

Condensed Thiophen Ring Systems. Part XI.¹ Synthesis of 2-Aryl[1]-benzothieno[3,2-*c*]pyrazoles and 2-Aryl[1]benzothieno[2,3-*c*]pyrazoles²

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2-Aryl[1]benzothieno[3,2-*c*]pyrazoles were prepared by reductive cyclisation of the corresponding *N*-(3-nitrobenzo[*b*]thiophen-2-ylidene)anilines with triethyl phosphite (20–30% yields) and by thermolysis in bis-(2-methoxyethyl) ether of the corresponding *N*-(3-azidobenzo[*b*]thiophen-2-ylidene)anilines (70–75% yields). Treatment of *N*-(2-nitrobenzo[*b*]thiophen-3-ylidene)anilines with triethyl phosphite gave mixtures of the corresponding 2-aryl[1]benzothieno[2,3-*c*]pyrazoles and benzo[*b*]thiophen-3-carbonitrile, whilst pyrolysis of *N*-(2-azidobenzo[*b*]thiophen-3-ylidene)aniline in bis-(2-methoxyethyl) ether gave a mixture of 2-phenyl[1]benzothieno[2,3-*c*]pyrazole and the anil of 2,3-dihydro-2-oxobenzo[*b*]thiophen-3-carbonitrile. Mechanistic aspects are discussed.

CONDENSATIONS of 3-nitrobenzo[*b*]thiophen-2-carbaldehyde and 2-nitrobenzo[*b*]thiophen-3-carbaldehyde with aniline, *o*-chloroaniline, and *p*-anisidine gave high yields of the anils (1) and (2) ($R^1 = \text{NO}_2$, $R^2 = \text{H}$, *o*-Cl, or *p*-OMe) (Table 1). By analogy with the synthesis of indazoles^{3,4} we prepared the 2-aryl[1]benzothieno[3,2-*c*]pyrazoles (3; $R = \text{H}$, *o*-Cl, *p*-OMe, or *p*-NMe₂) in moderate yields (20–30%) (Table 3) by reductive cyclisation of the anils (1; $R^1 = \text{NO}_2$, R^2 as before) with triethyl phosphite. A higher yield (45%) of 2-phenyl[1]benzothieno[3,2-*c*]pyrazole (3; $R = \text{H}$) was obtained when the anil (1; $R^1 = \text{NO}_2$, $R^2 = \text{H}$) was heated with triphenylphosphine in *p*-cymene.

In contrast, reductive cyclisation of the anils (2;

$R^1 = \text{NO}_2$, $R^2 = \text{H}$, *o*-Cl, *p*-OMe, or *p*-NMe₂) with triethyl phosphite gave in each case a mixture of a 2-aryl[1]benzothieno[2,3-*c*]pyrazole (4; $R = \text{H}$, *o*-Cl, *p*-OMe, or *p*-NMe₂) and benzo[*b*]thiophen-3-carbonitrile (8) (Scheme 1). The yield of the benzothieno[2,3-*c*]pyrazole (4) was highest (see Table 4), as expected, when the anil (2; $R^1 = \text{NO}_2$) carried an electron-donating substituent (*p*-OMe or *p*-NMe₂) and lowest with an electron-withdrawing substituent (2; $R^1 = \text{NO}_2$, $R^2 = \text{o-Cl}$). The yields (Table 4) of benzo[*b*]thiophen-3-carbonitrile (8) varied inversely with the yield of the benzothienopyrazole. These facts suggest that a nitrene is formed initially, which can either undergo an insertion reaction or a secondary reaction leading to the nitrile (see later).

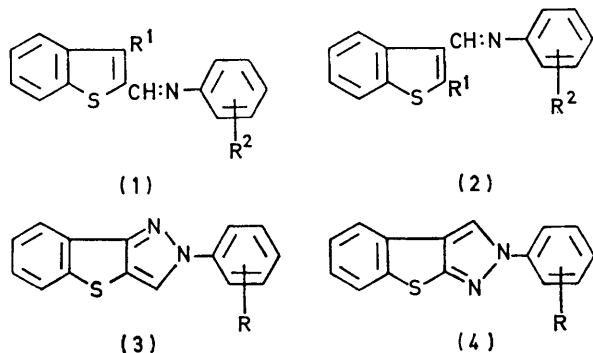
¹ Part X, K. E. Chippendale, B. Iddon, and H. Suschitzky, preceding paper.

² Presented at The Chemical Society Annual Meeting (Heterocyclic Section), Manchester, 10–14th April, 1972, abstract no. 9.9.

³ L. Krbeček and H. Takimoto, *J. Org. Chem.*, 1964, **29**, 1150 and 3630.

⁴ J. I. G. Cadogan, M. Cameron-Wood, R. K. Makie, and R. J. G. Searle, *J. Chem. Soc.*, 1965, 4831.

Higher yields (70–75%) (Table 3) of the 2-aryl-[1]benzothieno[3,2-*c*]pyrazoles (3; R = H, *o*-Cl, *p*-OMe, or *p*-NMe₂) were obtained by thermal decomposition of the azido-anils (1; R¹ = N₃, R² = H, *o*-Cl, *p*-OMe, or

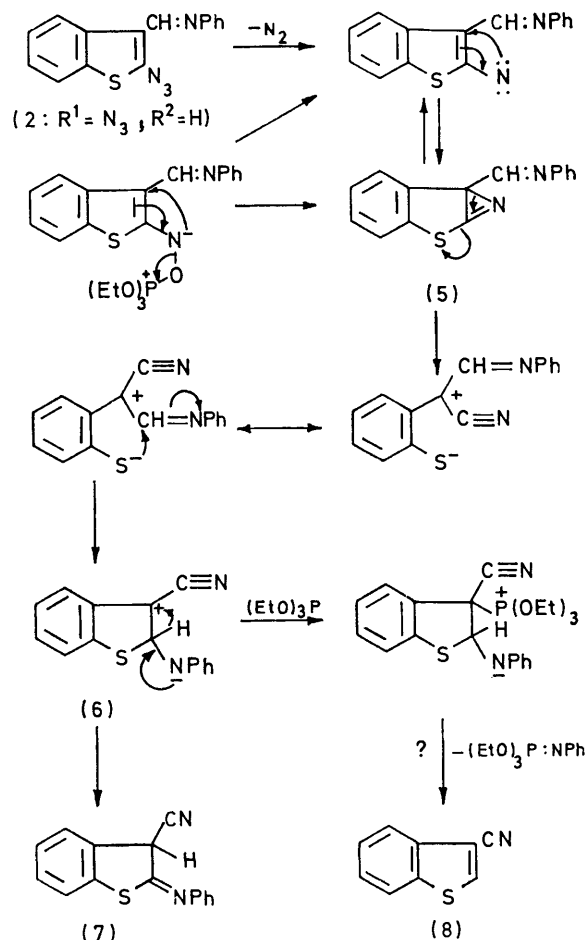


p-NMe₂) (Table 2) in bis-(2-methoxyethyl) ether. These anils were prepared through reduction of 3-nitrobenzo[*b*]thiophen-2-carbaldehyde with iron and aqueous ammonium chloride, diazotisation of the 3-aminobenzo[*b*]thiophen-2-carbaldehyde produced, treatment of the diazonium compound with sodium azide, and condensation of the resulting 3-azidobenzo[*b*]thiophen-2-carbaldehyde with the appropriate primary aromatic amine.

N-(2-Azidobenzo[*b*]thiophen-3-ylidene)aniline (2; R¹ = N₃, R² = H) was prepared similarly and decomposed thermally in bis-(2-methoxyethyl) ether. However, this gave a mixture of 2-phenyl[1]benzothieno[2,3-*c*]pyrazole (4; R = H) (7% yield) and the anil (7) (Scheme 1) whose structure followed from its spectroscopic properties. Thus, in the i.r. spectrum it had a strong absorption at 2220 cm⁻¹ (C≡N), but no band which could be assigned to an N-H bond, which excludes its tautomer. Similarly, we could not detect any NH signal in the n.m.r. spectrum of this compound and deuteration of the sample did not change the spectrum. Although 2-hydroxybenzo[*b*]thiophens, including the 3-formyl derivative of thio-oxindole, normally exist as their keto-tautomers, there have been no reports of a 2-aminobenzo[*b*]thiophen existing as an imine.⁵

The formation of benzo[*b*]thiophen-3-carbonitrile (8) on reductive cyclisation of the anils (2; R¹ = NO₂, R² as before) with triethyl phosphite and the formation of the anil (7) of 2,3-dihydro-2-oxobenzo[*b*]thiophen-3-carbonitrile on thermal decomposition of the anil (2; R¹ = N₃, R² = H) in bis-(2-methoxyethyl) ether suggests to us a common intermediate. This may be the azirine (5) (Scheme 1) formed from the azido-anil (2; R¹ = N₃, R² = H) *via* a nitrene, as shown, or from the corresponding nitro-compound (2; R¹ = NO₂, R² = H) either directly or indirectly, as shown (Scheme 1). Successive ring opening and ring closure of the common intermediate (5) followed by a prototropic shift in the resulting dipolar species (6) yields the anil (7), whilst formation of the nitrile (8) in the presence of triethyl phosphite can be explained by reaction of the dipolar species (6) with the reagent, to give

another dipolar species, which is capable of undergoing a Wittig-type elimination reaction. The formation of the nitrile (8) from the nitro-anils (2; R¹ = NO₂, R² = *o*-Cl, *p*-OMe, or *p*-NMe₂) is also accounted for by this Scheme. When 2-phenyl[1]benzothieno[2,3-*c*]pyrazole (4; R = H) is heated in bis-(2-methoxyethyl)



SCHEME 1

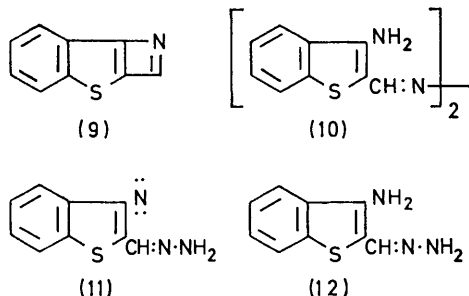
ether or triethyl phosphite, it remains unchanged. Thus, the anil (7) and the nitrile (8) are formed by secondary reactions. The anil (7) is not converted into benzo[*b*]thiophen-3-carbonitrile (8) on treatment with triethyl phosphite, which suggests that the latter is formed from another precursor, as shown in Scheme 1.

Attempts to convert the hydrazone of 3-azidobenzo[*b*]thiophen-2-carbaldehyde into the benzothioazete (9) by treatment with yellow mercuric oxide in ether heated under reflux and in benzene at 0 or 40° or under reflux gave only tars and starting material. The hydrazone was unstable at about 85° and darkened on exposure to light.

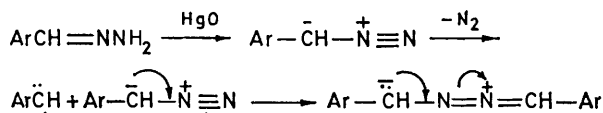
In an attempt to prepare 2-amino[1]benzothieno[3,2-*c*]pyrazole, we pyrolysed and photolysed the hydrazone in toluene. Besides tar, these reactions gave comparable yields (40%) of a compound to which we

⁵ B. Iddon and R. M. Scrowston, *Adv. Heterocyclic Chem.*, 1970, **11**, 177.

assign the azine structure (10) on the basis of its spectroscopic properties. An accurate mass measurement showed it to have the molecular formula $C_{18}H_{14}N_4S_2$, and i.r. bands at 3340 and 3260 cm^{-1} and a four-proton



n.m.r. signal at τ 3.14 which collapsed on deuteration confirmed the presence of two amino-groups. The methine proton signal (τ 0.81) was consistent with the proposed structure. Acetylation gave a diacetyl derivative with the expected spectroscopic properties. The formation of compound (10) can be rationalised by initial formation of the hydrazone (12) *via* the nitrene (11) followed by reaction with mercuric oxide as set out in Scheme 2. The formation of azines in this way has been observed previously.^{6,7}



SCHEME 2 (Ar = 3-amino-2-benzo[b]thienyl)

EXPERIMENTAL

Most of the spectroscopic instruments used and the precautions taken were described in Part VIII.⁸ The n.m.r. signals reported were singlets, unless stated otherwise. Molecular weights were determined by mass spectrometry; accurate mass measurements were determined on a G.E.C.-A.E.I. MS9 instrument.

Light petroleum refers to the fraction of b.p. 60–80°. The preparations of 3-nitrobenzo[b]thiophen-2-carbaldehyde, 2-nitrobenzo[b]thiophen-3-carbaldehyde, *p*-dimethylamino-*N*-(3-nitrobenzo[b]thiophen-2-ylidene)aniline, and *p*-dimethylamino-*N*-(2-nitrobenzo[b]thiophen-3-ylidene)aniline were described in Part X.¹

3-Aminobenzo[b]thiophen-2-carbaldehyde.—A solution of 3-nitrobenzo[b]thiophen-2-carbaldehyde (10.0 g, 48.3 mmol) in ethanol (50 ml) was added dropwise to a stirred mixture of ammonium chloride (10.5 g, 196 mmol), iron powder (10.5 g, 0.19 g atom), and water (100 ml) at room temperature, and the mixture was then heated under reflux with vigorous stirring for 3 h. Extraction with ether gave a product which was chromatographed on alumina. Chloroform eluted 3-aminobenzo[b]thiophen-2-carbaldehyde (4.6 g, 54%), m.p. 118–120° (sublimed, 110° at 1.0 mmHg), ν_{max} (Nujol) 3460, 3400, 3345, and 3230 cm^{-1} (NH_2) (multiplicity attributed to hydrogen bonding) and 1580 cm^{-1} (C:O), τ (CDCl_3) 0.20 (CHO), 2.10–2.73 (m, aromatic),

⁶ H. Reimlinger, *Chem. Ber.*, 1964, **97**, 339.

⁷ G. V. Garner, D. Mobbs, H. Suschitzky, and J. S. Millership, *J. Chem. Soc. (C)*, 1971, 3693.

and 3.35br (exchangeable, NH_2) (Found: C, 60.6; H, 3.9; N, 8.0%; *M*, 177. $\text{C}_9\text{H}_7\text{NOS}$ requires C, 61.0; H, 4.0; N, 7.9%; *M*, 177). Elution with other solvents gave intractable materials.

2-Aminobenzo[b]thiophen-3-carbaldehyde (58%) was prepared similarly. In this case, however, after the reaction was complete, the mixture was filtered hot. On cooling the filtrate, the product precipitated. It had m.p. 73–77° (sublimed, 100° at 1.0 mmHg), ν_{max} 3350, 3270, 3140, and 3070 cm^{-1} (NH_2) (multiplicity attributed to hydrogen bonding) and 1635 cm^{-1} (C:O), τ (CDCl_3) 0.80br (exchangeable, NH_2) and 2.10–2.90 (m, aromatic and aldehyde CHO) (integration ratio 2:5) (Found: C, 60.8; H, 4.0; N, 7.65%; *M*, 177).

3-Azidobenzo[b]thiophen-2-carbaldehyde.—Sodium nitrite (0.5 g, 6.33 mmol) was added in small portions to a stirred mixture of 3-aminobenzo[b]thiophen-2-carbaldehyde (1.1 g, 6.2 mmol) and 5*N*-hydrochloric acid (10 ml) at 0°, and the mixture was stirred at 0° for 30 min. It was then filtered and the filtrate was added dropwise to a stirred solution of sodium azide (0.5 g, 7.7 mmol) and sodium acetate (5.0 g, 61.0 mmol) in water (10 ml) at 0°. The resulting mixture was stirred at 0° for a further 1 h. The precipitate was filtered off and dried in air to give 3-azidobenzo[b]thiophen-2-carbaldehyde (0.8 g, 64%), m.p. 88–90° (decomp.), ν_{max} (Nujol) 2110s (N_3) and 1650 cm^{-1} (C:O) (Found: C, 53.45; H, 2.9; N, 20.6%; *M*, 203. $\text{C}_9\text{H}_5\text{N}_3\text{OS}$ requires C, 53.2; H, 2.5; N, 20.7%; *M*, 203).

2-Azidobenzo[b]thiophen-3-carbaldehyde (83%), prepared similarly, had m.p. 91–94° (decomp.), ν_{max} (Nujol) 2140s (N_3) and 1680 cm^{-1} (C:O). This azide rapidly darkened on exposure to light. It was therefore used immediately, as described later.

***N*-(3-Nitrobenzo[b]thiophen-2-ylidene)anilines** and ***N*-(2-Nitrobenzo[b]thiophen-3-ylidene)anilines.**—*General method.* A primary aromatic amine (1.1 equiv.) was added in small portions to a stirred solution of 3-nitrobenzo[b]thiophen-2-carbaldehyde or 2-nitrobenzo[b]thiophen-3-carbaldehyde (1.0 equiv.) in ethanol (10 ml g^{-1}) heated under reflux. The resulting mixture was then kept at room temperature for 4 h and the *anil* was filtered off, dried in air, and recrystallised from light petroleum. Details of the products are given in Table 1.

***N*-(3-Azidobenzo[b]thiophen-2-ylidene)anilines.**—*General method.* A primary aromatic amine (1.1 equiv.) was added in small portions to a stirred solution of 3-azidobenzo[b]thiophen-2-carbaldehyde (1.0 equiv.) in ethanol (10 ml g^{-1}) at 50°, and the mixture was then kept at room temperature for 4 h. The *anil* was filtered off and dried in air. A sample was recrystallised from light petroleum for microanalysis. Data for the products are given in Table 2.

***N*-(2-Azidobenzo[b]thiophen-3-ylidene)aniline** (57%), prepared similarly, had m.p. 62–65° (from light petroleum), ν_{max} (Nujol) 2110 cm^{-1} (N_3). This *anil* was unstable and was used immediately, as described later.

2-Aryl[1]benzothieno[3,2-*c*]pyrazoles.—(i) *Method A* (Table 3). A mixture of the *N*-(3-nitrobenzo[b]thiophen-2-ylidene)aniline (1.0 equiv.) and triethyl phosphite (8.0 equiv.) was heated under reflux for 4 h. The excess of triethylphosphite and the triethyl phosphate produced were distilled off at 0.1 mmHg and the residue was chromatographed on alumina. Ether–light petroleum (1:1) eluted the products. Details are given in Table 3.

⁸ Part VIII, K. E. Chippendale, B. Iddon, and H. Suschitzky, *J.C.S. Perkin I*, 1972, 2023.

(ii) *Method B* (Table 3). A solution of the *N*-(3-azido-benzo[*b*]thiophen-2-ylidene)aniline in bis-(2-methoxyethyl) ether (5% w/v) was heated under reflux for 1 h. The solvent was distilled off under reduced pressure and the residue was chromatographed on alumina. Ether-light

reflux for 6 h. The solvent was distilled off at 0.1 mmHg and the residue was chromatographed on alumina. Ether-light petroleum (1:1) eluted 2-phenyl[1]benzothieno[3,2-*c*]pyrazole (0.4 g, 45%), identical (m.p., i.r. and n.m.r. spectra) with the samples prepared as described in (i)

TABLE 1
N-(3-Nitrobenzo[*b*]thiophen-2-ylidene)anilines and *N*-(2-nitrobenzo[*b*]thiophen-3-ylidene)anilines

Compound	M.p. (°C)	Yield (%)	Chemical shifts (τ) ^a				Found (%)			Formula	Required (%)		
			CH:N	4-H	Me	Other	C	H	N		C	H	N
(1; R ¹ = NO ₂ , R ² = H)	151—153	77	0.54	1.45(m)		2.00—2.73(m)	63.5	3.7	10.1	C ₁₅ H ₁₀ N ₂ O ₂ S	63.8	3.6	9.9
(1; R ¹ = NO ₂ , R ² = <i>o</i> -Cl)	144—146	69	0.54	1.35(m)		2.00—2.60(m)	57.0	2.9	9.1	C ₁₅ H ₉ ClN ₂ O ₂ S	56.9	2.9	8.85
(1; R ¹ = NO ₂ , R ² = <i>p</i> -OMe)	143—145	86	0.54	1.45(m)	6.14	2.00—3.15(m)	61.1	3.9	9.15	C ₁₆ H ₁₂ N ₂ O ₃ S	61.5	3.9	9.0
(2; R ¹ = NO ₂ , R ² = H)	125—127	77	0.60	0.90(m)		1.75—2.73(m)	63.4	3.8	9.75	C ₁₅ H ₁₀ N ₂ O ₂ S			
(2; R ¹ = NO ₂ , R ² = <i>o</i> -Cl)	161—163	89	0.55	0.67(m)		2.05—2.85(m)	56.6	3.1	8.9	C ₁₅ H ₉ ClN ₂ O ₂ S			
(2; R ¹ = NO ₂ , R ² = <i>p</i> -OMe)	125—126	80	0.49	0.84(m)	6.18	2.05—3.15(m)	61.8	4.0	8.8	C ₁₆ H ₁₂ N ₂ O ₃ S			

^a Solvent CDCl₃.

TABLE 2
N-(3-Azidobenzo[*b*]thiophen-2-ylidene)anilines

Compound	M.p. ^a (°C)	Yield %	ν _{max.} (N ₃) (cm ⁻¹)	Found (%)			Formula	Required (%)		
				C	H	N		C	H	N
(1; R ¹ = N ₃ , R ² = H)	92—96	88	2100 ^d	64.9	3.3	20.1	C ₁₅ H ₁₀ N ₄ S	64.7	3.6	20.1
(1; R ¹ = N ₃ , R ² = <i>o</i> -Cl)	88—90	58	2100 ^e	57.7	3.2	17.7	C ₁₅ H ₉ ClN ₄ S	57.7	2.9	17.9
(1; R ¹ = N ₃ , R ² = <i>p</i> -OMe)	107—110 ^b	63	2100	62.8	3.9	18.0	C ₁₆ H ₁₂ N ₄ OS	62.3	3.9	18.2
(1; R ¹ = N ₃ , R ² = <i>p</i> -NMe ₂)	109—114 ^c	77	2100							

^a With decomposition. ^b Analysed immediately following its preparation. ^c This anil was too unstable for an accurate analysis to be obtained; each anil was used immediately following its preparation. ^d τ (CDCl₃) 1.10 (CH:N). ^e τ (CDCl₃) 1.17 (CH:N).

TABLE 3
2-Aryl[1]benzothieno[3,2-*c*]pyrazoles

Compound	M.p. (°C)	Yield (%) ^a		Chemical shifts ^b				Found (%)			Required (%)			
		Method A	Method B	3-H	8-H	Me	Other	C	H	N	Formula	C	H	N
(3; R = H)	102—104	27	72	1.90	1.76(m)		2.05—2.73(m)	71.9	4.0	11.3	C ₁₅ H ₁₀ N ₂ S	72.0	4.0	11.2
(3; R = <i>o</i> -Cl)	108—110	28	75	1.92	1.75(m)		2.06—2.73(m)	63.45	3.2	9.8	C ₁₆ H ₉ ClN ₂ S	63.25	3.2	9.8
(3; R = <i>p</i> -OMe)	139—141	30	66	2.00	1.75(m)	6.13	2.05—3.05(m)	68.6	4.5	10.0	C ₁₆ H ₁₂ N ₂ OS	68.55	4.3	10.0
(3; R = <i>p</i> -NMe ₂)	197—199	23	69	2.06	1.79(m)	7.00	2.10—3.30(m)	69.7	5.3	14.2	C ₁₇ H ₁₅ N ₃ S	69.6	5.2	14.3

^a Method A, from 3-nitro-anil; Method B, from 3-azido-anil. ^b Solvent CDCl₃.

TABLE 4
Products from the reactions of *N*-(2-nitrobenzo[*b*]thiophen-3-ylidene)anilines with triethyl phosphite
2-Aryl[1]benzothieno[2,3-*c*]pyrazoles

Starting material	Yield (%) of benzo[<i>b</i>]thiophen-3-carbonitrile	M.p. (°C) ^a	Yield (%)	Chemical shifts ^b			Found (%) ^c		
				3-H	Me	Other	C	H	N
(2; R ¹ = NO ₂ , R ² = H)	30	115—117	25	1.75		1.95—2.73(m)	71.95	4.0	11.1
(2; R ¹ = NO ₂ , R ² = <i>o</i> -Cl)	69	98—100	19	1.70		1.95—2.73(m)	63.6	3.4	10.0
(2; R ¹ = NO ₂ , R ² = <i>p</i> -OMe)	20	166—168	43	1.75	6.18	2.05—3.05(m)	68.7	4.5	9.8
(2; R ¹ = NO ₂ , R ² = <i>p</i> -NMe ₂)	Trace	174—176	42	1.80	7.00	2.10—3.00(m)	69.2	5.4	14.7

^a From light petroleum, except compound (2; R¹ = NO₂; R² = *p*-NMe₂), which was recrystallised from benzene-light petroleum (1:1). ^b Solvent CDCl₃. ^c For required figures see Table 3.

petroleum (1:1) eluted the product. Details are given in Table 3.

(iii) A mixture of *N*-(3-nitrobenzo[*b*]thiophen-2-ylidene)aniline (1.09 g, 3.87 mmol), triphenylphosphine (2.05 g, 7.83 mmol), and dry *p*-cymene (5 ml) was heated under

and (ii). Chloroform eluted triphenylphosphine oxide (1.85 g, 85%).

Reactions of N-(2-Nitrobenzo[*b*]thiophen-3-ylidene)anilines with Triethyl Phosphite.—*General method.* A mixture of the *N*-(2-nitrobenzo[*b*]thiophen-3-ylidene)aniline (1.0 equiv.)

and triethyl phosphite (8.0 equiv.) was heated under reflux for 4 h. Work-up in the usual manner gave a residue which was chromatographed on alumina. Light petroleum eluted benzo[b]thiophen-3-carbonitrile (yields given in Table 4), m.p. 69—71° (from light petroleum) (lit.,⁹ 71.5—72.5°), ν_{\max} 2215 cm⁻¹ (C:N), and ether-light petroleum (1:1) eluted the 2-aryl[1]benzothieno[2,3-*c*]pyrazole. Further details are given in Table 4.

Thermal Decomposition of N-(2-Azidobenzo[b]thiophen-3-ylidene)aniline.—A solution of the anil (0.8 g, 2.88 mmol) in bis-(2-methoxyethyl) ether (40 ml) was heated under reflux for 1 h. The solvent was distilled off and the residue chromatographed on alumina. Light petroleum eluted 2,3-dihydro-2-phenyliminobenzo[b]thiophen-3-carbonitrile (0.4 g, 56%), m.p. 121—122° (from light petroleum), ν_{\max} (Nujol) 2220s cm⁻¹ (C:N), τ (CDCl₃) 2.36—3.08 (m, aromatic and CH) (no change in spectrum on deuteration) (Found: C, 71.8; H, 4.0; N, 11.3%; *M*, 250). C₁₅H₁₀N₂S requires C, 72.0; H, 4.0; N, 11.2%; *M*, 250). Light petroleum-ether (1:1) eluted 2-phenyl[1]benzothieno[2,3-*c*]pyrazole (0.05 g, 7%), identical (m.p., i.r. and n.m.r. spectra) with the sample prepared as described before (Table 4).

3-Azidobenzo[b]thiophen-2-carbaldehyde Hydrazone.—A mixture of the aldehyde (1.0 g, 4.93 mmol) and hydrazine hydrate (0.61 g, 12.2 mmol) in ethanol (10 ml) was heated at 50°, then cooled and kept at room temperature for 1 h. The product (0.90 g, 88%) was filtered off and dried in air. It had m.p. 84—86° (decomp.), ν_{\max} (Nujol) 2110 cm⁻¹ (N₃) and, since it proved unstable to light, was used immediately.

Thermal Decomposition of 3-Azidobenzo[b]thiophen-2-carbaldehyde Hydrazone.—A solution of the hydrazone (0.90 g, 4.15 mmol) in dry toluene (3 ml) was added dropwise to dry toluene (17 ml) heated under reflux, and the mixture was

heated under reflux for a further 15 min. The volume of the resulting solution was then reduced to 10 ml and NN'-bis-(3-aminobenzo[b]thiophen-2-ylidene)hydrazine (0.29 g, 40%) was filtered off; m.p. 248—250°, ν_{\max} (Nujol) 3340w and 3260w cm⁻¹ (NH₂), τ (Me₂SO) 0.81 (CH), 2.00—2.48 (m, aromatic), and 3.14 (exchangeable, NH₂) (Found: *M*, 350.0666. C₁₈H₁₄N₄S₂ requires *M*, 350.0660).

Photolysis of 3-Azidobenzo[b]thiophen-2-carbaldehyde Hydrazone.—A solution of the hydrazone (1.50 g, 6.91 mmol) in dry toluene (150 ml) was irradiated for 10 h with a high-pressure Hg vapour lamp (Q81 Quarzlampen G.M.B.H. Hanau). The solvent was distilled off and the product chromatographed on alumina. Chloroform-benzene (1:1) eluted NN'-bis-(3-aminobenzo[b]thiophen-2-ylidene)hydrazine (0.40 g, 34%), m.p. 248—250°. Elution with other solvents gave only intractable tars.

NN'-Bis(3-acetamidobenzo[b]thiophen-2-ylidene)hydrazine.—A mixture of the amine (0.20 g, 0.57 mmol), acetic acid (2 ml), and acetic anhydride (1.0 ml) was heated under reflux for 30 min. It was then poured into an excess of water and the product (0.11 g, 44%) was filtered off and recrystallised from methanol; m.p. >360°, ν_{\max} (Nujol) 3250 (NH) and 1665 cm⁻¹ (C:O) (Found: *M*, 434.0881. C₂₂H₁₈N₄S₂O₂ requires *M*, 434.0872).

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⁹ R. B. Mitra, K. Rabindran, and B. D. Tilak, *J. Sci. Ind. Res. (India)*, 1956, 15B, 627.