Reactions of Dimethoxycarbene with Cyclic Perchlorinated Olefins and Ketones

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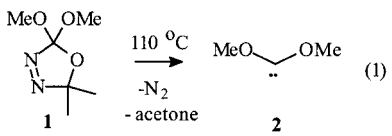
Reactions of dimethoxycarbene (**2**), a carbonyl group equivalent, with perchlorinated olefins and ketones were investigated. Thermolysis of 2,2-dimethoxy-5,5-dimethyl-Δ^3-1,3,4-oxadiazoline (**1**) at 110 °C generated **2**, which reacted with hexachlorocyclopentadiene (**4**), octachlorocycloheptatriene (**12**), octachlorobicyclo[3.2.0]hepta-3,6-diene (**24**), hexachlorotropone (**28**), hexachlorobicyclo[3.2.0]-hepta-3,6-dien-2-one (**32**), and tetrachloro-1,4-benzoquinone (**35**). Reactions of **2** with perchlorinated olefins **4**, **12**, and **24** led to esters or, in the case of **12**, to a ketene acetal. Their formation is rationalized in terms of Michael-like addition and displacement (S_N2' or S_N2'', if concerted) of allylic chlorine atoms by **2**, yielding ion pairs that either dechloromethylate to esters or dechlorinate to a ketene acetal. In contrast, the reactions of **2** with unsaturated perchloroketones **28**, **32**, and **35** led to ring contraction, ring expansion, and aromatization, respectively. The products from these reactions are consistent with nucleophilic addition of **2** at the carbonyl moiety rather than Michael-type addition. Dimethoxycarbene-d_3 was used to show that demethylation in the latter reaction was intermolecular. Mechanisms for the different reaction courses are proposed.

Introduction

Singlet dimethoxycarbene (**2**) is a nucleophile,[1] as a consequence of donation by the lone pairs of the methoxy oxygens into the formally vacant p-orbital of the carbene carbon, which strongly stabilizes the singlet state[2,3] and causes dipolar character. This resonance interaction stabilizes not only the ground state of **2** but also the transition states and dipolar intermediates arising from nucleophilic reactions of **2**.

Dimethoxycarbene (**2**) has been generated from 7,7-dimethoxynorbornadienes,[4] dimethoxydiazirine,[5] hexamethoxycyclopropane,[6] and 2,2-dimethoxy-5,5-dimethyl-Δ^3-1,3,4-oxadiazoline (**1**, eq 1).[7] We chose **1** to study the reactions of **2** with various perchlorinated olefins and perchloroketones.



(1)

The nucleophilic character of **2** is exemplified by its preference for reaction with electron-deficient olefins such as dimethylfumarate, dimethylmaleate,[8] and styrene,[4c] as well as strained olefins,[7d] over more electron-rich olefins such as tetramethylethylene.[1,9] It also undergoes [1+4] cycloadditions with tetraphenylcyclopentadienone,[10] with tropone to give **3** (eq 2),[10] and with tetrazines,[11] by either stepwise or concerted addition of **2**.

Addition of **2** to electron-deficient alkynes such as dimethyl acetylenedicarboxylate (DMAD)[8] can yield cyclopropenone acetal intermediates that can open thermally to give dioxyvinylcarbenes. Thermal ring openings

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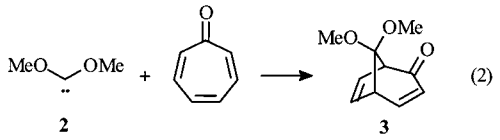


2 3 (2)

of cyclopropenone acetals were used in the construction of complex products, including the natural product colchicine, as well as its analogues, via Boger cycloadditions.[12−14]

Dipolar intermediates may be common in reactions involving nucleophilic attack by **2**. Thermal reactions of **2** with aryl isocyanates or aryl isothiocyanates yield 5,5-dimethoxyhydantoins or 5,5-(dimethoxy)thiohydantoins, respectively.[15] The proposed mechanism involves nucleophilic attack of **2** at the central carbon atom of the isocyanate or isothiocyanate to give a dipolar intermediate that adds to a second molecule of ArNCO or ArNCS. Competition experiments, involving aryl isocyanates,[16] gave a Hammett $\rho = +2.0$, consistent with the proposed mechanism. Reactions of **2** with vinylisocyanates lead to highly functionalized pyrrolinones via formal [1+4] cycloadditions[17] and constitute a key step in the synthesis of tazettine and some analogues,[17] and attack of **2** on 2,4-dinitrofluorobenzene and hexafluorobenzene affords acetals of aroyl fluorides, by nucleophilic aromatic substitution.[18]

In view of the diversity of the known reactions of **2** with unsaturated moieties, it was of interest to ask whether perchlorinated olefins and ketones would also react. Moreover, unsaturated perchloroketones would provide for internal competition between attack by **2** at CC and CO double bonds. Therefore, we undertook a study of reactions of **2**, a carbonyl group equivalent, with cyclic, unsaturated perchloro compounds.

Results and Discussion

Reaction of 2 with Hexachlorocyclopentadiene (4). Thermolysis of **1** at 110 °C in benzene containing **4** afforded **6**, **7**, and **8**, which were isolated by radial chromatography in 24%, 29%, and 34% yields, respectively (Scheme 1). Analysis by GC−MS prior to chromatography showed that **6**, **7**, and **8** were formed in 1.2:1.8:1 ratios. Isomers of **7** and **8** were detected by GC−MS, but they could not be isolated and characterized. Products with molecular weights corresponding to [1+2] or [1+4] adducts were not detected, and none of the minor products had a molecular weight exceeding that of **8**. Thermolysis of **1** in 10-fold excess (relative to **4**, 0.1 M) resulted in a change in the ratios of products. Only a trace of **6** was observed (GC−MS), whereas **7** and **8** were formed in 12% and 76% yields (isolated), respectively.

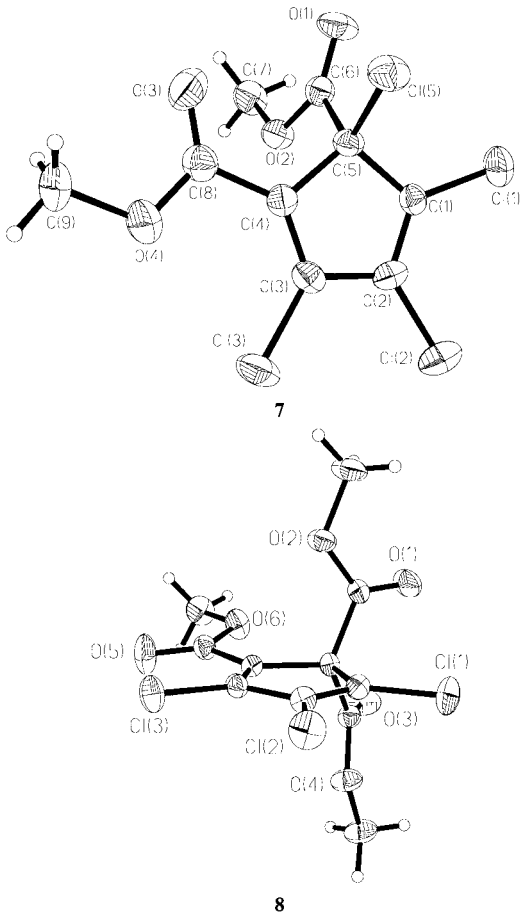
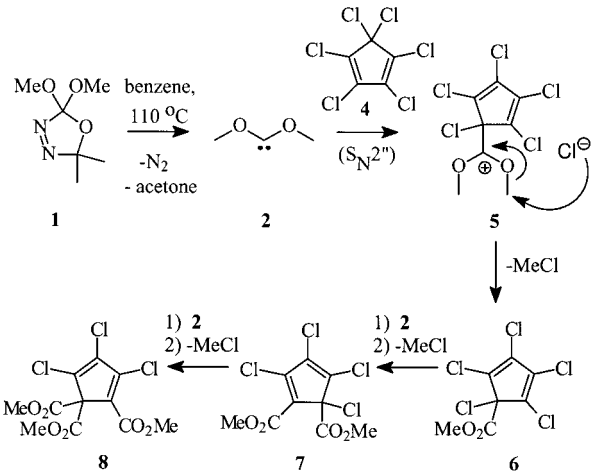


Figure 1.

Scheme 1



Structures of many of the perchloro products in this report could not be assigned unambiguously by means of ^{1}H and ^{13}C NMR spectroscopies and were confirmed by means of X-ray crystallography. Those of **7** and **8** are in Figure 1.

Variable-temperature ^{1}H NMR experiments with **6**, **7**, and **8**, from −80 to 0 °C (CD_2Cl_2) and from 25 to 110 °C (toluene-d_8), showed that the products did not result from 1,5-chlorine or 1,5-ester migrations. Ester groups attached to an sp^2 site, $\delta \sim 3.85$, were distinguishable from those on sp^3 hybridized centers, $\delta \sim 3.75$. Fluxionality in **6**−**8** was not observed. Compound **8** was stable in solution over a period of 24 h at 110−140 °C, and only

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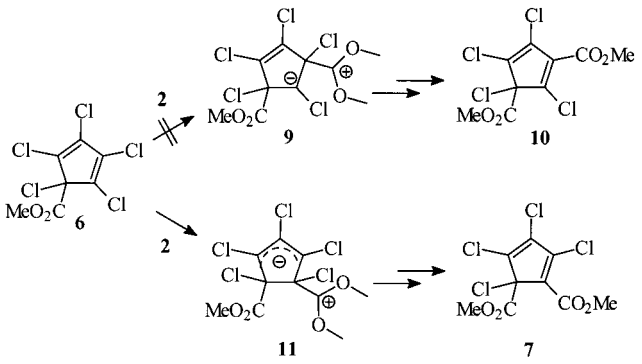
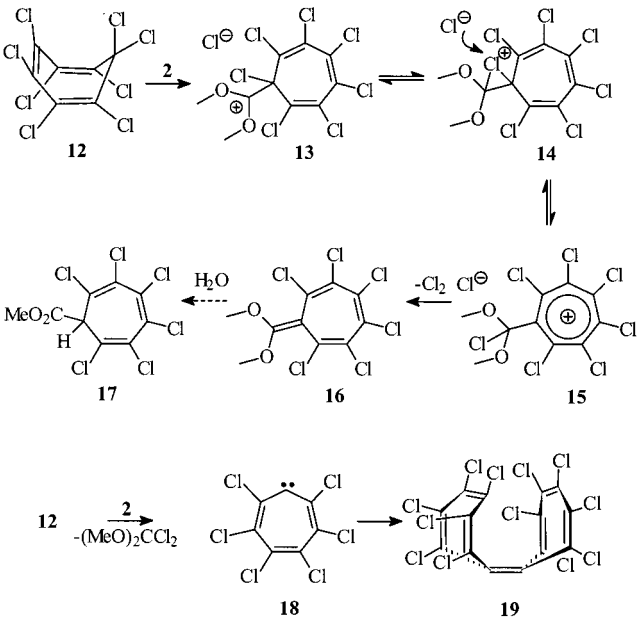
Scheme 2



Scheme 3



at ≥160 °C were products associated with 1,5-ester migrations observed (NMR, sealed tubes). These results are in keeping with high barriers for ester migrations in cyclopentadienes; the calculated barrier for a [1,5]-sigmatropic ester shift in 5-chloro-1,2,3,4,5-pentakis-(carbomethoxy)cyclopentadiene is ca. 32 kcal mol^{-1}.[19]

Of several hypothetical mechanisms that could account for **6**−**8** from the reaction of **2** with **4**, we favor a Michael type of addition and loss of Cl^-, possibly in concert, to produce the ion pair **5**, which affords **7** via **6**. Analogous subsequent processes provide a consistent account for the three products (Scheme 1). Insertions of **2** into a $C(sp^3)$-Cl bond by concerted, radical pair, or halonium ylide mechanisms are unlikely, given that chloroform and 1,1,2,2-tetrachloroethane did not react with **2**. Radical chemistry of **2** is unlikely in any case because its triplet state lies ca. 76 kcal/mol above the singlet.[3] The fact that coupling products (e.g., decachlorobi(2,4-cyclopentadien-1-yl) and/or octachloropentafulvalene)[20] were not seen from the reaction of **2** with **4** suggests that chlorine abstraction by singlet **2** is also not an accessible pathway.

It is not surprising that **7** is more reactive than **4**, because CO_2Me is more electron-withdrawing than Cl. The regioselectivity that leads to **7** but not **10** follows from the relative stabilities of transition states, modeled with the localized **9** and the allylic **11** (Scheme 2). We cannot account for the regioselective formation of **8** to the exclusion of the 1,2,3-triester that would result from addition at the alternative site of **7**.

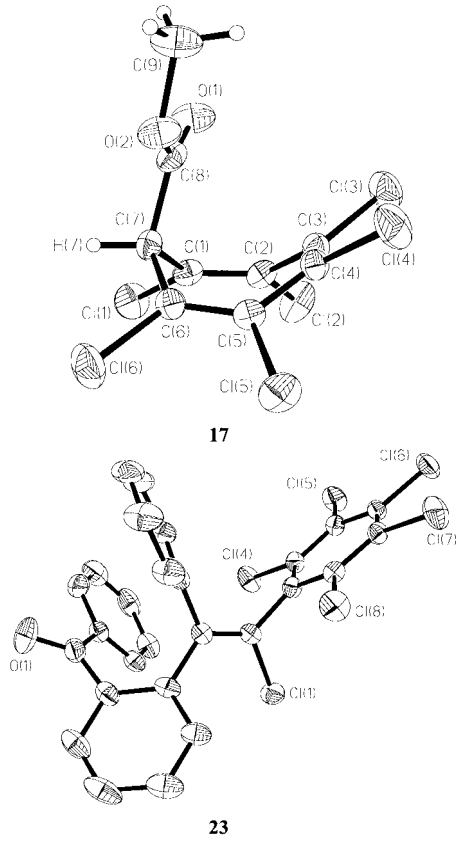


Figure 2.

Reaction of 2 with Octachlorocycloheptatriene (12).[21,22] Thermolysis of **1** at 110 °C in benzene containing **12** (initially 0.1 M) for 24 h yielded dimethoxy(hexachloro)heptafulvene (**16**, 12%) and dodecachloroheptafulvalene (**19**, 56%) as major products, Scheme 3. Analysis of the crude reaction mixture by GC−MS prior to chromatography revealed octachlorotoluene, a known product of thermal decomposition of **12**.[21] Heating of **12** in benzene (110 °C, 24 h) resulted in only 10% conversion to octachlorotoluene, but in two weeks it was fully converted.

Dimethoxy(hexachloro)heptafulvene (**16**), a ketene acetal, was stable enough to permit identification by conventional spectroscopic techniques. However, it was sensitive to atmospheric moisture that converted it into **17** (Scheme 3), the structure of which was secured by X-ray crystallography (Figure 2).

A straightforward mechanism for the formation of **16** involves addition of **2** at one of the terminal double bonds of **12** and loss of Cl^- to yield ion pair **13**. Subsequent rearrangement through chloronium ion **14** would then yield ion pair **15**. Heptachlorocycloheptatrienyl cation is known in a stable salt[22] and, although the geometry has

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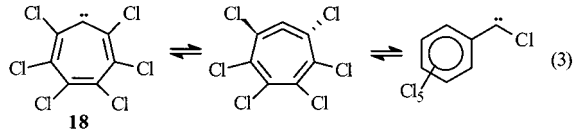
not been determined, it is unlikely to be planar.[23] One of the ion pairs, **14** or **15**, must then undergo dechlorination (the reverse of Cl_2 addition to **16**) rather than dechloromethylation.

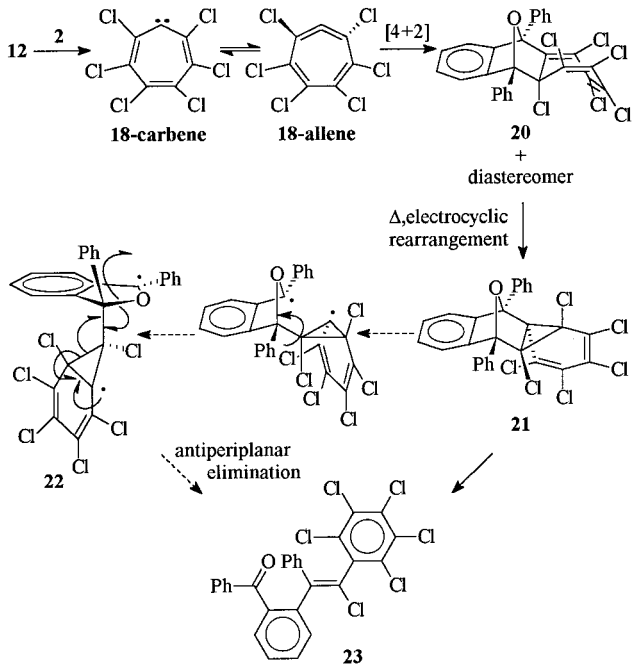
The formation of *syn*-dodecachloroheptafulvalene (**19**) was surprising. Selective formation of *syn*-**19** in reactions of *n*-BuLi[24] and of various metals[22] with **12** has been observed previously, and hexachlorocycloheptatrienylidene (**18**) was implicated in the selective formation of this kinetic product.[22,24b] *syn*-**19** is converted to *anti*-**19** at temperatures ≥270 °C.[24] We postulate that **12** and **2** afford the dimethoxyacetal of phosgene and **18**, which dimerizes to **19**. *gem*-Dechlorination (**12** + **2** → **18** + $(MeO)_2CCl_2$) is analogous to the reaction of organolithium reagents with **12**.[25] Moreover a "carbene-to-carbene transfer" (e.g., **2** + **12** → **18**) has been observed previously in reactions involving carbonyl groups.[26] Ketene acetal **16** was stable for several days in benzene at 110 °C and was therefore not the source of **18**.

Cycloheptatrienylidene is known to exist in equilibrium with cycloheptatetraene and phenylcarbene, as are benzannulated analogues of cycloheptatrienylidene.[27] We expect that the perchlorocycloheptatrienylidene would also exist in equilibrium with the analogous perchlorinated isomers (eq 3) and that the nonplanar perchlorocycloheptatetraene would be favored to alleviate steric interactions between the chlorine substituents.



Trapping of cycloheptatrienylidene/cycloheptatetraene and benzannulated analogues by way of [4+2] cycloadditions with diphenylisobenzofuran (DPIBF) has been reported.[28] We attempted to trap the proposed perchloro **18**/**18**-allene, from the reaction of **2** and **12**, with DPIBF. Thermolysis of **1** in benzene at 110 °C in the presence of **12** and DPIBF yielded **16** and **19**, as well as olefin **23** and an isomer of **23**, which could not be purified. The basic features of **23** followed from standard spectroscopic techniques, and the *Z*-configuration was determined by X-ray crystallography (Figure 2). One of several explanations would have **23** originate from the trapping of **18**/**18**-allene by DPIBF via a [4+2] cycloaddition to give **20**. An electrocyclic rearrangement would afford norcaradiene **21** (Scheme 4), and its fragmentation

Scheme 4



to either a diradical (**22**) or a zwitterion and rearrangement might be expected to give both *E*- and *Z*-**23**. Fragmentation of **22** from the conformer with the leaving groups antiperiplanar may account for the formation of the *Z*-isomer exclusively. Although we cannot prove that **23** arises from **20**,[29] Cope rearrangements of this type (Scheme 4) are known to occur readily at elevated temperatures in cycloheptatrienes.

Reaction of 2 with Octachlorobicyclo[3.2.0]hepta-3,6-diene (24). Thermolysis of **1** at 110 °C in benzene containing **24** (initially 0.1 M) for 24 h yielded dimethoxy(hexachloro)heptafulvene (**16**, 3%) and dodecachloroheptafulvalene (**19**, 11%). The remainder was unreacted **24** and carbene dimer (tetramethoxyethylene). The products from **24** are the same as those obtained with **12** in roughly the same ratio, suggesting that they are formed through a common intermediate. Following our previous interpretation, **2** attacks **24** to give ion pair **25** (Scheme 5). Rearrangement by way of chloronium ion **26** affords allylic cation **27**, which is analogous to the cation intermediate postulated for the aluminum chloride catalyzed conversion of **24** to octachlorocycloheptatriene (**12**).[21] Disrotatory ring opening[21] of **27** would lead to the cycloheptatrienyl cation in ion pair **15**, an intermediate common to the reactions of **2** with both **12** and **24**. The lower yields from the latter may mean that **24** is less reactive than **12** toward **2**, possibly because **24** cannot undergo overall S_N2'' substitution.

Reaction of 2 with Hexachlorotropone (28). Facile rearrangements of 2-substituted tropones or tropolones to benzenoid derivatives in reactions with nucleophiles have been explored vigorously.[30] Although the chemistries of **12** and **28** have been investigated less thoroughly, Scherer[31] and West et al.[21] reported independently that

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(29) Our attempts to trap **18**/**18**-allene, from the reaction of n-BuLi and **13**, with DPIBF led to minor products with the mass of **23**, which we could not isolate in pure form.

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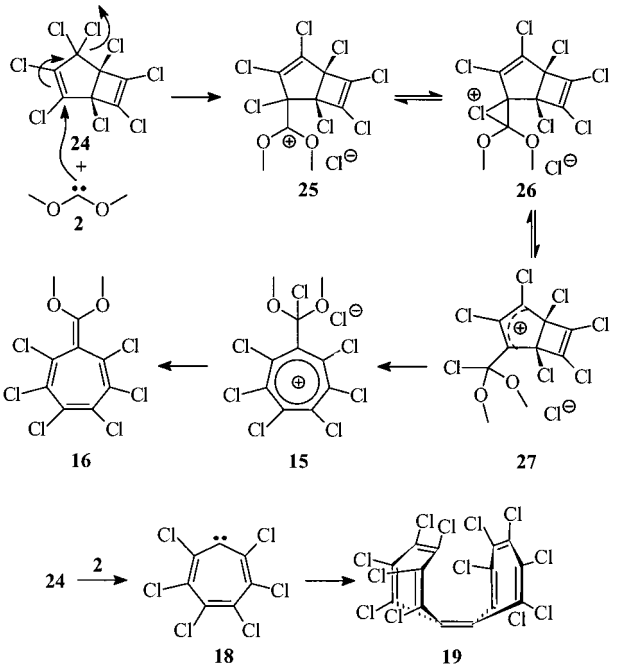
Scheme 5



both afford methyl pentachlorobenzoate upon dissolution in methanol. Thermolysis of **1** in benzene at 110 °C in the presence of **28** gave ester **31** as the major product (44%), in keeping with the reported rearrangements of troponoids to benzenoid derivatives.[30] Analysis of the crude product mixture by GC−MS prior to chromatography confirmed that **31** was the major fraction (ca. 69%) (Figure 3). Methyl pentachlorobenzoate (ca. 7%), pentachlorobenzoyl chloride (ca. 2%), and hexachlorobenzene (ca. 2%) were also found. The latter two are known products of thermal decomposition of **28** and presumably arise via a norcaradienone intermediate.[21b,32] We suggest that **31** arises through nucleophilic attack by **2** at the carbonyl carbon of **29**, generating a zwitterion intermediate **30** (Scheme 6), possibly in equilibrium with the corresponding oxirane (not shown). There is precedence for the formation of such intermediates in reactions of **2** with other carbonyl compounds.[33] Ring opening of **30** and demethylation is analogous to the formation of methyl pentachlorobenzoate from the reaction of **12** with methanol.[21]

Reactions of hexachlorotropone with nucleophiles, including thiols, amines, [30] and organolithium reagents,[34] give exclusively benzenoid products rather than products of nucleophilic addition without ring contraction. Although **31** could also arise from reaction of **2** with pentachlorobenzoyl chloride, analogous to the reaction of **2** with benzoyl chloride,[35] heating of **28** in benzene at 110 °C gave only ca. 5% of pentachlorobenzoyl chloride and ca. 2% of hexachlorobenzene. Therefore, reaction of pentachlorobenzoyl chloride with **2** can be only a minor contributor to the formation of **31**.

The origin of methyl pentachlorobenzoate is uncertain. Loss of CO from keto ester **31** is one possibility. Nucleophilic aromatic substitution by **2**, leading to products of formal carbon−halogen insertion, have been reported,[18] and insertion of **2** into a C−Cl bond of hexachlorobenzene, followed by hydrolysis on exposure to air, was also considered. However, thermolysis of **1** in the presence of hexachlorobenzene did not lead to methyl pentachlorobenzoate.

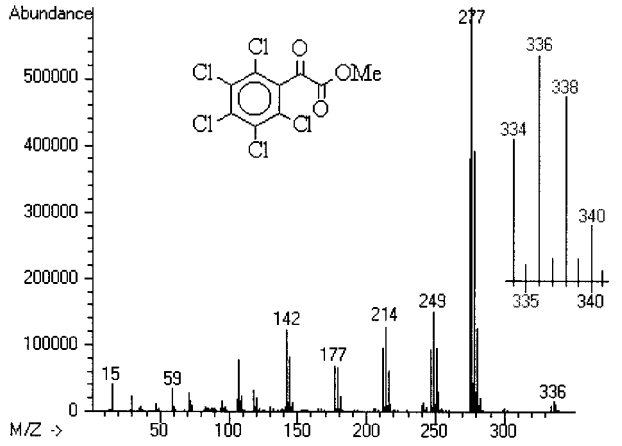
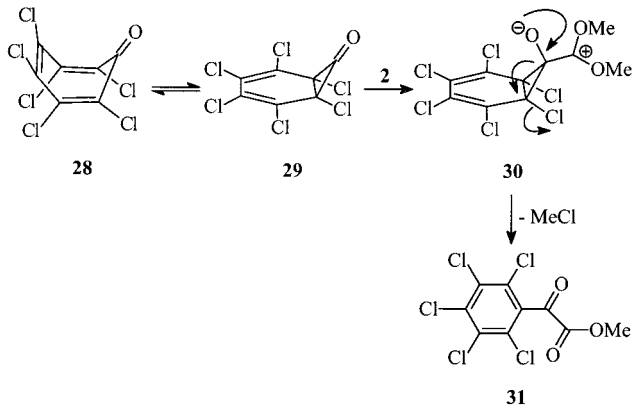


Figure 3.

Scheme 6



Although other mechanisms involving nucleophilic attack at the chlorine-bearing carbons have been suggested for analogous systems and cannot be discounted,[30a,b] they are less likely to occur in the formation of **31**, because **28** is far from planar.[36] The boatlike geometry of **28** should increase its susceptibility to attack at the carbonyl carbon while inhibiting the double bond shift associated with attack at C-2.[31] In contrast, C-7 in **12** should be more sterically encumbered, and as a result, the double bonds in **12** would be more likely sites for attack by **2**. Possible pathways which could result in the same end products have been reviewed for 2-chlorotropones and tropolones, and similar arguments probably apply to hexachlorotropone.[30]

Reaction of 2 and Hexachlorobicyclo[3.2.0]-3,6-dien-2-one (32). Ketone **32**[37] is known to react with anions (e.g., MeLi) to afford the corresponding alcohols,[37b] with no evidence for Michael addition products. Oxadiazoline **1** and **32**, when heated at 110 °C in benzene, gave 1,4,5,6,7,8-hexachloro-2,2-dimethoxybicyclo[4.2.0]-

(32) Mukai, T.; Nakazawa, T.; Okayama, K. *Tetrahedron Lett.* **1968**, *14*, 1695.

(33) For an example, see: Pole, D. L.; Warkentin, J. *J. Org. Chem.* **1997**, *62*, 4065.

(34) Dunn, J. A.; Pezacki, J. P.; Warkentin, J.; McGlinchey, M. J., manuscript in preparation.

(35) Hoffman, R. W.; Lilienblum, W.; Dittrich, B. *Chem. Ber.* **1974**, *107*, 3395.

(36) (a) Dodge, R. P.; Sime, R. J.; Templeton, D. H., personal communication cited in ref 31b. (b) Sünkel, R. *J. Organomet. Chem.* **1990**, *391*, 247.

(37) (a) Roedig, A.; Hörnig, L. *Liebigs Ann. Chem.* **1956**, *598*, 208. (b) Roedig, A.; Försch, M. *Liebigs Ann. Chem.* **1977**, 297.

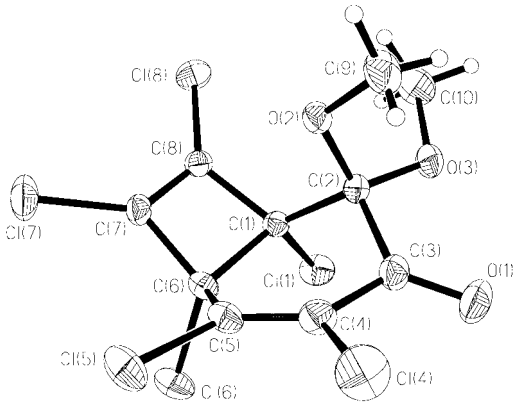
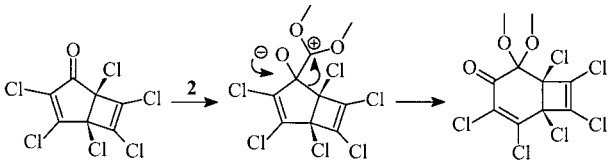


Figure 4.

Scheme 7



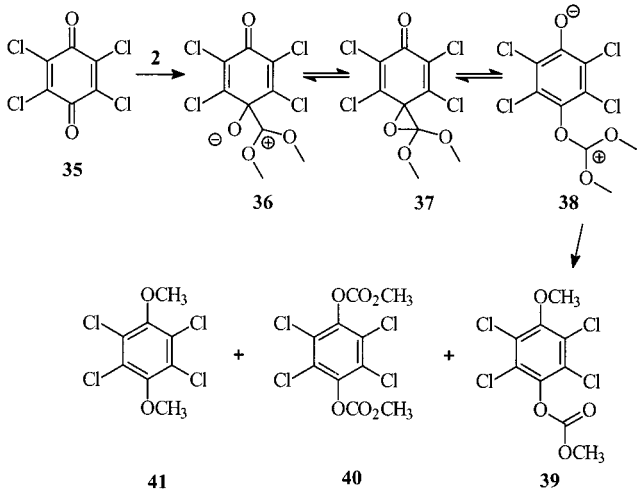
octa-4,7-dien-3-one (**34**) in quantitative yield. ^{1}H and ^{13}C NMR data included two methoxy signals, and in the IR, ν_{CO} = 1740 cm^{-1} suggested that the α,β-unsaturated carbonyl unit had remained intact; X-ray crystallography confirmed the structure, Figure 4.

Compound **34** is the result of a formal carbene insertion into a carbon−carbon bond. Reactions of **2** with carbonyl groups of anhydrides,[36] biacetyl, and benzoyl chloride[35] appear to involve nucleophilic addition of **2** at the carbonyl carbon, followed by rearrangement of the resulting dipolar intermediates. In the case of anhydrides, formal insertion of **2** into carbon−oxygen bonds occurs; analogous insertions into carbon−sulfur bonds have also been observed.[39]

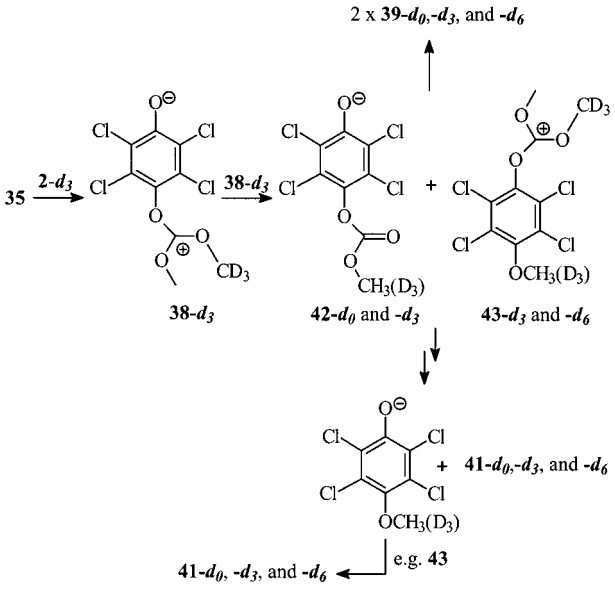
Formation of **34** probably involves nucleophilic attack by **2** at the carbonyl carbon of **32** to yield intermediate **33** (Scheme 7), which rearranges by a 1,2-carbon migration, with retention of stereochemistry, to form **34**. The reaction of **2** with **32** is the first example of an overall carbon−carbon bond insertion reaction for an alkoxy- or dialkoxycarbene.

Reaction of 2 with Tetrachloro-1, 4-benzoquinone (35). Thermolysis of **1** for 24 h at 110 °C in benzene containing **35** yielded 4-methoxy-2,3,5,6-tetrachlorophenyl methyl carbonate (**39**, 82% isolated yield), biscarbonate **40** (5%), and 1,4-dimethoxy-2,3,5,6-tetrachlorobenzene (**41**, 1%). Analysis by GC−MS prior to chromatography gave **39**:**40**:**41** ca. 57:4:1. Although **35** is a good one-electron acceptor,[40] an electron-transfer mechanism for the formation of the products is unlikely because the energy difference between dihydroxycarbene, a model for **2**, and its radical cation is ca. 120 kcal mol^{-1}.[41]

Scheme 8



Scheme 9



The aromatization of **35** presumably occurs via initial attack of **2** at the carbonyl carbon to yield dipolar structure **36**, which is probably equilibrated with oxirane **37** and dipole **38** (Scheme 8). An alternative pathway, from **35** directly to **38**, may also be feasible. The latter could then react with another **38** by way of a methyl transfer to give **42** and **43**, which undergo a subsequent intermolecular methyl transfer to yield the major product **39**. One possibility for the origins of the minor products **40** and **41** that is consistent with the labeling studies (below) is that they arise from the collapse of ions **42** and **43** (Scheme 9).

Carbene precursor **1**-d_3 was used to determine whether products **39**−**41** are formed via intermolecular or intramolecular methyl transfers. Methyl group transfer with crossover should lead to deuterium-labeled **39**−**41** with the isotopomer distribution ∼25% d_0, ∼50% d_3, and ∼25% d_6 based on statistics and ignoring kinetic isotope effects. Analysis by GC−MS showed that **39**−**41** had molecular ion isotopic distributions consistent with such a CD_3 crossover (Figure 5). Although those isotopic distributions were complicated somewhat by the Cl isotopes, the overlap of signals from d_3 and d_6 isotopomers

(38) Pole, D. L.; Warkentin, J. *Liebigs Ann. Chem.* **1995**, 1907.
(39) Reid, D.; Warkentin, J., unpublished results.
(40) (a) Eberson, L. *Electron-Transfer Reactions in Organic Chemistry*; Springer-Verlag: New York, 1987. (b) *Photoinduced Electron Transfer*, Vol. A−D; Fox, M. A., Chanon, M., Eds.; Elsevier: New York, 1988.
(41) (a) Burgers, P. C.; McGibbon, G. A.; Terlouw, J. K. *Chem. Phys. Lett.* **1994**, *224*, 539. (b) Burgers, P. C.; Mommer, A. A.; Holmes, J. L. *J. Am. Chem. Soc.* **1983**, *105*, 5976.

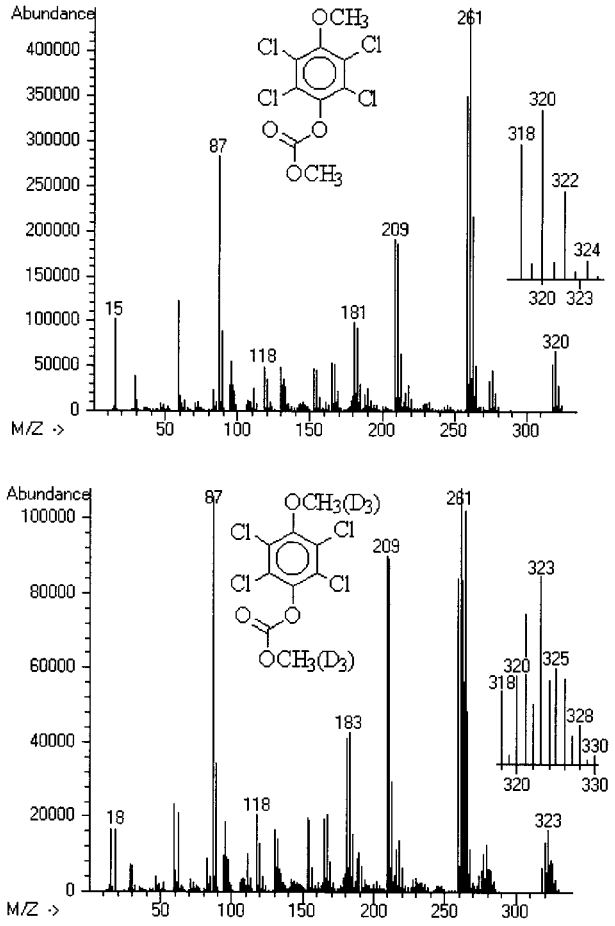


Figure 5.

could be corrected for. On the basis of these findings, a cascade of intermolecular methyl transfers is implicated.

Conclusions

Dimethoxycarbene reacts with perchloro olefins (e.g., **4** and **12**) by overall nucleophilic substitution leading to ion pair intermediates. The latter undergo nucleophilic substitution by Cl^- either at Me of $(MeO)_2C^+R$ to afford esters and MeCl or at Cl to afford a ketene acetal and Cl_2. These results are consistent with reaction of **2** as an "acyl anion" equivalent. Unsaturated perchloroketones, including tetrachloro-1, 4-benzoquinone, are attacked at the carbonyl carbon atom to afford dipolar intermediates that can rearrange without loss of a Cl^- moiety. Alternatively, such intermediates can form ion pairs that also lead to MeCl and esters.

Experimental Section

General Information. For GC−MS analyses, a gas chromatograph equipped with a mass-selective detector and a DB-1 capillary column (12 m × 0.2 mm) was used. Mass spectra were obtained with a double-focusing instrument, and infrared spectra (FT) are from samples in KBr windows. Frequencies below 1000 cm^{-1} are omitted. All values of *m*/*z* for polychlorinated compounds are the lowest in the envelope and correspond to ^{35}Cl; the signal intensities matched the pattern required for the number of Cl atoms in the fragment. Not all observed signals are listed.

Materials. Benzene (Aldrich) was distilled from sodium. All other solvents and reagents were of the highest purity commercially available (Aldrich) and were distilled/recrystallized prior to use if necessary. Purities of reagents and solvents were determined by GC and GC−MS.

2,2-Dimethoxy-5,5-dimethyl-Δ^3-1,3,4-oxadiazoline (1). Oxadiazoline **1** was prepared by oxidative cyclization of the carbomethoxyhydrazone of acetone with lead tetraacetate (LTA) as described previously.[7a] The product was purified by radial chromatography on SiO_2 using 10:1 hexanes/ethyl acetate as the eluent: yield 78%, clear oil; ^1H NMR (200 MHz, $CDCl_3$) δ 1.53 (s, 6 H), 3.45 (s, 6 H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 23.7, 51.5, 118.8, 137.0; IR (neat, KBr) 2982, 2949, 2887, 2847, 1577, 1459, 1448, 1376, 1137, 1078 cm^{-1}; MS (EI) *m*/*z* (molecular ion not observed), 129 $[M - OMe]^+$, 105, 91, 90, 75, 74, 73, 59 (100%); MS (CI, NH_3) *m*/*z* 178 $[M + NH_4]^+$; UV (pentane) λ_{max} 328 nm (ϵ 500).

2-Methoxy-2-methoxy-d_3-5, 5-dimethyl-Δ^3-1,3,4-oxadiazoline (1-d_3). Oxadiazoline **1**, prepared by LTA oxidation of the carbomethoxyhydrazone of acetone in CH_2Cl_2, was treated with methanol-d_4 as described previously.[33]

Octachlorobicyclo[3.2.0]hepta-3,6-diene (24). Diene **24** was synthesized according to a literature procedure:[37a] white solid, mp 53−54 °C (lit.[37a] 53 °C); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 137.4, 134.2, 133.4, 132.2, 89.0, 81.8, 78.7; MS (EI) *m*/*z* 364 $[M]^+$, 329 (100%) $[C_7Cl_7]^+$, 294 $[C_7Cl_6]^+$, 259 $[C_7Cl_5]^+$, 189 $[C_7Cl_3]^+$, 154 $[C_7Cl_2]^+$, 119 $[C_7Cl]^+$; MS (CI, NH_3) *m*/*z* 382 $[M + NH_4]^+$.

Octachlorocycloheptatriene(12). The triene, synthesized according to a literature procedure,[21] was a pale yellow solid: mp 85 °C (lit.[21] 86 °C); ^{13}C NMR (50.3 MHz, CD_2Cl_2) δ 134.5, 134.1, 129.2, 84.3; MS (EI) *m*/*z* 364 $[M]^+$, 329 (100%) $[C_7Cl_7]^+$, 294 $[C_7Cl_6]^+$, 259 $[C_7Cl_5]^+$, 189 $[C_7Cl_3]^+$, 154 $[C_7Cl_2]^+$, 119 $[C_7Cl]^+$; MS (CI, NH_3) *m*/*z* 382 $[M + NH_4]^+$.

Hexachlorotropone (28). A literature procedure[21b] for the synthesis of **28** gave a yellow solid: mp 82−83 °C (lit.[21b] 82.5 °C); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 177.5, 136.6, 134.5, 132.4; MS (EI) *m*/*z* 310 $[M]^+$, 284 (100%) $[M - CO]^+$, 247 $[C_7Cl_5]^+$, 212 $[C_7Cl_4]^+$, 177 $[C_7Cl_3]^+$, 142 $[C_7Cl_2]^+$, 107 $[C_7Cl]^+$; MS (CI, NH_3) *m*/*z* 328 $[M + NH_4]^+$.

Hexachlorobicyclo[3.2.0]hepta-3,6-dien-2-one (32). Dienone **32** was prepared by means of a modified literature procedure.[37a] Sulfuric acid (concentrated, 5.0 mL) was added to octachlorobicyclo[3.2.0]hepta-3,6-diene (**24**) (1.947 g, 5.30 mmol), and the solution was heated at 80 °C for 20 h. The solution was cooled, poured over ice, and extracted with ether. Radial chromatography of the extract using petroleum ether eluent yielded **32** as a white powder (1.034 g, 63%): mp 84.5−85 °C (lit.[37a] 85−86 °C); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 182.5, 157.0, 136.1, 132.1, 131.6, 75.6, 73.7; IR (neat, KBr) 1746, 1622, 1573, 1226, 1155, 1129, 1030 cm^{-1}; MS (EI) *m*/*z* 310 $[M]^+$, 282 $[M - CO]^+$, 247 $[C_6Cl_5]^+$, 212 $[C_6Cl_4]^+$, 177 $[C_6Cl_3]^+$, 142 (100%) $[C_6Cl_2]$; MS (CI, NH_3) *m*/*z* 328 $[M + NH_4]^+$, 311 $[M + H]^+$; HRMS calcd for C_7Cl_6O 309.8080, found 309.8092.

Reaction of 2 with 4. A solution of **1** (0.268 g, 1.68 mmol) in freshly distilled benzene (18.3 mL) containing **4** (0.1 M, 0.500 g, 1.83 mmol), in a 40 mL thermolysis tube fitted with Teflon valves, was degassed by means of three successive freeze−pump−thaw cycles. The sealed tube was then heated at 110 °C in a constant temperature oil bath for 24 h. Immediate analysis by GC−MS showed **6**, **7**, and **8** as major products in a 1.2:1.8:1 ratio, respectively. These products were isolated by means of radial chromatography, with hexanes and 1:1 hexanes/CH_2Cl_2. Minor isomers of **6**, **7**, and **8** were detected by GC−MS, but they could not be isolated by chromatography. A degassed solution of **1** (0.587 g, 3.67 mmol) in benzene (3.7 mL) containing **4** (0.100 g, 0.37 mmol) was also heated in a thermolysis tube at 110 °C for 24 h. Analysis by GC−MS gave **8**:**7** ≈ 4:1 with only trace amounts of **6** present. The identities of **7** and **8** were confirmed by isolation of those products.

5-Carbomethoxy-1,2,3,4,5-pentachlorocyclopentadiene (6). Yield 24%, white solid, mp 93−94 °C; ^1H NMR (500 MHz, CD_2Cl_2) δ 3.82 (s); ^{13}C NMR (125.7 MHz, CD_2Cl_2) δ 162.5, 131.0, 130.1, 72.6, 55.1; IR (neat, KBr) 2956, 2920, 2850, 1756, 1648, 1601, 1448, 1441, 1283, 1234, 1179, 1148, 1123, 1010 cm^{-1}; MS (EI) *m*/*z* 294 $[M]^+$ (100%), 259 $[C_7H_3O_2Cl_4]^+$, 235 $[C_5H_3O_2Cl_4]^+$ (based on the isotopic distribution within the

fragment envelope); MS (CI, NH_3) *m/z* 312 $[M + NH_4]^+$; HRMS calcd for $C_7H_3O_2Cl_5$ 293.8576, found 293.8573.

4,5-Dicarbomethoxy-1,2,3,5-tetrachlorocyclopentadiene (7). Yield 28%, white solid, mp 84−85 °C; ^{1}H NMR (500 MHz, CD_2Cl_2) δ 3.84 (s, 3 H), 3.75 (s, 3 H); ^{13}C NMR (125.7 MHz, CD_2Cl_2) δ 163.4, 159.9, 143.7, 137.0, 132.3, 132.0, 68.4, 54.9, 52.7; IR (neat, KBr) 3007, 2956, 2848, 1783, 1756, 1697, 1681, 1653, 1628, 1603, 1557, 1436, 1327, 1289, 1254, 1226, 1161, 1120, 1094, 1048 cm^{-1}; MS (EI) *m/z* 318 $[M]^+$, 287 $[C_8H_3O_3Cl_4]^+$, 274 $[C_8H_6O_2Cl_4]^+$ (based on isotopic distribution within the fragment envelope), 259 $[C_7H_3O_2Cl_4]^+$, 228 $[C_6OCl_4]^+$, 180 $[C_6H_3Cl_3]^+$, 165 $[C_5Cl_3]^+$, 130 $[C_5Cl_2]^+$, 95 $[C_5Cl]^+$, 59 $[CO_2Me]^+$ (100%), 43; MS (CI, NH_3) *m/z* 338 $[M + NH_4]^+$; HRMS calcd for $C_9H_6O_4Cl_4$ 317.9020, found 317.9012.

4,5,5-Tricarbomethoxy-1,2,3-trichlorocyclopentadiene (8). Yield 33%, white solid, mp 104−105 °C; ^{1}H NMR (200 MHz, CD_2Cl_2) δ 3.80 (s, 3 H), 3.75 (s, 6 H); ^{13}C NMR (50.3 MHz, CD_2Cl_2) δ 162.8 (*C*O_2Me), 160.5 (*C*O_2Me), 142.4, 133.2, 132.0, 129.0, 71.1, 54.5, 52.3; IR (neat, KBr) 3013, 2959, 2848, 1785, 1754, 1625, 1597, 1552, 1437, 1325, 1290, 1255, 1228, 1161, 1055, 1043 cm^{-1}; MS (EI) *m/z* 342 $[M]^+$, 298 $[C_{10}H_9O_4Cl_3]^+$, 267 $[C_{11}H_9O_6Cl_3]^+$; MS (CI, NH_3) *m/z* 360 $[M + NH_4]^+$, 343 $[M + H]^+$; HRMS (EI) HRMS calcd for $C_{11}H_9O_6Cl_3$ 341.9465, found 341.9463.

Reaction of 2 with 12. A solution of **1** (0.118 g, 0.74 mmol) in benzene (8.1 mL) containing **12** (0.1 M, 0.300 g, 1.1 mmol) was heated as described above. Major products **16** and **19** were isolated using radial chromatography with a gradient of solvents ranging from hexanes to 1:1 hexanes/CH_2Cl_2. Octachlorotoluene was isolated as a minor product. Heating of **12** under identical conditions converted ∼10% to octachlorotoluene, whereas heating for two weeks resulted in complete conversion.

Dimethoxy(hexachloro)heptafulvene (16). Yield 12%, white solid, mp 91−91.5 °C; ^{1}H NMR (500 MHz, CD_2Cl_2) δ 3.89 (s, 6 H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 162.1, 132.0, 130.4, 126.0, 86.8, 57.9; IR (neat, KBr) 3007, 2956, 2856, 1618, 1555, 1467, 1430, 1320, 1266, 1223, 1192, 1165, 1120 cm^{-1}; MS (EI) *m/z* 368 $[M]^+$, 353 $[C_9H_3O_2Cl_6]^+$, 333 $[C_{10}H_6O_2Cl_5]^+$; MS (CI, NH_3) *m/z* 369 $[M + H]^+$; HRMS calcd for $C_{10}H_6O_2Cl_6$ 367.8499, found 367.8492.

Dodecachloroheptafulvalene (19). Fulvalene **19** was identified from MS (EI) and ^{13}C NMR data, which were consistent with those in the literature;[22,24b] yield 56%. **Octachlorotoluene.** Yield 5%, white solid, mp 69−71 °C (lit.[21b] 71−72 °C); ^{13}C NMR (50.3 MHz, CD_2Cl_2) δ 138.0, 136.1, 134.7, 132.9, 93.5; MS (EI) *m/z* 364 $[M]^+$, 329 (100%) $[C_7Cl_7]^+$, 294 $[C_7Cl_6]^+$; MS (CI, NH_3) *m/z* 382 $[M + NH_4]^+$.

Attempted Thermolysis of Dimethoxy(hexachloro)heptafulvene (16). A solution of **16** (0.05 M, 0.020 g, 0.054 mmol) in 1 mL of benzene-d_6 in an NMR tube was degassed by means of three successive freeze−pump−thaw cycles before the tube was flame-sealed. The solution was heated at 110 °C for 24 h and then analyzed by ^{1}H NMR (500 MHz) spectroscopy. Thermal decomposition products of **16** were not observed.

Reaction of 2 with 24. A solution of **1** (0.118 g, 0.74 mmol) in benzene (8.1 mL) containing **24** (0.1 M, 0.300 g, 0.82 mmol) was heated as described above. Products **16** (11%) and **19** (3%) were isolated by means of radial chromatography.

7-Carbomethoxy-1,2,3,4,5,6-hexachlorocycloheptatriene (17). Ketene acetal **16** hydrolyzed to **17** on prolonged exposure to air. In a deliberate hydrolysis, a solution of **16** (0.05 M, 0.100 g, 0.27 mmol) in dichloromethane (5.5 mL) was stirred with 2 mL of distilled water at room temperature for 2 days. Radial chromatography (hexanes) gave **17** as a white solid (85 mg, 89%): mp 86−87 °C; ^{1}H NMR (200 MHz, CD_2Cl_2) δ 4.65 (s, 1H), 3.71 (s, 3H); ^{13}C NMR (50.3 MHz, CD_2Cl_2) δ 165.4, 133.2, 130.6, 127.9, 60.4, 54.2; IR (neat, KBr) 3007, 2954, 2844, 1751, 1641, 1616, 1597, 1575, 1449, 1436, 1291, 1274, 1230, 1152, 1090, 1003 cm^{-1}; MS (EI) *m/z* 354 $[M]^+$, 319 $[C_9H_4O_2Cl_5]^+$, 295 (100%) $[C_7HCl_6]^+$; MS (CI, NH_3) *m/z* 372 $[M + NH_4]^+$; HRMS calcd for $C_9H_4O_2Cl_6$ 353.8342, found 353.8339.

Reaction of 2 with 12 Containing Diphenylisobenzofuran. A solution of **1** (0.1 M, 0.087 g, 0.54 mmol) in benzene (5.4 mL) containing **12** (0.1 M, 0.200 g, 0.54 mmol) and diphenylisobenzofuran (0.2 M, 294 mg, 1.09 mmol) was heated as described above. Radial chromatography with a solvent gradient ranging from hexanes to 1:1 hexanes/ethyl acetate yielded **16**, **19**, and **23**, as well as the product of hydrolysis of diphenylisobenzofuran. An isomer of **23** (identical mass spectrum) was also isolated, but it could not be obtained in either a high enough purity or yield to be fully characterized.

(*Z*)-2-(2-Benzoylphenyl)-1-chloro-1-pentachlorophenyl-2-phenylethene (23). Yield 16%, white solid, mp 158−9 °C; ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.05−7.80 (m, 14 H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 126.9, 128.1, 128.2, 128.4, 128.5, 128.7, 128.8, 129.5, 130.1, 130.4, 130.6, 130.8, 131.1, 131.3, 132.3, 132.9, 133.3, 134.8, 137.7, 140.4,196.7; IR (neat, KBr) 2924, 2852, 1771, 1736, 1661, 1597, 1579, 1492, 1447, 1315, 1276, 1199, 1179, 1154, 1103, 1074, 1061, 1025, 1001 cm^{-1}; MS (EI) *m/z* 564 $[M]^+$, 529$[C_{27}H_{14}OCl_5]^+$, 494 $[C_{27}H_{14}OCl_4]^+$, 459 $[C_{27}H_{14}OCl_3]^+$, 209 (100%); MS (CI, NH_3) *m/z* 582 $[M + NH_4]^+$; HRMS calcd for $C_{27}H_{14}OCl_6$ 563.9176, found 563.9179.

Reaction of 2 with 28. A solution of **1** (0.093 g, 0.58 mmol) in benzene (6.4 mL) containing **28** (0.1 M, 0.200 g, 0.64 mmol) was heated as described above. Analysis by GC−MS revealed methyl 2-pentachlorophenyl-2-oxo-ethanoate (**31**) (69%), pentachlorobenzoyl chloride (2%), methyl pentachlorobenzoate (7%), hexachlorobenzene (1%), and remaining **28** (20%). Ketoester **31** was isolated using radial chromatography with a gradient of solvents ranging from hexanes to 1:1 hexanes/CH_2Cl_2. Hexachlorotropone (**28**), heated under identical conditions, gave (by GC−MS) pentachlorobenzoyl chloride (5%), hexachlorobenzene (2%), and starting material (93%). Prolonged thermolysis times (2.5 weeks) converted hexachlorotropone fully to hexachlorobenzene and pentachlorobenzoyl chloride. A solution of **1** (0.102 g, 0.64 mmol) in freshly distilled benzene (7.0 mL) containing hexachlorobenzene (0.1 M, 0.200 g, 0.70 mmol) was heated as described previously. The only product from this reaction, other than acetone, detected by GC−MS was tetramethoxyethylene.

Methyl 2-Pentachlorophenyl-2-oxo-ethanoate (31). Yield 44%, white solid, mp 127−28 °C; ^{1}H NMR (300 MHz, CD_2Cl_2) δ 3.95; ^{13}C NMR (75 MHz, CD_2Cl_2) δ 181.3, 159.0, 136.2, 135.4, 132.8, 129.4, 54.1; IR (neat, KBr) 3046, 2967, 2850, 1763, 1738, 1646, 1545, 1439, 1352, 1322, 1273, 1230, 1138, 1031 cm^{-1}; MS (EI) *m/z* 334 $[M]^+$, 275 (100%) $[C_7OCl_5]^+$; MS (CI, NH_3) *m/z* 352 $[M + NH_4]^+$; HRMS (EI) calcd for $C_9H_3O_3Cl_5$ 333.8525, found 333.8536.

Pentachlorobenzoyl Chloride. Identified from the mass spectral (GC−MS) fragmentation pattern:[21] MS (EI) *m/z* 310 $[M]^+$, 275 (100%) $[C_7OCl_5]^+$, 247 $[C_6Cl_5]^+$, 212 $[C_6Cl_4]^+$, 177 $[C_6Cl_3]^+$, 142 $[C_6Cl_2]^+$, 107 $[C_6Cl]^+$.

Methyl Pentachlorobenzoate. Identified from the mass spectral (GC−MS) fragmentation pattern: MS (EI) *m/z* 306 $[M]^+$, 275 (100%) $[C_7OCl_5]^+$, 247 $[C_6Cl_5]^+$, 212 $[C_6Cl_4]^+$, 177 $[C_6Cl_3]^+$, 142 $[C_6Cl_2]^+$, 107 $[C_6Cl]^+$, 83, 71, 59 $[CO_2Me]^+$.

Hexachlorobenzene. Yield 1%, white solid, mp 225−227 °C (lit.[21] 227−29 °C); ^{13}C NMR (50.3 MHz, CD_2Cl_2) δ 132.3; MS (EI) *m/z* 282 (100%) $[M]^+$, 247 $[C_6Cl_5]^+$; MS (CI, NH_3) *m/z* 300 $[M + NH_4]^+$.

Reaction of 2 with 32. A solution of **1** (0.1 M, 116 mg, 0.73 mmol) in benzene (8.0 mL) containing **32** (0.1 M, 0.250 mg, 0.80 mmol) was heated as described above. Analysis by TLC suggested that only **34** was formed during the thermolysis. It was purified by recrystallization from a 19:1 hexanes/CH_2Cl_2 solvent mixture.

2,2-Dimethoxy-1,4,5,6,7,8-hexachlorobicyclo[4.2.0]octa-4,7-dien-3-one (34). Yield 98%, white solid, mp 154.5−155 °C; ^{1}H NMR (500 MHz, CD_2Cl_2) δ 3.52 (s, 3H), 3.18 (s, 3H); ^{13}C NMR (125.7 MHz, CD_2Cl_2) δ 183.2, 143.3, 133.5, 132.3, 129.8, 100.3, 80.0, 77.0, 52.0, 51.4; IR (neat, KBr) 2996, 2986, 2944, 2984, 1740, 1637, 1592, 1530, 1458, 1441, 1249, 1194, 1181, 1161, 1086, 1019 cm^{-1}; MS (EI) *m/z* (molecular ion not obsd) 349 (100%) $[C_{10}H_6O_3Cl_5]^+$, 321 $[C_9H_6O_2Cl_5]^+$; MS (CI, NH_3) *m/z* 402 $[M + NH_4]^+$; HRMS calcd for fragment $C_{10}H_6O_3Cl_5$ 348.8760, found 348.8762.

Reaction of 2 with 35. A solution of **1** (0.296 g, 1.85 mmol) in benzene (20.3 mL) containing **35** (0.1 M, 0.500 g, 2.03 mmol) was heated as described above. Analysis by TLC and by GC−

MS indicated **39**:**40**:**41** in ca. 57:4.1:1 ratio (GC−MS). They were isolated by means of radial chromatography with a gradient of solvents ranging from hexanes to 20% CH_2Cl_2 in hexanes.

4-Methoxy-2,3,5,6-tetrachlorophenyl Methyl Carbonate (39). Yield 82%, yellow solid, mp 106.5−108 °C; ^{1}H NMR (500 MHz, CD_2Cl_2) δ 3.95 (s, 3 H), 3.91 (s, 3 H); ^{13}C NMR (125.7 MHz, CD_2Cl_2) δ 152.8, 152.1, 142.2, 128.3, 127.5, 61.3, 57.0; IR (neat, KBr) 2952, 1784, 1462, 1443, 1408, 1383, 1316, 1254, 1199, 1166, 1031 cm^{-1}; MS (EI) *m*/*z* 318 $[M]^+$, 274 $[C_8H_6O_2Cl_4]^+$, 259 (100%) $[C_7H_3O_2Cl_4]^+$, 228 $[C_6OCl_4]^+$; MS (CI, NH_3) *m*/*z* 336 $[M + NH_4]^+$; HRMS calcd for $C_9H_6O_4Cl_4$ 317.9020, found 317.9004.

1,4-(2,3,5,6-Tetrachlorophenyl) Bis(methyl carbonate) (40). Yield 5%, orange solid, mp 169−170.5 °C; ^{1}H NMR (500 MHz, CD_2Cl_2) δ 3.95 (s, 6 H); ^{13}C NMR (50.3 MHz, CD_2Cl_2) δ 151.8, 144.0, 127.9, 57.2; IR (neat, KBr) 3005, 2847, 1779, 1715, 1688, 1574, 1455, 1442, 1414, 1384, 1330, 1247, 1194, 1171 cm^{-1}; MS (EI) *m*/*z* 362 $[M]^+$, 318 $[C_9H_6O_4Cl_4]^+$, 274 $[C_8H_6O_2Cl_4]^+$, 259 (100%) $[C_7H_3O_2Cl_4]^+$; MS (CI, NH_3) *m*/*z* 380 $[M + NH_4]^+$; HRMS calcd for $C_{10}H_6O_6Cl_4$ 361.8918, found 361.8933.

1,4-Dimethoxy-2,3,5,6-tetrachlorobenzene (41). Yield 1%, yellow solid, mp 98−99 °C; ^{1}H NMR (500 MHz, CD_2Cl_2) δ 3.92; ^{13}C NMR (50.3 MHz, CD_2Cl_2) δ 61.5, 128.7, 152.0; MS (EI) *m*/*z* 274 $[M]^+$, 259 (100%) $[C_7H_3O_2Cl_4]^+$.

Reaction of Dimethoxycarbene-*d*$_3$ (2-*d*$_3$) with 35. A solution of 2-methoxy-2-methoxy-*d*$_3$-5,5-dimethyl-Δ^3-1,3,4-oxadiazoline (**1-*d*$_3$**, 0.120 g, 0.74 mmol) in benzene (8.1 mL) containing **35** (0.1 M, 0.200 g, 0.82 mmol) was heated as described above. Analysis by GC−MS revealed that the ratio **39**:**40**:**41** was again 57:4:1. The isotopic distribution of the molecular ion envelope (IDME) from **39** was consistent with a 1:2:1 distribution of isotopomers containing all hydrogens (*m*/*z* 318), 3 deuterium atoms (*m*/*z* 321), and 6 deuterium atoms (*m*/*z* 324), respectively. Relative intensities of the signals from the molecular ion were 318 (8.1%), 319 (0.9%), 320 (9.7%), 321 (16.4%), 322 (6.6%), 323 (20.5%), 324 (9.2%), 325 (10.5%), 326 (9.4%), 327 (3.1%), 328 (4.2%), 329 (0.5%), and 330 (1.0%). The IDME of **40** was also consistent with a 1:2:1 distribution of isotopomers containing all hydrogens (*m*/*z* 362), 3 deuterium atoms (*m*/*z* 365), and 6 deuterium atoms (*m*/*z* 368), respectively. Relative intensities of the signals from the molecular ion were 362 (5.8%), 363 (<0.1%), 364 (13.1%), 365 (19.4%), 366 (5.5%), 367 (29.4%), 368 (3.2%), 369 (11.3%), 370 (9.4%), 371 (<0.1%), 372 (2.9%), 373 (<0.1%), and 374 (<0.1%). Finally, the IDME of **41** was consistent with a 1:2:1 distribution of isotopomers containing all hydrogens (*m*/*z* 274), 3 deuterium atoms (*m*/*z* 277), and 6 deuterium atoms (*m*/*z* 280). The relative intensities of the signals from the molecular ion were 274 (4.4%), 275 (<0.1%), 276 (10.9%), 277 (19.1%), 278 (5.6%), 279 (22.4%), 280 (11.8%), 281 (12.5%), 282 (10.2%), 283 (<0.1%), 284 (3.1%), 285 (<0.1%), and 286 (<0.1%).

X-ray Crystallographic Data. Summaries of the crystal data and structure refinement parameters are in Supporting Information, Table S1. All crystals were grown by slow evaporation of the solvent and were mounted on fine glass fibers with epoxy cement. X-ray crystallographic data were collected with a P4 Siemens diffractometer, equipped with a Siemens SMART 1K charge-coupled device (CCD) area detector (employing the program SMART[42]) and a rotating anode utilizing graphite-monochromated Mo Kα radiation (λ = 0.71703 Å). The crystal-to-detector distance was 3.991 cm, and the data collection was carried out in 512 × 512 pixel mode, employing 2 × 2 pixel binning. In all cases, the initial unit cell parameters were determined by a least-squares fit of the angular settings of the strong reflections, collected using three 4.5° scans (15 frames each) over three different parts of reciprocal space, and one complete hemisphere of data was collected, to better than 0.8 Å resolution. Processing of the data was carried out using the program SAINT,[43] which applied Lorentz and polarization corrections to three-dimensionally integrated diffraction spots. The program SADABS[44] was employed for the scaling of diffraction data, the application of a decay correction, and an empirical absorption correction based on redundant reflections. All structures were solved by the direct methods routine outlined in the Siemens SHELXTL program library[45] followed by full-matrix least-squares refinement on F^2 with anisotropic thermal parameters for all nonhydrogen atoms. For **7**, **17**, and **34**, hydrogen positions were located on a Fourier difference map and then the coordinates were refined with isotropic thermal parameters, whereas for **8** and **23**, hydrogen atoms were added as fixed contributors at calculated positions riding on the relevant carbon atoms.

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Supporting Information Available: Crystal and structure refinement data for compounds **7**, **8**, **17**, **23**, and **34**. This material is available free of charge via the Internet at http://pubs.acs.org.

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