of sulphur dioxide and hydrogen chloride. The products were isolated by distillation, no other purification being necessary. Variations in technique or in dilution had no effect on the proportions of isomers isolated (see Table), indicating that selective removal of isomers by further phenylation is improbable. The close correspondence of the isomer percentages with those obtained with benzoyl peroxide confirms the homolytic character of the reaction.[4,6] The yields (*ca.* 40%, based on benzenesulphonyl chloride) are lower than for other substrates,[4] but it seems that the formation of chlorobenzene and of phenylsulphonyldibenzothiophens are the only side reactions and that these probably proceed by a free-radical mechanism.

Isomer percentages in free-radical phenylation * and reactivity indices for dibenzothiophen.

Posn. of substitn.	B.S.C.			B.P.	Fr	Ar
	(*a*)	(*b*)	(*c*)			
1-	29·0	30·0	32·8	31·0	0·440	1·658
2-	12·8	12·4	12·0	12·0	0·423	1·758
3-	21·8	21·4	20·2	21·0	0·407	1·778
4-	35·6	34·7	30·2	28·0	0·464	1·571

* B.S.C. = benzenesulphonyl chloride: (*a*) B.S.C. : dibenzothiophen, 1 : 15; (*b*) 1 : 3; (*c*) gradua addition of B.S.C. to dibenzothiophen. B.P. = benzoyl peroxide. Fr and Ar = free valency and radical localisation energies (Berthier and Pullmann [7]).

The surprising feature of the results is the high proportion of the sterically hindered[3] 1- and 4-phenyl isomers, particularly when comparison is made with the phenylation of phenanthrene.[5] In the latter case no substitution could be detected at the 4-position (corresponding to the 1-position in dibenzothiophen) and this was attributed to steric hindrance. If steric effects are important in the phenylation of dibenzothiophen, they must be counterbalanced by an inherent high reactivity of the 1- and the 4-position. Unfortunately, two of the available theoretical discussions[7,8] which treat dibenzothiophen as a non-alternant molecule[7] or as an alternant molecule related to phenanthrene[8] seem inadequate in dealing with reactivity. These treatments are alike in predicting superior reactivity for the 1- and the 4-position in radical substitutions, but they cannot account for the order ($1 \sim 4 > 3 > 2$) observed here for the 2- and the 3-position. They are similarly unable to account for the order ($2 > 3 > 4 > 1$) observed for electrophilic substitution.[1,2]

EXPERIMENTAL

Analyses of isomer mixtures were carried out on CS_2 solutions by using a Unicam S.P. 100/130 spectrometer and the absorption bands, 791 (1-phenyl), 884 (2-), 875 (3-), and 1103 cm.$^{-1}$ (4-).

Materials.—Dibenzothiophen was prepared according to the method of Gilman and Jacoby[9] and, after distillation, was recrystallised from ethanol to m. p. 98—99·5°. Benzenesulphonyl chloride was commercial material, f. p. 14·5°, d_{20}^{4} 1·3770, n_D^{25} 1·5494 (fractionation did not improve these properties). Benzoyl peroxide was purified according to the method of Augood, Hey, and Williams.[10]

Dibenzothiophen and Benzoyl Peroxide.—Benzoyl peroxide (20 g., 0·083 mole) was added slowly to molten dibenzothiophen (100 g., 0·544 mole) at 110° and the whole was kept at this temperature for a further 17 hr., then dissolved in light petroleum–benzene (1 l.) and extracted with aqueous potassium carbonate. Acidification of the aqueous layer gave benzoic acid (2·5 g.),

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[6] G. H. Williams, " Homolytic Aromatic Substitution," Pergamon Press, London, 1960, p. **68.**

[7] Berthier and Pullmann, *Compt. rend.*, 1950, **231**, 774.

[8] Koutecky, Zahradnik, and Paldus, *J. Chim. phys.*, 1959, **56**, 455.

[9] Gilman and Jacoby, *J. Org. Chem.*, 1938, **3**, 108.

[10] Augood, Hey, and Williams, *J.*, 1952, 2094.

m. p. 120—121°. The hydrocarbon layer, after drying ($MgSO_4$), was evaporated, and the residue boiled under reflux with 10% ethanolic potassium hydroxide (300 ml.) for 17 hr. The solvent was removed under reduced pressure and the residue treated with water (500 ml.) and benzene (1 l.). The aqueous layer was filtered from gum and saturated with carbon dioxide. The precipitated materials were extracted with ether. The aqueous solution was then acidified with hydrochloric acid and extracted with ether, to yield slightly impure benzoic acid (9·9 g.), m. p. 115—121°. The benzene solution was evaporated and the residue distilled to give dibenzothiophen (79·8 g.) and a brown solid (4·4 g., 20·4%), b. p. 172—193°/0·2 mm. The solid had composition: 1- (31%), 2- (12%), 3- (21%), and 4-phenyldibenzothiophen (28%) and dibenzothiophen 5,5-dioxide (2%; isolated as material insoluble in carbon disulphide and identical in mixed m. p. and infrared spectrum with an authentic sample [11]).

Dibenzothiophen and Benzenesulphonyl Chloride.—(*a*) Dibenzothiophen (200 g., 1·10 moles) and benzenesulphonyl chloride (13·78 g., 0·078 mole) were heated at 250—270° for 5 hr.; evolution of sulphur dioxide and hydrogen chloride had then ceased. Distillation gave unchanged dibenzothiophen and a solid (11·0 g., 54·5%), b. p. 193—250°/1 mm., of composition as stated in the Table (plus dibenzothiophen 0·8%). The residues were not examined. (*b*) Dibenzothiophen (708 g., 3·83 moles) and benzenesulphonyl chloride (206 g., 1·28 moles) were heated at 240—250° for 10 hr. The gases evolved were absorbed in aqueous sodium hydroxide. Hydrogen chloride was determined, after expulsion of sulphur dioxide, by titration with silver nitrate; sulphur dioxide was determined, after oxidation with iodine, by back-titration with sodium thiosulphate. During reaction 70% of the theoretical amount of hydrogen chloride and 65% of sulphur dioxide were evolved, both values being based on benzenesulphonyl chloride assumed to be completely consumed in production of phenyldibenzothiophens. The excess of dibenzothiophen was distilled from the reaction mixture and the residue fractionated at 1 mm. (38 × 2·5 cm. column packed with $\frac{1}{8}''$ glass rings). Individual fractions were analysed for the phenyl isomers until absorption characteristic of sulphone appeared in the infrared spectrum. The mixture of phenyldibenzothiophens (133 g., 0·51 mole, 40% based on benzenesulphonyl chloride) had the composition shown in the Table. (*c*) (With R. J. ROBERTS.) Benzenesulphonyl chloride (249·1 g., 1·41 moles) was added slowly to stirred dibenzothiophen (780 g., 4·24 moles) at 250—270° during 12 hr. Reaction was continued at this temperature for 2 hr., evolution of gases being followed as for reaction (*b*). After reaction, determination of benzenesulphonyl chloride (Jensen and Brown [12]) showed that 96% had been consumed; sulphur dioxide and hydrogen chloride corresponded to 70% of the theoretical amount, complete conversion into phenyldibenzothiophens being assumed. The mixture (900 g.) was distilled, yielding chlorobenzene (12·2 g.), dibenzothiophen (639·7 g.), a mixture (M; 199·7 g.) consisting largely of phenyldibenzothiophens, and a residue (32·3 g.) containing a large proportion of sulphone (infrared spectrum). The mixture M was fractionated and yielded a mixture of phenyldibenzothiophens (148 g., 40%) having the composition shown in the Table. The residue from the fractionation also contained a large proportion of sulphone. There was therefore total consumption of the benzenesulphonyl chloride with production of 70% of the equivalent amount of sulphur dioxide and hydrogen chloride and 40% of phenyldibenzothiophens. This can be interpreted if it is assumed that 30% of the benzenesulphonyl chloride decomposes to produce chlorobenzene with evolution of sulphur dioxide and 30% gives rise to phenylsulphonyldibenzothiophens with evolution of hydrogen chloride.

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MONSANTO CHEMICALS LIMITED,
RUABON, WREXHAM, DENBIGHSHIRE.

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[11] Gilman and Nobis, *J. Amer. Chem. Soc.*, 1945, **67**, 1479.
[12] Jensen and Brown, *J. Amer. Chem. Soc.*, 1958, **80**, 4038.