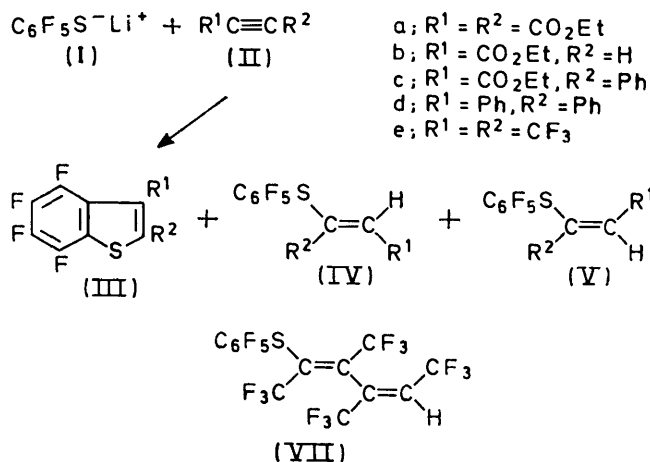


Partially Fluorinated Heterocyclic Compounds. Part XI.¹ The Reactions of Lithium Pentafluorobenzenethiolate with Acetylenic Compounds Giving Benzo[*b*]thiophen Derivatives and/or Olefins

By G. M. Brooke* and Md. Abul Quasem, Chemistry Department, Science Laboratories, South Road, Durham City

Lithium pentafluorobenzenethiolate reacts (i) with diethyl acetylenedicarboxylate to give diethyl 4,5,6,7-tetrafluorobenzo[*b*]thiophen-2,3-dicarboxylate; (ii) with ethyl phenylpropiolate to give ethyl 4,5,6,7-tetrafluoro-2-phenylbenzo[*b*]thiophen-3-carboxylate and a small amount of the product of thiol addition to the triple bond; (iii) with hexafluorobut-2-yne to give 4,5,6,7-tetrafluoro-2,3-bistrifluoromethylbenzo[*b*]thiophen and the all-*trans*-1-pentafluorophenylthio-1,2,3,4-tetrakis(trifluoromethyl)butadiene; (iv) with ethyl propiolate to give ethyl *cis*- and *trans*-β-(pentafluorophenylthio)acrylate; and (v) with diphenylacetylene to give *cis*- and *trans*-α-pentafluorophenylthiostilbene. The failure to trap olefinic material in (i), and the absence of cyclised materials in (iv) and (v) have not been rationalised.

In Part II² we reported the formation of diethyl 4,5,6,7-tetrafluorobenzo[*b*]thiophen-2,3-dicarboxylate (IIIa) in 49% yield by the reaction of lithium pentafluorobenzenethiolate (I) with diethyl acetylenedicarboxylate (IIa) in tetrahydrofuran at reflux temperature. When the thiolate was treated under similar conditions with ethyl propiolate (IIb), preliminary experiments³ surprisingly showed that no cyclised product (IIIb) was formed; a mixture of geometrically isomeric olefins (IVb) and (Vb) was obtained as a result of the overall *cis*- and *trans*-addition of C₆F₅S⁻H to the triple bond.



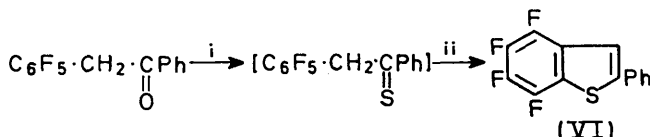
We have reinvestigated the reaction of lithium pentafluorobenzenethiolate with these two acetylenes (IIa and b) and extended our studies to include other acetylenic compounds in an attempt to discover the factors responsible for promoting the formation of benzo[*b*]thiophen derivatives. In each experiment, the reaction products were separated by column chromatography and each component was examined by mass spectroscopy.

When the reaction of lithium pentafluorobenzenethiolate (I) with diethyl acetylenedicarboxylate in

tetrahydrofuran was repeated at low temperature (−70 to −58°), the cyclised material (IIIa) was formed in 74% yield and *no* simple adducts of type (IVa) and (Va) were formed.

In contrast, ethyl propiolate and (I) in tetrahydrofuran at −70 to −25° gave *no* cyclised product (IIIb); a mixture of ethyl *trans*-β-(pentafluorophenylthio)acrylate (IVb) (10%) and the *cis*-isomer (Vb) (69%) was formed. The structure and stereochemistry of each ester were readily deduced from the characteristic coupling constants of vicinal vinylic protons in the ¹H n.m.r. spectra⁴ (*J* 10 Hz for the *cis*- and 15 Hz for the *trans*-protons). No cyclised material (IIIb) was formed when the reaction was carried out at reflux temperature.

Lithium pentafluorobenzenethiolate reacted with ethyl phenylpropiolate (IIc) in tetrahydrofuran at reflux temperature to give ethyl 4,5,6,7-tetrafluoro-2-phenylbenzo[*b*]thiophen-3-carboxylate (IIIc) (72%) and *ca.* 5% of olefin [*M*⁺ 374; presumably (IVc) and/or (Vc)] which was not investigated further. Hydrolysis of the cyclised material (IIIc) with sodium hydroxide and acidification gave the 3-carboxylic acid, which was decarboxylated by copper-quinoline to 4,5,6,7-tetrafluoro-2-phenylbenzo[*b*]thiophen (VI). This compound (VI) was synthesised by an alternative route which identified the orientation of addition of the thiolate to the acetylenic ester. 2-(Pentafluorophenyl)acetophenone⁵ was treated with hydrogen sulphide and hydrogen chloride in ethanol and the crude purple product (which presumably



Reagents: i, H₂S-HCl in EtOH; ii, NaOH in dry pyridine

contained the thioketone) isolated by evaporation of the solvent was treated with sodium hydroxide in dry pyridine to give compound (VI) (27%).

¹ Part X, G. M. Brooke, W. K. R. Musgrave, R. J. D. Rutherford, and T. W. Smith, *Tetrahedron*, 1971, **27**, 5653.

² G. M. Brooke and Md. Abul Quasem, *J. Chem. Soc. (C)*, 1967, 865.

³ Md. A. Quasem, Thesis, 1967, University of Durham.

⁴ R. M. Silverstein and G. C. Bassler, 'Spectrometric Identification of Organic Compounds,' 2nd edn., Wiley, New York, 1967, pp. 144, 145.

⁵ G. M. Brooke, W. K. R. Musgrave, and T. R. Thomas, *J. Chem. Soc. (C)*, 1971, 3596.

In an analogous reaction sequence reported earlier,⁶ 2-(pentafluorophenyl)acetone was converted into 4,5,6,7-tetrafluoro-3-methylbenzo[*b*]thiophen *via* a stable *gem*-dithiol, but there was no indication that such an intermediate was formed in the reaction described in here: the presence of thioketone was inferred from the colour of the crude product, as it proved so sensitive to hydrolysis as to preclude its isolation in the pure state.

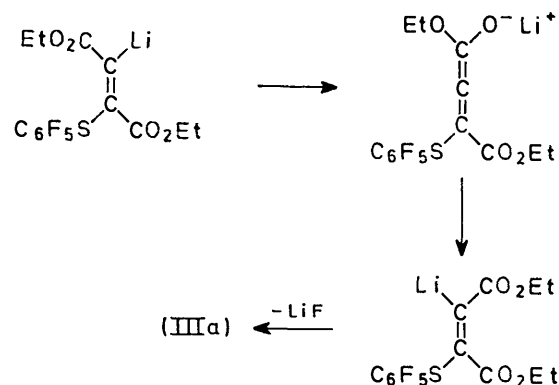
No cyclised product (III_d) was formed in the reaction of diphenylacetylene (II_d) with (I) in tetrahydrofuran at reflux temperature. In an extremely clean reaction, a mixture of geometrically isomeric olefins, *cis*- [(IV_d), 60%] and *trans*- [(V_d), 40%] α -pentafluorophenylthiostilbene, was formed in 98% yield. The ratio of the two isomers was determined from the integration of the easily identifiable *para*-fluorine signals in the ¹⁹F n.m.r. spectrum. The major component was obtained pure by fractional crystallisation; the absorption at highest field (τ 3.12) in the ¹H n.m.r. spectrum, due to the vinylic proton, was also the absorption at highest field in the mixture of isomers. Since it has been shown that a vinylic proton in *cis*-stilbenes absorbs at higher fields than in the isomeric *trans*-stilbenes,^{7,8} the absorption at τ 3.12 might be assignable to the vinylic proton in the *cis*-stilbene (IV_d). However, since the chemical shift of this proton is lower than expected, the stereochemistry given as (IV_d) is only regarded as tentative.

Lithium pentafluorobenzenethiolate and hexafluorobut-2-yne (II_e) in tetrahydrofuran at -70° gave a complex mixture from which two components have been isolated and identified: the cyclised material 4,5,6,7-tetrafluoro-2,3-bistrifluoromethylbenzo[*b*]thiophen [(III_e), 11%] and the all-*trans*-1-pentafluorophenylthio-1,2,3,4-tetrakistrifluoromethylbutadiene [(VII), 2%]. The stereochemistry of the diene was shown by the small coupling constants (*ca.* 2 Hz) between the aliphatic fluorine atoms, which is characteristic of vicinal vinylic CF₃ groups orientated *trans* to each other.⁹

We explained the formation of compound (III_a) in our earlier paper² in terms of an intermediate carbanion (although a partially covalent carbon-lithium bond is probably nearer the truth), resulting from the *cis*-addition of the lithium thiolate to the triple bond. Although *trans*-addition is the usual, kinetically controlled mode of reaction,¹⁰ the presence of the ethoxycarbonyl group would permit isomerisation of the initially formed lithio-derivative, followed by the irreversible intramolecular nucleophilic displacement of fluoride ion.

The formation of cyclised material (III_c) in high yield from (I) and ethyl phenylpropiolate can readily be accommodated by an analogous reaction mechanism. However, ethyl propiolate failed to give any benzo[*b*]thiophen derivative (III_b) with lithium pentafluoro-

benzenethiolate, which was particularly surprising in view of the presence of a significant amount (10%) of ethyl *trans*- β -(pentafluorophenylthio)acrylate (IV_b) in the product, since both (III_b) and (IV_b) would be expected to be derived from the same intermediate



lithio-derivative. The major product from the reaction was ethyl *cis*- β -(pentafluorophenylthio)acrylate [(V_b), 69%] due to the overall *trans*-addition of the thiol to ethyl propiolate, but isomerisation of this compound under the prevailing mild conditions was shown in a control experiment not to be responsible for the *trans*-acrylate (IV_b) found in the product: isomerisation of the initial thiolate adduct took place in the solvent *prior* to protonation during work-up. The absence of both the benzo[*b*]thiophen derivative (III_b) and the olefinic products (IV_a) and (V_a) in the reactions of lithium pentafluorobenzenethiolate with ethyl propiolate and diethyl acetylenedicarboxylate, respectively, coupled with the extreme reactivity of the latter system present problems which cannot be resolved on the basis of the data available. The lithium thiolate adducts are clearly far more complex than represented here.

The reaction of thiolates with diphenylacetylene has not been described previously, but Truce and Simms have examined the stereochemistry of addition of sodium toluene-*p*-thiolate to phenylacetylene in alcoholic solutions at reflux temperature.¹⁰ After 15 h at reflux only one product (*cis*-PhCH=CH·S·C₆H₄Me; 79% yield) was obtained, resulting from *trans*-addition of *p*-MeC₆H₄S-H to the triple bond. The addition of lithium pentafluorobenzenethiolate to diphenylacetylene in tetrahydrofuran at reflux temperature gave a mixture of *cis*- and *trans*- α -pentafluorophenylthiostilbenes which had a particularly high proportion (60%) of (IV_d) formed as a result of overall *cis*-addition of the thiol to the acetylene. The apparent violation of Truce's *trans*-addition rule can be explained on the basis of the kinetically controlled formation of a vinyl-lithium intermediate by *trans*-addition of the lithium thiolate across the triple bond and subsequent isomerisation of the

⁶ G. M. Brooke, *Tetrahedron Letters*, 1968, **37**, 4049.

⁷ J. E. Mulvaney, Z. G. Gardlund, S. L. Gardlund, and D. J. Newton, *J. Amer. Chem. Soc.*, 1966, **88**, 476.

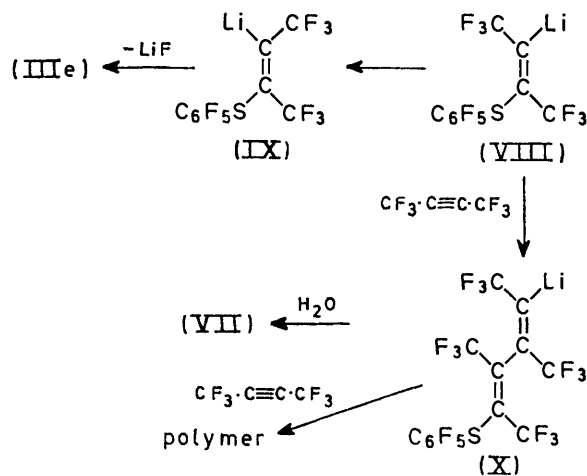
⁸ D. Y. Curtin, H. Gruen, and B. A. Shoulders, *Chem. and Ind.*, 1953, 1205.

⁹ J. W. Emsley, J. Feeney, and L. H. Sutcliffe, 'High Resolution Nuclear Magnetic Resonance Spectroscopy', vol. 2, Pergamon, Oxford, 1966, p. 911.

¹⁰ W. E. Truce and J. A. Sims, *J. Amer. Chem. Soc.*, 1956, **78**, 2756.

vinyl-lithium derivative. This explanation is consistent with the observation that derivatives of *cis*- and *trans*- α -stilbenyl-lithium compounds are configurationally isomerised at elevated temperatures (25–80°), and especially in tetrahydrofuran as solvent.¹¹ The problem remaining, and which is still unanswered, is why no benzo[*b*]thiophen derivative (III_d) was formed, since both (III_d) and the *cis*-stilbene derivative (IV_d) would again be expected to be derived from the same intermediate lithio-derivative.

The formation of both 4,5,6,7-tetrafluoro-2,3-bis(trifluoromethyl)benzo[*b*]thiophen (III_e) and the butadiene derivative (VII) from lithium pentafluorobenzenethiolate (I) and hexafluorobut-2-yne (II_e) in tetrahydrofuran at –70° can be explained by a mechanism analogous to the one described for the formation of (III_a) from (I) and diethyl acetylenedicarboxylate. The initially formed lithio-derivative (VIII) (formed by *trans*-addition of the lithium thiolate to the triple bond reacts in two ways: (i) is isomerised to give (IX) which cyclises to (III_e); and (ii) it combines with further hexafluorobut-2-yne to give the alkadienyl-lithium compound (X) [since protonation of this gives (VII)]. Only a small portion of (X) remained in solution at the end of the experiment however; the major part of it reacted with further hexafluorobut-2-yne to give increasingly higher molecular weight components. The formation of polymeric olefins has been observed previously in the reaction of hexafluorobut-2-yne with fluoride ion in the presence of polyfluoro-aromatic¹² and -heterocyclic¹³ compounds.



The nucleophilic additions of alcohols under base catalysis^{14,15} and of amines¹⁶ to hexafluorobut-2-yne have been reported. The stereochemistry of the 1:1 adducts obtained from reactions with methanol and ethanol was not established, but with dimethylamine a

¹¹ D. Y. Curtin and W. J. Koel, jun., *J. Amer. Chem. Soc.*, 1962, **84**, 1967.

¹² W. T. Flowers, R. N. Haszeldine, and P. G. Marshall, *Chem. Comm.*, 1970, 371.

¹³ R. D. Chambers, W. K. R. Musgrave, and S. Partington, *Chem. Comm.*, 1970, 1050.

¹⁴ A. L. Henne and M. Nager, *J. Amer. Chem. Soc.*, 1952, **74**, 650.

mixture of isomers (*cis*:*trans*, 1:6) was obtained. No nucleophilic additions of thiolates to hexafluorobut-2-yne have been reported, but hydrogen sulphide has been added under the influence of X-rays to give a 1:1 adduct¹⁷ which has recently been assigned the *cis*-configuration.¹⁸ Haszeldine¹² has described the reaction of hexafluorobut-2-yne with caesium fluoride in the presence of pentafluorobenzonitrile in dimethylformamide at 125°. The proposed *trans*-vinyl carbanion (CF₃·CF=C·CF₃) initially formed displaced the *para*-fluorine atom in pentafluorobenzonitrile to give a product containing both a *trans*- and a *cis*-perfluorobut-2-enyl group in the ratio 5:1. However, these isomers were shown to be in equilibrium with each other, though partial isomerisation of the *trans* vinylic carbanion prior to reaction can not be ruled out under these conditions. Particularly noteworthy in the reaction of (I) with (II_e) described here is the case of isomerisation of (VIII) to (IX) under extremely mild conditions prior to cyclisation.

EXPERIMENTAL

Reactions of Lithium Pentafluorobenzenethiolate with Acetylenic Compounds.—With diethyl acetylenedicarboxylate. Pentafluorobenzenethiol (1.71 g) in dry tetrahydrofuran (25 ml) was treated at –70° with *n*-butyl-lithium in hexane (5.0 ml; 2.0N). Diethyl acetylenedicarboxylate (2.10 g) was added during 5 min (exothermic reaction), the temperature being kept below –60°. The mixture was maintained at –70° for 30 min, then warmed to –58°, and absolute ethanol (10 ml) was added. The mixture was acidified with hydrochloric acid (4N) and extracted with ether; the extracts were dried (MgSO₄) and evaporated. Four components were present, which were separated by chromatography on silica (benzene as eluant). The third component from the column was diethyl 4,5,6,7-tetrafluorobenzo[*b*]thiophen-2,3-dicarboxylate³ (III_a) (2.225 g), identified by its i.r. spectrum. None of the other components were identified, but their mass spectra showed that none of them was the olefin (*M* 370) resulting from the overall addition of pentafluorobenzenethiol to the acetylenic compound.

With ethyl propiolate. (A) *Low temperature reaction.* Pentafluorobenzenethiol (5.06 g) in dry tetrahydrofuran (25 ml) was treated at –70° with *n*-butyl-lithium in hexane (12.0 ml; 2.0M). Ethyl propiolate (2.52 g) was added and the mixture was stirred for 3 h at –70°. The solution was then warmed rapidly to –25°, the mixture was cooled to –35°, and worked up as before. Three components were present, which were separated by chromatography on silica (benzene as eluant). The first component was not identified, but its mass spectrum showed the absence of cyclised product (III_b) (ethyl 4,5,6,7-tetrafluorobenzo[*b*]thiophen-3-carboxylate). The second component was ethyl *cis*-β-(pentafluorophenylthio)acrylate (V_b) (5.21 g), m.p. 48–49° [from light petroleum (b.p. 40–60°)] (Found: C, 44.1; H, 2.4. C₁₁H₇F₅O₂S requires C, 44.3; H, 2.4%), τ (CCl₄) 3.15 and 4.02 (doublets, *J* 10.0 Hz, vicinal vinylic protons⁴).

¹⁵ R. N. Haszeldine, *J. Chem. Soc.*, 1952, 3490.

¹⁶ W. R. Cullen, D. S. Dawson, and G. E. Styan, *Canad. J. Chem.*, 1965, **43**, 3392.

¹⁷ F. W. Stacey and J. F. Harris, *J. Amer. Chem. Soc.*, 1963, **85**, 963.

¹⁸ M. J. Bruce and W. R. Cullen, *Fluorine Chem. Rev.*, 1969, **4**, 96.

The third component was *ethyl trans-β-(pentafluorophenylthio)acrylate* (IVb) (0.75 g), b.p. 73° at 0.01 mmHg (Found: C, 44.2; H, 2.6%), τ (CCl₄) 2.56 and 4.37 (doublets, J 15 Hz, vinylic protons⁴). The compound contained ca. 10% of the *cis*-olefin. The pure *cis*-olefin in carbon tetrachloride was not measurably isomerised at 100° over 16 h, but after 185 h at 100°, the *cis*- and *trans*-olefins were present in the ratio of 35 : 65.

(B) *High temperature reaction.* Pentafluorobenzenethiol (5.01 g) in dry tetrahydrofuran (25 ml) was treated at -70° with *n*-butyl-lithium in hexane (11.5 ml; 2.0M). Ethyl propiolate (2.49 g) was added over 5 min, and the mixture was warmed rapidly to reflux temperature and heated under reflux for 1.5 h. It was worked up as before and shown to contain at least five components, from which the ester (Vb) (0.33 g) was readily identified. All the other components were examined by mass spectroscopy, but none showed *m/e* 278 due to cyclised material (IIIb).

With ethyl phenylpropiolate. Pentafluorobenzenethiol (1.81 g) in dry tetrahydrofuran (50 ml) was treated at -70° with *n*-butyl-lithium in hexane (4.8 ml; 2.0M). Ethyl phenylpropiolate (1.81 g) was added; the mixture was warmed rapidly, heated under reflux for 3 h, and worked up as before. The four components present were separated by chromatography on silica (benzene as eluant). The second component, contaminated with yellow material, was shown to contain ethyl β -phenyl- β -(pentafluorophenylthio)acrylate (0.18 g) from its mass spectrum (M^+ 374); the third component was *ethyl 4,5,6,7-tetrafluoro-2-phenylbenzo[b]thiophen-3-carboxylate* (IIIc) (2.30 g), m.p. 67.5—68.0° [from light petroleum (b.p. 60—80°)] (Found: C, 57.9; H, 2.9. C₁₇H₁₀F₄O₂S requires C, 57.6; H, 2.8%), δ (¹⁹F) (CDCl₃) 20.8, 19.9, 3.6, and 2.9 p.p.m. downfield from internal C₆F₆ (four multiplets of equal intensity).

The ester (IIIc) (0.0714 g) was hydrolysed with sodium hydroxide; acidification gave *4,5,6,7-tetrafluoro-2-phenylbenzo[b]thiophen-3-carboxylic acid* (0.027 g), m.p. 174—176° (Found: C, 55.5; H, 2.0. C₁₅H₆F₄O₂S requires C, 55.2; H, 1.8%).

The carboxylic acid (0.31 g) in quinoline (10 ml) was heated under reflux with copper powder (1.45 g) for 2.5 h to give *4,5,6,7-tetrafluoro-2-phenylbenzo[b]thiophen* (VI) (0.15 g), m.p. 130.5—131.5° (Found: C, 59.3; H, 2.3. C₁₄H₆F₄S requires C, 59.6; H, 2.1%), δ (¹⁹F) (CDCl₃) 20.4, 16.8, and 1.6 p.p.m. downfield from internal C₆F₆ (multiplets with intensities 1 : 1 : 2).

Compound (VI) was prepared by a second method⁶ from 2-(pentafluorophenyl)acetophenone.⁵ The ketone (1.00 g) in dry ethanol (150 ml) was treated at 0° with a mixture of hydrogen chloride and hydrogen sulphide, bubbled simultaneously through the mixture for 23 h. The solution was dried (MgSO₄), filtered under dry nitrogen through a sinter, and evaporated *in vacuo* at room temperature during 3 h. The purple semi-solid material remaining was heated under reflux for 1 h with dry pyridine (50 ml) and sodium hydroxide (0.25 g). The mixture was cooled, diluted with ether, and washed with excess of hydrochloric acid (4N). The ethereal solution was dried (MgSO₄) and evaporated and the residue chromatographed on silica [benzene-light petroleum (b.p. 60—80°) (50% v/v) as eluant] to give a crude yellow product (0.72 g). This was

rechromatographed on silica [light petroleum (b.p. 60—80°) as eluant]; the first fraction was pure *4,5,6,7-tetrafluoro-2-phenylbenzo[b]thiophen* (VI) (0.27 g), m.p. 130.5—131.5°, identical (i.r. spectrum) with the material prepared by the earlier method.

With diphenylacetylene. Pentafluorobenzenethiol (4.58 g) in dry tetrahydrofuran (25 ml) was treated at -70° with *n*-butyl-lithium in hexane (13.0 ml; 2.0M). Diphenylacetylene (2.22 g) was added; the mixture was warmed rapidly, heated under reflux for 16.5 h, and worked up as before. The three components were separated by chromatography on silica (benzene as eluant). The first component was a mixture of *cis*- and *trans*- α -pentafluorophenylthiostilbenes [(IVd) and (Vd)] (4.61 g), m.p. 60—67° (Found: C, 63.3; H, 2.8. Calc. for C₂₀H₁₁F₅S: C, 63.5; H, 2.9%). The *cis-trans* ratio was shown to be 60 : 40 from integration of the *para*-fluorine signals in the ¹⁹F n.m.r. spectrum (CCl₄): δ 9.0 and 10.1 p.p.m., respectively, downfield from internal C₆F₆. The ¹H n.m.r. spectrum (CCl₄) showed no absorption with $\tau > 3.12$. Recrystallisation of the mixture from light petroleum (b.p. 40—60°) gave pure *cis*- α -pentafluorophenylthiostilbene (IVd), m.p. 77.5—78.5° (Found: C, 63.6; H, 3.0%), τ (CCl₄) 3.12 (one vinylic proton).

The other two components were not characterised, but their i.r. and mass spectra showed that neither of them was the cyclised material *4,5,6,7-tetrafluoro-2,3-diphenylbenzo[b]thiophen* (IIIId).

With hexafluorobut-2-yne. Pentafluorobenzenethiol (5.56 g) in dry tetrahydrofuran (100 ml) was treated at -70° with *n*-butyl-lithium in hexane (13 ml; 2.0N). The pressure in the apparatus was reduced by 8 cmHg and hexafluorobut-2-yne (7.3 g), contained in a rubber bladder, was admitted into the system during 45 min, the temperature being maintained at -70° throughout. The mixture was worked up as before and the product distilled *in vacuo* to give a fraction (1.91 g), b.p. $\leq 83^\circ$ at 0.05—0.10 mmHg. Column chromatography on silica [light petroleum (b.p. 60—80°) as eluant] gave *4,5,6,7-tetrafluoro-2,3-bistrifluoromethylbenzo[b]thiophen* (IIIe) (1.00 g), b.p. 45° at 0.01—0.05 mmHg and 203° at 760 mmHg (Found: F, 55.5%; M^+ , 342. C₁₀F₁₀S requires F, 55.55%; M , 342) followed by the *all-trans-1-pentafluorophenylthio-1,2,3,4-tetrakis(trifluoromethyl)butadiene* (VII) (0.345 g), b.p. 51—70° at 0.01—0.05 mmHg (Found: C, 32.9; H, 0.4; F, 61.9. C₁₄HF₁₇S requires C, 32.1; H, 0.2; F, 61.6%).

The ¹⁹F n.m.r. spectrum of (IIIe) (neat liquid) showed δ 109.7, 106.6, 27.7, 24.0, 11.3, and 9.8 p.p.m. downfield from external C₆F₆ (ratio 3 : 3 : 1 : 1 : 1 : 1). The ¹⁹F n.m.r. spectrum of (VII) (CCl₄) showed δ 107.7, 107.1, 103.4, 99.4, 34.3, 16.9, and 4.8 p.p.m. downfield from external C₆F₆ (ratio 3 : 3 : 3 : 3 : 2 : 1 : 2). Under high resolution, the aliphatic fluorine signals showed only very weak splitting [J_{trans} (CF₃, CF₃) ca. 2 Hz].

We thank Professor W. K. R. Musgrave for his interest in this work, Dr. R. D. Chambers for encouraging us to perform the reaction with hexafluorobut-2-yne, the former Government of East Pakistan (now Bangladesh) for providing a scholarship (to Md. A. Q.), and the Imperial Smelting Corporation, Avonmouth, for gifts of chemicals.

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