

Chlorocyclopropenes, Chloropropenyl Cations, and Cyclopropenone^{1a}

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Abstract: Treatment of tetrachlorocyclopropene with tri-*n*-butyltin hydride in hydrocarbon solvents effects successive removal of chlorines, leading to 1,2,3- and 1,3,3-trichlorocyclopropenes II and III, 1,3- and 1,1-dichlorocyclopropenes IV and VI, 3-chlorocyclopropene VII, and cyclopropene. Appropriate conditions were devised for the preparation of a II, III equilibrating mixture, a IV, VI equilibrating mixture, and VII. In ether solvents, or with ether or tin oxide impurities, the product distribution changes and 1,2-dichlorocyclopropene V and 1-chlorocyclopropene VIII are formed. Nmr studies show that in the II, III and IV, VI equilibria the isomer with fewer vinyl chlorines is preferred under some solvent and temperature conditions, in contrast to the situation in other systems. Further, IV equilibrates with its enantiomer and/or *congruent isomer* more rapidly than with its isomer VI. The nmr spectra of III, IV, VIII, IX, and X show a shielding, not deshielding, effect by chlorine, which is explained using the McConnell equation. ¹³C coupling constants and infrared spectra of the chlorocyclopropenes are in line with those of other cyclopropene derivatives. With Lewis acids these chlorocyclopropenes have been converted to dichlorocyclopropenyl cation IX and monochlorocyclopropenyl cation X. The IV, VI mixture hydrolyzes to cyclopropenone; the *d*₂ and ¹⁸O derivatives have also been prepared and examined spectroscopically. The II, III mixture hydrolyzes with ring opening to dichloroacrolein. Diels-Alder additions of the chlorocyclopropenes to a number of dienes have been examined. The products involve *exo* addition, except for VII which goes both *exo* and *endo*.

Although derivatives of cyclopropenyl cation² and cyclopropenone³ have been known for several years now, and their properties⁴ fully confirm quantum mechanical predictions of aromaticity in these systems, the parent compounds were still of interest. After a number of abortive approaches to these species,⁵ we settled on a route involving reductive dechlorination of West's tetrachlorocyclopropene⁶ to appropriate precursors. As we have reported earlier, hydrolysis of appropriate dichlorocyclopropenes in fact leads to the parent cyclopropenone,⁷ while 3-chlorocyclopropene can be converted to salts of the parent cyclopropenyl cation.⁸ In this paper we will describe the preparation and properties of trichloro-, dichloro-, and chlorocyclopropenes, and their conversion to chlorocyclopropenyl cations and cyclopropenone. In the accompanying paper we describe the preparation and properties of cyclopropenyl cation itself.

Results and Discussion

Synthesis of Chlorocyclopropenes. Treatment of tetrachlorocyclopropene with tri-*n*-butyltin hydride in high-boiling hydrocarbons led to successive replacement of chlorines with hydrogen. Although mixtures resulted in all cases, conditions were devised (*cf.* Experimental Section) by which it was possible to maximize the yields of trichloropropenes, dichlorocyclopropenes, or

monochlorocyclopropene; the pure materials were isolated by preparative vapor phase chromatography.

Reaction conditions are of some importance, and in particular it is critical that the tri-*n*-butyltin hydride be free of oxides, and that there be no traces of ether solvents (*e.g.*, residual dimethoxyethane in the tetrachlorocyclopropene). Pure decalin or hexadecane could be used as solvents, but high-boiling paraffin (Nujol) proved most satisfactory. Under these conditions the most likely path involves the usual free-radical dechlorination mechanism.⁹ The sequence is outlined in Scheme I.

Only allylic, not vinylic, chlorine should be removable, so radical A should be the first intermediate. This must then form 1,2,3-trichlorocyclopropene (II), but II can isomerize to III, 1,3,3-trichlorocyclopropene, *via* dichlorocyclopropenyl cation. In accord with this hypothesis, we find that in some runs an excess of II over III is immediately formed (nmr spectrum of the crude product) although on equilibration III predominates over II by *ca.* 5:1.

It is interesting that III is of lower energy than II. The dipole-dipole repulsion energy in III, with geminal chlorines, should be higher. One explanation of the observed trend is that II has two vinylic chlorines, and III has only one. In ordinary systems¹⁰ chlorine on a double bond has a stabilizing resonance interaction which outweighs the unfavorable interaction of electronegative chlorine with electronegative vinyl carbon. This latter factor, however, becomes dominant for fluorine, and explains the preference of fluorobullvalene (but not chlorobullvalene) for a structure with halogen on a saturated carbon.¹¹ In our system the increased electronegativity of a cyclopropenyl carbon¹² causes

(1) (a) Support of this work by the National Institutes of Health is gratefully acknowledged; (b) NIH Trainee, 1965-1969; (c) NIH Pre-doctoral Fellow, 1966-1969.

(2) (a) R. Breslow, *J. Am. Chem. Soc.*, **79**, 5318 (1957); (b) R. Breslow and H. W. Chang, *ibid.*, **83**, 2367 (1961); (c) R. Breslow, H. Höver, and H. W. Chang, *ibid.*, **84**, 3168 (1962).

(3) (a) R. Breslow, R. Haynie, and J. Mirra, *ibid.*, **81**, 247 (1959); (b) M. E. Vol'pin, Y. D. Koreshkov, and D. N. Kursanov, *Dokl. Akad. Nauk SSSR*, 506 (1959); (c) R. Breslow, T. Eicher, A. Krebs, R. Peterson, and J. Posner, *J. Am. Chem. Soc.*, **87**, 1320 (1965).

(4) A. Krebs, *Angew. Chem. Intern. Ed. Engl.*, **4**, 10 (1965).

(5) G. Ryan, Ph.D. Thesis, Columbia University, 1969.

(6) S. Tobey and R. West, *J. Am. Chem. Soc.*, **88**, 2481 (1966).

(7) R. Breslow and G. Ryan, *ibid.*, **89**, 3073 (1967).

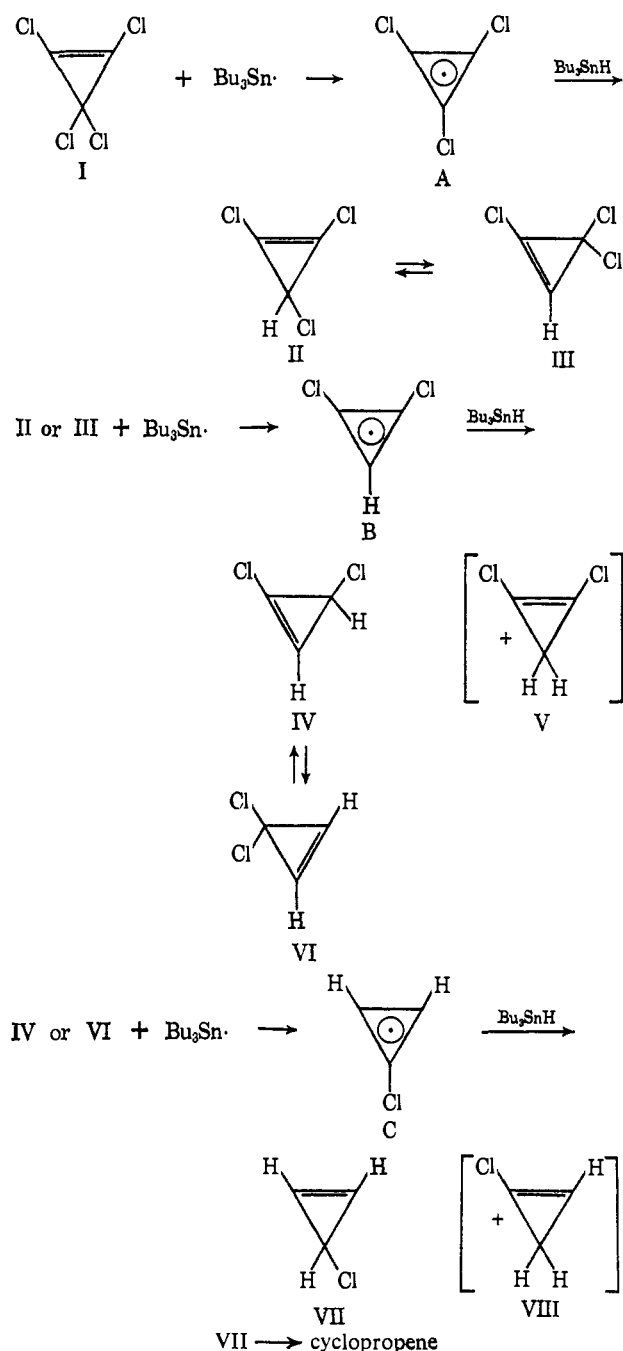
(8) R. Breslow, J. T. Groves, and G. Ryan, *ibid.*, **89**, 5048 (1967).

(9) H. G. Kuivila in "Advances in Organometallic Chemistry," Vol. I, Academic Press, New York, N. Y., 1964, pp 47-87.

(10) K. V. Scherer, Jr., and T. J. Meyers, *J. Am. Chem. Soc.*, **90**, 6253 (1968).

(11) J. F. M. Oth, R. Merenyi, J. Nielsen, and G. Schroder, *Chem. Ber.*, **98**, 3385 (1965).

Scheme I. Sequential Reductive Dechlorination by Free-Radical Chain Mechanisms

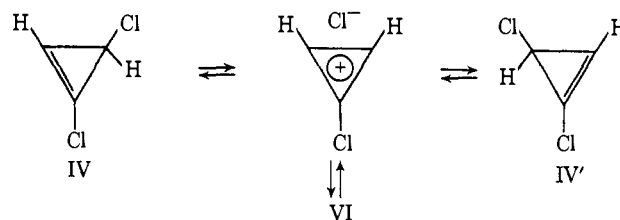


the effect of opposing σ -electron demands in II to outweigh conjugative effects, so structure III with one less vinyl chlorine and one more chlorine on the more electropositive saturated carbon is preferred.

Removal of an allylic chlorine from either II or III leads to B, dichlorocyclopropenyl radical. This can pick up a hydrogen to give either 1,3-dichlorocyclopropene (IV) or 1,2-dichlorocyclopropene (V); under these conditions IV, which is statistically favored, is the chief product. By allylic rearrangement IV equilibrates with 3,3-dichlorocyclopropene (VI).

The equilibrium between IV and VI has been studied by the use of nmr. At 40° in CCl_4 solution VI shows a singlet at δ 8.1 while IV has an AB quartet at δ 7.2 and 4.5; the IV/VI ratio is 1.5/1. In dimethoxyethane at

40° the ratio is the same, but the signals of IV at δ 7.2 and 4.5 are broadened. In acetonitrile at 40° the signal of VI at δ 8.1 is still sharp, but those of IV are broadened so as to be barely discernible. In nitromethane at 40° only the signal of VI can be seen, although quantitative comparison of this signal with that of a chloroform internal standard indicates that IV is still present. These experiments indicate that IV equilibrates with IV' (this is either the enantiomer of IV or superimposable on IV, depending on the stereochemistries at the saturated carbons. Since the $\text{IV} \rightleftharpoons \text{IV}'$ interconversion is detectable by nmr methods even if IV' is "identical" with IV, we propose that such a superimposable form be called a *congruent isomer*) more rapidly than it equilibrates with VI. It seems most likely, both *a priori* and from the effect of polar solvents in increasing



the IV \rightarrow IV' rate, that the equilibration involves an intermediate chlorocyclopropenyl chloride salt. Collapse of this ion pair occurs preferentially to IV (and IV'), and formation of the ion pair from VI is also slower than from IV (the IV/VI equilibrium is near unity). The transition state between VI and the ion pair would involve charge localization next to chlorine, while the transition state to (and from) IV localizes positive charge next to hydrogen.

At +40°, in acetonitrile, the ratio of IV/VI is 1.4, but at -40° they are in a 1:5 ratio. A similar temperature effect is noted in the trichlorocyclopropene equilibrium: the III/II ratio goes from 5:1 at +40° to 10:1 at -40°. Furthermore, in SO_2 at -40° we can detect VI but not IV, and III but not II, and quantitative studies with internal standards show that we are not dealing with nmr invisibility of one of the isomers. As we pointed out earlier, the dipole-dipole repulsion raises the energy of III, and VI, with their geminal chlorines. At low temperature a polar solvent can be oriented (at a smaller cost in $T\Delta S^\circ$) so as to minimize this repulsion. Then the preference we described for chlorine to avoid vinyl carbon becomes dominant, so VI and III are strongly favored in the equilibria.

Either IV or VI can lose the allylic chlorine to tributyltin radical forming C, chlorocyclopropenyl radical. This may then go to 3-chlorocyclopropene (VII) or 1-chlorocyclopropene (VIII); although probability favors the latter, we find that no appreciable amount of VIII is formed under these conditions. Nmr studies show that VII is in equilibrium among its three congruent isomers: in CCl_4 or CHCl_3 at 40° an AX_2 pattern is seen, while in SO_2 at -40° there is a sharp singlet at the weighted average position. In CH_2Cl_2 or CH_3CN , over the temperature range of -40 to +40°, an intermediate velocity of equilibration among congruent isomers (with a remarkably low temperature coefficient) leads to signals broadened beyond detectability, while in CH_3NO_2 a sharp singlet at 40° broadens to 25-Hz half-width at -40°. The conversion of VII to C_3H_5^+ is the subject of the accompanying paper.

(12) G. L. Closs, *Advan. Alicyclic Chem.*, **1**, 53 (1966).

We have stressed the importance of reaction conditions in this reduction sequence. If an ether such as tetraglyme is used as solvent, or if there are impurities of dimethoxyethane or tin oxides in the reagents, then varying amounts of 1,2-dichlorocyclopropene (V) and 1-chlorocyclopropene (VIII) are formed. In fact, in ether solvents the 3-chlorocyclopropene (VII) is not a detectable product while in pure hydrocarbon solvents VIII is not present at a detectable level.

This difference in products most likely reflects a change in mechanism, rather than a subtle solvent effect on the position of a reaction of radicals B and C. It is striking that the products of reduction by tri-*n*-butyltin hydride in ether solvents—II, III, V, VIII, with only occasional traces of the IV, VI mixture and no VII—correspond to the products from reduction of tetrachlorocyclopropene with LiAlH₄. This latter reaction also affords ring-opened materials, but the cyclopropenes are II, III, V, and VIII. Neither tin hydride in ether nor LiAlH₄ affords cyclopropene itself, a relatively stable compound which is always a by-product of the tin hydride-hydrocarbon solvent reductions. The LiAlH₄ reaction certainly has an ionic mechanism, and we suggest that the reaction of tri-*n*-butyltin hydride in ether is ionic as well.¹³ One possible process involves SN2' reaction, in which the chloride ion which leaves becomes coordinated to aluminum or tin. Alternatively, the metal hydrides may reduce cyclopropenyl chloride ion pairs. We have shown that the IV, VI mixture is reduced to VIII with the tin hydride in ether, but not in hydrocarbons, but more work would be needed to establish the exact mechanisms involved.

Spectra. Closs has reviewed the infrared spectra of cyclopropenes¹⁴ and has pointed out the extent to which the "C=C stretching" mode is coupled with single-bond vibrations. Wilcox and Craig¹⁵ have shown that the apparently high frequency of double-bond vibration in cyclopropene, at 1641 cm⁻¹, can be related to the coupling with stretching and bending modes of the single bonds. We have examined the infrared spectra of our cyclopropenes, including deuterated compounds prepared from tri-*n*-butyltin deuteride, and present the "double bond" bonds in Table I, along with data on methylcyclopropenes tabulated by Closs.¹⁴ It is apparent that the two series correspond well, and that vibrations of substituents on the vinyl carbons are strongly coupled with the C=C vibration.

The nmr data on compounds II–VIII are summarized in Table II. The most striking observation is the up-field shift of the vinyl proton when there is a chlorine at the other vinyl position. The effect, *ca.* 0.35 ppm, is seen in the comparison of III with VI, IV with VII, and VIII with cyclopropene. A related but smaller effect has been noted by Paquette¹⁶ in some chlorocyclobutenes; it may be explained by use of the McConnell equation¹⁷

$$\Delta\sigma = \frac{\chi}{3R^3}(1 - 3\cos^2\gamma)$$

(13) Cf. A. J. Leusink, H. A. Budding, and W. Drenth, *J. Organometal. Chem.*, **9**, 295 (1967).

(14) Reference 12, p 70 ff.

(15) C. F. Wilcox, Jr., and R. R. Craig, *J. Am. Chem. Soc.*, **83**, 3866 (1961).

(16) (a) L. A. Paquette, J. H. Barrett, R. P. Spitz, and R. Pitcher, *ibid.*, **87**, 3417 (1965); (b) L. A. Paquette and W. C. Farley, *J. Org. Chem.*, **32**, 2725 (1967).

(17) H. M. McConnell, *J. Chem. Phys.*, **27**, 226 (1957).

Table I. "Double Bond" Stretching Vibrations of Substituted Cyclopropenes

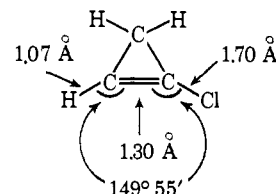
Cyclopropene derivative	Frequency, cm ⁻¹	Reference
Cyclopropene	1641	<i>b</i>
3-Chloro (VII)	1615	<i>a</i>
3-Methyl	1638	<i>b</i>
3,3-Dichloro (VI)	1624	<i>a</i>
3,3-Dimethyl	1632	<i>b</i>
1-Chloro (VIII)	1725	<i>a</i>
1-Methyl	1780	<i>b</i>
1,3-Dichloro (IV)	1723	<i>a</i>
1,3-Dimethyl	1773	<i>b</i>
1,3,3-Trichloro (III)	1723	<i>a</i>
1,3,3-Trimethyl	1768	<i>b</i>
1,2-Dichloro (V)	1805	<i>a</i>
1,2-Dimethyl	1885	<i>b</i>
1,2,3-Trichloro (II)	1808	<i>a</i>
1,2,3-Trimethyl	1880	<i>b</i>
Tetrachloro	1810	<i>b</i>
1,2-Dideuterio-3,3-dichloro	1512	<i>a</i>
1,2-Dideuterio-3,3-dimethyl	1525	<i>b</i>
1,2,3-Trideuterio-3-chloro	1515	<i>a</i>
1,3-Dideuterio-2,3-dichloro	1671	<i>a</i>
1-Deuterio-2,3,3-trichloro	1672	<i>a</i>
1-Deuterio-2,3,3-trimethyl	1718	<i>b</i>

^a Current work, in CCl₄ solution. ^b Reference 14.

Table II. Nmr Data on Chlorocyclopropenes

Compd	Chemical shifts, δ (\mathcal{J}) in CCl ₄
II	4.72
III	7.67
IV	7.20, 4.48 (2 Hz)
V	2.07
VI	8.00 (1.0 Hz, from ¹³ C satellites)
VII	7.57, 4.23 (1.5 Hz)
VIII	6.65, 1.61 (1.5 Hz)
Cyclopropene	7.01, 0.92 (1.8 Hz)

Here $\Delta\sigma$, the chemical shift difference induced by the magnetic anisotropy of the chlorine, is related to the magnetic susceptibility of chlorine (χ), the distance from the proton to the center of the C–Cl bond (R), and the angle between the C–X bond and the line R (γ). For ordinary olefins this angle is such that $\Delta\sigma$ is positive, and a *cis*-chlorine on a double bond deshields the adjacent vinyl proton. However, using known¹⁴ distances and angles for cyclopropenes and estimating the C–Cl distance as 1.70 Å, intermediate between typical vinylic and acetylenic values, we calculate that the vinyl proton should be shielded by the chlorine. In fact, for the HC=C–Cl system with the expected values for a cyclopropene as shown, $\Delta\sigma$ is calculated to be –0.56 ppm. A number of other effects are ignored in this treatment, so even this degree of

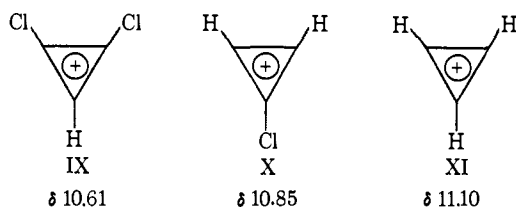


quantitative agreement with experiment is fortuitous.

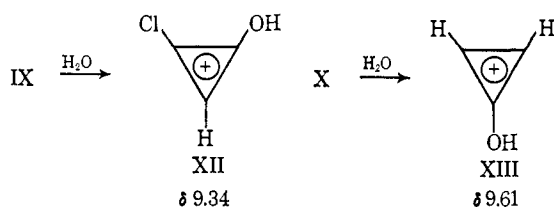
The other point of interest in the nmr spectra is the very large ¹³C–H coupling constants. For 1,3,3-trichlorocyclopropene (III) $J_{13\text{C-H}} = 240 \pm 2$ Hz, and for 3,3-dichlorocyclopropene $J_{13\text{C-H}} = 239 \pm 2$ Hz.

The vinyl ^{13}C -H coupling constants¹⁴ for the corresponding trimethyl- and dimethylcyclopropenes, 218 and 221 Hz, respectively, have been interpreted as indicating 44% s character in the carbon orbital of the vinyl C-H bond.

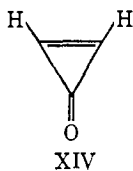
Reactions. Treatment of the mixture of trichlorocyclopropenes (II and III) with SbCl_5 affords the hexachloroantimonate salt of dichlorocyclopropenyl cation (IX). With Cl^- this can be reconverted to the trichlorocyclopropenes. Similarly, the dichlorocyclopropene mixture (IV and VI) affords chlorocyclopropenyl cation (X) as its hexachloroantimonate. Conversion of VII to C_3H_3^+ (XI) is the subject of the accompanying paper. The nmr spectra of these cations show the same type of shielding by chlorines as we have discussed above for the chlorocyclopropenes, and again shielding, not deshielding, is predicted from the McConnell equation.



On treatment with moisture, cations IX and X are converted to new species with nmr singlets at δ 9.34 and 9.61, respectively, apparently chlorohydroxycyclopropenyl (XII) and hydroxycyclopropenyl (XIII) cations. With PCl_5 both XII and XIII are reconverted to the parent chlorocyclopropenes (II, III and IV, VI).



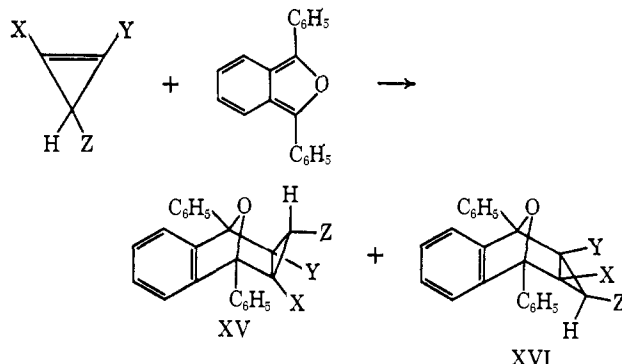
With further addition of H_2O , XIII is converted to cyclopropenone (XIV). Cyclopropenone can also be prepared⁷ by direct hydrolysis of the mixture of IV and VI. The nmr signal of XIV, at δ 9.08, shifted gradually to δ 9.30 in CH_3NO_2 on addition of H_2SO_4 (H bond-



ing?) and then suddenly shifts to δ 9.6 with further acid (formation of XIII). The ^{13}C satellites of XIV indicate a ^{13}C -H coupling constant of 230 ± 2 Hz, and an H-H coupling of 3.0 ± 0.2 Hz. In the infrared, XIV has bands at 1864 and 1833 cm^{-1} , but not in the 1600- cm^{-1} region, while XIV- d_2 (from hydrolysis of dideuterodichlorocyclopropenes) has bands at 1858 and 1779 cm^{-1} . Hydrolysis with 85% enriched H_2^{18}O affords XIV- ^{18}O , with bands at 1834 and 1817 cm^{-1} , while XIV- $^{18}\text{O}-d_2$ has bands at 1858 and 1764 cm^{-1} . On standing with H_2O , XIV is slowly hydrolyzed to acrylic acid. Further studies of the chemistry of XIV will be reported elsewhere.

Direct hydrolysis of the trichlorocyclopropenes (II, III) affords *cis*-2,3-dichloroacrolein, and in nonpolar solvents the hydrolysis of IV, VI affords both XIV and *trans*-3-chloroacrolein. These ring openings are reminiscent of the chemistry⁶ of tetrachlorocyclopropene.

A number of studies of Diels-Alder reactions with cyclopropene derivatives have been reported.¹⁸ As part of our characterization of the chlorocyclopropenes we converted them to adducts with diphenylisobenzofuran



furan. Thus, with 3-chlorocyclopropene (VII) we obtained two adducts, (XV, X = Y = H; Z = Cl) and (XVI, X = Y = H; Z = Cl), in a ratio of 4.5/1. The assignment is based on nmr data; both XV and XVI show AB_2 patterns, $J = 2$ Hz, but the single proton in XV is at δ 3.80 while in XVI it comes at δ 2.0. In view of the unreactivity of *gem*-dichlorocyclopropenes in this reaction (*vide infra*) we exclude structures related to XV or XVI with H and Z interchanged. Furthermore, the 2-Hz AB coupling is consistent with *trans* protons on a cyclopropane. We assume that the *endo* proton in XVI will be shielded by the benzene ring relative to the proton in XV, in line with nmr observations¹⁸ on other *endo*-cyclopropene adducts.

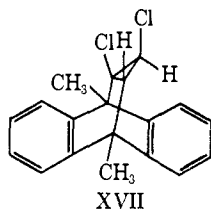
Reaction of diphenylisobenzofuran with the mixture of dichlorocyclopropenes IV and VI afforded only the *exo* adduct of IV (XV, X = H; Y = Z = Cl). The reaction is quantitative: as IV is removed more is formed by isomerization of VI. The assignment of structure XV is based on the nmr chemical shift of the H, 0.52 ppm lower than in the XV from chlorocyclopropene (VII) as expected because of the extra chlorine. Only a tiny trace of an nmr signal can be seen in the region expected for XVI (X = H; Y = Z = Cl). Similarly, 1,2-dichlorocyclopropene (V) adds to afford the *exo* adduct (XV, X = Y = Cl; Z = H).

Reaction of the mixture of trichlorocyclopropenes (II, III) affords the *exo* adduct XV (X = Y = Z = Cl), with its single proton at δ 4.73. Again only the isomer (II) without a *gem*-dichloro group reacts, and the equilibrium between II and III is displaced as II is removed. The mixture of dichlorocyclopropenes (IV, VI) also adds to 9,10-dimethylantracene to afford a single adduct XVII derived from IV.

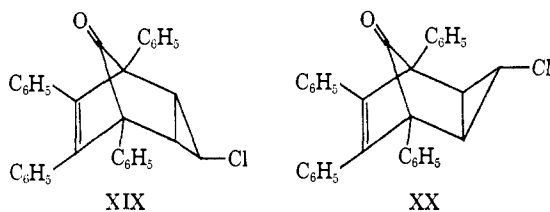
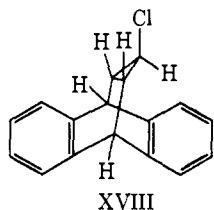
3-Chlorocyclopropene was added to anthracene to afford XVIII, which had been prepared by Cristol¹⁹ in a

(18) (a) K. B. Wiberg and W. J. Bartley, *J. Am. Chem. Soc.*, **82**, 6375 (1960); (b) M. A. Battiste, *Tetrahedron Letters*, 3795 (1964); (c) G. L. Closs, L. E. Closs, and W. A. Boll, *J. Am. Chem. Soc.*, **85**, 3796 (1963); (d) M. A. Battiste, *ibid.*, **85**, 2175 (1963); (e) D. C. F. Law and S. W. Tobey, *ibid.*, **90**, 2376 (1968).

(19) (a) S. J. Cristol, R. M. Sequeira, and C. H. DePug, *ibid.*, **87**, 4007 (1965); (b) S. J. Cristol, T. W. Russell, J. R. Mohrig, and D. E. Plorde, *J. Org. Chem.*, **31**, 581 (1966).



different fashion. With tetracyclone, 3-chlorocyclopropene gives two adducts, assigned structures XIX and XX. The structure assignment was made by assuming that the H-C-Cl proton in XIX would be shielded in



the nmr relative to that in XX. Consistent with this assignment, XIX was thermally unstable relative to XX. A similar difference in the ease of thermal decarbonylation between *endo*- and *exo*-tricyclooctenones has been observed by other investigators.²⁰

It is interesting that these Diels-Alder reactions of chlorocyclopropenes afford *exo* as well as the "normal" *endo* products. In fact, only with 3-chlorocyclopropene is any *endo* product formed at all. Thus in this series Alder's *endo* rule is of no predictive value.

Experimental Section

Warning: Exposure to volatile chlorocyclopropenes causes severe headaches and may be dangerous. Some have also proved explosive and shock sensitive, and they should not be handled as pure liquids in large quantities.

1,2,3- and 1,3,3-Trichlorocyclopropene. A flask was charged with 100 ml of paraffin oil (purified by prior heating at 80° and 0.1 mm to remove low-boiling materials) and 3 g (0.0168 mole) of tetrachlorocyclopropene (I).⁶ The system was cooled to 20° and flushed with N₂; then 8.5 g (0.029 mole) of tri-*n*-butyltin hydride²¹ was added in a steady stream with good stirring (under N₂). After 45 min stirring at 20–23° the reaction products were distilled in a trap at –70° at 0.1 mm with warming of the reaction flask to 35°. The clear colorless distillate, *ca.* 1.3 g, was fractionated by vpc on a 5 ft × 3/8 in. stainless steel column of 3% SE-30 on Chromosorb G at 40°. With a He flow of 1 cc/sec, the retention time of the trichlorocyclopropenes was 8 min, while dichlorocyclopropenes had retention time 5 min and tetrachlorocyclopropene 9 min. The mixture of 10% Cl₄, 60% Cl₃, and 30% Cl₂ cyclopropenes gave, by vpc fractionation, an overall 36% yield of the colorless lachrymatory trichlorocyclopropene mixture. The mass spectrum had *m/e* 142, with P, P + 2, P + 4, and P + 6 ratios of 100:99:30:4. The nmr spectrum (CCl₄) showed a singlet at δ 7.67 (assigned to the vinyl proton of 1,3,3-trichlorocyclopropene, III) and at 4.72 (assigned to 1,2,3-trichlorocyclopropene, II). In some runs the latter was the major component, but on standing the two reached equilibrium at a 5:1 ratio of III to II.

(20) (a) H. Tanida, T. Tsuji, and T. Irie, *J. Am. Chem. Soc.*, **89**, 1953 (1967); (b) M. A. Battiste, *Chem. Ind. (London)*, 550 (1961).

(21) H. G. Kuivila and O. F. Beumel, Jr., *J. Am. Chem. Soc.*, **83**, 1246 (1961).

1,3- and 3,3-Dichlorocyclopropenes. The reaction was performed as above, but 14.7 g of tri-*n*-butyltin hydride was used, and the reaction mixture was stirred for 1 hr. The clear product was collected at –70° by evacuation to 0.1 mm and warming of the reaction flask to 40°. The total product, 1.1 g, contained 85% Cl₂, 13% Cl₃, and 2% Cl₄ cyclopropenes and it was fractionated by vpc as above. The overall yield of isolated dichlorocyclopropenes was 47%, based on tetrachlorocyclopropene. The dichlorocyclopropene mixture showed *m/e* 108, with P, P + 2, and P + 4 ratios of 100:65:11. The nmr (CCl₄) showed a singlet at δ 8.0 (3,3-dichlorocyclopropene, IV) and a pair of doublets at δ 7.67 and 4.72 (*J* = 2 Hz) for 1,3-dichlorocyclopropene (IV).

3-Chlorocyclopropene (VII). Tri-*n*-butyltin hydride (17.2 g) was added over 40 min to 3.0 g of tetrachlorocyclopropene in 50 ml of purified paraffin oil under argon. The mixture was then heated to 80° for 30 min and quickly cooled to 30–40°. The volatile product was then distilled into a trap at –78° under vacuum. The crude product, 0.60 g, was a colorless mixture of dichlorocyclopropenes (17.5% yield) and 3-chlorocyclopropene (22.5%), which was fractionated by vpc as above. The 3-chlorocyclopropene was a clear mobile liquid which solidified at –77°. The mass spectrum showed *m/e* 74 (and 76) in a 3:1 ratio, 73 and 75, and a base peak at 39 (80% of total intensity). The infrared spectrum (CCl₄) had bands at 3080, 2970, 1615, 1245, 1155, 1120, 1025, and 865 cm⁻¹. The nmr spectrum (CCl₄) had a two-proton doublet at δ 7.57 (*J* = 1.5 Hz) and a one-proton triplet at 4.23 (*J* = 1.5 Hz). The compound could be stored under argon at –78°, but deteriorates after several days.

1,2-Dichlorocyclopropene (V). A solution of tetrachlorocyclopropene (3.0 g) in 75 ml of dry tetraglyme was held at 0° under argon while tri-*n*-butyltin hydride (14.7 g) was added in a slow stream. The mixture was stirred for 20 min at 0°, 10 min at room temperature, and the volatile products were collected in a trap at –78° (0.1 mm). During this distillation the reaction flask was warmed to 40°. The clear distillate (0.4 g) was diluted with 0.75 ml of toluene (warning: without dilution the distillate has exploded on occasion), and fractionated by vpc as above. The 1,2-dichlorocyclopropene had a retention time of 2 min and was collected as a 5–10% yield of colorless lachrymatory liquid. The nmr (CCl₄) showed a singlet at δ 2.0, while the infrared had bands at 2941, 2860, 1808, 1472, 1058, and 948 cm⁻¹.

1-Chlorocyclopropene (VIII). This compound was also isolated from the above mixture in 5–10% yield with a retention time of 1 min. The nmr (CCl₄) had a one-proton triplet (*J* = 2 Hz) at δ 6.65 and a two-proton doublet (2 Hz) at δ 1.61. The infrared spectrum had bands at 3105, 2950, 2865, 1725, 1475, 1043, and 952 cm⁻¹. The mass spectrum had *m/e* 74, with a P/P + 2 ratio of 3:1.

Reduction of Tetrachlorocyclopropene with Lithium Aluminum Hydride. A solution of LiAlH₄ (2.01 g) in 100 ml of tetraglyme was cooled to 0° and 3 g of tetrachlorocyclopropene was added dropwise cautiously with good stirring. After the addition the reaction mixture was stirred for 10 min at 0° and the volatile products were transferred *in vacuo* into a trap at –78°. The distillate, 0.3 g, showed the nmr peaks characteristic of the trichlorocyclopropenes, 1,2-dichlorocyclopropene, and 1-chlorocyclopropene. The compounds were also identified by vpc and infrared characteristics. No other dichloro- or monochlorocyclopropenes were present; occasionally propargyl chloride was identified (δ 2.2 and 4.0, *J* = 2.5 Hz) along with other unknown ring-opened materials.

Reaction of 1,3-Diphenylisobenzofuran with the Trichlorocyclopropenes. A solution of 1.89 g of diphenylisobenzofuran in 10 ml of CHCl₃ was added to 0.98 g of the trichlorocyclopropene mixture in 2 ml of CHCl₃. The yellow color discharged in 30 sec, and the product was isolated by silica gel chromatography. The *exo* adduct (XV, X = Y = Z = Cl) crystallized (petroleum ether), mp 146–148°, in 46% overall yield. *Anal.* Calcd for C₂₃H₁₅OCl₃: C, 66.75; H, 3.63; Cl, 25.75. Found: C, 66.78; H, 3.35; Cl, 25.63. The mass spectrum had *m/e* 412 with appropriate P + 2, P + 4, and P + 6 peaks. The nmr spectrum (CDCl₃) had 14 protons in a multiplet at δ 7.3–7.8 and one proton as a singlet at 4.73.

Reaction of 1,3-Diphenylisobenzofuran with 1,3- and 3,3-Dichlorocyclopropenes. Reaction as above gave, after chromatography, an almost quantitative yield of XV (Y = Z = Cl; X = H), mp 117–118°. *Anal.* Calcd for C₂₃H₁₆OCl₂: C, 72.82; H, 4.23; Cl, 18.72. Found: C, 72.31; H, 4.06; Cl, 18.78. The mass spectrum had *m/e* 378 (380,382), and the nmr spectrum (CDCl₃) had one proton at δ 2.18 as a doublet (3 Hz), one proton at 4.32 as a doublet (3 Hz), and 14 protons in a multiplet at 7.5–7.8.

Reaction of 9,10-Dimethylantracene with 1,3- and 3,3-Dichlorocyclopropenes. A solution of 0.108 g of the dichlorocyclopropene mixture and 0.315 g of 9,10-dimethylantracene in 25 ml of benzene was kept at room temperature for 2 days. Removal of the solvent and silica gel chromatography afforded a 65% yield of adduct (XVII), mp 167–168° (ethanol). *Anal.* Calcd for $C_{19}H_{16}Cl_2$: C, 72.38; H, 5.08; Cl, 22.54. Found: C, 71.94; H, 4.96; Cl, 22.50. The mass spectrum had m/e 314 (316, 318) and the nmr ($CDCl_3$) showed one proton at δ 1.7 (doublet, 3 Hz), one proton at 2.5 (doublet, 3 Hz), a three-proton singlet at 2.1 and another at 2.2, and eight protons in a multiplet at 7.2.

Reaction of 1,3-Diphenylisobenzofuran with 1,2-Dichlorocyclopropene. Approximately 20 mg of 1,2-dichlorocyclopropene was treated with 1,3-diphenylisobenzofuran in $CHCl_3$ to afford, after chromatography, 70 mg (quantitative yield) of an adduct (XV, X = Y = Cl; Z = H), mp 160–164°. The mass spectrum had m/e 378 (380, 382) and the nmr ($CDCl_3$) showed one proton at δ 2.05 (doublet, 7.5 Hz), one proton at 3.01 (doublet, 7.5 Hz), and 14 protons at 7.2–7.8.

Reaction of Anthracene with 3-Chlorocyclopropene. A solution of 50 mg of 3-chlorocyclopropene and 120 mg of anthracene in 4 ml of benzene was heated on a steam bath for 30 min. The unreacted anthracene was removed by filtration and the benzene was evaporated to afford crude XVIII, 0.105 g (65%). The product, after crystallization from ethanol, had mp 173–174.5° (lit.²¹ mp 173–175°). The nmr spectrum (CCl_4) had a multiplet at δ 1.79 (two protons), a triplet at 1.98 (one proton, $J = 2$ Hz), a multiplet at 4.46 (two protons), and a multiplet at 7.07 (eight protons).

Reaction of Tetracyclone with 3-Chlorocyclopropene. A solution of 3-chlorocyclopropene (50 mg) and tetracyclone (387 mg) in 15 ml of CCl_4 was allowed to stand overnight. The solvent was removed and the residue crystallized from ether. A first crop of XX (100 mg) was recrystallized to pure XX, mp 200° dec.

Anal. Calcd for $C_{32}H_{23}ClO$: C, 83.73; H, 5.05; Cl, 7.72. Found: C, 83.64; H, 5.16; Cl, 6.60.

The mass spectrum (75 V) had m/e (relative intensity) 460 (0.7), 458 (2.3), 432 (6.9), 430 (16.7), 395 (100), 317 (61). The infrared (CCl_4) had a band at 1780 cm^{-1} ; the nmr ($CDCl_3$) had a one-proton triplet at δ 3.35 ($J = 1.5$ Hz), a two-proton doublet at 2.67 ($J = 1.5$ Hz), and 20 protons at 6.83, 7.17. The isomer XIX was unstable and could not be isolated pure, but showed in the nmr ($CDCl_3$) a one-proton triplet at δ 3.0 ($J = 1.5$ Hz), a two-proton doublet at 2.54 ($J = 1.5$ Hz), and the 20 protons at 6.81, 7.17.

Reaction of Diphenylisobenzofuran with 3-Chlorocyclopropene. A solution of 1,3-diphenylisobenzofuran (290 mg) and 3-chlorocyclopropene (80 mg) in 5 ml of CCl_4 was allowed to stand 1 hr under argon. Chromatography on silica afforded XV (X = Y = H; Z = Cl), mp 117–119°.

Anal. Calcd for $C_{23}H_{17}ClO$: C, 80.10; H, 4.97; Cl, 10.29. Found: C, 79.92; H, 5.01; Cl, 10.28.

The nmr (CCl_4) had a two-proton doublet at δ 2.15 ($J = 2$ Hz), a one-proton triplet at 3.80 ($J = 2$ Hz), and 14 protons at 7.0–7.8. The other isomer (XVI, X = Y = H; Z = Cl) did not survive chromatography, but it showed a one-proton triplet at 2.0 ($J = 2$ Hz), and a two-proton doublet at 2.7 ($J = 2$ Hz).

Cyclopropenone. A water solution of cyclopropenone⁷ could be prepared by adding 5 ml of H_2O (or D_2O) to 5 ml of CCl_4 containing 0.5 g of the 1,3- and 3,3-dichlorocyclopropene mixture at 0°. After 2–3 hr hydrolysis is complete and the water layer contains cyclopropenone; nmr δ 9.08, infrared 1850 cm^{-1} (broad). Dilute ($\sim 0.1 M$) solutions have a half-life of 1 week or more at room temperature, but concentrated solutions deteriorate within 1 day.

Solutions in organic solvents miscible with H_2O were obtained by adding a few drops of H_2O to the organic solution of the dichlorocyclopropenes. A CH_2Cl_2 solution could be obtained by (inefficient) extraction of the above H_2O solution. The organic solutions of cyclopropenone all showed infrared bands at 1864 and 1833 cm^{-1} , and an nmr singlet at δ 9.1. The ^{13}C satellites ($J^{13}C-H = 230$ Hz) are doublets ($J_{H-H} = 3$ Hz).

A solution of 50 mg of cyclopropenone in 1 ml of CH_3NO_2 , free of dichlorocyclopropene starting materials as judged by nmr and vpc analysis, was treated with 0.5 g of PCl_5 for a few minutes. The nmr now revealed the singlet at δ 8.2 characteristic of 3,3-dichlorocyclopropene, while the cyclopropenone signal at 9.1 had disappeared. The volatile material was collected and fractionated by vpc; the mixture of 1,3- and 3,3-dichlorocyclopropenes was collected and identified by retention time, nmr, infrared, and re-conversion to cyclopropenone (infrared bands) on exposure to moisture.

Dichlorocyclopropenyl Hexachloroantimonate (IX). A solution of this cation was prepared by adding 50 mg of the mixture of trichlorocyclopropenes in 0.3 ml of CH_3NO_2 to 0.1 ml of $SbCl_5$ in 0.7 ml of CH_3NO_2 at 0°. The nmr showed a singlet at δ 10.61 assigned to a dichlorocyclopropenyl cation. In the presence of moisture varying amounts of a singlet at δ 9.34 also appeared. The signal at δ 10.61 could be decreased in favor of that at δ 9.34 by addition of 1 drop of H_2O .

A white solid precipitate of this salt was obtained by carrying out the reaction of 0.1 ml of $SbCl_5$ with 70 mg of the trichlorocyclopropenes in 5 ml of CH_2Cl_2 at -70° . The salt showed infrared bands (Nujol) at 3080 (m), 1330 (m), 1271 (m), and 874 cm^{-1} (s), and the nmr signal (CH_3NO_2) at δ 10.61.

A solution of 150 mg of the salt in 1 ml of CH_3NO_2 was added to 0.82 g of tetraethylammonium chloride in 1 ml of CH_3NO_2 . The volatile products consisted of the trichlorocyclopropenes, identified by nmr, vpc, and infrared.

Chlorocyclopropenyl Hexachloroantimonate (X). A mixture of 1,3- and 3,3-dichlorocyclopropenes was treated with $SbCl_5$ in CH_3NO_2 as above. The nmr spectrum of the cation showed a singlet at δ 10.85. The precipitated salt could be prepared, as above, from CH_2Cl_2 solution, and the salt was reconverted to the dichlorocyclopropene mixture, as above, with tetraethylammonium chloride. Addition of a drop of H_2O to the CH_3NO_2 of the chlorocyclopropenyl cation produced a new nmr signal at δ 9.61 which shifted to δ 9.25 with further H_2O .

Hydrolysis of Trichlorocyclopropenes. Treatment of the trichlorocyclopropene mixture in ether solution with a few drops of H_2O for 10 min led to formation of *cis*-2,3-dichloroacrolein as the major (and only identified) product, identical with an authentic sample.