data suggest they are mono- and bicyclic substances. These compounds are relatively inactive.[29]

I wish to thank the National Institutes of Health for support of that porton of the described work performed in my laboratories. I especially express my gratitude to Drs. Roeller and Dahm for a fruitful, enjoyable, and exciting collaboration in our work on juvenile hormone.

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(29) NOTE ADDED IN PROOF. Two recent articles report testing a wide range of compounds for juvenile hormonal activity—many related to the *cecropia* hormone. See V. B. Wigglesworth, *J. Insect Physiol.*, **15**, 73 (1969); V. Jarolim, K. Hejno, F. Sehnal, and F. Sorm, *Life Sci.*, Part II, **8**, 831 (1969).

Conjugated Cyclic Chlorocarbons

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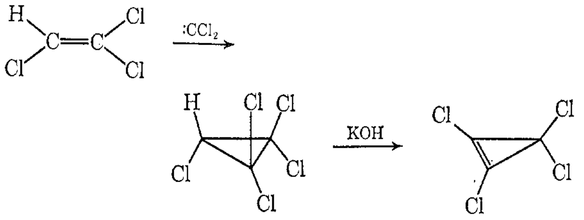
The chlorocarbons—highly or fully chlorinated organic compounds—have long been known and are manufactured on a large scale as solvents, insecticides, and flame retardants. The chemistry of the chlorocarbons has, however, been relatively underdeveloped in recent decades. Chlorocarbon chemistry now is undergoing a rebirth in which many of the most interesting findings are concerned with the family of cyclic conjugated polyenes, $(CCl)_n^{m\pm}$ (Figure 1). Of these compounds, only hexachlorobenzene (**5**) was known before 1964, but within the last 5 years the species $C_3Cl_3^+$, $C_7Cl_7^+$, and C_8Cl_8 have been isolated, and excellent evidence has been presented for the existence of C_4Cl_4, $C_5Cl_5^+$, and $C_5Cl_5^-$. Many of these species are highly reactive and give rise to derivatives with unusual electronic structures.

The family of species in Figure 1, like the cyclic polyenes from which they are derived, can be classified as aromatic if they contain $4n + 2$ and antiaromatic if they contain $4n$ π electrons.[1] Thus **1**, **4**, **5**, and **6** can be considered aromatic and so are expected to be stabilized, but **2**, **3**, and **7** are antiaromatic and should be destabilized, at least when planar. However, the chlorine substituents may perturb the carbocyclic π system by either withdrawing electronic charge inductively through the C–Cl σ bonds or by direct participation of the nonbonding pairs on the chlorine in π interaction with carbon. Fragmentary evidence suggests that both effects may be significant in certain delocalized chlorocarbons.

Trichlorocyclopropenium Ion. The smallest of the new species, and the first to be isolated, was the trichlorocyclopropenium ion, $C_3Cl_3^+$ (**1**).[2] The discovery of trichlorocyclopropenium followed closely upon the synthesis of tetrachlorocyclopropene (**9**).[3] A tetrahalocyclopropene was desired as a precursor to the still-unknown compound "deltic acid," or dihydroxycyclopropenone.[4] A logical route to **9** is dehydrochlorination of pentachlorocyclopropane (**8**), which in turn might be prepared by addition of dichlorocarbene to trichloroethylene (eq 1). The difficulty is that trichloroethylene is a rather unreactive olefin toward carbene addition. However, when CCl_2 is obtained by thermolysis of sodium trichloroacetate in dimethoxyethane at 80°, it will add to trichloroethylene in 25% yield to produce **8**,[5] which is smoothly dehydrochlorinated by warm concentrated aqueous KOH to give **9**, a colorless liquid, bp 130–131°.[6] This method has recently found use in the commercial synthesis of tetrachlorocyclopropene, which is an effective fumigant as well as a useful intermediate.[7]



8 **9**

(1)

When **9** was mixed with aluminum chloride or other powerful chloride acceptor Lewis acids ($SbCl_5$, $GaCl_3$, or $FeCl_3$), stable, colorless crystalline salts of the trichlorocyclopropenium ion (**1**) were formed.[8] These compounds all have very simple infrared spectra, consistent with the symmetrical formulation for **1**. At the time it was discovered, **1** was the simplest aromatic species known[9] and seemed well suited for structural studies. Vibrational analysis was used to investigate the chemical bonding in **1**. The infrared and Raman frequen-

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(1) R. Breslow, J. Brown, and J. Gajewski, *J. Am. Chem. Soc.*, **89**, 4383 (1967).

(2) S. W. Tobey and R. West, *ibid.*, **86**, 1459 (1964).

(3) S. W. Tobey and R. West, *Tetrahedron Letters*, 1179 (1963).

(4) Hydrolysis of **9** gives, however, none of the desired dihydroxycyclopropenone, but leads instead to the ring-opened product α,β-dichloroacrylic acid or its anhydride.

(5) S. W. Tobey and R. West, *J. Am. Chem. Soc.*, **88**, 2478 (1966).

(6) S. W. Tobey and R. West, *ibid.*, **88**, 2481 (1966).

(7) E. E. Gilbert, U. S. Patent 3,251,735 (May 17, 1966); *Chem. Abstr.*, **65**, 2944*h* (1966).

(8) R. West, A. Sadô, and S. W. Tobey, *J. Am. Chem. Soc.*, **88**, 2488 (1966).

(9) The cyclopropenium ion itself, $C_3H_3^+$, has recently been prepared. See R. Breslow, J. Groves, and G. Ryan, *ibid.*, **89**, 5048 (1967).

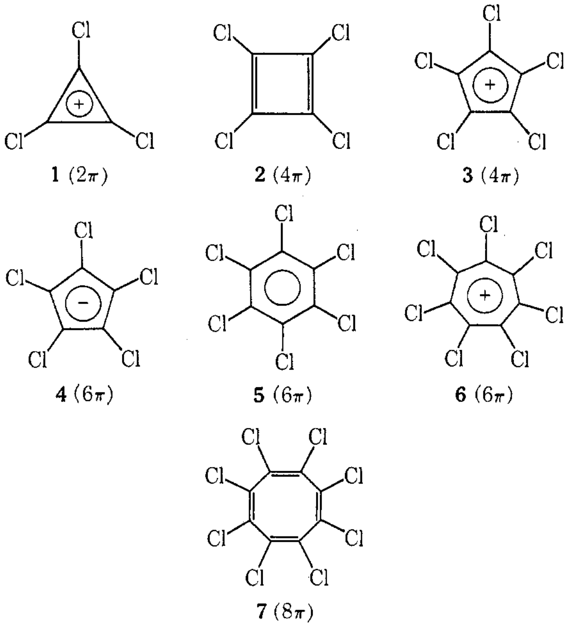

Figure 1. The known cyclic conjugated chlorocarbons. The number of π electrons in the carbocyclic system is given in parentheses below each structure.

cies for the trichlorocyclopropenium ion and their assignments are given in Table I. Normal coordinate analysis using the Urey–Bradley force field led to force constants, of which the most important are the C–C and C–Cl stretching constants, given in Table II along with similar data for other aromatic species. The carbon–carbon stretching force constant for **1** is much larger than for benzene, hexachlorobenzene, etc.[8] Therefore the C–C bond in **1**, and probably in cyclopropenium ions generally,[10] must be *shorter and stronger than in any other known aromatic compounds.*

Table I
Vibrational Frequencies for $C_3Cl_3^+$

Cm^{-1}	Ir	Raman	Assignment
200	s		E
459		s, polarized	A_1
735	s	vw	E
1312	vs	s, depolarized	E
1348	s		
1791		m, polarized	A

Table II
C–C and C–Cl Stretching Force Constants for Aromatic Species[8]

	Kcc	*Kcx*	ρ^a
C_6H_6	5.59	4.67	0
	5.15	4.79	0.35
$C_5H_5^-$	5.39	4.79	0.21
C_6Cl_6	4.81	2.30	0.37
$C_3Cl_3^+$	6.32	2.99	0

[a] ρ = resonant constant.

Why should the C–C bond in cyclopropenium ions be so strong? Simple Hückel calculations predict a π bond order of 0.667 for cyclopropenium, identical with that for benzene. The σ bonding in cyclopropenium ions is probably external to the ring and "bent" even more strongly than in cyclopropane or cyclopropene (Figure 2); if so, the σ bonds should be weaker than those in benzene. However, bending of the σ bonds may bring the carbon atoms closer together, allowing for much increased overlap of p orbitals on adjacent carbon atoms. According to this model the unprecedented bond strength in **1** arises from the increased π bonding in cyclopropenium ions, which more than makes up for the decreased σ bond strength.[11]

In **1**, contributions from the chlorine atoms to the π bonding may also aid in raising the C–C bond strength and force constant. The C–Cl stretching force constant for **1** is also abnormally large; nuclear quadrupole resonance measurements give a value of 0.35 for the asymmetry parameter η for the ^{35}Cl nuclei in **1**.[12] This asymmetry parameter can be related directly to the partial double bond character, which is found to be 0.16. Both the asymmetry parameter and the bond order are higher than for any other known carbon–chlorine compound. The data suggest that about half of the positive charge on the ring (3 × 0.16) is delocalized through the π system onto the chlorine atoms.[12]

Not only is **1** unusually interesting from the structural point of view, it is also a highly versatile species in chemical reactions. Rapid hydrolysis, as by quenching in water, converts the tetrachloroaluminate salt of **1** back to **9**. Formation of this product indicates that water attacks $AlCl_4^-$ much more rapidly than it does **1**, forming chloride ion which combines with **1**.[13] Slow hydrolysis of **1** with water or alcohols leads, however, to an intermediate aluminum complex (**10**) which can be further hydrolyzed to dichlorocyclopropenone (**11**)[14] (Scheme I). We found the latter to be a treacherously unstable liquid, but before this was known a 40-g sample detonated in our laboratories, causing serious damage.[15] Controlled decomposition of **10** leads to the spirolactone **12** (similar spirolactone formation is known for other cyclopropenones).[16] On further alcoholysis, **10** is converted to alkoxychlorocyclopropenones (**13**).[17]

A most useful reaction of **1** is Friedel–Crafts-type condensation with aromatic hydrocarbons, leading to

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[10] The C–C bond length in the three-membered ring in triphenylcyclopropenium perchlorate is 1.373 Å, compared to 1.39 Å for benzene. See M. Sundralingham and L. H. Jensen, *J. Am. Chem. Soc.*, **88,** 198 (1966).

[11] If this reasoning is correct for cyclopropenium ions generally, it follows that large repulsion forces involving the σ electrons must limit the C–C bond distance in conventional aromatic hydrocarbons.

[12] E. A. C. Lucken and C. Mazeline, *J. Chem. Soc., A,* 153 (1968). The nqr assignments for C_3Cl_4 given in this paper are in error; see R. M. Smith and R. West, *Tetrahedron Letters,* 2141 (1969).

[13] Regeneration of a chlorocarbon from its ionic $AlCl_3$ adduct on hydrolysis is frequently observed. See, for example, R. West and P. T. Kwitowski, *J. Am. Chem. Soc.*, **88,** 5280 (1966).

[14] R. West. J. Chickos, and E. Ōsawa, *ibid.*, **90,** 3885 (1968).

[15] Amounts of 11 up to 1 g have been made repeatedly in our laboratories. Such small samples occasionally undergo rapid decomposition between 0° and room temperature, but without explosion.

[16] A. Krebs, *Angew. Chem., Intern. Ed. Engl.*, **4,** 10 (1965). This paper gives a good review of cyclopropenium ion chemistry through 1964.

[17] J. Chickos and R. West, unpublished work.

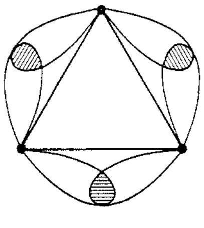
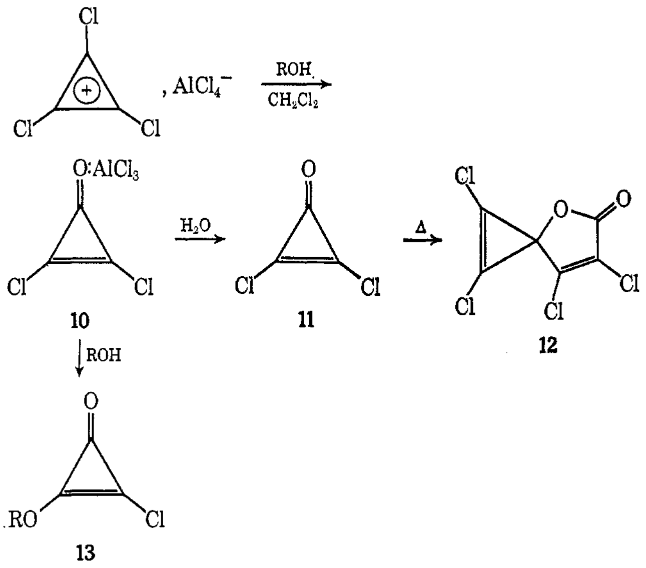


Figure 2. Schematic drawing of orbitals forming C–C bonds in cyclopropenium ions, indicating overlap external to the three-membered ring.

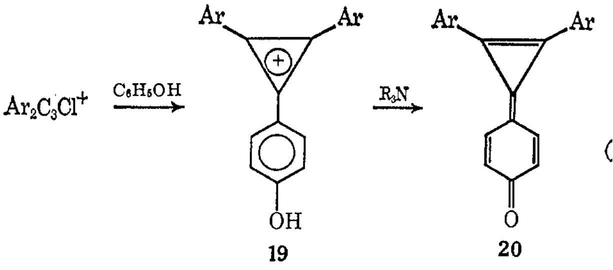
Scheme I



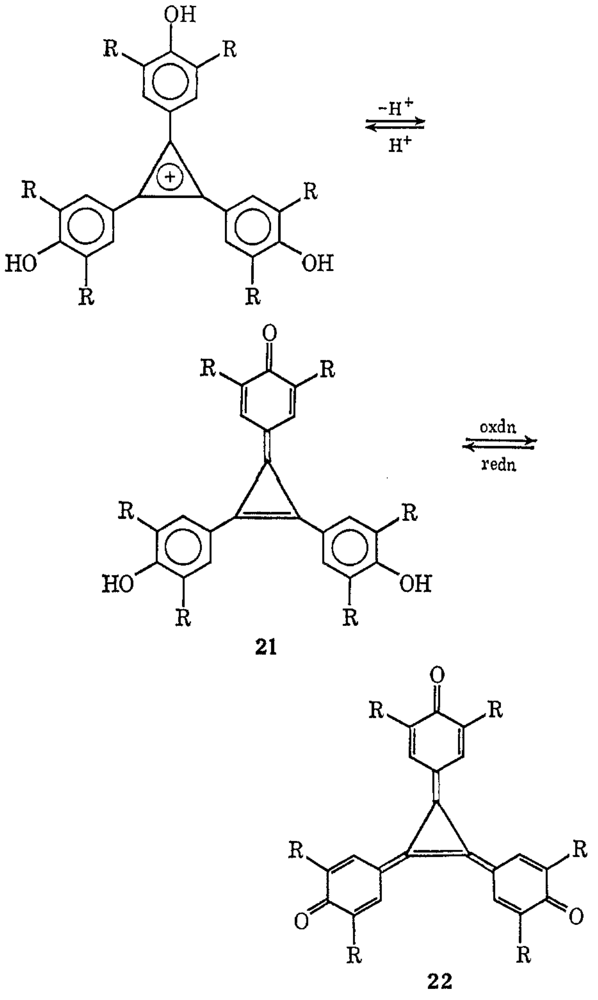
mono-, di-, or triarylcyclopropenium ions[18] (Scheme II). The three substitutions can be carried out either stepwise or all at once, so the three aryl groups can be the same or different. However, the final step to form the *tri*arylcyclopropenium salt apparently requires use of an activated aromatic compound.

The various arylchlorocyclopropenium salts give rather different products on hydrolysis. Quenching with water converts aryldichlorocyclopropenium compounds to 1-aryltrichlorocyclopropenes (**14**), which can be further hydrolyzed, probably *via* arylchlorocyclopropenones, to arylhydroxycyclopropenones (**15**).[14,17] The latter are, like phenylhydroxycyclobutenedione,[19] strong acids (p$K \sim 2$) because of extensive delocalization of the negative charge in the anion.[17,20] Diarylchlorocyclopropenium salts hydrolyze to covalent 1,2-diaryl-3,3-dichlorocyclopropenes (**16**) and thence to diarylcyclopropenones (**17**), which can be reconverted to **16** with thionyl chloride.[21] Finally, the triarylcyclopropenium salts, as Breslow has shown earlier,[22] hydrolyze reversibly to triarylcyclopropenyl ethers (**18**).

Particularly interesting products are obtained when phenols are used as the aromatic compounds in reactions in Scheme II. If a diarylchlorocyclopropenium ion, for instance, is treated with a phenol, the product is a *p*-hydroxyaryldiphenylcyclopropenium salt (**19**), as expected. The latter, however, contains a phenolic proton easily removed by treatment with mild base, converting **19** to an orange or yellow diarylquinocyclopropene (**20**) (eq 2).[23] If all three aromatic groups allowed to react with **1** are phenols (preferably 2,6-disubstituted), tris(*p*-hydroxyaryl)cyclopropenium ions are formed; these readily lose protons to form bis(hydroxyaryl)quinocyclopropenes (**21**). The latter undergo reversible oxidation to yield a remarkable new class of compounds, the triquinocyclopropanes (**22**) (eq 3).[23]



(2)



(3)

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[18] R. West, D. C. Zecher, and W. Goyert, *J. Am. Chem. Soc.*, **92**, 149 (1970).

[19] E. J. Smutny, M. C. Caserio, and J. D. Roberts, *ibid.*, **82**, 1793 (1960).

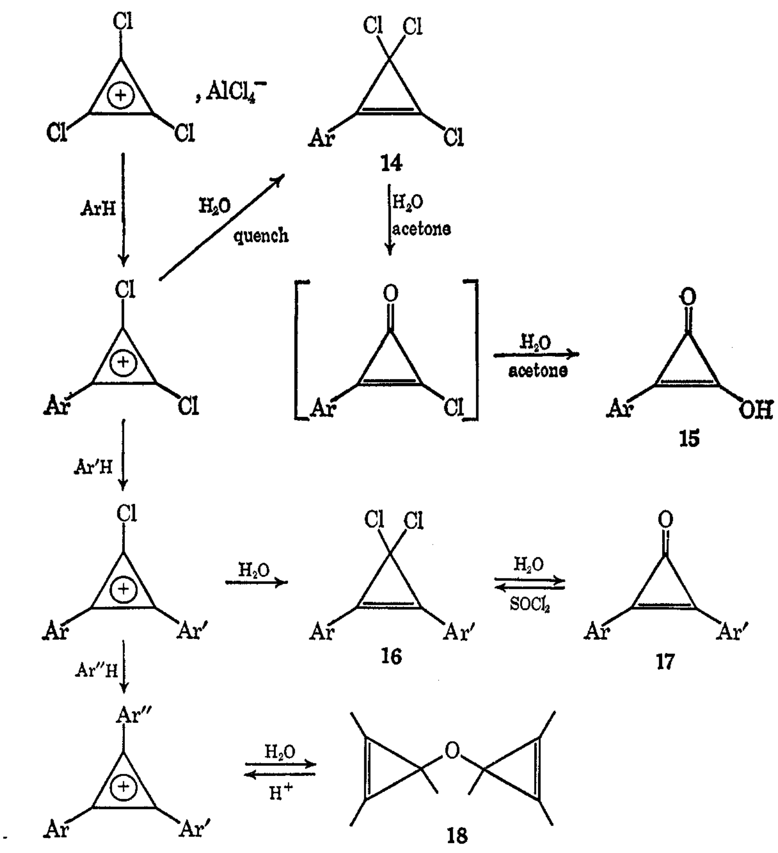
[20] D. Farnum, J. Chickos, and P. Thurston, *ibid.*, **88**, 3075 (1966).

[21] S. W. Tobey and R. West, *ibid.*, **86**, 4215 (1964); R. West, D. C. Zecher, and S. W. Tobey, *ibid.*, **92**, 168 (1970).

[22] R. Breslow and H. W. Chang, *ibid.*, **83**, 2367 (1961).

[23] R. West and D. C. Zecher, *ibid.*, **89**, 152 (1967); **92**, 155 (1970).

Scheme II

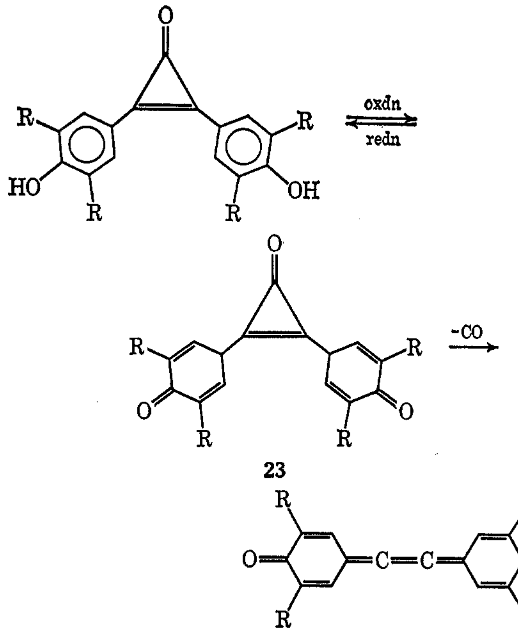


Triquinocyclopropanes are intensely purple crystalline solids, with electronic absorption throughout the visible and extending into the near-infrared region, corresponding to very easy electronic excitation. Although they are derivatives of 3-radialene, they are very much more stable than other known 3-radialenes. The compound **22** with R = *t*-butyl will withstand brief heating to 280°.

Other compounds with novel electronic structures are obtained when phenol condensation with **1** is carried only to the disubstitution stage. Hydrolysis gives a dihydroxydiarylcyclopropenone, which on oxidation gives a violet diquinocyclopropanone, **23**. This spontaneously decarbonylates, yielding a diquinoethylene, **24**, a cumulene derivative[24] (eq 4).

Recently Tobey has found that **1** will also react with certain partially halogenated olefins such as 1,1-dichloroethylene, to give (after hydrolysis) divinylcyclopropenones[25] (eq 5).

A final reaction of interest is halogen exchange, which leads to new halogenated cyclopropenes and cyclopropenium ions. If **9** is simply mixed with liquid boron tribromide a self-warming reaction takes place in which BCl_3 is liberated and *all four* chlorine atoms in **9** are replaced by bromine.[3] The reaction most probably takes place through the formation of **1** as an intermediate and successive Br–Cl exchange reactions (Scheme III). The resulting tetrabromocyclopropene gives salts of the tribromocyclopropenium ion $C_3Br_3^+$ with, *e.g.*, aluminum bromide. Reactions of $C_3Br_3^+$ have not been studied but will probably resemble those of **1**.



(4)

Exchange of fluorine for chlorine on **9** takes place with the SbF_3–$SbCl_5$ mixture often used for fluorination of

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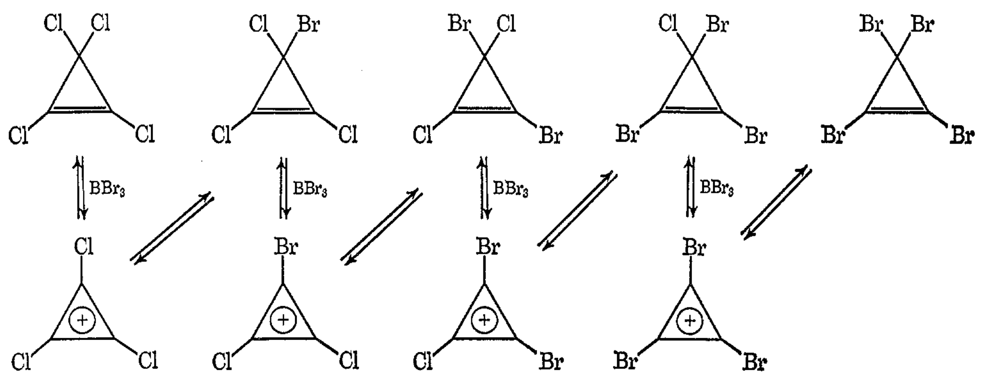
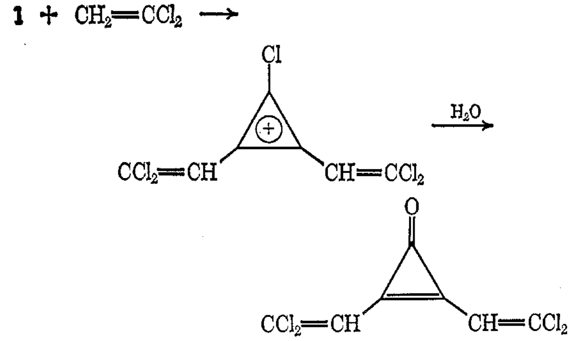
[24] D. C. Zecher and R. West, *J. Am. Chem. Soc.*, **89**, 153 (1967).

[25] S. W. Tobey, K. S. Wittemore, and M. Z. Laurandos, Abstracts of Papers, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968, No. ORGN 168.

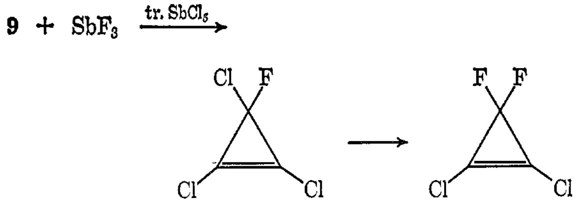
Scheme III





(5)

organic chlorides, in a reaction which also probably proceeds through **1**. However, only the two geminal chlorines are replaced under these conditions, in a stepwise reaction[3,26] (eq 6).



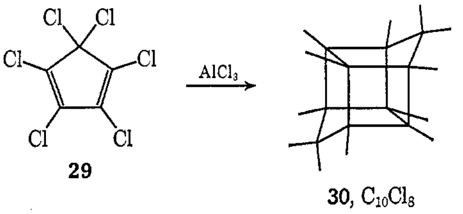
(6)

Tetrachlorocyclobutadiene (2). Evidence for this antiaromatic chlorocarbon as a reaction intermediate results from Scherer's[27] recent experiments on the dehydrohalogenation of 3H-pentachlorocyclobutene with KOH in refluxing benzene. In the presence of styrene or cyclohexadiene the *c*-C_4Cl_4 fragment is trapped stereospecifically as **25** or **26**, respectively (Scheme IV). In the absence of a reactive diene or dienophile a C_8Cl_8 isomer is produced. The latter compound has been studied by X-ray crystallography with results which agree well for octachlorocubane (**28**). However, the infrared spectrum (showing double bond absorptions) and the ultraviolet maximum at 238 nm are both inconsistent with **28** but fit the proposed structure, **27** (Scheme IV). Scherer suggests that the nearly cubic molecules of **27** pack into the crystal lattice with random orientation, leading to averaging of the atomic coordinates.[27]

Tetrachlorocyclobutadiene is almost certainly an intermediate in the reactions described above, and if so is generated with remarkable ease, perhaps because of stabilization of the cyclobutadiene structure by π bonding involving the chlorine p orbitals.[27] Further studies of perhalocyclobutadienes should be of considerable interest in this connection.

Pentachlorocyclopentadiene Cation (3). The $C_5Cl_5^+$ cation has only four π electrons from the carbon atoms and so, like tetrachlorocyclobutadiene, can be classed as antiaromatic. In agreement with this prediction $C_5Cl_5^+$ is highly reactive. There is, however, some indication that π donation from chlorine increases the net charge in the carbocyclic ring and so stabilizes $C_5Cl_5^+$ somewhat.

The $C_5Cl_5^+$ cation is most probably involved in the well-known dimerization of hexachlorocyclopentadiene (**29**) to the "Prins dimer" (**30**), which takes place in the presence of strong Lewis acids such as $AlCl_3$[28] or $SbCl_5$ (eq 7). With $AlCl_3$ an intermediate red complex $C_5Cl_6 \cdot AlCl_3$ can be isolated.[29] The latter is not an ionic salt, but seems to be a partially ionic, chlorine-bridged complex, **31**.



(7)

Evidence for the actual existence of $C_5Cl_5^+$ comes from electron spin resonance experiments on solutions of C_5Cl_6 in antimony pentafluoride. Like other antiaromatic species, **3** is potentially capable of existence in

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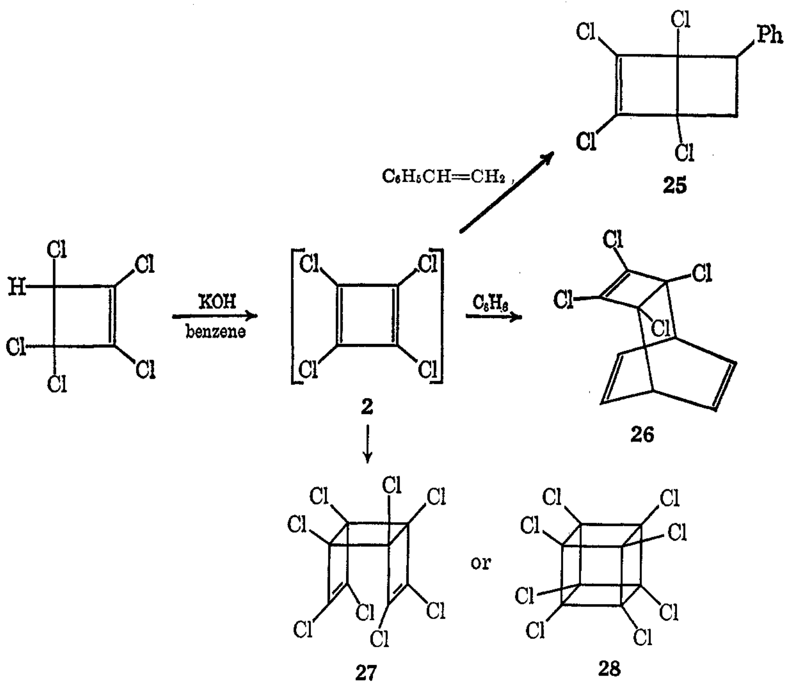
[26] Other methods have recently been used to obtain chlorotrifluorocyclopropene and tetrafluorocyclopropene; the latter gives trifluorocyclopropenium ion with SbF_5. See D. C. F. Law, Ph.D. Thesis, University of Wisconsin, 1967, and P. B. Sargeant and C. G. Krespan, *J. Am. Chem. Soc.*, **91**, 415 (1969).

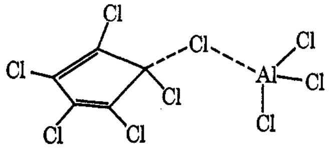
[27] K. V. Scherer, Jr., and T. J. Meyers, *ibid.*, **90**, 6253 (1968).

[28] H. J. Prins, *Rec. Trav. Chim.*, **65**, 455 (1946). For other reactions of **2a** which might involve the ion **3**, see H. E. Ungnade and E. T. McBee, *Chem. Rev.*, **58**, 249 (1958).

[29] H. P. Fritz and L. Schäfer, *J. Organometal. Chem.*, **1**, 318 (1964). A similar red complex is formed between **29** and $SbCl_5$; see P. T. Kwitowski, Ph.D. Thesis, University of Wisconsin, 1966.

Scheme IV

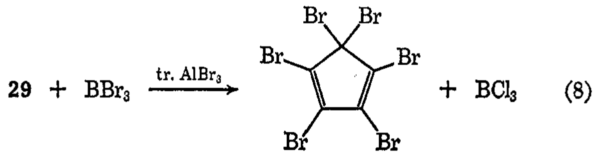




31

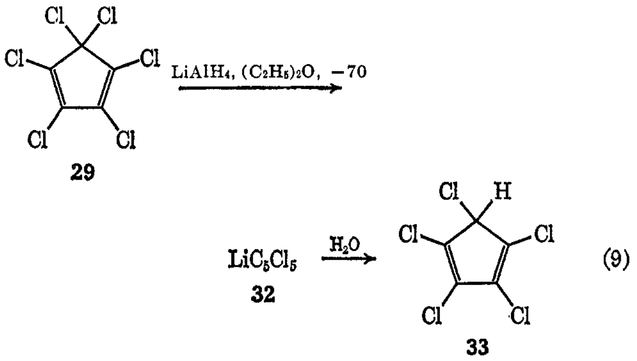
a triplet state, with two unpaired electrons. Esr lines for the triplet species were observed, showing that $C_5Cl_5^+$ exists at least in part in a triplet state below 77°K, and temperature variation experiments indicated that the triplet state is the ground state for **3**. However, conversion of **29** to **3** is low.[30]

Ionic chlorine–bromine exchange does not take place between **29** and boron tribromide. No reaction occurs even at elevated temperatures, probably because BBr_3 is not sufficiently strong as a Lewis acid to remove chloride from C_5Cl_6. With aluminum tribromide, **29** gives only the Prins dimer, **30**. However, if **29** is dissolved in BBr_3 and a *trace* of $AlBr_3$ is added, halogen exchange takes place smoothly (eq 8) and C_5Br_6 is formed,[31] undoubtedly through $C_5Cl_5^+$ and partially brominated cyclopentadiene cations as intermediates. C_5Br_6 itself reacts with $AlBr_3$ to form a perbrominated dimer, $C_{10}Br_{12}$, isostructural with **30**.



Pentachlorocyclopentadienide (4). This ion has six π electrons and so should be aromatic, but recent experiments show that $C_5Cl_5^-$ is rather unstable, decomposing above 0°.

Lithium pentachlorocyclopentadienide (**32**) was first mentioned in 1955 as the probable product of $LiAlH_4$ reduction of C_5Cl_6 at low temperature, which produced hydrogen gas and (after hydrolysis) 1,2,3,4,5-pentachlorocyclopentadiene (**33**)[32] (eq 9). The chemistry of the lithium derivative **32** has recently been investigated by McBee, Halling, and Morton.[33] These workers found that **32** can be made from **29** and lithium metal, either with or without zinc chloride as a catalyst. We have obtained the same lithium derivative from **33** and alkyllithium compounds.[34] **32** is a remarkably weak nucleophile, perhaps reflecting its aromatic stabilization. In the absence of Lewis acids it is unreactive



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(30) R. Breslow, H. Chang, R. Hill, and E. Wasserman, *J. Am. Chem. Soc.*, **89**, 1112 (1967).

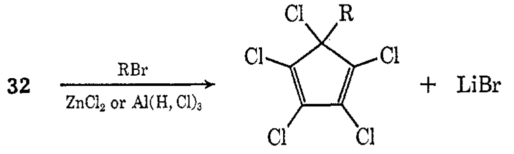
(31) R. West and P. T. Kwitowski, *ibid.*, **90**, 4697 (1968). Hexabromocyclopentadiene has long been known as a product of other syntheses, and some of its reactions are known. See, for example, R. G. Pews and C. W. Roberts, *J. Org. Chem.*, **34**, 2029 (1969).

(32) E. T. McBee and D. K. Smith, *J. Am. Chem. Soc.*, **77**, 389 (1955).

(33) E. T. McBee, R. A. Halling, and C. J. Morton, unpublished studies. R. A. Halling, Ph.D. Thesis, Purdue University, 1965; *Dissertation Abstr.*, **B27** (2), 409 (1966).

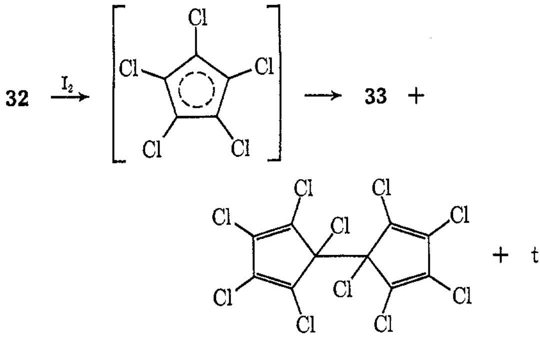
(34) G. Wulfsberg and R. West, unpublished results.

toward alkyl halides, but with $ZnCl_2$ or aluminum chlorohydrides present it gives 5-alkyl derivatives[33] (eq 10). However, even in the presence of Lewis acids,



(10)

32 does not react with ketones or aldehydes. Iodine oxidizes **32** to a mixture of products including **33** and bis(pentachlorocyclopentadienyl) (**34**), probably through the intermediate formation of the $C_5Cl_5\cdot$ radical[33] (eq 11).



(11)

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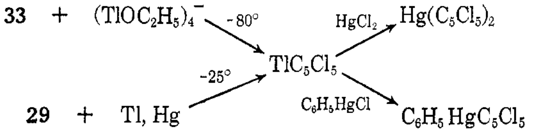
Decomposition of LiC_5Cl_5 takes place above 0°, forming mostly tarry products. No structural work on **32** has been carried out, so it is not known whether it is an ionized salt of **4** or a covalent, σ-bonded lithium compound. Recently the unstable thallium derivative of C_5Cl_5 has been made by several methods and used to prepare the first stable organometallic derivatives, $C_6H_5HgC_5Cl_5$ and $Hg(C_5Cl_5)_2$.[34] The latter compounds appear to have σ-bonded covalent structures.

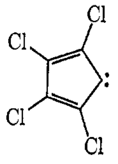


Very recently true salts of $C_5Cl_5^-$ have also been made from **33** and tetraalkylammonium hydroxides at low temperature.[34] The tetra-*n*-butylammonium salt

$$\mathbf{33} + n\text{-}Bu_4N\ {}^+OH^- \longrightarrow n\text{-}Bu_4N\ {}^+C_5Cl_5^-,\ \mathbf{35}$$

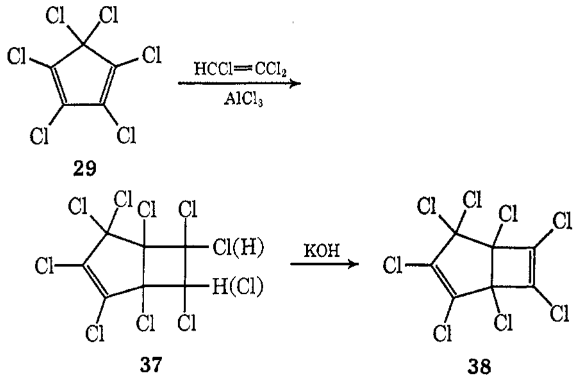
(**35**) is a colorless crystalline compound which decomposes slowly at 0° and within 30 min at 25° to **33**, **34**, and polymeric products. Salts of **4** with smaller tetraalkylammonium counterions decompose at still lower temperatures.

It is evident that **4** is quite unstable, in spite of the fact that it has six π electrons and so can be considered aromatic. Salts or covalent organometallic derivatives of **4** are nevertheless usable at low temperatures, and further developments in their chemistry may be expected. In particular, they may prove convenient sources of the useful carbene, tetrachlorocyclopentadienylidene[35] (**36**).

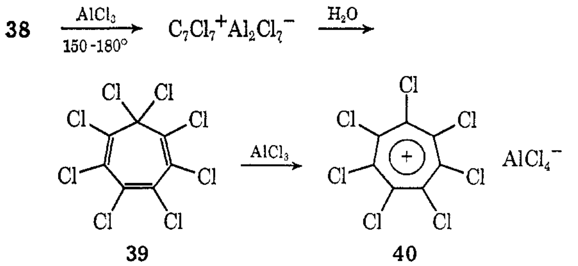


36

Heptachlorotropylium Ion (**6**). Tropylium ion, $C_7H_7^+$, is well known as a stable, six-π-electron cation. Following isolation of $C_3Cl_3^+$, attention was turned to synthesis of the seven-membered ring analog, $C_7Cl_7^+$. Starting material for this synthesis was the bicyclic compound **37** made from **29**, trichloroethylene, and aluminum chloride.[36] Dehydrohalogenation leads to the octachlorobicycloheptadiene **38** (eq 12). Compound **38** reacts with aluminum chloride on warming. Below 150° **38** is regenerated on hydrolysis, and above 180° complete fragmentation occurs, but in the intermediate 30° temperature range isomerization takes place to heptachlorocycloheptatrienium heptachlorodialuminate, which hydrolyzes to octachlorocycloheptatriene (**39**). This is a colorless crystalline compound, mp 86°, which reacts with $AlCl_3$ to form the yellowish tetrachloroaluminate salt **40**[37] (eq 13). With



(12)



$$\mathbf{38} \xrightarrow[150\text{-}180°]{AlCl_3} C_7Cl_7^+Al_2Cl_7^- \xrightarrow{H_2O}$$

(13)

sulfuric acid **39** is transformed to the interesting greenish yellow perchlorotropone (**41**) which has also been synthesized photochemically by Scherer[38] (Scheme V).

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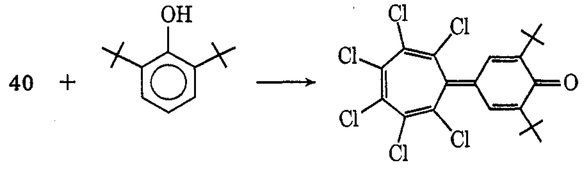
(35) E. T. McBee, J. A. Bosoms, and C. J. Morton, *J. Org. Chem.*, **31**, 768 (1966); E. T. McBee, G. W. Calundann, and T. Hodgins, *ibid.*, **31**, 4260 (1966).

(36) Preparations of **37** and **38** were first reported by J. A. Krynitski and R. W. Bost, *J. Am. Chem. Soc.*, **69**, 1918 (1947), and J. S. Newcomer and E. T. McBee, *ibid.*, **71**, 952 (1949), but the correct structures were assigned only later by A. Roedig and L. Hörnig, *Ann. Chem.*, **598**, 208 (1956).

(37) R. West and K. Kusuda, *J. Am. Chem. Soc.*, **90**, 7354 (1968), and unpublished studies.

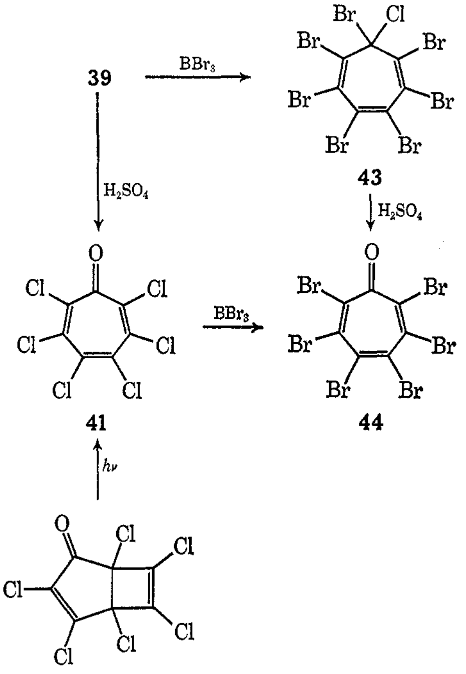
Models indicate that lone pairs on adjacent chlorine atoms would interfere strongly in the ion **6** if it were planar. The geometry of **6** is unknown, but it seems to have much of the aromatic character of tropylium ions generally. It is at least as stable with respect to **39** and Lewis acids as **1** is with respect to its parent chlorocarbon C_3Cl_4. The chemical reactions of **6** also resemble those of **1**. Arylation of **40** takes place with aromatic hydrocarbons. With phenols, arylation is followed by loss of a proton to give "quinotropones"; for example, **42** is obtained from 2,6-di-*t*-butylphenol.[37,39]



42

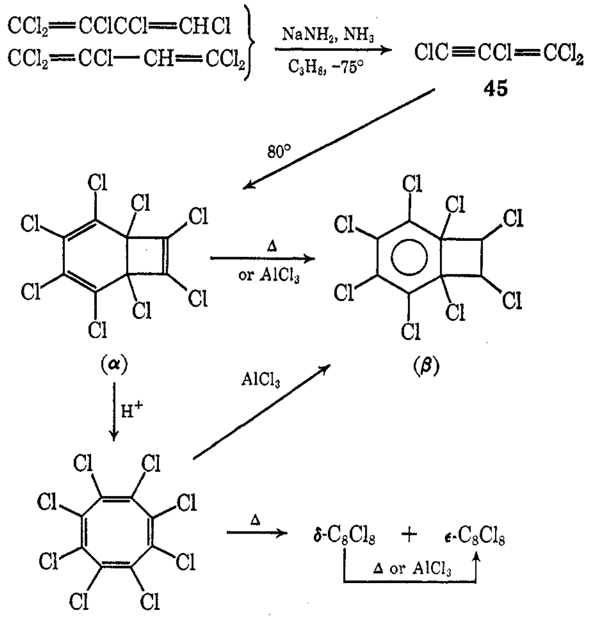
Halogen-exchange reactions involving **6** also take place. When **39** is warmed with boron tribromide, *seven* of the eight chlorine atoms are replaced by bromine, giving C_7Br_7Cl (**43**). The remaining chlorine probably is in the geminal position and resists replacement for steric reasons. With sulfuric acid, C_7Br_7Cl is converted to perbromotropone (**44**), which can also be made from **41** and BBr_3 (Scheme V).[37]

Scheme V



The chemical reactions of **6** and **39** are still little known, but these compounds seem likely to be every bit as useful for further syntheses as their three-membered ring counterparts **1** and **9**.

Scheme VI



Octachlorocyclooctatetraene (7). The highly reactive substance perchlorobuteneyne (**45**) was synthesized by Roedig and Kohlhaupt in 1964.[40] Above 80° **45** spontaneously dimerizes to crystalline α-C_8Cl_8, mp 103° (Scheme VI). This dimer is in turn unstable, isomerizing at 160–180° to octachlorobenzocyclobutene (or β-C_8Cl_8).[41] Lewis acids also convert α- to β-C_8Cl_8, but protonic acids transform α- to yet a third isomer, γ-C_8Cl_8, colorless crystals melting at 172°. The structures of these three C_8Cl_8 isomers have recently been assigned mainly from their ^{35}Cl nuclear quadrupole resonance spectra. γ-C_8Cl_8 is believed to be octachlorocyclooctatetraene.[42]

The evidence for the octachlorocyclooctatetraene structure is the nuclear quadrupole resonance spectrum, which shows all eight chlorines in a narrow frequency range (36.6–37.3 MHz) in the vinyl Cl region; the extremely simple infrared spectrum (only four bands at 1570, 1160, 900, and 730 cm^{-1}) and the ultraviolet spectrum (λ_{max} 237 nm (log ϵ 4.47)) resemble that for octamethylcyclooctatetraene. γ-C_8Cl_8 is such an unreactive compound that the cyclooctatetraene structure was not initially considered. It is inert to halogens, mineral acids, and potassium permanganate, and even survives long boiling with fuming nitric acid.[42] Octakis(trifluoromethyl)cyclooctatetraene, however, is similarly unreactive toward mineral acids and oxidizing agents.[43] Aluminum chloride converts γ-C_8Cl_8 to the β isomer, and upon strong heating γ-C_8Cl_8 is transformed into a mixture of two new C_8Cl_8 isomers, δ and ϵ, whose structures are still uncertain. No other reac-

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(38) K. V. Scherer, Jr., *J. Am. Chem. Soc.*, **90,** 7352 (1968).

(39) Other stable quinotropones have been reported only recently. See J. J. Looker, *J. Org. Chem.*, **32,** 2941 (1967), and B. Föhlisch, *et al.*, *Chem. Ber.*, **101,** 2717, 3990, 4004 (1968).

(40) A. Roedig and R. Kohlhaupt, *Tetrahedron Letters*, 1107 (1964).

(41) A. Roedig, *Angew. Chem.*, **81,** 157 (1969).

(42) A. Roedig, R. Helm, R. M. Smith, and R. West, *Tetrahedron Letters*, 2137 (1969).

(43) B. Ekström, *Chem. Ber.*, **92,** 749 (1959).

tions of γ-C_8Cl_8 have yet been described, but very recently Meyers and Scherer[44] have reported the synthesis of octachlorocyclooctatetraene by thermolysis of **27**.

Conclusions

The discovery of $C_3Cl_3{}^+$ heralded in the presently burgeoning chemistry of the aromatic and antiaromatic cyclic chlorocarbons. All of the family of compounds shown in Figure 1 have now been synthesized, or at least detected in solution. The chlorine substituents appear to stabilize cyclic cations, probably by Cl–C π bonding and consequent charge delocalization. Chlorine may also stabilize the neutral C_nCl_n species.

With the exceptions of **5** and **7**, the cyclic conjugated chlorocarbons are highly reactive species, which give rise to products having unusual and interesting structures. Further important developments in the reaction chemistry of these substances can be expected. Synthesis of the bromine and fluorine ring species analogous to **1–7**, at present mostly unknown, can also be anticipated, as can synthesis of new polycyclic conjugated halocarbons.

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(44) T. J. Meyers and K. V. Scherer, Abstracts of Papers, 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969, No. ORGN-59.