

The Synthesis of Some Thiophenophanes and Attempted Cyclisations to Polycyclic Thiophenium Salts

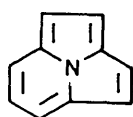
R. Morrin Acheson* and Gary C. M. Lee

Department of Biochemistry, University of Oxford, South Parks Road, Oxford OX1 3QU

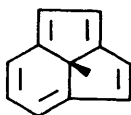
5,10-Diphenylcyclotrideca-2,4,10,12-tetraene-6,8-diyn-1-one (**28**), 5,6,7,8-tetrahydrodibenzo[*a,g*]cyclotridecen-15-one (**21**), and 13,14,16,17-tetrahydro-5,6,7,8-tetrahydrodibenzo[*a,g*]cyclotridecen-15-one (**40**) were synthesized. All attempts to add hydrogen sulphide across the triple bonds of these compounds to give thiophenes failed. 13,14,16,17-Tetrahydro-5,8-epithiodibenzo[*a,g*]cyclotridecen-15-one (**43**), from which hydrogen sulphide was removed by DDQ or chloroanil to give the ketone (**40**), was synthesized *via* the copper(II) acetate oxidation of 1,5-bis(2-ethynylphenyl)pentan-3-one (**36**). This ketone was obtained from 2-iodobenzaldehyde which on successive treatment with acetone, and ethynyltrimethylsilane yielded 1,5-bis(2-trimethylsilylethynylphenyl)penta-1,4-dien-3-one (**18**). Tributyltin hydride reduced the vinyl double bonds only in this ketone, and subsequent hydrolysis gave the ketone (**36**). Reduction of the cyclic ketone (**40**) with sodium borohydride gave the alcohol (**41**), sodium sulphide converted the diyne grouping into a thiophene ring giving the thiophene alcohol (**42**), and chromic acid now yielded the ketone (**43**). Attempts to convert this alcohol (**42**) and ketone (**43**) into pentacyclic sulphonium salts or related compounds resulted in elimination of oxygen and the formation of olefins.

Although [2.2.3]cyclazine (**1**) was synthesized¹ over 20 years ago the carbocyclic aromatic [10]annulene (**2**) has only recently been obtained.² The charged sulphur analogue (**3**) might be more umbrella shaped, because of the relatively long C-S bond, and is not known. Very few of the many sulphonium salts reported³ possess a thiophenium type of sulphur atom [*cf.* (**3**)] and of these the only two possessing a bridgehead sulphur atom are the salts (**4**)⁴ and (**5**).⁵ X-Ray crystal structure data for 1,2,3,5-tetramethylbenzo[*b*]thiophenium tetrafluoroborate [*cf.* (**6**)].⁶ and for 1*H*-thiophenium 1-(bismethoxycarbonyl)methyl-

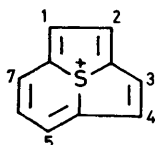
of (**6**),⁸ ¹³C n.m.r. resonance positions⁶ and an *ab initio* calculation performed for the hypothetical 1-protothiophenium cation which gave an energy maximum when the S-H atom was coplanar with the ring.⁶ It is extremely likely, therefore, that the salt (**4**) has a structure resembling that of (**6**) and that the carbocyclic rings of the thianthrene (**5**) are not coplanar as they subtend 28° to each other in the parent molecule.⁹ Some aryl sulphonium salts can invert their configuration quite easily¹⁰ as a flattening of an sp³ sulphur atom might be possible at some cost in energy. A structure such as the 10π system (**3**), although thought¹¹ to be capable of existence on the basis of calculations which ignored 3d orbital participation by sulphur, appeared to be very strained, and so we made the 12π 6*aH*-10*b*-thioniacyclopenta[*e,f*]heptalene system (**7**), and the 14π aromatic ylide (**8**)



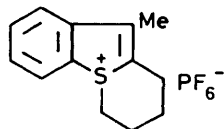
(1)



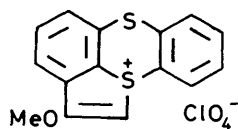
(2)



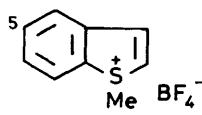
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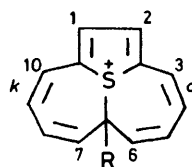
(4)



(5)

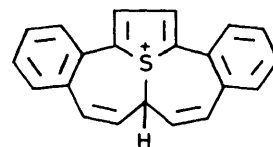


(6)

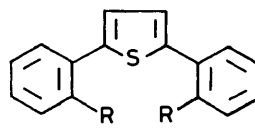


(7) R = H

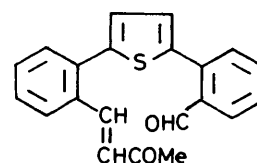
(8) R = -



(9)



(10) R = CHO

(11) R = CH=CH₂

(13)



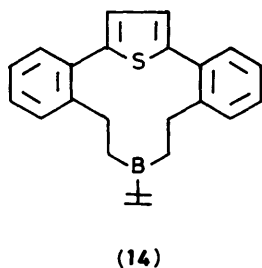
(12)

ide⁷ shows that the sulphur atoms exhibit pyramidal bonding. It seems likely under these circumstances that the lone pairs formally associated with the sulphur atoms are not involved with the aromatic systems to a significant extent and this is consistent with the addition of bromine across the 2,3-positions

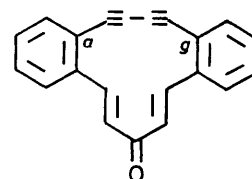
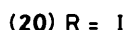
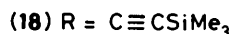
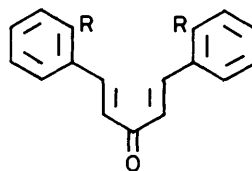
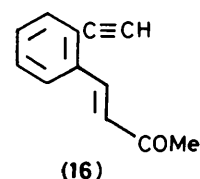
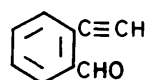
theoretically obtainable by proton loss, our objectives, the immediate aim being the 3,10-diphenyl- and the [*d,k*]-dibenzo derivatives where synthetic problems appeared to be less.

There are many possible ways of building a molecule such as (9), and the first routes envisaged involved the synthesis of a symmetrically 2,5-disubstituted thiophene, adding on the saturated carbon atom in (9) to the ends of the substituents either as a one-carbon or three-carbon fragment to yield a thiophenophane, followed by cyclisation. Very few thiophenophanes are known and no general synthesis has been developed.¹²

2,5-Bis(2-formylphenyl)thiophene (10), described earlier,¹³ was treated with the bis-phosphorane (12), obtained from the corresponding bis-phosphonium chloride¹⁴ and 1,8-diazabicyclo[5.4.0]undec-7-ene which is known to react with carbonyl compounds.^{15,16} Combination required boiling tetrahydrofuran (THF) and gave a poor yield of the ketone (13). Prolonged reaction times failed to cause cyclization which was surprising in view of Büchi's preparation¹⁷ of macrocyclic ketones by this sort of procedure. The dialdehyde (10) was now converted by triphenylphosphonium methylide into the 2,5-bis(2-styrylphenyl)thiophene (11). Concurrent attempts to obtain this thiophene from 2-styrylphenylmagnesium bromide, 2,5-dibromothiophene, and dichloro[1,3-bis(diphenylphosphino)propane]nickel(II) and Kumada's conditions,¹⁸ which we confirm give the reported yields of 2,5-diphenylthiophene from phenylmagnesium bromide, gave a complex mixture containing only 9% of the desired compound (11), 2,2'-styrylbiphenyl, and other products. *o*-Tolylmagnesium bromide gave a similar mixture, and although many successful examples of the use of substituted phenylmagnesium bromides are reported by Kumada none possessed a 2-substituent; steric hindrance may interfere with the condensation. Attempts to prepare (11), from 2,5-dilithiothiophene, generated from the 2,5-dibromo compound and butyl-lithium, 2-bromostyrene and tetrakis(triphenylphosphine)palladium(0), used¹⁹ in a related instance, gave only 2,5-dibutylthiophene, and *t*-butyl-lithium, used to circumvent halogen exchange²⁰ which may have been the cause of our results, was not successful. Styrene undergoes hydroboration easily²¹ but the thiophene (11) was recovered unchanged from treatment with tetrabutylborane at high dilution²² so the desired (14) could not be cyanoborated²³ to (43).



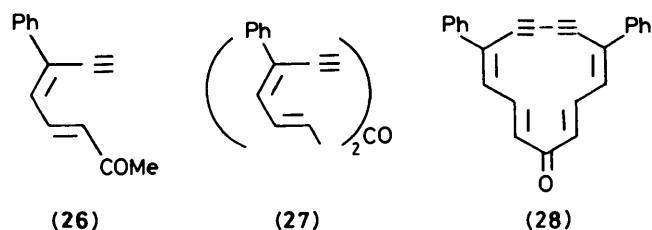
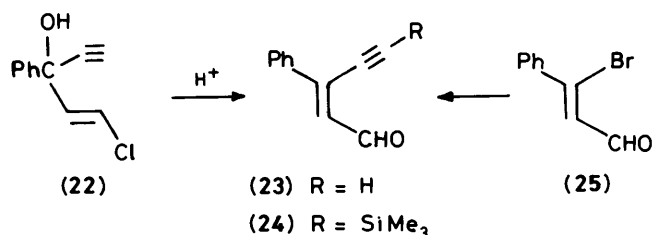
As the approaches had failed it was decided to build a carbocyclic-1,3-diyne and form the thiophene ring by addition of hydrogen sulphide to the diyne system at a late stage. Ojima *et al.* have described²⁴ the synthesis of 5,6,7,8-tetrahydrodibenzo[*a,g*]cyclotridecen-15-one (21) starting from 2-ethynylbenzaldehyde (15) which was obtained in eight steps from 2-(2-aminoethyl)benzaldehyde.²⁵ Recently Austin *et al.*²⁶ obtained 2-ethynylbenzaldehyde by the more convenient process of a palladium catalysed coupling of 2-bromobenzaldehyde with pure ethynyltrimethylsilane followed by hydrolysis. In our hands the literature preparations of ethynyltrimethylsilane from chlorotrimethylsilane and sodium acetylide²⁷ or ethynylmagnesium bromide²⁸ did not give the reported 30% yield, and a better synthesis was sought. Monolithium acetylide, prepared



at -78°C ²⁹ from butyl-lithium and acetylene in THF with chlorotrimethylsilane, gave a solution containing 75–80% of the desired ethynyltrimethylsilane. This solution with 2-bromobenzaldehyde in the presence of palladium(II) acetate and triethylamine, essentially under Austin's conditions,²⁶ gave a 91% yield of the trimethylsilylethynyl compound. The time-consuming isolation and purification of the ethynyltrimethylsilane was therefore quite unnecessary for our reactions and this may well be true in other cases. As noted by Austin *et al.*²⁶ the source of the triethylamine used for the coupling was critical. That from Fluka gave satisfactory and reproducible results, but that from Aldrich or British Drug Houses did not; the reason has not been investigated. Desilylation was effected initially by anhydrous potassium carbonate in methanol as described.²⁶ On one occasion, however, an explosive decomposition took place. This was probably due to the extreme sensitivity of 2-ethynylbenzaldehyde to base, especially above 40°C , and perhaps all the potassium carbonate had not been completely removed. Potassium fluoride in dimethylformamide (DMF) proved equally effective as a desilylator and no explosive decompositions followed its use.

Treating 2-ethynylbenzaldehyde (15) with 0.5 mol equiv. of acetone and base gave 27% of the dienone (17); altering the conditions or carrying out the reaction in two stages, *via* compound (16) as described,³⁰ gave much poorer results. An alternative route to (17) was examined. Although 2-bromobenzaldehyde with acetone gave a high yield of the dienone (19), the best yield of the bis-trimethylsilylethynyl derivative (18) obtainable from this [(19)] under a variety of conditions with trimethylsilylacetylene was only 5%. Oxidation of the diyne (17) under the conditions of Sondheimer *et al.*³⁰ gave the tricyclic diyne (21) which had properties similar to those reported by Ojima *et al.*²⁴

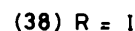
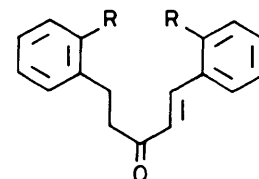
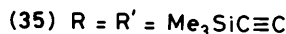
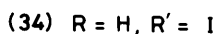
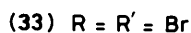
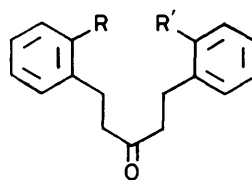
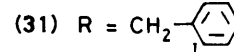
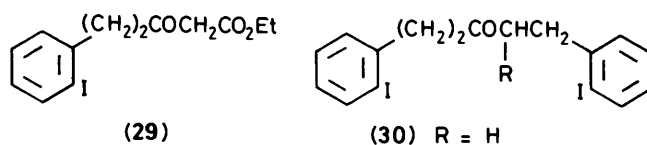
Concurrently with this work the diyne (28) was synthesized *via* 3-phenylpent-2-en-4-ynal (23). This aldehyde was first obtained, in only 9.7% overall yield, from benzoyl chloride which, with acetylene and aluminium chloride, yielded³¹ 2-chlorovinyl phenyl ketone. The best conversion of this into 1-chloro-3-phenylpent-1-en-4-yn-3-ol (22) was with lithium acetylide prepared from butyl-lithium as described by Midland,²⁹ but despite very careful temperature control explosive decomposition always took place towards the end of every distillation; treatment of compound (22) with acid gave the ynal (23). An alternative route, which proved much easier



to carry out, required 3-bromo-3-phenylpropen-1-al (25) which was obtained from DMF, acetophenone and phosphorus tribromide as described by Arnold and Holý,³² but in half their yield. Nevertheless, the reaction of compound (25) with ethynyltrimethylsilane, in the presence of tetrakis(triphenylphosphine)palladium and copper(I) iodide gave the hygroscopic ethynyl derivative (24) which hydrolysed readily to the acetylene (23). An aldol condensation with acetone under the conditions of Nakagawa *et al.*³³ gave almost twice the yield of compound (26) as obtained using Sondheimer *et al.*'s procedure,³⁰ but a further aldol reaction using Sondheimer's conditions³⁰ gave (27), converted by copper(II) acetate and pyridine into 5,10-diphenyl-2,4,10,12-cyclotridecatetraene-6,8-diyn-1-one (28). The ¹H n.m.r. spectrum is similar to that reported³⁰ for the corresponding 5,10-dimethyl analogue, but the 3, 4, 11, and 12 protons are at slightly lower field.

Every attempt to add the elements of hydrogen sulphide across the triple bond system of compound (21) either caused no reaction, or using conditions successful in other cases for making thiophenes,³⁴⁻³⁶ or hydrogen sulphide and 1,8-diazabicyclo[5.4.0]undecene in methylene dichloride, caused reaction but gave none of the desired (48). The i.r. spectrum of the products, which could not be separated, showed that the acetylenic absorption had disappeared and that the carbonyl absorption had moved from 1660 cm⁻¹ into the saturated region at 1710 cm⁻¹, and the ¹H n.m.r. spectrum showed no resonance in the region expected of hydrogen atoms at the 3,4-positions of a thiophene. It was clear that the electrophilic activity of the olefinic double bonds in (21) had to be suppressed before the thiophene ring could be formed. Attempts to form the diethyl acetal of (21) from triethyl orthoformate and ammonium chloride³⁷ gave a low conversion while long reaction times caused decomposition. Reduction of the ketone (21) by sodium borohydride as described³⁸ did not give the reported 91% yield of the corresponding alcohol, but gave a six or more component mixture. The proportion of the desired alcohol, detected by 300 MHz ¹H n.m.r., could not be increased by altering the reaction conditions. Reduction of the ketone (17) by borohydride was now examined, and, again contrary to the short communication,³⁸ the reaction gave a high yield of the corresponding alcohol with the described³⁸ spectroscopic properties. Oxidative cyclization by copper(II) acetate unfortunately also oxidized the alcohol group to give the ketone (21).

As the activated olefinic double bonds of (21) were the prime cause of the difficulties a direct synthesis of the saturated analogue (40) was undertaken, for a selective reduction of (21)



did not seem possible with contemporary reagents.¹² 2-Iodobenzyl bromide with dilithium ethyl acetoacetate yielded the expected product (29), which could not be purified by distillation, but nevertheless, on further alkylation by the same bromide, acid hydrolysis and concurrent decarboxylation yielded a mixture of the desired ketone (30) and the further alkylation product (31), the formation of which could not be eliminated. An alternative synthesis of (30) began with 2-iodobenzoyl chloride. It was reduced to the alcohol, oxidized to the aldehyde, and converted into 2-iodostyrene with a Wittig reagent. Hydroboration with hexyl borane,²² under standard conditions,³⁹ gave the trialkylborane [*cf.* (14)], and treatment with sodium cyanide followed by trifluoroacetic anhydride and hydrogen peroxide³⁹ yielded mainly the ketone (32). This was separated chromatographically from 2-(2-iodophenyl)ethanol which arose from oxidation of 2-(2-iodophenyl)ethylhexylborane. Although the ketone (32) had essentially the same spectra as the sample obtained from the previous route it did not solidify and could not be separated from what were thought to be boron-containing impurities.

The conjugate reduction of the bromo dienone (19) with 2.2 mol equiv. of butyltin hydride and tetrakis(triphenylphosphine)palladium(0) under published conditions⁴⁰ gave the saturated ketone (33), the partially saturated ketone (37) also being detected by n.m.r. in the reaction mixture before reduction was complete. Under identical conditions the iodo compound (20) lost an iodine atom yielding (34). House has reported⁴¹ the direct displacement of iodine by butyltin hydride. Reducing the amount of butyltin hydride to 2 mol equiv. gave a 1:1 molar mixture of compounds (32) and (38).

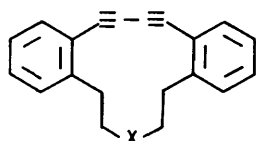
The reaction of 1,5-bis(2-iodophenyl)pentan-3-one (32) with ethynyltrimethylsilane in THF-hexane under our usual conditions gave the bistrimethylsilylethynyl derivative (35), which was desilylated by potassium fluoride in dimethylformamide to the ketone (36).

Because it was so difficult to synthesize the ketone (32) in quantity it was decided to try an alternative route and to insert the ethynyl group at an earlier stage. The iodo ketone (20), in contrast to the bromo compound (19), gave a 63% yield of the bistrimethylsilylethynyl derivative (18) with ethynyltrimethylsilane, copper(I) iodide, tetrakis(triphenylphosphine)palladium(0), and triethylamine; the stepwise replacement of the iodine atoms was strongly suggested by t.l.c. monitoring. The same derivative (18) was obtained from the diacetylene (17) and

chlorotrimethylsilane under Yamaguchi's conditions⁴² in much poorer yield, while a bis-Wittig reaction between 2-trimethylsilyl ethynylbenzaldehyde and the phosphorane (13) gave unresolvable mixtures.

In 1964 Shakhovskoi *et al.*,⁴³ and later others,⁴⁴ found that a triple bond attached to a trimethylsilyl group was not reduced by hydrogen and palladium. This could be due in part for steric reasons, so the conjugate reduction of the diethynyl dienone (18) with tributyltin hydride in the presence of tetrakis(triphenylphosphine)palladium(0) and acetic acid was examined under the general conditions reported.⁴⁰ One equivalent of the hydride caused reduction of one of the olefinic bonds giving 85% of the diethynyl enone (39), with a little (35), and further reduction to the ketone (35) was achieved in very high yield by more reagent. This highly effective protection of ethynyl groups by trimethylsilylation to reduction by tributyltin hydride, a reagent which can add to an unactivated alkyne,⁴⁵ appears to be the first example of such a selective reaction and may be a useful procedure in other syntheses.

The intramolecular oxidative coupling of the ketone (36) by copper(II) acetate initially gave problems but cyclization to the first example (40) of a partially saturated dibenzo[13]annulene was effected in 78% yield using the precise conditions and precautions suggested by Sondheimer³⁰ for similar reactions. The ¹H and ¹³C n.m.r. spectra of (40) showed no unusual



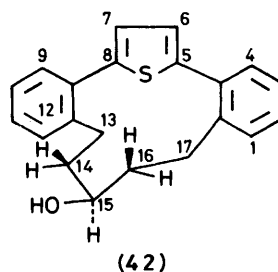
(40) X = C=O

(41) X = CHO

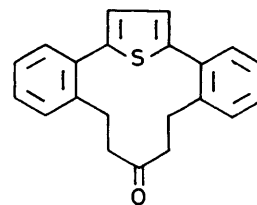
features but the carbonyl absorption at 1 695 cm⁻¹ was outside the normal saturated ketone range and the triple bond appeared at 2 200 cm⁻¹. The u.v. spectrum showed more fine structure than that of (21). The structure of the compound was confirmed by X-ray diffraction studies⁴⁶ which showed that the diyne system was slightly bowed, and that the planar phenyl rings subtended an angle of 27° to each other.

Refluxing the diyne (40) with sodium sulphide in methanol failed to give a thiophene derivative but, instead, gave a compound isomeric with the starting material which possessed no normal carbonyl absorption in the i.r. region and has not been identified. Reduction of the diyne (40) to the alcohol (41), in order to protect the carbonyl and prevent the α-carbon atoms reacting in an undesired fashion, was achieved with sodium borohydride. The n.m.r. spectrum of the resulting alcohol (41) confirmed its structure and now treatment with sodium sulphide yielded the thiophenophane alcohol (42), which was easily oxidized by chromic acid to the ketone (43). The best synthesis of this ketone followed the route 2-iodobenzaldehyde → (20) → (18) → (35) → (36) → (40) → (41) → (42) → (43).

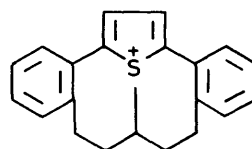
Attempts to obtain suitable crystals of compounds (42) and (43) for X-ray crystallography were unsuccessful,⁴⁶ but the structures of the compounds were clear from their ¹H n.m.r. spectra. The thiophene protons appeared in both compounds as singlets at *ca.* δ 6.9, clearly differentiated from the benzenoid protons at *ca.* δ 7.4. In the alcohol (42) the CHOH proton appeared as a triple triplet due to coupling (9 + 2 Hz) with the adjacent methylene groups. A model suggests the stereochemical arrangement shown and the values of the coupling constants suggest dihedral angles of *ca.* 160 and 60° which are consistent with 'axial-axial' and 'axial-equatorial' coupling. The u.v. spectrum of the alcohol (42), and that of the ketone (43), show



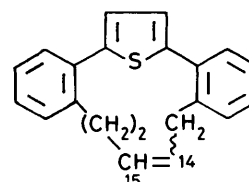
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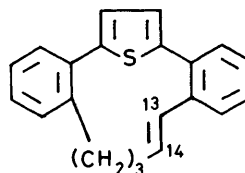


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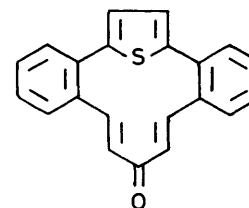


(45) E - isomer

(46) Z - isomer



(47)



(48)

small shifts to longer wavelengths compared with that of 2,5-diphenylthiophene which indicates that the aromatic rings in the compounds subtend different average angles to each other. The mass spectrum of compound (42) showed the molecular ion as the base peak, a very unusual feature for a secondary alcohol, while the ion corresponding to the loss of water was less than 5%. Under similar conditions the molecular ion of 1,5-diphenylpenta-4-ol was not observed and the [M - H₂O]⁺ peak was *ca.* 20% of the base peak. The molecular ion for the ketone (43) was the base peak and there was little fragmentation.

Attempts were now made to cyclise the alcohol (42) to the thiophenium cation (44). Alkyl triflates are exceptionally powerful alkylating agents⁴⁷ and so the alcohol was treated with triflic anhydride and sodium carbonate using the general conditions reported⁴⁷ first at -40 °C and working up at room temperature. Some of the alcohol was recovered, and an oil which was identified as the olefin (45) from its ¹H n.m.r. and mass spectra was produced. In order to see whether decomposition of the triflate of (42) took place during the work-up, the reaction was monitored by observing the thiophene proton resonances. The singlet observed for the alcohol (42) in CDCl₃ at -40 °C remained after the addition of the anhydride, it started to collapse at -20 °C, and had changed completely to the double doublet characteristic of (45) as the temperature was slowly increased to +20 °C over 20 min. As no base had been added it is possible that electron donation by the sulphur, even to the extent of forming (44), may be a factor in the rapid elimination. The alcohol (42) was now converted into the iodide by iodotrimethylsilane, but treatment of this in dichloromethane with silver tetrafluoroborate, conditions which give 1-isopropylation of benzothiophenes,⁸ again only gave the olefin (45).

Since the trapping of a carbene by a sulphur lone pair is

Table. 300 MHz n.m.r. spectra in δ (J Hz)

Proton assignment	Compound		
	(45) ^a	(46) ^a	(47) ^a
6-H (or 7-H)	6.84d (3.75)	6.89 ^d (3.75)	7.00d(3.75)
7-H (or 6-H)	6.95d (3.75)	6.99d (3.75)	7.06d (3.75)
13-H _A	3.32dd (15 + 10)	3.20m ^c	6.35d (16.3)
13-H _B	3.20d ^b (15)	3.20m ^c	—
14-H	4.92m	5.22m	5.22m
15-H or H ₂	4.92m	5.35m	1.82m
16-H ₂	1.65m	1.50m	1.50m
17-H ₂	2.92m	2.75m	2.75m

^a Aromatic protons 7.16—7.50m. ^b Decoupling at δ 3.20 converts 14-H into a doublet (J 15) and 15-H to a dd (J 10 + 3). ^c Decoupling at δ 3.20 converts 14-H into a d (J 10) and 15-H into a dt (J 10 + 7.5 + 7.5).

known^{7,48} to give an ylide [cf. (8)] the ketone (43) was converted into the toluene-*p*-sulphonylhydrazone and this was treated with lithium di-isopropylamide.⁴⁹ The product was a mixture of the olefin (45), obtained previously, and compounds (46) and (47) which were identified from their mass and ¹H n.m.r. spectra.

It was now hoped that dehydrogenation of ketone (43) to the unsaturated ketone (48) and cyclization to the dibenzo derivative of (8) could be effected. Treatment with palladium(II) chloride in *t*-butyl alcohol and hydrochloric acid⁵⁰ caused no dehydrogenation and benzeneselenic anhydride⁵¹ gave polymers. Bromination could not be controlled in acetic acid, and mass spectrometry showed that three hydrogen atoms had been replaced by bromine. Dehydrogenation by 2,3-dichloro-5,6-dicyano-1,4-benzoquinone and by 3,4,5,6-tetrachloro-1,2-benzoquinone was now examined and both removed the elements of hydrogen sulphide from the thiophene to give back the strained di-acetylene (40). The identity of this product, in view of its very unexpected nature, was rigorously established by the identity of its ¹H n.m.r., mass, u.v., and i.r. spectra with those of authentic material. This appears to be the first direct conversion of a thiophene into a 1,3-diyne, and must be associated with the particular properties of our ring system because neither of the quinones reacted with 2,5-diphenylthiophene or 2,5-bis(2-bromophenyl)thiophene.

The mass spectra of ketone (43) gave the molecular ion as the base peak, and the loss of 33 m.u. gave the next most intense peak. This corresponds to the loss of 'HS,' a fragment also apparently lost from the molecular ion derived from the olefin (45) to give in fact the base peak for this compound. The successive loss of 'HO' and 'HS' from the molecular ion, which is also the base peak, in the mass spectrum of the alcohol (42) again indicates that the thiophene ring in these compounds is being disrupted by the oxidative process of mass spectrometry.

Experimental

M.p.s were taken on a Kofler hot stage apparatus and are uncorrected. I.r. spectra were recorded on a Perkin-Elmer Model 257 spectrometer and are normally reported for the 3 350—1 000 region; fuller data are available.¹² N.m.r. spectra were measured in deuteriochloroform and are recorded in δ (δ_H at 60 MHz and δ_C at 75.5 MHz) (J in Hz) using internal tetramethylsilane as standard; off resonance multiplicities for δ_C resonances are noted. Low resolution mass spectra were determined at 70 eV on a VG Micromass ZAB-16F spectrometer. Field ionization and chemical ionization mass spectra were recorded on a VG Micromass ZAB-1F spectrometer. Flash column chromatography was performed using a flash

column technique⁵² with silica (Merck Kieselgel 60 No. 9385) or alumina (Merck Aluminium oxide 90 aktiv neutral 70—230 mesh) grade I or III having 1 or 4.7% water respectively. T.l.c. was carried out using CamLab pre-coated plates, or for preparative purposes using 1.25 mm thick Merck silica gel 60 GF 254 No. 7730. Anhydrous magnesium sulphate was used for drying extracts and evaporation refers to removal of solvent on a Büchi evaporator under reduced pressure. *n*- And *t*-butyllithium were standardized by the method of Watson and Eastham.⁵³ THF was distilled from calcium hydride immediately before use. Light petroleum was of b.p. 40—60 °C.

2-(2-Formylphenyl)-5-[2-(3-oxobut-1-enyl)phenyl]thiophene (13).—Carbonyldimethylenebis(triphenylphosphonium) dichloride (540 mg), 1,8-diazabicyclo[5.4.0]undec-7-ene (250 mg) and THF (30 ml) were refluxed under N₂ for 1 h after which 2,5-bis(2-formylphenyl)thiophene (10)¹³ (240 mg) in THF (10 ml) was added and refluxing continued for a further 20 h. The mixture was poured into water, acidified (HCl aqueous 2M), and extracted with ether; evaporation of the washed and dried extracts afforded yellow crystals. Flash chromatography (silica) and elution with ether (30%)—light petroleum gave 2,5-bis(2-formylphenyl)thiophene (10) (R_F 0.33) (86.4 mg) and the title compound (13) (R_F 0.14) (65 mg) as an oil; m/z 332 (M^+ , 10), 317 (M^+ - 15, 2), 289 (M^+ - MeCO, 56), and 271 (100); δ 2.32 (3 H, s, Me), 6.66 (1 H, d, J 15.3, vinyl H), 7.03 (2 H, s, 3,4-H), 6.90—7.70 (8 H, m, ArH), 7.90 (1 H, d, J 15.3, vinyl H), and 10.31 (1 H, s, CHO). A longer reaction time (30 h) or reaction at 90 °C with dimethyl sulphoxide (DMSO) as solvent led to no improvement.

2,5-Bis(2-vinylphenyl)thiophene (11).—(i) Methyltriphenylphosphonium bromide (1.83 g) was suspended in THF (20 ml) and butyl-lithium in hexane (5.14 mmol) was added dropwise, with stirring, under nitrogen at 0 °C. After 35 min at 0 °C, 2,5-bis(2-formylphenyl)thiophene (10) (0.5 g) in THF (5 ml) was added, stirring was continued (18 °C, 90 min) and water (25 ml), methanol (25 ml), and ether (50 ml) were added. The organic phase was washed (brine), dried, and the brown oil obtained on solvent evaporation chromatographed (silica). Elution with light petroleum containing ether (10%) gave the title compound (11) which recrystallized from light petroleum (cooling to -78 °C), as very pale yellow prisms (0.36 g, 74%), m.p. 48—49 °C (Found: C, 82.2; H, 5.6. C₂₀H₁₆S·0.25H₂O requires C, 82.1; H, 5.6%; m/z 288 (M^+ , 100), 273 (39), 141 (61), 128 (51), and 115 (64); v_{max} (neat) 3 380 (H₂O), 1 625, 1 595, 1 475, 1 465, 1 440, and 1 410 cm⁻¹; δ 5.20 (1 H, dd, J 11.3 + 1.3, vinyl H₂), 5.63 (1 H, dd, J 17.3 + 1.3, vinyl H₂), 6.95 (2 H, s, 3,4-H), and 7.25 (10 H, m, ArH + vinyl H₂).

(ii) 2-Styrylphenylmagnesium iodide [from 2-iodostyrene (10 g) magnesium (1.04 g)] in ether was added dropwise, with stirring, under nitrogen, to 2,5-dibromothiophene (4.16 g) and [Ni(dppp)Cl₂] (30 mg) in ether (40 ml) at 0 °C. The mixture was refluxed for 9 h after which it was poured into aqueous hydrochloric acid (2M; 100 ml) and extracted with dichloromethane; the extract was washed (H₂O), dried, and evaporated to give a light brown oil, which was purified by preparative t.l.c. using ether (10%) in light petroleum as eluant. Three major bands appearing as purple, green, and yellow respectively (under u.v. λ 254) were isolated. The first band (R_F 0.63) afforded yellow prisms (300 mg, 9.3%), with physical and spectral properties identical with those of authentic 2,5-bis(2-vinylphenyl)thiophene (11) prepared by an alternative route. The second band (R_F 0.50) gave 2,2'-styrylbiphenyl as a yellow oil (310 mg, 8.7%); m/z 206 (M^+ , 21), 178 (M^+ - C₂H₄, 100), 152 (39), 103 (M^+ /2, 77); δ 5.24 (2 H, dd, J 11 + 1.3), 5.65 (2 H, dd, J 18 + 1.3), and 6.90—7.60 (10 H, m, ArH). The third band (R_F 0.38) recrystallized (from chloroform—light petroleum

cooling to -78°C) as yellow prisms (280 mg, 4.3%), provisionally identified as 2,2'-bis[5-(2-styrylphenyl)thiophene], m.p. $105-106^{\circ}\text{C}$ (Found: C, 74.2; H, 4.5. $\text{C}_{24}\text{H}_{18}\text{S}_2 \cdot 0.17\text{CHCl}_3$ requires C, 74.3; H, 4.7%); m/z 370 (M^+ , 92), 185 ($M^+ / 2$, 46), and 152 (39); δ 5.26 (2 H, dd, J 10.7 + 1.3), 5.68 (2 H, dd, J 17 + 1.3), 7.27 (CHCl_3), and 6.80–7.70 (14 H, m). Employing refluxing THF (21 h) caused no improvement.

Ethynyltrimethylsilane in THF.—Butyl-lithium (0.3 mol) in hexane was added dropwise, with stirring, under N_2 at -78°C to THF (500 ml) saturated with acetylene (purified by passing through a trap cooled to -78°C , concentrated sulphuric acid and soda-lime). The flow of acetylene was maintained throughout the addition of the butyl-lithium and for 20 min afterwards. Now chlorotrimethylsilane (0.306 mol) was added and after stirring overnight (10 h), while the cooling bath warmed slowly to room temperature, the mixture was allowed to settle. The solution of ethynyltrimethylsilane was decanted off carefully and was used directly in subsequent experiments.

2-Ethynylbenzaldehyde (15).—A deaerated solution of 2-bromobenzaldehyde (18.5 g, 100 mmol), triphenylphosphine (400 mg), and palladium(II) acetate (200 mg) in anhydrous triethylamine (300 ml) was treated with ethynyltrimethylsilane in THF–hexane (150 mmol) under nitrogen. The mixture was rapidly heated and kept at $80-90^{\circ}\text{C}$ for 5 h. After being cooled, the mixture was filtered and the filtrate concentrated, mixed with water (100 ml), and extracted with dichloromethane. Distillation of the dried extract gave 2-(trimethylsilyl)ethynylbenzaldehyde as a yellow oil (18.4 g, 91%), b.p. 98°C at 0.2 mmHg (lit.,²⁶ 108°C at 2 mmHg); δ 0.09 (9 H, s, SiMe_3), 7.27 (3 H, m, ArH), 7.67 (1 H, m, 6-H), and 10.32 (1 H, s, CHO).

This compound (18.4 g) was treated with potassium fluoride dihydrate (19 g) in DMF (60 ml) under nitrogen at room temperature and then left overnight. It was then poured into water and extracted with dichloromethane; work-up of the extract and recrystallization of the product from light petroleum (cooling to -78°C) gave 2-ethynylbenzaldehyde (15) (11.7 g, 99%), m.p. $60-61^{\circ}\text{C}$ (lit.,²⁵ $60-60.5^{\circ}\text{C}$); m/z 130 (M^+ , 28), 129 (6), 105 (7), and 102 ($M^+ - \text{CO}$, 100); ν_{max} (Nujol) 3 230 ($\equiv\text{CH}$), 2 840, 2 740, 2 090 ($\text{C}\equiv\text{C}$), 1 680, 1 660, 1 590, 1 270, and 1 200 cm^{-1} ; δ 3.45 (1 H, s, $\equiv\text{CH}$), 7.45 (3 H, m, ArH), 7.80 (1 H, m, 6-H), and 10.43 (1 H, s, CHO).

4-(2-Ethynyl)phenylbut-3-en-2-one (16).—A mixture of aqueous sodium hydroxide (0.65M; 6.8 ml) and ethanol (6.8 ml) was added over 10 min to an ice-cooled stirred solution of 2-ethynylbenzaldehyde (15) (3.25 g) in acetone (13.5 ml). The mixture was stirred for 4 h at 0°C and then aqueous sulphuric acid (2M; 2.65 ml) was added. Dilution with water (150 ml), extraction with ether, and evaporation of the washed (saturated aqueous sodium hydrogencarbonate) dried extracts gave an oil which was chromatographed over alumina (grade III). Elution with light petroleum containing ether (20%) afforded the ketone (16) as a yellow oil (2.43 g, 57%) which could not be induced to crystallize (lit.,⁵⁴ m.p. 64.5°C); m/z 170 (M^+ , 32), 169 (11), 155 (61), and 127 ($M^+ - \text{MeCO}$, 85); ν_{max} (film) 3 300 ($\equiv\text{CH}$), 2 100 ($\text{C}\equiv\text{C}$), 1 670, 1 620, 1 610, 1 590, 1 475, 1 360, and 1 260 cm^{-1} ; δ 2.34 (3 H, s, Me), 3.40 (1 H, s, $\equiv\text{CH}$), 6.67 (1 H, d, J 16.7, vinyl H), 7.35 (4 H, m, ArH), and 8.00 (1 H, d, J 16.7, vinyl H).

1,5-Bis(2-ethynylphenyl)penta-1,4-dien-3-one (17).—(i) Methanolic potassium hydroxide (3.6M; 1.89 ml) was added to a stirred solution of 4-(2-ethynyl)phenylbut-3-en-2-one (16) (2.42 g) and 2-ethynylbenzaldehyde (15) (1.85 g) in ether (60 ml, previously passed through basic alumina and flushed with nitrogen). After 4 h at room temperature, acetic acid (2.8 ml) was added, the mixture stirred for 15 min and then diluted with

water (100 ml). The combined ether extracts were washed (saturated aqueous sodium hydrogencarbonate), dried, evaporated and the residue chromatographed (alumina, grade III). Elution with light petroleum containing ether (30%) gave the ketone (17) as yellow crystals (0.85 g, 21%), m.p. $101-102^{\circ}\text{C}$ (lit.,²⁴ m.p. $101.3-101.7^{\circ}\text{C}$); m/z 155 ($M^+ - \text{C}_{10}\text{H}_7$, 75), 127 (100), and 102 (30); ν_{max} (CH_2Cl_2) 3 300 ($\equiv\text{CH}$), 2 250 ($\text{C}\equiv\text{C}$), 1 650, 1 620, 1 600, 1 590, 1 470, and 1 090 cm^{-1} ; δ 3.41 (2 H, s, $2 \times \equiv\text{CH}$), 7.09 (2 H, d, J 16.0, 2,4-H), 7.30 (8 H, m, ArH), and 8.29 (2 H, d, J 16.0, 1,5-H).

(ii) 2-Ethynylbenzaldehyde (6.82 g) in ether [20 ml, purified as in (i)] was added during 25 min, under nitrogen, to a solution of acetone (1.92 ml) and methanolic potassium hydroxide (1.41M; 4.68 ml) in ether (30 ml) at room temperature (cf. Sondheimer *et al.*³⁰). After being stirred for 4 h, the mixture was worked up as in (i). Recrystallization of the product from the column from ethanol gave the ketone (15) (1.95 g) with the properties described under (i).

1,5-Bis(2-bromophenyl)penta-1,4-dien-3-one (19).—2-Bromobenzaldehyde (41.4 g) in ethanol (20 ml) was added over 3 h at room temperature, with stirring, to a solution of sodium hydroxide (1.2 g) in acetone (10.67 ml), ethanol (340 ml) and water (340 ml); yellow crystals soon separated. The mixture was left in a refrigerator overnight after which the upper layer was decanted from a heavy bright yellow oil; the latter was collected with chloroform (150 ml), and the extract washed (H_2O), dried, and evaporated. Recrystallization (acetone) of the residue afforded the title compound (19) as yellow prisms (14.7 g, 34%), m.p. $126-127^{\circ}\text{C}$ (Found: C, 52.3; H, 3.1. $\text{C}_{17}\text{H}_{12}\text{Br}_2\text{O}$ requires C, 52.1; H, 3.1%); m/z 394 + 392 (M^+ , 12 + 14), 313 + 311 ($M^+ - \text{Br}$, 67), and 211 (32); ν_{max} (Nujol) 1 650, 1 590, 1 580, and 1 190 cm^{-1} ; δ 6.78 (2 H, d, J 16.7, 2,4-H), 7.09 (4 H, m, ArH), 7.55 (4 H, m, ArH), and 7.96 (2 H, d, J 16.7, 1,5-H).

Although treating this compound with triphenylphosphine, palladium(II) acetate, triethylamine, and ethynyltrimethylsilane using the general conditions reported,²⁶ or adding xylene and using 100°C (23 h) failed to give compound (17), using dioxane as co-solvent (13 h reflux) 5% of (18) was obtained.

1,5-Bis(2-ethylphenyl)penta-1,4-dien-3-ol.—Powdered sodium borohydride (0.27 g) was added to 1,5-bis(2-ethynylphenyl)penta-1,4-dien-3-one (17) (0.5 g) in methanol (25 ml) and the mixture stirred at room temperature for 3 h. It was then poured into water and the organic material collected with dichloromethane. Work-up of the extract and chromatography (alumina, grade III) of the product with ether (30%) in light petroleum as eluant gave the title compound as a yellow oil (0.36 g, 72%) with spectra similar to those reported:³⁸ m/z 267 ($M^+ - \text{OH}$, 2), 157 (18), 128 (100), and 127 (40); ν_{max} (film) 3 400, 3 300, 2 100, 1 645, 1 595, 1 560, 1 075, 1 040, and 1 020 cm^{-1} ; δ 2.6 (1 H, br, exchanged by D_2O), 3.30 (2 H, s), 5.00 (1 H, t, J 6), 6.33 (2 H, dd, J 16 + 6), and 7.20 (10 H, m).

5,6,7,8-Tetradehydrodibenzo[a,g]cyclotridecen-15-one (21).—(i) 1,5-Bis(2-ethynylphenyl)penta-1,4-dien-3-one (17) (4.7 g) in pyridine (200 ml) and dry ether (100 ml) was added dropwise during 5 h to a stirred solution of anhydrous copper acetate⁵⁵ (21.4 g) in pyridine (525 ml) and dry ether (175 ml) at 60°C (bath) according to a published procedure.³⁰ The solution was stirred at 60°C for a further 1.5 h and was then cooled. The residue after solvent evaporation was taken up in aqueous hydrochloric acid (0.1M) and extracted with dichloromethane (3×150 ml). The combined extracts were washed with saturated aqueous sodium hydrogencarbonate, dried, and evaporated. The residue on recrystallization from chloroform–light petroleum gave the annulene (21) as yellow prisms (2.96 g, 62%),

m.p. 196 °C (decomp.), [lit.,²⁴ m.p. 194 °C (decomp.)]; m/z 280 (M^+ , 7), 252 ($M^+ - CO$, 15), 154 (7), 126 (7); $\nu_{\max.}$ (CH_2Cl_2) 2 180 ($C\equiv C$), 1 660, 1 640, 1 620, 1 590, 1 090, 1 010, and 975 cm^{-1} ; δ 6.78 (2 H, d, J 16.6, vinyl-H), 7.40 (8 H, m), and 8.48 (2 H, d, J 16.6, vinyl-H). The elemental analysis was always low in carbon as reported previously.²⁴

(ii) Oxidation of 1,5-bis(2-ethynylphenyl)penta-1,4-dien-3-ol (1.0 g) in pyridine and dry ether with copper(II) acetate (4.43 g) exactly as above gave the ketone (21) (0.45 g) which had spectra and m.p. identical with those described above.

This compound (21) (200 mg) in ether (5 ml) with sodium borohydride (108 mg) in ethanol (30 ml) at room temperature as described³⁸ afforded a brown oil, which was flash chromatographed (silica) eluting with ethyl acetate–light petroleum (3:7 v/v). The product contained at least six components (t.l.c.), showed a very complex ¹H n.m.r. spectrum (300 MHz) but resonances due to the expected alcohol were observed at δ 5.08 (1 H, t, J 5.5) and 5.88 (2 H, dd, J 5.5 + 15). Similar results were obtained using THF or methanol as reaction solvent and longer times (16 h).

2-Chlorovinyl Phenyl Ketone.—The procedure of Price and Pappalardo³¹ was modified. The benzoyl chloride was added without cooling and then the mixture was refluxed on a water-bath for 5 h. Work-up gave 2-chlorovinyl phenyl ketone as a pale yellow oil (45%), b.p. 136–138 °C at 22 mmHg (lit.,³³ 134–136 °C at 17 mmHg).

1-Chloro-3-phenylpent-1-en-4-yn-3-ol (22).—2-Chlorovinyl phenyl ketone (42.65 g) in THF (50 ml) was added dropwise, with stirring, under nitrogen to lithium acetylide (0.33 mol) in THF²⁹ at –78 °C. Stirring was continued overnight while the cooling bath attained room temperature. With cooling, saturated aqueous ammonium chloride (200 ml) was added. The mixture was extracted with Et_2O and the extract worked up to give a viscous brown oil, which was distilled (explosive decomposition occurred towards the end) to give the title compound (22) as a colourless oil (20.0 g, 40%), b.p. 133–136 °C at 0.8 mmHg (lit.,³³ 118–119 °C at 0.35 mmHg); $\nu_{\max.}$ (film) 3 460, 3 300, 3 060, 3 020, 2 110, 1 670, 1 635, 1 600, 1 500, 1 490, 1 450, and 1 030 cm^{-1} ; δ 2.74 (1 H, s, 5-H), 3.48 (1 H, s, exchanged with D_2O , OH), 6.07 (1 H, d, J 13, vinyl-H), 6.57 (1 H, d, J 13, vinyl-H), and 7.45 (5 H, m, ArH).

3-Phenylpent-2-en-4-ynal (23).—(i) This compound, prepared from compound (22) as reported,³³ formed yellow prisms (from tetrachloromethane–cyclohexane, 2:1, v/v) (54% yield), m.p. 59.5–60 °C (lit.,³³ ca. 65 °C); δ 3.75 (1 H, s, 5-H), 6.80 (1 H, d, J 7.8, 2-H), 7.40 (3 H, m, ArH), 7.75 (2 H, m, ArH), and 10.28 (1 H, d, J 7.8, 1-H).

(ii) **3-Bromo-3-phenylpropen-1-al (25).** This was obtained as described,³² but in 23% yield, as a yellow oil, b.p. 92 °C at 0.3 mmHg (lit.,³² 106–107 °C at 0.7 mmHg); δ 6.70 (1 H, d, 6.5, 2-H), 7.40 (3 H, m, ArH), 7.60 (2 H, m, ArH), and 10.02 (1 H, d, J 6.5, 1-H).

Modifying earlier procedures,^{26,56} a deaerated solution of this aldehyde (25) (18.6 g, 88 mmol), copper(I) iodide (18 mg), and tetrakis(triphenylphosphine)palladium(0) (0.2 g) in anhydrous triethylamine (200 ml) was treated with ethynyltrimethylsilane (132 mmol, in THF and hexane prepared as described) under nitrogen. The mixture was rapidly heated to ca. 90 °C and kept there for 18 h. After work-up²⁶ distillation gave 3-phenyl-5-trimethylsilylpent-2-en-4-ynal (24) as a yellow oil (11.5 g, 57.3%), b.p. 130–134 °C at 1 mmHg; m/z 228 (M^+ , 1), 213 (16), 199 (6), and 73 (100); $\nu_{\max.}$ (film) 3 060, 2 960, 2 930, 2 900, 2 830, 2 740, 2 140, 1 670, 1 580, 1 560, 1 495, 1 450, 1 325, 1 250, 1 135, and 1 000 cm^{-1} ; δ 0.20 (9 H, s), 6.55 (1 H, d, J 7.8), 7.25 (3 H, m), 7.55 (2 H, m), and 10.15 (1 H, d, J 7.8). The

compound was extremely hygroscopic and hydrolysed to the aldehyde (23) on exposure to air, as shown by the i.r. spectrum and microanalysis. Compound (24) (11.5 g) and potassium fluoride dihydrate (10.9 g) in DMF (60 ml) was stirred under nitrogen at room temperature overnight. The mixture was then poured into water and extracted with dichloromethane. Work-up of the extract and recrystallization of the product gave 3-phenylpent-2-en-4-ynal (23) (7.02 g, 90%) with the properties described under (i).

6-Phenylocta-3,5-dien-7-yn-2-one (26).—Using a modified procedure,³³ sodium hydroxide in ethanol (4.4 ml) and water (4.4 ml) was added over 20 min to a stirred solution of 3-phenylpent-2-en-4-ynal (3.0 g) in acetone (31 ml) in an ice-bath. After 2 h under these conditions the mixture was neutralized with sulphuric acid (1M), diluted with water (200 ml), extracted with ether, and the extracts washed with saturated aqueous sodium hydrogen carbonate. The extracts were dried and evaporated and the residue was chromatographed (alumina grade III) with light petroleum containing ether (20%) as eluant to afford the ketone (26) as yellow crystals (2.50 g, 67%), m.p. 69–72 °C (lit.,³³ 70–72 °C); m/z 196 (M^+ , 59), 195 (21), 181 (24), 153 (100), and 127 (14); $\nu_{\max.}$ (Nujol) 3 240, 2 080, 1 700, 1 680, 1 650, 1 585, 1 495, 1 445, 1 360, 1 280, and 1 250 cm^{-1} ; δ (90 MHz) 2.28 (3 H, s, 1-H), 3.65 (1 H, s, 8-H), 6.28 (1 H, d, J 16, 3-H), 7.01 (1 H, d, J 11, 5-H), 7.40 (3 H, m, ArH), 7.65 (2 H, m, ArH), and 7.75 (1 H, dd, J 16 + 11, 4-H).

3,11-Diphenyl-3,5,8,10-tridecatetraene-1,12-diyn-7-one (27).—The ketone (26) and the aldehyde (23) were condensed using the procedure of Sondheimer *et al.*³⁰ and the residue after solvent evaporation was chromatographed (alumina grade III). Fractions eluted with light petroleum–ether (1:1, v/v) yielded the ketone (27) as a yellow solid from chloroform–hexane (20% yield), m.p. 113–114 °C (Found: C, 86.3; H, 5.0. $C_{25}H_{18}O \cdot 0.13 CHCl_3$ requires C, 86.3; H, 5.2%, the chloroform was not removed at 100 °C under high vacuum); m/z 334 (M^+ , 8), 181 (18), and 153 (15); $\nu_{\max.}$ (dichloromethane) 3 300, 2 920, 2 840, 2 090, 1 660, 1 640, 1 600, 1 590, 1 580, 1 570, 1 550, 1 345, and 1 080 cm^{-1} ; δ 3.66 (1 H, s, 1-H), 6.65 (1 H, d, J 15.3, 6-H), 7.10 (1 H, d, J 11.3, 4-H), 7.40 (3 H, m, ArH), 7.70 (2 H, m, ArH), and 7.98 (1 H, dd, J 15.3 + 11.3, 5-H); $\lambda_{\max.}$ (EtOH) 247 (ϵ 8 546), 277 (10 268), 389 (31 600), and 396 nm (31 355); $\lambda_{\max.}$ (EtOH + 1 drop $HClO_4$) 249 (ϵ 9 142), 280 (10 600), 403 (31 490), and 410 nm (31 220).

5,10-Diphenylcyclotrideca-2,4,10,12-tetraene-6,8-diyn-1-one (28).—The ketone (27) was oxidized using Sondheimer's procedure.³⁰ Recrystallization of the ether-soluble material from chloroform–hexane gave the annulenone (28) (65% yield) as a deep red solid, m.p. 192–193 °C (decomp.) (Found: C, 86.7; H, 4.6. $C_{25}H_{16}O \cdot 0.15 CHCl_3$ requires C, 86.8; H, 4.6%, the chloroform was not removed at 100 °C under high vacuum); m/z 332 (M^+ , 7), 303 (10), 185 (100), and 157 (22); $\nu_{\max.}$ (dichloromethane) 2 900, 2 850, 2 100, 2 160, 1 650, 1 620, 1 600, 1 100, and 1 000 cm^{-1} ; δ 6.10 (2 H, d, J 16.7, 2,13-H), 6.90 (2 H, d, J 9.8, 4,12-H), 7.35 (10 H, m, ArH), and 9.84 (2 H, dd, J 16.7 + 9.8, 3,12-H); u.v. (EtOH) 237 nm (ϵ 11 462), 269 (9 635), and 307 (7 973); $\lambda_{\max.}$ (EtOH + 1 drop $HClO_4$) 236.5 nm (ϵ 11 733) and 314 (7 844); both spectra showed tailing down to 700 nm.

2-Iodobenzaldehyde.—(i) 2-Iodobenzoyl chloride (82.6 g) in dioxane (ca. 100 ml) was added over 25 min to a well-stirred suspension of sodium borohydride (23.4 g) in dioxane (200 ml) cooled in an ice-bath using a reported procedure.⁵⁷ The mixture was heated on a steam-bath for 1 h and cooled (ice-bath) while water (50 ml) was added cautiously. 2-Iodobenzyl alcohol,

collected with dichloromethane, was obtained as colourless needles (71.1 g, 98%) and used in the next stage without further purification. Lithium aluminium hydride as reductant⁵⁸ gave only benzyl alcohol.

2-Iodobenzyl alcohol (71.1 g) in dichloromethane (200 ml) was added to a well-stirred suspension of pyridinium dichromate⁵⁹ (174.9 g) (0.47 mol) in dichloromethane (500 ml). After 3 h at room temperature, the mixture was diluted with ether (200 ml), filtered (Celite), and distilled to give 2-iodobenzaldehyde as a pale yellow oil (53.2 g, 76.4%), b.p. 98–100 °C at 2.0 mmHg (lit.,⁶⁰ 129 °C at 14 mmHg); δ 7.35 (3 H, m, ArH), 7.85 (1 H, m, 6-H), and 10.04 (1 H, s, CHO).

(ii) 2-Iodobenzoyl chloride (39.98 g) in acetone (75 ml) was added dropwise over 10 min to a stirred slurry of bis(triphenylphosphine)copper(I) tetrahydroborate⁶¹ (90.47 g) and triphenylphosphine (78.7 g) in acetone (250 ml). The mixture became warm and after 1 h was filtered and the precipitate washed with acetone (250 ml). Water (500 ml) and methanol (500 ml) were added to the combined filtrate and washings and the mixture was filtered; the filtrate was then concentrated to 1.5 l and extracted with ether. Distillation of the washed (brine, 200 ml) and dried extracts under reduced pressure gave 2-iodobenzaldehyde (13.9–17.2 g) as described above.

2-Iodostyrene.—In a modification of Harrison and Lythgoe's procedure⁶² methyltriphenylphosphonium bromide (128.5 g, 0.359 mol) was suspended in THF (300 ml) and butyl-lithium in hexane (0.359 mol) was added dropwise, with stirring, under nitrogen at 0 °C. After 30 min at 0 °C 2-iodobenzaldehyde (79.32 g, 0.342 mol) in THF (100 ml) was added, stirring was continued at room temperature for 1 h and methanol (100 ml), water (100 ml), and light petroleum (200 ml) were added. The mixture was extracted with light petroleum and the extract washed (H₂O), dried, and evaporated to afford a light orange oil, which was distilled in the presence of hydroquinone (500 mg) to give 2-iodostyrene (56.4 g) as a yellow oil, b.p. 69–70 °C at 0.3 mmHg (lit.,⁶³ 88–90 °C at 3 mmHg); δ 5.16 (1 H, dd, *J* 10.6 + 0.7, 2'-H), 5.46 (1 H, dd, *J* 17.3 + 0.7, 2'-H), 6.83 (1 H, dd, *J* 17.3 + 10.6, 1'-H), and 7.00–7.80 (4 H, m, ArH). Doubling the scale gave a 57% yield and only 44% was obtained using methyltriphenylphosphonium iodide.⁶⁴ No reaction occurred when sodium methyl sulphanyl carbanion⁶⁵ was used instead of butyl-lithium.

1,5-Bis(2-iodophenyl)pentan-3-one (30).—(i) Following the procedure of Pelter *et al.*³⁹ diborane-THF (85 mmol, 1M) was added dropwise to 2,3-dimethylbut-2-ene (7.15 g) in a flame-dried nitrogen filled round-bottomed flask sealed with a rubber septum and cooled in an ice-bath. The mixture was stirred for 1 h, after which the cooling bath was removed and stirring was continued for a further 1 h. 2-Iodostyrene (38.9 g) was added dropwise over 30 min and stirring was continued for 10 h (or overnight). The solution was transferred, under nitrogen, to a flame-dried flask equipped with a magnetic stirrer and sodium cyanide (4.46 g, oven-dried at 100 °C at 20 mmHg for 6 h prior to use). After being stirred overnight the solution was cooled to –78 °C (dry ice-acetone bath) and trifluoroacetic anhydride (13.0 ml) added dropwise over 20 min. The cooling bath was removed and on warming to room temperature the solid mixture became syrupy and yellow. After 2 h, the septum cap was removed and methanol (47 ml) added followed by aqueous sodium hydroxide (77.5 ml, 5M), with stirring. Finally hydrogen peroxide (30%; 77.5 ml) was slowly added upon which there was an exothermic reaction with much effervescence. After 3 h the mixture was extracted with dichloromethane (3 × 200 ml). Evaporation of the washed [aqueous sodium hydroxide (3M; 400 ml) followed by aqueous hydrochloric acid (3M; 400 ml) and

water (500 ml)] and dried extract gave a viscous pale yellow oil, which was chromatographed over silica. Elution with light petroleum gave unchanged 2-iodostyrene (4.17 g) and light petroleum containing ether (20%) gave 1,5-bis(2-iodophenyl)pentan-3-one (30) (20.7 g); subsequent elution with dichloromethane gave 2-(2-iodophenyl)ethanol (6.4 g). The ketone (30), a pale yellow viscous oil, failed to crystallize; *m/z* 491 (*M*⁺ + 1, 25), 363 (39), 231 (33), 217 (100), 104 (46), and 91 (33); ν_{\max} (film) 1 710, 1 620, 1 585, 1 560, 1 465, 1 432, and 1 010 cm⁻¹; δ 2.50–3.20 (8 H, m, 4 × CH₂), 6.70–7.30 (6 H, m, ArH), 7.78 (2 H, d, *J* 8.0, 3,3'-H). The 2,4-dinitrophenylhydrazone, orange prisms (from ethanol), had m.p. 128–129 °C (Found: C, 41.7; H, 3.0; N, 8.4. C₂₃H₂₀I₂N₄O₄ requires C, 41.2; H, 3.0; N, 8.4%). The 2-(2-iodophenyl)ethanol was a yellow viscous oil, b.p. 138–140 °C at 2.2 mmHg (lit.,⁶⁶ 100 °C at 0.5 mmHg); *m/z* 248 (*M*⁺, 38), 231 (10), 217 (53), 121 (86), and 81 (100); ν_{\max} (film) 3 350, 1 630, 1 585, 1 560, 1 465, 1 430, 1 050, and 1 010 cm⁻¹; δ 2.40 (1 H, br, exchanged by D₂O, OH), 2.90 (2 H, t, *J* 7.9, CH₂), 3.75 (2 H, t, *J* 7.9, CH₂), 6.65–7.40 (3 H, m, ArH), and 7.79 (1 H, d, *J* 7.7, 3-H).

(ii) Using a procedure described⁶⁷ butyl-lithium in hexane (70 mmol) was added, with stirring, under nitrogen at 0 °C to di-isopropylamine (6.81 g, 68 mmol, freshly distilled from calcium hydride) in THF (200 ml). After 20 min, methyl acetoacetate (3.91 g) was added slowly and after a further 20 min at 0 °C 2-iodobenzyl bromide (10 g) in THF (50 ml) was added dropwise to the orange solution. The colour faded gradually. After being stirred at room temperature for 10 h the mixture was poured into aqueous hydrochloric acid (2M; 100 ml). Ether extraction, washing (saturated aqueous sodium hydrogen carbonate, then water), drying, and evaporation gave a viscous oil, which was chromatographed (silica). Fractions eluted with light petroleum containing ether (30%) afforded ethyl 5-(2-iodophenyl)-3-oxopentanoate (29) as a pale yellow oil (8.46 g, 75%) which decomposed on attempted distillation under reduced pressure; *m/z* 332 (*M*⁺, 1), 259 (6), 231 (20), 217 (43), 205 (100), 173 (23), 163 (49), 145 (86), 131 (31), and 103 (33); ν_{\max} (Nujol) 3 400w, 1 745, 1 710, 1 650, 1 630, 1 560, 1 465, 1 435, 1 405, 1 320, and 1 010 cm⁻¹; δ 2.90 (4 H, s), 3.40 (2 H, s), 3.67 (3 H, s), 4.97 (1 H, s; vinyl proton of the enol form, *ca.* 8% from integral), 6.70–7.20 (4 H, m), and 7.80 (1 H, d, *J* 8).

2-Iodobenzyl bromide (7.15 g) in acetone (100 ml) was added to a well-stirred refluxing mixture of compound (29) (8.0 g), anhydrous potassium carbonate (3.65 g), and acetone (100 ml),⁶⁸ and after 11 h it was poured into water (200 ml). The dichloromethane-soluble material, a viscous oil was refluxed with aqueous sulphuric acid (150 ml, 20%) and acetic acid (150 ml) for 10 h, cooled and the organic phase separated. It was dissolved in dichloromethane, washed with water, and dried; the solvent was evaporated and the residue was taken up in the minimum amount of chloroform. Addition of light petroleum now precipitated 2-(2-iodobenzyl)-1,5-bis(2-iodophenyl)pentan-3-one (31) (2.26 g) as colourless prisms, m.p. 159–160 °C (Found: C, 41.0; H, 2.8. C₂₄H₂₁I₃O requires C, 40.8; H, 3.0%); ν_{\max} 1 690, 1 435, 1 380, 1 270, 1 240, and 1 012 cm⁻¹; δ 2.80–3.20 (9 H, m), 6.50–7.30 (9 H, m), and 7.75 (3 H, d, *J* 7.3). On cooling the mother liquor a solid precipitated and this on recrystallization from dichloromethane–light petroleum yielded 1,5-bis(2-iodophenyl)pentan-3-one (30) as colourless prisms (2.9 g), m.p. 71–72 °C (Found: C, 41.3; H, 3.1. C₁₇H₁₆I₂O requires C, 41.6; H, 3.3%), with spectra identical with those of the sample described under (i).

1,5-Bis(2-bromophenyl)pentan-3-one (33).—1,5-Bis(2-bromophenyl)penta-1,4-dien-3-one (19) (0.5 g) was reduced by tributyltin hydride (0.7 ml) in the presence of tetrakis(triphenylphosphine)palladium(0) using the reported procedure.⁴⁰ After 40 min, the reaction mixture was chromatographed (silica). Light petroleum containing ether (10%) eluted the *title*

compound (33) as colourless needles (0.32 g), m.p. 79–79.5 °C (Found: C, 51.4; H, 4.2. $C_{17}H_{14}Br_2O$ requires C, 51.5; H, 4.0%); m/z 397 ($M^+ + 1$, 36), 396 (M^+ , 5), 395 (21), 316 (87), 315 (100), 183 (25), 169 (56), and 91 (33); ν_{max} (Nujol) 3 060, 1 710, 1 565, 1 290, 1 120, 1 090, and 1 020 cm^{-1} ; δ 2.50–3.20 (8 H, m), 6.90–7.30 (6 H, m), and 7.50 (2 H, d, J 6.7, 3',3''-H). Work-up of the reaction mixture after 10 min and isolation by t.l.c. [silica, developing with light petroleum containing ether (10%)] gave 1,5-bis(2-bromophenyl)pent-1-en-3-one (37) (R_F 0.1), δ 3.05 (4 H, m, $2 \times CH_2$), 6.55 (1 H, d, J 16.7, 2-H), 6.90–7.60 (8 H, m, ArH), and 7.90 (1 H, d, J 16.7, 1-H).

1,5-Bis(2-iodophenyl)penta-1,4-dien-3-one (20).—Replacement of benzaldehyde, by 2-iodobenzaldehyde, in the synthesis of dibenzylideneacetone,⁶⁹ gave 1,5-bis(2-iodophenyl)penta-1,4-dien-3-one (20) (75%) as yellow prisms (from ethyl acetate), m.p. 131–132 °C (Found: C, 42.1; H, 2.6. $C_{17}H_{12}I_2O$ requires C, 42.0; H, 2.5%); m/z 359 ($M^+ - I$, 7), 232 ($M^+ - 2 I$, 100); δ 6.95–8.05 (8 H, m, ArH), 7.20 (2 H, d, J 16.7, 2,4-H), and 7.85 (2 H, d, J 16.7, 1,5-H); λ_{max} (EtOH) 235 (ϵ 5 442) and 313 nm (11 338).

This compound was reduced, as for the dibromo analogue (19), by tributyltin hydride (2.4 mol equiv.) and work-up in the same way afforded 1-(2-iodophenyl)-5-phenylpentan-3-one (34) as a viscous yellow oil (0.21 g); m/z 364 (2), 363 (8), 237 (28), 133 (31), 105 (67), and 91 (100); ν_{max} (film) 1 710 (C=O) and 1 600 cm^{-1} ; δ 2.50–3.10 (8 H, m, $4 \times CH_2$), 6.70–7.40 (8 H, m, ArH), and 7.75 (1 H, d, J 7.9, 3'-H). Tributyltin hydride (1 mol equiv.) gave (from 1H n.m.r.) a 1 : 1 mixture of compounds (32) and (38).

1,5-Bis(2-trimethylsilylethynylphenyl)penta-1,4-dien-3-one (18).—(i) 1,5-Bis(2-iodophenyl)penta-1,4-dien-3-one (20) (30 g), tetrakis(triphenylphosphine)palladium(0) (0.5 g), copper(I) iodide (36 mg), triethylamine (250 ml), and xylene (200 ml, sodium dried) were placed in a 3-necked flask with a nitrogen gas inlet, a dry-cold condenser, and a stopper. The mixture was deaerated for 5 min after which ethynyltrimethylsilane (186 mmol, in THF–hexane) was added. The mixture was warmed to ca. 85 °C slowly on an oil-bath and maintained at 85 °C for 11 h. After being cooled, the solution was filtered; the filtrate was concentrated, ether (200 ml) was added, and the solution washed successively with aqueous hydrochloric acid (5%), saturated aqueous sodium hydrogen carbonate (200 ml), and water (200 ml), and dried. The solution was concentrated, filtered through a silica column (5 \times 8 cm) and the organic materials washed through with ether and light petroleum. The solvents were evaporated and the residue diluted with an equal volume of light petroleum and cooled at –78 °C. This precipitated 1,5-bis(2-trimethylsilylethynylphenyl)penta-1,4-dien-3-one (18) as bright yellow prisms (16.7 g, 63.0%) (from light petroleum), m.p. 102–103 °C (Found: C, 76.0; H, 7.1. $C_{27}H_{30}OSi_2$ requires C, 76.1; H, 7.0%); m/z 426 (M^+ , 4), 411 (3), 227 (7), and 73 (100); ν_{max} (Nujol) 2 160, 2 070, 1 660, 1 620, 1 600, 1 590, 1 275, 1 250, 1 185, and 1 090 cm^{-1} ; δ 0.30 (18 H, s, $6 \times Me$), 7.15 (2 H, d, J 16.7, 2,4-H₂), 7.45 (8 H, m, ArH), and 8.27 (2 H, d, J 16.7, 1,5-H); λ_{max} (EtOH) 225 (ϵ 31 030), 251 (29 640), and 325 nm (19 590).

(ii) 1,5-Bis(2-ethynylphenyl)penta-1,4-dien-3-one (17) (0.5 g) and 1,8-diazabicyclo[5.4.0]undec-7-ene (0.65 g) were successively added to a stirred suspension of silver nitrate (30 mg) in dichloromethane (2 ml) and the mixture heated at 40 °C; chlorotrimethylsilane (0.46 g) was then added as in a similar case.⁴² After being stirred for 30 h at 40 °C, the mixture was cooled and silica (2 g) was added. After evaporation to dryness, the residue was chromatographed (silica). Elution with light petroleum containing ether (30%) gave the dienone (18) (297 mg) identical with the analysed specimen.

1,5-Bis(2-ethynylphenyl)pentane-3-one (36).—(i) A deaerated solution of 1,5-bis(2-iodophenyl)pentan-3-one (19.6 g), copper(I) iodide (36 mg), and tetrakis(triphenylphosphine)palladium(0) (0.5 g) in anhydrous triethylamine (300 ml) was treated with ethynyltrimethylsilane (11.76 g, in THF–hexane) under nitrogen, and rapidly heated to 90 °C for 16 h. The mixture was worked up as for compound (18) but the product was chromatographed (silica). Elution with light petroleum containing ether (10%) afforded 1,5-bis(2-trimethylsilylethynylphenyl)pentan-3-one (35) (9.97 g, 58%); m/z 430 (M^+ , 2), 357 (3), 284 (7), 128 (2), and 73 (100); ν_{max} (film) 3 060, 2 960, 2 900, 2 860, 2 150, 2 110, 1 720, 1 600, 1 480, 1 450, 1 410, 1 250, 1 070, and 1 040 cm^{-1} ; δ 0.23 (18 H, s, $6 \times Me$), 2.50–3.20 (8 H, m, $4 \times CH_2$), and 7.00–7.50 (8 H, m, ArH).

Unpurified compound (35) was treated with potassium fluoride dihydrate (5.8 g) in DMF (60 ml) under nitrogen at room temperature for 1 h and poured into water (100 ml). The organic material, extracted with dichloromethane, was chromatographed (silica) with light petroleum containing ether (20%) as eluant to afford 1,5-bis(2-ethynylphenyl)pentan-3-one (36) as a pale brown oil (88–92%); m/z 294 (M^+ , 1), 269 (7), 129 (70), and 115 (100); ν_{max} (film) 3 300, 3 060, 2 100, 1 710, 1 600, 1 485, 1 450, 1 370, and 1 080 cm^{-1} ; δ 2.50–3.15 (8 H, m, $4 \times CH_2$), 3.15 (2 H, s, $\equiv CH$), and 6.95–7.50 (8 H, m, ArH). The 2,4-dinitrophenylhydrazone derivative, orange prisms (from acetone), had m.p. 114–115 °C (Found: C, 57.3; H, 4.3; N, 10.1. $C_{27}H_{22}N_4O_4 \cdot H_2SO_4$ requires C, 57.4; H, 4.3; N, 9.9%).

(ii) Tributyltin hydride (19.7 ml) was added dropwise at room temperature over 10 min to a stirred deaerated solution of 1,5-bis(2-trimethylsilylethynylphenyl)penta-1,4-dien-3-one (18) (13 g), acetic acid (3.67 ml), and tetrakis(triphenylphosphine)palladium(0) (0.7 g) in benzene (120 ml). After 20 min, the solvent was removed and the residue chromatographed (alumina grade I). Fractions eluted with light petroleum containing ether (40%) afforded 1,5-bis(2-trimethylsilylethynylphenyl)pentan-3-one (35) which, when desilylated with potassium fluoride as in (i), gave 1,5-bis(2-ethynylphenyl)pentan-3-one (36) (6.1 g, 70%).

Reduction of the penta-1,4-dien-3-one (18) with equimolar quantities of tributyltin hydride gave 1,5-bis(2-trimethylsilylethynylphenyl)pent-1-en-3-one (39) (85%), prisms (from light petroleum), m.p. 72–73 °C (Found: C, 75.7; H, 7.4. $C_{27}H_{32}OSi_2$ requires C, 75.7; H, 7.5%); m/z 428 (M^+ , 1), 413 (7), 355 (15), 227 (5), and 73 (100); ν_{max} (Nujol) 2 160, 1 665, 1 620, 1 590, 1 300, 1 250, and 1 172 cm^{-1} ; δ 0.2 (18 H, s, $6 \times Me$), 3.10 (4 H, m, $2 \times CH_2$), 6.72 (1 H, d, J 16.7, 2-H), 7.05–7.70 (8 H, m, ArH), and 8.10 (1 H, d, J 16.7, 1-H); λ_{max} (EtOH) 243 nm (ϵ 5 465), 249 (13 940), and 292 (5 440).

Further reduction of this compound (39) with butyltin hydride (1.2 equiv.) under our usual conditions, gave the pentan-3-one (35) (80% yield).

13,14,16,17-Tetrahydro-5,6,7,8-tetradehydrodibenzo[a,g]-cyclotridecen-15-one (40).—1,5-Bis(2-ethynylphenyl)pentan-3-one (36) (1 g) in pyridine (52.5 ml, freshly distilled from calcium hydride) and dry ether (17.5 ml) was added dropwise during 3 h to a stirred suspension of anhydrous copper acetate⁵⁵ (4.4 g) in pyridine (127.5 ml) and dry ether (42.5 ml) at 50 °C (oil bath); stirring was continued at 50 °C for 30 min after which the mixture was cooled. The residue, after solvent removal, was chromatographed (silica). Elution with light petroleum containing ether (40%) gave the title compound (40) (761 mg, 76.8%) as yellow rods (from ether), m.p. 175–176 °C (decomp.) (Found: C, 89.0; H, 5.2. $C_{22}H_{16}O$ requires C, 88.7; H, 5.6%); m/z 284 (M^+ , 100), 255 (30), and 128 (24); ν_{max} (Nujol) 2 200, 1 695, 1 160, 1 100, and 1 035 cm^{-1} ; δ (300 MHz) 2.92 (4 H, m), 3.08 (4 H, m), 7.17–7.38 (8 H, m); δ_c (75.5 MHz) 32.3 (t), 42.3 (t), 80.8 (s), 88.9 (s), 122.3 (s), 126.7 (d), 129.7–129.8 (3 \times sp²-CH),

145.9 (s), and 211.8 (s); λ_{\max} . (EtOH) 200 (ϵ 22 460), 220 (15 700), 277 (4 040), 288 (6 430), 296 (8 280), 310 (9 871), 317 (11 590), 332 (9 080), and 339 nm (9 210); addition of 1 drop of HClO_4 shifted the whole spectrum by 2 nm to longer wavelengths. Longer reaction times or wet solvents caused a dramatic decrease in yield.

This compound (**40**) (200 mg), sodium sulphide nonahydrate (680 mg), and methanol (10 ml) were refluxed for 5.5 h. Most of the solvent was evaporated and water (20 ml) was added. Evaporation of the washed (water) and dried ethyl acetate extract gave an oil, which was chromatographed (silica) eluting with dichloromethane. A yellow eluate yielded a compound (25 mg), off-white needles (from dichloromethane–light petroleum, cooled to -78°C), m.p. 215–216 $^\circ\text{C}$ (decomp.) (Found: C, 88.5; H, 5.8. $\text{C}_{21}\text{H}_{16}\text{O}$ requires C, 88.7; H, 5.6%); m/z 284 (M^+ , 72), 256 ($M^+ - \text{CO}$, 16), 156 ($M^+ - \text{C}_{10}\text{H}_8$, 100), and 128 ($\text{C}_{10}\text{H}_8^+$, 100); ν_{\max} . (Nujol) 1 602, 1 585, and 1 570 cm^{-1} ; δ 3.11 (4 H, br s), 3.83 (4 H, br s), and 7.00–7.70 (8 H, m); λ_{\max} . (EtOH) 233 (ϵ 9 320), 315 (7 370), and 370 (17 200) nm.

13,14,16,17-Tetrahydro-5,6,7,8-tetrahydridibenzo[a,g]-cyclotridecen-15-ol (**41**).—Powdered sodium borohydride (182 mg) was added to compound (**40**) (343 mg) in ethanol (25 ml). The reduction was complete after 10 min (t.l.c.). Most of the solvent was removed and water (30 ml) was added. The mixture was extracted with dichloromethane (3×10 ml) and the extract dried and evaporated to give the title compound (**41**) as colourless needles from chloroform–light petroleum (cooling to -78°C) (321 mg, 93.6%), m.p. 146–147 $^\circ\text{C}$ (Found: C, 88.0; H, 6.6. $\text{C}_{21}\text{H}_{18}\text{O}$ requires C, 88.1; H, 6.3%); m/z 287 ($M^+ + 1$, 36), 286 (M^+ , 100), 285 (21), 269 (77), 141 (50), 128 (50), and 115 (31); ν_{\max} . (Nujol) 3 360 (OH), 3 060, 2 200, 1 375, 1 180, and 1 050 cm^{-1} ; δ (300 MHz) 1.58 (1 H, d, exchanged with D_2O , OH), 1.83 (2 H, m), 2.17 (2 H, m), 2.87 (4 H, m), 4.07 (1 H, m), and 7.13–7.38 (8 H, m, ArH).

13,14,16,17-Tetrahydro-5,8-epithiodibenzo[a,g]cyclotridecen-15-ol (**42**).—Compound (**41**) (1 g), sodium sulphide nonahydrate (3.36 g), and methanol (60 ml) were refluxed for 17 h as described³⁶ in other cases. After most of the solvent had been removed, the residue was treated with water and extracted with ethyl acetate. Evaporation of the washed (water) and dried extract gave a brown viscous oil which was chromatographed (silica). Elution with light petroleum containing ethyl acetate (30%) gave a yellow foamy solid which on recrystallization from ether–light petroleum (cooling to -78°C) gave the tridecen-15-ol (**42**) (333 mg, 29.8%) as yellow prisms, m.p. 92–93 $^\circ\text{C}$ (Found: C, 78.3; H, 5.9; S, 10.2. $\text{C}_{21}\text{H}_{20}\text{OS}$ requires C, 78.7; H, 6.2; S, 10.0%); m/z 321 ($M^+ + 1$, 85), 320 (M^+ , 100), 303 (57), 269 (25), and 115 (28); ν_{\max} . (Nujol) 3 340, 3 080, 1 620, 1 595, 1 370, 1 365, 1 050, and 1 035 cm^{-1} ; δ_{H} (300 MHz) 1.42 (1 H, br, exchanged by D_2O , OH), 1.58 (2 H, m, 14,16-H), 1.82 (2 H, m, 14,16-H), 2.60 (4 H, m, 13,17- H_4), 3.78 (1 H, tt, J 9 + 9 + 2 + 12, 15-H), 6.93 (2 H, s, 6,7-H), 7.28 (6 H, m, ArH), 7.55 (2 H, m, ArH); assignment of 14,16- H_4 was made from the results obtained by adding [$\text{Eu}(\text{fod})_3$]; δ_{C} (75.5 MHz) 30.13 (t, CH_2), 32.95 (t, CH_2), 71.44 (d, 15-C), 126.20 (d), 126.90 (d), 128.55 (d), 128.89 (d), 130.37 (d), 134.17 (s), 142.02 (s), and 142.93 (s); λ_{\max} . (EtOH) 196 nm (ϵ 25 600), 277 (10 470), and 332 (2 440); λ_{\max} . (EtOH + 1 drop HClO_4) 190.5 (ϵ 25 610), 270 (9 350), and 328 nm (1 120).

Reaction between 13,14,16,17-Tetrahydro-5,8-epithiodibenzo[a,g]cyclotridecen-15-ol (**42**) and Trifluoromethanesulphonic Anhydride.—Trifluoromethanesulphonic anhydride (180 mg) and dichloromethane (5 ml, distilled over P_2O_5) were placed in a 2-necked flame-dried flask, with a nitrogen inlet and a pressure equalizing funnel. The reaction mixture was cooled to -40°C

and solid sodium carbonate (36 mg, dried *in vacuo* at 200°C overnight) was added, followed by a solution of the alcohol (**42**) (161 mg) in dichloromethane (10 ml) over 20 min at the same temperature. After 2 h, the cooling bath was removed and 1 h later the dark brown solution was poured into water. The dichloromethane extract was washed (water), dried, and evaporated to leave an oil, which was chromatographed (silica). Elution with light petroleum containing ethyl acetate (10%) afforded the E-olefin (**45**) (60 mg, 48.5%) as an oil which decomposed on attempted distillation in high vacuum; m/z 302 (M^+ , 34), 269 ($M^+ - \text{SH}$, 100), and 115 (30); ν_{\max} . (film) 3 060, 3 020, 2 930, 2 860, 1 600, 1 480, 1 450, 1 218, and 1 105 cm^{-1} ; δ ^1H n.m.r. see the Table. Elution with light petroleum containing ethyl acetate (40%) gave back compound (**42**) (30 mg).

15-Iodo-13,14,16,17-tetrahydro-5,8-epithiodibenzo[a,g]-cyclotridecene.—Iodotrimethylsilane (223 mg) in dichloromethane (1 ml) was added to the cyclotridecen-15-ol (**42**) (179 mg) in dichloromethane under nitrogen at room temperature.⁷⁰ After 2 h, the mixture was washed with aqueous sodium metabisulphite and water, dried, and the solvent evaporated. Chromatography (silica) and elution with dichloromethane afforded the 15-iodocyclotridecene (163.5 mg) as very pale yellow prisms (from light petroleum, cooled to -78°C), m.p. 78–79 $^\circ\text{C}$. The last traces of solvent were not removed in high vacuum and satisfactory analytical data could not be obtained; m/z 430 (M^+ , 11), 302 (100), 269 (80), 146 (46), 128 (56), and 115 (43); ν_{\max} . (Nujol) 3 060, 1 262, 1 180, 1 140, 1 040, and 1 030 cm^{-1} ; δ (300 MHz), 2.00 (4 H, m, $2 \times \text{CH}_2$), 2.65 (4 H, m, $2 \times \text{CH}_2$), 4.44 (1 H, m, 15-H), 6.94 (2 H, s, 6,7-H), and 7.00–7.62 (8 H, m, ArH).

The iodo compound (48 mg) in 1,2-dichloroethane (2 ml, distilled over P_2O_5) was added to silver tetrafluoroborate (21.7 mg) suspended in the same solvent (2 ml). After 15 min, a yellow solid began to precipitate out. After 75 min, the mixture was filtered through Celite and evaporation of the solvent under reduced pressure at 20°C afforded the olefin (**45**) as a brown oil (26.8 mg), identified from its ^1H n.m.r. (300 MHz) spectrum (Table).

13,14,16,17-Tetrahydro-5,8-epithiodibenzo[a,g]cyclotridecen-15-one (**43**).—A chromium trioxide solution [0.5 ml of a mixture of chromium trioxide (2.67 g), concentrated sulphuric acid (2.3 ml) and water (7.7 ml)] was added to a stirred solution of the cyclotridecen-15-ol (**42**) (150 mg) in acetone (6 ml) at room temperature. After 1 h, saturated aqueous sodium metabisulphite (5 ml) was added. The mixture was extracted with dichloromethane and the extract, washed (H_2O), dried, and evaporated to afford a yellow oil, which was dissolved in dichloromethane and filtered through a small silica column. After evaporation the residue was recrystallized from dichloromethane–light petroleum (cooling to -78°C) to give the tridecen-15-one (**43**) (186.3 mg) as colourless prisms, m.p. 132–133 $^\circ\text{C}$ (Found: C, 78.7; H, 5.7; S, 10.3. $\text{C}_{21}\text{H}_{18}\text{OS}$ requires C, 79.2; H, 5.7; S, 10.1%); m/z 318 (M^+ , 100), 290 (3), 185 (14), and 228 (9); ν_{\max} . (Nujol) 3 058, 1 715, 1 415, 1 380, and 1 080 cm^{-1} ; δ 2.48 (4 H, m), 2.92 (4 H, m), 6.86 (2 H, s), and 7.30 (8 H, m); λ_{\max} . (EtOH) 206 (ϵ 55 250), 215 (33 930), 293 (13 600), 299 (16 270), 313 (18 510), 320 (21 310), 334 (16 550), and 342 nm (16 410); λ_{\max} . (EtOH + 1 drop HClO_4) 216 (ϵ 54 410), 224 (32 810), 292 (13 180), 298 (15 990), 312 (18 230), 319 (21 030), 33 (15 990), and 341 nm (15 990).

The ketone (**43**) (174 mg), toluene-*p*-sulphonylhydrazide (102 mg), concentrated aqueous hydrochloric acid (4 drops), and ethanol (15 ml, 95%) were refluxed for 30 min. Filtration and thorough washing with light petroleum gave the *p*-tosylhydrazone (228 mg) as shiny, colourless prisms, m.p. 231–232 $^\circ\text{C}$ (Found: C, 69.2; H, 5.3; N, 5.9. $\text{C}_{28}\text{H}_{26}\text{N}_2\text{O}_2\text{S}_2$ requires C, 69.1;

H, 5.4; N, 5.8%); m/z 487 ($M^+ + 1$, 36), 333 (56), 318 (26), and 303 (100); v_{\max} (Nujol) 3 200, 3 060, 1 598, 1 490, 1 375, 1 340, 1 170, 1 150, 1 085, and 1 030 cm^{-1} ; $\delta[(\text{CD}_3)_2\text{SO}]$ 1.90–2.95 (8 H, m), 2.35 (3 H, s), 3.12 (1 H, s), 6.93 (2 H, s), 7.35 (10 H, m), and 7.78 (2 H, d, J 8).

Reaction of Tosylhydrazone of (43) and Lithium Di-isopropylamide.—A solution of 13,14,16,17-tetrahydro-5,8-epithiodibenzo[*a,g*]cyclotridecen-15-one tosylhydrazone (200 mg, 0.41 mmol) in tetrahydrofuran (15 ml) was added to lithium diisopropylamide (4.1 mmol, prepared as described previously) at 78 °C over 5 min. A pale yellow colour developed. After 15 min at –78 °C, the temperature was allowed to rise slowly to 0 °C and was kept there for 2 h. The mixture was poured into saturated aqueous ammonium chloride (50 ml) and extracted with dichloromethane. The extracts were washed (H_2O), dried, and evaporated to give a brown oil which was flash chromatographed over silica using ethyl acetate–light petroleum (3:7, v/v) as eluant. A mixture of the alkenes (45), (46), and (47) was obtained as a pale brown oil (68 mg); m/z 302 (M^+ , 55), 269 ($M^+ - \text{SH}$, 100), 268 ($M^+ - \text{H}_2\text{S}$, 21), 253 (18), 239 (15), 215 (13), 141 (28), 128 (27), and 115 (41). The alkenes were identified from their ^1H n.m.r. spectra (Table).

Conversion of 13,14,16,17-Tetrahydro-5,8-epithiodibenzo[*a,g*]cyclotridecen-15-one (43) into 13,14,16,17-tetrahydro-5,6,7,8-tetrahydrodibenzo[*a,g*]cyclotridecen-15-one (40).—(i) The tridecen-15-one (43) (91.7 mg), 2,3-dichloro-4,5-dicyano-1,4-benzoquinone (327 mg) and dioxane (10 ml) were refluxed for 23 h. The solvent was evaporated and the residue was chromatographed (alumina, grade I). Fractions eluted with ethyl acetate–light petroleum (1:1, v/v) afforded yellow crystals (27.8 mg) which were identical with an authentic sample of the title compound (40) in m.p., mass, and ^1H n.m.r. spectra.

(ii) A mixture of compound (43) (50 mg, 0.16 mmol) and 3,4,5,6-tetrachloro-1,2-benzoquinone (120 mg) was refluxed in ether⁷¹ for 3 h. Work-up as above afforded compound (40) (30 mg) identified as in (i). The ketone (43) was unchanged by palladium(II) chloride in hydrochloric acid in *t*-butyl alcohol.⁵⁰

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References

- V. Boekelheide and R. J. Windgassen, *J. Am. Chem. Soc.*, 1958, **80**, 2020; R. J. Windgassen, W. H. Saunders, and V. Boekelheide, *ibid.*, 1959, **81**, 1459.
- R. McCague, C. J. Moody, and C. W. Rees, *J. Chem. Soc., Chem. Commun.*, 1982, 622.
- C. J. M. Stirling (ed.), 'The Chemistry of the Sulphonium Group,' John Wiley, Chichester, 1981.
- J. A. Coturo and I. Degani, *J. Chem. Soc., Chem. Commun.*, 1971, 436.
- R. M. Acheson and M. W. Cooper, *J. Chem. Soc., Perkin Trans. 1*, 1980, 1185.
- R. M. Acheson, R. J. Prince, G. Procter, J. D. Wallis, and D. J. Watkin, *J. Chem. Soc., Perkin Trans. 2*, 1981, 266.
- R. J. Gillespie, J. Murray-Rust, P. Murray-Rust, and A. E. A. Porter, *J. Chem. Soc., Chem. Commun.*, 1978, 83.
- R. M. Acheson and D. R. Harrison, *J. Chem. Soc. C*, 1970, 1764.
- 'Tables of Interatomic Distances and Configurations in Molecules and Ions,' ed. L. E. Sutton, Supplement 1956–1959, p. M167s, special publication No. 18, The Chemical Society, London, 1965.
- D. Darwish and C. E. Scott, *Can. J. Chem.*, 1973, **51**, 3647; K. K. Andersen in reference 3, Part 1, Ch. 10.
- R. Zahradnik, *Adv. Heterocycl. Chem.*, 1965, **5**, 1; R. Zahradnik and C. Párkányi, *Collect. Czech. Chem. Commun.*, 1965, **30**, 3016 and references cited.
- G. C. M. Lee, D.Phil. Thesis, Oxford University, 1983.
- R. M. Acheson and G. C. M. Lee, *J. Chem. Res.*, 1986, (S), 380; (*M*) 3020.
- H. Oediger, A. J. Kable, F. Möller, and K. Eiter, *Chem. Ber.*, 1966, **99**, 2012.
- D. B. Denney and J. Song, *J. Org. Chem.*, 1964, **29**, 495.
- H. J. Bestmann and W. Schlosser, *Synthesis*, 1979, 201.
- G. Büchi and H. Wüest, *Helv. Chim. Acta*, 1979, **62**, 2661.
- K. Tamao, S. Kodama, I. Nakajima, and M. Kumada, *Tetrahedron*, 1982, **38**, 3347.
- S. Murahashi, M. Yamamura, K. Yanagisawa, N. Mita, and K. Kondo, *J. Org. Chem.*, 1979, **44**, 2408.
- D. Seebach and H. Neumann, *Chem. Ber.*, 1974, **107**, 847; E. J. Corey and D. J. Beames, *J. Am. Chem. Soc.*, 1972, **94**, 7210.
- H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, 1960, **82**, 4708; H. C. Brown and R. L. Sharp, *ibid.*, 1966, **88**, 5851.
- G. Zweifel and H. C. Brown, *J. Am. Chem. Soc.*, 1963, **85**, 2066.
- M. E. Garst, J. N. Bonfiglio, and J. Marks, *J. Org. Chem.*, 1982, **47**, 1494, and earlier papers cited.
- J. Ojima, Y. Yokoyama, and T. Yokoyama, *Chem. Lett.*, 1974, 1261; J. Ojima, Y. Yokoyama, and M. Enkaku, *Bull. Chem. Soc. Jpn.*, 1977, **50**, 1522; J. Ojima, K. Kanazawa, K. Kusaki, and K. Wada, *J. Chem. Soc., Perkin Trans. 1*, 1980, 473.
- J. Ojima, T. Yokomachi, and T. Yokoyama, *Chem. Lett.*, 1972, 633.
- W. B. Austin, N. Bilow, W. J. Kellegan, and K. S. Y. Lau, *J. Org. Chem.*, 1981, **46**, 2280.
- H. G. Viehe and V. Jager, 'Methoden der Organischen Chemie (Houben-Weyl), Vol. V/2a, ed. E. Muller, Georg Thieme Verlag, Stuttgart, 1977, p. 391.
- L. Brandsma and H. D. Verkruijsse, 'Synthesis of Acetylenes, Allenes, and Cumulenes,' Elsevier Press, 1981, p. 55.
- M. M. Midland, *J. Org. Chem.*, 1975, **40**, 2250.
- T. M. Cresp, J. Ojima, and F. Sondheimer, *J. Org. Chem.*, 1977, **42**, 2130.
- C. C. Price and J. A. Pappalardo, *Org. Synth.*, Coll. Vol. IV, 1963, 186.
- Z. Arnold and A. Holý, *Collect. Czech. Chem. Commun.*, 1961, **26**, 3059.
- T. Katakami, K. Fukui, T. Okamoto, and M. Nakagawa, *Bull. Chem. Soc. Jpn.*, 1976, **49**, 297.
- J. P. Beny, S. N. Dhawan, J. Kagan, and S. Sundlass, *J. Org. Chem.*, 1982, **47**, 2201.
- A. G. Voronkov, B. A. Trofimov, V. V. Kruchkov, S. V. Amosova, Yu. M. Skwrotsa, A. N. Volkov, A. G. Mal'kina, and R. Mushii, *Khim. Geterotsykl., Soedin.*, 1981, **12**, 1694.
- K. E. Schulte, J. Reisch, W. Herrmann, and G. Bohn, *Arch. Pharm.*, 1963, **296**, 456 (*Chem. Abstr.*, 1963, **59**, 13916f).
- M. Fieser and L. F. Fieser, 'Reagents for Organic Synthesis,' Wiley Interscience, New York, Vol. 1, p. 1206.
- J. Ojima, Y. Yokoyama, and T. Yokoyama, *Chem. Lett.*, 1975, 487.
- A. Pelter, K. Smith, M. G. Hutching, and K. Rowe, *J. Chem. Soc., Perkin Trans. 1*, 1975, 129, and personal communication from Professor A. Pelter.
- P. Four and F. Guibe, *Tetrahedron Lett.*, 1982, 1825.
- H. O. House, S. G. Boots, and V. K. Jones, *J. Org. Chem.*, 1965, **30**, 2519.
- Y. Taniguchi, J. Inanaga, and M. Yamaguchi, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 3229.
- B. G. Shakhovskoi, M. D. Standnichuk, and A. A. Petrov, *J. Gen. Chem. USSR*, 1964, **34**, 2646.
- H. M. Schmidt and J. F. Arens, *Recl. Trav. Chim. Pays-Bas*, 1967, **86**, 1138.
- E. J. Corey and J. W. Suggs, *J. Org. Chem.*, 1975, **40**, 2554.
- Unpublished observations, Dr. C. D. Reynolds.
- E. Vedejs, D. A. Engles, and M. J. Mullins, *J. Org. Chem.*, 1977, **42**, 3109; P. J. Stang and A. G. Anderson, *J. Am. Chem. Soc.*, 1978, **100**, 1520.
- W. Ando, *Acc. Chem. Res.*, 1977, **10**, 179.
- R. H. Shapiro, *Org. React.*, 1976, **23**, 405.
- B. Bierling, K. Kirschke, and H. Oberzender, *J. Prakt. Chem.*, 1972, **314**, 170.
- D. H. R. Barton, D. L. Lester, and S. V. Ley, *J. Chem. Soc., Perkin Trans. 1*, 1980, 2209.

- 52 W. C. Still, M. Kahn, and A. Mitra, *J. Org. Chem.*, 1978, **43**, 2923.
53 S. C. Watson and J. F. Eastham, *J. Organomet. Chem.*, 1967, **9**, 165.
54 J. Ojima, M. Ishiyama, A. Kimura, and Y. Yokoyama, *Tetrahedron Lett.*, 1975, 1909.
55 A. A. Clifford and W. A. Waters, *J. Chem. Soc.*, 1963, 3056.
56 K. Sonogashira, Y. Tohda, and N. Hagihara, *Tetrahedron Lett.*, 1975, 4467.
57 S. W. Chaikin and W. B. Brown, *J. Am. Chem. Soc.*, 1949, **71**, 122.
58 R. F. Nystrom and W. G. Brown, *J. Am. Chem. Soc.*, 1947, **69**, 2548;
B. O. Field and J. Brundy, *J. Chem. Soc.*, 1955, 1110.
59 E. J. Corey and G. Schmidt, *Tetrahedron Lett.*, 1979, 399.
60 W. S. Rapson and R. G. Shuttleworth, *J. Chem. Soc.*, 1941, 487.
61 G. W. J. Fleet and P. J. C. Harding, *Tetrahedron Lett.*, 1979, 975.
62 I. T. Harrison and B. Lythgoe, *J. Chem. Soc.*, 1958, 837.
63 M. M. Koton and E. P. Moskvina, *Zh. Prikl. Khim.*, 1953, **26**, 660
(*Chem. Abstr.*, 1954, **48**, 8747c).
64 G. Wittig and U. Schölkopf, *Chem. Ber.*, 1954, **87**, 1318.
65 E. J. Corey and M. Chaykovsky, *Org. Synth.*, Coll. Vol. V, 1973, 755;
R. Green, M. Chaykovsky, and E. J. Corey, *J. Org. Chem.*, 1963, **28**,
1128.
66 C. E. Castro, R. Havlin, H. K. Honward, A. Malte, and S. Moje, *J.*
Am. Chem. Soc., 1969, **91**, 6464.
67 S. N. Huckin and L. Weiler, *J. Am. Chem. Soc.*, 1974, **96**, 1082.
68 *cf.* A. Barco, S. Benetti, and G. P. Pollini, *Synthesis*, 1973, 316.
69 C. R. Conrad and M. A. Dolliver, *Org. Synth.*, Coll. Vol. II, 1943, p.
167.
70 *cf.* M. E. Jung and P. L. Ornstein, *Tetrahedron Lett.*, 1977, 2659.
71 *cf.* N. Latif, N. Mishvikiy, and N. S. Girgis, *Chem. Ind. (London)*,
1976, 28.

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