

General Synthesis of Dibenzotetrathiafulvalenes

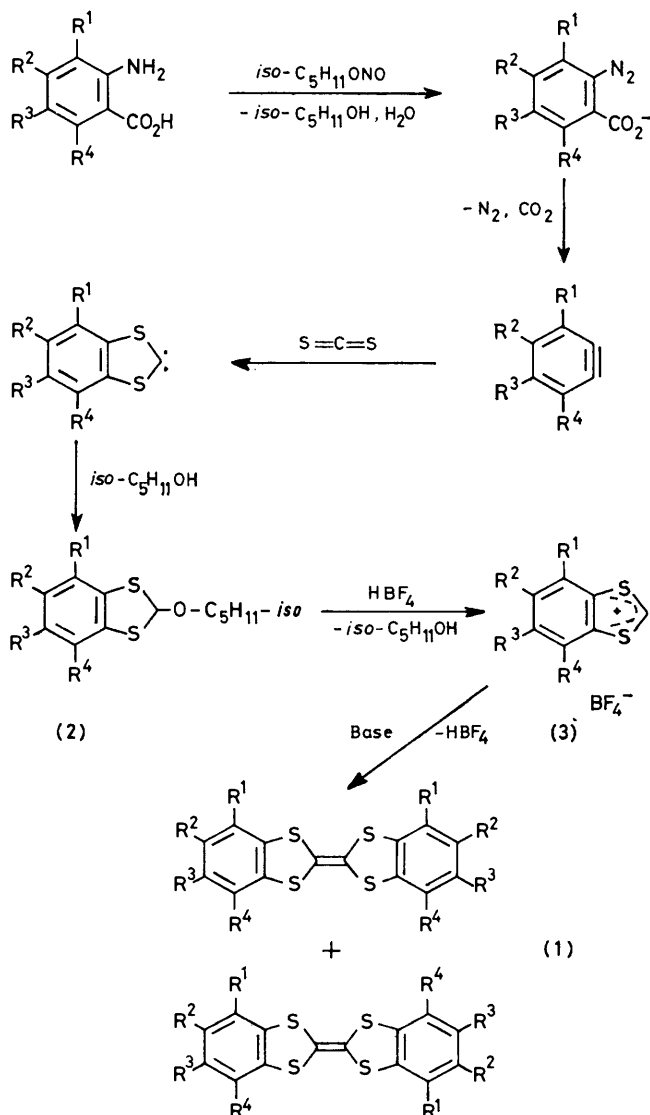
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A wide variety of dibenzotetrathiafulvalenes (1) were synthesized starting from anthranilic acids. Aprotic diazotization of anthranilic acids by isopentyl nitrite in the presence of carbon disulphide and isopentyl alcohol in boiling 1,2-dichloroethane gave 2-isopentoxy-1,3-benzodithioles (2). Compounds (2) were converted into 1,3-benzodithiolylium tetrafluoroborates (3) by treatment with tetrafluoroboric acid. Treatment of the salts (3) with base afforded tetrathiafulvalenes (1).

THE recent discovery of the highly conducting charge transfer salt of tetrathiafulvalene with 7,7,8,8-tetracyanoquinodimethane has prompted extensive investigation into convenient synthetic methods of tetrathiafulvalenes.¹ Dibenzotetrathiafulvalene (1a) has been prepared from various precursors which were derived in common from benzene-1,2-dithiol.² The synthesis of benzene-1,2-dithiol is, however, tedious.³ Recently a one-step synthesis of 2-isopentoxy-1,3-benzodithiole (2a) has been developed by one of us.⁴ Thus, compound (1a) can now be easily obtained by conversion of (2a) into 1,3-benzodithiolylium tetrafluoroborate (3a) with tetrafluoroboric acid and subsequent treatment of (3a) with base.^{2h,i} We have now extended this synthetic method to the preparation of a variety of dibenzotetrathiafulvalenes (1).

The synthesis of 2-isopentoxy-1,3-benzodithioles (2) consists of four steps: (a) aprotic diazotization of anthranilic acids by isopentyl nitrite to give benzene-diazonium-2-carboxylates, (b) thermal decomposition of the carboxylates to benzyne, (c) reaction of benzyne with carbon disulphide to lead to 1,3-benzodithiol-2-ylidenes, and (d) addition of isopentyl alcohol, resulting from the diazotization of anthranilic acids or added prior to the reactions, to the carbenes. This reaction was effected by addition of a solution of an anthranilic acid in dioxan to a stirred refluxing mixture of isopentyl nitrite, carbon disulphide, and isopentyl alcohol in 1,2-dichloroethane. 3-Amino-2-naphthoic acid is poorly soluble in dioxan and was dissolved in dimethyl sulph-

oxide instead of dioxan. 4-Nitroanthranilic acid is scarcely soluble in ordinary organic solvents and,



¹ M. Narita and C. U. Pittman, jun., *Synthesis*, 1976, 489.

² (a) W. R. H. Hurlley and S. Smiles, *J. Chem. Soc.*, 1926, 1821; 1926, 2263; (b) G. S. Pajwa, K. D. Berlin, and H. A. Pohl, *J. Org. Chem.*, 1976, **41**, 145; (c) S. Hünig, G. Kiesslich, H. Quast, and D. Scheutzow, *Annalen*, 1973, 310; (d) G. Scherowsky and J. Weiland, *ibid.*, 1974, 403; (e) J. Nakayama, *J.C.S. Perkin I*, 1975, 525; (f) J. Nakayama, *Synthesis*, 1975, 168; (g) D. Buza A. Gryff-Keller, and S. Szymański, *Roczniki Chem.*, 1970, **44**, 2319; (h) J. Nakayama, K. Fujiwara, and M. Hoshino, *Chem. Letters*, 1975, 1099; (i) J. Nakayama, K. Fujiwara, and M. Hoshino, *Bull. Chem. Soc. Japan*, 1976, **49**, 3567.

³ A. Ferretti, *Org. Synth.*, 1973, Coll. Vol. 4, 419; S. Hünig and E. Fleckenstein, *Annalen*, 1970, **738**, 192; I. Degani and R. Fochi, *Synthesis*, 1976, 471.

⁴ J. Nakayama, *Synthesis*, 1975, 38.

therefore, isopentyl nitrite dissolved in 1,2-dichloroethane was added to a refluxing mixture of the anthranilic acid, carbon disulphide, and isopentyl alcohol in 1,2-dichloroethane. Results are listed in Table 1. The yields of benzodithioles (2) are satisfactory. This indicates that a wide variety of benzyne can undergo

Treating the salts (3) with base gave dibenzotetra-thiafulvalenes in excellent yields. Results are listed in Table 4. Triethylamine is the most common base used for conversion of 1,3-dithiolium salts into tetrathiafulvalenes.¹ We have found that *NN*-dimethylformamide and 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU)

TABLE I
Synthesis of 2-isopentoxy-1,3-benzodithioles (2)

Compound	R ¹	R ²	R ³	R ⁴	Yield (%)	B.p. [°C (<i>p</i> /mmHg)] or M.p. (°C)	Found (%)			Formula	Required (%)		
							C	H	S		C	H	S
(2a)	H	H	H	H	50 ^a		61.1	7.05	24.9	C ₁₃ H ₁₆ OS ₂	61.4	7.15	25.15
(2b)	Me	H	H	H	65 ^b	129 (0.1)	61.1	7.05	24.9	C ₁₃ H ₁₆ OS ₂	61.4	7.15	25.15
(2c)	H	Me	H	H	35.5 ^c	131 (0.1)	60.9	6.9	25.1	C ₁₃ H ₁₆ OS ₂	61.4	7.15	25.15
(2d)	H	Cl	H	H	34 ^d	135 (0.5)	52.0	5.45	23.6	C ₁₂ H ₁₅ ClOS ₂	52.45	5.5	23.35
(2e)	H	I	H	H	49 ^e	50—51 ^g	39.35	4.1	17.5	C ₁₂ H ₁₅ IOS ₂	39.35	4.15	17.5
(2f)	H	NO ₂	H	H	46 ^f	62—64 ^g	50.25	5.2	22.4	C ₁₂ H ₁₅ NO ₃ S ₂	50.5	5.3	22.45
(2g)	H	-CH=CH-		H	24	86—87 ^g	66.5	6.0	22.4	C ₁₆ H ₁₈ OS ₂	66.2	6.25	22.05
(2h)	Cl	Cl	Cl	Cl	73	91—92 ^g	38.15	3.3	(Cl, 37.5)	C ₁₂ H ₁₂ Cl ₄ OS ₂	38.1	3.2	(Cl, 37.5)
(2i)	Br	Br	Br	Br	57	92—92.5 ^g	26.05	2.15	(Br, 57.55)	C ₁₂ H ₁₂ Br ₄ OS ₂	25.9	2.2	(Br, 57.5)

^a Yield reported in ref. 3. ^b From 3-methylantranilic acid. ^c From 5-methylantranilic acid. ^d From 4-chloroantranilic acid. ^e From 5-iodoantranilic acid. ^f From 4-nitroantranilic acid. ^g Recrystallized from *n*-hexane.

TABLE 2
Synthesis of 1,3-benzodithiolium tetrafluoroborates (3)

Compound	R ¹	R ²	R ³	R ⁴	Yield (%)	M.p. (°C) (decomp.)	Found (%)			Formula	Required (%)		
							C	H	S		C	H	S
(3a)	H	H	H	H	96 ^a	150—150.5 ^a				C ₈ H ₇ S ₂ BF ₄	37.75	2.95	25.2
(3b)	Me	H	H	H	92	150—152	37.6	2.8	25.6	C ₉ H ₇ S ₂ BF ₄	37.75	2.95	25.2
(3c)	H	Me	H	H	89	130—132	37.65	2.8	25.5	C ₉ H ₇ S ₂ BF ₄	37.75	2.95	25.2
(3d)	H	Cl	H	H	91	>200	30.6	1.5	23.75	C ₇ H ₄ ClS ₂ BF ₄	30.65	1.45	23.35
(3e)	H	I	H	H	87	>210	23.1	1.15	17.85	C ₇ H ₄ IS ₂ BF ₄	22.95	1.1	17.5
(3f)	H	NO ₂	H	H	79	>180	29.55	1.45	22.45	C ₇ H ₄ NO ₂ BF ₄	29.5	1.4	22.45
(3g)	H	-CH=CH-		H	88	>230	45.45	2.45	22.45	C ₁₁ H ₇ S ₂ BF ₄	45.55	2.45	22.1

^a From refs. 2*h* and *i*.

1,3-dipolar cycloaddition with carbon disulphide to give 1,3-benzodithiol-2-ylidenes and that isopentyl alcohol smoothly adds to these nucleophilic carbenes.

Benzodithioles (2) thus obtained, except the tetrachloro- and tetrabromo-derivatives, gave excellent yields of the corresponding 1,3-benzodithiolium tetrafluoroborates (3) by treatment with 42% tetrafluoroboric acid in acetic anhydride. The failure of the synthesis of the tetrachloro- and tetrabromo-1,3-benzodithiolium salts may be the result of destabilisation of the salts by the four strongly electronegative halogen substituents. Results are summarized in Table 2. The salts (3*f* and *g*) are pale yellow and the others are near white. I.r. spectra of (3) are characterized by a strong broad absorption at 1000—1100 cm⁻¹ due to the tetrafluoroborate anion. The C-2 protons of 5-substituted 1,3-benzodithiolium salts (3*c*—*f*) resonated in the region δ 11.41—12.00 in deuteriotrifluoroacetic acid depending upon the nature of the substituent on the benzene ring; the electron-donating methyl substituent gave a high-field shift and the strongly electron-withdrawing chloro- and nitro-substituents caused a low-field shift (Table 3).

are also useful for this conversion; DBU especially gave excellent results. Dibenzotetra-thiafulvalenes (1) are scarcely soluble in organic solvents [compounds (1*b*

TABLE 3

¹H N.m.r. data for 1,3-benzodithiolium tetrafluoroborates (3)^a

Compound	2-H	ArH
(1a)	11.50	8.06—8.26, 8.66—8.86 (4 H, AA'XX'm) ^b
(1b)	11.58	7.8—8.3 (2 H, m), 8.6 (1 H, dd), 3.10 (3 H, s, Me)
(1c)	11.41	8.00 (1 H, dd), 8.5—8.7 (2 H, m), 2.80 (3 H, s, Me)
(1d)	11.59	8.15 (1 H, dd), 8.6—8.9 (2 H, m)
(1e)	11.48	8.45br (2 H, s), 9.15br (1 H, s)
(1f)	12.00	8.8—9.2 (2 H, m), 9.75 (1 H, m)
(1g)	11.60	7.8—8.5 (4 H, AA'BB'm), 9.28 (2 H, s)

^a δ Values. Deuteriotrifluoroacetic acid as solvent. ^b From refs. 2*h* and *i*.

and *c*) are soluble in carbon disulphide]. In all cases reported here except (1*g*), the formation of both *Z*- and *E*-isomers would be expected. In the ¹H n.m.r. spectra, the methyl proton signals of (1*b* and *c*) appeared at

δ 2.26 and 2.29,* respectively, as only one sharp singlet in carbon disulphide (the aromatic protons of both compounds resonated at δ 6.9—7.2 as complex multiplets). It may be the case that the chemical shift of the methyl protons of the *Z*- and *E*-isomers are identical rather than that a single isomer is formed preferentially.

EXPERIMENTAL

¹H N.m.r. spectra were recorded with a Varian A60 instrument (tetramethylsilane as internal reference). I.r. spectra were recorded for Nujol mulls with a JASCO

carbon disulphide (24 ml), and isopentyl alcohol (2.5 g) in 1,2-dichloroethane (300 ml) and then refluxing the mixture for 0.5 h (the resulting mixture was treated as described above).

In the case of the benzodithiole (2f), isopentyl nitrite (8.6 g, 74 mmol) dissolved in 1,2-dichloroethane (30 ml) was added dropwise to a refluxing mixture of 4-nitroanthranilic acid (11.3 g, 60 mmol), carbon disulphide (30 ml), and isopentyl alcohol (10.8 g) in 1,2-dichloroethane (250 ml) over a period of 1.5 h and the mixture was refluxed for 2 h.

1,3-Benzodithiolylium Tetrafluoroborates (3).—To a stirred and ice-cooled solution or suspension of benzodithioles

TABLE 4

Synthesis of dibenzotetrathiafulvalenes (1)

Compound ^a	R ¹	R ²	R ³	R ⁴	Yield (%)	Base	M.p. (°C) ^b	Formula	Analysis (%) ^c		
									C	H	S
(1a)	H	H	H	H	81 ^d	Et ₃ N					
(1b)	Me	H	H	H	94	Et ₃ N	248—249 ^e	C ₁₆ H ₁₂ S ₄	57.55	3.65	38.1
					67	DMF ^f			(57.85	3.65	38.5)
(1c)	H	Me	H	H	67	DMF	260—262 ^g	C ₁₆ H ₁₂ S ₄	57.75	3.7	38.3
(1d)	H	Cl	H	H	88	Et ₃ N	315—318	C ₁₄ H ₆ Cl ₂ S ₄	45.1	1.65	34.3
									(45.05	1.65	34.3)
(1e)	H	I	H	H	95	DBU ^h	303—304	C ₁₄ H ₆ I ₂ S ₄	30.45	1.1	23.15
									(30.25	1.1	23.05)
(1f)	H	NO ₂	H	H	60	Et ₃ N	366—360 (decomp.)	C ₁₄ H ₆ N ₂ O ₄ S ₄	42.65	1.6	N, 7.0
									(42.65	1.55	N, 7.1)
(1g)	H	—CH=CH—CH=CH—		H	88	Et ₃ N	>400	C ₂₂ H ₁₂ S ₄	65.45	3.1	31.45
					99	DBU			(65.35	3.0	31.65)

^a Compound (1f) is russet and the others are yellow. ^b Recrystallized from pyridine. Compound (1g) did not dissolve in hot solvents and could not be purified by recrystallization (crude product gave satisfactory elemental analysis). ^c Required values in parentheses. ^d From refs. 2h and i. ^e Recrystallization from pyridine gave a mixture of long yellow needles and granules; these had identical m.p.s. Recrystallization of the needles also gave a mixture of needles and granules. ^f DMF = *NN*-dimethylformamide. ^g Lit.^{2b} m.p. 260—262°. ^h DBU = 1,8-diazabicyclo[5,4,0]undec-7-ene.

IRA-2 instrument. Tetrachloro- and tetrabromo-anthranilic acids ⁵ and 2-amino-3-naphthoic acid ⁶ were prepared by literature methods and other anthranilic acids were commercial materials and were used without further purifications.

2-Isopentoxo-1,3-benzodithioles (2).—To a stirred and gently refluxed solution of isopentyl nitrite (7.6 g, 70 mmol), carbon disulphide (27 ml), and isopentyl alcohol (9.1 g) in 1,2-dichloroethane (200 ml) was added dropwise a solution of 3-methylanthranilic acid (8.3 g, 55 mmol) in dioxan (30 ml) over a period of 40 min. After the addition was completed, the red mixture was refluxed for 30 min. The solvents and excess of reagents were removed under reduced pressure. The residue dissolved in ether (200 ml) was washed successively with water, aqueous sodium carbonate, and water and dried (Na₂SO₄). The ether was evaporated and the residue was distilled to give the dithiole (2b) (9.1 g, 65%) as a viscous pale yellow oil, b.p. 129° at 0.1 mmHg. Dithioles (2c—e, h, and i) were prepared in similar ways.

The dithiole (2g) was prepared by adding a solution of 3-amino-2-naphthoic acid (2.55 g, 13.6 mmol) in dimethyl sulphoxide (15 ml) dropwise over a period of 1.5 h to a refluxing solution of isopentyl nitrite (2.0 g, 17 mmol),

* Berlin *et al.* have reported that compound (2c), prepared by condensation of 4-methylbenzene-1,2-dithiol with tetrachloroethylene, exhibits only one sharp singlet resonance peak for methyl protons at δ 1.65 in deuteriochloroform.^{2b} However, the methyl proton signal of our compound appeared at δ 2.30 in deuteriochloroform. Berlin's value must be erroneous since the chemical shift for methyl protons attached to a benzene ring generally occurs in the range δ 1.7—2.5.⁵

(2) (10 mmol) in acetic anhydride (30 ml) was added dropwise 42% tetrafluoroboric acid (4.3 g, 22 mmol) over 15 min. In most cases, a crystalline product began to precipitate near the end point of the addition. After being stirred for 30 min at room temperature, anhydrous ether (60 ml) was added to the mixture to precipitate the product completely. The precipitate was collected and washed with anhydrous ether (20 ml). The salts (3) thus obtained gave satisfactory elemental analyses and were used for the synthesis of dibenzotetrathiafulvalenes (1) without further purification. However, they must be protected from moisture and light if not required for immediate use. Benzodithioles (2h and i) gave unidentified products (having a carbonyl absorption at 1730 cm⁻¹) by the procedure described above, the expected fluoroborate salts not being obtained. Benzodithiole (2i) also did not give the expected salt by treatment with trityl tetrafluoroborate in acetonitrile [we have recently reported the synthesis of 1,3-benzodithiolylium tetrafluoroborate (3a) by treatment of 2-isopentoxo-1,3-benzodithiole (2a) with trityl tetrafluoroborate in acetonitrile⁶].

Dibenzotetrathiafulvalenes (1).—(a) *Triethylamine and DBU as base.* To a stirred solution of fluoroborate salts (3) (5 mmol) in anhydrous acetonitrile (15 ml) was added triethylamine (1 ml) or DBU (1 ml) at room temperature. Immediately a crystalline product precipitated. After

⁵ N. F. Chamberlain, 'The Practice of N.M.R. Spectroscopy,' Plenum Press, New York and London, 1974, p. 123.

⁶ J. Nakayama, K. Fujiwara, M. Imura, and M. Hoshino, *Chem. Letters*, 1977, 127.

being stirred for 0.5 h, the product was collected, washed with benzene (10 ml), and recrystallized.

(b) *NN-Dimethylformamide as base*. The fluoroborate salt (3b) (1.27 g, 5 mmol) was dissolved in anhydrous *NN*-dimethylformamide (15 ml) and allowed to stand at room temperature. After *ca.* 5 min, yellow crystals of the

dibenzotetrathiafulvalene (1b) began to precipitate. After 2 h the product was collected and washed with benzene (10 ml). The dibenzotetrathiafulvalene (1c) was prepared from the salt (3c) in a similar way.

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