

Reaction of Phenyl-lithium and Bromobenzene with Carbon Disulphide

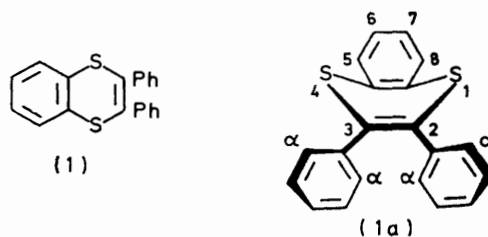
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2,3-Diphenyl-1,4-benzodithiin (1) was prepared from the reaction of phenyl-lithium and bromobenzene with carbon disulphide. 2-(Biphenyl-2-yl)-3-phenyl-1,4-benzodithiin (2), 3-(biphenyl-2-yl)-2-phenylbenzo[*b*]thiophen (3), and 2,3-dihydro-2,3-diphenyl-1,4-benzodithiin were isolated as by-products. Pyrolysis of (1) afforded tetraphenylthiophen. A reaction mechanism involving a benzyne intermediate is suggested.

DITHIO-1-NAPHTHOIC ACID has been obtained by treatment of 1-naphthyl-lithium with carbon disulphide.¹ We now report that, although phenyl-lithium reacts similarly with an excess of carbon disulphide to give dithiobenzoic acid,[†] reaction with a limited amount of carbon disulphide affords a different product, C₂₀H₁₄S₂, identified as 2,3-diphenyl-1,4-benzodithiin (1) on the basis of its hydrogenolysis to give benzene and bibenzyl, and spectroscopic evidence. The mass spectrum showed fragmentation to the ions (M - H)⁺, (M - S)⁺, and (M - C₆H₅CS)⁺, analogous to those observed with 3,6-diphenyl-1,4-dithiin.⁴ The n.m.r. data are consistent with the conformation (1a); other dithiins have been shown by X-ray crystallography to exist as boat forms.⁵ Compound (1) could not be isolated from the reaction of phenyl-lithium, bromobenzene, and a large excess of carbon disulphide.

Compound (1) was not oxidised by dichromate or permanganate, but decomposed when heated above its m.p. to give tetraphenylthiophen, which afforded 1,2,3,4-tetraphenylbutane on hydrogenolytic desulphurisation

with Raney nickel.⁶ Tetraphenylthiophen is obtained in a remarkable number of reactions involving heating compounds containing Ph-C and S components.⁷ Its formation appears to involve free-radical intermediates.



Other products isolated from the reaction leading to (1) were 2-(biphenyl-2-yl)-3-phenyl-1,4-benzodithiin (2), 3-(biphenyl-2-yl)-2-phenylbenzo[*b*]thiophen (3), and 2,3-dihydro-2,3-diphenyl-1,4-benzodithiin. Compound (2) was desulphurised with Raney nickel to give 2-phenethylbiphenyl, identical with a sample prepared by Kuhn's method.⁸ The mass spectrum of (2) was similar to

[†] Identified by comparison with material obtained by Houben's method;² the reaction is analogous to carboxylation with carbon dioxide.³

¹ A. Schönberg, A. Stephenson, H. Kaltschmitt, E. Petersen, and H. Schulten, *Ber.*, 1933, **66**, 237.

² J. Houben, *Ber.*, 1906, **39**, 3219.

³ H. Watanabe, R. A. Schwarz, and C. R. Hauser, *Canad. J. Chem.*, 1969, **47**, 1543; J. E. Mulvaney, *J. Amer. Chem. Soc.*, 1966, **88**, 476.

⁴ C. M. Buess, V. O. Brandt, R. C. Strivastava, and W. R. Carper, *J. Heterocyclic Chem.*, 1972, **9**, 887.

⁵ T. Sasaki, 'The Chemistry of Heterocyclic Compounds,' Tokyo Kagakudozin, 1972, p. 205.

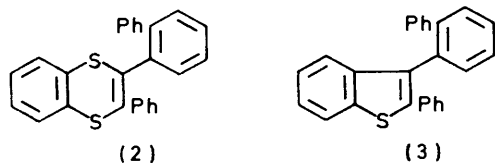
⁶ G. M. Badger, B. J. Christie, J. M. Pryke, and W. H. F. Sasse, *J. Chem. Soc.*, 1957, 4417.

⁷ G. Purrello and A. L. Vullo, *Boll. Sedute Accad. Gioenia Sci. Nat. Catania*, 1967, **9**, 46; G. Montando and G. Purrello, *Ann. chim. (Italy)*, 1961, **51**, 865.

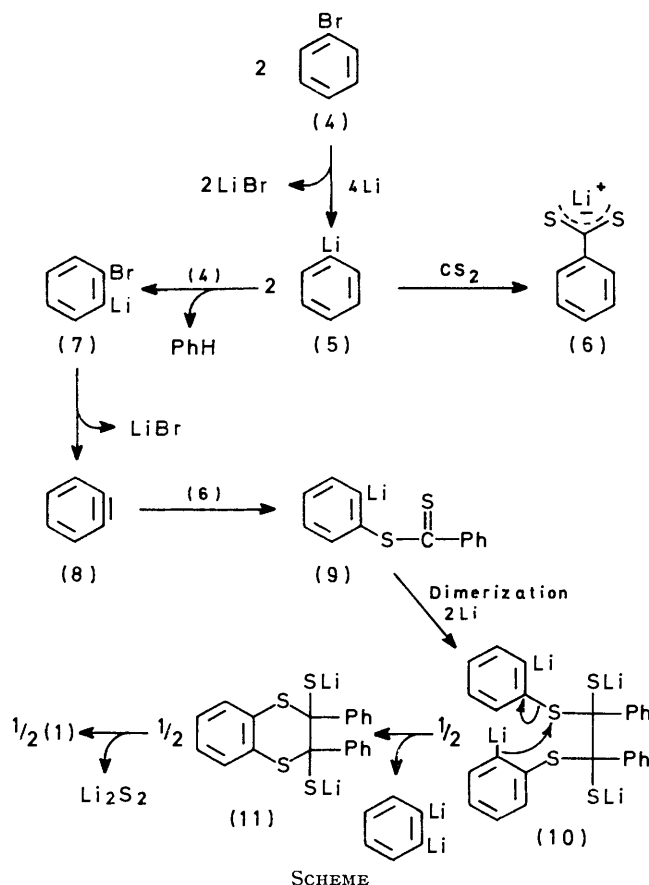
⁸ R. Kuhn and A. Deutch, *Ber.*, 1932, **65**, 43.

that of compound (1). The structure of compound (3) was determined from i.r. and n.m.r. data. The isomeric 2-(biphenyl-2-yl)-3-phenylbenzothiophen structure was ruled out, because the mass spectrum showed the ion $(M - C_6H_5CS)^+$ and no peak corresponding to $(M - PhC_6H_4CS)^+$.

Compound (1) could be formed by a mechanism involving benzyne (8) on the basis of the following evidence: (a) benzyne prepared from fluorobenzene and phenyl-lithium⁹ reacted with lithium dithiobenzoate to



give compound (1); (b) biphenyl and benzene were detected in the reaction mixture; and (c) a 2:1:1 molar ratio of phenyl-lithium, bromobenzene, and carbon disulphide gave the optimum yield (30%) of compound (1) (Scheme). Although many mechanisms for the process $(8) + (6) \rightarrow (1)$ could be advanced,

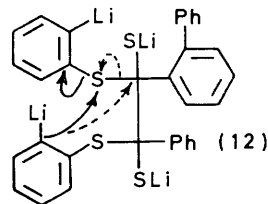


SCHEME

we favour a mechanism involving the dimer (10) of 2-lithiophenyl dithiobenzoate (9) formed in the presence

* The separation of unchanged lithium before the reaction was complete caused a large decrease in the yield of (1).

of metallic lithium.* The formation of compounds (2) and (3) can be explained in terms of an intermediate



(12), similar to (10), and 2,3-dihydro-2,3-diphenyl-1,4-benzodithian could be derived from the intermediate (11). An attempt to isolate benzene-1,2-dithiol was unsuccessful.

EXPERIMENTAL

2,3-Diphenyl-1,4-benzodithiin (1).—To dry ether (100 ml), lithium wire (3.5 g, 0.5 mol) and bromobenzene (40 g, 0.25 mol) were added with stirring in a current of dry nitrogen. After *ca.* 2 min, the mixture started to boil and the boiling was continued for 30 min. The resulting solution, diluted with ether (50 ml), was refluxed for 30 min, then carbon disulphide (3.8 g, 0.05 mol) in ether (50 ml) was added with cooling (ice-water). Stirring was continued for 30 min, then bromobenzene (8 g, 0.05 mol) in ether (50 ml) was added dropwise with stirring at room temperature. After 3 h stirring, the reaction mixture was filtered through glass-wool to separate unchanged lithium, and ice-water (100 ml) was added dropwise with stirring (the addition of *ca.* 20 ml of ice-water afforded a yellow material, which readily dissolved when the rest was added).

The aqueous and ethereal layers were separated, and the aqueous layer was set aside at room temperature. Yellow crystals began to precipitate gradually after 1 day and were collected (6 g, 30%) after 2 weeks. Recrystallisation from acetic acid gave the *dithiin* (1) as needles, m.p. 157–158°; ν_{\max} (KBr) 3060s, 1575s, and 1475s cm^{-1} (arom. CH); λ_{\max} (EtOH) 209 (log ϵ 4.63) and 273 nm (3.26); δ (CDCl_3) 6.90 [4H, s, C(α)H], 7.08 (8H, m, other protons), and 7.15 [2H, q, C(5,8)H]; *m/e* 318 (M^+ , 100%), 317 ($M - H$, 54), 286 ($M - S$, 6), 285 ($M - HS$, 19), 210 ($M - SC_6H_4$, 69), and 197 ($M - C_6H_5CS$, 12) (Found: C, 75.0; H, 4.85; S, 20.05. $C_{20}H_{14}S_2$ requires C, 75.0; H, 4.95; S, 20.05%).

When the filtrate was condensed to *ca.* 30 ml and acetone was added, a mixture of dilithium disulphide and lithium bromide was deposited.

Compound (1) was also obtained as follows. To ethereal phenyl-lithium containing fluorobenzene was added ethereal dithiobenzoic acid [prepared from the Grignard reagent² and dried over anhydrous sodium sulphate (1 day), Zeolite (1 day), and lithium wire (3 h)]. The mixture was stirred at room temperature for 3 h and then (1) was isolated as above (yield *ca.* 20%).

Desulphurisation of the Benzodithiin (1).—Compound (1) (1.2 g, 3.7 mmol) was refluxed with the activated¹⁰ Raney nickel (48%; 30 g) in absolute ethanol (150 ml) for 8 h. The mixture was separated by decantation, centrifugation, and filtration. The nickel was washed with ethanol and the washing was also centrifuged. The combined ethanolic solution was evaporated to *ca.* 30 ml under vacuum and cooled in ice to afford material which was recrystallised

⁹ G. Wittig, G. Pieper, and G. Fuhrmann, *Ber.*, 1940, **73**, 1193.

¹⁰ H. C. Horning, *Org. Synth.*, 1967, Coll. Vol. III, p. 181.

from methanol to give bibenzyl as prisms (0.4 g, 60%), m.p. 52–53° (lit.,¹¹ 52°); δ (CDCl₃) 2.89 (4H, s, 2 × CH₂) and 7.18 (10H, s, 2 × Ph), as reported¹² [Found: C, 91.95; H, 7.75%; *M*, 186 (osmometry in acetone). C₁₄H₁₄ requires C, 92.2; H, 7.75%; *M*, 182].

G.l.c. showed the presence of benzene in the mother liquor (Hitachi K 23; 20% w/w TCP, 30–60 mesh, 1 m column, N₂ at 20 ml min⁻¹, t_R 4.2 min).

Pyrolysis of the Benzodithiin (1).—Compound (1) (0.3 g, 0.9 mmol) was heated above its m.p. for ca. 5 min to give a deep red oil. When the oil was stirred with a glass rod with a small amount of ethanol, a yellow-brown powder was obtained; recrystallisation from ethanol gave tetraphenylthiophen (0.1 g, 58%) as light yellow needles, m.p. 186–187° (lit.,¹³ 183–184°); λ_{\max} (EtOH) 239 (log ϵ 4.28), 263 (4.25), and 314 nm (4.08) (identical with reported data¹⁴) (Found: C, 86.35; H, 5.1; S, 8.15%; *M*⁺, 388. Calc. for C₂₈H₂₀S: C, 86.55; H, 5.2; S, 8.25%; *M*, 388).

The product was desulphurised with Raney nickel in the usual way to give 1,2,3,4-tetraphenylbutane (0.1 g) as colourless needles, m.p. 178–179°; ν_{\max} (KBr) 3030s, 1595s, 1490s (benzene CH), and 2900s (CH) cm⁻¹ (Found: C, 92.6; H, 7.4%; *M*⁺, 362. Calc. for C₂₈H₂₆: C, 92.75; H, 7.25%; *M*, 362).

2-(Biphenyl-2-yl)-3-phenyl-1,4-benzodithiin (2).—The yellow material obtained in the preparation of (1) by addition of ca. 20 ml of ice-water (see above) was collected quickly at this stage and then dissolved in an excess of water. To the solution, cooled in ice-water, was added dimethyl sulphate (2.5 ml, 25 mmol), and the mixture was set aside overnight. Methanolic potassium hydroxide (100 ml) was then added to decompose unchanged dimethyl sulphate. A red lower layer was separated and concentrated to ca. 20 ml under diminished pressure. Addition of a small amount of acetic acid gave yellow crystals, which were recrystallised from acetic acid to give the *dithiin* (2) as yellow plates (0.6 g), m.p. 259–260°; ν_{\max} (KBr) 3040s, 1578s, and 1480s (benzene CH) cm⁻¹; δ (CDCl₃) 7.22 [3H, s,

C(α)H], 7.25 (13H, m, other protons), and 7.32 [2H, s, C(5,8)H] [for proton numbering see (1a)]; λ_{\max} (EtOH) 247 (log ϵ 3.18) and 348 nm (4.38); *m/e* 394 (100%, *M*⁺), 393 (8, *M* – H), 362 (14, *M* – S), 361 (3, *M* – HS), and 273 (6, *M* – C₆H₅CS) (Found: C, 79.2; H, 4.65; S, 16.15. C₂₆H₁₈S₂ requires C, 79.15; H, 4.6; S, 16.25%).

Hydrogenolytic desulphurisation of (2) (0.5 g) afforded a colourless oil (0.1 g), b.p. 205–210° at 10 mmHg.

3-(Biphenyl-2-yl)-2-phenylbenzo[b]thiophen (3).—The ethereal layer separated in the isolation of (1) was evaporated to a deep red oil (24 g), which was dissolved in ethanol (50 ml). To the solution was added a small amount of water to give a deep red oily material. This was collected, left in a vacuum desiccator for 24 h, and washed with acetic acid to give yellow crystals of 2,3-dihydro-2,3-diphenyl-1,4-benzodithiin (1.2 g) (22%), m.p. 95–96° (from acetic acid); ν_{\max} (KBr) 3030s (benzene CH) and 2900 (CH) cm⁻¹; δ (CDCl₃) 2.90 (2H, d, CH) and 7.04 (14H, m, other protons) (Found: C, 74.95; H, 5.3; S, 19.75%; *M*⁺, 320. C₂₀H₁₆S₂ requires C, 74.95; H, 5.1; S, 20.0%; *M*, 320). This compound readily afforded compound (1) on addition of bromine water.

When the alcoholic solution separated from the above oily product was set aside for ca. 1 week, the *benzothiophen* (3) precipitated as yellow plates (0.25 g), m.p. 142–143° (from acetic acid); ν_{\max} (KBr) 3020s, 1575s, and 1480s (benzene CH) cm⁻¹; δ (CDCl₃) 6.98 [3H, s, C(α)H], 7.00 (13H, m, other protons), and 7.06 [2H, s, C(4,7)H]; *m/e* 362 (100%, *M*⁺), 285 (3, *M* – C₆H₅), 254 (50, *M* – C₆H₄S), and 241 (12, *M* – C₆H₅CS) (Found: C, 86.1; H, 4.9. C₂₆H₁₈S requires C, 86.2; H, 4.95%).

The foregoing ethereal layer also contained crude biphenyl (ca. 0.2 g), identical (i.r. spectrum) with an authentic sample, and benzene (2.3 g, 60%), estimated by g.l.c.

We thank Drs. T. Hayashi and J. Nakayama for discussions.

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¹¹ 'Encyclopedia Chimica,' Kyoritu, 1969, vol. 7, p. 511.

¹² H. A. Szymanski and R. E. Yelin, 'NMR Band Handbook,' Plenum Press, New York-Washington, 1968, p. 189.

¹³ L. Fortina, *Ann. chim. (Italy)*, 1959, **49**, 2047.

¹⁴ L. Fortina and G. Montaudo, *Gazzetta*, 1960, **90**, 987.