As a final remark, one can state that even though the reported data do not allow one to draw a complete kinetic formulation of the reaction mechanism and further experimental work is needed these data do unambiguously demonstrate that ethylation of PAN in the presence of concentrated aqueous NaOH occurs via an interfacial mechanism.

Experimental Section

All starting materials and final products were characterized by nuclear magnetic resonance spectra recorded on a Varian T-60 NMR spectrometer using Me_4Si as internal standard.

Gas chromatographic analyses were performed on a Perkin-Elmer F30 gas chromatograph equipped with a 6 ft × $^1/_8$ in., 2% silicon gum rubber SE-30 on high-performance Chromosorb W (AW-DMCS, 80–100 mesh) column.

Reagents. Commercial grade phenylacetonitrile (PAN) and bromoethane (EtBr) were purified by distillation. Tetra-*n*-butylammonium bromide (TBAB) was prepared as reported in the literature.[21]

Alkylation Reactions. The reactions were carried out in a 250-mL, three-necked flask equipped with a condenser, thermometer, and mechanical stirrer. To a mixture of PAN, EtBr, and TBAB at a given temperature was added a solution of aqueous NaOH, preheated at the same temperature, with stirring. Stirring rates were adjusted within 1% by a Rotor revolution counter. The reaction temperature was kept constant within ±1 °C by a thermostated oil bath. Small samples of the reaction mixture were withdrawn by a syringe at intervals, quenched with dilute HCl, and extracted with diethyl ether, and the extracts were tested by GLC. Runs R1–R5 were carried out with the same general procedure but by using a reactor and a stirrer provided with additional baffles. The details of the individual experiments are given under the corresponding tables.

The initial rate of disappearance of PAN (v_0) was evaluated as the tangent to the origin of the kinetic curve.

Registry No. Phenylacetonitrile, 140-29-4; ethyl bromide, 74-96-4.

(21) E. Gravenstein, Jr., E. P. Blanchard, Jr., B. A. Gordon, and R. W. Stevenson, *J. Am. Chem. Soc.*, **81**, 4842 (1959).

Strained Aromatic Systems. Synthesis of Cyclopropabenzocyclobutenes, Cyclopropanaphthocyclobutenes, and Related Compounds

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The diene **9**, prepared in four steps from diethyl cyclohex-4-ene-1,2-dicarboxylate, was converted into cyclopropa[4,5]benzocyclobutene (**3**) by photoirradiation to the cyclobutene **20** followed by treatment with KO-*t*-Bu and into cyclopropa[*e*]cyclobuta[*b*]naphthalene (**45**) by Diels–Alder addition to diethyl cyclobutene-1,2-dicarboxylate, oxidation, and treatment with KO-*t*-Bu. Attempts to convert **9** into cyclopropa[*b*]anthracene were unsuccessful. The corresponding diene **15** could not be converted into cyclopropa[3,4]cyclobutabenzene (**4**), but this compound was prepared by treatment of **27**, obtained from chlorocarbene addition to bicyclo[4.2.0]octa-2,4-diene, with KO-*t*-Bu. Unsuccessful attempts to prepare substituted derivatives of **3**, **4**, and cyclopropa[*b*]anthracene as well as cyclopropa[*d*]cyclobuta[*b*]naphthalene and dicyclopropa[*b*,*d*]naphthalene are described. The chemical and physical properties of **3**, **4**, and **45** and the chemistry of the dienes **9**, **15**, and **36** are outlined, and some conclusions are drawn regarding the scope of the Billups reaction.

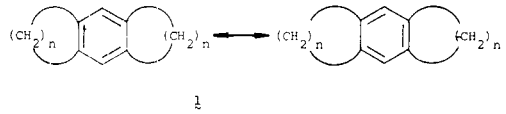
The extent to which the benzene ring can be distorted from its planar, hexagonal configuration before it loses its aromatic character has long interested both theoretical and experimental chemists. It is known that the out-of-plane force constants are smaller than the in-plane ones,[1] and this has been exploited in the formation of bent benzene rings, as in the paracyclophanes,[2] and in twisted benzene rings, as in layered systems.[3] Although bent and battered,[4] nevertheless the benzene rings have largely maintained the physical characteristics of the unperturbed system. Since in-plane distortions of benzene are more strongly resisted, the enforcement of changes in the in-plane geometry of benzene might be expected to more readily affect the aromatic character of the system. Such a disruption might be brought about by the introduction of large groups at adjacent positions on the ring, causing a preferred bond elongation and bond angle distortion, although the relief by an out-of-plane arrangement of the two groups can moderate such effects.[5] Alternatively, the fusion of small rings to the benzene nucleus should cause changes to both bond angles and lengths, and these would not be alleviated by the molecule becoming nonplanar. The synthesis of benzene annelated by small rings began with the preparation of biphenylene by Lothrop in 1941.[6] However, the first major impetus to work in this area was provided by Cava and his co-workers, who succeeded in preparing benzocyclobutene,[7] *sym*-dicyclobutabenzene,[8] and the two isomeric naphthocyclobutenes[9] in the late 1950's and early 1960's. The properties of these compounds showed that the benzene rings were insufficiently perturbed for their aromatic character to be disrupted. Other four-membered-ring compounds were subsequently prepared, but the next major event was the preparation of the first benzocyclopropene derivative by Anet and Anet[10] in 1964,

(1) See: Callomon, J. H.; Dunn, T. M.; Mills, I. M. *Philos. Trans. R. Soc. London, Ser. A.* **1966**, *259*, 499.
(2) Farthing, A. C. *J. Chem. Soc.* **1953**, 3261. Brown, C. J. *Ibid.* **1953**, 3265. Cram, D. J.; Steinberg, H. *J. Am. Chem. Soc.* **1951**, *73*, 5691.
(3) See: Hubert, A. J. *J. Chem. Soc. C* **1967**, 13; Longone, D. T.; Chow, H. S. *J. Am. Chem. Soc.* **1970**, *92*, 994; Misumi, S.; Otsubo, T. *Acc. Chem. Res.* **1978**, *11*, 251.
(4) Cram, D. J.; Cram, J. M. *Acc. Chem. Res.* **1971**, *4*, 204.
(5) See: van Tamelen, E. E.; Pappas, S. P. *J. Am. Chem. Soc.* **1962**, *84*, 3789; Burgstahler, A. W.; Chien, P.-L.; Abdel-Rahman, M. O. *Ibid.* **1964**, *86*, 5281.
(6) Lothrop, W. C. *J. Am. Chem. Soc.* **1941**, *63*, 1187.
(7) Cava, M. P.; Napier, D. R. *J. Am. Chem. Soc.* **1956**, *78*, 500.
(8) Cava, M. P.; Deana, A. A.; Muth, K. *J. Am. Chem. Soc.* **1960**, *82*, 2524.
(9) Cava, M. P.; Shirley, R. L. *J. Am. Chem. Soc.* **1960**, *82*, 654. Cava, M. P.; Shirley, R. L.; Erickson, B. W. *J. Org. Chem.* **1962**, *27*, 755.
(10) Anet, R.; Anet, F. A. L. *J. Am. Chem. Soc.* **1964**, *86*, 525.

0022-3263/80/1945-4183$01.00/0

which was followed the next year by the synthesis of the parent molecule by Vogel and co-workers.[11] Since then a variety of aromatic compounds annelated by three-membered rings have been prepared and their properties studied,[12] but little evidence has been found for bond localization in these systems.

One way in which the distortion of the benzene ring can be increased is to fuse two small rings onto the molecule. Further, the consequences of such a double fusion may be different if the rings are fused symmetrically or asymmetrically, since in the first case (**1**) the Kekulé structures



1

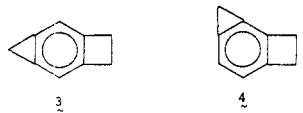
2

are identical whereas in the second case (**2**) they are not. A preference for the double bond being exocyclic or endocyclic to the small ring would then favor one of the Kekulé structures of **2**, and some disruption of delocalization might be detected.

We now describe some of our work directed both toward the synthesis of benzene derivatives annelated by two small rings and toward the preparation of related annelated polycyclic systems.[13]

Results and Discussion

Cyclopropabenzocyclobutenes. We chose as our original synthetic goals the two isomeric cyclopropabenzocyclobutenes **3** and **4**. We considered that closing the

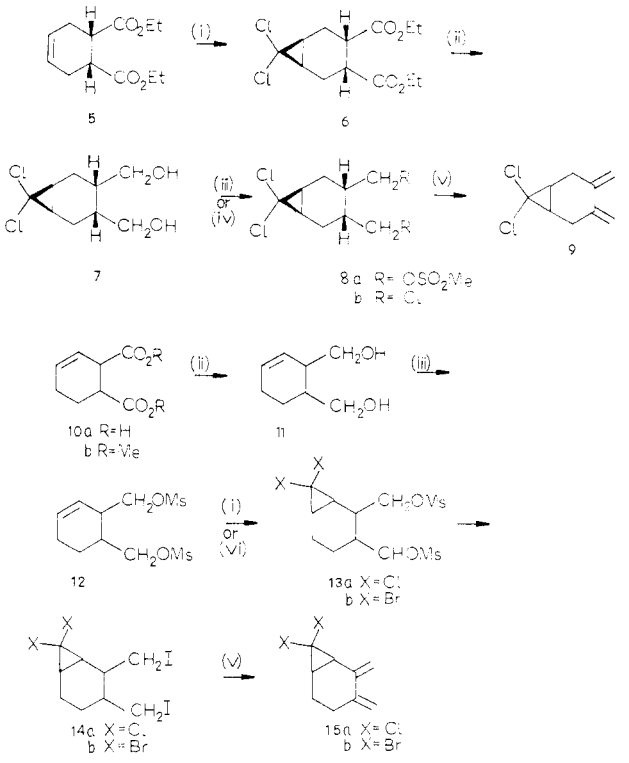


3 **4**

second small ring on a preformed benzocyclopropene or benzocyclobutene would be difficult[14] because of the large increase in strain engendered by such a reaction. We therefore decided to initially synthesize the complete carbon skeleton and then introduce the unsaturation, hoping in this way to have some strain already present and to offset the further strain by the delocalization energy. The Billups reaction[15] to convert 7,7-dichlorobicyclo[4.1.0]hepta-3-enes into benzocyclopropenes seemed eminently suited for the final reaction, and in consequence, we chose the compounds **9** and **15** as our initial target molecules since on photoirradiation[1]- these should give the desired cyclobutene precursors **20** and **21**. The syntheses of **9** and **15** are outlined in Scheme I.

The diester **5** was prepared by the Diels–Alder reaction of butadiene with maleic anhydride.[17] Reaction of **5** in

Scheme I



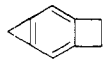
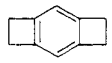
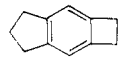
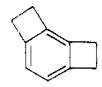
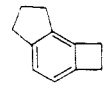
[a] (i) $CHCl_3$, NaOH, Et_3PhCH_2NCl. (ii) $LiAlH_4$. (iii) CH_3SO_2Cl. (iv) $SOCl_2$. (v) KOtBu, THF. (vi) $CHBr_3$, NaOH, Et_3PhCH_2NCl.

$CHCl_3$ with sodium hydroxide in the presence of benzyltriethylammonium chloride[18] gave **6** as one isomer, presumably that in which the cyclopropane ring is anti to the cis ester groups. The ester **6** was reduced with lithium aluminum hydride to the diol **7** which was converted to the mesylate **8a**. Reaction of **8a** with KO-*t*-Bu in THF gave the desired diene **9**. This diene could also be prepared by similar base treatment of the tetrachloride **8b**, which was prepared from **7** by reactions with thionyl chloride. Preparation via **8a** was the preferred method, and the overall yield from **5** was 32%. The diene **9** is a colorless oil, the ^1H and ^{13}C NMR spectra being in accord with the assigned structure.

The diacid **10a**, prepared by the Diels–Alder reaction of 2,4-pentadienoic acid and acrylic acid,[19] was esterified to give **10b** which was then reduced with lithium aluminum hydride to **11**. The diol **11** was converted into the mesylate **12** which on reaction with chloroform or bromoform and base gave the cyclopropanes **13a,b**. This order of reaction was used as reaction of the ester **10b** with chloroform and base gave the desired adduct contaminated with dimethyl cyclohex-2-ene-1,2-dicarboxylate. When the mesylates **13a,b** were treated with KO-*t*-Bu in THF, only low yields of the desired dienes **15a,b** were obtained. Consequently **13a,b** were converted into the corresponding diiodides **14a,b** which reacted with KO-*t*-Bu to give, respectively, the diene **15a** in good yield and the diene **15b** in moderate yield. The ^1H NMR spectrum of **15a** showed three singlets at δ 5.53, 5.12, and 4.70 and a multiplet centered at δ 2.10, while the ^{13}C NMR spectra showed the presence of nine carbon atoms. The electronic spectrum had a maximum at 243 nm. The diene **15b** has similar spectroscopic

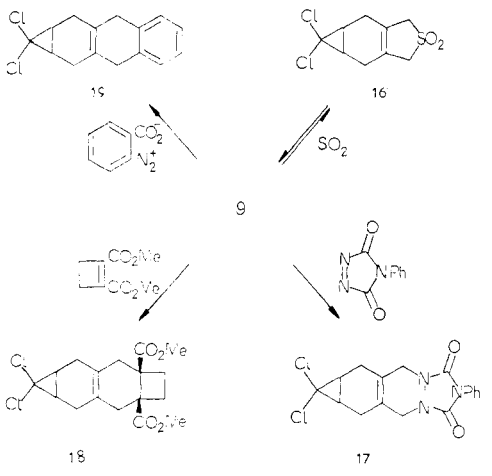
(11) Vogel, E.; Grimme, W.; Korte, S. *Tetrahedron Lett.* **1965**, 3625.
(12) See: Halton, B. *Chem. Rev.* **1973**, *73*, 113; Billups, W. E. *Acc. Chem. Res.* **1978**, *11*, 245.
(13) For preliminary accounts of parts of this work, see: Davalian, D.; Garratt, P. J. *J. Am. Chem. Soc.* **1975**, *97*, 6883; *Tetrahedron Lett.* **1976**, 2815; Davalian, D.; Garratt, P. J.; Mansuri, M. M. *J. Am. Chem. Soc.* **1978**, *100*, 980.
(14) However, see: Saward, C. J.; Vollhardt, K. P. C. *Tetrahedron Lett.* **1975**, 4539.
(15) Billups, W. E.; Blakeney, A. J.; Chow, W. Y. *J. Chem. Soc. D* **1971**, 1461.
(16) Garrett, J. M.; Fonken, G. J. *Tetrahedron Lett.* **1969**, 191.
(17) Cope, A. C.; Herrick, E. *Org. Synth.* **1950**, *30*, 29.
(18) Makosza, M.; Wawrzyniewicz, M. *Tetrahedron Lett.* **1969**, 4659.
(19) Muskat, I. E.; Becker, B. C.; Lowenstein, J. S. *J. Am. Chem. Soc.* **1930**, *52*, 326.

Table I. ^{1}H NMR and Electronic Spectra of 3, 4, Dicyclobutabenzenes, and Cyclopentabenzocyclobutenes

	^{1}H NMR, δ (J, Hz)	electronic spectrum, nm (ε)	ref
	6.85, 2 H; 3.08, 6 H	284 (1000),[a] 287.5 (1000), 294 (630)	
	6.64, 2 H; 2.99, 8 H	276 (4570), 280 (5125), 286 (3890)	26
	6.91, 2 H; 3.08, 4 H; 2.86, 2.00, 6 H	276 (4570), 280 (4380), 286 (3752)	26
	7.04, 6.82, 2 H (6.5); 3.24, 4 H; 3.18, 2 H	264 (1250),[a] 270 (1600), 276.5 (1600)	
	6.88, 2 H; 3.14, 8 H	266 (1360), 269 (1370), 275 (1540)	26
	7.07, 6.08, 2 H (7.5); 3.12, 4 H; 2.85, 2.77, 2.03, 6 H	267 (972), 271 (879), 276 (1037)	26

[a] Extinction coefficients are minimal values.

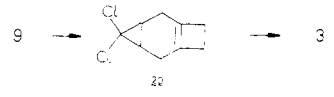
Scheme II



properties except that in the electronic spectrum the maximum was shifted to 253 nm.

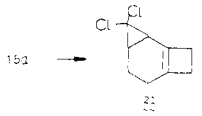
The diene **9** readily underwent Diels–Alder reactions with a variety of dienophiles (Scheme II). The adduct with sulfur dioxide, **16**, could be thermally reconverted to **9** and provides a stable crystalline source for the generation of this diene. The dienes **15a,b** also react with dienophiles (vide infra).

For our projected synthesis of **3** the diene **9** had to be converted to the cyclobutene **20**; photoirradiation[16] of **9**



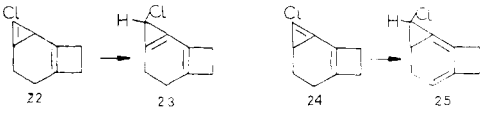
produced **20** in 50% yield. Compound **20** was then dehydrochlorinated by treatment with KO-*t*-Bu in Me_2SO to give **3** in 25–40% yield. Freshly sublimed KO-*t*-Bu gave higher and more consistent yields. The 60-MHz ^{1}H NMR spectrum (CCl_4) of **3** showed only two singlets (Table I), but the ^{13}C NMR spectrum showed five types of carbon atoms (vide infra). The IR spectra showed a band at 1665 cm^{-1} characteristic for benzocyclopropenes.[12]

Photoirradiation of **15a** give the cyclobutene **21**, the desired precursor for the synthesis of **4**, in 45% yield.

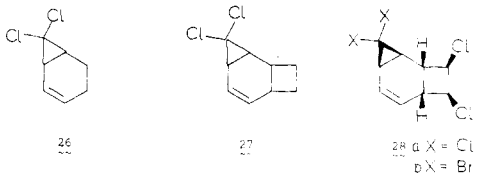


However, all attempts to convert **21** into **4** by treatment with KO-*t*-Bu in either Me_2SO or THF failed, none of the desired product being detected.[20] Since the dibromo analogue of **21** should be more readily rearranged, we investigated its preparation from **15b**. However, in this case photoirradiation provided a variety of products but none of the desired cyclobutene.

The failure of **21** to rearrange to **4** may be ascribed to a number of causes. Billups' method had previously been applied only to compounds with the double bond in the position 4,5 to the cyclopropane ring, and elimination of HCl from such a system gives only one intermediate. When the double bond is at the 3,4-position, as in **21**, elimination of HCl can lead initially to two different compounds, **22** and **24**. For **22** to undergo further reaction



the double bond has to migrate into the ring to give, assuming conjugation of the double bonds is preferred, **23**. Compound **23**, with a double bond endocyclic to both rings, is highly strained.[21] The other intermediate, **24**, like the 4,5 isomer, should be capable of rearranging to the less strained system **25**. However, the rearrangement of **24** to **25** shifts one double bond from a tetra- to a trisubstituted position which is also unfavorable. In order to examine these problems in a simpler system, we prepared 7,7-dichlorobicyclo[4.1.0]hept-2-ene (**26**) and treated this with



KO-*t*-Bu in Me_2SO whereupon rearrangement to benzocyclopropene occurred. This reaction did, however, appear to be slower than that of 7,7-dichlorobicyclo[4.1.0]hept-3-ene, and this difference has been independently and more quantitatively described by Halton and co-workers.[22]

Since it appeared that the problems with **21** might be associated with this specific isomer, we decided to examine

(20) The benzocyclopropenes have a characteristic and exceptionally pungent smell which makes it difficult for them to elude detection.
(21) Closs, G. L.; Böll, W. A. *J. Am. Chem. Soc.* **1963**, *85*, 3904.
(22) Banwell, M. G.; Blattner, R.; Browne, A. R.; Craig, J. T.; Halton, B. *J. Chem. Soc., Perkin Trans. 1* **1977**, 2165.

the preparation of an isomer in which the double bond is in a different position. We chose **27** in which the double bond is disubstituted but in which one of the intermediates would still require a double bond to become endocyclic to both rings.

Our initial attempt to prepare **27** was via the tetrachloride **28a**, which was readily available from the reaction of 7,8-dichlorobicyclo[4.2.0]octa-2,4-diene[23] with KO-*t*-Bu and $CHCl_3$. The dibromide dichloride could be prepared by the corresponding reaction with bromoform. All attempts to remove the cyclobutyl chlorine atoms from **28a** failed, and an attempt to replace them with iodine via the Finkelstein reaction gave a mixture of tetrachlorides, probably the *trans*-7,8-dichloro isomers. Reaction of **28a** with KO-*t*-Bu gave no identifiable product.

Accordingly, we abandoned this route and investigated the addition of dichlorocarbene to bicyclo[4.2.0]octa-2,4-diene, prepared by the method of Alder and Dortmann.[24] Treatment of bicyclo[4.2.0]octa-2,4-diene with $CHCl_3$ and KO-*t*-Bu gave **27** as a pale yellow oil in 28% yield. Reaction of **27** with freshly sublimed KO-*t*-Bu in Me_2SO gave **4** in 4–10% isolated yield. The ^1H NMR (Table I) and ^{13}C NMR spectra were consistent with **4**. A comparison of the ^1H NMR and electronic spectra of **3**, **4**, *sym*-[8] and *as*-dicyclobutabenzene,[25] cyclopenta[4,5]benzocyclobutene,[26] and cyclopenta[3,4]benzocyclobutene[26] is made in Table I.

In the ^1H NMR spectrum the cyclobutyl and cyclopropyl protons of **3** are at lower field (0.16, 0.10 ppm) than those of **4**, a finding in keeping with the observed differences in the cyclobutyl protons of the dicyclobutabenzenes (0.15 ppm) and cyclopentabenzocyclobutenes (0.04 ppm). Thummel and Nutakul[26] have suggested that this difference reflects a decrease in shielding in the distorted aromatic system, the difference being smaller in the less strained cyclopentabenzocyclobutenes. That the distortions in **3** and **4** are somewhat differently apportioned is supported by a comparison of the ^{13}C NMR spectra (vide infra).

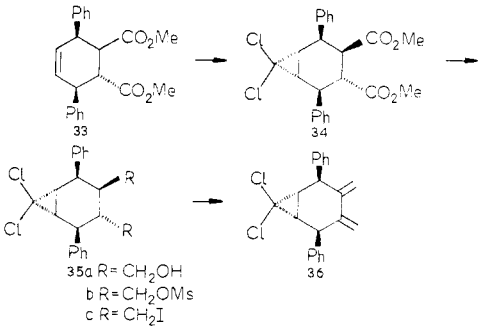
The electronic spectrum of **3** shows a considerable bathochromic shift (ca. 8 nm) of all three maxima as compared to those of *sym*-dicyclobutabenzene and cyclopenta[4,5]benzocyclobutene, and the maximum at 296 nm is the longest wavelength band known for a simple alkylated benzene.[27] The electronic spectrum of **4** is very similar to those of *as*-dicyclobutabenzene and cyclopenta[3,4]benzocyclobutene, the shortest wavelength band showing a small hypsochromic shift. It has been generally observed that symmetrically annelated benzenes show a bathochromic shift (ca. 10 nm) over the 1,2,4,5-tetraalkylated benzenes whereas the asymmetrically annelated benzenes have maxima at the same positions as those for 1,2,3,4-tetraalkylated benzenes. The spectrum of **3** suggests that those factors contributing to the bathochromic shift in symmetrically annelated benzenes have been intensified in this molecule.

The ^{13}C NMR spectra of **3** and **4** show clearly that these are similarly strained molecules. With values obtained from benzocyclopropene and benzocyclobutene for the upfield shift of an aromatic carbon next to a three- or four-membered ring (14.1 and 3.7 ppm, respectively[28]), the chemical shifts of the carbons in **4** can be calculated by taking the shifts in **3** as the standard values. For example, C-1 of **3**, the common carbon atom to both the benzene and cyclobutene rings, is at 145.5 ppm; C-2 in **4** is similarly situated except that it is adjacent to the cyclopropyl ring and should be shifted upfield by 14.1 ppm, giving a predictable position at 131.4 ppm. The observed and predicted chemical shifts of the carbons in **4** are given in Table II.

Table II. Observed and Calculated ^{13}C Chemical Shifts for the Benzene Carbon Atoms in 4

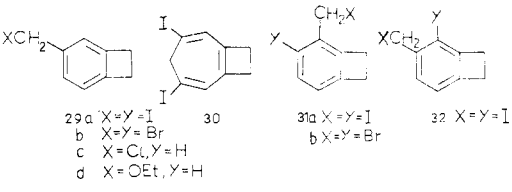
	^{13}C NMR, ppm					
	C-1	C-2	C-3	C-4	C-5	C-6
obsd	148.0	135.9	119.6	126.0	112.4	121.0
calcd	145.5	131.4	119.1	122.8	114.7	122.1
difference	+2.5	+4.5	+0.5	+3.2	−2.3	−1.1

Scheme III



It can be seen that there are small differences in the predicted and found chemical shifts shown in Table II. The annelated ring carbon atoms are shifted upfield less than is calculated, whereas the nonannelated carbon atoms (C-5, C-6) are shifted more upfield than calculated. These differences can tentatively be attributed to an increase in strain in the nonannelated fragment of the benzene ring with a concomitant relaxation of strain in the annelated portion of the ring.

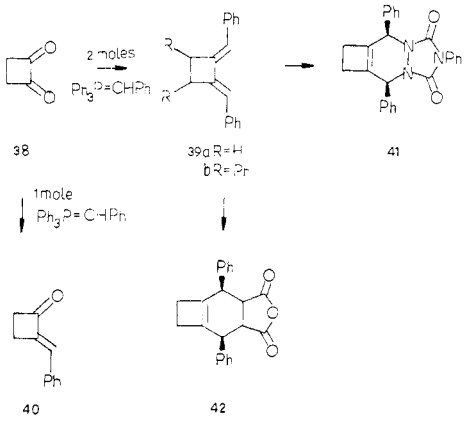
Both **3** and **4** react readily with electrophiles to give products resulting from the cleavage of the three-membered ring. Thus reaction of **3** with iodine, bromine, hydrogen chloride, and ethanol in the presence of silver ions gave the substituted benzocyclobutenes **29a–d**. In the case



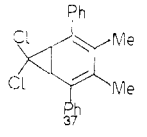
of iodine, none of the cycloheptatrienyl derivative **30** could be detected, this type of ring cleavage being a major pathway for the reaction of benzocyclopropene.[11] With **4**, two modes of ring opening are possible to give compounds of types **31** and **32**. Bromine gave solely and iodine mainly compounds of type **31**, whereas hydrogen chloride and silver-assisted ethanolysis gave only compounds of type **32** (**29c**, **29d**). An explanation for this difference has been discussed elsewhere in conjunction with other experiments.[29]

(23) See: Huisgen, R.; Boche, G.; Hecht, W.; Huber, H. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 585.
(24) Alder, K.; Dortmann, H. A. *Chem. Ber.* **1954**, *87*, 1492.
(25) Thummel, R. P. *J. Am. Chem. Soc.* **1976**, *98*, 628.
(26) Thummel, R. P.; Nutakul, W. *J. Org. Chem.* **1977**, *42*, 300.
(27) Hexamethylbenzene has a maximum at 278 nm: Stern, E. S.; Timmons, C. J. "Electronic Absorption Spectroscopy in Organic Chemistry", 3rd ed.; Arnold: London, 1970. Cyclophanes have bands at longer wavelength; cf. ref 3.
(28) Günther, H.; Jikeli, G.; Schmickler, H.; Prestien, J. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 762.
(29) Bee, L. K.; Garratt, P. J.; Mansuri, M. M. *J. Am. Chem. Soc.*, in press.

Scheme IV



Substituted Cyclopropabenzocyclobutenes. In the hope of preparing crystalline compounds, we investigated the synthesis of cyclopropabenzocyclobutenes substituted by phenyl groups. By analogy with our synthesis of **3** we treated compound **33**, prepared by Diels–Alder addition of dimethyl fumarate to 1,4-diphenylbutadiene, with chloroform and sodium hydroxide at 10 °C. The resulting dichlorocarbene adduct **34** (Scheme III) was reduced with lithium aluminum hydride to the diol **35a** which was then treated with methanesulfonyl chloride to give the dimesylate **35b**. Reaction of **35b** with KO-*t*-Bu gave none of the desired diene **36** but instead norcaradiene **37**, identified

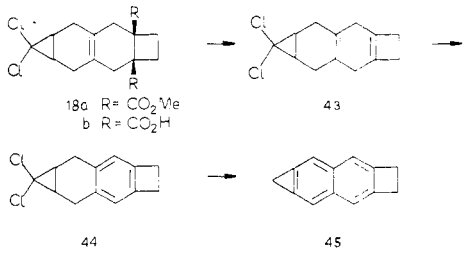


by its ^1H NMR and electronic spectra. The diene **36** could be prepared by first converting the dimesylate to the corresponding diiodide **35c** by a Finkelstein reaction, followed by treatment with KO-*t*-Bu to give the exocyclic diene. The ^1H NMR spectrum of **36** showed multiplets at δ 7.35 (10 H), 5.25, 4.50 (4 H), 3.80 (2 H), and 2.20 (2 H), and the ^{13}C NMR spectrum showed eight signals, two of the aromatic carbon atoms having coincidental chemical shifts. The reduction in the complexity of the ^{13}C NMR spectrum of **36** compared to those of its precursors clearly illustrated that this complexity arose from the trans arrangement of the diester functions and their subsequent transformation products.

All attempts to convert the diene **36** into the cyclobutene by photoirradiation were unsuccessful. We therefore explored a second route to the desired cyclobutene. *trans,trans*-1,2-Dibenzylidenecyclobutane (**39a**) was prepared by the Wittig reaction between cyclobutane-1,2-dione (**38**)[30] and 2 molar equiv of the ylide prepared from benzyltriphenylphosphonium chloride and methyllithium (Scheme IV). The all-trans stereochemistry was assigned because of the similarity of the electronic spectrum to that of 3,4-diphenyl-*trans,trans*-1,2-dibenzylidenecyclobutane (**39b**)[31] and from the simplicity of its ^{13}C NMR spectrum. With 1 molar equiv of the ylide, **38** gave the monoalkene **40**.

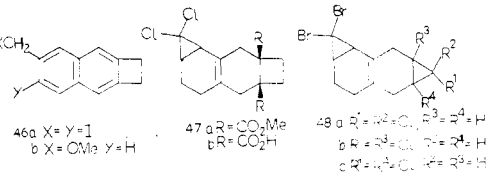
Unlike **39b** the diene **39a** reacted readily in a [4 + 2] manner with dienophiles, giving the adduct **41** with 4-phenyl-1,2,4-triazoline-3,5-dione[32] and the adduct **42** with maleic anhydride. However all attempts to react **39a** with a mixture of 1,3- and 3,3-dichlorocyclopropenes were unsuccessful.

Scheme V



Cyclopropanaphthocyclobutenes and Dicyclopropanaphthalene. The adduct **18a** had been synthesized since it appeared to be an ideal precursor for the preparation of cyclopropa[*e*]cyclobuta[*b*]naphthalene (**45**, Scheme V). Hydrolysis of **18a** gave the diacid **18b** (205–210 °C dec) which was electrolyzed in pyridine containing triethylamine to give the diene **43** (mp 96–98 °C, 20% yield) contaminated by a little of its dehydrogenation product, **44**. Reaction of this mixture with pyridinium hydrobromide perbromide gave **44**: mp 88–90 °C; 55% yield. Treatment of **44** with KO-*t*-Bu gave **45**: mp 144–146 °C; 50% yield. The ^1H NMR spectra showed four singlets at δ 9.52 (2 H), 7.47 (2 H), 3.45 (2 H) and 3.28 (4 H), and the ^{13}C NMR spectra showed the presence of seven different carbon atoms. The electronic spectrum showed an absorption maximum at 226.5 nm (ϵ 3500) and two broad bands with maxima at 256 (ϵ 3120), 267 (4830), and 288 (1910) and 304 (2210), 310 (3620), and 324 (5430). These three principal bonds can be assigned to the ^1B, ^1L_a, and ^1L_b bands of naphthalene.[33] A comparison of the electronic and ^{13}C NMR spectra of **45** with related naphthalenes has been made by Thummel and Nutakul.[34]

The three-membered ring **45** is readily cleaved by electrophiles to give substituted cyclobutanaphthalenes. Thus with iodine **45** gave the diiodide **46a**, and with methanol in the presence of silver ions it gave **46b**.

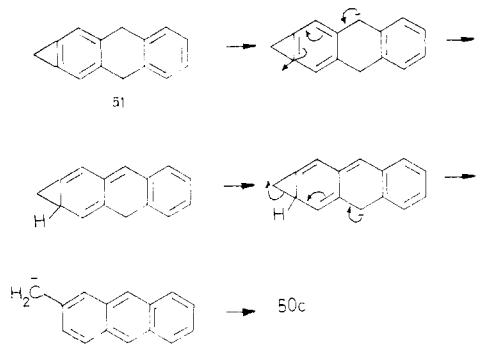


We examined the preparation of cyclopropa[*d*]cyclobuta[*b*]naphthalene by the same sequence of reactions using the diene **15a**, which was treated with dimethyl cyclobutene-1,2-dicarboxylate to give the Diels–Alder adduct **47a** in 60% yield. The diester was saponified to the diacid **47b**, but all attempts to oxidatively decarboxylate **47b** electrolytically failed. Observations of Vogel and coworkers[35] on the reactivity of cyclopropa[*a*]naphthalene, together with our and others[22] difficulties in synthesizing polyaromatic systems asymmetrically annelated with a cyclopropane ring via the Billups reaction, caused us to abandon this approach.

We also prepared a mixture of adducts by the Diels–Alder reaction between **15b** and a mixture of 1,3- and 3,3-dichlorocyclopropene.[36] This mixture probably con-

(30) Heine, H.-G. *Chem. Ber.* **1971**, *104*, 2869.
(31) Dehmlow, E. V. *Chem. Ber.* **1967**, *100*, 3260.
(32) Cookson, R. C.; Giliani, S. S. H.; Stevens, I. D. R. *Tetrahedron Lett.* **1962**, 615.
(33) Clar, E. *Spectrochim. Acta* **1950**, *4*, 117. The ^1L_a band is reduced and the ^1L_b band increased in intensity compared to those bands in naphthalene.
(34) Thummel, R. P.; Nutakul, W. *J. Am. Chem. Soc.* **1978**, *100*, 6171.
(35) Tanimoto, S.; Schäfer, R.; Ippen, J.; Vogel, E. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 613.

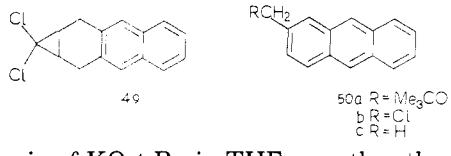
Scheme VI



sisted of **48b,c** since Breslow et al.[36] have observed that 3,3-dichlorocyclopropene does not readily undergo Diels–Alder reactions. All attempts to convert the mixture of adducts into dicyclopropa[*a*,*e*]naphthalene failed, probably for the reasons outlined above.

Similar, but symmetric, adducts were formed from the diene **36** and the mixture of dichlorocyclopropenes, but again, none of the desired diphenyldicyclopropa[*b*,*e*]-naphthalene was formed when the mixture was treated with base.

Cyclopropanthracenes. We have made a number of attempts to synthesize cyclopropanthracenes, all of which were ultimately unsuccessful. The adduct **19** was treated with pyridinium hydrobromide perbromide to give the naphthalene **49** in 60% yield. Reaction of **49** with 20

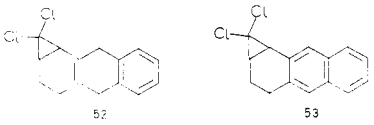


molar equiv of KO-*t*-Bu in THF gave the ether **50a** and not the desired cycloprop[*b*]anthracene. Reaction of **49** with 2 molar equiv of KO-*t*-Bu for a shorter time gave the chloride **50b**. This could be converted into **50a** under the reaction conditions and is presumably the primary product of the reaction. Hoping to prepare 9,10-dihydrocycloprop[*b*]anthracene (**51**), we treated the adduct **19** directly with KO-*t*-Bu, but only 2-methylanthracene (**50c**) was obtained.

The rearrangement of **19** to **50c** may involve the desired **51** which then undergoes deprotonation at a C-9,10 position followed by a prototropic shift, deprotonation, and ring cleavage (Scheme VI).

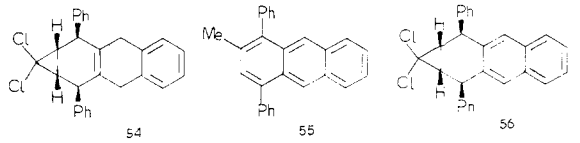
The failure to form cycloprop[*b*]anthracene under these conditions, which were milder than those used to prepare cyclopropa[*b*]naphtho[*e*]cyclobutene, may reflect a greater degree of bond localization in the anthracene, with the annelated ring having the dimethylenecyclopropane structure as a major contributor.

The synthesis of cycloprop[*a*]anthracene was approached in a similar manner. A Diels–Alder reaction between the diene **15a** and benzenediazonium-2-carboxylate gave the adduct **52** which could be converted



into the naphthalene **53** by treatment with pyridinium hydrobromide perbromide. Reaction of **53** with base gave none of the desired compound nor, in this case, any anthracene products.

We also examined the synthesis of phenyl-substituted cyclopropanthracenes, hoping that the phenyl groups might render the three-membered ring less prone to open. The diene **36** was reacted with benzenediazonium-2-carboxylate to give the adduct **54**. Reaction of **54** with



KO-*t*-Bu gave 1,4-diphenyl-2-methylanthracene (**55**). Again, this reaction may proceed through the 9,10-dihydrocycloprop[*b*]anthracene. Some support for this view was found by examining the reaction mixture after partial reaction had occurred at which point, in the ^{1}H NMR spectrum, besides the signals due to **54** and **55**, there was a singlet at δ 3.35 at somewhat lower field than that for 9,10-dihydroanthracene itself (δ 3.90).[37] Attempts to isolate the compound responsible for this absorption were unsuccessful.

The adduct **54** could be converted to the naphthalene **56**, but attempts to convert this into the cyclopropanthracene were also unsuccessful.

The Billups reaction,[15] which is extremely useful for the synthesis of benzocyclopropenes and cyclopropa[*b*]-naphthalenes, does not readily give cyclopropa[*a*]-naphthalenes, cyclopropanthracenes, or higher derivatives. With cyclopropa[*a*]naphthalenes, rearrangement of the precursor may, if the double bond has to be in the 4,5-position, require disruption of a benzene ring, and other reactions are probably preferred. This is not the case for the cycloprop[*b*]anthracenes, and the fact that neither our route from the naphthalene nor that from the dihydronaphthalene precursor was successful suggests that cycloprop[*b*]anthracene is not stable under the reaction conditions employed. Vogel and co-workers[35] have shown that their retro-Diels–Alder method can lead to the preparation of cyclopropa[*a*]naphthalene, and nonbasic syntheses of the cyclopropanthracenes would seem worth exploring. If bond fixation in the cyclopropanthracene is leading to instability, it may transpire that dicycloprop-[*b*,*e*]anthracene, in which both Kekulé structures are identical, may be more stable. We continue to explore routes to these compounds.

Experimental Section

^{1}H NMR spectra were obtained on either a Varian T-60 or HA-100 spectrometer and are reported in δ units with Me_4Si as internal standard. ^{13}C NMR spectra were obtained on a Varian CFT-20 spectrometer in $CDCl_3$ and are reported in parts per million from Me_4Si as the internal standard. Mass spectra were taken on an AEI MS-12 or MS-9 spectrometer. Melting points were taken on a Kofler hot stage and are uncorrected. Silica for TLC was Merck Kieselgel GF_{254} and for preparative TLC was PF_{254}. Woelm alumina (neutral or basic) and silica gel were used for column chromatography. Petroleum ether is the fraction boiling below 40 °C unless stated otherwise. Solvents were purified by standard methods. Unless stated otherwise, reactions were worked up by addition of water followed by extraction with ether. The ethereal layer was dried and the solvent removed under reduced pressure.

Preparation of 7,7-Dichloro-3,4-bis(carboethoxy)bicyclo-[4.1.0]heptane (6). A chilled solution of NaOH (50%, 400 cm^3) was added to a stirred solution of diethyl cyclohex-4-ene-1,2-dicarboxylate[17] (45.2 g, 0.2 mol) and Et_3PhCH_2NCl (20 g, 0.09 mol) in alcohol-free $CHCl_3$ (240 g, 2.0 mol) at room temperature.

(36) Breslow, R.; Ryan, G.; Groves, J. T. *J. Am. Chem. Soc.* **1970**, *92*, 988.

(37) Smith, W. B.; Shoulders, B. A. *J. Phys. Chem.* **1965**, *69*, 2022.

The mixture was vigorously stirred for 6 h at 40–50 °C and worked up, the ethereal layer being washed with HCl (5%, 2 × 200 cm^3) to give **6**: 51.9 g (84%); bp 120–130 °C (0.08 mm); mass spectrum, *m/e* (relative intensity) 312, 310, 308 (M^+, 1:6:9, 80), 267, 265, 263 ($M^+ - OC_2H_5$, 1:6:9, 100), 257, 255, 253 ($M^+ - C_2H_5CO_2$, 1:6:9, 16); ^1H NMR 4.14 (q, 4 H), 2.9–1.6 (m, 8 H), 1.22 (t, 6 H).

Reduction of 6. $LiAlH_4$ (12 g, 0.3 mol) was added to a stirred solution of **6** (62.2 g, 0.2 mol) in dry ether at ice-bath temperature under N_2. Stirring was continued at room temperature for 8 h, and excess $LiAlH_4$ was destroyed by addition of water (25 cm^3) and then concentrated HCl (30 cm^3). Workup gave an oil which was crystallized from CH_2Cl_2/petroleum ether as colorless crystals of **7**: 29.69 g (66%); mp 75–79 °C; mass spectrum, *m/e* (relative intensity) 228, 226, 224 (M^+, 1:6:9, 5), 211, 209, 207 ($M^+ - HO$, 1:6:9, 66), 191, 189 ($M^+ - Cl$, 1:3, 100); ^1H NMR 4.20 (s, 2 H), 3.60 (d, 4 H), 2.4–1.5 (m, 8 H); ^{13}C NMR 67.25, 63.4, 36.3, 25.2, 20.75. Anal. Calcd for $C_9H_{14}Cl_2O_2$: C, 48.0; H, 6.2; Cl, 31.5. Found: C, 48.32; H, 6.02; Cl, 31.62.

Preparation of the Dimesylate 8a. Methanesulfonyl chloride (30.0 g, 0.26 mol) was added over a period of 20 min to a stirred solution of the diol **7** (22.4 g, 0.1 mol) and Et_3N (30.0 g, 0.29 mol) in dry CH_2Cl_2 (500 cm^3) cooled in an ice bath under N_2. Stirring was continued for a further 1 h at 0 °C, the mixture was washed with chilled water (100 cm^3), cold HCl (10%, 50 cm^3), saturated $NaHCO_3$ (50 cm^3), and water (2 × 100 cm^3), and the organic layer was dried ($MgSO_4$). The solvent was removed under reduced pressure and the resulting solid crystallized from CH_2Cl_2/petroleum ether to give **8a**: 31.7 g (85%); mp 99–100 °C; mass spectrum, *m/e* (relative intensity) 384, 382, 380 (M^+, 1:6:9, 2), 305, 303, 301 ($M^+ - SO_2Me$, 1:6:9, 60), 268, 266 ($M^+ - SO_2MeCl$, 1:3, 100); ^1H NMR 4.20 (d, 4 H), 3.07 (s, 6 H), 2.40–1.80 (m, 8 H). Anal. Calcd for $C_{11}H_{18}S_2Cl_2O_6$: C, 34.64; H, 4.72; Cl, 18.63. Found: C, 34.56; H, 4.75; Cl, 18.59.

Preparation of the Dichloride 8b. The diol **7** (11.2 g, 0.05 mol) was added to a stirred mixture of freshly distilled thionyl chloride (24.0 g, 0.2 mol) and pyridine (16.0 g, 0.2 mol) cooled in an ice bath. After 30 min the bath was removed and the reaction mixture heated under reflux for 20 min. Excess thionyl chloride was removed under reduced pressure, CH_2Cl_2 (100 cm^3) was added, and the organic layer was washed with $NaHCO_3$ solution (5%, 2 × 50 cm^3) and water (2 × 50 cm^3) and dried. Evaporation of the solvent gave a residue which was crystallized from pentane (−20 °C) as **8b**: 2.27 g (18%); mp 74–75 °C; mass spectrum, *m/e* (relative intensity) 268, 266, 264, 262, 260 (M^+, 1:12:55:114:87, 13) 231, 229, 227, 225 ($M^+ - Cl$, 1:9:28:28, 36), 194, 192, 190 ($M^+ - Cl_2$, 1:6:9, 55), 166, 164, 162 ($M^+ - C_2H_4Cl_2$, 1:6:9, 100); ^1H NMR 3.46 (d, 4 H), 2.40–1.70 (m, 8 H). Anal. Calcd for $C_9H_{12}Cl_4$: C, 41.22; H, 4.58; Cl, 54.19. Found: C, 41.20; H, 4.61; Cl, 54.32.

Preparation of the Diene 9. (a) From the Dimesylate 8a. KO-*t*-Bu (16.8 g, 0.15 mol) was added to a stirred solution of **8a** (15.24 g, 0.04 mol) in dry THF (500 cm^3) under N_2. The solution was stirred for 1.5 h and worked up. Distillation in vacuo gave the colorless oil **9**: 4.91 g (65%); bp 50–60 °C (0.02 mm); mass spectrum, *m/e* (relative intensity) 188.0162 ($C_9H_{10}{}^{35}Cl_2$ requires 188.0172), 192, 190, 188 (M^+, 1:6:9, 50), 155, 153 ($M^+ - Cl$, 1:3, 100); ^1H NMR 5.20 (s, 2 H), 4.80 (s, 2 H), 3.06–2.00 (m, 4 H), 1.83 (m, 2 H); ^{13}C NMR 142.35, 109.9, 96.4, 28.8, 27.9; λ_{max} (cyclohexane) 243 nm (ϵ 7000).

(b) From the Tetrachloride 8b. KO-*t*-Bu (5.6 g, 0.05 mol) was added to a stirred solution of **8b** (5.24 g, 0.02 mol) in THF (70 cm^3) under N_2, and the mixture was stirred for 1.5 h. Workup gave **9** (1.70 g, 45%) identical in all observed respects with that prepared from the dimesylate.

Preparation of 11. A solution of diethyl 3-cyclohexene-1,2-dicarboxylate (**10b**) in dry ether (100 cm^3) was added to a stirred suspension of $LiAlH_4$ (20.0 g, 0.52 mol) in dry ether (600 cm^3) cooled in an ice bath under N_2. The ice bath was removed and the mixture stirred for 12 h. Excess $LiAlH_4$ was destroyed with water (60 cm^3) and HCl (25%, 30 cm^3), the solution filtered, and the filtrate worked up. Evaporation of the solvent under reduced pressure gave the diol **11** as a colorless oil: 31.3 (85%); bp 100–110 °C (0.08 mm); ^1H NMR 5.60 (2 H, m), 4.15 (2 H, s), 3.60 (4 H, m), 2.50 (1 H, m), 2.00 (3 H, m), 1.53 (2 H, t); ^{13}C NMR 128.65, 126.7, 64.3, 62.3, 39.3, 37.7, 24.2, 21.95; IR (film) 3300, 3020, 2900, 1430, 1030 cm^{-1}.

Preparation of the Dimesylate 12. Methanesulfonyl chloride (30 g, 0.26 mol) was added over 30 min to a stirred solution of **11** (14.2 g, 0.1 mol) and Et_3N (30 g, 0.29 mol) in dry CH_2Cl_2 (500 cm^3) cooled in an ice bath under N_2. The mixture was stirred for a further 1 h and then washed with ice water (2 × 500 cm^3), cold HCl (10%, 2 × 100 cm^3), and $NaHCO_3$ solution (10%, 100 cm^3) and dried ($MgSO_4$). The solvent was removed under reduced pressure to give the dimesylate **12** (25.3 g, 85%) which was used for the next step without further purification: ^1H NMR 5.56 (2 H, m), 4.03 (4 H, m), 2.86 (6 H, s), 2.56 (1 H, m), 1.93 (3 H, m), 1.56 (2 H, m); ^{13}C NMR 130.28, 124.16, 70.24, 69.01, 37.15, 37.08, 35.87, 35.01, 23.62, 21.35.

Reaction of 12 with Dichlorocarbene. A chilled solution of NaOH (50%, 500 cm^3) was added to a stirred solution of **12** (15 g, 50 mmol) and $Et_3C_6H_5CH_2NCl$ (0.5 g, 2 mmol) in alcohol-free $CHCl_3$ (20 g, 0.17 mol). The reaction was stirred for 10 h, water (500 cm^3) added, and the mixture extracted with $CHCl_3$ (2 × 100 cm^3). The organic layer was washed with water (2 × 200 cm^3), HCl (10%, 2 × 50 cm^3), and water (2 × 200 cm^3) and dried ($MgSO_4$). Removal of the solvent under reduced pressure and crystallization of the residue from CH_2Cl_2/petroleum ether gave **13a**: 9.1 g (47%); mp 105–108 °C; ^1H NMR 4.40 (2 H, d), 4.18 (2 H, m), 3.06 (6 H, d), 2.24 (2 H, m), 1.82 (4 H, m), 1.56 (2 H, m); ^{13}C NMR 67.5, 65.8, 62.5, 35.0, 34.8, 30.9, 28.75, 24.2, 23.05, 19.6, 12.15. Anal. Calcd for $C_{11}H_{18}Cl_2S_2O_6$: C, 34.64; H, 4.72; Cl, 18.63; S, 16.79. Found: C, 34.75; H, 4.88; Cl, 18.46; S, 16.38.

Reaction of 12 with Dibromocarbene. A chilled solution of NaOH (50%, 300 cm^3) was added to a stirred solution of **12** (11.43 g, 38 mmol) and $Et_3C_6H_5CH_2NCl$ (0.3 g, 1.2 mmol) in bromoform (50 g, 198 mmol). Stirring was continued for a further 5 h, and the mixture was worked up as for the proceeding experiment except that the initial residue after removal of the solvent was extracted into $CHCl_3$–Et_2O (1:1, 200 cm^3) and filtered. **13b**: 10.7 g (59%); mp 119–120 °C; ^1H NMR 4.44 (2 H, d), 4.20 (2 H, m), 3.06 (6 H, d), 2.42–1.40 (8 H, m). Anal. Calcd for $C_{11}H_{18}Br_2S_2O_6$: C, 28.08; H, 3.82; Br, 34.04; S, 13.61. Found: C, 28.35; H, 3.85; Br, 34.24; S, 13.79.

Preparation of 14a. A solution of **13a** (7.62 g, 20 mmol) and sodium iodide (30.0 g, 200 mmol) in dry acetone (20 cm^3) was heated to reflux for 15 h under N_2. The reaction mixture was filtered and worked up to give a dark brown oil which crystallized from methanol as pale yellow crystals of **14a**: 4.40 g (50%); mp 88–89 °C; mass spectrum, *m/e* (relative intensity) 448, 446, 444 (M^+, 1:6:9, 7), 321, 319, 317 ($M^+ - I$, 1:6:9, 45), 194, 192, 190 ($M^+ - 2I$, 1:6:9, 100); ^1H NMR 3.30 (3 H, m), 2.83 (1 H, t), 2.0–2.3 (2 H, m), 1.60–1.96 (4 H, m), 1.20–1.60 (2 H, m); ^{13}C NMR 46.5, 45.15, 38.2, 34.0, 33.75, 21.45, 17.0, 16.6, 12.05. Anal. Calcd for $C_9H_{12}Cl_2I_2$: C, 24.27; H, 2.70; I, 57.07. Found: C, 24.22; H, 2.67; I, 56.81.

Preparation of 14b. The preparation was carried out as for **14a**, the dibromide **14b** being isolated as pale yellow crystals: 45%; mp 99–100 °C; mass spectrum, *m/e* (relative intensity) 536, 534, 532 (M^+, 1:2:1, 66), 409, 407, 405 ($M^+ - I$, 1:2:1, 100); ^1H NMR 3.28 (3 H, m), 2.86 (1 H, t), 1.20–2.10 (8 H, m); ^{13}C NMR 39.3, 35.75, 35.35, 29.65, 25.4, 24.2, 13.5, 7.35, 2.75. Anal. Calcd for $C_9H_{12}Br_2I_2$: C, 20.22; H, 2.24; Br, 29.96. Found: C, 20.21; H, 2.26; Br, 29.81.

Preparation of 15a. KO-*t*-Bu (1.23 g, 11 mmol) was added to a solution of **14a** (2.25 g, 5 mmol) in dry THF (40 cm^3) cooled in an ice bath under N_2. The ice bath was removed and the reaction stirred for 20 min. Workup gave an oil which was bulb to bulb distilled in vacuo to give **15a**: 0.70 g (80%); mass spectrum, *m/e* (relative intensity) 192, 190, 188 (M^+, 1:6:9, 60), 155, 153 ($M^+ - Cl$, 1:3, 100); ^1H NMR, see Results and Discussion; ^{13}C NMR 146.95, 141.7, 117.75, 112.45, 68.85, 36.4, 33.9, 31.4, 23.3; λ_{max} (hexane) 218 nm (ϵ 14000), 243 (5000). Anal. Calcd for $C_9H_{10}Cl_2$: C, 57.14; H, 5.29. Found: C, 57.20; H, 5.40.

Preparation of 15b. The diene **15b** was prepared in the same way as **15a** except that it was purified by TLC (Al_2O_3, pentane): yield 40%; mass spectrum, *m/e* (relative intensity) 282, 280, 278 (M^+, 1:2:1, 20), 201, 199 ($M^+ - Br$, 1:1, 100); ^1H NMR 5.66 (1 H, s), 5.23 (2 H, s), 4.76 (1 H, s), 2.50–1.75 (6 H, m); ^{13}C NMR 144.4, 140.5, 115.4, 110.35, 39.05, 34.6, 31.5, 29.75, 22.85; λ_{max} (hexane) 223 nm (ϵ 10000), 253 (3500).

Reaction of the Diene 9 with SO_2. The diene **9** (0.94 g, 5 mmol) and liquid SO_2 (2 cm^3) were heated at 40 °C in a sealed,

evacuated tube for 5 h. The excess SO_2 was driven off, and the residue was dissolved in CH_2Cl_2 (5 cm^3) and filtered. Pentane was added dropwise to the filtrate to precipitate the pale yellow crystals of **16**: 1.20 g (95%); mp 195–196 °C; mass spectrum (30 eV), *m/e* (relative intensity) 256, 254, 252 (M^+, 1:6:9, 95), 192, 190, 180 ($M^+ - SO_2$, 1:6:9, 100); ^1H NMR 3.60 (s, 4 H), 2.33 (s, 4 H), 1.93 (m, 2 H). Anal. Calcd for $C_9H_{10}Cl_2SO_2$: C, 42.68; H, 3.95; Cl, 28.06; S, 12.64. Found: C, 42.63; H, 3.93; Cl, 27.83; S, 12.78.

Pyrolysis of 16. The sulfone **16** (0.25 g, 1 mmol) was heated at 200 °C in a Pyrex tube (20 × 40 mm) held horizontally and equipped with a cold finger under vacuum (14 mm) for 5 min. Solid which accumulated on the cold finger was dissolved in CH_2Cl_2 (5 cm^3). The solvent was removed under reduced pressure to give **9** (0.18 g, 95%) identical in all observed respects with that previously reported.

Reaction of 9 with 4-Phenyl-1,3,4-triazole-2,4-dione. A solution of 4-phenyl-1,3,4-triazole-2,4-dione (0.56 g, 3.2 mmol) in dry acetone (15 cm^3) was added over 30 min to a stirred solution of **9** (0.60 g, 3.2 mmol) in dry, ice-cold acetone (10 cm^3) under N_2. The ice bath was then removed and the mixture stirred for 1 h. The solvent was removed under reduced pressure, the residue dissolved in CH_2Cl_2 (20 cm^3), and pentane added dropwise until precipitation occurred. After the mixture had been allowed to stand, the precipitate was removed by filtration as pale yellow crystals of **17**: 1.0 g (86%); mp 200–202 °C dec; ^1H NMR 7.43 (s, 5 H), 3.93 (s, 4 H), 2.33 (m, 4 H), 1.96 (m, 2 H). Anal. Calcd for $C_{17}H_{15}N_3Cl_2O_2$: C, 56.00; H, 4.12; N, 11.53. Found: C, 56.04; H, 4.09; N, 11.89.

Reaction of 9 with Dimethyl Cyclobut-1-ene-1,2-dicarboxylate. The diene **9** (2.05 g, 11 mmol) and dimethyl cyclobut-1-ene-1,2-dicarboxylate (1.65 g, 9.7 mmol) were dissolved in dry benzene (3 cm^3) and the solution was stirred and heated at 60 °C for 24 h. The reaction mixture was chromatographed on a column of silica gel, eluting with $CHCl_3$, to give a solid which was recrystallized from petroleum ether (60–80 °C) as pale yellow crystals of **18**: 2.61 g (75%); mp 131–134 °C; mass spectrum, *m/e* (relative intensity) 358.0739 ($C_{17}H_{20}{}^{35}Cl_2O_4$ requires 358.0724), 362, 360, 358 (M^+, 1:6:9, 10), 331, 329, 327 ($M^+ - OCH_3$, 1:6:9, 95), 303, 301, 299 ($M^+ - CO_2Me$, 1:6:9, 100); ^1H NMR 3.70 (s, 6 H), 2.80–2.20 (m, 8 H), 2.20–1.80 (m, 4 H), 1.70–1.40 (m, 2 H).

Reaction of 9 with Benzyne. The diene **9** (0.95 g, 5 mmol) was added to a stirred solution of benzenediazonium-2-carboxylate (1.03 g, 7 mmol) in dry CH_2Cl_2 (10 cm^3) under N_2. The mixture was heated under reflux for 2.5 h on an oil bath. The solvent was removed under reduced pressure and the dark red residue chromatographed on a column of Al_2O_3 (neutral, grade V; petroleum ether) to give the adduct **19**, purified by recrystallization from methanol as white crystals: 0.795 g (60%); mp 129–130 °C; mass spectrum, *m/e* (relative intensity) 264.0414 ($C_{15}H_{14}{}^{35}Cl_2$ requires 264.0472), 268, 266, 264 (M^+, 1:6:9, 100), 213, 229 ($M^+ - Cl$, 1:3, 35), 194 ($M^+ - 2Cl$, 95); ^1H NMR 7.10 (s, 4 H), 3.20 (s, 4 H), 2.26 (m, 4 H), 1.90 (m, 2 H).

Photoirradiation of 9. A solution of the diene **9** (1.89 g, 10 mmol) in dry pentane (800 cm^3) was flushed with argon for 5 min and then irradiated with an Hanovia 250-W medium-pressure lamp through quartz for 8 h under argon.[16] The mixture was then filtered to remove polymer and the solvent removed under reduced pressure. The residue was distilled in vacuo to give **20**: 0.945 g (50%); bp 40–46 °C (0.01 mm); mass spectrum, *m/e* (relative intensity) 188.0160 (calcd for $C_9H_{10}{}^{35}Cl_2$, 188.0170) 192, 190, 188 (M^+, 1:6:9, 62), 155, 153 ($M^+ - Cl$, 1:3, 100); ^1H NMR 2.6–2.0 (m, 8 H), 1.75 (m, 2 H); ^{13}C NMR 137.4, 66.3, 30.3, 25.1, 19.4.

Preparation of Cyclopropa[4,5]benzocyclobutene (3). A solution of **20** (94.5 mg, 0.5 mmol) in dry Me_2SO (0.5 cm^3) was added dropwise to a stirred solution of KO-*t*-Bu (224 mg, 2 mmol) in dry Me_2SO (2 cm^3) under N_2. The dark brown mixture was stirred for 30 min and then distilled into a trap under low pressure (0.1 mm) at room temperature. CCl_4 (4 cm^3) was added to the distillate, and the organic layer was separated, washed with brine (4 × 20 cm^3) and water (2 × 10 cm^3), and dried (Na_2SO_4). The solvent was removed under reduced pressure (50 mm) to leave the pale yellow oil **3**: 12.4 mg (25%); yield varied from 20 to 40%; mass spectrum, *m/e* (relative intensity) 116.0609 (C_9H_9 requires 116.0625), 116 (M^+, 95), 115 ($M^+ - H$, 100); ^1H NMR, see Table I; ^{13}C NMR 145.5, 110.0, 122.8, 29.0, 19.2; IR (CCl_4) 3060, 2960, 2940, 2920, 2880, 2840, 2820, 1665, 1450, 1350, 1260, 1090, 1060, 850 cm^{-1}; λ_{max} (cyclohexane) 284 nm (ϵ 1100), 287.5 (1100), 294 (sh, 800).

Photoirradiation of 15a. A solution of **15a** (1.89 g, 10 mmol) in dry pentane (800 cm^3) was irradiated as for **9** above for 4 h. Workup as for **20** gave **21**: 0.85 g (40%); mass spectrum, *m/e* (relative intensity) 188.0151 ($C_9H_{10}{}^{35}Cl_2$ requires 188.0159), 192, 190, 188 (M^+, 1:6:9, 48), 155, 153 ($M^+ - Cl$, 1:3, 100); ^1H NMR 2.62 (2 H, m), 2.45 (2 H, m), 1.94 (6 H, m); ^{13}C NMR 145.4, 136.75, 70.0, 33.4, 32.05, 29.3, 23.15, 18.2.

Photoirradiation of 15b. A solution of **15b** was irradiated as for **15a** both at room temperature and at −40 °C. The diene disappeared, but none of the desired cyclobutene was obtained.

Reaction of 21 with Base. The dichloride **21** (94.5 mg, 0.5 mmol) in dry Me_2SO (0.5 cm^3) was added dropwise to a stirred solution of KO-*t*-Bu (2.24 mg, 2 mmol) in dry Me_2SO (2 cm^3) at room temperature under N_2, and the resulting mixture stirred for 30 min. Workup as for **3** gave none of the desired product.

Preparation of 26. Alcohol-free $CHCl_3$ (2.98 g, 25 mmol) in dry pentane (5 cm^3) was added to a stirred mixture of 1,3-cyclohexadiene (1.60 g, 20 mmol) and KO-*t*-Bu (3.36 g, 30 mmol) in dry pentane (20 cm^3) at −20 °C under N_2. The reaction mixture was stirred for 1 h at −20 °C and then for 20 h during which the mixture was allowed to come to room temperature. The precipitate was removed by filtration and the filtrate evaporated under reduced pressure to give **26**: 1.30 g (75%); mass spectrum, *m/e* (relative intensity) 166, 164, 162 (M^+, 1:6:9, 23), 129, 127 ($M^+ - Cl$, 1:3, 100); ^1H NMR 5.90 (m, 2 H), 1.20 (s, 6 H).

Reaction of 26 with Base. A solution of **26** (81.5 mg, 0.5 mmol) in dry Me_2SO (0.5 cm^3) was added dropwise to a stirred solution of KO-*t*-Bu (224 mg, 2 mmol) in dry Me_2SO (2 cm^3) under N_2. The dark brown reaction mixture was stirred for 30 min and the volatile material removed under low pressure. CCl_4 (4 cm^3) was added to the distillate, and the organic phase was separated, washed with brine (4 × 20 cm^3) and water (2 × 10 cm^3), and dried (Na_2SO_4) to give benzocyclopropene (18 mg, 40%) identical in all observed respects with an authentic sample.

Preparation of 28a. KO-*t*-Bu (22.4 g, 0.2 mol) was added carefully to a vigorously stirred mixture of 7,8-dichlorobicyclo-[4.2.0]octa-2,4-diene (17.5 g, 0.1 mol) and alcohol-free $CHCl_3$ (36.0 g, 0.3 mol) in dry pentane (500 cm^3) at −20 °C under N_2. The reaction mixture was stirred at −20 °C for a further 2 h and was then allowed to warm to room temperature and stirred for a further 1 h. Workup followed by chromatography on silica (pentane) gave the tetrachloride **28a**, recrystallized from pentane as white crystals: 7.5 g (29%); mp 78–79 °C; mass spectrum, *m/e* (relative intensity) 262, 260, 258, 256 (M^+, 1:4.5:9:7); ^1H NMR 6.12 (ddd, 1 H, J = 9, 6, 1 Hz), 5.84 (dd, 1 H, J = 10, 2 Hz), 4.30 (m, 2 H), 3.38 (t, 1 H, J = 10 Hz), 2.86 (m, 1 H), 2.18 (m, 2 H); ^{13}C NMR 126.15, 122.3, 65.1, 60.8, 56.6, 40.5, 37.5, 28.8, 26.7. Anal. Calcd for $C_9H_8Cl_4$: C, 41.86; H, 3.10; Cl, 55.04. Found: C, 41.73; H, 3.11; Cl, 55.01.

Preparation of 28b. This compound was prepared in the same manner as **28a** with $CHBr_3$. Compound **28b** was isolated as white crystals (pentane): yield 22%; mp 83–85 °C; mass spectrum, *m/e* 350, 348, 346, 344 (M^+); ^1H NMR 6.18 (ddd, 1 H), 5.85 (dd, 1 H), 4.35 (m, 2 H), 3.38 (t, 1 H), 2.88 (m, 1 H), 2.28 (m, 2 H).

Preparation of 27. KO-*t*-Bu (0.9 g, 8 mmol) was added to a vigorously stirred mixture of bicyclo[4.2.0]octa-2,4-diene[24] (0.5 g, 4 mmol) and alcohol-free $CHCl_3$ (1.44 g, 12 mmol) in dry pentane (100 cm^3) at −20 °C under N_2. The reaction mixture was stirred for 2 h, allowed to warm to room temperature, and stirred for a further 1 h. After workup the solvent was removed to give an oil which was distilled to give **27**: 0.26 g (28%); bp 42–44 °C (0.01 mm); mass spectrum, *m/e* (relative intensity) 188.0155 ($C_9H_{10}{}^{35}Cl_2$ requires 188.0159), 192, 190, 188 (M^+, 1:6:9, 4), 155, 153 ($M^+ - Cl$, 1:3, 25), 125 ($M^+ - C_2H_4Cl$, 100), 117 ($M^+ - Cl_2$, 62); ^1H NMR 6.0 (m, 2 H), 3.2–1.2 (m, 8 H).

Reaction of 27 with Base. Compound **27** (300 mg, 1.6 mmol) in dry Me_2SO (5 cm^3) was added to a stirred solution of resublimed KO-*t*-Bu (672 mg, 6 mmol) in dry Me_2SO (6 cm^3) under N_2, the reaction flask being cooled in a water bath and the addition made at such a rate that the temperature did not rise above 15 °C. The volatile material was then removed under low pressure, the distillate extracted with CCl_4 (3 × 5 cm^3), and the organic phase washed with water (8 × 10 cm^3) and dried (Na_2SO_4). Removal

of the solvent under reduced pressure (25 °C, 40 mm) gave an oil which on distillation (bath temperature 40 °C, 10^{-4} mm) gave cyclopropa[3,4]benzocyclobutene (**4**) as a colorless, pungent liquid: 7–18 mg (4–10%); ^{1}H NMR of CCl_4 extract indicates 15–20% yield; mass spectrum, *m/e* (relative intensity) 116.0632 (C_9H_8 requires 116.0625), 116 (M^+, 45), 115 ($M^+ - 1$, 100); ^{1}H NMR, see Table I; ^{13}C NMR, see Table II; electronic spectrum, see Table I.

Reaction of 3 with Iodine. A solution of iodine (25.4 mg, 0.1 mmol) in CCl_4 (5 cm^3) was added dropwise to a stirred solution of **3** (10 mg, 0.08 mmol) in CCl_4 (1 cm^3) at 0 °C. The solution was stirred for 10 min, the solvent removed under reduced pressure, and the resultant solid chromatographed (Al_2O_3, CH_2Cl_2) to give pale yellow crystals of the diiodide **29a**: 28.0 mg (95%); mp 138–139 °C; mass spectrum, *m/e* (relative intensity) 369.8698 ($C_9H_8I_2$ requires 369.8719), 370 (M^+, 10), 243 ($M^+ - I$, 100), 116 ($M^+ - I_2$, 46); ^{1}H NMR 7.36 (s, 1 H), 7.17 (s, 1 H), 4.50 (s, 2 H), 3.13 (s, 4 H); λ_{max} (cyclohexane) 231 nm (ϵ 17 000), 260 (5860).

The reaction of 3 with bromine was carried out in essentially the same way as that with iodine to give pale yellow crystals of **29b**: yield 80%; mp 84–87 °C; mass spectrum, *m/e* (relative intensity) 273.8975 ($C_9H_8{}^{79}Br_2$ requires 273.8994), 278, 276, 274 (M^+, 1:2:1, 6), 197, 195 ($M^+ - Br$, 1:1, 100), 116 ($M^+ - Br_2$, 70); λ_{max} (hexane) 217 nm (ϵ 15 000), 240 (sh, 7400), 275 (1500), 283 (1950), 292 (1500).

The reaction of 3 with hydrogen chloride was carried out in essentially the same way as that with iodine to give a colorless oil (**29c**): yield 80%; mass spectrum, *m/e* (relative intensity) 154, 152 (M^+, 1:3, 20), 117 ($M^+ - Cl$, 100); ^{1}H NMR 6.98 (dd, 2 H, J = 7.5 Hz), 6.96 (s, 1 H), 4.42 (s, 2 H), 3.10 (s, 4 H); λ_{max} (hexane) 223 nm (ϵ 14 000), 265 (2210), 270 (2800), 274 (2940), 279 (3168).

Reaction of 3 with Ethanolic Silver Nitrate. A solution of **3** (4 mg, 0.03 mmol) in CCl_4 (2 cm^3) was added to a stirred solution of silver nitrate (1.0 mg, 0.005 mmol) in dry ethanol (2 cm^3) under N_2. The mixture was stirred for 15 min, the solvent removed under reduced pressure, and the residue extracted with ether (10 cm^3) and worked up. Removal of the solvent gave the ester **29d**: 4.3 mg (90%); mass spectrum, *m/e* (relative intensity) 162.1038 ($C_{11}H_{14}O$ requires 162.1045), 162 (M^+, 29), 133 ($M^+ - C_2H_5$, 35), 117 ($M^+ - C_2H_5O$, 100); ^{1}H NMR 6.93 (m, 3 H), 4.36 (s, 2 H), 3.43 (q, 2 H), 3.13 (s, 4 H), 1.10 (t, 3 H); λ_{max} (hexane) 215 nm (ϵ 16 000), 263 (940), 270 (960), 276 (950).

The reaction of 4 with iodine was carried out in essentially the same way as for **3** with iodine to give white crystals of **31a** (containing ca. 10% **32a**), which decomposed on being allowed to stand in the light: yield 95%; mp 79–81 °C; mass spectrum, *m/e* (relative intensity) 370 (M^+, 9), 243 ($M^+ - I$, 100), 116 ($M^+ - I_2$, 50); ^{1}H NMR 7.24, 6.88 (dd, 2 H, J = 7.5 Hz), 4.52 (s, 2 H), 3.12 (s, 4 H); λ_{max} (hexane) 226 nm (ϵ 16 600), 255 (7000), 285 (2630).

The reaction of 4 with bromine was carried out in essentially the same way as for **3** with iodine to give white crystals of **31b**: yield 73%; mp 77–78 °C; mass spectrum, *m/e* (relative intensity) 278, 276, 274 (M^+, 1:2:1, 15), 197, 195 ($M^+ - Br$, 100), 116 ($M^+ - Br_2$, 70); ^{1}H NMR 7.24, 6.90 (dd, 2 H, J = 7.5 Hz), 4.52 (s, 2 H), 3.12 (s, 4 H); λ_{max} (cyclohexane) 236 nm (ϵ 6300), 275 (830), 283 (690).

The reaction of 4 with hydrogen chloride was carried out in essentially the same way as for **3** with iodine to give **29c** (71%) identical in all observed respects with the previously prepared sample.

The reaction of 4 with ethanolic silver nitrate was carried out in essentially the same way as for **3** with ethanolic silver nitrate to give **29d** (72%), identical in all observed respects with the previously prepared sample.

Reaction of 33 with Dichlorocarbene. Sodium hydroxide (120 cm^3, 50%) was added to a stirred solution of **33** (17.5 g, 50 mmol) and Et_3PhCH_2NCl (200 mg) in $CHCl_3$ (100 cm^3) at 10 °C. The mixture was kept in an ice bath for 2 h, allowed to warm to room temperature, and stirred for 14 h. The mixture was poured into water (400 cm^3) and extracted with $CHCl_3$ (3 × 100 cm^3), the organic extracts were dried ($MgSO_4$), and the solvent was removed under reduced pressure to give a solid, recrystallized from MeOH as **34**: 17.5 g (80%); mp 107–108 °C; mass spectrum, *m/e* (relative intensity) 432 (M^+, 45); ^{1}H NMR 7.35 (m, 5 H), 7.30 (m, 5 H), 4.05–2.75 (m, 2 H), 3.40 (s, 3 H), 3.30 (s, 3 H), 2.25 (d, 2 H); ^{13}C NMR 172.2, 140.0, 139.8, 131.7, 128.3, 127.9, 127.2, 66.1, 52.4, 51.4, 47.0, 38.4, 31.4. Anal. Calcd for $C_{23}H_{22}Cl_2O_4$: C, 63.75; H, 5.12. Found: C, 63.63; H, 5.10.

Reduction of 34. $LiAlH_4$ (1.0 g, 26 mmol) in THF (150 cm^3) was added slowly to a stirred and cooled solution of **34** (10 g, 23 mmol) in THF (50 cm^3). Stirring was continued at room temperature for 14 h, water (1 cm^3), sodium hydroxide (1 cm^3, 15%), and water (3 cm^3) were added, the mixture was filtered, the filtrate was dried ($MgSO_4$), and the solvent was evaporated to give a solid, recrystallized from the MeOH/petroleum ether (bp 60–80 °C) as **35a**: 4.9 g (58%); mp 171–172 °C; ^{1}H NMR 7.30 (s, 10 H), 4.10–3.30 (m, 6 H), 2.80–2.20 (m, 6 H); ^{13}C NMR 147.7, 144.7, 133.0, 132.6, 132.1, 131.7, 131.5, 131.0, 130.9, 67.7, 53.5, 52.8, 49.4, 46.7, 42.8, 39.6, 35.9. Anal. Calcd for $C_{21}H_{22}O_2Cl_2$: C, 66.85; H, 5.88. Found: C, 66.78; H, 5.82.

Preparation of 35b. Methanesulfonyl chloride (3.4 g, 26 mmol) was added dropwise to a cooled, stirred solution of **35a** (4.5 g, 12 mmol) and Et_3N (3.6 g, 36 mmol) in dry CH_2Cl_2 (150 cm^3).[38] The solution was allowed to warm to room temperature (1 h), the precipitate was removed by filtration, and the filtrate was extracted with water (100 cm^3), HCl (2 M, 2 × 100 cm^3), saturated $NaHCO_3$ solution (100 cm^3) and dried ($MgSO_4$). Evaporation of the solvent gave a solid, recrystallized from CH_2Cl_2–pentane as **35b**: 4.35 g (80%); mp 51–53 °C; ^{1}H NMR 7.35 (m, 5 H), 7.30 (m, 5 H), 4.15 (d, 4 H, J = 5 Hz), 2.85 (s, 6 H), 3.80–2.10 (m, 6 H).

Reaction of 35b with Base. KO-*t*-Bu (1 g, 9 mmol) was added to a stirred solution of **35b** (0.50 g, 1.1 mmol) in dry THF (50 cm^3) and the mixture stirred for 1 h. Workup gave, after evaporation of the solvent, **37**: 0.21 g (55%); mass spectrum, *m/e* (relative intensity) 340 (M^+, 30); ^{1}H NMR 7.35 (m, 10 H), 2.25 (m, 2 H), 1.10 (s, 6 H).

Preparation of 35c. A stirred mixture of **35b** (2.33 g, 5.1 mmol) and sodium iodide (7.5 g, 50 mmol) in dry acetone (75 cm^3) was heated under reflux for 8 h. The white precipitate was removed by filtration, the filtrate worked up, and the solvent removed to give a solid, recrystallized from ether as **35c**: 1.8 g (59%); mp 135–136 °C; ^{1}H NMR 7.25–7.15 (m, 10 H), 3.60–2.75 (m, 6 H), 2.50–2.05 (m, 2 H), 1.90–1.45 (m, 2 H); ^{13}C NMR 141.6, 139.1, 129.3, 128.9, 128.1, 127.4, 127.3, 65.3, 47.0, 44.2, 43.0, 41.0, 34.2, 30.0, 18.4, 10.5. Anal. Calcd for $C_{21}H_{20}Cl_2I_2$: C, 42.23; H, 3.35. Found: C, 42.19; H, 3.47.

Preparation of 36. KO-*t*-Bu (0.57 g, 5.1 mmol) was added to a stirred solution of **35c** (1.53 g, 2.56 mmol) in dry THF (15 cm^3) under N_2. The reaction was stirred for 30 min and then worked up. Evaporation of the solvent gave a solid which was recrystallized from EtOH as **36**: 0.765 g (88%); mp 112–114 °C; mass spectrum, *m/e* 340.0786 (calcd for $C_{21}H_{18}{}^{35}Cl_2$ 340.0792); ^{1}H NMR 7.35 (s, 10 H), 5.25 (m, 2 H), 4.50 (m, 2 H), 3.80 (m, 2 H), 2.20 (m, 2 H); ^{13}C NMR 147.8, 142.8, 128.7, 126.9, 112.7, 64.9, 44.8, 34.3; λ_{max} (pentane) 243 nm (ϵ 8350).

Preparation of 39. Methyllithium in ether (25 cm^3, 50 mmol) was added to a stirred suspension of benzyltriphenylphosphonium chloride[39] (19.5 g, 50 mmol) in dry ether (300 cm^3). The resulting orange suspension was stirred at room temperature for 2 h and cooled to −78 °C, and cyclobutane-1,2-dione[30] (1.2 g, 14 mmol) in dry ether (10 cm^3) was added. The reaction mixture was stirred and allowed to warm to room temperature, the precipitate removed by filtration and washed with CH_2Cl_2 (30 cm^3), the combined filtrate evaporated, and the resulting solid chromatographed on Al_2O_3 (eluting with pentane) to give **39**: 1.35 g (42%); mp 114–115 °C; mass spectrum, *m/e* 232.1252 (calcd for $C_{18}H_{16}$, 232.1244); ^{1}H NMR 7.30 (m, 10 H), 6.65 (s, 2 H), 3.15 (s, 4 H); ^{13}C NMR 143.8, 137.5, 128.6, 127.9, 126.6, 117.6, 30.7; λ_{max} (cyclohexane) 328 nm (ϵ 30 000), 344 (41 000), 363 (3050).

Reaction of 39 with 4-Phenyl-1,2,4-triazoline-3,5-dione. A solution of 4-phenyl-1,2,4-triazoline-3,5-dione (46 mg, 0.25 mmol) in dry acetone (2 cm^3) was added to a stirred solution of **39** (58 mg, 0.25 mmol) in dry acetone (2 cm^3) at −10 °C over a period of 5 min. The reaction mixture was allowed to warm to room temperature, the solvent removed under reduced pressure, and the residue recrystallized from CH_2Cl_2–pentane as **41**: 72 mg (69%); mp 182–184 °C; mass spectrum, *m/e* 407.1634 (calcd for

(38) See: Crossland, R. K.; Servis, K. L. *J. Org. Chem.* **1970**, *35*, 3195.
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$C_{26}H_{21}N_3O_2$, 407.1630); ^1H NMR 7.55–7.00 (m, 15 H), 5.50 (m, 2 H), 2.55 (m, 4 H); λ_{max} (ether) 261 nm (ϵ 9600), 270 (11 500), 282 (8600).

Reaction of 39 with Maleic Anhydride. A solution of **39** (100 mg, 0.43 mmol), maleic anhydride (49 mg, 0.5 mmol), and hydroquinone (3 mg) in dry benzene (6 cm^3) was heated to reflux for 14 h. Removal of the solvent under reduced pressure gave a solid recrystallized from ether as **42**: 60 mg (36%); mp 146–148 °C; mass spectrum, m/e 330.1275 (calcd for $C_{22}H_{18}O_3$, 330.1271); ^1H NMR 7.40–7.20 (m, 10 H), 4.20–3.75 (m, 4 H), 2.75–2.45 (m, 4 H); λ_{max} (ether) 252 nm (ϵ 450), 256 (520), 262 (570), 268 (470).

Reaction of 39 with a Mixture of Dichlorocyclopropenes. A solution of **39** (170 mg, 0.7 mmol) and dichlorocyclopropenes[36] (160 mg, 1.5 mmol) in dry benzene (10 cm^3) was heated under reflux under N_2 for 14 h. Removal of the solvent gave a residue which contained neither the desired product nor **39**. Substitution of THF for benzene as solvent gave the same result. Heating the compounds in a sealed tube at 80 °C without solvent gave polymer.

The preparation of 40 was carried out in essentially the same way as for the preparation of **39** except equimolar amounts of ylide and dione were used. Chromatography on Al_2O_3 (eluting with ether) gave **40**: yield 62%; mp 83–84 °C; mass spectrum, m/e 158.0732 (calcd for $C_{11}H_{10}O$, 158.0735); ^1H NMR 7.75–7.20 (m, 5 H), 7.20–7.00 (m, 1 H), 3.25–2.65 (m, 4 H); λ_{max} (ethanol) 303 nm (ϵ 14 200). Anal. Calcd for $C_{11}H_{10}O$: C, 83.52; H, 6.37. Found: C, 83.23; H, 6.30.

Hydrolysis of 18a. Potassium hydroxide (0.45 g, 8 mmol) in aqueous ethanol (80%, 4 cm^3) was added to a solution of the diester **18a** (0.722 g, 2 mmol) in aqueous ethanol (80%, 6 cm^3). The mixture was heated under reflux for 24 h, the solvent removed under reduced pressure, and water added (20 cm^3). The aqueous solution was acidified (HCl, pH 2), and the resulting precipitate was collected by filtration and dried to give **18b** (0.496 g, 75%) as an off-white solid (mp 205–210 °C dec) which was used without further purification.

Oxidative Decarboxylation of 18b. Et_3N (1.02 g, 10 mmol) was added to a stirred solution of **18b** (1.33 g, 4 mmol) in aqueous pyridine (90%, 100 cm^3) in an ice bath. An initial current of 0.6 A at 50 V was applied to platinum electrodes, and electrolysis was continued for 4.5 h, with the temperature of the electrolyte maintained between 15 and 20 °C. Water (10 cm^3) was added, and the reaction was worked up, the ethereal layer being washed with hydrochloric acid (20%, 3 × 100 cm^3). Chromatography on Al_2O_3 (eluting with pentane) gave **43** (contaminated with some **44**): 0.192 g (20%); mp 96–98 °C; mass spectrum, m/e (relative intensity) 244, 242, 240 (M^+, 1:6:9, 100%), 242, 240, 238 ($M^+ - H_2$, 1:6:9, 50), 207, 205 ($M^+ - Cl$, 1:3, 40), 205, 203 ($M^+ - H_2Cl$, 1:3, 60); ^1H NMR 2.52 (s, 4 H), 2.44 (s, 4 H), 2.21 (m, 4 H), 1.90 (m, 2 H).

Oxidation of 43. Pyridinium hydrobromide perbromide (480 mg, 150 mmol) in dry THF (5 cm^3) was added over 30 min to a stirred solution of **43** (162 mg, 0.67 mmol) in dry THF (10 cm^3) under N_2. The solvent was removed under reduced pressure and the residue chromatographed on basic Al_2O_3 (eluting with pentane) to give a solid, recrystallized from CH_3OH as white crystals of **44**: 88.0 mg (55%); mp 88–90 °C; mass spectrum, m/e (relative intensity) 238.0325 ($C_{13}H_{12}{}^{35}Cl_2$ requires 238.0316), 242, 240, 238 (M^+, 1:3:9, 100), 205, 203 ($M^+ - Cl$, 1:3, 60); ^1H NMR 6.86 (s, 2 H), 3.6–2.4 (m, 4 H), 3.08 (s, 4 H), 2.05 (m, 2 H); λ_{max} (hexane) 220 nm (ϵ 5100), 266 (2000), 271 (2760), 275 (3350), 281 (3370), 285 (1550).

Preparation of 45. KO-*t*-Bu (748 mg, 7 mmol) was added to a stirred solution of **44** (76 mg, 0.3 mmol) in dry THF (7 cm^3) under N_2. The mixture was stirred for 19 h and then eluted through a column of basic Al_2O_3 (eluting with pentane). Sublimation (70–90 °C, 0.05 mm) gave white crystals of **45**: 24.9 mg (50%); mp 144–146 °C; mass spectrum, m/e (relative intensity) 166.0780 (calcd for $C_{13}H_{10}$, 166.0782), 166 (M^+, 100), 165 ($M^+ - 1$, 95); ^1H NMR, see Results and Discussion; ^{13}C NMR 144.3, 136.2, 122.1, 121.5, 112.7, 29.3, 19.3; electronic spectrum see Results and Discussion.

The reaction of 45 with iodine was carried out in essentially the same way as for **3** with iodine except $CHCl_3$ was used as solvent to give pale yellow crystals of **46a**: yield 90%; mp 140–142 °C; mass spectrum, m/e (relative intensity) 419.8883 (calcd for $C_{13}H_{10}I_2$, 419.8876), 420 (M^+, 3), 293 ($M^+ - I$, 100), 166 ($M^+ - I_2$, 100); ^1H NMR 8.28 (s, 1 H), 7.86 (s, 1 H), 7.30 (s, 1 H), 7.23 (s, 1 H), 4.66 (s, 2 H), 3.33 (s, 4 H).

The reaction of 45 with methanolic silver nitrate was carried out in essentially the same way as for **3** with ethanolic silver nitrate to give pale yellow crystals of **46b**: yield 97%; mp 47–50 °C; mass spectrum, m/e (relative intensity) 198.1033 (calcd for $C_{14}H_{14}O$, 198.1044), 198 (M^+, 100), 183 ($M^+ - CH_3$, 13), 167 ($M^+ - OCH_3$, 79); ^1H NMR 7.70 (s, 2 H), 7.43 (s, 3 H), 4.76 (s, 2 H), 3.43 (s, 3 H), 3.36 (s, 4 H).

Preparation of 47a. A solution of **15a** (6.15 g, 33 mmol) and dimethyl cyclobutene-1,2-dicarboxylate (4.95 g, 29.1 mmol) in dry benzene (15 cm^3) was stirred and heated to 50 °C for 24 h under N_2. Chromatography on basic Al_2O_3 (eluting with petroleum ether) gave a mixture of **47a** and unchanged ester. These were separated by high-pressure LC on Porasil to give **47a**, recrystallized from petroleum ether (bp 60–80 °C): 7.0 g (60%); mp 66–68 °C; mass spectrum, m/e (relative intensity) 362, 360, 358 (M^+, 1:6:9, 10), 331, 329, 327 ($M^+ - OCH_3$, 40), 303, 301, 299 ($M^+ - CO_2CH_3$, 100); ^1H NMR 3.65 (s, 6 H), 2.80–1.2 (m, 14 H). Anal. Calcd for $C_{17}H_{20}O_4Cl_2$: C, 56.82; H, 5.57; Cl, 19.78. Found: C, 56.44; H, 5.62; Cl, 19.46.

Hydrolysis of 47a. Potassium hydroxide (4.5 g, 80 mmol) in aqueous ethanol (80%, 40 cm^3) was added to a solution of the diester (7.0 g, 20 mmol) in aqueous ethanol (80%, 40 cm^3). The mixture was heated to reflux for 24 h, the solvent removed under reduced pressure, and water (120 cm^3) added to the residue followed by concentrated HCl to pH 4. The precipitate was collected, the filtrate extracted with ethyl acetate (6 × 200 cm^3), the ethyl acetate removed under reduced pressure, and the residue combined with the precipitate obtained previously as the diacid: 3.44 g (55%); mp 215–220 °C dec. The crude acid was used without further purification.

Preparation of 48a–c. A solution of the diene **15b** (142 mg, 0.5 mmol) and a mixture of dichlorocyclopropenes (109 mg, 1.0 mmol) in dry benzene (0.5 cm^3) was stirred for 14 h under N_2. The solvent was removed under reduced pressure and the residue chromatographed on Al_2O_3 to give **48a–c**: 150 mg (78%); mass spectrum, m/e (relative intensity) 392, 390, 388, 386, 384 (M^+, 10:25:23:8:1, 100), 311, 309, 307, 305 ($M^+ - Br$, 9:15:7:1, 3); ^1H NMR 3.0–1.0 (m).

Oxidation of 19. A solution of pyridinium hydrobromide perbromide (0.89 g, 2.8 mmol) in dry THF (10 cm^3) was added dropwise to a solution of **19** (0.36 g, 1.3 mmol) in dry THF (30 cm^3) under N_2. The reaction was stirred for 1 h, and the solution was reduced to half its volume and then chromatographed on silica gel to give **49**, recrystallized from methanol as white crystals: 0.20 g (60%); mp 180–182 °C; mass spectrum, m/e (relative intensity) 262.0305 (calcd for $C_{15}H_{12}{}^{35}Cl_2$, 262.0316), 266, 264, 262 (M^+, 1:6:9, 100), 229, 227 ($M^+ - Cl$, 91); ^1H NMR 7.97 (m, 2 H), 7.24–6.60 (m, 4 H), 2.50 (m, 6 H); λ_{max} (hexane) 227 nm (63 300), 259 (2585), 268 (3450), 278 (3790), 288 (2815).

Reaction of 49 with Base. A solution of **49** (26.3 mg, 0.1 mmol) in dry THF (0.5 cm^3) was added to a stirred solution of KO-*t*-Bu (25 mg, 0.2 mmol) in dry THF (1.0 cm^3) under N_2. After 2 h the stirring was stopped and the mixture chromatographed on Al_2O_3 [petroleum ether–CH_2Cl_2, 19:1] to give pale yellow crystals of **50b**: 9.0 mg (40%); mp 192–195 °C; mass spectrum, m/e (relative intensity) 228, 226 (M^+, 1:3, 66), 191 ($M^+ - Cl$, 100); ^1H NMR 8.40 (s, 2 H), 8.03 (m, 4 H), 7.47 (m, 3 H), 4.83 (s, 3 H); λ_{max} (hexane) 256 nm (ϵ 100 000), 325 (900), 339 (1400), 353 (1900), 363 (1600). Reaction with a 12 molar excess of KO-*t*-Bu gave, after chromatography on Florisil, the ether **50a** (40%) as a yellow solid: mp 142–145 °C; mass spectrum, m/e (relative intensity) 264.1511 (calcd for $C_{19}H_{20}O$, 264.1514), 264 (M^+, 20), 203 ($M^+ - C_3H_9O$, 100); ^1H NMR 8.33 (s, 2 H), 7.93 (m, 4 H), 7.40 (m, 3 H), 4.60 (s, 2 H), 1.37 (s, 9 H); λ_{max} (cyclohexane) 308 nm (ϵ 90 000), 323 (1250), 338 (2000), 356 (2430), 376 (2000).

Reaction of 19 with Base. The adduct **19** (132 mg, 0.5 mmol) in degassed Me_2SO (0.5 cm^3) was added to a stirred solution of KO-*t*-Bu (150 mg, 1.3 mmol) in degassed Me_2SO (2 cm^3) under N_2. The reaction was stirred for 15 min and the mixture chromatographed at −10 °C on Al_2O_3 (eluting with petroleum ether) to give 2-methylanthracene: 38.4 mg (40%); mp 205–206 °C (lit.[40]

(40) Martin, E. L. *J. Am. Chem. Soc.* **1936**, *58*, 1438.

mp 209–209.5 °C); mass spectrum, *m/e* (relative intensity) 192.0932 (calcd for $C_{15}H_{12}$, 192.0939), (M^+, 100); ^1H NMR 8.33 (d, 2 H), 7.87 (m, 4 H), 7.38 (m, 3 H), 2.53 (s, 3 H); λ_{max} (cyclohexane) 323 nm (ϵ 110 000), 325 (1075), 342 (1790), 360 (2500), 380 (2100).

Reaction of 15a with Benzyne. The diene **15a** (0.700 g, 3.7 mmol) was added to a stirred solution of benzenediazonium-2-carboxylate (1.03 g, 7 mmol) in dry CH_2Cl_2 (10 cm^3) under N_2. The mixture was then heated to reflux for 1 h, the solvent removed under reduced pressure, and the residue chromatographed on Al_2O_3 (eluting with petroleum ether) to give a white solid, recrystallized from methanol as **52**: 0.800 g (80%); mp 93–95 °C; mass spectrum, *m/e* (relative intensity) 264.0430 (calcd for $C_{15}H_{14}{}^{35}Cl_2$, 264.0472), 268, 266, 264 (M^+, 1:6:9, 100), 231, 229 (M^+ – Cl, 1:3, 60); ^1H NMR 7.00 (s, 4 H), 3.33 (m, 4 H), 1.96 (s, 6 H).

Oxidation of 52. A solution of pyridinium hydrobromide perbromide (1.78 g, 5.6 mmol) in dry THF (15 cm^3) was added dropwise to a solution of **52** (0.720 g, 2.6 mmol) in dry THF (30 cm^3) under N_2. The reaction was stirred for a further 2 h, the solution reduced to half its volume by evaporation under reduced pressure, and the remaining solution chromatographed on Al_2O_3 (eluting with petroleum ether) to give a white solid, recrystallized from methanol as **53**: 0.30 g (45%); mp 110–112 °C; mass spectrum, *m/e* (relative intensity) 266, 264, 262 (M^+, 1:6:9, 35), 229, 227 (M^+ – Cl, 1:3, 100); ^1H NMR 7.78 (m, 2 H), 7.44 (m, 4 H), 3.00–1.80 (m, 6 H); λ_{max} (hexane) 227 nm (ϵ 70 000), 265 (3900), 275 (4780), 284 (4780), 294 (2980). Anal. Calcd for $C_{15}H_{12}Cl_2$: C, 68.44; H, 4.56; Cl, 26.99. Found: C, 68.10; H, 4.63; Cl, 26.03.

Reaction of 53 with Base. A solution of **53** (83 mg, 3.1 mmol) in dry THF (1 cm^3) was added to a stirred solution of KO-*t*-Bu (336 mg, 3 mmol) in dry THF (4 cm^3) under N_2. Stirring was continued for 3 h, and the mixture was chromatographed on Al_2O_3 (eluting with petroleum ether–CH_2Cl_2, 9:1) to give a yellow oil which was not the desired product.

Reaction of 36 with Benzyne. The diene **36** (0.510 g, 1.8 mmol) and benzenediazonium-2-carboxylate (0.450 g, 3 mmol) in dry CH_2Cl_2 (30 cm^3) were heated to reflux for 2 h. Evaporation of the solvent gave a solid residue which was recrystallized from ethanol as **54**: 0.600 g (80%); mp 178–180 °C; mass spectrum, *m/e* (relative intensity) 420, 418, 416 (M^+, 1:6:9, 100); ^1H NMR 7.40 (m, 14 H), 3.65 (s, 2 H), 3.20 (s, 4 H), 2.10 (s, 2 H).

Reaction of 54 with Base. KO-*t*-Bu (0.800 g, 7 mmol) was added to a solution of **55** (0.140 g, 0.34 mmol) in dry THF and the mixture stirred under N_2 for 90 min. Further KO-*t*-Bu (0.800 g, 7 mmol) was then added and stirring continued for a further 1 h. The mixture was filtered through Al_2O_3 (eluting with ether), the extracts were washed with water (2 × 50 cm^3) and dried (Na_2SO_4), and the solvent was removed by evaporation to give **55**: 20 mg (19%); mass spectrum, *m/e* (relative intensity) 344 (M^+, 100); ^1H NMR 8.05–7.10 (m, 17 H), 2.30 (s, 3 H).

Oxidation of 54. Bromine (0.800 g, 10 mmol) was added to a solution of **55** (1.0 g, 2.4 mmol) in CCl_4 (15 cm^3) at 0 °C, and the mixture was then warmed to 60 °C for 1.5 h. The solvent was removed under reduced pressure to give **56** (0.600 g, 60%): mass spectrum, *m/e* (relative intensity) 418, 416, 414 (M^+, 1:6:9, 100); ^1H NMR 7.65–6.85 (m, 16 H), 4.10 (m, 2 H), 2.15 (m, 2 H).

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Registry No. **3**, 57867-58-0; **4**, 65886-90-0; **5**, 4841-85-4; **6**, 57867-52-4; **7**, 57867-53-5; **8a**, 57867-54-6; **8b**, 57867-55-7; **9**, 57867-56-8; **10b**, 74663-82-4; **11**, 74725-24-9; **12**, 74725-25-0; **13a**, 74725-26-1; **13b**, 74725-27-2; **14a**, 74725-28-3; **14b**, 74725-29-4; **15a**, 65886-85-3; **15b**, 65886-87-5; **16**, 74725-30-7; **17**, 74725-31-8; **18a**, 61603-44-9; **18b**, 61603-45-0; **19**, 61603-52-9; **20**, 57867-57-9; **21**, 65886-86-4; **26**, 5296-51-5; **27**, 65886-89-7; **28a**, 74778-31-7; **28b**, 74725-32-9; **29a**, 57867-59-1; **29b**, 74725-33-0; **29c**, 65886-91-1; **29d**, 74725-34-1; **31a**, 74725-35-2; **31b**, 74725-36-3; **33**, 74725-37-4; **34**, 74725-38-5; **35a**, 74725-39-6; **35b**, 74725-40-9; **35c**, 74725-41-0; **36**, 74725-42-1; **37**, 74725-43-2; **38**, 33689-28-0; **39a**, 74725-44-3; **40**, 74725-45-4; **41**, 74725-46-5; **42**, 74725-47-6; **43**, 61603-46-1; **44**, 61603-47-2; **45**, 61603-48-3; **46a**, 61603-49-4; **46b**, 74725-48-7; **47a**, 74725-49-8; **47b**, 74725-50-1; **48a**, 74725-51-2; **48b**, 74725-52-3; **48c**, 74725-53-4; **49**, 61603-51-8; **50a**, 61603-50-7; **50b**, 885-90-5; **50c**, 613-12-7; **52**, 74725-54-5; **53**, 74725-55-6; **54**, 74725-56-7; **55**, 74725-57-8; **56**, 74725-58-9; sulfur dioxide, 7446-09-5; 4-phenyl-1,2,4-triazole-3,5-dione, 4233-33-4; dimethyl cyclobut-1-ene-1,2-dicarboxylate, 1128-10-5; benzenediazonium-2-carboxylate, 1608-42-0; 1,3-cyclohexadiene, 592-57-4; 7,8-dichlorobicyclo[4.2.0]octa-2,4-diene, 40229-61-6; 7,8-dibromobicyclo[4.2.0]-octa-2,4-diene, 27587-70-8; bicyclo[4.2.0]octa-2,4-diene, 3725-28-8; maleic anhydride, 108-31-6.

Electrolysis of Potassium Butyrate in Acetonitrile. A Deuterium NMR Study

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The anodic oxidation of 2,2-dideuteriobutyrate ion in acetonitrile gives rise to radical-derived and cation-derived C_3 products. By ^2H FT NMR spectroscopy, the radical-derived propane and propene are found to be formed without scrambling of the label. Similarly, the products derived from the intermediate isopropyl cation, i.e., the remainder of the propene and *N*-isopropylamides, bear deuterium only at the terminal C-1 and C-3 positions of the C_3 fragment. However, the 1:1:1 label distribution found in the *N*-*n*-propylamides and the formation of cyclopropane strongly suggest that ring closure of the *n*-propyl cation to rapidly scrambling protonated cyclopropane is an important reaction pathway. Atom scrambling at the level of protonated cyclopropane shows a large H/D isotope effect.

Introduction

The fundamental structures and interconversions of cationic C_3H_7 species have received much attention, both from experimental[1-3] and theoretical viewpoints.[4-6] There is general agreement that the *n*-propyl cation (**1**) is the highest metastable species on the ground-state energy

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