group, proceeds through an intermediate and is subject to catalysis, which has been interpreted as proton donation to the leaving imidazole. Again, the absence of a proton on the thiol anion or the sulfur atom in the addition intermediate precludes general base catalysis of the kind suggested here for aminolysis reactions and catalysis of imidazole expulsion is brought about by protonation of the leaving group.

The thiol reaction undergoes a change in rate-determining step at high catalyst concentrations. This is interpreted as a change to rate-determining attack of thiol anion, which occurs as a consequence of the relatively high affinity (small k_{-a}, eq 2) of sulfur toward carbonyl carbon; no such change in rate-determining step is seen in aminolysis, presumably because of the rapid rate of expulsion of protonated amine. The rate constant k_a for the attack of mercaptoethanol anion on acetylimidazole is $2.3 \times 10^3 \ M^{-1} \ \text{sec}^{-1}$, whereas the rate constant for the uncatalyzed reaction of hydrazine with acetylimidazole is only 1.5 $M^{-1} \ \text{sec}^{-1}$; the corresponding ratio $k_{\text{RS}^-}/k_{\text{N}_2\text{H}_4}$ is 1.8 for the reactions of these compounds with p-nitrophenyl acetate.[13] This suggests that the rate constant k_a for the attack of hydrazine on acetylimidazole is >1.5 and is consistent with an estimated value of $k_a \geq 100$ $M^{-1} \ \text{sec}^{-1}$, assuming the previously noted values of $K_a = k_a/k_{-a} = 10^{-6} \ M^{-1}$ and $k_{-a} \geq 10^8 \ \text{sec}^{-1}$. In other words, this comparison suggests that the attack

of hydrazine on acetylimidazole to form T$^\pm$ is sufficiently fast that it does not become rate determining, in agreement with the proposed mechanisms.

In summary, the available data for acyl aminolysis reactions are consistent with a sequence of mechanisms that are determined by the nature of the leaving group: (a) for methyl formate, with a relatively poor leaving group, there is a stepwise mechanism of catalysis but the free intermediate has a sufficient lifetime that its breakdown may become rate determining at low pH values;[29,34] (b) for somewhat better leaving groups (e.g., free acetylimidazole) there is a stepwise mechanism of catalysis and an intermediate, but the lifetime of the intermediate is so short that the rates of proton transfer steps are always kinetically significant for the catalyzed reaction pathway. Breakdown of the immediate product of the proton transfer step, T$^-$, can occur either before or after diffusion away of BH$^-$, depending on its lifetime; (c) for still better leaving groups (e.g., acetylimidazolium ion) the "intermediate" is too unstable to exist and the reaction must proceed through a concerted rather than a stepwise mechanism. It may be significant that many of the cases in which addition intermediates have been demonstrated, kinetically or otherwise, involve acyl-activated compounds with relatively poor leaving groups;[2] in other cases the reason that such intermediates have not been detected may be simply that they do not exist.

Synthesis and Thermal Rearrangements of Spiro[2.3]hexadiene and Spiro[2.3]hex-4-ene Derivatives

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Contribution from the Department of Chemistry, Cornell University, Ithaca, New York 14850. Received June 14, 1972

Abstract: The reaction of n-butyllithium and hexachlorocyclobutene in the presence of alkenes produced 4,5,6,6-tetrachlorospiro[2.3]hex-4-ene derivatives; with 2-butyne in place of the alkenes, the corresponding spiro[2.3]-hexadiene was obtained in 40% yield. With n-butyllithium and 3-H-pentachlorocyclobutene, reaction occurs predominately by α dechlorination and, in the presence of alkenes, leads to 4,5,6-trichlorospiro[2.3]hex-4-enes. The latter compounds were also obtained in a more efficient way, by controlled potential electroreduction of the 4,5,6,6-tetrachlorospiro[2.3]hex-4-enes and the 4,5,6,6-tetrachlorospiro[2.3]hexadiene. The formation of spirocycles in these reactions is in contrast to earlier reports where tetrachlorocyclobutadiene was postulated as intermediate in related reactions. The spirocycles are generally stable toward isomerization at ambient temperature but rearranged at elevated temperatures (265–450° in a flow system, 60° and above in solution). The spiro[2.3]-hexadienes produce labile products which are tentatively identified as allylidenecyclopropenes, while the spiro[2.3]-hex-4-enes undergo ring opening to allylidenecyclopropanes, which rearrange further to derivatives of 3-methylene-cyclopentene. In certain cases, the latter products spontaneously lose hydrogen chloride to afford a series of fulvenes.

S pirocyclic molecules consist of two perpendicular rings joined by a common carbon atom of tetrahedral geometry. This special geometry has provoked detailed theoretical studies of unique π-electron delocalization (spiroconjugation,[1] spiroaromaticity[2]) and

provides an array of molecular rearrangements, especially in highly strained or highly unsaturated spirocycles. In this paper we report the synthesis of the first unsaturated representatives of the spiro[2.3]hexane ring system (e.g., 1–3) and the series of molecular rearrangements which occur at elevated temperatures.[3]

(1) (a) H. E. Simmons and T. Fukunaga, *J. Amer. Chem. Soc.*, **89**, 5208 (1967); (b) R. Boschi, A. Dreiding, and E. Heilbronner, *ibid.*, **92**, 123 (1970).

(2) (a) R. Hoffmann, A. Imamura, and G. D. Zeiss, *ibid.*, **89**, 5219 (1967); (b) M. J. Goldstein and R. Hoffmann, *ibid.*, **93**, 6193 (1971); (c) A. Tajiri and T. Nakajima, *Tetrahedron*, **26**, 6089 (1971).

(3) For a preliminary account of part of this work, see: (a) M. F. Semmelhack and R. J. DeFranco, *Tetrahedron Lett.*, 1061 (1971); (b) M. F. Semmelhack and R. J. DeFranco, *J. Amer. Chem. Soc.*, **94**, 2116 (1972); (c) M. F. Semmelhack, R. J. DeFranco, and J. Stock, *Tetrahedron Lett.*, 1371 (1972).

In a forthcoming paper, experimental scrutiny of the possibility of spiroaromaticity in an anion derived from **1** is discussed.
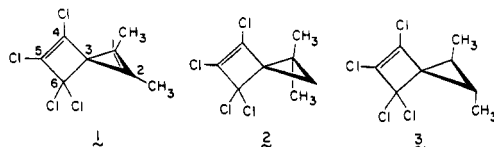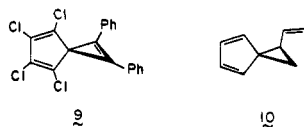

Highly strained spiropolyenes have been the subject of many synthetic exercises. The pinnacle of this effort, spiropentadiene (**4**), has yet to be prepared even as a substituted derivative. A calculation places the strain energy for **4** at 145 kcal/mol,[4] making isolation a dubious possibility even though there is no obvious symmetry-allowed pathway for relief of strain. Two examples (**5** and **6**) of the spiropentene system have been synthesized,[5] in each case by carbene-like addition to a carbon–carbon π bond, and are estimated to bear 90 kcal/mol of bond angle strain.[5a]
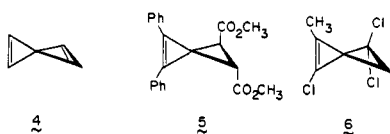
Before this work, no examples of the spiro[2.3]hexadiene or spiro[2.3]hex-4-ene ring systems were known, although an interesting relative, **7**, was prepared by Dolbier and coworkers.[6] Assuming additivity of strain effects, the minimum strain energy of spiro[2.3]-hexadiene (**8**) is about 82 kcal/mol (56 kcal/mol for cyclopropene[4] and 26 kcal/mol for cyclobutene[4]). However, constraint of the rings in the spiro arrangement
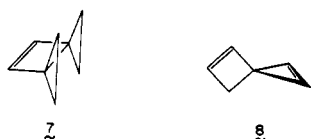
would undoubtedly contribute about 5 kcal/mol of additional strain,[7] for a total of approximately 87 kcal/mol. Examples of the spiro[2.4]hepta-4,6-diene (*e.g.*, **10**) and spiro[2.4]heptatriene (*e.g.*, **9**) systems are accessible *via* catalyzed thermal[8] or photochemical[9] decomposition of diazacyclopentadienes in the presence of alkenes or alkynes.

Thermal rearrangements of spirocycles lead to bond migration from the spiro atom to a radial atom, usually affording a product with less bond angle distortion. The well-studied isomerization of spiropentane to methylenecyclobutane typifies this pathway (eq 1).[10] Spiropentene **5** rearranges upon heating (or upon treatment with acid) to methylenecyclopropene **11**; this process may proceed *via* initial rupture of a radial bond followed by hydrogen atom transfer (eq 2a) or by heterolytic cleavage of the same bond followed by proton transfer (eq 2b).

$$(1)$$
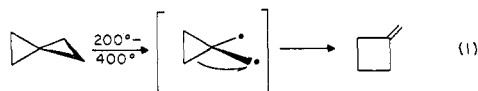
erolytic cleavage of the same bond followed by proton transfer (eq 2b). Pathway 2b is uniquely applicable

$$(2)$$
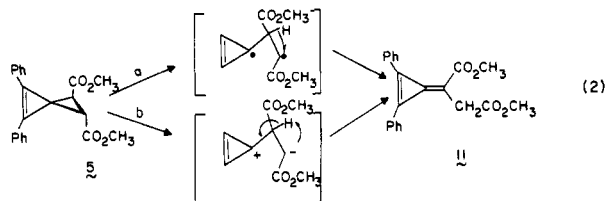
to spirocyclopropene rings, due to the special stabilization accruing to a cyclopropenium ion. For spirocycles in which one ring is a cyclopentadiene ring, an initial concerted suprafacial 1,5-sigmatropic alkyl migration generally accounts for the observed products[11] (eq 3a), although in spiro[2.4]hepta-4,6-diene a diradical pathway is also observed (eq 3b).[11a]

$$(3)$$
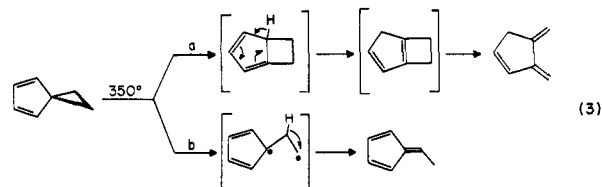
Only a few simple spirocyclobutene compounds are known, and no thermal isomerization has been reported, although such spiro[3.*n*]alk-1-enes (*e.g.*, **12**) have a unique symmetry-allowed concerted pathway (eq 4) to partial relief of strain *via* electrocyclic opening of the cyclobutene ring.[12] For the spirocyclobutenes **1**, **2**, and **3**, this process leads to an allylidenecyclopropene

$$(4)$$

(from **1**) and an allylidenecyclopropane (from **2** and **3**), both of current interest.[13,14]

(4) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1970, p 461.

(5) (a) W. M. Jones, M. E. Stowe, E. E. Wells, Jr., and E. W. Lester, *J. Amer. Chem. Soc.*, **90**, 1849 (1968); (b) J. P. Zahra and B. Waegell, *Tetrahedron Lett.*, 2537 (1970).

(6) W. R. Dolbier, Jr., D. Lomas, and O. Tarrant, *J. Amer. Chem. Soc.*, **90**, 3594 (1968).

(7) The observed strain energy of spiropentane is 61.4 kcal/mol compared to 55 kcal/mol for two isolated cyclopropane rings.[4]
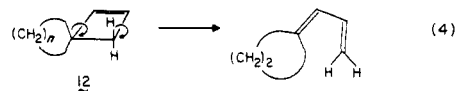
(8) (a) E. T. McBee, J. A. Bosoms, and C. J. Morton, *J. Org. Chem.*, **31**, 768 (1966); (b) E. T. McBee, G. W. Calundann, and T. Hodgins, *ibid.*, **31**, 4260 (1966); (c) D. Schönleber, *Chem. Ber.*, **102**, 1789 (1969).

(9) (a) H. Dürr, R. Sergio, and W. Gombler, *Angew. Chem., Int. Ed. Engl.*, **11**, 224 (1972); (b) H. Dürr and B. Ruge, *ibid.*, **11**, 225 (1972); (c) M. Jones, Jr., R. N. Hochman, and J. D. Walton, *Tetrahedron Lett.*, 2617 (1970).

(10) For leading references, see J. J. Gajewski, *J. Amer. Chem. Soc.*, **92**, 3688 (1970).

(11) (a) J. M. E. Krekels, J. W. de Haan, and H. Kloosterzeil, *Tetrahedron Lett.*, 2751 (1970); (b) L. M. Dane, J. W. de Haan, and H. Kloosterzeil, *ibid.*, 2755 (1970).

(12) R. B. Woodward and R. Hoffmann, "Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1969, p 43.

(13) No allylidenecyclopropenes have been reported, but certain simple derivatives of methylenecyclopropene are known; see (a) A. W. Krebs, *Angew. Chem., Int. Ed. Engl.*, **4**, 10 (1965); (b) E. D. Bergmann, *Chem. Rev.*, **68**, 41 (1968); (c) Z. Yoshida and Y. Tawara, *Tetrahedron Lett.*, 3613 (1971).

(14) Allylidenecyclopropanes are of interest because of the question of concertedness in thermal isomerizations; see (a) T. C. Shields, W. E. Billups, and A. R. Lepley, *J. Amer. Chem. Soc.*, **90**, 4749 (1968); (b) W. R. Roth and Th. Schmidt, *Tetrahedron Lett.*, 3639 (1971); (c) A. S. Kende and E. E. Riecke, *J. Amer. Chem. Soc.*, **94**, 1397 (1972).

Synthesis. The preparation of the spiro[2.3]hex-4-enes is based on the familiar addition of an α-halolithium derivative to a carbon–carbon π bond. Addition of *n*-butyllithium to a solution of hexachlorocyclobutene in hexane containing a large excess of alkene leads to a single type of adduct, the spiro[2.3]-hex-4-enes (eq 5). In the same way, 2-butyne reacts with carbenoid **13** to produce **1**, the first example of a spiro[2.3]hexadiene. No direct evidence is available to support the intermediacy of **13**; it is assumed in analogy with the results of other studies of the interaction of alkyllithium reagents with *gem*-dichlorides.[15]
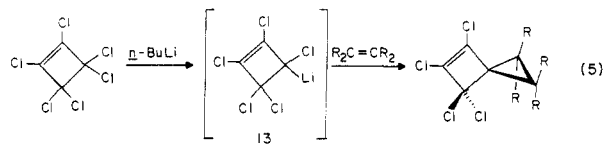
The definitive spectral data for **1** include infrared absorption at 1885 cm^{-1}, characteristic of 1,2-dimethylcyclopropenes,[16] and at 1630 cm^{-1} (1,2-dichlorocyclobutene[17]). Catalytic hydrogenation of **1** over palladium-on-carbon in ethyl alcohol produces a single dihydro product, the spiro[2.3]hex-4-ene **14**, identical to one of the isomeric adducts from addition of **13** to *cis*-2-butene (see below). Addition of 1 equiv of bromine produces the expected product (**16**) from selective addition to the cyclopropene π bond. X-Ray diffraction data from crystals of **1** at −70° are in complete accord with the spirocyclic structure.[18]

The carbenoid **13** reacts with *cis*-2-butene to give a pair of adducts (**14** and **15**) in nearly equal amounts; *trans*-2-butene affords a single product (**3**, racemic mixture) in 40% yield. This stereospecificity is consistent with the general behavior of carbenoids or carbenes in the singlet state.[15] The structural assignments for **3**, **14**, and **15** are based on ^{1}H nmr spectral data. The
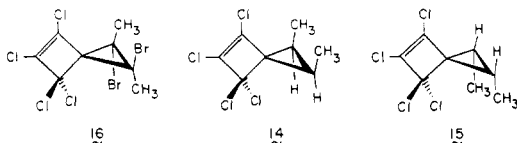

through-space deshielding effect of the *gem*-dichloro group[19] results in the methyl resonance for **15** appearing downfield (δ 1.38, accidental degeneracy of all signals) relative to the methyl resonance from **14** (centered at δ 1.26, multiplet). The spectrum of the adduct **3** shows two broad singlets at δ 1.26 and 1.42 due to the signals from the methyl groups overlapping on the signals from the cyclopropylmethine hydrogens. The chemical shift of one signal (δ 1.26) matches that for the methyl groups in **14**, while the downfield signal (δ 1.42) nearly matches the position of the peak due to the methyl groups in **15**.

The reaction of *n*-butyllithium with 3-*H*-pentachlorocyclobutene in the presence of isobutene exposed two

examples of remarkable selectivity. The reaction gave two products (**2** and **19**) in 1:8 ratio; the combined yield was 45%. The major product, **19**, arises from initial chlorine–lithium exchange to give carbene **17**: only a minor amount of α-dehydrohalogenation (leading to **2**) was observed. Addition of carbene **17** to isobutene (Scheme I) proceeds with >99% stereospecificity to give the more crowded product, **19**. The less crowded epimer **20** was produced during electrochemical reduction of **2** (see below) and was differentiated from **19** by a ^{1}H nmr double resonance experiment. Irradiation of the methyl resonance of **20** at 1.33 δ produced an 18 ± 2% enhancement of the integrated intensity of the resonance due to the hydrogen at C-6 (δ 4.78), an example of the internal nuclear Overhauser effect[20] which confirms the proximity of a methyl substituent and the hydrogen at C-6. A similar irradiation of **19** failed to cause a detectable change in the intensity of absorption due to the hydrogen at C-6.

The exclusive formation of **19** from addition of carbene **17** to isobutene is consistent with efficient steric approach control and a two-step mechanism, parallel with the suggestions of Newman and Patrick.[21a] A possible reaction path is outlined in Scheme I. The

Scheme I
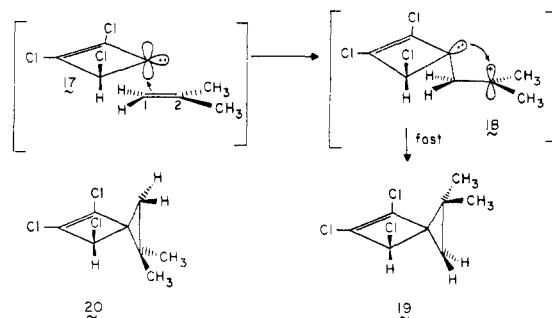
isobutene approaches carbene **17** from the less crowded side and interacts with the empty p orbital of **17** to give an intermediate which is represented as the dipolar species **18**. Rapid ring closure completes the reaction without inversion at the incipient spiro atom.

A series of 4,5,6-trichlorospirocycles (**19**–**23**) was desired for further study because of their relatively facile thermal isomerization compared to the 4,5,6,6-tetrachlorospirocycles (*e.g.*, **1** and **2**), and because kinetic acidity measurements would allow a test for spiroaromaticity. The route discussed above (Scheme I) is satisfactory for the preparation of 4,5,6-trichlorospiro-[2.3]hex-4-enes such as **19** which are stable enough to be isolated from the complex product mixture. However, the more interesting spiro[2.3]hexadiene **21** isomerizes very readily and could not be isolated efficiently by this route. Reaction of the tetrachlorospirocycles with lithium aluminum hydride or tri-*n*-butyltin hydride[22] failed to give selective reduction. Electrolytic reduction, a technique observed to effect selective reduc-

(15) G. Köbrich, *Angew. Chem., Int. Ed. Engl.*, **6**, 41 (1967).

(16) G. Closs, *Advan. Alicyclic Chem.*, **1**, 53 (1966); see also a discussion of this unique ir absorption by C. F. Wilcox, Jr., and R. Craig, *J. Amer. Chem. Soc.*, **83**, 3866 (1961).

(17) R. Criegee and R. Huber, *Angew. Chem., Int. Ed. Engl.*, **8**, 759 (1969).

(18) B. E. Robertson, manuscript in preparation. We thank Professor Robertson (University of Saskatchewan, Regina) for disclosure of these results prior to publication.

(19) R. C. Fort, Jr., G. W. H. Cheeseman, and E. C. Taylor, *J. Org. Chem.*, **29**, 2440 (1964).

(20) W. Philipsborn, *Angew. Chem., Int. Ed. Engl.*, **10**, 472 (1971).

(21) (a) M. S. Newman and T. B. Patrick, *J. Amer. Chem. Soc.*, **92**, 4312 (1970); see also (b) R. A. Moss in "Selective Organic Transformations," B. S. Thyagarajan, Ed., Vol. I, Wiley, New York, N. Y., 1970, p 55ff.

(22) (a) D. Seyferth, H. Yamazoki, and D. L. Alleston, *J. Org. Chem.*, **28**, 703 (1963); (b) T. Ando, F. Namigata, H. Yamanaka, and W. Funasaka, *J. Amer. Chem. Soc.*, **89**, 5719 (1967).
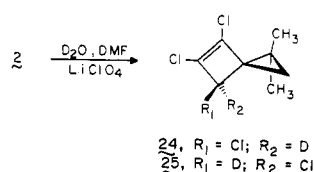
tion of one halogen in gem-dihalogen compounds,[23] was much more promising as polarographic studies indicated that half-wave potentials for the spirocycles 1–3 lay in the easily accessible range of −1.58 to −1.68 V vs. the saturated calomel reference electrode.

Preparative electrolysis on a several mmol scale involved a water-jacketed three-compartment cell with a stirred mercury pool cathode, and with the potential controlled at −2.05 V by a potentiostat. In dimethylformamide containing 0.2 M lithium perchlorate as electrolyte, the spirocycles 1, 2, and 3 were converted to the corresponding 6-H derivatives in 85–90% yield after isolation by extraction into n-pentane and short-path distillation (Scheme II). The products were char-

Scheme II
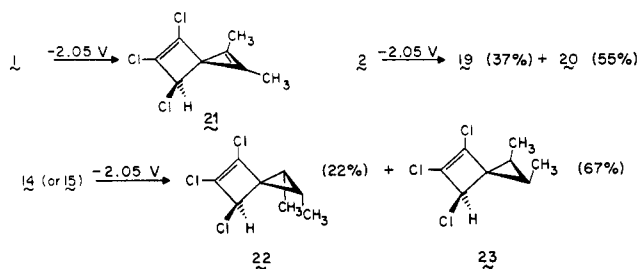
acterized primarily by ^{1}H nmr spectroscopy, including typical absorption at ca. δ 4.60 due to the hydrogen at C-6. The isomers (22 and 23) from reduction of 3 have not been separated. The relative amounts of each isomer were obtained from integrated intensity of the ^{1}H nmr peaks due to the hydrogen at C-6 [δ 4.57 (67%) and 4.80 (22%)]. The major isomer is assigned structure 23 based on the fact that irradiation in the region of the methyl resonances (δ 1.30) produces an enhancement (12%) in the area of the signal at δ 4.80; irradiation at δ 1.30 or other frequencies in the methyl region produces no change in the signal at δ 4.57. The process is expected to involve two electrons[24] via an intermediate anion and subsequent proton transfer. Small amounts of adventitious water or dimethylformamide itself[25] may be the source of the proton; with a twofold molar excess of deuterium oxide added to the electrolyte, reduction leads to efficient incorporation of deuterium (24 + 25, >98% D at C-6, 88% yield). In addition to verifying the source of the proton, this general technique has produced a series of spirocycles (19–23) with tritium enrichment at C-6, greatly simplifying the determination of kinetic acidity.
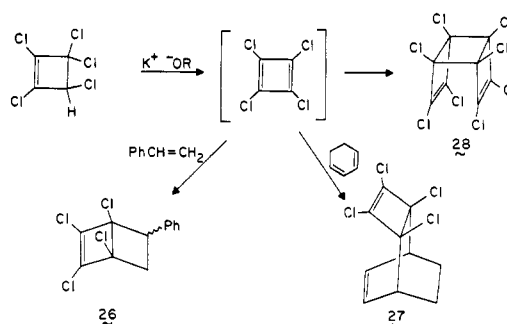

While the formation of cyclopropane rings by addition of α-halolithium reagents to alkenes is well documented, the particular example presented here is surprising in light of brief communications from Scherer

and Meyers.[26] They isolate products from the β-dehydrohalogenation of 3-H-pentachlorocyclobutene in the presence of alkenes (e.g., styrene, 1,3-cyclohexadiene) to which they assign structures (26, 27) which

imply the intermediacy of tetrachlorocyclobutadiene. No adduct with 2-hexyne was isolated.[26c] Because of the surprising contrast that chlorine–lithium exchange (to give 13) affords adducts from α elimination only, while dehydrohalogenation with potassium hydroxide appears to produce β-elimination product, we attempted to confirm the preparation and structures of the tetrachlorocyclobutadiene adducts.

Surprisingly, in view of the earlier reports,[26] we obtain spirocycles by dehydrohalogenation under conditions parallel with those of Scherer and Meyers. For example, a solution of 3-H-pentachlorocyclobutene, potassium tert-butoxide, and styrene in benzene produces a complex reaction mixture from which was isolated dimer 28 and two liquid adducts (combined yield: 15%). From spectral data and characteristic electroreduction behavior, the adducts are assigned spirocyclic structures 29 and 30. The major isomer is obtained in high purity by repeated preparative layer chromatography and shows ^{1}H nmr signals at δ 1.77 (2 H, broadened doublet, J = 9 Hz) and δ 2.98 (1 H, broadened triplet, J = 9 Hz), in addition to the aromatic singlet (5 H) at δ 7.24. The polarographic half-wave potential is −1.55 V; macroscale controlled-potential electrolysis produces a mixture of three products, with ^{1}H nmr peaks appearing at δ 4.48, 4.70, and 4.82, consistent with the expected reduction products (for example, 31 and 32). The alternative structure (26) for the styrene adducts is inconsistent with the electrochemical behavior; simple chlorocarbons (in contrast to gem-dichloro derivatives) are generally not reduced at potentials less negative than −2.0 V. For example, the
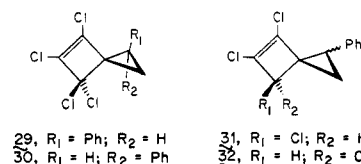
dimer 28 and the cyclohexadiene adduct 27 show $E_{1/2}$ ca. −2.1 V. The adducts we obtain (29 and 30) are clearly different from those (26) obtained by Scherer and Meyers.[27] The presence of small quantities of 26

(23) (a) R. E. Erickson, R. Annino, M. D. Scanlon, and G. Zon, J. Amer. Chem. Soc., 91, 1767 (1969); (b) A. J. Fry and R. H. Moore, J. Org. Chem., 33, 1283 (1968).
(24) I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. 2, Interscience, New York, N. Y., 1952, p 647.
(25) Dimethylformamide is an effective proton donor for strong bases; cf. D. D. Perrin, W. L. F. Armarego, and D. R. Perrin, "Purification of Laboratory Chemicals," Pergamon Press, Oxford, 1966, p 143.

(26) (a) K. V. Scherer, Jr., and T. J. Meyers, J. Amer. Chem. Soc., 90, 6253 (1968); (b) T. J. Meyers and K. V. Scherer, Jr., Abstracts, 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969, ORGN 59; (c) presented in detail by T. J. Meyers at the 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969.
(27) Through personal communication, Professor Scherer has provided the spectral data for 26, which unambiguously distinguish it from the spirocycles.

in the crude reaction mixture from which **29** and **30** are isolated cannot be ruled out because of the complexity of the mixture. The simplest explanation of our results compared to those of Scherer and Meyers[26] is that the product mixtures are similar but different isolation procedures led to isolation of different (minor) products.

Similarly, in the presence of 2-butyne, 3-*H*-pentachlorocyclobutene and potassium *tert*-butoxide react to give a single adduct (15% yield) which is identical with spirohexadiene **1**. The result is essentially the same in either benzene or tetrahydrofuran solvents. With isobutene as trapping agent, spirocycle **2** is obtained as the only adduct (10% yield). On the other hand, the adduct formed in 25% yield from a mixture of potassium *tert*-butoxide, 3-*H*-pentachlorocyclobutene, and 1,3-cyclohexadiene in pentane does possess the structure proposed by Scherer and Meyers, according to an X-ray diffraction study.[28]

The formation of dimer **28** is also presented[26] as evidence for the intermediacy of tetrachlorocyclobutadiene. We find that dimer **28** is a ubiquitous byproduct even during the formation of spirocycles according to eq 5. The yields of spirocycles are highest from the reaction of *n*-butyllithium and hexachlorocyclobutene in *n*-pentane at -30 to $0°$; in ethereal solvents, or with methyllithium, the yield of dimer **28** is sharply increased (Table I) reaching a maximum of 80%, at the expense of the spirocycle. The absence of tetrachlorocyclobutadiene adducts with 2-butyne in those reactions which produce substantial amounts of dimer **28** is consistent with at least two interpretations: (1) the rate of cycloaddition of tetrachlorocyclobutadiene with 2-butyne is very slow relative to cyclodimerization of the cyclobutadiene, even with the alkyne in high concentration; or (2) tetrachlorocyclobutadiene is *not* the reactive intermediate; instead a nonconcerted mechanism is operating, such as the series of steps outlined in eq 6. The latter possibility cannot be rigorously excluded at present, but it fails to account for the isolation of at least one well-characterized cycloadduct, **27**, and the failure to isolate the less crowded anti dimer **33**, which

(6)
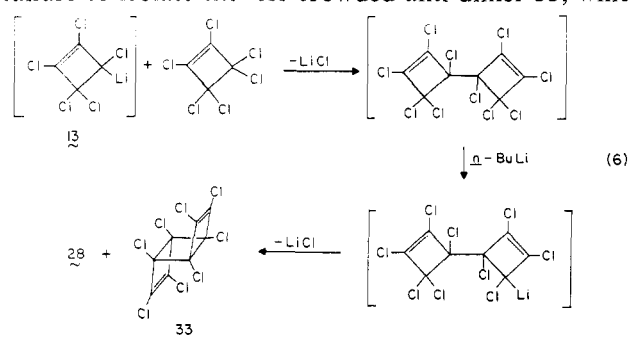
is a reasonable product of the stepwise mechanism.

We favor an interpretation of these results based on the initial formation of an α-halolithium (or potassium) intermediate (*e.g.*, **13**), which can follow two independent pathways—reaction as a carbenoid or β elimination to tetrachlorocyclobutadiene—with a remarkable solvent effect in the partitioning between the two pathways.[29]

(28) R. E. Hughes, J. Lemley, J. Stezowski, and M. F. Semmelhack, manuscript in preparation.
(29) A referee has suggested the possible interconversion of carbene **17** and tetrachlorocyclobutadiene, with a solvent effect on the rate of interconversion or on the position of equilibrium, as an explanation of the results in Table I. We have no data which bear on this question.

Table I. Reaction of Hexachlorocyclobutene with Alkyllithium Reagents and 2-Butyne

Alkyllithium	Solvent	Temp, °C	Yield of 1, %	Yield of 28, %
n-BuLi	Pentane	-78	28	<5
n-BuLi	Pentane	-30	40	<5
n-BuLi	Pentane–ether (10:1)	0	10	30
n-BuLi	Ether	-78	5	50
CH₃Li	Ether	-78	5	65
CH₃Li	Pentane	0	15	80
t-BuLi	Pentane	-30	25	<5

Thermal Rearrangements. The tetrachlorospirocycles **1**, **2**, and **3** are remarkably stable toward heating. They are unchanged over many weeks at 25°, and decompose rapidly only above 120°. When distilled through a low pressure flow–pyrolysis apparatus at 330° (residence time *ca.* 20 sec), spirohexadiene **1** is converted to a labile product (singlet at δ 2.37 in the ¹H nmr spectrum) which has not been obtained pure and is incompletely characterized, while spirohexene **2** rearranges (450°) with loss of hydrogen chloride to 6,6-dimethyl-1,2,3-trichlorofulvene (**34**), a relatively stable yellow solid [mp 26–28° (78%)]. In order to clarify the mechanism of these rearrangements, a detailed study of the thermal properties of trichlorospirocycles **19**, **20**, and **21** was undertaken, employing both low-pressure flow systems and solution studies. Compounds **20** and **21** are particularly interesting because they rearrange under mild conditions, and because the hydrogen at C-6 provides an additional structural probe for ¹H nmr spectroscopy.

All flow pyrolyses were carried out in a gas phase system consisting of a glass tube wrapped with Briskeat heavy-duty heating tape and filled with glass helices. The sample was distilled through the hot tube at 0.01 Torr, and the products were collected at $-78°$ in a simple apparatus that allows transfer of the pyrolysate to an nmr sample tube without exposure to air or warming to ambient temperature (see Experimental Section).

When samples of **20** are distilled through the pyrolysis apparatus at 265° (0.01 Torr), 40% conversion to one product was observed, allylidenecyclopropane **35** (70% yield based on unrecovered starting material). Higher temperature (440°) led to compete conversion to a mixture of fulvene **36** and methylenecyclopentene **37** (1:2.5 ratio, 80%). Spirocycle **19**, the more crowded epimer, should rearrange on heating to a geometric isomer of **35** (either **38** or **39**) according to orbital symmetry theory. However, as **19** is distilled through the pyrolysis apparatus at various temperatures, no products are observed until 360°, at which point low conversion to **36** and **37** occurs. Conversion to the same two products is complete at 440° (yield 80%) and the ratio (**36**:**37** = 1:2.2) is closely similar to the mixture from **20**. It is likely that the allylidenecyclopropanes **38** or **39** are intermediates in the rearrangement of **19**, but cannot be detected because the minimum temperature for their formation is above that necessary for further rearrangement. The fulvene **36** has not been isolated in high purity due to instability toward oxygen and polymerization; however, both the related fulvene **34** and compound **37** have been fully characterized.
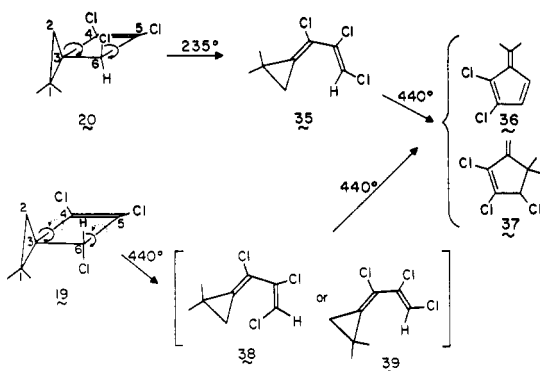
The rearrangement of spirocycle **20** is also observed in solution, with a half-life of 36 hr at 125° in carbon tetrachloride. The peaks characteristic of **35** grow into the ^{1}H nmr spectrum, reaching a maximum intensity after 25 hr, and then disappear with time, leaving a mixture from which **37** is isolated in moderate yield by short-path distillation.

The near identity of the product mixtures from the 440° pyrolyses of **19** and **20** suggests that a common intermediate might be involved in the rearrangements. A second series of spirocycles (**3, 14,** and **15**) led to precisely identical product mixtures. The ^{1}H nmr spectra of the products from pyrolysis (450° (0.01 Torr)) of each spirocycle were superimposable and fully consistent with two products (**40** and **41**) in the ratio 1.7:1 (yield 80%). The fulvenes **40** and **41** are unstable and have not been separated; the structural assignments are based on spectral data (^{1}H nmr, uv, ir) from the mixture.
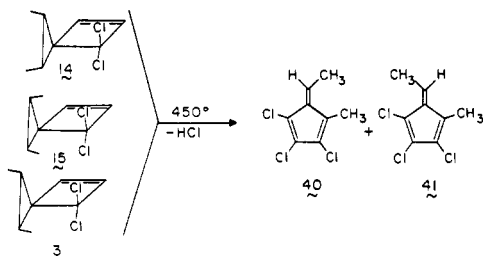

The more highly strained spirocycle **21** is even more labile. Distillation through the pyrolysis apparatus at 225° (0.01 Torr) gave complete conversion to an exceedingly elusive substance which polymerized on the cold collector surface to an amorphous, insoluble yellow solid. The product expected in analogy with the spirohexenes is 3-(1,2,3-trichloro-Z-prop-2-enyl-idene)-1,2-dimethylcyclopropene (**42**), which, if formed during pyrolysis, must be very sensitive toward self-polymerization. This behavior is, of course, not unexpected for a derivative of methylenecyclopropene, although certain stabilized derivatives are known.[13] In solution, spirocycle **21** rearranges with a half-life of 17 hr at 25° (10 min at 90°). During the initial stages of the reaction, transient singlets appear in the ^{1}H nmr spectrum at δ 6.25 (1 H) and 2.33 (6 H), each somewhat broadened, consistent with structure **42**. However, as the concentration of the new product rises, its rate of disappearance increases; after 40 min at 95°, the ^{1}H nmr spectrum shows no signals attributable to **21** or **42**. The final product is nonvolatile and could not be characterized. The disappearance of **21** at 60° in carbon tetrachloride solution is cleanly first order ($k = 8.5 \times$

10^{-5} sec^{-1}, $R = 0.96$ from a least-squares analysis), consistent with unimolecular isomerization.

Further support for the structural assignment of **42** is available from comparison of the chemical shifts for the vinylic proton in **42** (δ 6.25) and the corresponding proton in the allylidenecyclopropane **35** (δ 7.06). The difference of δ 0.81 is consistent with the difference (δ 0.9) found in the chemical shifts of the vinylic protons in a methylenecyclopropene compared to a methylene-cyclopropane. The difference is attributed to an important contribution from a dipolar structure for **42**, which increases the electron density along the 1,3-diene unit.[30]
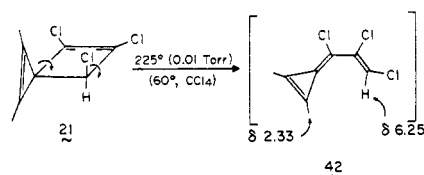
Mechanism. Ring opening of the spirocycles to form **35** and **42** follows directly from orbital symmetry considerations. The higher temperatures necessary to cause isomerization of **19** and the tetrachlorospirocycles (**1, 2, 3, 14, 15**) are also consistent with initial concerted conrotatory ring opening, now with a large steric barrier due to interaction between a chlorine at C-6 and the substituents at C-2 as illustrated for **2** (eq 7).
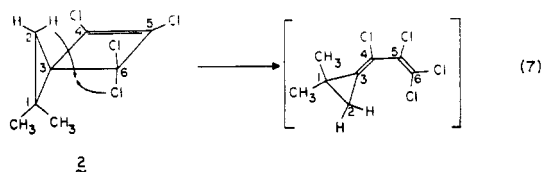
The mechanism of further rearrangement of allyl-idenecyclopropane derivatives has been the subject of recent activity. The best interpretation appears to be that of Roth[14b] and of Kende,[14c] with which our results are completely consistent. For illustrative purposes, consider the rearrangement of **20** (Scheme III). The

Scheme III
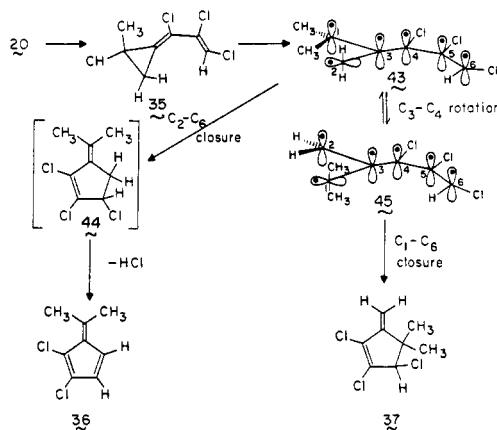
first product is **35**, which then undergoes homolytic cleavage of C_1–C_2 to give a trimethylenemethane singlet diradical (**46**), most likely not completely planar,[14] with one or more of the p orbitals being in the plane of the original ring. Rapid rotation about the partial π bonds (C_1–C_3, C_2–C_3, C_3–C_4) in **43** would afford geometric

(30) G. Closs, *Advan. Alicycl. Chem.*, **1,** 125 (1966).

isomers of **43**. Then bond formation between C_2 and C_6 gives compound **44**, which loses hydrogen chloride spontaneously to produce one of the observed products, the fulvene **36**. Other geometric isomers of **43** (e.g., **45**) have C_1 and C_6 in proximity; bond formation leads to the stable methylenecyclopentene **37**.

Intermediates such as **46** and **47**, which would have
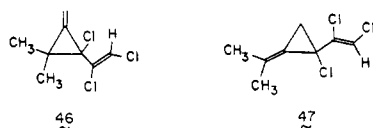
been expected according to the suggestions of Kende,[14c] have not been observed; however, they would be present in very small amounts at most and may have been undetected. The results presented here are inconsistent with concerted sigmatropic rearrangement, which must be regiospecific, leading to a single methylenecyclopentene isomer from a particular allylidenecyclopropene (eq 8).

$$R_1 = Cl; R_2 = H$$
$$R_1 = H; R_2 = Cl$$
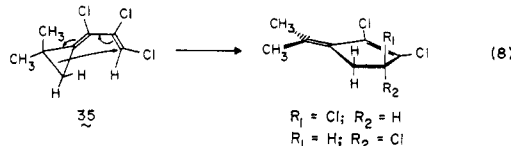
Experimental Section

General. All solvents used were ACS reagent grade and were not further purified unless otherwise noted. Boiling points and melting points are uncorrected. Infrared spectra were obtained using a Perkin-Elmer Infracord Model 137 spectrophotometer on samples prepared as neat films between sodium chloride plates unless otherwise specified. [1]H nmr spectra were obtained on carbon tetrachloride solutions using a Varian A-60A spectrometer with chemical shifts reported in parts per million (δ) downfield of internal tetramethylsilane. Ultraviolet spectra were obtained on isooctane (Fisher Spectranalyzed) solutions using a Cary Model 14 spectrophotometer. All mass spectral data were obtained from an Associated Electrical Industries Model MS-902 spectrometer. Microanalytical data were obtained from Scandanavian Microanalytical Laboratory. The terms "under argon" or "in an argon atmosphere" imply that the reaction system is alternately evacuated to aspirator pressure and filled with argon at least three times.

1,2-Dimethyl-4,5,6,6-tetrachlorospiro[2.3]hexadiene (1). To a solution of hexachlorocyclobutene[31] (20.00 g, 76.5 mmol) and 2-butyne (50 ml, ca. 700 mmol, Farchan Chemical Co.) in 500 ml of dry n-pentane under argon at $-30°$ was added 70 ml of a 1.6 M solution of n-butyllithium in hexane (112 mmol of n-butyllithium, Foote Mineral Co.) over 10 min. The solution was stirred at $-30°$ for 45 min, during which time it became milky (lithium chloride). The mixture was then allowed to come to 25° and 100 ml of water was added with vigorous stirring. The organic phase was washed three times with 100-ml portions of water, dried over anhydrous magnesium sulfate, and concentrated *in vacuo* to yield a yellow oil. Short-path distillation (40° (0.001 Torr)) into a trap cooled to $-78°$ gave a colorless semisolid material. Repeated crystallization from methylene chloride at $-78°$ yielded 7.64 g (41%) of **1** as a colorless solid: mp 36–37°;[32] [1]H nmr δ 2.17; ir 1885 (C=C for 1,2-dimethylcyclopropene)[16] and 1630 cm^{-1} (C=C for 1,2-dichlorocyclobutene);[17] uv max (isooctane) 231 nm (ϵ 5360); mass spectrum (70 eV) parent ion at m/e 242 with an isotopic distribution pattern consistent with the presence of four chlorine atoms;[33] calcd for $C_8H_6{}^{35}Cl_4$, 242.

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(31) Hexachlorocyclobutene was prepared by the method of W. C. Solomon, L. A. Dee, and D. W. Schults, *J. Org. Chem.*, **31**, 1551 (1966), using 1,2-dichlorotetrafluorocyclobut-1-ene (Peninsular Chem Research, Inc.) as the precursor and methylene chloride as the solvent.

(32) The principal impurities in the distillate have been tentatively identified (nmr, mass spectra) as hexachlorocyclobutene, and the spiro compound on which a chlorine atom has been replaced by an n-butyl group. No further effort was made to characterize these high-boiling side products, nor was this aspect of the reaction pursued.

(33) F. W. McLafferty, "Interpretation of Mass Spectra," W. A. Benjamin, New York, N. Y., 1967, p 22.

Anal. Calcd for $C_8H_6Cl_4$: C, 39.39; H, 2.48; Cl, 58.13. Found: C, 39.34; H, 2.51; Cl, 58.16.

1,1-Dimethyl-4,5,6,6-tetrachlorospiro[2.3]hex-4-ene (2). Hexachlorocyclobutene (20.00 g, 76.5 mmol) was placed in a dry flask under an argon atmosphere and 250 ml of isobutene (Matheson Gas Products) was passed through a Drierite-filled drying tower and condensed in the flask using a Dry Ice cooled Dewar condenser. To the stirred refluxing solution was added a solution of n-butyllithium in hexane (1.6 M, 90 ml, 144 mmol of n-butyllithium) over 10 min. The resulting milky suspension was stirred at reflux for 30 min. Water (100 ml) was added and the mixture was stirred vigorously while being allowed to warm to 25° with evolution of the excess isobutene. After foaming ceased, 75 ml of pentane was added and the mixture was treated as above to yield, after short-path distillation (35° (0.001 Torr)), 7.75 g (41%) of **2** as a colorless liquid: [1]H nmr δ 1.45 (s, 3 H), 1.32 (s, 3 H), 1.15 (d, 1 H, $J = 6$ Hz), 0.97 (d, 1 H, $J = 6$ Hz); ir 1630 cm^{-1} (C=C for 1,2-dichlorocyclobutane);[17] uv max (isooctane) 230 nm (ϵ 5710); mass spectrum (70 eV) parent ion at m/e 244 with an isotopic distribution pattern consistent with the presence of four chlorine atoms; calcd for $C_8H_8{}^{35}Cl_4$, 244.

Anal. Calcd for $C_8H_8Cl_4$: C, 39.07; H, 3.28; Cl, 57.66. Found: C, 39.07; H, 3.25; Cl, 57.85.

***trans*-1,2-Dimethyl-4,5,6,6-tetrachlorospiro[2.3]hex-4-ene (3).** Hexachlorocyclobutene (10.00 g, 38.3 mmol) was dissolved in 100 ml of refluxing *trans*-2-butene (Matheson Gas Products, C.P. grade) in the manner described for the preparation of **2**. A solution of n-butyllithium in hexane (1.6 M, 35 ml, 57 mmol) was added and the reaction mixture was treated as in the preparation of **2**. The distillate (35° (0.001 Torr)) was purified by preparative glpc [10 ft × 0.375 in., 20% FFAP (Varian Aerograph) on 60–80 mesh Chromosorb P, 155°] to yield **3** (3.39 g, 36%) as a colorless liquid; ^{1}H nmr shows two broad singlets at δ 1.42 and 1.26 in a ratio of 1:1, corresponding to the two methyl groups, with the cyclopropyl protons appearing as a broad multiplet from δ 1.2 to 1.45 (see text for discussion); ir 1630 cm^{-1} (C=C for 1,2-dichlorocyclobutene);[17] mass spectrum (70 eV) parent ion at m/e 243.9377; calcd for C_8H_8-$^{35}Cl_4$, 243.9380.

***syn*(15)- and *anti*(14)-*cis*-1,2-Dimethyl-4,5,6,6-tetrachlorospiro-[2.3]hex-4-ene.** The reaction between hexachlorocyclobutene (10.00 g, 38.3 mmol) and n-butyllithium (1.6 M in hexane, 35 ml, 57 mmol) in the presence of *cis*-2-butene (Matheson Gas Products, C.P. grade) was performed as described above for **2** and **3**, except that a mixture of 85 ml of dry n-pentane (dried over activated Linde Molecular Sieves Type 51) and 50 ml of *cis*-2-butene was used as the reaction medium, rather than the pure alkene as in the previous procedures. Preparative glpc (10 ft × 0.375 in., 20% Carbowax 20M on 60–80 mesh Chromosorb A, 160°) afforded approximately equimolar quantities of the pure isomers **14** and **15** (1.78 g of **14** and 1.54 g of **15**) in a combined yield of 35%, with **14** having the shorter retention time. The anti isomer **14** forms colorless crystals: mp 34–35°; ^{1}H nmr δ 1.28 (m, 6 H, –CH$_3$) and 1.75 (m, 2 H, –CH–);[34] ir 1630 cm^{-1} (C=C for 1,2-dichlorocyclobutene);[17] mass spectrum (70 eV) parent ion at m/e 244 in a pattern consistent with the presence of four chlorines; calcd for $C_8H_8{}^{35}Cl_4$, 244.

Anal. Calcd for $C_8H_8Cl_4$: C, 39.07; H, 3.28; C, 57.66. Found: C, 39.11; H, 3.34; C, 57.55.

The syn isomer **15** forms colorless crystals: mp 45–46°; ^{1}H nmr δ 1.48 (s, accidental degeneracy of all protons); ir 1630 cm^{-1} (C=C for 1,2-dichlorocyclobutene);[17] mass spectrum (70 eV) parent ion at m/e 243.9386; calcd for $C_8H_8{}^{35}Cl_4$, 243.9380.

Catalytic Reduction of 1. A solution of spirodiene **1** (0.100 g, 0.41 mmol) in 5 ml of 95% ethanol was injected through a serum stopper into a 25-ml sidearm flask containing a stirred suspension of 10% palladium-on-charcoal catalyst (50 mg) in 10 ml of 95% ethanol under hydrogen (1 atm). Over a 1-hr period the mixture took up 10.9 ml of hydrogen (corrected to standard temperature and pressure, 106% of theory for saturation of one double bond). The mixture was filtered, concentrated *in vacuo*, and distilled in a short-path apparatus (40° (0.001 Torr)) to yield 0.068 g (67%) of a colorless semisolid; ^{1}H nmr revealed this to be a mixture of 96-98% **14** and 2-4% **15**. There was no evidence of any cyclopropane ring cleavage or hydrogenation of the cyclobutene double bond.

Bromination of 1. A solution of 0.100 g of **1** (0.41 mmol) in *ca.* 5 ml of carbon tetrachloride was treated with *ca.* 1 equiv of bromine

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(34) The splitting pattern, which is quite complex, is virtually superimposable on that of 3,3-dichloro-*cis*-1,2-dimethylcyclopropane.[35]

(35) "Sadtler Nmr Spectra Index," Spectrum 5130M, Sadtler Research Laboratories, Inc., 1967.

(0.41 mmol, 0.065 g, 22 μl) at 25°. Approximately 15 min was required for the bromine color to disappear completely, after which the solvent was removed (aspirator, followed by 0.001 Torr (25°) for 30 min) to leave crystals: mp 55–56°, weighing 0.138 g (83%) of the pure dibromide **16**; ^{1}H nmr δ 2.35 and 2.23 (singlets in a 1:1 ratio); ir (CCl$_4$) 1635 cm^{-1} (C=C for 1,2-dichlorocyclobutene),[17] with no trace of the 1885-cm^{-1} peak characteristic of the 1,2-dimethylcyclopropene; mass spectrum (70 eV) showed the parent ions (low abundance) at m/e 400 and abundant fragments with the expected isotope distribution patterns at m/e 365 (loss of ^{35}Cl) and m/e 321 (loss of ^{79}Br); calcd for C$_8$H$_6$^{79}Br$_2$^{35}Cl$_6$, 400.

Reaction of 3-*H*-Pentachlorocyclobutene with *n*-Butyllithium in Isobutene. To a solution of 3-*H*-pentachlorocyclobutene[36] (0.849 g, 3.75 mmol) in *ca*. 50 ml of isobutene (condensed in the manner described above for the preparation of **2**) was added a solution of *n*-butyllithium in hexane (1.6 M, 3.5 ml, 5.60 mmol). The mixture was stirred at reflux for 45 min, during which time a white solid (lithium chloride) formed. Isolation as for **2**, including short-path distillation (30° (0.001 Torr)), gave 0.437 g of colorless distillate. Five components were detected by glpc (10 ft × 0.375 in., 20% Carbowax 20M on 60–80 mesh Chromosorb A, 150°). The major products, isolated by preparative glpc under the same conditions, were **2** (7–10% of the distillate, *ca*. 5% overall) and *anti*-6-*H*-1,1-dimethyl-4,5,6-trichlorospiro[2.3]hex-4-ene, **19** (70–75% of the distillate, *ca*. 40% overall); ^{1}H nmr δ 4.70 (s, 1 H, C=CC*H*Cl), 1.26 (s, 3 H, –CH$_3$), 1.17 (s, 3 H, –CH$_3$), 1.02 (d, *J* = 6 Hz, 1 H, cyclopropyl –H), 0.96 (d, *J* = 6 Hz, 1 H, cyclopropyl –H); ir 1630 cm^{-1} (C=C for 1,2-dichlorocyclobutene);[17] uv max (isooctane) 227 nm (ε 6400); mass spectrum (70 eV) parent ion at m/e 209.9761; calcd for C$_8$H$_5$^{35}Cl$_3$, 209.9770. There was less than 2% of the syn isomer, **20**, in the product mixture, as ascertained by comparison of the ^{1}H nmr spectrum of the sample with those of samples of both **19** and **20** prepared by another route (see below). The configurations of the spirocycles were determined by means of the internal Overhauser effect (see below).

Reaction of 3-*H*-Pentachlorocyclobutene with *n*-Butyllithium in the Presence of 2-Butyne. To a solution of 0.856 g of 3-*H*-pentachlorocyclobutene (3.78 mmol) in 20 ml of dry *n*-pentane and 5 ml (13.5 mmol) of 2-butyne (Farchan Chemical Co.) at −30° under an argon atmosphere was added 3.8 ml of a 1.6 M solution of *n*-butyllithium in hexane (6.07 mmol). The mixture was allowed to stir at −30° for 45 min, during which time a white solid formed. Isolation according to the procedure described for the preparation of **1** gave, after short-path distillation (35° (0.001 Torr)), 0.355 g of colorless oil. Analysis of the mixture by ^{1}H nmr revealed the following composition: 25% 3-*H*-pentachlorocyclobutene, 20% alkylated byproducts (see ref 30 for a discussion of the analogous byproducts in the formation of **1**), and 55% (*ca*. 25% overall yield) of a compound which was characterized after inefficient (25% recovery) preparative glpc (10 ft × 0.375 in., 20% Versamide 900 on 60–80 Chromosorb W, 140°) isolation as 1,2-dimethyl-4,5,6-trichlorospiro[2.3]hexadiene **21**; ^{1}H nmr δ 4.67 (s, 1 H, C=CC*H*Cl), 2.13 (m, 6 H, –CH$_3$); ir 1860 (C=C for 1,2-dimethylcyclopropene),[16] 1620 cm^{-1} (C=C for 1,2-dichlorocyclobutene);[17] mass spectrum (70 eV) parent ion at m/e 207.9611; calcd for C$_8$H$_7$^{35}Cl$_3$, 207.9613.

Polarographic Determination of Half-Wave Reduction Potentials for Hexachlorocyclobutene, Tetrachlorospirocycles 1, 2, 14, and 15, and Cyclohexadiene Adduct 27. Approximately 1 m*M* solutions of each of the samples were prepared under argon in acetonitrile (Fisher Spectranalyzed) which was 0.10 *M* in tetraethylammonium perchlorate (Alfa Inorganics, Inc.). Determinations of the half-wave potentials were made using a modular Heath-Built polarograph, Model EUA-19, equipped with a dropping mercury cathode, a platinum wire anode, and a saturated calomel reference (sce) electrode in a 10-ml cell. The voltage was swept toward negative potential at 0.2 V/min from −0.50 to −2.25 V *vs*. the sce. The half-wave potentials determined by this method are −1.68 ± 0.03 for **1**, −1.58 ± 0.02 for **2**, −1.63 ± 0.02 for **14**, −1.61 ± 0.02 for **15**, −1.26 ± 0.02 for hexachlorocyclobutene, and −2.15 ± 0.02 V for **27**, relative to the sce. Each result is the average of four identical determinations.

General Procedure for the Electrochemical Synthesis of Trichlorospirocycles 19, 20, 21, 22, and 23. Preparative controlled-potential

electrolyses were carried out in a water-jacketed three-compartment cell using a Wenking Model 68-FR-0.5 potentiostat to maintain a preset constant potential difference between the working and reference electrodes. The working electrode, a magnetically stirred mercury pool, was in the central compartment, while the reference electrode, a saturated calomel electrode, and the counter electrode, a platinum sheet (1 cm^2), were in separate sidearms isolated by means of coarse fritted glass disks. To the central compartment was added *ca*. 20 ml of the electrolyte solution [0.2 *M* lithium perchlorate (anhydrous, Alfa Inorganics, Inc.) in dimethylformamide] and sufficient quantities were added to the side compartments to fill all three sections to equal height. Argon was then bubbled through the electrolyte in the central compartment for *ca*. 10 min to remove dissolved oxygen, and the potentiostat controls were set to maintain −2.05 ± 0.01 V (approximately the maximum potential at which the solvent itself will not be reduced) between the working electrode and the reference electrode. With a continuous slow flow of argon through the electrolyte being maintained, the potentiostat was disengaged, the tetrachlorospirocycle (3–5 mmol) was added to the central compartment, and the potentiostat was reengaged. The initial current of 200–250 mA decreased over a period of 2–3 hr, reaching a constant background level of 5–10 mA. The resulting brown solution in the central compartment was diluted with 120 ml of water and extracted four times with 40-ml portions of *n*-pentane. The combined pentane extracts were washed four times with 50-ml portions of water, dried over anhydrous magnesium sulfate, concentrated under aspirator pressure, and distilled in a short-path apparatus (25° (0.001 Torr)) to give the trichlorospirocycle in 85–95% yield and >98% purity (by ^{1}H nmr and/or glpc analysis). Careful drying of the electrolyte solution over activated Linde Molecular Sieves, Type 4A, and addition of *ca*. 2 molar equiv of deuterium oxide resulted in the isolation of trichlorospirocycles in similar yield with deuterium at C-6 in 98% isotopic purity.

a. Reduction of 1 to Give 21. The tetrachlorospirocycle **1** (0.750 g, 3.07 mmol) was reduced during a 3-hr period to yield, upon isolation, 0.572 g (89%) of pure **21**, identical with the sample produced by the reaction of 3-*H*-pentachlorocyclobutene described in an earlier procedure.

b. Reduction of 2 to Give 19 and 20. The tetrachlorospirocycle **2** (0.900 g, 3.66 mmol) was reduced during a 3-hr period to yield, upon isolation, a colorless oil (0.705 g, 92%) consisting of a mixture of the two isomeric trichlorospirocycles. Preparative glpc (10 ft × 0.375 in., 20% Carbowax on 60–80 mesh Chromosorb A, 155°) afforded the pure isomers **19** (40% of the mixture, 37% overall; identical in all respects with the sample produced by the reaction of 3-*H*-pentachlorocyclobutene described in an earlier procedure) and **20** (60% of the mixture, 55% overall); ^{1}H nmr δ 4.78 (s, 1 H, C=CC*H*Cl), 1.34 (s, 3 H, –CH$_3$), 1.31 (s, 3 H, –CH$_3$), 0.88 (s, 2 H, cyclopropyl –H); ir 1630 cm^{-1} (C=C for 1,2-dichlorocyclobutene);[17] uv max (isooctane) 227 nm (ε 7200); mass spectrum (70 eV) parent ion at m/e 209.9777; calcd for C$_8$H$_5$^{35}Cl$_3$, 209.9770.

c. Reduction of 14 (or 15) to Give 22 and 23. The tetrachlorospirocycle **14** (0.200 g, 0.81 mmol) was reduced during a 2-hr period to yield, upon isolation, a colorless oil (0.155 g, 90%) consisting of a mixture of the isomeric trichlorospirocycles **23** (75% of the mixture, 67% overall) and **22** (25% of the mixture, 22% overall). Although the components of the mixture could not be separated by the usual techniques, the relative amounts of each isomer could be determined by integration of the easily distinguishable ^{1}H nmr signals due to the proton at C-6; ^{1}H nmr of the mixture δ 4.80 (s, 0.25 H, C=C*H*Cl), 4.57 (s, 0.75 H, C=CC*H*Cl), *ca*. 1.30 (m, 8 H, –CH$_3$ and cyclopropyl –H); ir 1630 cm^{-1} (C=C for 1,2-dichlorocyclobutene);[17] mass spectrum (70 eV) parent ion at m/e 210; calcd for C$_8$H$_9$^{35}Cl$_3$, 210. The relative configurations of the two isomers were determined by means of a ^{1}H nmr double-resonance experiment (see below). Reduction of the tetrachlorospirocycle **15** yielded identical results, no doubt due to the intermediacy of the same allylic anion.

d. Reduction of 2 to Give 24 and 25. To electrolyte solution (dried over Linde Molecular Sieves, Type 2A, for 24 hr) was added tetrachlorospirocycle **2** (0.500 g, 2.03 mmol) and deuterium oxide (75 μl, 4.17 mmol). Reduction and isolation by the usual procedure gave a colorless oil (0.430 g, 88%) consisting of a mixture of the two isomeric trichlorospirocycles. ^{1}H nmr analysis of the mixture revealed it to be identical with that obtained in procedure **b** except that the signals due to the protons at C-6 (δ 4.70 and 4.78) were greatly diminished. Utilizing the methyl and cyclopropyl proton resonances as internal standards, the area of the two peaks at δ 4.70 and 4.78 was estimated to be less than 2% of the corresponding area for the mixture of isomers **19** and **20**, indicating greater than 98% incorporation of deuterium at C-6 of **24** and **25**.

(36) 3-*H*-Pentachlorocyclobutene was prepared by reduction of 1,2-dichlorotetrafluorocyclobutene-1 (Peninsular Chem Research, Inc.) according to the method of D. J. Burton and R. L. Johnson, *J. Amer. Chem. Soc*., **86**, 5361 (1964), followed by heterogeneous chlorination by the method of Solomon, *et al*.[31] See also ref 26a.

Determination of the Relative Configuration about C-6 for 19, 20, 22, and 23 by Means of the Internal Nuclear Overhauser Effect. Pure samples of the isomeric trichlorospirohexenes 19 and 20 and the inseparable mixture 22 and 23 (50–100 mg of each) were placed in 5-mm nmr sample tubes. To each of the tubes was added 0.3 ml of deuteriochloroform containing ca. 5% tetramethylsilane; the samples were degassed by means of several freeze–evacuate–thaw cycles and sealed under argon. The ¹H nmr spectra of the samples were observed using a Varian HA-100 spectrometer in the frequency-sweep mode with tetramethylsilane providing the lock signal, while a Hewlett-Packard 4204A oscillator provided a 2.5-V external signal. In each case, the oscillator signal was applied at a frequency 10.0 Hz downfield of the downfield cyclopropylmethyl signal and was swept in 2.0-Hz increments through the methyl resonance region to 10.0 Hz beyond on the upfield site. After each incremental shift, the integral of the signal due to the proton at C-6 was measured six times and an average value was obtained. By this means the following observations were made. Irradiation at the methyl proton resonance frequency (δ 1.33–1.32) for 20 caused an $18 \pm 2\%$ increase in the area of the signal from the proton at C-6 (δ 4.78), while irradiation at the methyl proton resonance frequencies (δ 1.26 and 1.17) or the cyclopropyl proton resonance frequencies (δ 1.02 and 0.96) for 19 failed to cause any change in the area of the signal from the proton at C-6 (δ 4.70). It was unfortunately impossible to determine which of the two methyl groups was responsible for the signal involved in the Overhauser effect, due to the rather broad power bandwidth of the oscillator and the very small shift difference between the methyl group resonances. Irradiation in the vicinity of the methyl proton resonance frequencies (ca. δ 1.3) for the mixture 22 and 23 caused a $12 \pm 2\%$ increase in the area of the signal from the C-6 proton at δ 4.80 (corresponding to the minor component of the mixture); no change, however, was observed in the area of the signal at δ 4.57 (corresponding to the major component of the mixture) upon irradiation in the region δ 1.5–0.9.

Reaction of 3-H-Pentachlorocyclobutene with Potassium tert-Butoxide and Styrene in Benzene. To a solution under argon of potassium tert-butoxide (MSA, Inc., 1.46 g, 13.0 mmol) and distilled styrene (10.0 ml, ca. 100 mmol) in 50 ml of dry benzene at 25° was added through a serum stopper 2.26 g (10.0 mmol) of 3-H-pentachlorocyclobutene and the mixture was left to stir ca. 12 hr. The brown reaction mixture was partitioned between pentane and water and the organic phase was washed with water, dried over anhydrous magnesium sulfate, and concentrated in vacuo (0.5 Torr). Short-path distillation of the oily residue gave 0.62 g of unreacted starting material (25–30° (0.003 Torr)), and 0.32 g (15%) of a mixture of styrene adducts 29 and 30 (65° (0.003 Torr)). Repeated preparative layer chromatography afforded 0.15 g of the major isomer in high purity: ¹H nmr δ 7.23 (s, 5 H, aromatic H), 2.98 (broad t, J = 9 Hz, 1 H, benzylic H), 1.77 (d, J = 9 Hz, 2 H, cyclopropyl H); mass spectrum (70 eV) parent ion at m/e 291.9374; calcd for $C_{12}H_9{}^{35}Cl_3$, 291.9390. Trituration with methylene chloride at –30° of the pot residue after distillation gave 1.04 g (55%) of dimer 28. mp 164–166° dec (lit. mp[26] 161–163° dec).

Measurement of the polarographic half-wave reduction potential under the usual conditions (see above) gave a value of -1.55 ± 0.02 V vs. the sce. Electroreduction of a 0.100-g sample of the adduct at -2.05 V gave, after the usual isolation procedures (see above), 0.078 g (89%), apparently a mixture of three of the four possible isomeric reduction products (31, 32) with the three ¹H nmr signals due to the proton at C-6 (δ 4.82, 4.70, and 4.48) in the ratio, respectively, of 1:4.5:2. The mass spectrum of the mixture (70 eV) gave a parent ion at m/e 257.9769 with an isotope distribution pattern typical of an ion containing three chlorine atoms;[33] calcd for $C_{12}H_9{}^{35}Cl_3$, 257.9783.

Reaction of 3-H-Pentachlorocyclobutene with Potassium tert-Butoxide and 2-Butyne in Benzene. To a solution under argon of potassium tert-butoxide (0.68 g, 6.05 mmol) and 2-butyne (5.0 ml, ca. 60 mmol) in 30 ml of dry benzene at 25° was added 0.80 g (3.52 mmol) of 3-H-pentachlorocyclobutene and the mixture was left to stir ca. 12 hr. Isolation as above gave, after short-path distillation (30° (0.001 Torr)), 0.141 g (16%) of 1, identical with material prepared by the method above. Trituration of the pot residue with diethyl ether at $-30°$ gave 0.38 g (57%) of dimer 28.

Reaction of 3-H-Pentachlorocyclobutene with Potassium tert-Butoxide and 2-Butyne in Tetrahydrofuran. Reaction as above, but at 0 using tetrahydrofuran (freshly distilled from lithium aluminum hydride) as the solvent, gave, after isolation, 0.103 g (12%) of 1 and 0.33 g (49%) of 28.

Reaction of 3-H-Pentachlorocyclobutene with Potassium tert-Butoxide and 1,3-Cyclohexadiene in n-Pentane. To a mixture under

argon of potassium tert-butoxide (1.17 g, 10.4 mmol) and 1,3-cyclohexadiene (Aldrich Chemical Co., 5.0 ml, ca. 50 mmol) in 50 ml of dry n-pentane (dried over Linde Molecular Sieves, type 4A) at 0° was added 1.36 g (6.00 mmol) of 3-H-pentachlorocyclobutene, and the mixture was left to stir ca. 12 hr, warming to 25°. Diethyl ether (20 ml) was added and the mixture was washed several times with water. The organic phase was dried over anhydrous magnesium sulfate and concentrated in vacuo to yield a mixture of yellow oil and white solid. Trituration of this mixture with diethyl ether at $-30°$ gave a white crystalline residue of dimer 28 (0.71 g, 62%), while concentration of the ether washes in vacuo and recrystallization of the residue from ethanol gave 0.398 g (25%) of adduct 27, mp 103–104°, identical (¹H nmr, ir, mp) with the compound described in the literature.[26]

Reaction of 3-H-Pentachlorocyclobutene with Potassium tert-Butoxide and Isobutene. To a mixture under argon of potassium tert-butoxide (0.55 g, 4.90 mmol) in 50 ml of refluxing isobutene was added 0.80 g (3.52 mmol) of 3-H-pentachlorocyclobutene and the mixture was left to stir at reflux ($-6°$) for ca. 12 hr. The solvent was allowed to evaporate and the mixture was partitioned between n-pentane and water. The organic phase was washed with water, dried over anhydrous magnesium sulfate, and concentrated in vacuo to give a mixture of yellow oil and white solid. Short-path distillation (35° (0.001 Torr)) gave 0.363 g of colorless oil, identified by ¹H nmr and analytical glpc (6 ft × 0.25 in., 3% SE-30 on 100–120 mesh Chromosorb W, 110°) as a mixture of unreacted 3-H-pentachlorocyclobutene and spirocycle 2 in the respective ratio 4:1 (13% overall yield of 2 based on starting material not recovered). Trituration (diethyl ether) of the pot residue after distillation at $-30°$ gave 0.317 g (74% based on starting material not recovered) of dimer 28.

Reaction of Hexachlorocyclobutene with Alkyllithium Reagents and 2-Butyne. To a solution under argon of hexachlorocyclobutene (1.00 g, 3.83 mmol) of 2-butyne (5.0 ml, ca. 60 mmol) in 50 ml of one of several solvents [pentane, pentane–ether (10:1), ether] cooled to the specified temperature was added a solution containing 1.5 molar equiv of the alkyllithium reagent in the solvent in which it was supplied (n-butyllithium as a hexane solution, methyllithium as an ether solution, tert-butyllithium as a pentane solution). The reaction was allowed to proceed for ca. 1 hr and then quenched with 10 ml of water. The organic phase was washed with water, dried over anhydrous magnesium sulfate, concentrated in vacuo, and distilled in a short-path apparatus (35° (0.001 Torr)). The distillate was weighed, analyzed by ¹H nmr and analytical glpc (6 ft × 0.25 in., 3% SE-30 on 100–120 Chromosorb W, 110°), and the yield of 1 (presented in Table I) was calculated based on unrecovered starting material. The residue after distillation was triturated several times with diethyl ether at $-30°$ to remove alkylated cyclobutenes (the principle side products of these reactions)[37] and the remaining white solid, dimer 28, was weighed (yield of 28 presented in Table I).

General Procedure for High-Vacuum Flow Pyrolyses. The pyrolyses were carried out in a 27 cm × 1.1 cm Pyrex tube equipped with an inner ⟆ 14/35 joint at both ends, packed with ³/₃₂-in. Pyrex helices, and wrapped with a Briskeat heavy-duty heating tape and an outer layer of glass wool. The temperature of the tube (after equilibration for at least 2 hr) was measured by means of a dual-junction iron–constantan thermocouple with one junction placed between the heating tape and the wall of the tube and the other immersed in ice–water. Material to be pyrolyzed was placed in a 10-ml flask and affixed to one end of the tube, with the special receiver shown in Figure 1 affixed to the other end. The apparatus was evacuated (0.001–0.01 Torr), the receiver was cooled to $-78°$ with a Dry Ice–acetone mixture, and the sample was warmed to ca. 40° to promote distillation of the sample through the hot tube. When the sample had completely distilled, the vacuum was released with argon using a syringe needle inserted through the rubber septum on the top of the receiver. The receiver was allowed to warm to $-63°$ (melting point of chloroform) or $-23°$ (melting point of carbon tetrachloride), and the pyrolysate was rinsed from the receiver into the attached nmr tube by injecting 0.3 ml of deuteriochloroform or carbon tetrachloride (containing ca. 1% tetramethylsilane) through the top septum. (Draining of the receiver into the nmr tube is facilitated if the nmr tube–septum assembly is gently "pumped" up and down on the receiver delivery tube.)

a. Pyrolysis of 1. The tetrachlorospirocycle 1 (0.100 g, 0.41 mmol) was passed through the pyrolysis tube at 330° (0.003 Torr)

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(37) R. Huisgen and U. Burger, *Tetrahedron Lett.*, 3053 (1970).

with the collector cooled to 0°. ^{1}H nmr spectral analysis of the light yellow pyrolysate (0.087 g) revealed only two peaks, a singlet at δ 2.17, corresponding to unreacted **1** (22% of the total integrated area), and a singlet at δ 2.37, corresponding, by analogy to other pyrolyses reported herein, to 3-(1,2,3,3-tetrachloroprop-2-enylidene)-1,2-dimethylcyclopropene (78% of the total integrated area, 83% yield based on unrecovered starting material). Although the product could not be purified due to its propensity for thermal and oxidative decomposition, other spectral data, consistent with the proposed structure, were obtained from the mixture: ir 1870 (C=C for 1,2-dimethylcyclopropene)[16] and 1570 cm^{-1} (s, exocyclic double bond of methylenecyclopropene);[16] uv max (isooctane) 303 (ϵ ~10,000) and 260 nm (sh, ϵ ~3000).[16]

b. Pyrolysis of 2. Tetrachlorospirocycle **2** (0.300 g, 1.22 mmol) was distilled through the pyrolysis tube at 460° (0.003 Torr) with the collector cooled to −78°. The product was obtained as a bright yellow oil (0.200 g, 68% based on conversion to C$_8$H$_7$Cl$_3$) which was recrystallized from n-pentane at −78° to yield 0.110 g (0.52 mmol, 55%) of the fulvene **34** as bright yellow needles: mp 26–28°; ^{1}H nmr δ 6.50 (s, 1 H, vinyl H), 2.45 (s, 3 H, CH$_3$), 2.20 (s, 3 H, CH$_3$); ir 1630 (s), 1550, 1440, 1375, 1330 (s), 1280, 1105 cm^{-1}; uv max (isooctane) 378 (ϵ 394), 303 (sh, ϵ 8350), 291 (ϵ 15,300), 284 (ϵ 15,600); mass spectrum (70 eV) parent ion at m/e 207.9613; calcd for C$_8$H$_7{}^{35}$Cl$_3$, 207.9613. The spectral data for this compound are consistent with those observed for similar fulvenes.[8a]

c. Pyrolysis of 20. Samples of trichlorospirocycle **20** (0.150 g, 0.71 mmol) were passed through the pyrolysis tube heated at the following temperatures at 0.008 Torr with the collector cooled to −78° (Dry Ice–acetone). **(1) At 265°.** ^{1}H nmr spectral analysis of the pyrolysate (0.132 g) revealed the presence of only two compounds, unreacted starting material (60% of the mixture) and allylidenecyclopropane **35** (40% of the mixture); δ 7.06 (t, J = 0.8 Hz, 1 H, vinyl H), 1.32 (s, 6 H, CH$_3$), 1.23 (d, J = 0.8 Hz, 2 H, cyclopropyl H). The allylidenecyclopropane, obtained in 72% yield (based on unrecovered starting material), was purified by preparative glpc (10 ft × 0.375 in., 20% FFAP on 60–80 mesh Chromosorb W, 150°): ir 3090 (vinyl H), 1740, 1580 cm^{-1}; uv max (isooctane) 253 (sh, ϵ 18,300), 246 (ϵ 22,300), 239 nm (sh, ϵ 18,500); mass spectrum (70 eV) parent ion at m/e 209.9827; calcd for C$_8$H$_9{}^{35}$Cl$_3$, 209.9770. **2. At 440°.** ^{1}H nmr spectral analysis of the pyrolysate (0.117 g) revealed the presence of only two compounds, fulvene **36** [δ 6.52 (d, J = 6 Hz, 1 H, vinyl H), 6.23 (d, broad, J = 6 Hz, 1 H, vinyl H), 2.45 (s, broad, 3 H, CH$_3$), 2.23 (s, broad, 3 H, CH$_3$)] and methylenecyclopentene **37** [δ 5.34 (s, 1 H, vinyl H), 5.04 (s, 1 H, vinyl H), 4.61 (s, 1 H, C=CCHCl), 1.35 (s, 3 H, CH$_3$), 1.28 (s, 3 H, CH$_3$)] in the respective ratio 1:2.5 (81% yield overall). The fulvene **36** was found to be quite thermally labile and oxygen-sensitive, rapidly forming a dark intractable tar at 25°, and has thus far not been isolated in high purity. However, titration of the mixture of **36** and **37** with a solution of 4-phenyltriazoline-3,5-dione in methylene chloride at 0° until the red color of the dienophile persisted,[38] although not yielding an isolable adduct of **36**, gave, upon removal of the solvent in vacuo and shortpath distillation (30° (0.001 Torr)) of the residue, a pure sample of **37** as a light-yellow oil: ir 1640, 1590, 885 cm^{-1} (C=CH$_2$); uv max (isooctane) 247 nm (ϵ 15,000); mass spectrum (70 eV) parent ion at m/e 209.9752; calcd for C$_8$H$_9{}^{35}$Cl$_3$, 209.9770.

d. Pyrolysis of 35. The allylidenecyclopropane **35** (0.050 g, 0.24 mmol) was passed through the pyrolysis tube at 440° (0.01 Torr) with the collector at −78° (Dry Ice–acetone). ^{1}H nmr spectral analysis of the bright-yellow pyrolysate (0.041 g, 86%) revealed a mixture identical in composition with that obtained from pyrolysis at **20** under the same conditions (see above).

e. Pyrolysis of 19. The tetrachlorospirocycle **19** (0.100 g, 0.47 mmol) was passed through the pyrolysis tube at 440° (0.01 Torr) with the collector cooled to −78° (Dry Ice–acetone). ^{1}H nmr spectral analysis (CDCl$_3$) of the bright-yellow pyrolysate (0.074 g, 84%) revealed the presence of only two compounds, fulvene **36** and methylenecyclopentene **37** (see section c, part 2 above) in the respective ratio 1:2.2.

f. Pyrolysis of 3, 14, and 15. Individual samples of the tetrachlorospirocycles **3, 14,** and **15** (0.050 g, 0.20 mmol) were passed through the pyrolysis tube at 450° (0.003 Torr) with the collector cooled to −78° (Dry Ice–acetone). ^{1}H nmr spectral analysis of each of the bright-yellow pyrolysates (ca. 85% yield in each case) revealed a complex pattern, in each case completely superimposable with that obtained for the other two samples: δ 6.58 (six peaks, 1 H), 2.2 (six peaks, 6 H). ^{1}H nmr spectra at 100 MHz were much

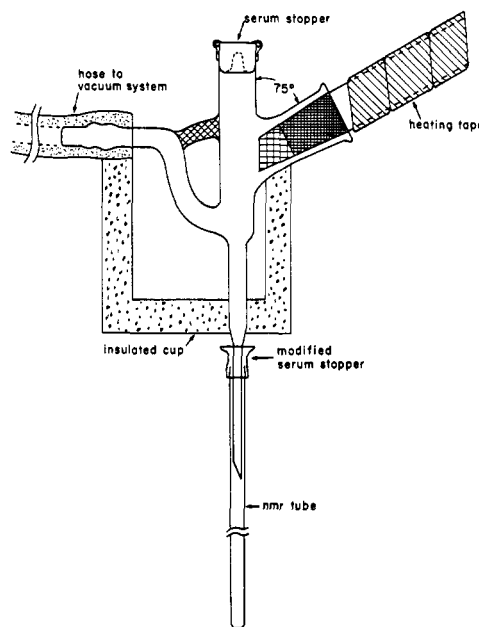(38) J. C. Stickler and W. H. Pirkle, J. Org. Chem., **31**, 3444 (1966).

Figure 1. Pyrolysate collector.

simpler, revealing a downfield pattern consisting of two overlapping quartets (J = 8.0 Hz for each) centered at δ 6.67 and 6.55 in the respective ratio 1:1.7. The upfield pattern became two sets of doublets (J = 8.0 Hz, 3 H each) at δ 2.20 and 2.35 and two singlets (3 H each) at 2.23 and 2.00 in the identical ratio (1:1.7), completely consistent with the postulated mixture of fulvenes **40** and **41**. Efforts to separate and purify these labile compounds have thus far met with failure, so that no other data on the individual components are yet available.

g. Pyrolysis of 21. The trichlorospirocycle **21** (0.100 g, 0.48 mmol) was passed through the pyrolysis tube at 225° (0.01 Torr) with the collector cooled to −78° (Dry Ice–acetone). The pyrolysate collected as an amorphous yellow-white solid which proved to be practically insoluble in carbon tetrachloride or deuteriochloroform. No data could be obtained on the material.

Thermal Rearrangement of 20 in Carbon Tetrachloride Solution. Trichlorospirocycle **20** (0.075 g, 0.35 mmol), dissolved in 0.3 ml of carbon tetrachloride containing ca. 1% tetramethylsilane, was sealed in a standard 5-mm nmr sample tube and immersed in an oil bath heated to 125 ± 2°. ^{1}H nmr spectra of the contents of the tube were obtained at intervals of 4–6 hr. Spirocycle **20** was observed to disappear with a half-life of ca. 36 hr. The peaks characteristic of **35** appeared, reaching maximum intensity after ca. 25 hr, then disappeared with concomitant appearance of peaks assigned to **36** and **37**. After 144 hr, only the signals due to the methylenecyclopentene **37** were observed from the dark-brown sample. The contents of the tube were distilled in a short-path apparatus (35° (0.001 Torr)) to give 0.041 g (55%) of **37**.

Thermal Rearrangement of 21 in Carbon Tetrachloride Solution. A sample of trichlorospirocycle **21** (0.075 g, 0.36 mmol), dissolved in 0.3 ml of carbon tetrachloride containing ca. 10 μl of 1,4-dioxane as an internal standard, was sealed in a standard 5-mm nmr sample tube and inserted into an ^{1}H nmr probe heated to 60 ± 1°. The ^{1}H nmr spectrum was observed at intervals of 5–10 min and the concentration of **21** was determined as the ratio of the integral of the signal due to the proton at C-6 (δ 4.67) to the dioxane signal. The disappearance of **21** was found to be cleanly first order, with k_1 = 8.47 ± 0.88 × 10^{-5} sec^{-1} (R = 0.96 from a least-squares analysis) over an observation period of ca. 3 hr, giving a half-life of 8200 sec. Similar determinations at 25 and 90° gave half-lives of, respectively, ca. 17 hr and ca. 10 min. During all of these experiments, new signals appeared at δ 6.25 (s, 1 H) and 2.33 (s, 6 H) during the initial stages but disappeared rapidly to leave only broad absorptions in these regions. No identifiable products were isolated from the final mixture.

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