

Reaction of Benzyne with Carbon Disulphide: Formation and Reaction of 1,3-Benzodithiol-2-ylidene

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Benzyne, generated by oxidation of 1-aminobenzotriazole and by decomposition of benzenediazonium-2-carboxylate or 2-carboxybenzenediazonium chloride, reacts with carbon disulphide to give the resonance-stabilized and nucleophilic carbene 1,3-benzodithiol-2-ylidene. This carbene can be effectively trapped by protic substrates by protonation to give the 1,3-benzodithiolium ion, which further reacts with nucleophiles to yield final products, although in the absence of protic substrates it dimerizes to give bi-(1,3-benzodithiol-2-ylidene). However, the reaction of carbon disulphide with benzyne generated from 1-(2-carboxyphenyl)-3,3-dimethyltriazeno gives products unexplainable in terms of the carbene intermediate.

HARTZLER¹ and Coffen² have shown independently that acetylenes having at least one electron-attracting group react with carbon disulphide to give nucleophilic carbenes (1,3-dithiol-2-ylidenes). Furthermore carbon disulphide can add to the double bonds of norbornenes to give dithiocarbenes under drastic conditions (at 10⁴ atm and 100°).³ The reaction of carbon disulphide with benzyne, which can be considered to possess a highly strained and reactive triple bond, would thus be expected to lead to 1,3-benzodithiol-2-ylidene (1). The carbene (1) has been suggested as intermediate in the reaction of 1,3-benzodithiolium salts with base.^{4,5} Tabushi *et al.* have reported that the reaction of carbon disulphide with benzyne, generated by the action of sodium amide on bromobenzene in liquid ammonia, gives benzenethiol, thioanisole, and diphenyl sulphide.⁶ In this reaction, however, the species which reacts with benzyne is not carbon disulphide itself but its adduct with sodium amide. More recently Fields and Meyerson have suggested the transient formation of the carbene (1) from carbon disulphide and benzyne generated by the pyrolysis of phthalic anhydride at 700° in the vapour phase, on the grounds that a product corresponding to the dimer of (1) was indicated by mass spectroscopy.⁷ We have reported briefly evidence for the formation of the carbene (1) from carbon disulphide and benzyne generated by oxidation of 1-aminobenzotriazole.⁸ We now report the formation of (1) from carbon disulphide and benzyne from other origins, and its characteristic reactions.

Heating benzenediazonium-2-carboxylate (as benzyne source⁹) with carbon disulphide in boiling methylene chloride gave bi-(1,3-benzodithiol-2-ylidene)⁴ (2) (22%) and low yields of 2,2'-spirobis-(1,3-benzodithiole)¹⁰ (3) (1.0%), 2,2'-(*o*-phenylenedithio)bis-1,3-benzodithiole⁵ (4) (1.7%), and 1,3-benzodithiol-2-one¹¹ (5) (1.6%). Evidently compound (2) is the result of dimerization of the carbene (1) produced by 1,3-dipolar cycloaddition

¹ H. D. Hartzler, *J. Amer. Chem. Soc.*, 1970, **92**, (a) p. 1412; (b) p. 1413.

² D. L. Coffen, *Tetrahedron Letters*, 1970, 2633.

³ H. Plieninger, C. C. Heuck, and R. Bühler, *Tetrahedron*, 1972, **28**, 73.

⁴ W. R. H. Hurlley and S. Smiles, *J. Chem. Soc.*, 1926, 2263.

⁵ D. Buza, A. Gryff-Keller, and S. Szymański, *Roczniki Chem.*, 1970, **44**, 2319; D. Buza and S. Szymański, *ibid.*, 1971, **45**, 501.

⁶ I. Tabushi, K. Okazaki, and R. Oda, *Tetrahedron Letters*, 1967, 3827.

⁷ E. K. Fields and S. Meyerson, *Tetrahedron Letters*, 1970, 629; E. K. Fields and S. Meyerson, *Internat. J. Sulfur Chem. (C)*, 1971, 51.

⁸ J. Nakayama, *J.C.S. Chem. Comm.*, 1974, 166.

of benzyne with carbon disulphide. The dipolarophilic capacity of benzyne has been well documented.¹² The carbene (1) may be resonance-stabilized by participation of the *p* orbital of the carbene carbon atom (which is formally empty and hence can accept electrons¹³) and the *d* orbitals of the sulphur atoms in the constitution of a conjugated system, and therefore the species (1) is expected to be nucleophilic. All the materials used in this reaction are not necessarily free from water, which is presumably involved in the formation of compounds (3)–(5). Because of its nucleophilicity the carbene (1) can be trapped effectively by water, with the result that equilibration takes place amongst the species (1), (6a), and (7a). The dithiolium ion (6a), the conjugate acid of (1), is iso- π -electronic with the benzotropylium ion (by virtue of replacement of two sulphur atoms by two double bonds)¹⁴ and it is well known that disproportionation between tropylium ion and troyl alcohol gives tropone and cycloheptatriene.¹⁵ Consequently it is probable that (5) is produced by disproportionation between (6a) and (7a), although we have failed to isolate 1,3-benzodithiole (8). On the other hand, electrophilic attack of (6a) on the sulphur atom of (7a) could give the sulphonium ion (9a) which could either give compound (3) with loss of 'dihydroxymethane' or rearrange to (10a). Finally electrophilic attack of (6a) on the sulphur atom attached to the dihydroxymethyl group of (10a), followed by elimination of 'trihydroxymethane' (formic acid and water) would afford compound (4). However the formation of (4) could be also explained by the reaction of two molecules of (6a) with benzene-1,2-dithiol produced by ring opening of (6a) and subsequent hydrolysis of the resulting thioformate (12). Such a mechanism has been postulated⁵ for the formation of (4) by the action of water on 1,3-benzodithiolium perchlorate.⁵

⁹ F. M. Logullo, A. H. Seitz, and L. Friedman, *Org. Synth.*, 1968, **48**, 12; M. Stiles and R. G. Miller, *J. Amer. Chem. Soc.*, 1960, **82**, 3802; M. Stiles, R. G. Miller, and U. Burckhardt, *ibid.*, 1963, **85**, 1792; R. G. Miller and M. Stiles, *ibid.*, 1963, **85**, 1798.

¹⁰ R. Huisgen and V. Weberndörfer, *Experientia*, 1961, **17**, 566; V. Weberndörfer, Ph.D. Thesis, University of Munich, 1964.

¹¹ W. R. H. Hurlley and S. Smiles, *J. Chem. Soc.*, 1926, 1821.

¹² R. W. Hoffmann, 'Dehydrobenzene and Cycloalkynes,' Academic Press, New York, 1967.

¹³ R. Gleiter and R. Hoffmann, *J. Amer. Chem. Soc.*, 1968, **90**, 5457.

¹⁴ H. Prinzbach and E. Futterer, *Adv. Heterocyclic Chem.*, 1966, **7**, 39.

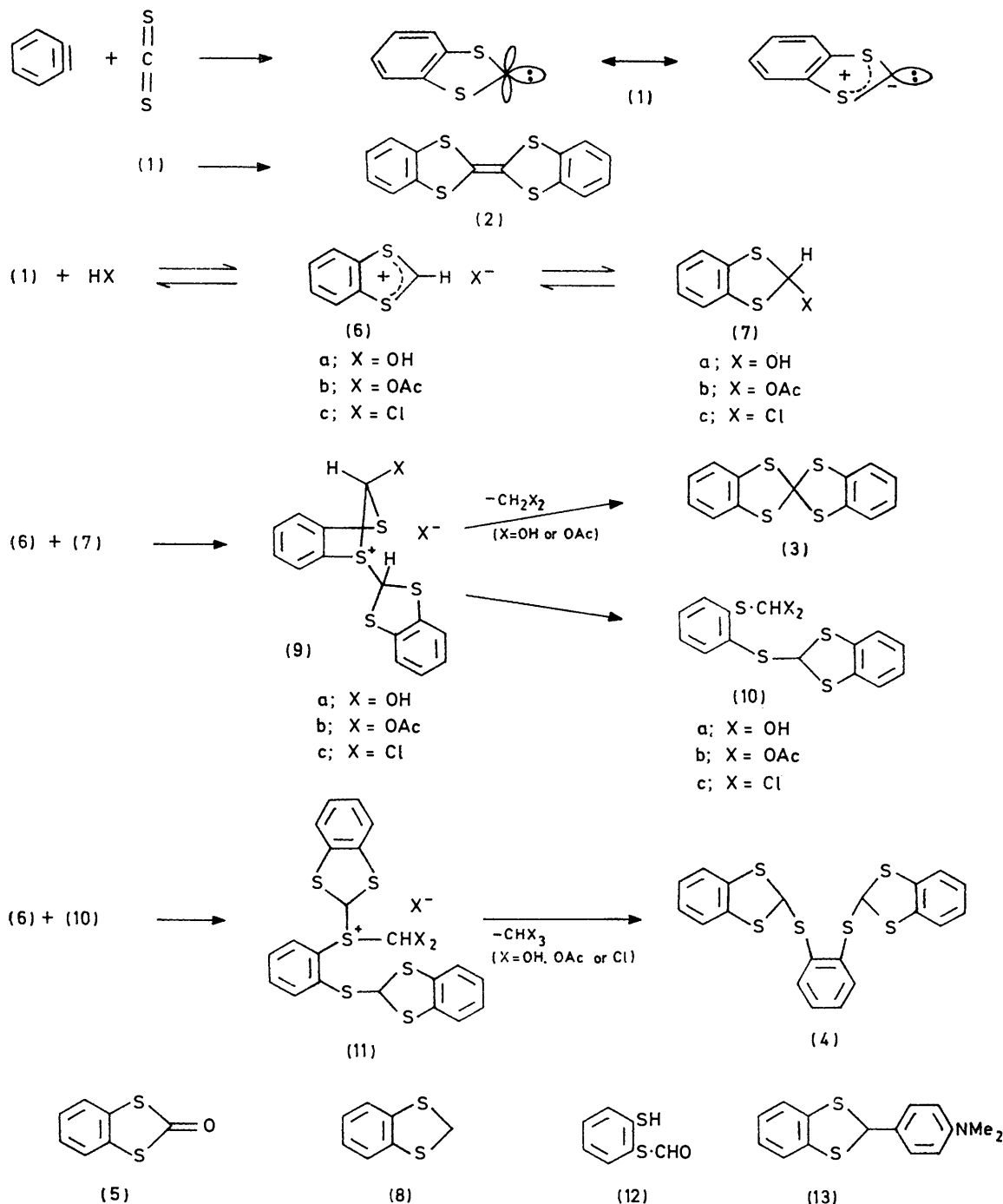
¹⁵ T. Ikemi, T. Nozoe, and S. Sugiyama, *Chem. and Ind.*, 1960, 932; A. P. Ter Borg, R. van Helden, A. F. Bickel, W. Renold, and A. S. Dreiding, *Helv. Chim. Acta*, 1960, **43**, 457.

Dimerization of the carbene (1) provides a convenient synthetic route to compound (2); the synthesis of benzene-1,2-dithiol,^{11,16} from which (2) can be prepared by condensation with tetrachloroethylene⁴ is laborious.

1,3-Dithiolylenes, produced by addition of carbon

of benzyne is too short in this system. This hypothesis is partially supported by the absence of biphenylene (benzyne dimer) in the reaction products.

Supporting data for the participation of water in the formation of compounds (3) and (4) were obtained



disulphide to acetylenes, do not dimerize in the absence of acids, but react further with the acetylenes to give other carbenes.^{1a} In the present case, however, the corresponding reaction of the carbene (1) with benzyne was not observed, probably because the lifetime

by heating benzenediazonium-2-carboxylate with carbon disulphide and water in boiling tetrahydrofuran. In this reaction, compounds (3) and (4) were obtained in

^{1a} R. Adams and A. Ferretti, *J. Amer. Chem. Soc.*, 1959, **81**, 4939; S. Hünig and E. Fleckenstein, *Annalen*, 1970, **738**, 192.

respective yields of 1.1 and 11%, but no carbene dimer was observed, suggesting that water effectively traps the carbene (1).

Oxidation of 1-aminobenzotriazole as benzyne source with lead tetra-acetate (LTA)¹⁷ in a mixture of carbon disulphide and methylene chloride at room temperature gave compounds (3) (6%) and (4) (67%) along with a small amount of two unidentified products. Oxidation of the triazole in carbon disulphide alone gave a higher yield of (4) (86%) and a trace of (3). Compounds (3) (2.0%) and (4) (26%) were also obtained in addition to the carbene dimer (2) (5.2%) by heating benzenediazonium-2-carboxylate with carbon disulphide and acetic acid in boiling methylene chloride. In these cases, the intervention of acetic acid either formed by oxidation of 1-aminobenzotriazole by LTA or added prior to the reaction, results in equilibration amongst the species (1), (6b), and (7b), as observed with 1,3-dithiolylenes.^{1a} Reaction of (6b) with (7b) gives (3) and (4) in a manner similar to the formation of these compounds from (6a) and (7a). The intermediacy of the dithiolylium ion (6b) was strongly supported by the oxidation of 1-aminobenzotriazole in the presence of carbon disulphide and *NN*-dimethylaniline which afforded 2-(4-dimethylaminophenyl)-1,3-benzodithiole¹⁸ (13) (15%) by electrophilic substitution of (6b) with *NN*-dimethylaniline. The alkylation of *NN*-dimethylaniline by 1,3-dithiolylium ion has been reported.¹⁹ However, (6b) failed to react with anisole, the sole product isolated being (4) (54%).

On oxidation of 1-aminobenzotriazole in a mixture of carbon disulphide and pyridine [to suppress the protonation of (1) by acetic acid] nearly half of the triazole was recovered, along with intractable tars. In this case primary product, *e.g.* the carbene dimer (2) must be oxidized by LTA in preference to the triazole.

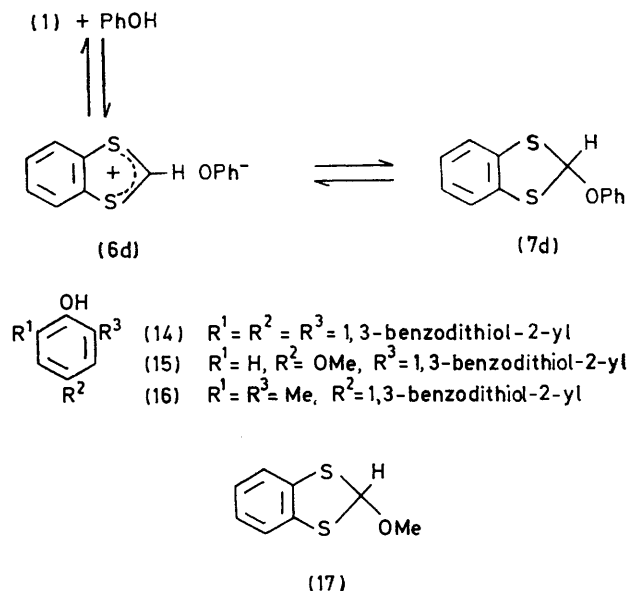
Heating 2-carboxybenzenediazonium chloride²⁰ as benzyne source with carbon disulphide in the presence of propylene oxide in boiling 1,2-dichloroethane gave compound (4) (7.3%) along with a considerable amount of unidentified oily products. The formation of (4) may be explained by the reaction of the species (6c) and (7c) which were formed by addition of hydrogen chloride (produced by decomposition of the diazonium salt and not trapped by propylene oxide) to the carbene (1).

It is noteworthy that compounds (3) and (4) were produced from the carbene (1) and acids, whereas 1,3-dithiolylenes give dimerization products exclusively in the presence of acids.^{1a}

Benzenediazonium-2-carboxylate prepared from 15 mmol of anthranilic acid was heated with carbon disulphide and phenol (15 mmol) in boiling methylene chloride. Unexpectedly the sole product isolated was 2,4,6-tris-(1,3-benzodithiol-2-yl)phenol (14) (17%); no mono- or di-alkylated phenols nor the carbene dimer (2)

* We cannot fully explain why two sets of aromatic protons should give rise to an A_2B_2 spectrum, whereas the third set affords an A_4 singlet. Of the derivatives of 1,3-benzodithiole reported here, only the spiro-compound (3) gives rise to an A_4 spectrum; all the others give A_2B_2 spectra.

were obtained. In a separate reaction, benzenediazonium-2-carboxylate prepared from 10 mmol of anthranilic acid was heated with carbon disulphide and phenol (7 mmol) to give compound (14) (6.7%) in addition to (4) (14%). Strongest support for structure of (14) was provided by the ¹H n.m.r. spectrum: δ [(CD₃)₂SO] 6.24 (1H, s, methine), 6.51 (2H, s, methine), 6.98–7.34 (8H, two equivalent $A_2B_2m^*$, aromatic), 7.12 (4H, A_4s^* , aromatic), 7.69 (2H, s, phenol ring), and 9.82 (1H, s OH). The phenol (14) is insoluble in aqueous alkali, like other hindered phenols.²¹ Protonation of (1) by phenol produces a dithiolylium ion (6d) and this subsequently undergoes a Friedel-Crafts-type alkylation reaction with phenol or phenolate ion to give a mono-(1,3-benzodithiol-2-yl)phenol, which is then twice alkylated by (6d) to yield (14). This suggests that (6d) is not such a strong alkylating reagent that it reacts with the monosubstituted phenol, somewhat activated by a 1,3-benzodithiolylium group, in preference to phenol itself, in keeping with the fact that the dithiolylium ion (6b) fails to alkylate anisole. The formation of (4) may be explicable in terms of reaction of (6d) with (7d) in a manner similar to the formation of (4) from (6a) and (7a). Similarly 4-methoxy- and 2,6-dimethyl-phenols reacted with the carbene (1) to give the phenols (15) (6.0%) and (16) (42%), respectively. The phenols (14)–(16) are susceptible to oxidation



in air and persistently retain a faint pink tinge in accord with the behaviour of 2-(4-hydroxyphenyl)-1,3-benzodithiole.²²

¹⁷ C. D. Campbell and C. W. Rees, *J. Chem. Soc. (C)*, 1969, 742, 748, 752.

¹⁸ O. Neunhoeffer and A. Nowak, *Naturwiss.*, 1958, 45, 491.

¹⁹ E. Klingsberg, *J. Amer. Chem. Soc.*, 1962, 84, 3410.

²⁰ B. H. Klanderma and T. R. Criswell, *J. Org. Chem.*, 1969, 34, 3426.

²¹ G. H. Stillson, D. W. Sawyer, and C. K. Hunt, *J. Amer. Chem. Soc.*, 1945, 67, 303.

²² W. R. H. Hurtley and S. Smiles, *J. Chem. Soc.*, 1927, 534.

Oxidation of 1-aminobenzotriazole with LTA in a 1:1 mixture of carbon disulphide and methanol gave 2-methoxy-1,3-benzodithiole (17) (78%). Heating the benzenediazonium-2-carboxylate with carbon disulphide and methanol in boiling methylene chloride also gave (17) (40%), in addition to the carbene dimer (2) (4.0%). The dithiole (17) is the adduct of methanol with the carbene (1), produced presumably *via* protonation, and is stable at room temperature, suggesting that it no longer dissociates into 1,3-benzodithiolylum and methoxide ions to an appreciable extent.* The present reaction also shows that carbon disulphide is more reactive than methanol towards benzyne, since the carbene (1) is produced in preference to anisole, the adduct of benzyne with methanol.¹²

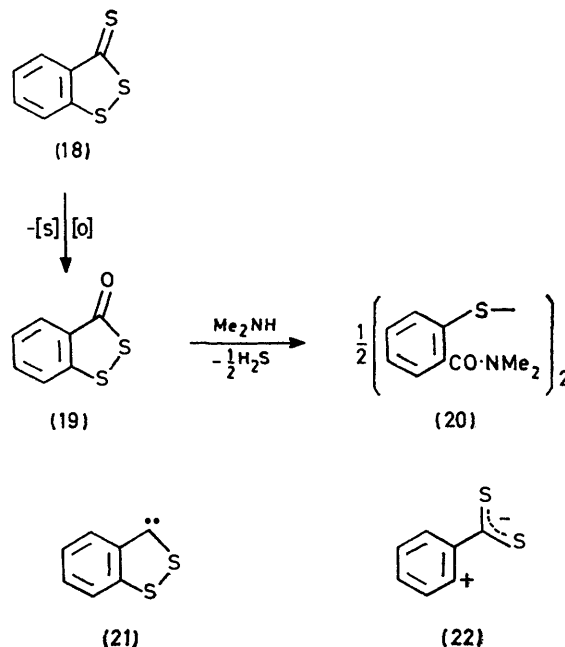
The carbene (1), generated from carbon disulphide and benzyne from benzenediazonium-2-carboxylate, was treated with diethyl acetylenedicarboxylate. However the sole product isolated was the carbene dimer (2) (11%). Similarly the reaction of (1) with tetrachloroethylene was attempted, but the products were (2) (5.3%) and small amounts of unidentified compounds. 1,3-Dithiolylidenes alkylate aldehydes and ketones.^{1b} However an attempted reaction of (1) with acetone gave only (2) in 9.4% yield.

Benzyne is also generated by thermal decomposition of 1-(2-carboxyphenyl)-3,3-dimethyltriazenes.²⁴ Heating this reagent in carbon disulphide at 175–185° for 2 h in a steel bomb yielded 1,2-benzodithiole-3-thione²⁵ (18) (4.8%), 1,2-benzodithiole-3-one^{26a} (19) (31%), and 2,2'-dithiobis-(*NN*-dimethylbenzamide)²⁷ (20) (28%). The same products were also obtained by heating the triazene in a mixture of carbon disulphide and benzene at 135–145° for 5 h.

The formation of compounds (19) and (20) may be best explained by a sulphur-oxygen exchange reaction of (18) and subsequent reaction of the resulting (19) with dimethylamine produced by decomposition of the triazene. The reaction of (19) with primary amines to give 2,2'-dithiobisbenzamides has been reported.²⁶ However the mechanism of the sulphur-oxygen exchange reaction is unclear, except that the origin of the oxygen is the carboxy-group of the triazene: the reaction was carried out under anhydrous conditions and the i.r. spectrum of the crude reaction products already showed the carbonyl bands due to (19) and (20), excluding the possibility of conversion of (18) into (19) and (20) during work-up.

At first we thought that the thione (18) might be produced by subsequent reaction of 1,2-benzodithiol-3-ylidene (21), formed by rearrangement of the carbene (1) produced by carbon disulphide addition to benzyne. Therefore the triazene was heated with carbon disulphide and methanol in order to trap the carbene (1) or (21) as an adduct with methanol. Neither 2-methoxy-

1,3-benzodithiole (17) nor 3-methoxy-1,2-benzodithiole was obtained, however; the products were (18) (9.2%), (19) (21%), and (20) (20%). Fields and Meyerson have reported the formation of the thione (18) by reaction of benzyne with carbon disulphide at 700° in the vapour phase, and they have postulated that (18) is produced by reaction of benzyne with carbon trisulphide generated from carbon disulphide under high energy conditions, or by reaction of a zwitterionic adduct (22) of benzyne and carbon disulphide with sulphur produced from carbon disulphide.⁷



EXPERIMENTAL

I.r. spectra of solids were taken for Nujol mulls, and those of liquids for films. ¹H N.m.r. spectra were determined at 100 MHz for solutions in deuteriochloroform with tetramethylsilane as internal reference. Mass spectra were taken with an ionization voltage of 75 eV. Carbon disulphide was refluxed over and distilled from phosphorus pentoxide and stored over molecular sieves. Methylene chloride and 1,2-dichloroethane were washed with concentrated sulphuric acid and then water and dried over calcium chloride. Methylene chloride used in oxidation of 1-aminobenzotriazole was distilled from phosphorus pentoxide prior to use. Benzene was refluxed over and distilled from calcium hydride. Other commercial materials were used without further purification. Benzyne precursors benzenediazonium-2-carboxylate,⁹ 1-aminobenzotriazole,¹⁷ 2-carboxylbenzenediazonium chlor-

²³ J. Nakayama, unpublished result.

²⁴ R. Gompper, E. Kutter, and G. Seybold, *Chem. Ber.*, 1968, **101**, 2340; J. Nakayama, O. Simamura, and M. Yoshida, *Chem. Comm.*, 1970, 1222; J. Elks and D. H. Hey, *J. Chem. Soc.*, 1943, 441.

²⁵ E. W. McClelland, L. A. Warren, and J. H. Jackson, *J. Chem. Soc.*, 1929, 1582.

²⁶ (a) S. Smiles and E. W. McClelland, *J. Chem. Soc.*, 1922, **121**, 86; (b) E. W. McClelland and J. Longwell, *ibid.*, 1923, **123**, 3310.

²⁷ F. Gialdi, R. Ponci, and A. Baruffini, *Farmaco (Pavia) Ed. sci.*, 1959, **14**, 648.

* At elevated temperatures (17) dissociates into 1,3-benzodithiolylum and methoxide ions. Deprotonation of the former then gives the carbene (1), and the final products are (2) and (3), formed by reaction of these species.²³

ide,²⁰ and 1-(2-carboxyphenyl)-3,3-dimethyltriazene²⁴ were prepared by literature methods. Lead tetra-acetate (LTA) was prepared from trilead tetraoxide and acetic acid.²⁸

Formation and Reactions of 1,3-Benzodithiol-2-ylidene (1) from Carbon Disulphide and Benzyne generated from Benzene-diazonium-2-carboxylate.—(a) *Without addition of a further reactant.* The diazonium carboxylate [prepared from anthranilic acid (10 g)] was suspended in carbon disulphide (50 ml) and methylene chloride (450 ml), and the mixture was heated under reflux for 1.5 h. A small amount of precipitate was filtered off and the dark brown filtrate, concentrated to ca. 150 ml, was left overnight. The crystalline precipitate was collected and washed with methylene chloride (10 ml) to give bi-(1,3-benzodithiol-2-ylidene) (2) as brownish yellow crystals (1.36 g, 12%), m.p. 234—236° (lit.,⁴ 234°). The filtrate and washings combined were evaporated and the residue chromatographed on silica gel (150 g). Elution with carbon tetrachloride gave a mixture of compound (2) and 2,2'-spirobi-(1,3-benzodithiole) (3). The mixture was washed with ether (10 ml) to leave the dimer (2) (1.0 g, 10%), m.p. 236°, as yellow leaflets (from benzene). The washings were evaporated and the residue was rechromatographed on silica gel to give compound (3) (1.0%), m.p. 120—121° (from ethanol) (lit.,¹⁰ 120—121°). Further elution of the original column gave 2,2'-(*o*-phenylenedithio)bis-1,3-benzodithiole (4) (1.7%), m.p. 130—131° (from chloroform-petroleum) (lit.,⁶ 127.5—130°) and then 1,3-benzodithiol-2-one (5) (1.6%), m.p. 78.5—79° (from ethanol) (lit.,¹¹ 78—79°). Finally carbon tetrachloride eluted an unidentified product (120 mg), m.p. 289—293° (decomp.), ν_{\max} 1640 cm⁻¹ (C=O), *m/e* 332 (*M*⁺, C₁₅H₈OS₄). The m.p. of this compound fell to 280—285° (decomp.) on recrystallization from dimethyl sulphoxide; this was accompanied by a considerable change in its i.r. spectrum.

(b) *In the presence of water.* A suspension of the diazonium carboxylate [from anthranilic acid (10 mmol)] in tetrahydrofuran (60 ml), carbon disulphide (5 ml), and water (0.4 ml) was heated under reflux for 1 h. The homogeneous orange mixture was evaporated and the residue chromatographed on silica gel to give compounds (3) (1.1%), m.p. 116—118°, and (4) (11%), m.p. 127—129°.

(c) *In the presence of acetic acid.* A suspension of the diazonium carboxylate [from anthranilic acid (10 mmol)] in methylene chloride (100 ml), carbon disulphide (5 ml), and acetic acid (20 mmol) was heated under reflux for 1 h. The homogeneous red mixture was evaporated and the residue chromatographed on silica gel. Carbon tetrachloride first eluted a mixture of compounds (2) (5.2%), m.p. 236—237°, and (3) (2.0%), m.p. 116—118°, which were separated by the procedure described in (a). Further elution gave an unidentified product (20 mg), m.p. 237—241°, and then compound (4) (26%), m.p. 126—129°.

(d) *In the presence of phenols.* (i) *Phenol.* The diazonium carboxylate [from anthranilic acid (15 mmol)] was heated with carbon disulphide (5 ml) and phenol (15 mmol) in boiling methylene chloride (120 ml) for 1 h. The red mixture was washed with aqueous sodium carbonate and extracted with 3*N*-NaOH (2 × 25 ml). Work-up of the alkaline layer gave phenol (60% recovery). The organic layer was washed with water, dried, and evaporated, and the residue was chromatographed on silica gel. Elution with carbon tetrachloride gave a small amount of an unidentified product, m.p. 141—143°. Elution with

carbon tetrachloride-benzene (9 : 1) then gave 2,4,6-*tris*-(1,3-benzodithiol-2-yl)phenol (14) (17%) as granules retaining a pink tinge (from dimethyl sulphoxide-methanol), m.p. 223—224° (decomp.) (Found: C, 58.5; H, 3.2; S, 34.8. C₂₇H₁₈OS₆ requires C, 58.9; H, 3.3; S, 34.9%), ν_{\max} 3375 cm⁻¹ (OH), *m/e* 550 (*M*⁺).

A suspension of the diazonium carboxylate [from anthranilic acid (10 mmol)] in methylene chloride (100 ml), carbon disulphide (5 ml), and phenol (7 mmol) was heated under reflux for 1 h. Purification of products by column chromatography and recrystallization gave compounds (4) (14%), m.p. 129—131°, and (14) (6.7%), m.p. 223—226°.

(ii) *4-Methoxyphenol.* A suspension of the diazonium carboxylate [from anthranilic acid (10 mmol)] in carbon disulphide (5 ml), 4-methoxyphenol (10 mmol), and methylene chloride (100 ml) was heated under reflux for 1 h. The dark red mixture was evaporated and the residue chromatographed on silica gel. Elution with benzene gave 2-(1,3-benzodithiol-2-yl)-4-methoxyphenol (15) (6.0%) as pink granules, m.p. 138—141° (from methanol) (Found: C, 61.0; H, 4.6; S, 22.8. C₁₄H₁₂O₂S₂ requires C, 60.9; H, 4.4; S, 23.3%), ν_{\max} 3375 cm⁻¹ (OH), *m/e* 276 (*M*⁺).

(iii) *2,6-Dimethylphenol.* A suspension of the diazonium carboxylate [from anthranilic acid (10 mmol)] in methylene chloride (100 ml), carbon disulphide (5 ml), and 2,6-dimethylphenol (10 mmol) was heated under reflux for 1 h. The red mixture was evaporated and the residue chromatographed on silica gel. Elution with carbon tetrachloride-benzene (4 : 1) gave 4-(1,3-benzodithiol-2-yl)-2,6-dimethylphenol (16) contaminated with 2,6-dimethylphenol, which was washed with petroleum (10 ml). Compound (16) (42%) had m.p. 108—109° (from ethanol) (Found: C, 65.7; H, 5.0; S, 23.1. C₁₅H₁₄OS₂ requires C, 65.7; H, 5.2; S, 23.3%), ν_{\max} 3450 cm⁻¹ (OH), δ 2.18 (6H, s), 4.67 (1H, s, OH), 6.20 (1H, s), 6.9—7.3 (4H, A₂B₂m), and 7.19 (2H, s), *m/e* 274 (*M*⁺).

(e) *In the presence of methanol.* A suspension of the diazonium carboxylate [anthranilic acid (30 mmol)] in methylene chloride (200 ml), carbon disulphide (10 ml), and methanol (5 ml) was heated under reflux for 1 h. The red mixture was washed successively with aqueous sodium carbonate and water, dried, and evaporated. The oily residue was distilled to give 2-methoxy-1,3-benzodithiole (17) (40%), b.p. 105—106° at 2 mmHg (Found: C, 52.2; H, 4.1; S, 34.6. C₈H₆OS₂ requires C, 52.2; H, 4.4; S, 34.8%), δ 3.22 (3H, s), 6.75 (1H, s), and 7.0—7.4 (4H, A₂B₂m), ν_{\max} 1060 cm⁻¹ (C-O), *m/e* 184 (*M*⁺).

(f) *With diethyl acetylenedicarboxylate.* A suspension of the diazonium carboxylate [from anthranilic acid (20 mmol)] in diethyl acetylenedicarboxylate (20 mmol), carbon disulphide (8 ml), and methylene chloride (120 ml) was heated under reflux for 1 h. The mixture was evaporated and the residue chromatographed on silica gel to give compound (2) (11%), m.p. 235—236°, diethyl acetylenedicarboxylate (almost quantitative), and intractable tars.

(g) *In the presence of tetrachloroethylene.* A suspension of the diazonium carboxylate [from anthranilic acid (15 mmol)] in carbon disulphide (5 ml), tetrachloroethylene (25 ml), and methylene chloride (100 ml) was heated under reflux for 1 h. Evaporation, followed by chromatography of the residue on silica gel, gave compound (2) (5.3%), m.p. 235—236°, and small amounts of two unidentified products (one with m.p. 166—167°, the other with m.p. 204°).

(h) *In the presence of acetone.* A suspension of the

²⁸ O. Dimroth and R. Schweizer, *Ber.*, 1923, 56, 1375.

diazonium carboxylate [from anthranilic acid (30 mmol)] in carbon disulphide (10 ml), acetone (15 ml), and methylene chloride (150 ml) was heated under reflux for 1 h. Evaporation, followed by chromatography of the residue, gave compound (2) (9.4%), m.p. 235—236°, and intractable tars.

Formation and Reactions of the Carbene (1) from Carbon Disulphide and Benzyne generated by Oxidation of 1-Aminobenzotriazole.—(a) *Without addition of a further reactant.* A solution of the triazole (6 mmol) in methylene chloride (30 ml) was added dropwise during 30 min to a stirred mixture of LTA (7 mmol), carbon disulphide (30 ml), and methylene chloride (60 ml). The inorganic precipitate was filtered off and the filtrate was evaporated; the residue was chromatographed on silica gel. Elution with carbon tetrachloride gave compound (3) (6%), m.p. 120°. Further elution gave a mixture of compound (4) (67%), m.p. 129—130°, and a product (30 mg) insoluble in chloroform, m.p. 152—154° (Found: C, 55.6; H, 3.1%). Final elution with carbon tetrachloride gave a yellow crystalline product (30 mg), m.p. 185—186°.

LTA (2.2 mmol) was added in portions during 5 min to a stirred suspension of the triazole in carbon disulphide (30 ml). The mixture was stirred for 30 min and was evaporated. Chromatography of the residue on silica gel gave a trace of compound (3) and an 86% yield of (4), m.p. 131—131.5°.

(b) *In the presence of NN-dimethylaniline.* LTA (2.2 mmol) was added in portions to a stirred mixture of the triazole (2 mmol), *NN*-dimethylaniline (2 mmol), carbon disulphide (10 ml), and methylene chloride (25 ml). After 30 min the mixture was evaporated. Ether (50 ml) was added to the residue and insoluble material was filtered off. The filtrate was extracted with 4*N*-HCl (2 × 25 ml). Work-up of the aqueous layer gave a crystalline product contaminated with *NN*-dimethylaniline, which was recrystallized from methanol to give 2-(4-dimethylaminophenyl)-1,3-benzodithiole (13) (15%), m.p. 117.5—118.5° (lit.,¹⁸ 116°).

(c) *In the presence of anisole.* LTA (1.1 mmol) was added in portions to a stirred mixture of the triazole (1 mmol), anisole (6 ml), and carbon disulphide (14 ml). After 30 min the precipitate was filtered off and the filtrate evaporated under reduced pressure. The residue was chromatographed on silica gel to give compound (4) (54%), m.p. 127—129°.

(d) *In the presence of methanol.* LTA (2.2 mmol) was added in portions to a stirred mixture of the triazole (2 mmol), carbon disulphide (20 ml), and methanol (20 ml). After 1 h the precipitate was filtered off and the filtrate was evaporated to leave a yellow oily residue, whose i.r. spectrum showed no absorption attributable to the Ph-O stretching

vibration of anisole. The oil was chromatographed on silica gel. Elution with carbon tetrachloride gave a trace of crystalline product and then compound (17) (78%), b.p. 145—150° at 4 mmHg.

(e) *In the presence of pyridine.* A solution of the triazole (2 mmol) in pyridine (5 ml) was added to a stirred mixture of LTA (2.2 mmol), pyridine (10 ml), and carbon disulphide (20 ml) at 0° during 30 min. The dark brown mixture was evaporated under reduced pressure after 30 min, and the residue chromatographed on silica gel. Elution with carbon tetrachloride gave a trace of a few unidentified products; elution with chloroform gave 1-aminobenzotriazole (40%) along with a considerable amount of intractable tar.

Reaction of Carbon Disulphide with Benzyne generated from 2-Carboxybenzenediazonium Chloride.—A suspension of the diazonium salt (10 mmol) in carbon disulphide (5 ml), propylene oxide (3 ml), and 1,2-dichloroethane (100 ml) was heated under reflux for 1 h. The red mixture was evaporated and the residue chromatographed on silica gel. Carbon tetrachloride eluted first a mixture of oily products having almost same R_F values (t.l.c.). Further elution gave compound (4) (7.3%), m.p. 129—131°.

Reaction of Carbon Disulphide with Benzyne generated from 1-(2-Carboxyphenyl)-3,3-dimethyltriazene.—(a) In a steel bomb the triazene (10 mmol) in carbon disulphide (50 ml) was heated at 175—185° for 2 h. The red mixture was evaporated to give oily residue. The i.r. spectrum showed carbonyl bands due to 1,2-benzodithiol-3-one (19) and 2,2'-dithiobis-(*NN*-dimethylbenzamide) (20). Chromatography of the oil on silica gel (elution with carbon tetrachloride) gave 1,2-benzodithiole-3-thione (18) (4.8%), m.p. 96—98° (lit.,²⁵ 94—95°), as red needles (from acetic acid), and then compound (19) (31%), m.p. 77—78° (lit.,^{26a} 77°), as yellow needles from (ethanol). Elution with acetone then gave compound (20) (28%), m.p. 128—129° (from benzene-ether) (lit.,²⁷ 128—129°).

In a steel bomb the triazene (10 mmol) in benzene (50 ml) and carbon disulphide (20 ml) was heated at 135—145° for 5 h. Chromatographic purification of the products gave compounds (18) (3.0%), m.p. 94—96°, (19) (4.2%), m.p. 77—78°, and (20) (31%), m.p. 128—129°.

(b) *In the presence of methanol.* In a steel bomb the triazene (10 mmol) in methanol (5 ml) and carbon disulphide (50 ml) was heated at 165—175° for 2 h. Chromatographic purification of the products gave compounds (18) (9.2%), m.p. 96—97°, (19) (21%), m.p. 77—78°, and (20) (20%), m.p. 128—129°.

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