POLYCYCLIC SYSTEMS CONTAINING SMALL-MEMBERED RINGS

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ABSTRACT

The syntheses of a number of polycyclic systems containing potential cyclobutadiene rings are described. The main route to these compounds involved a bis-Wittig reaction with a compound containing a four-membered ring, but alternative routes are also discussed. The properties of the compounds are described, and it is shown that, in those cases in which delocalization occurs, the nuclear magnetic resonance spectra are consistent with those systems having a paratropic contribution from the four-membered ring. In the case of 2-thianorbiphenylene, the paratropic component can be removed by oxidation to 2-thianorbiphenylene 2,2-dioxide. The electronic spectra of biphenylene, 2-thianorbiphenylene, and tetraphenyl-2,5-dithiabisnorbiphenylene were found to be similar.

At a time when we can profitably hold a second International Symposium on the Chemistry of Nonbenzenoid Aromatic Compounds in the space of four years, it is perhaps instructive to recall the position in this field 30 years ago. We are conveniently able to do this because at that time Wilson Baker gave a Chemical Society Tilden Lecture entitled 'Nonbenzenoid aromatic hydrocarbons'[1]. The Tilden Lectures are meant to be reviews of a field, and at the beginning of his lecture Professor Baker remarked 'In dealing with the present position of our knowledge of the chemistry of nonbenzenoid hydrocarbons the lecturer is aware that there are few outstanding recent developments to report.' The lecture discusses the evidence for and against Willstätter synthesis of cyclooctatetraene (1911), Reppe's work at that time not being known, and also the evidence for Lothrop's biphenylene structure (1942). Of particular interest to the subject which I would like to consider here is this discussion of biphenylene and related systems. The dominance of the idea of strain on the thinking of chemists at that time is well illustrated by the statement 'It (biphenylene) is probably also the only type of molecule in which it is possible to have an aromatic nucleus fused to a four-membered ring' and further emphasized by the heading to the final section 'Non-existence of compounds containing a four-membered ring fused to an aromatic nucleus'.

Professor Baker's lecture, given in 1944, was published in 1945, and if given in that year it would probably have been rather different, for Dewar's now classical analysis of the stipitatic acid and colchicine structures had by then appeared. Fifteen years later, in 1959, when *Nonbenzenoid Aromatic Compounds*[2] was published, considerable advances had occurred. For our purposes in particular, benzocyclobutene, if I might use this incorrect but

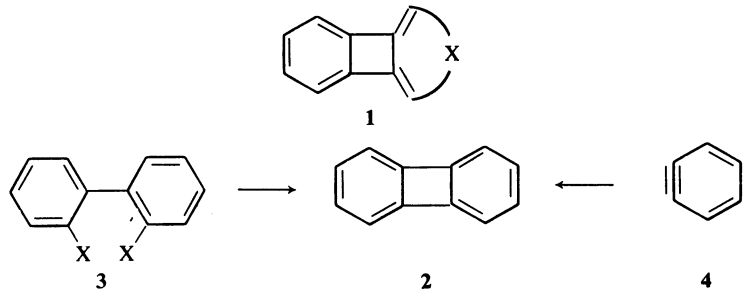
comprehensible name, had been synthesized by Cava and his co-workers[3], and was shown to be a fairly normal compound, and benzocyclobutadiene was a popular fleeting intermediate[4]. The avalanche of results which have been reported since then is reflected in the plethora of volumes now available in this area of chemistry[5]. We now know the annelation of four- or even three-membered rings to benzenoid systems gives compounds which are relatively stable, and the concept of strain as a barrier preventing synthesis has become much less important in the thinking of the chemist.

My interest in fused small ring compounds originated in the middle 1960s and arose from two sources. The first was the concept of anti-aromaticity, independently suggested by Breslow[6] and Dewar[7], who proposed that $4n$ π-electron systems, rather than being merely non-stabilized, were actually destabilized by conjugation. The second was the observation that $4n$ annulenes exhibit magnetic properties opposite in type to those of the $4n+2$ annulenes[8]. This was accounted for on theoretical grounds[9], the $4n$ systems exhibiting a paramagnetic ring current in contrast to the diamagnetic ring current of the $4n + 2$ systems. In order to separate these observable magnetic effects from the emotive concepts of aromaticity and anti-aromaticity the terms diatropic, paratropic and atropic were coined to describe molecules possessing diamagnetic, paramagnetic and no ring currents[10]. It is, of course, hoped that in most cases aromatic compounds will be diatropic, and anti-aromatic compounds paratropic, but such a correspondence is not necessary[11].

Now it appeared clear that, in the same way that benzene is the archetypal aromatic molecule, being the only annulene able to enjoy a planar structure with no bond angle or non-bonding strain, cyclobutadiene should be the archetypal anti-aromatic, paratropic compound, in that it cannot distort from planarity to remove the effect of conjugation. Since cyclobutadiene itself appeared to be a molecule whose properties would be difficult to observe, though many of these difficulties have now been elegantly solved by a number of groups of workers[12], we decided to attempt to synthesize a number of fused systems containing potential cyclobutadiene rings. It was hoped that by varying the type of fusion we would be able to obtain an estimate of the magnitudes both of the magnetic and destabilizing effects of introducing the cyclobutadiene ring.

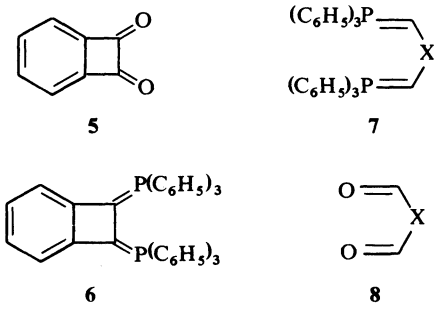
Our initial approach was directed towards the preparation of biphenylene analogue (**1**) in which one of the benzene rings had been replaced by a different $4n + 2$ or $4n$ system. Neither of the classical methods of preparing biphenyl-

Scheme 1



enes (**2**), closure of a 2,2′-biphenyl derivative (**3**) or dimerization of a benzyne (**4**), appeared suitable for our purpose (*Scheme 1*). We considered that a method involving the formation of one of the $4n + 2$ rings in the final step would be the most versatile synthesis. A bis-Wittig reaction looked to be an attractive method, and we examined the possible precursors for this reaction as the ultimate synthetic step. These are shown in *Scheme 2*. Benzocyclo-

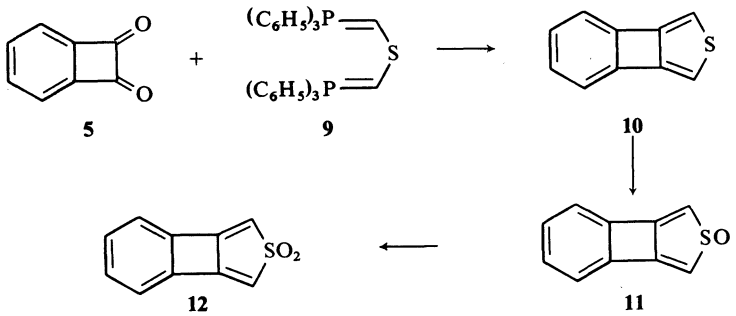
Scheme 2



butadienequinone (**5**) had been prepared by Cava *et al.*[13], and was known to undergo Wittig reactions, although no cyclic products had been reported. 1,2-Bis(triphenylphosphoranyl)benzocyclobutene (**6**) had been prepared by Blomquist and Hruby[14], and although no Wittig reaction had been described when we commenced our investigations, such reactions were subsequently reported[14b]. However, again none of the products were cyclic, and in fact an attempt to prepare benzo[b]biphenylene (**1**, X = C_6H_4) by this route failed.

The required precursors being available, reaction with either a bis-ylide (**7**) or a dicarbonyl compound (**8**) could lead to a range of biphenylene derivatives.

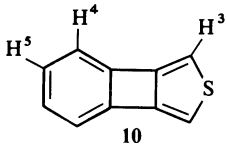
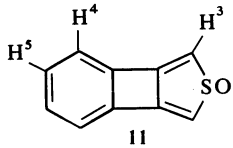
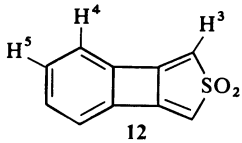
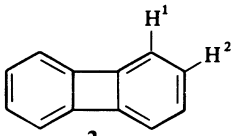
The reaction of benzocyclobutadienequinone (**5**) with the bis-ylide (**9**), derived from α,α′-dichlorodimethyl sulphide by the method of Dimroth *et al.*[15], in ether at room temperature or below gave a 14 per cent yield of the crystalline 2-thianorbiphenylene (**10**), m.pt 98–98.5°[16]. Oxidation of **10** with hydrogen peroxide in acetic acid gave first the sulphoxide **11** and then the sulphone **12**. The second oxidation appears to occur at about the same



rate as the first, but pure sulphoxide could be obtained by interrupting the reaction and separating the mixture.

A comparison of the n.m.r. and electronic spectra of these compounds with those of biphenylene is of interest. The n.m.r. chemical shifts are given in *Table 1*.

Table 1

	$CDCl_3$, 100MHz, τ	
	H^3	H^4, H^5
 **10**	3.51(s)	3.14 (bs)
 **11**	3.35 (s)	2.49 (m)
 **12**	3.60 (s)	2.37 (m)
 **2**		3.30 (H^1), 3.40 (H^2)

In 2-thianorbiphenylene (**10**) both the thiophene ring protons and the benzene protons are at higher field than is normal in such systems, and we attribute this shift as due to the paratropic contribution of the four-membered ring. Oxidation of **10** to **11** leads to a downfield shift of the benzene type protons (0.65 p.p.m.) and further oxidation to **12** results in a further small downfield shift. These shifts we consider to be due to the removal of the paratropic component of the ring current. In the case of the thiophene protons oxidation has two consequences: the diamagnetic ring current of the heterocyclic is removed, but so also is the paratropic contribution from the four-membered ring. These two effects are opposed, and the small change in chemical shift of the thiophene protons on oxidation indicates that the contribution of the diatropic and paratropic components to the chemical shift of the thiophene proton in **10** are of similar magnitude. Further evidence supporting this conclusion will be discussed later.

The electronic spectra of **10** and biphenylene are shown in *Figure 1*. These spectra are quite similar, that of **10** showing a small hypsochromic shift by comparison with that of biphenylene.

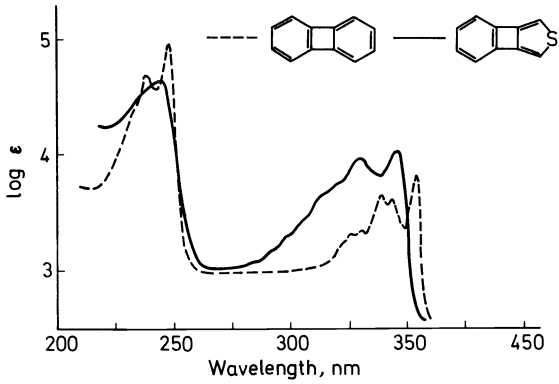
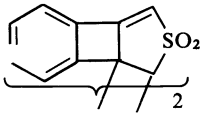


Figure 1. The electronic spectra of 2-thianorbiphenylene (**10**) and biphenylene (**2**) in ethanol.

Neither the sulphoxide **11** nor the sulphone **12** shows any tendency to dimerize via a Diels–Alder reaction, presumably because of the benzocyclobutadiene character of the product that would result. However, the sulphone **12** does give a dimer **13** on photoirradiation, formally derived from a $2\pi + 2\pi$ addition. The stereochemistry of this product, that is whether it is head to head or head to tail, and *anti* or *syn*, is not known.



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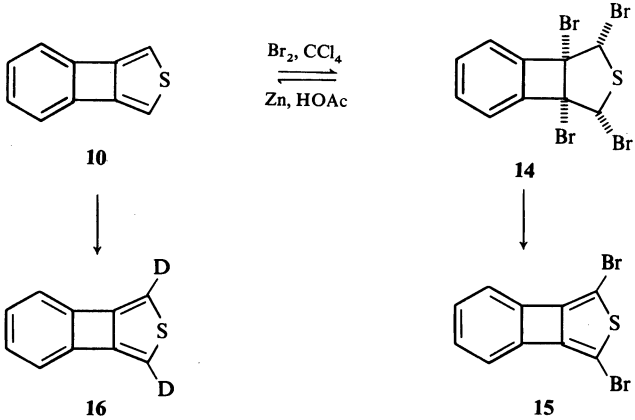
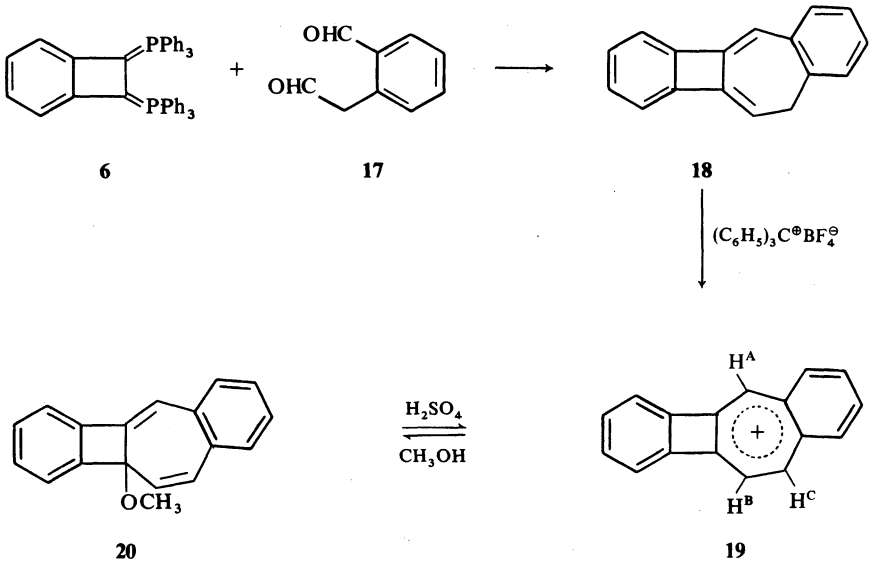
The chemical properties of 2-thianorbiphenylene indicate that the thiophene ring is abnormally reactive towards addition reactions. Thus **10** reacts with bromine to give the tetrabromide **14**, which can be reconverted into **10** by treatment with zinc, or dehydrobrominated to 1,3-dibromo-2-thianorbiphenylene (**15**).



Treatment of **10** with deuterotrifluoroacetic acid in ether containing deuterosulphuric acid gave 1,3-dideutero-2-thianorbiphenylene (**16**). Attempts to deuterate the benzene ring under more acid conditions led only to decomposition.

Attempts to extend this sequence to give oxygen and carbon analogues of **10** from benzocyclobutadienequinone were unsuccessful. Reaction occurred but the products did not contain five-membered rings.

The reactions of the bis-ylide **6** were then explored. Treatment of **6** with homophthaldehyde (**17**) gave, in two per cent yield, the cycloheptatriene derivative **18**[17]. Reaction of **18** with trityfluoroborate in acetonitrile gave a deep green solution of the homobiphenylene cation **19**. The n.m.r. spectrum of **19** shows a doublet at τ 1.09, attributed to H^C, and a complex band at τ 1.6–3.1, which included signals from triphenylmethane.



Quenching **19** with methanol gave the methyl ether **20**, from which the cation **19** could be regenerated by treatment with concentrated sulphuric acid. The electronic spectrum of **19** in sulphuric acid was complex (*Figure 2*, *Table 2*), the absorption bands extending to 618 nm. The ⟪p*K*⟫ of the cation was determined by the method of Meuche *et al.*[18], and it was found to be −1.3. Comparison with the ⟪p*K*⟫ values of the benzotropylium and 1,2:4,5-dibenzotropylium cations indicates that the destabilizing effect of annelation by the benzocyclobutadiene group is similar to that of annelation by benzene (*Table 2*).

The cation **19** was the first homobiphenylene cation to be prepared. Subsequently Lombardo and Wege[19] prepared the parent cation **23** by the route shown. The spectral properties and chemical behaviour of **23** are

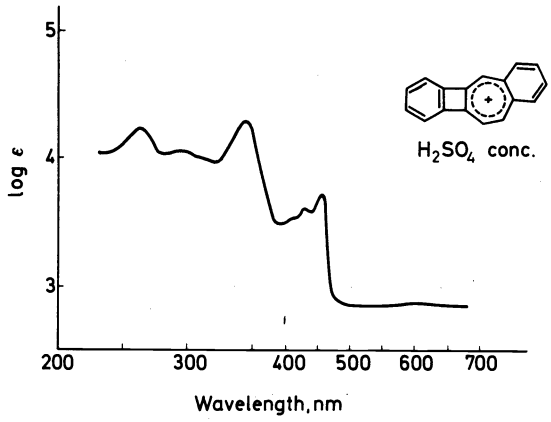
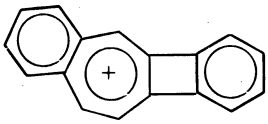
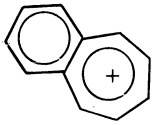
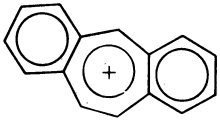


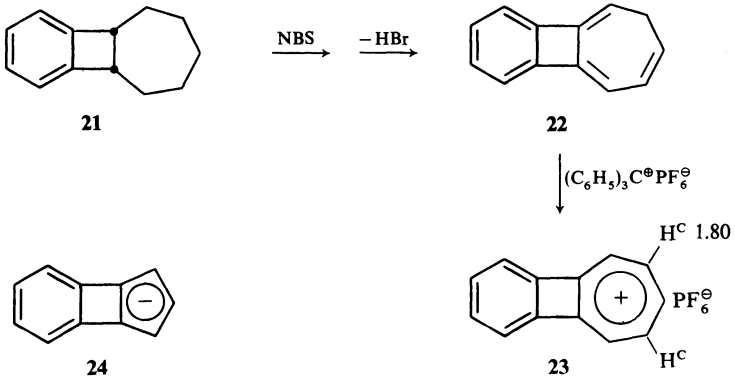
Figure 2. Electronic spectrum of the cation (**19**) in sulphuric acid.

similar to those of **19**. Thus, in the n.m.r. spectrum the H^C proton in **23** appears at τ 1.80, with the remaining three tropylium protons at τ 2.2–2.5. In both of these cations there thus appears to be an upfield shift of the protons adjacent to the four-membered ring, presumably due to a paratropic contribution.

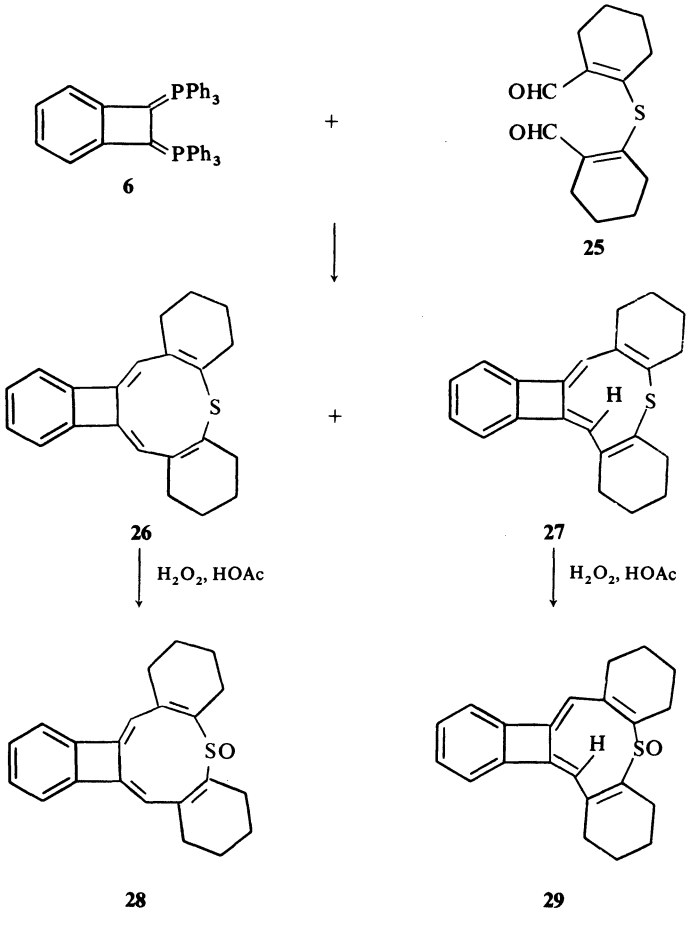
Table 2

	λ_{max}, nm		⟪pK⟫
	263	17 500	
	295	11 500	
	344	19 700	−1.3
	428	4 100	
	456	5 300	
	598	750	
	234	17 800	
	282	50 000	+1.7
	338	3 150	
	425	1 650	
	237	14 800	
	306	123 000	−1.9
	379	10 200	
	397	8 700	
	508	3 250	
	540	3 250	

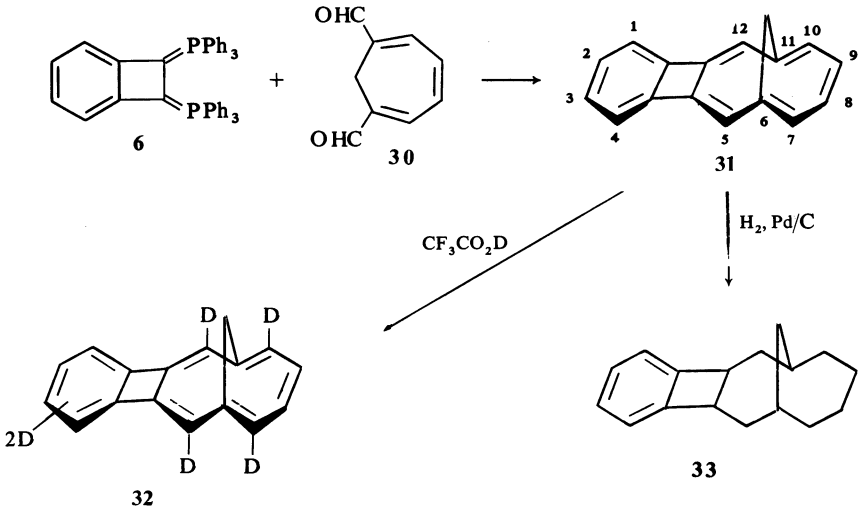
G. Naville, H. Strauss and E. Heilbronner, *Helv. Chim. Acta*, 43, 1221 (1960).



The series of 12π carbocyclic systems of the biphenylene type is complete, as the norbiphenylene anion **24** has been prepared by Cava and his co-workers[20].



We next explored the possibility of synthesizing rings containing more than six π-electrons, and the reaction of the bis-ylide with the readily available dialdehyde **25** was examined. Treatment of **6** with **25** in dry ether gave the cyclic systems **26** and **27**[21]. Both **26** and **27** have the same molecular formula; and both are analogues of biphenylene in which one benzene ring has been replaced by a nine-membered thionin ring, the compounds differing only in the stereochemistry of one of the double bonds.



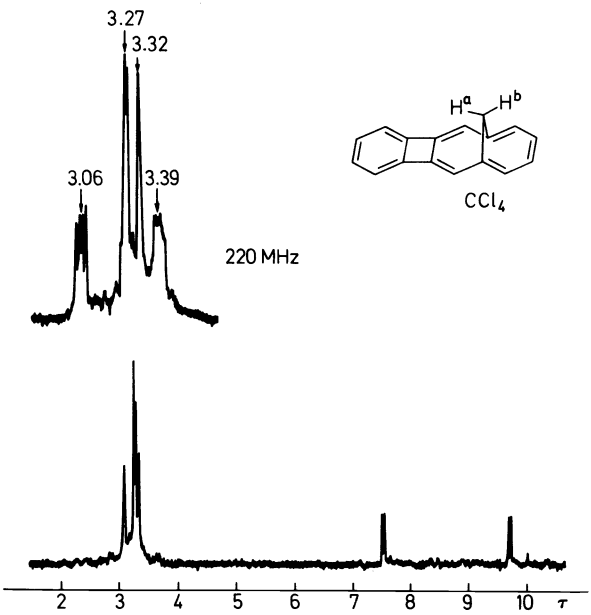
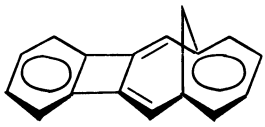


Figure 3. The 220 MHz n.m.r. spectrum of 6,11-methanocyclobutabenzo[1,2-*a*][10]annulene (**31**) in carbon tetrachloride.

Compound **26** had only one type of olefinic proton resonance in the n.m.r. spectrum, and its electronic spectrum resembled that of the other bis-methylenebenzocyclobutenes, whereas compound **27** had two olefinic resonance signals, and its electronic spectrum was unlike those of the other bis-methylenebenzocyclobutenes. Compound **26** was therefore assigned the all-*cis* stereochemistry, and compound **27** the mono-*trans* stereochemistry shown. Oxidation of **26** with hydrogen peroxide in acetic acid gave the sulphoxide **28**, while oxidation of **27** gave two sulphoxides of gross structure **29**, but differing with regard to the orientation of the SO group and the internal proton. The latter observation, together with the small change of the spectral properties in oxidation, strongly suggests that **26** and **27** have non-planar nine-membered rings and are not delocalized systems. Compound **27** appears to be the only fully unsaturated nine-membered ring compound having a *trans* double bond to have been isolated[22].

The success of Vogel and others in preparing stable ten π-electron systems containing a 1,6-bridge encouraged us to examine the synthesis of a biphenylene analogue of this type. Reaction of **6** with cycloheptatriene-1,6-dialdehyde (**30**)[23] gave, in low yield, the 1,6-methano[10]annulene derivative **31**[24]. The electronic spectrum of **31** was quite similar to that of 1,6-methano[10]annulene, while the n.m.r. spectrum (*Figure 3*) consisted of an AA′BB′ multiplet at τ 3.06 (H^8, H^9) and 3.99 (H^7, H^{10}) and an AA′BB′ multiplet at τ 3.27 (H^1, H^2, H^3, H^4), a singlet at τ 3.32 (H^5, H^{12}) and an AB system at high field (7.55, 9.71, J = 10 Hz) due to the methylene protons. Treatment of **31** with deuterotrifluoroacetic acid, deuterosulphuric acid in ether caused the successive disappearance of the bands at τ 3.39, 3.32 and part of the band at 3.27, and eventually led to the hexadeutero derivative **32**. The n.m.r. spectrum of **32** shows two singlets at τ 3.06 and 3.27 (1:1), which supports the assignment given for **31**. Catalytic hydrogenation of **31** using palladium on charcoal gave the decahydro derivative **33**, no evidence for cleavage of the 1,6-methano bridge being detected.

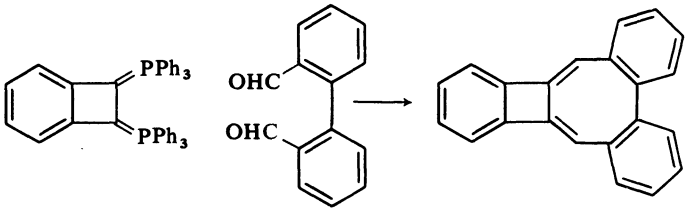
The large difference in chemical shift of the two methylene bridge protons, and the observed ^{13}C chemical shifts[25], suggest that **31** is best represented by **31a**, in which delocalization in that part of the ten-membered ring annelated to the benzocyclobutadiene is diminished.



31a

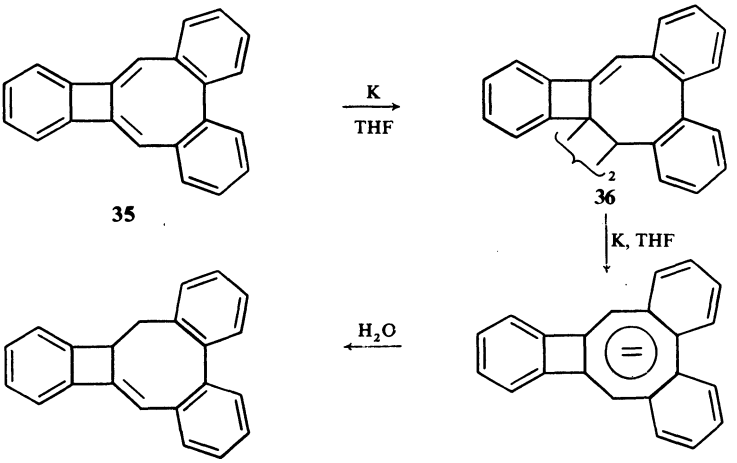
Besides the synthesis of biphenylene analogue containing $4n + 2$ rings, the synthetic method can also be applied to the preparation of systems containing $4n$ rings. The fusion of a $4n$ ring gives a system containing $4n + 2$ π-electrons, and this contradiction of 'magic numbers' invoked interest.

Reaction of **6** with biphenyl dialdehyde **34** gave the bicyclo[6.2.0] decapentaene derivative **35**[26], in which a $4n$ ring has replaced one of the benzene rings in biphenylene. The n.m.r. spectrum of **34** clearly indicates that it is not a delocalized system, and the molecule is almost certainly non-planar.



6 **34** **35**

By analogy with cyclooctatetraene, the eight-membered ring in **35** might be capable of reduction to a 10π-electron system. However, in the case of **35** such a reduction would be opposed by an increase in steric interference in the planar form and also by the increase of the cyclobutadiene character of the system. Treatment of **35** with potassium in tetrahydrofuran led to the formation of a radical anion which is rapidly converted to the dimer **36**. This overall reaction does not represent a reduction, but reduction does occur in a subsequent step in which the dimer **36** is cleaved to the dianion **37**. The dianion **37** can be quenched with water to give the dihydro derivative **38**[27].



35 **36** **38** **37**

The n.m.r. spectrum of **37** is shown in *Figure 4*, together with that of the dianion of *sym*-dibenzocyclooctatetraene (**39**)[28]. The cyclooctatetraene protons, which appear as a singlet at τ 2.92 in the n.m.r. spectrum of **39**, appear as a singlet at τ 4.23 in the n.m.r. spectrum of **37**. The protons on the benzocyclobutene rings in **37** are also at extremely high field (τ 4.51, 4.87).

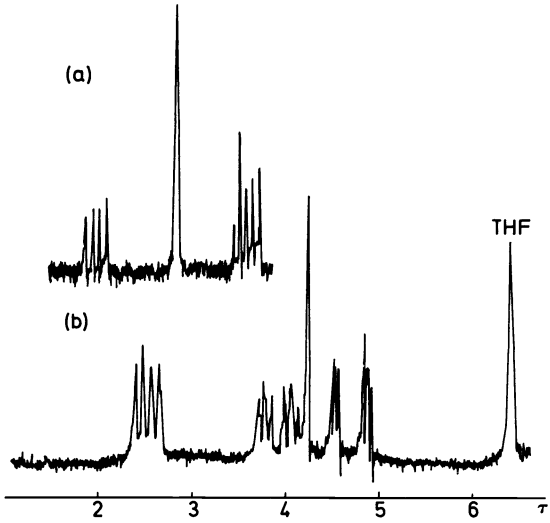
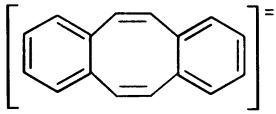


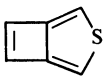
Figure 4. The n.m.r. spectrum of *sym*-dibenzocyclooctatetraenyl dianion (**39**) (a) and 3,4:5,6:9,10-tribenzobicyclo[6.2.0]decapentaenyl dianion (**37**) (b), both in tetrahydrofuran-d_8. Spectrum (a) is taken from T. J. Katz, M. Yoshida and L. C. Siew, *J. Amer. Chem. Soc.* **87**, 4516 (1961) by permission of the authors and the American Chemical Society.

These shifts cannot be simply accounted for on the basis of the negative charge, and we attribute these high field shifts to a large paratropic contribution to the ring current arising from the cyclobutadiene form of the four-membered ring in **37**.



39

Since the bis-Wittig method had proved successful in the synthesis of biphenylene-type systems, we considered its possible use as a method for preparing benzocyclobutadiene-type systems. Further, the properties of 2-thianorbiphenylene suggested that 3-thiabicyclo[3.2.0]heptatriene (**40**) and its derivatives might, unlike benzocyclobutadiene, be isolable compounds. Cava's finding that the phenyl substituent in the 3,4-positions of naphtho[b]cyclobutadiene increases the stability sufficiently to allow isolation[29], made 6,7-diphenyl-3-thiabicyclo[3.2.0]heptatriene (**41**) the target system.



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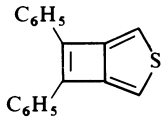


41

Reaction of 3,4-diphenylcyclobutadienequinone (**42**) with the bis-ylide **9** gave the bright red crystalline **41** in four per cent yield[30]. The n.m.r. spectrum (*Figure 5*) shows signals at τ 2.37 (dd, $J = 9$, 1.5 Hz, 4H, *o*-phenyl), 2.70 (m, 6H, *m*, *p*-phenyl) and 3.84 (s, 2H, H^2, H^4). The electronic spectrum (*Figure 6*) was similar to, but less complex than that of 3,4-diphenylnaphtho-[b]cyclobutadiene. Reaction of **41** with Raney nickel gave *meso*-3,4-diphenylhexane (**43**).

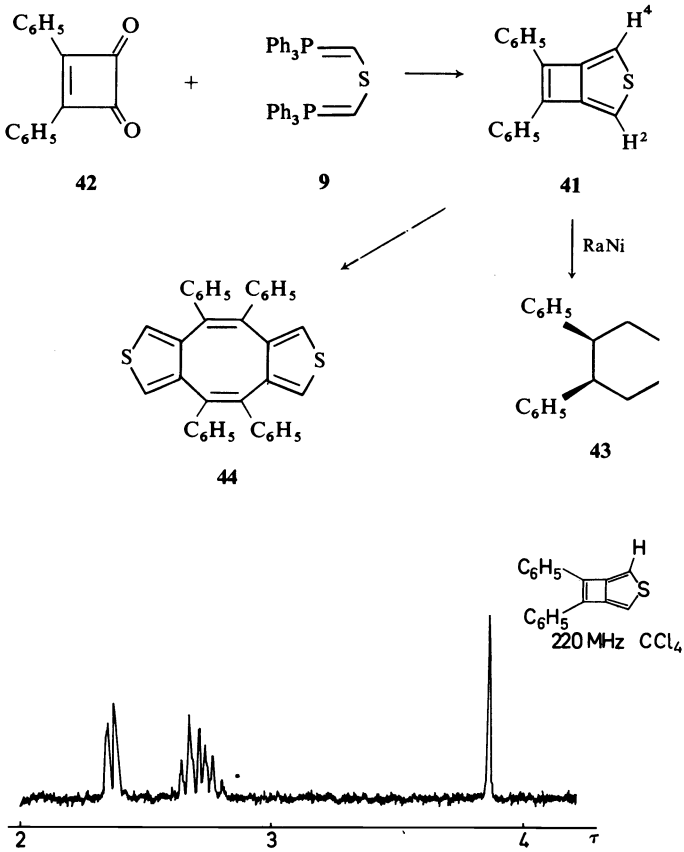


Figure 5. The 220 MHz n.m.r. spectrum of 6,7-diphenyl-3-thiabicyclo[3.2.0]heptatriene (**41**) in carbon tetrachloride.

The compound **41** forms a 2,4,7-trinitrofluorene complex, and it is decolorized on heating, giving a dimer to which we assign the structure **44**. This dimer presumably arises from a $2\pi + 2\pi$ addition followed by subsequent rearrangement. On warming in chlorinated solvents a trimer is produced.

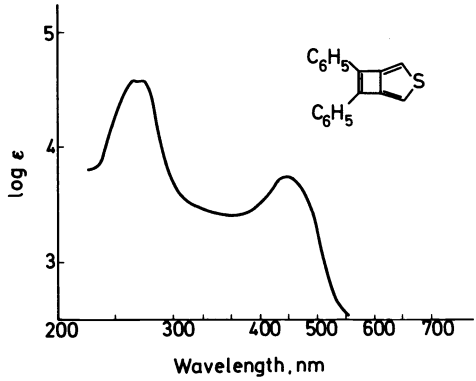
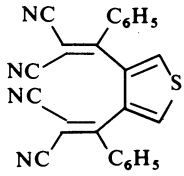
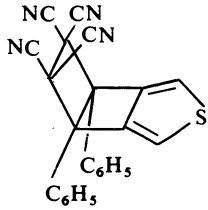


Figure 6. The electronic spectrum of 6,7-diphenyl-3-thiabicyclo[3.2.0]heptatriene (**41**) in ethanol.

The compound **41** is thermochromic and changes from deep reddish orange to pale orange on cooling. Diels–Alder reactions were unsuccessful, but a 1:1 adduct was formed with tetracyanoethylene, which probably has the formula **45**, although **46** has not been rigorously excluded.



45



46

The high field position of the H^2, H^4 protons in the n.m.r. spectrum of **41** we consider again to be due to a paratropic contribution from the four-membered component. The electronic spectrum suggests that the phenyl

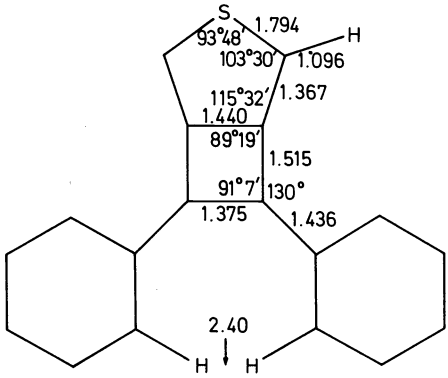
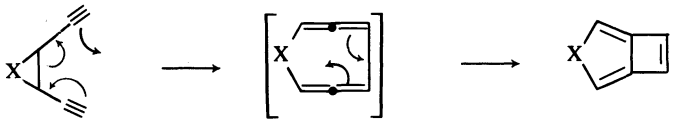


Figure 7. The x-ray crystallographic structural parameters of 6,7-diphenyl-3-thiabicyclo-[3.2.0]heptatriene (**41**).

rings are approximately co-planar with the double bond of the four-membered ring, allowing extensive conjugation. An x-ray crystallographic analysis of **41** (*Figure 7*) shows that in the crystalline state the phenyl rings are twisted about 23° out of the plane, and the four-membered ring is approximately rectangular, but with the double bonds longer than usual, and the single bonds shorter, indicating some interaction between the double bonds[31].

Subsequent to this synthesis, Bergman and Vollhardt have prepared the parent 3-oxabicyclo[3.2.0]heptatriene (**49a**)[32] and 3-thiabicyclo[3.2.0]-heptatriene (**49b**)[33] by the route shown. The parent compound **49b** is much less stable than **41**, but the n.m.r. spectra of both **49a** and **49b** were obtained



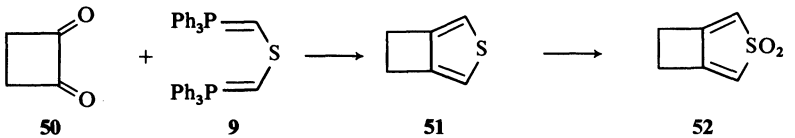
47a X = O
47b X = S

48

49a X = O
49b X = S

and the high field position of both the heterocyclic and olefin protons strongly suggests that these compounds have a paratropic contribution to the ring current.

In order to have available a model compound with which to compare the chemical shift of the thiophene protons in **41**, and further, to examine the properties of annelating a small ring to a heterocyclic system, we investigated the preparation of 3-thiabicyclo[3.2.0]hepta-1,4-diene (**51**). Reaction of the diketone **50** with the ylid **9** gave **51** as an oil in *ca.* 10 per cent yield [34]. The n.m.r. spectrum of **51** had two singlets at τ 3.24 and 6.98 in the ratio 1:2, and the electronic spectrum showed a maximum at 244 nm, characteristic of a

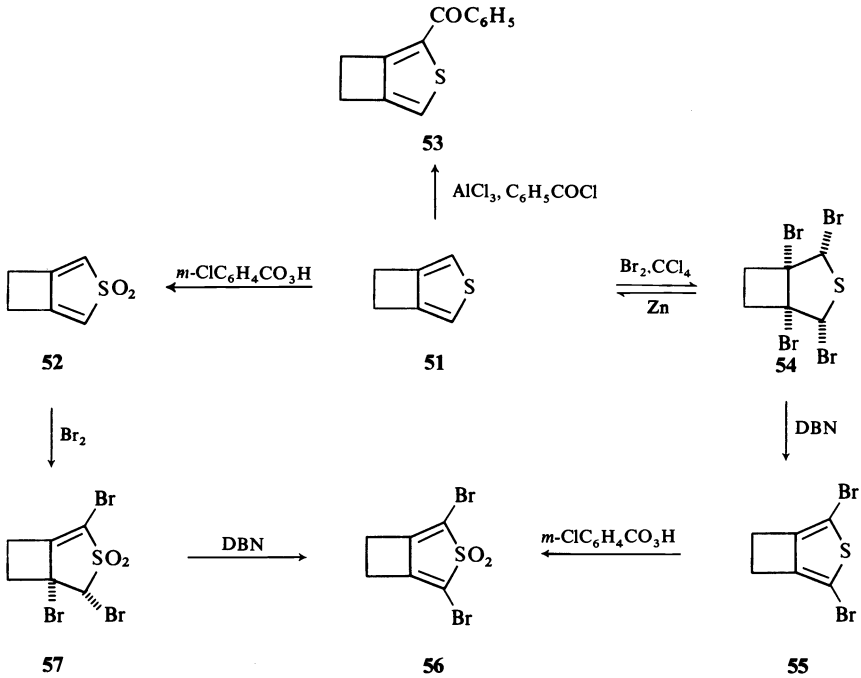


50 **9** **51** **52**

thiophene. Oxidation of **51** with *m*-chloroperoxybenzoic acid gave the sulphone **52**, the n.m.r. spectrum of which had singlets at τ 3.98 and 6.67, in the ratio 1:2. The electronic spectrum of **52** had maxima at 225 nm (ε 3300) and 292 nm (1300), characteristic of a thiophene sulphone.

The compound **51** undergoes electrophilic substitution with benzoyl chloride in the presence of aluminium chloride to give **53**. However, when treated with bromine in carbon tetrachloride addition occurs and the tetrabromide **54** is obtained. Reaction of **54** with zinc regenerates **51**, while treatment with diazabicyclo[3.4.0]nona-5-ene (DBN) gives the dibromide **55**. Oxidation of **55** with *m*-chloroperoxybenzoic acid gives the sulphone **56**,

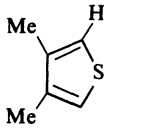
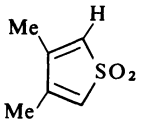
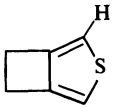
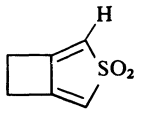
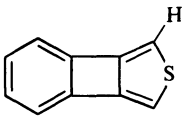
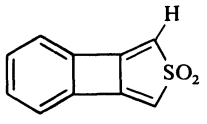
and this compound can also be obtained from the sulphone **52** via the tribromide **57**.



A comparison of the change in chemical shift of a heterocyclic ring proton on conversion of the thiophene to the corresponding sulphone is shown in *Table 3*. It can be seen that on oxidizing 3,4-dimethylthiophene to the sulphone there is an upfield shift of the thiophene proton (0.54 p.p.m.), and a similar upfield shift is observed on oxidizing **51** to **52** (0.74 p.p.m.). However, when 2-thianorbiphenylene (**10**) is oxidized only a small upfield shift is observed (0.09 p.p.m.). In our view this small change is due to the unusual chemical shift of the heterocyclic proton in **10**, owing to the paratropic contribution from the four-membered ring. On oxidation both the paratropic and diatropic contributions are removed, and as these approximately balance, the change in chemical shift is small. *Table 4* shows the effect of introducing the double bond into the 3-heterobicyclo[3.2.0]heptadiene system by comparison of **49b** with **51**, and of **49a** with **58**, also prepared by Bergman and Vollhardt[35].

Two other routes to the 3-thiabicyclo[3.2.0]hepta-1,4-diene system have been described. Longworth and McOmie[36] prepared the halogenated derivative **60a, b** by treatment of the thiophenes **59a, b** with sodium iodide, and Cava and his co-workers[37] synthesized the phenyl-substituted derivative **62** by photoirradiation of the corresponding sulphones **61**.

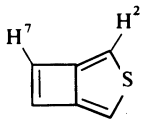
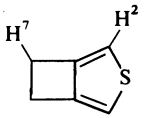
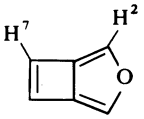
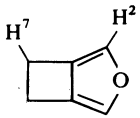
Table 3. Comparison of the n.m.r. proton shifts of some thiophenes and the corresponding sulphones

	$CHCl_3$, τ, 100MHz	$\Delta\tau$
	3.16	0.54
	3.70	
	3.24	0.74
	3.98	
	3.51	0.09
	3.60	

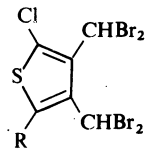
We have investigated two other possible routes to the 3-heterobicyclo-[3.2.0]heptadienes. Base treatment of bis-propargyl systems of type **63** might be expected to lead to the corresponding bis-allenes **64**, which would be envisaged to ring close to the biradical **65**. The diradical **65** can potentially ring close to the desired 3-heterobicyclo[3.2.0]heptadiene under suitable conditions. In fact treatment of **63a** with potassium *t*-butoxide gave the dimer **66a** in 15 per cent yield as the only characterized product.

Similarly, the sulphur and nitrogen analogues **63b** and **63c** give the corresponding dimers **66b** and **66c**. The structures assigned to **66a–c** are based on the spectral properties.

Table 4. Comparison of the n.m.r. proton shifts of some 3-heterobicyclo[3.2.0]heptatrienes and the corresponding 3-heterobicyclo[3.2.0]hepta-1,4-dienes

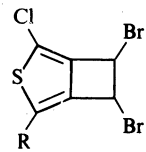
	H^2	τ $\Delta\tau$	H^7
	3.99		3.25
	3.23	0.76	6.98
	3.89		3.67
58 	3.12	0.77	6.87

R. G. Bergman and K. P. C. Vollhardt, *J. Amer. Chem. Soc.* **94**, 8950 (1972); **95**, 7538 (1973).
R. G. Bergman and K. P. C. Vollhardt, *Chem. Commun.* 214 (1973).

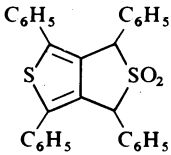


59a R = Cl
59b R = Br

NaI / DMF →

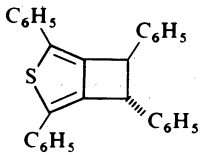


60a R = Cl (*cis, trans*)
60b R = Br (*cis, trans*)



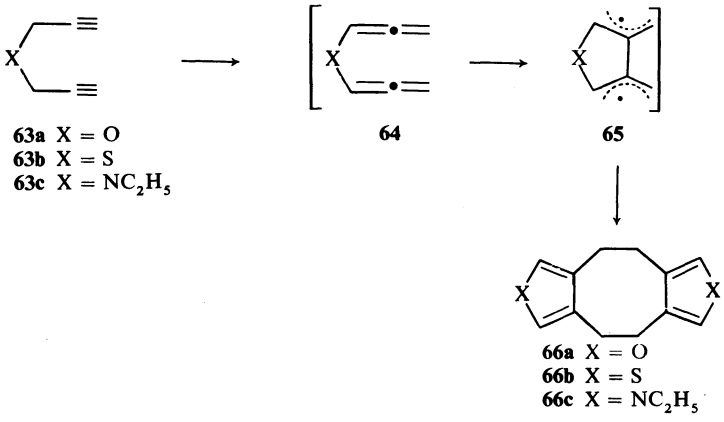
61

hν →



62

Hoping that substitution of the acetylene might impede dimerization and lead to the desired monomer, we prepared the *t*-butyl acetylene **67**. Base rearrangement of this compound, however, again gave the corresponding

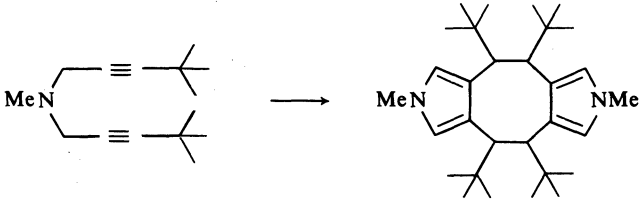


63a X = O
63b X = S
63c X = NC_2H_5

64 **65**

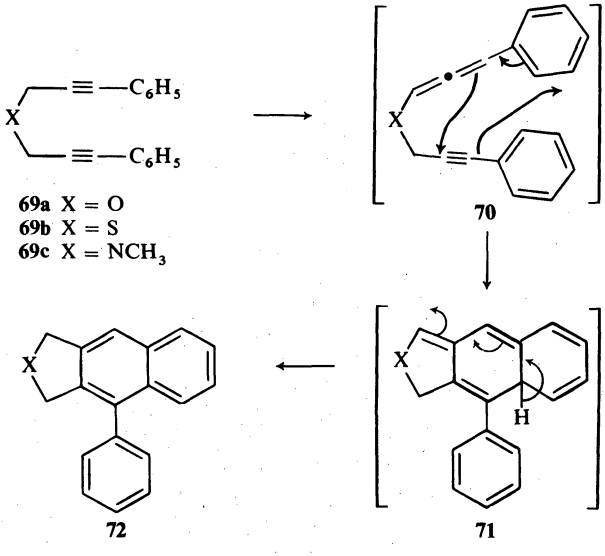
66a X = O
66b X = S
66c X = NC_2H_5

dimer **68**, albeit in lower yield. The related sulphur and oxygen analogues are currently under investigation.



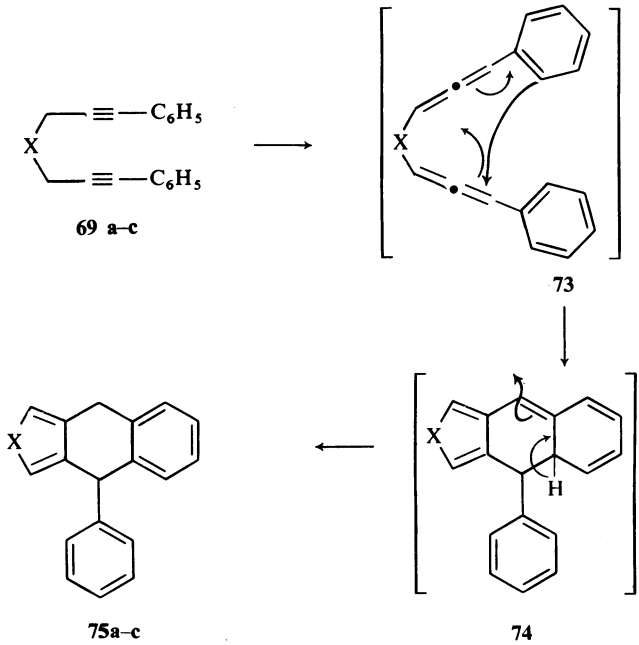
67 **68**

The phenyl-substituted derivative **69a–c** had been examined earlier by Iwai and Ide[38]. These authors found that base rearrangement gave naphthalenes **72a–c**, and they suggested that these compounds arose from the

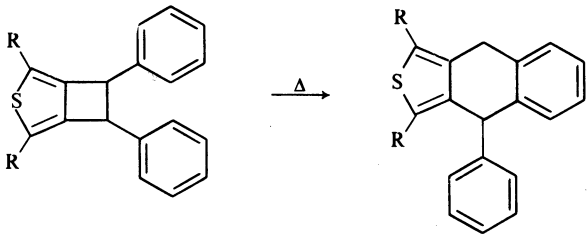


69a X = O
69b X = S
69c X = NCH_3

70 **71** **72**



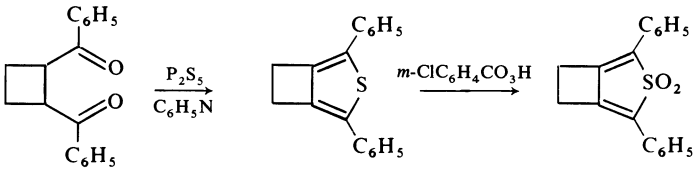
monoallene-monoacetylene intermediate **70** which cyclized by a Cope reaction to **71** and that this then underwent a prototropic rearrangement to the naphthalene **72**. This plausible mechanism has been adopted by others[39], but it is in fact incorrect for the compounds **69a–c**, as the naphthalenes are not the primary products of the reaction. Iwai and Ide monitored their reaction by the electronic spectrum, and the reactions required a fairly long time to go to completion. If the reaction is monitored by other methods, for example t.l.c., the first product observed is not the naphthalene but the heterocycle **75**. This presumably arises from the bis-allene **73** which can cyclize to **74**, either by a concerted route as shown, or via a diradical intermediate. Prototropic rearrangement of **74** then gives **75**. Base treatment of **75** under conditions similar to those employed by the Japanese authors leads to the naphthalene derivative **72**, the rate of reaction being fastest for **75c**. We are currently attempting to elucidate the mechanism of this rearrangement, and



76 **77**

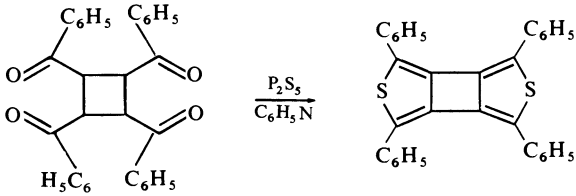
are trying to obtain further intermediates in the sequence **67** to **75**. I should perhaps point out that the desired bicyclo[3.2.0]heptadiene **76** is also a possible intermediate in this sequence, although probably less likely, as related compounds are known to rearrange thermally to derivatives of type **75** [e.g. **76**→ **77**(R = C_6H_5)][37].

The other method which we investigated was the classical formation of five-membered heterocycles from 1,4-diketones. We re-examined this reaction because of the observed stability of the parent sulphur compound **51**. Reaction of the diketone **78** with phosphorus pentasulphide in pyridine gave, in about five per cent yield, 2,4-diphenyl-3-thiabicyclo[3.2.0]hepta-1,4-diene (**79**), m.pt 150–150.5°. The n.m.r. spectrum ($CDCl_2$) of **79** showed a multiplet centred at τ 2.65 and a singlet at τ 6.74 (5:2), and the electronic spectrum [234.5 nm (ε 12000), 242sh (11000), 327sh (29900), 338.5 (35900), 352 (26400)] was very similar to those of the related compounds prepared by Cava *et al.* Oxidation of **79** with *m*-chloroperoxybenzoic acid gave the sulphone **80**, m.pt 224–246°. The n.m.r. spectrum (CD_2Cl_2) showed a multiplet at τ 2.46 and a singlet at τ 6.30. The characteristic downfield shift of the cyclobutene protons on oxidation of the thiophene to the sulphone is again observed.



78 **79** **80**

Attempts to prepare the other heterocycles by the analogous reactions were unsuccessful. However, the phosphorus pentasulphide reaction was applied to the tetraketone **81**, when tetraphenyl-2,5-dithiabisnorbiphenylene **82**, m.pt 194–194.5°, was obtained in about five per cent yield[40]. This represents the synthesis of the first potential cyclobutadiene fused to two five-membered heterocyclic rings. The n.m.r. spectrum of **82** showed only a multiplet centred at τ 2.60. The electronic spectrum [298 nm sh (ε 31000), 322 (34800)] does not resemble that of **79**, but is more like that of biphenylene

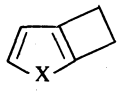


81 **82**

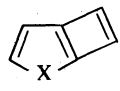
and 2-thianorbiphenylene. Clearly some interaction between the thiophene rings is indicated.

Unfortunately, the yield of **82** in the reaction is not reproducible, and appears to be susceptible to small changes in the reaction conditions. We are currently trying to optimize and control these conditions in order to make sufficient **82** available to be able to study its chemistry. Whether dithiabisnorbiphenylenes will have a paratropic component from the four-membered ring must await the synthesis of simpler derivatives, and routes to these are also being explored.

The properties of 3-thiabicyclo[3.2.0]heptadiene (**51**) and heptatriene (**49b**) aroused our interest in the analogous compounds (**83**, **84**) in which the cyclobutene ring is fused to the 2,3-position of the heterocycle rather than the 3,4-position. We have therefore examined possible routes to these compounds[41].

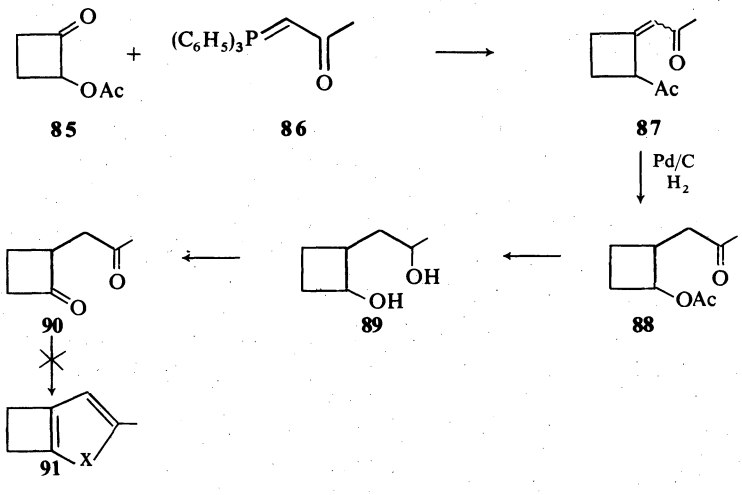


83



84

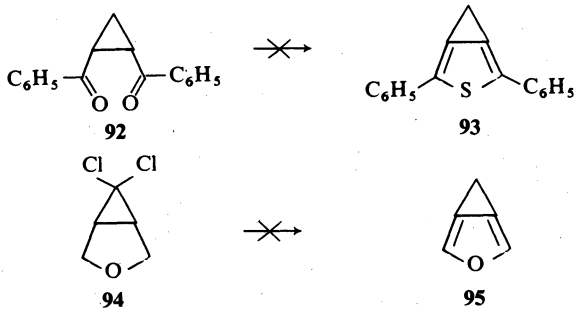
Reaction of the cyclobutanone **85** with the ylide **86** gave, in high yield, the methylenecyclobutene **87**. Hydrogenation of **87** over palladium on charcoal proceeded smoothly to give the saturated acetate **88**. Hydrolysis of the acetate gave only a low yield of the desired alcohol, and compound **88** was therefore treated with lithium aluminium hydride when the diol **89** was obtained in high yield. Oxidation of **89** with chromium trioxide in pyridine gave the diketone **90**. Unfortunately all attempts to convert **90** to compounds of type **91** have so far been unsuccessful.



85 **86** **87** **88** **89** **90** **91**

We have also investigated routes to five-membered heterocycles fused to three-membered rings. The diketone **92** failed to give any of the desired product **93** under a variety of conditions, whereas the corresponding acyclic analogue reacted smoothly. Attempts to dehydrochlorinate **94**, by analogy

with the Billups method[42], also failed to give **95**. We are continuing our investigations in both these areas.



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