Approaches to Bridged Thia[17]annulenes

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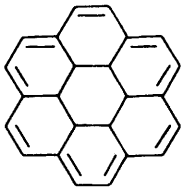
The macrocyclic trisulphide (5) has been prepared from 2,5-bis-(*p*-bromomethylphenylmethylthiomethyl)thiophen (7) but attempts to convert it into the triolefin (2) *via* a Stevens rearrangement of the derived trimethylsulphonium salt and elimination of sulphur were frustrated by the intractability of the salt. In other experiments 15,17-dimethyl-16-thiabicyclo[12.3.0]heptadeca-2,12,14,17-tetraen-6,8-diyne (9) was prepared but attempted base-catalysed rearrangement to the bridged thia-annulene 15,17-dimethyl-16-thiabicyclo[12.3.0]heptadeca-2,4,6,8,10,12,14,17-octaene (8) led to a product of uncertain structure.

RECENT reports[1] on the synthesis of the bridged [18]-annulene (1) and some related compounds prompt us to record our attempts to prepare the triene (2) which we hoped to convert into the bridged thia[17]annulene (3) by photocyclisation.[2]



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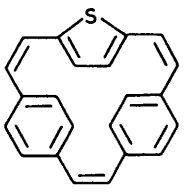

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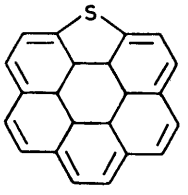

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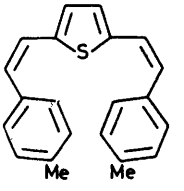
We aimed first to proceed *via* *cis,cis*-di-(*p*-methylstyryl)thiophen (4) by appropriate manipulation of the methyl substituents, but this approach was frustrated by the very ready isomerisation of the *cis,cis*-compound into the *trans,trans*-isomer. Catalytic hydrogenation of the corresponding dialkyne, obtained from 2,5-diiodothiophen and the copper salt of *p*-methyltolane,[3] gave a product which consisted mainly of the crystalline *trans,trans*-diolefin. Reduction of the diyne with diimide gave similar results. Isomerisation to the *trans,trans*-derivative on bromination with *N*-bromosuccinimide similarly frustrated an alternative approach to (2) from 4,4'-dimethyl-*cis*-stilbene.

The failure of these attempts led us to consider the possibility of introducing the double bonds in compound (2) after construction of the macrocyclic trisulphide (5) which, on analogy with recorded examples,[2,4] was expected to form compound (2) by Stevens rearrangement of the derived trimethylsulphonium salt followed by Hoffmann elimination. The synthetic route to (5) is shown in the Scheme. We had it in mind to convert the dibromide (7) into the macrocycle (6) by an intramolecular Wittig reaction using the bis(triphenylphosphonium) periodate,[5] but treatment of the bis-(triphenylphosphonium) bromide with sodium periodate led only to an intractable gum from which no useful



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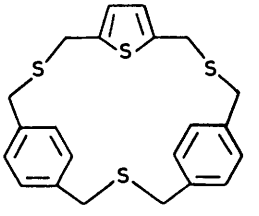

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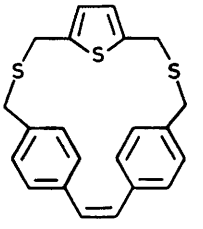


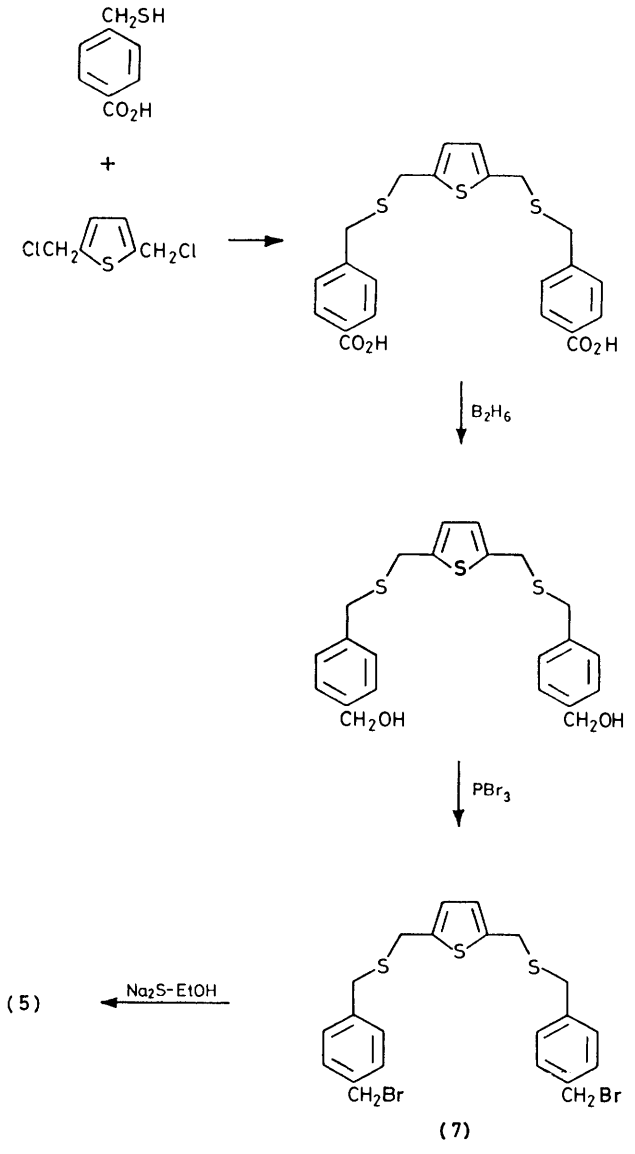
(6)

product could be obtained on treatment with base. However, with sodium sulphide in ethanol the bromide (7) was smoothly converted into the crystalline trisulphide (5) in 82% yield.

Reaction of the trisulphide (5) with dimethoxycarbonium fluoroborate gave an almost quantitative yield of a purple microcrystalline product, presumably a methylsulphonium salt, but the extreme insolubility of this product prevented characterisation and we have been unable to convert it into the triolefin (2). Sodium hydride or potassium t-butoxide in tetrahydrofuran were without effect on the compound. 1,5-Diazobicyclo-[4.3.0]non-5-ene (DBN) in dimethylformamide caused rapid dissolution but the product consisted almost

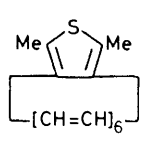
entirely of material which did not move from the base line on layer chromatography.

In separate experiments we have explored the possibility of preparing the bridged thia[17]annulene (8) by prototropic rearrangement of the cyclic diyne (9). The compound (9) was smoothly obtained by Glaser



SCHEME

coupling of the diyne (10), itself prepared as a mixture of double-bond isomers from 3,4-diformyl-2,5-dimethylthiophen and pent-4-ynyltriphenylphosphonium ylide (see Experimental section). Prototropic rearrangement of compound (9) with potassium t-butoxide in t-butyl alcohol gave a product isolated by preparative-layer chromatography as a bright yellow gum. Although this material ran as a single spot on thin-layer chromatography it could not be crystallised and we have been unable to establish conclusively that it is the desired annulene (8). The gross structure is supported by the molecular weight, determined by mass spectrometry, by the i.r. spectrum in which the peaks at 2 258 cm^{-1} (C≡C) and 963 cm^{-1} (*trans*-CH=CH) in the spectrum of (9) have disappeared, and by hydrogenation to the crystalline macrocycle (11) identical with that obtained



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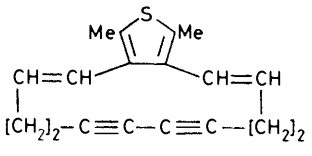

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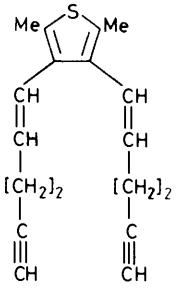

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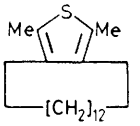

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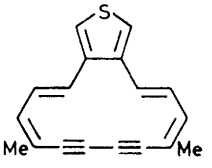

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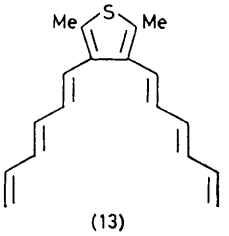

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by hydrogenation of compound (9). The Raman spectrum of the rearrangement product, in contrast to those of (9) and (10) showed no signal in the acetylenic region and this, together with the absence of allenic signals in the i.r. spectrum appears to eliminate the possibility of incomplete rearrangement during base treatment of (9). Taken together with the formation of the macrocycle (11) on hydrogenation, this would seem to suggest that the rearrangement product has the desired conjugated structure (8). Curiously, however, the u.v. absorption [$\lambda_{max.}$ 246 nm (ε 16 600), 285 nm (ε 6 530) tailing into the visible] is less intense and less extensive than might have been expected for a completely conjugated structure (8) and is certainly less intense and less extensive than that of the related bisdehydro-analogue (12), which was reported [6] after our own experiments were completed. These compounds may not be strictly comparable, however, for in compound (12) the rigid diyne system will favour a planar configuration whereas with compound (8) it is conceivable that the molecule

is non-planar and that some of the double bonds may be only formally in conjugation.

The interest in compound (8) lies in establishing whether or not it behaves as an 18π electron thia-annulene and shows a diamagnetic ring current. Unfortunately the ^{1}H n.m.r. evidence is inconclusive. The spectrum, which is essentially unchanged between 37 and −50 °C, shows three complex groups of signals. Comparison (see Table) with the spectra of the precursor (9) and the open-chain polyene (13) suggests that the

^{1}H N.m.r. parameters in $CDCl_3$ at 100 MHz; τ values, $SiMe_4$ internal standard (figures in parentheses represent) approximate relative numbers of protons)

' Thia-annulene ' (8)	2.2—3.1 (4)	3.2—4.2 (5)	7.4—7.9 (9)
Cyclic diyne (9)	3.6—4.0 (1)	4.1—4.6 (1)	7.5—7.9 (7)
Open-chain polyene (13)	2.8—4.2 (5)	4.6—5.0 (2)	7.4—7.8 (3)

signals due to some of the olefinic protons of (8) occur among the high field group at τ 7.4—7.9 along with the signals due to the protons of the methyl groups but whether this is indicative of the effect of a diamagnetic ring current on ' inside ' protons of some configurational isomer(s) of (8) remains to be seen. Clearly further work needs to be done on this interesting compound but since resources to complete the work are not forthcoming the results are recorded as they stand at present.

EXPERIMENTAL

I.r. spectra were determined with a Perkin-Elmer 357 Grating Spectrometer, mass spectra with a Perkin-Elmer Hitachi RM06 instrument, and ^{1}H n.m.r. spectra with a Perkin-Elmer R10 spectrometer at 60 MHz or a Jeol MH-100 at 100 MHz. Light petroleum refers to the fraction b.p. 60—80 °C.

2,5-*Bis*-(p-*tolylethynyl*)*thiophen*.—A solution of copper(I) *p*-tolylacetylide (32.0 g) and 2,5-di-iodothiophen (23 g) in pyridine (1 l) was boiled under nitrogen for 10 h. Most of the pyridine was removed under reduced pressure and the residue was taken up in ether and the solution washed with 2M-hydrochloric acid. Chromatography of the crude product on silica gel and elution with light petroleum gave 2,5-*bis*-(p-*tolylethynyl*)*thiophen* (4.5 g, 17%) as yellow needles, m.p. 141—142 °C (from methanol–chloroform); $\lambda_{max.}$ (ether), 232, 239, 274, 293, 311, 332, and 349 nm (ε 28 030, 23 890, 9 650, 13 325, 26 190, 39 510, and 35 875); δ($CDCl_3$) 7.40 (d, *J* 9 Hz, 4 H), 7.15 (d, *J* 9 Hz, 4 H), 7.10 (s, 2 H thiophen protons), and 2.35 (s, 6 H, ArMe); *m/e* 312 (Found: C, 84.5; H, 5.5; S, 9.9. $C_{22}H_{16}S$ requires C, 84.6; H, 5.2; S, 10.2%).

trans,trans-2,5-*Bis*-(p-*methyl*-α-*styryl*)*thiophen*.—The diyne described above (500 mg) was hydrogenated in toluene (20 ml) containing quinoline (200 mg) in the presence of palladium–barium sulphate (5%; 200 mg). Absorption of hydrogen ceased after up-take of 2 mol equiv. (72 ml). Quinoline was washed out with hydrochloric acid and the crude product crystallised from light petroleum, giving *trans,trans*-2,5-*bis*-(p-*methyl*-α-*styryl*)*thiophen* as bright yellow needles, m.p. 193—194 °C (156 mg, 31%); $\nu_{max.}$ (KBr) 955 and 815 cm^{-1}; δ($CDCl_3$) 7.36 (4 H, d, *J* 9 Hz), 7.12 (4 H, d, *J* 9 Hz), 7.16 (2 H, d, *J* 16 Hz, *trans*-olefinic H) 6.84 (2 H, d, *J* 16 Hz, *trans*-olefinic H), 6.92 (2 H, s), and 2.35 (6 H, s, ArMe); *m/e* 316 (Found: C, 83.4; H, 6.6; S, 9.8. $C_{22}H_{20}S$ requires C, 83.5; H, 7.6; S, 10.1%).

cis-4,4′-*Dimethylstilbene*.—This compound was prepared by partial hydrogenation of 4,4′-dimethyltolane, itself obtained (21%) by a Castro reaction [3] as described above, between *p*-iodotoluene and copper(I) *p*-tolylacetylide, m.p. 134—135 °C (lit.,[7] m.p. 136 °C). It is reported that this compound is reduced to the *cis*-stilbene in 24% yield using an unspecified palladium–barium sulphate catalyst in ethanol. In our hands much better results were obtained by hydrogenation in toluene using 10% palladium–charcoal as catalyst, with interruption of the reaction after absorption of 1 equiv. of hydrogen. Chromatography of the product on alumina and distillation at 90 °C/0.02 mmHg gave the *cis*-stilbene as colourless crystals (61%), m.p. 33—34 °C (lit.,[8] m.p. 34 °C); δ($CDCl_3$) 7.10 (4 H, d, *J* 9 Hz), 6.90 (4 H, d, *J* 9 Hz), 6.45 (2 H, s, *cis*-olefinic H), and 2.25 (6 H, s, ArMe).

trans-4,4′-*Dibromomethylstilbene*.—A solution of *cis*-4,4′-dimethylstilbene (120 mg), *N*-bromosuccinimide (200 mg), and benzoyl peroxide (5 mg) in carbon tetrachloride (4 ml) was boiled by 3 h. The recovered product was purified by preparative layer chromatography, giving *trans*-4,4′-dibromomethylstilbene as colourless crystals (41%), m,p. 188—190 °C, undepressed when mixed with an authentic specimen.

p-*Mercaptomethylbenzoic Acid*.—A solution of *p*-bromomethylbenzoic acid (2.16 g) and thiourea (0.76 g) in water (10 ml) was refluxed for 1 h, after which the solution was cooled, a solution of sodium hydrogen carbonate (2.1 g) in water (20 ml) added, and the refluxing continued until all the precipitate had dissolved. The cooled solution was acidified and the precipitate collected and washed with water. Crystallisation from ethanol–light petroleum gave p-*mercaptomethylbenzoic acid* (1.2 g, 71%) as colourless platelets, m.p. 179—180 °C; M^+ 168 (Found: C, 57.0; H, 4.7. $C_8H_8O_2S$ requires C, 57.1; H, 4.8%).

2,5-*Bis*-(p-*carboxyphenylmethylthiomethyl*)*thiophen*.—A solution of *p*-mercaptomethylbenzoic acid (7.1 g) in methanol (50 ml) was added to a stirred solution of potassium hydroxide (4.7 g) in methanol under nitrogen, followed, 30 min later, by a solution of 2,5-dichloromethylthiophen (3.8 g) in methanol (10 ml). The mixture was refluxed for 12 h, cooled, poured into water (500 ml), extracted with ether to remove neutral material, and acidified. Crystallisation of the product from acetic acid gave *the disulphide* as a cream-coloured microcrystalline powder (5.5 g, 60%), m.p. 238—239 °C (decomp.); δ($CDCl_3$) 7.90 (4 H, d, *J* 9 Hz), 7.35 (4 H, d, *J* 9 Hz), 6.75 (2 H, s), 3.80 (4 H, s, CH_2), and 3.75 (4 H, s, CH_2) (Found: C, 59.6; H, 4.5. $C_{22}H_{20}O_4S_3$ requires C, 59.4; H, 4.5%).

2,5-*Bis*-(p-*hydroxymethylphenylmethylthiomethyl*)*thiophen*.—A solution of borane–tetrahydrofuran complex (1M; 150 ml) was added dropwise to a stirred solution of the above dicarboxylic acid (5.5 g) in tetrahydrofuran (200 ml) and the mixture was stirred at room temperature for 2 h. Excess of diborane was destroyed by addition of digol and the reaction mixture was poured into dilute hydrochloric acid and extracted with chloroform. The recovered product was crystallised from ethanol–light petroleum to give the *bishydroxymethyl compound* as colourless platelets (4.2 g, 81%), m.p. 109—110 °C; δ($CDCl_3$) 7.25 (8 H, s, benzene ring H), 6.70 (2 H, s, thiophen ring H), 4.60 (4 H, s, CH_2OH), 3.70 (4 H, s, CH_2), 3.65 (4 H, s, CH_2) (Found: C, 63.1; H, 5.8. $C_{22}H_{24}O_2S_3$ requires C, 63.4; H, 5.8%).

2,5-*Bis*-(p-*bromomethylphenylmethylthiomethyl*)*thiophen* (7).—Phosphorus tribromide (1 g) in benzene (5 ml) was added dropwise to a stirred suspension of the above bis-benzyl alcohol (1 g) in benzene (30 ml). After 1 h the mixture was poured into water and the product extracted with ether. Chromatography on silica gel and elution with toluene gave the bisbromomethyl compound as a colourless oil (890 mg, 68%) which showed only one spot on thin layer chromatography; δ($CDCl_3$) 7.25 (8 H, s, benzene H), 6.65 (2 H, s, thiophen H), 4.40 (4 H, s, CH_2Br), 3.65 (4 H, s, CH_2), and 3.60 (4 H, s, CH_2).

The Trithiacyclophane (5).—A solution of 2,5-bis[(*p*-bromomethylphenylmethylthiomethyl)thiophen (7) (284 mg) in benzene (30 ml) was added dropwise to a briskly stirred solution of sodium sulphide nonahydrate (130 mg) in ethanol–water (20 : 1). After 12 h ethanol was removed under reduced pressure and the residual solid was extracted with chloroform. The recovered product was purified by repeated precipitation from solution in chloroform by addition of ether and obtained as a colourless powder (178 mg, 82%), m.p. 140—142 °C; *m/e* 414 (M^+, 47%), 304 (24%), 136 (32%), 110 (63%), 104 (100%), 103 (42%), and 92 (34%); δ($CDCl_3$) 7.25 (8 H, s), 6.72 (2 H, s), and 3.76, 3.70, and 3.60 (12 H, three overlapping singlets, CH_2) (Found: M^+ 414.0603. $C_{22}H_{22}S_4$ requires 414.0605).

Addition of this compound (100 mg) in dichloromethane (10 ml) to a briskly stirred suspension of dimethoxycarbonium fluoroborate (120 mg) in dichloromethane (10 ml) at −30 °C led to rapid formation of a purple precipitate. Reaction was continued for 12 h more at room temperature, methanol (10 ml) was added and the precipitated salt filtered off and washed with chloroform to give a purple powder (168 mg, 97%), melting range 140—145 °C. No solvent was found in which this salt would dissolve.

3,4-*Diformyl*-2,5-*dimethylthiophen*.—This compound was prepared by an improved procedure [9] as follows. 2-Nitropropane (30.5 g) was added to a solution of sodium (5.8 g) in ethanol (500 cm^3) followed, after 2 h, by 3,4-dichloromethyl-2,5-dimethylthiophen (22 g). The mixture was stirred for 24 h at room temperature, ethanol was removed under reduced pressure and the residue diluted with water (500 cm^3). The recovered product (ether) was filtered through a column of silica gel (200 g) in benzene and gave the aldehyde as light yellow flakes (15.1 g), from light petroleum–benzene, m.p. 92—93 °C, identical with the product prepared by the method of Dimroth, Follmann, and Pohl.[10]

3,4-*Bis*-(*hex*-1-*en*-5-*ynyl*)-2,5-*dimethylthiophen* (10).—Pent-4-ynyl(triphenyl)phosphonium iodide [11] (20 g) was added under nitrogen to an ice-cold suspension of sodium ethoxide (from 1.1 g sodium) in dimethylformamide (100 cm^3). After 3 h a solution of 3,4-diformyl-2,5-dimethylthiophen (3.0 g) in dimethylformamide was added dropwise, at 0 °C, over a period of 5 h. The temperature was raised to 80 °C and reaction was continued until all the aldehyde had been consumed (3 days). The reaction mixture was diluted with water (1 000 cm^3) and extracted with ether and the recovered oily residue was chromatographed on silica gel (150 g). Elution with light petroleum–ether (20 : 1) gave 3,4-*bis*-(*hex*-1-*en*-5-*ynyl*)-2,5-*dimethylthiophen* (3.6 g) as a yellow oil. A portion was distilled at 125 °C (bath) 0.05 mmHg (Found: C, 80.9; H, 7.6; S, 11.8%; M^+, 268. $C_{18}H_{20}S$ requires C, 80.6; H, 7.5; S, 11.9%; *M*, 268); $\lambda_{max.}$ (cyclohexane) 237 and 268 nm (log ε 4.31 and 3.82); $\nu_{max.}$ (film) 3 290, 2 115, and 963 cm^{-1}; τ 3.5—4.4 (m, 4 H, *cis*- and *trans*-olefinic H), 7.6—7.8 (14 H, overlapping m and s, CH_2 and CH_3), 8.1br (2 H, s, C≡C–*H*). Analytical t.l.c. of this material showed three overlapping spots and this was confirmed by g.l.c. at 160 °C, which gave three peaks in the ratio 4 : 5 : 2. Attempted separation of the isomers by preparative-layer chromatography was unsuccessful.

Refluxing a solution of the mixture in light petroleum (b.p. 100—120 °C) with a crystal of iodine for 12 h left the isomer composition unchanged. Irradiation of a solution of the mixture of isomers (135 mg) and eosin (325 mg) in ether–benzene (1 : 1; 200 cm^3) with light from a 125 W Hanovia medium-pressure mercury-vapour lamp gave a photostationary state after 30 h (g.l.c.) in which the peak of longest retention time in the starting material had completely disappeared and the peak of shortest retention time was 90% of the two-component mixture; the n.m.r. and i.r. spectra strongly suggest that the product is mainly the *cis,cis*-isomer. Distillation gave a yellow oil b.p. 125 °C at 0.05 mmHg; τ 3.0 (2 H, d, *J* 10 Hz, olefinic H adjacent to thiophen ring), 3.4 (2 H, m, olefinic H adjacent to CH_2), 7.80—7.85 (14 H, overlapping m and s, CH_2 and CH_3), 8.10 (2 H, s, C≡C–H); on irradiating at 204 Hz to decouple the CH_2 protons, the multiplet at τ 3.4 collapsed to a doublet, *J* 10 Hz; in the i.r. spectrum there was a marked decrease in the peak at 963 cm^{-1} (*trans*-CH=CH) compared with that in the starting material. Irradiation in presence of benzophenone instead of eosin gave a similar, but a less pure, product.

Oxidative Cyclisation of the Di-yne (10).—A solution of the mixture of diynes (300 mg) obtained as described above and cupric acetate (1.4 g) in pyridine (120 cm^3) and methanol (60 cm^3) was stirred under nitrogen at 60 °C for 60 h. The cooled mixture was poured into water (2 l) extracted with ether, and the ether extract washed with water and dilute hydrochloric acid to remove pyridine. The recovered gummy product on g.l.c. at 180 °C showed two peaks in the ratio 5 : 1, but the individual components could not be separated. Preparative layer chromatography gave the mixture as a yellow gum (120 mg) which decomposed on attempted distillation (Found: M^+ 266.1135. $^{12}C_{18}{}^{1}H_{18}{}^{32}S$ requires *M*, 266.1130); $\nu_{max.}$ (film) 2 258, 963, and 680 cm^{-1}; τ 3.6—4.1 (m, 2 H, olefinic protons adjacent to thiophen ring), 4.1—4.8 (m, 2 H, olefinic protons adjacent to CH_2), and 7.5—7.9 (m, 14 H, CH_2, and CH_3); $\lambda_{max.}$ 237 and 269 nm (log ε 4.27 and 3.84).

Hydrogenation of this material (80 mg) in benzene with palladium–charcoal (10%) as catalyst for 18 h gave a crude product which showed a single peak on g.l.c. Crystallisation from benzene–methanol gave 15,17-*dimethyl*-16-*thiabicyclo*[12.3.0]*heptadeca*-14,17-*diene* (11) as needles (55 mg), m.p. 113 °C (Found: C, 77.7; H, 10.5; S, 11.5%; M^+, 278. $C_{18}H_{30}S$ requires C,77.6; H, 10.8; S, 11.5%; *M*, 278); $\lambda_{max.}$ 243 nm (log ε 3.88); τ 7.5—7.7 (10 H, overlapping m and s, Ar-CH_2 and CH_3), and 8.4—8.8 (m, 20 H).

Base-catalysed Rearrangement of Compound (9).—A solution of the cyclisation product (9) (70 mg) in ether (3 cm^3) was added to a solution of potassium t-butoxide (from 300 mg potassium) in t-butyl alcohol (20 cm^3) and the solution was stirred under nitrogen at 60 °C for 5 h. The solution was diluted with water and extracted with ether and the recovered product purified by preparative layer chromatography. Elution with light petroleum–ether (20 : 1) gave a bright yellow gum (18 mg) which ran as a single spot on analytical t.l.c. (Found: M^+, 266.1138. $^{12}C_{18}{}^{1}H_{18}{}^{32}S$ requires *M*, 266.1130).

Hydrogenation of a sample (25 mg) with palladium–charcoal (10%) in benzene gave one main product (g.l.c.); crystallisation from benzene–methanol afforded the macrocycle (11) (14 mg), m.p. and mixed m.p. 113 °C. The two samples were also identical by g.l.c. and t.l.c.

2,5-Dimethyl-3,4-bis-(hexa-1,3,5-trienyl)thiophen (13).—A solution of the mixture of diynes (10) from the Wittig reaction (300 mg) in ether (5 cm^3) was stirred under nitrogen at 60 °C for 18 h with a solution of potassium t-butoxide (from 1.0 g potassium) in t-butyl alcohol (80 cm^3). The cooled mixture was poured into water, extracted with ether, and the recovered product purified by preparative layer chromatography. The rearranged product was obtained as a bright yellow gum (60 mg) which showed a single spot on analytical t.l.c. but decomposed on attempted distillation (Found: M^+, 268. Calc. for $C_{18}H_{20}S$: M, 268); $\lambda_{max.}$ 247, 293, 320, and 335 nm (log ε, 4.36, 4.47, 4.30, and 4.10); $\nu_{max.}$ (film) 990, 972, and 900 cm^{-1}.

Determination of Raman Spectra (By Dr. D. N. Waters, Brunel University).—The spectra were determined on a Spex Ramalab instrument with sample excitation by a Coherent Radiation Model 52MG argon–krypton ion laser, using the exciting lines at 568.2 and 647.1 nm. Rather low powers (*ca.* 20 mW) were necessary to avoid overheating the samples. Some fluorescence was encountered, especially with the cyclic di-yne (9) and compound (8) and as a result the overall signal to noise ratio was only moderate. Nevertheless, the intrinsically strong symmetrical triple-bond vibrations of the acetylenic groups present in the terminal di-acetylene (10) and the cyclic di-yne (9) (in $CHCl_3$) were readily apparent at 2 116 and 2 258 cm^{-1}, the latter corresponding to that shown by hexa-2,4-diyne in carbon tetrachloride at 2 264 cm^{-1}. The success of these observations can be attributed, in part, to the high red-sensitivity of the (cooled) R.C.A. type C31034 photomultiplier used in the spectrometer. The samples were examined by transverse illumination in 1 mm diameter capillary tubes; they were introduced into the tubes by suction after dilution with a little chloroform to reduce the viscosities.

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