and cycloheptyl methyl ether in the ethereal solution. The total yield was 91.8%.

Anodic Oxidation of Bicyclo[3.1.0]hexane (2).—The electrolysis of a solution of 8.2 g (0.1 mol) of **2** and 3.0 g (0.01 mol) of tetraethylammonium *p*-toluenesulfonate in 40 ml of methanol was carried out by the same method used in the anodic oxidation of **1**. The gas chromatographic analysis indicated the formation of compounds **7a,b**, **8a,b**, and **9**, the total yield being 50%. The identifications of **7a,b** and **8a,b** were accomplished by the comparisons of their nmr data and gas chromatographic retention times with those of authentic samples. The nmr spectrum and elemental analysis of **9** coincided with the assigned structure: nmr (CCl_4) τ 8.5 (m, 4, CH_2), 7.95 (m, 2, CH_2CH=), 6.88 (s, 6, OCH_3), 5.73 (t, 1, OCHO), 5.05 (m, 2, =CH_2), and 4.35 (m, 1, CH=).

Anal. Calcd for $C_8H_{16}O_2$: C, 66.63; H, 11.18. Found: C, 66.68; H, 11.32.

Acidic Methanolysis of 2.—A solution of 2.1 g (0.025 mol) of bicyclo[3.1.0]hexane and 0.98 g (0.005 mol) of *p*-toluenesulfonic acid in 10 ml of methanol was refluxed for 26 hr. Work-up of the reaction mixture and product identification were carried out by the same method used in the methanolysis of **1**. The total yield of products (Table II) was 90%.

Registry No.—**1**, 286-08-8; **2**, 285-58-5; **6**, 28995-68-8; **9**, 28995-69-9.

Acknowledgment.—The authors are grateful for the kind encouragement of Dr. Ryohei Oda.

Mechanism of the Diels–Alder Reaction of Halocyclopropenes[1a]

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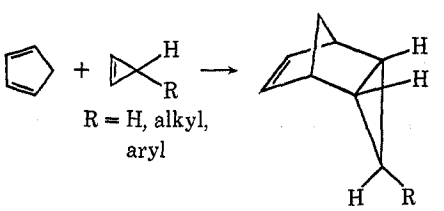
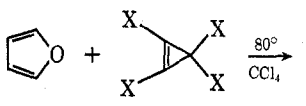
The possibility that perhalocyclopropenes undergo Diels–Alder reaction by first dissociating to a cyclopropenium halide ion pair which then reacts with diene is discussed. Several criteria for deciding between the one-step direct Diels–Alder mechanism and the two-step ionic process are described. Stereochemical studies and kinetic data (the order of the reaction, solvent polarity rate effects, activation parameters) appear to be consistent with the simple direct cycloaddition mechanism.

The great majority of cyclopropenes are excellent dienophiles in the Diels–Alder reaction, undergoing rapid cycloaddition with cyclopentadiene, for example, to produce the endo adduct;[2-4] monosubstitution at C_3 leads to formation of the endo–anti adduct[2a,b,d] and geminal disubstitution often inhibits reaction completely.[2a-d] This substituent effect has most reasonably been interpreted as being steric in origin.

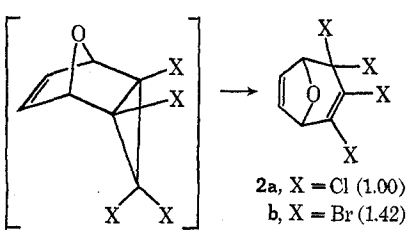


In contrast to these observations with alkyl- and aryl-substituted cyclopropenes, Law and Tobey[5] have argued that the Diels–Alder reactivity of perhalocyclopropenes, and the stereochemistry of their cycloadducts, has an electronic basis. Their study of the cycloadditions of six different perhalocyclopropenes with cyclopentadiene, furan, or butadiene revealed that all products have endo stereochemistry (or are derived from initial endo adducts by the cyclopropyl halide to allyl halide electrocyclic reaction[6]) and that the rate of cycloaddition to furan is greatest when the largest halogen (Br > Cl > F) is at C_3 of the starting material. Thus, relative to tetrachlorocyclopropene (**1a**), tetrabromocyclopropene (**1b**) reacts more rapidly, whereas all products from **3** and **6a–c** are formed more slowly (k_{rel} in parentheses).

Based upon these observations, Law and Tobey conclude (1) when the initially formed endo adduct has Br or Cl syn to the ethylene bridge, concerted ionization and disrotatory ring opening occurs[6] yielding the corresponding bicyclic diene (**2a,b**, **5**), and, when F is syn, the initial adduct is stable (**4**, **7a–c**); (2) since the rate of reaction increases as the C_3 substituent is changed from F to Cl to Br, neither the steric argument (above)



1a, X = Cl
b, X = Br



2a, X = Cl (1.00)
b, X = Br (1.42)

(1) (a) Partial support of this work by the Robert A. Welch Foundation is gratefully acknowledged, as is the assistance of the National Science Foundation in the purchase of a Varian Associates A-56/60A nmr spectrometer. (b) To whom inquiries should be addressed at the Department of Chemistry, The University of Tennessee, Knoxville, Tenn. 37916. (c) National Defense Education Act Fellow, 1966–1969.

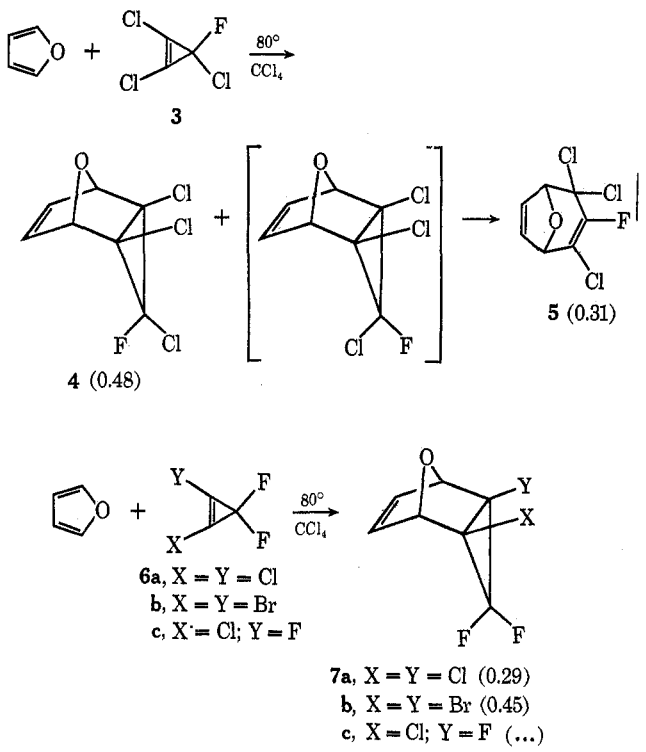
(2) (a) G. L. Closs, *Advan. Alicycl. Chem.*, **1**, 53 (1966); (b) G. L. Closs, L. E. Closs, and W. A. Böll, *J. Amer. Chem. Soc.*, **85**, 3796 (1963); (c) J. A. Berson and M. Pomerantz, *ibid.*, **86**, 3896 (1964); (d) M. A. Battiste, *Tetrahedron Lett.*, 3795 (1964); (e) S. C. Clarke, K. J. Frayne, and B. L. Johnson, *Tetrahedron*, **25**, 1265 (1969); (f) J. S. Haywood-Farmer and R. E. Pincock, *J. Amer. Chem. Soc.*, **91**, 3020 (1969).

(3) Some examples of exo addition have recently been reported,[4] most of them involving dienes like cyclopentadienones and furans for which nonbonded interactions in the exo transition state are less severe than with cyclopentadiene.

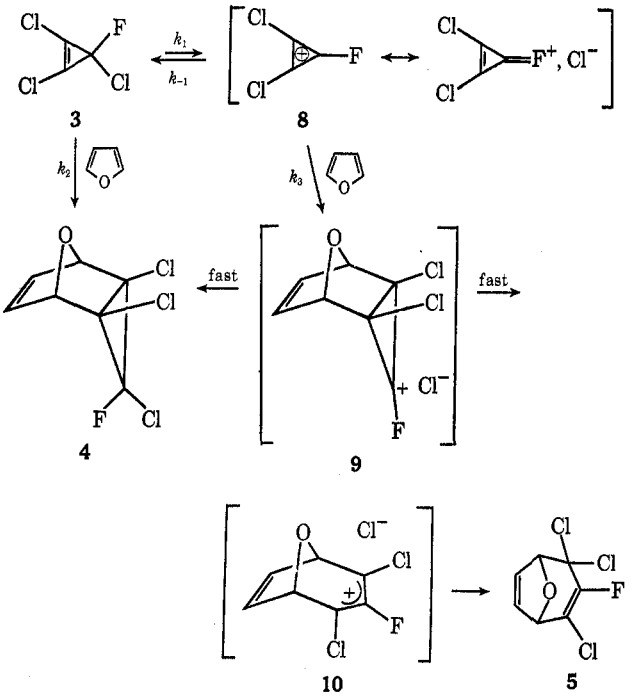
(4) (a) R. Breslow and J. T. Groves, *J. Amer. Chem. Soc.*, **92**, 984 (1970); (b) R. Breslow, G. Ryan, and J. T. Groves, *ibid.*, **92**, 988 (1970); (c) P. B. Sargeant, *ibid.*, **91**, 3061 (1969); (d) H. Monti and M. Bertrand, *Tetrahedron Lett.*, 2587, 2591 (1970); (e) J. P. Zahra and B. Waegell, *ibid.*, 2537 (1970); (f) M. A. Battiste and C. T. Sprouse, Jr., *ibid.*, 3165, 3893 (1969); (g) D. T. Longone and D. M. Stehouwer, *ibid.*, 1017 (1970).

(5) D. C. F. Law and S. W. Tobey, *J. Amer. Chem. Soc.*, **90**, 2376 (1968).

(6) See the following recent papers and references cited therein: (a) U. Schöllkopf, *Angew. Chem., Int. Ed. Engl.*, **7**, 588 (1968); (b) P. v. R. Schleyer, T. M. Su, M. Saunders, and J. C. Rosenfeld, *J. Amer. Chem. Soc.*, **91**, 5174 (1969); (c) T. M. Su, W. F. Sliwinski, and P. v. R. Schleyer, *ibid.*, **91**, 5386 (1969); (d) J. M. Bollinger, J. M. Brinich, and G. A. Olah, *ibid.*, **92**, 4025 (1970); (e) D. T. Clark and G. Smale, *Chem. Commun.*, 868, 1050 (1969); (f) W. E. Parham and K. S. Yong, *J. Org. Chem.*, **35**, 683 (1970).



SCHEME I



nor the Alder rule for dienophile reactivity appears to be operative; an argument based upon stabilization of the ground-state reactant (F > Cl > Br) is suggested.

There is another explanation, however, that is consistent not only with these rate and product studies but also with the steric effect expected for a C_3 halogen. This alternate mechanism is based upon a prior ionization of the cyclopropene followed by cycloaddition of the resulting ion pair with diene,[7] shown in Scheme I for the reaction of 1,2,3-trichloro-3-fluorocyclopropene (**3**) with furan.

In support of this scheme are the following considerations.

(1) Any *direct* Diels–Alder reaction (k_2) should produce only **4**, consistent with the smaller steric demands of F.

(2) Adduct **4** may be formed, in part, *via* cycloaddition of ion pair **8**, but this should not be a major route since 3,3-difluorocyclopropenes (**6a–c**) readily give adduct but are unlikely to ionize.

(3) The postulated equilibrium between covalent compound **3** and ion pair **8** is a well-established and facile process for 3-chlorocyclopropenes in a variety of solvents;[4a,b] the equilibrium should lie far to the left.

(4) The cationic moiety of the ion pair is stablized by fluorine, perhaps by the contributing structure having positive charge on the halogen.[4a,b,11] Because of this and because of the greater leaving-group ability of Cl relative to F, ion pair **8**, alone, is formed.

(5) Partial localization of the π electrons[11e] as implied by the second contributing structure serves to guarantee that cycloaddition will occur exclusively across the vic dichloro substituted bond; ion-pair return to **3** rather than its gem dichloro isomer is well established.[11e]

(6) Cycloaddition of a cyclopropenium ion with a diene is a thermally allowed process[12] and should occur on the face of the three-membered ring anti to the gegenion. By analogy to the reaction of other cyclopropenes, endo cycloadduct **9** is shown; analogy to the [4 + 2] cycloaddition of dienes with allylic cations,[13] however, might suggest that exo adduct would be favored. Although the overall conversion of a cyclopropenium ion into an allylic cation should be endothermic by nearly 20 kcal/mol,[4a] the process is made feasible here by the exothermic formation of two σ bonds.

(7) Ionic cycloadduct **9** can either collapse to **4** (which is stable because of the reluctance of F to ionize in the recognized disrotatory mode[6]) or, because there are no restrictions on the disrotatory opening of an already formed cyclopropyl cation, can yield allylic cation **10** which collapses to **5**.

(8) Generalizing from this scheme, *gem*-difluorocyclopropenes **6a–c** react exclusively by the single-step mechanism (k_2) because of the low steric requirement coupled with poor leaving-group ability. Conversely, *gem*-dibromo- and *gem*-dichlorocyclopropenes **1b** and **1a** undergo the two-step process (k_3), exclusively, the

(7) A similar multistep ionic scheme has been advanced for the cycloaddition reactions of cyclopropanones,[8] aziridines,[9] and epoxides.[10]

(8) (a) S. S. Edelson and N. J. Turro, *J. Amer. Chem. Soc.*, **92**, 2770 (1970); (b) N. J. Turro, S. S. Edelson, and R. B. Gagosian, *J. Org. Chem.*, **35**, 2058 (1970).

(9) (a) R. Huisgen, W. Scheer, and H. Mäder, *Angew. Chem., Int. Ed. Engl.*, **8**, 602 (1969); (b) R. Huisgen, W. Scheer, H. Mäder, and E. Brunn, *ibid.*, **8**, 604 (1969); (c) R. Huisgen and H. Mäder, *ibid.*, **8**, 604 (1969); (d) P. B. Woller and N. H. Cromwell, *J. Org. Chem.*, **35**, 888 (1970).

(10) (a) T. Do-Minh, A. M. Trozzolo, and G. W. Griffin, *J. Amer. Chem. Soc.*, **92**, 1402 (1970); (b) D. R. Arnold and L. A. Karnischky, *ibid.*, **92**, 1404 (1970); (c) W. F. Bayne and E. I. Snyder, *Tetrahedron Lett.*, 2263 (1970).

(11) (a) R. West, A. Sâdo, and S. W. Tobey, *J. Amer. Chem. Soc.*, **88**, 2488 (1966); (b) R. West, *Accounts Chem. Res.*, **3**, 130 (1970); (c) R. M. Smith and R. West, *Tetrahedron Lett.*, 2141 (1969); (d) M. A. Battiste and B. Halton, *Chem. Commun.*, 1368 (1968); (e) D. J. Burton and G. C. Briney, *J. Org. Chem.*, **35**, 3036 (1970).

(12) For a discussion of cycloaddition reactions of aromatic compounds, see D. Bryce-Smith, *Chem. Commun.*, 806 (1969).

(13) (a) H. M. R. Hoffmann, D. R. Joy, and A. K. Suter, *J. Chem. Soc. B*, 57 (1968); (b) H. M. R. Hoffmann and D. R. Joy, *ibid.*, 1182 (1968).

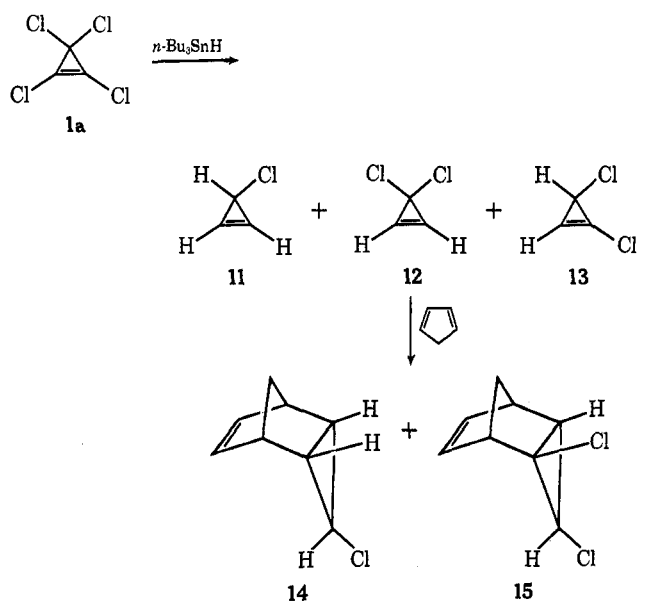
faster reaction of **1b** being due to its more ready bond heterolysis.

A number of approaches may be used to probe for the validity of the two-step mechanism. Several of these are described in the following section.

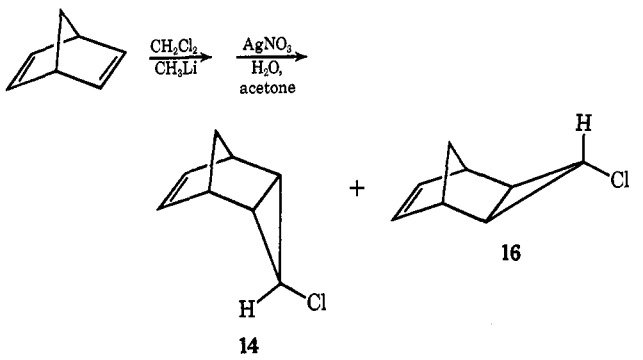
Results and Discussion

Our initial studies focused on a possible stereochemical distinction between the one-step and two-step mechanisms. The accumulated data from the cyclopropene literature strongly support the contention that direct Diels–Alder reaction (k_2) of perhalocyclopropenes with cyclopentadiene will lead to endo product.[2] On the other hand, a firm prediction of product stereochemistry in the two-step ionic mechanism is more difficult to make; as was discussed earlier, analogy to the known [4 + 2] chemistry of allylic cations[13] would suggest exo adduct as a distinct possibility. Whether exo or endo adduct is initially formed is a moot question for cyclopropenes **1a** and **1b** since only ring-opened products **2a** and **2b** are produced. We considered the possibility of trapping the initial cyclopropyl adduct by reductive removal of the halogens but were unable to find conditions suitable for this task.

We therefore turned to an investigation of adduct stereochemistry from less highly halogenated cyclopropenes for which the initially formed cyclopropanes are stable. Following the procedure of Breslow, *et al.*,[4b] reduction of tetrachlorocyclopropene (**1a**) with tri-*n*-butyltin hydride in paraffin oil affords a mixture consisting of 59% 3-chlorocyclopropene (**11**), 14% 3,3-dichlorocyclopropene (**12**), and 27% 1,3-dichlorocyclopropene (**13**). Reaction of this mixture with an excess of cyclopentadiene in CCl_4 at room temperature produces two adducts, **14** and **15**, whose endo structures and additional stereochemistry can be rigorously assigned. There is no evidence for the formation of any exo adduct.

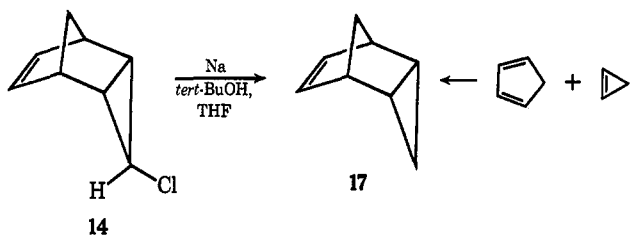


Adduct **14** is identical with the minor product (26%) formed by reaction of chlorocarbenoid with norbornadiene, followed by treatment with aqueous silver nitrate to remove any allylic chlorides; the major product (74%) from this reaction is the exo isomer **16**.[14]



Structures **14**, **15**, and **16** are strongly supported by nmr data on these compounds (see Experimental Section for the complete spectra). Briefly, endo–anti structure **14** is suggested by the small coupling constant of the proton on the chlorine-bearing carbon (J = 1.5 Hz),[2a,14,15a] by its relatively high chemical shift (δ 2.48),[2d] by the relatively high chemical shift of the vinyl protons (δ 5.85),[2e] and by the nearly identical chemical shifts of the two methylene protons (*ca.* δ 1.7).[14a,15b] The exo–anti structure **16** is suggested by the small coupling constant (J = 1.5 Hz) but relatively low chemical shift (δ 3.68) of the proton on the chlorine-bearing carbon, by the relatively low chemical shift of the vinyl protons (δ 6.45), and by the nonequivalence and upfield shift of the two methylene protons (δ *ca.* 0.8 and 1.1). Similar arguments lead to the endo–anti structure **15** for the dichloro compound.

Chemical confirmation of the endo stereochemistry of **14** is obtained from its reduction by sodium in *tert*-butyl alcohol[16] to the known tricyclic olefin **17**, the Diels–Alder adduct of cyclopropene and cyclopentadiene.[2a,17]



Thus, both mono- and dichlorocyclopropenes **11** and **13** yield endo adducts exclusively, a result allowed by either the one-step or two-step mechanisms. It should be noted that, according to our general formulation of the ionic mechanism, it is not unreasonable to expect **11** and **13** to react entirely by direct Diels–Alder reaction since intervention of the ionic mechanism is predicated upon there being severe steric interactions in the one-step cycloaddition of 3,3-dihalocyclopropenes. We therefore decided to concentrate all of our efforts on

(14) In general, carbene additions to norbornenes and related compounds preferentially give exo product: (a) C. W. Jefford and W. Wojnarowski, *Tetrahedron*, **25**, 2089 (1969); (b) C. W. Jefford and D. T. Hill, *Tetrahedron Lett.*, 1957 (1969), and references cited therein.

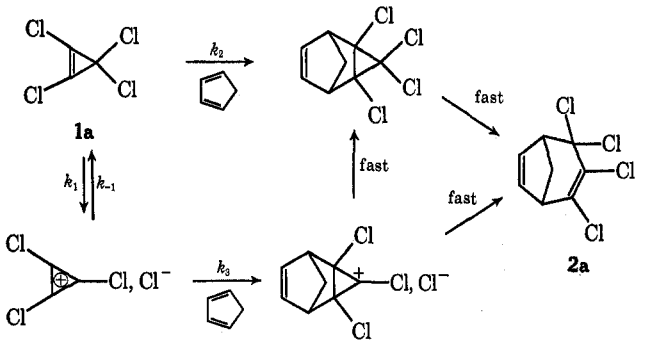
(15) (a) C. W. Jefford, E. H. Yen, and R. Medary, *ibid.*, 6317 (1966); (b) C. W. Jefford and R. T. Medary, *Tetrahedron*, **23**, 4123 (1967).

(16) P. G. Gassman and P. G. Pape, *J. Org. Chem.*, **29**, 160 (1964).

(17) K. B. Wiberg and W. J. Bartley, *J. Amer. Chem. Soc.*, **82**, 6375 (1960).

securing meaningful mechanistic data for tetrachlorocyclopropene (**1a**).

Depending upon the relative magnitudes of the rate constants, investigation of the kinetics of the cycloaddition could reveal which mechanism is operative. Under pseudo-first-order conditions (large excess of cyclopentadiene), the rate expression for the direct Diels–Alder reaction is given by eq 1 and the observed rate constant by eq 2. By application of steady-state principles, the rate law for the two-step mechanism is again given by eq 1 but the observed rate constant by eq 3.



$$\frac{d[2a]}{dt} = k_{obsd}[1a] \quad (1)$$

$$k_{obsd} = k_2[\text{diene}] \quad (2)$$

$$k_{obsd} = \frac{k_1k_3[\text{diene}]}{k_{-1} + k_3[\text{diene}]} \quad (3)$$

For the two-step mechanism (eq 3), three possibilities exist. (a) k_1 is rate determining, in which case the reaction rate is independent of diene concentration ($k_{obsd} = k_1$). (b) k_3 is rate determining, in which case the kinetics cannot distinguish between the one-step and two-step processes ($k_{obsd} = k_1k_3[\text{diene}]/k_{-1}$). (c) k_{-1} and $k_3[\text{diene}]$ are of comparable magnitude, in which case a plot of the observed pseudo-first-order rate constant *vs.* [diene] increases linearly at low concentrations but bends and approaches k_1 asymptotically at high concentrations $\{k_{obsd} = k_1k_3[\text{diene}]/(k_{-1} + k_3[\text{diene}])\}$.

Thus, unless condition b arises, the ion-pair mechanism is kinetically distinguishable from the direct cycloaddition. Even if b persists for a given diene, changing to a more reactive diene could alter the relative magnitudes of k_{-1} and $k_3[\text{diene}]$ (the rates of the reverse and forward reactions of the ion pair) such that condition c is achieved.

In addition, the rate of the two-step mechanism should be substantially more sensitive to changes in solvent polarity than should that of the direct Diels–Alder reaction.[18] At one extreme, condition a, a clear increase in rate with increasing solvent polarity should be observed. Even at the other extreme, condition b, the rate should be sensitive to solvent polarity; although k_3 will not vary appreciably, k_1/k_{-1} (the equilibrium constant for ion-pair formation) should show a marked solvent dependence.[4a,b]

Reaction of tetrachlorocyclopropene (**1a**) with a 20-fold excess of cyclopentadiene in a variety of solvents produces adduct **2a** as the only product (>95% isolated yields in all cases). The rate of product formation is conveniently monitored by quantitative glpc analysis (internal standard method). In every solvent system investigated, the kinetics are cleanly pseudo-first-order. The second-order rate constants, k, in Table I are obtained by dividing k_{obsd} by [diene].

TABLE I
RATE CONSTANTS FOR THE REACTION OF TETRACHLOROCYCLOPROPENE WITH CYCLOPENTADIENE IN VARIOUS SOLVENTS

Solvent	E_T[a]	Temp, °C	$k \times 10^5$,[b] l. mol^{-1} sec^{-1}
Carbon tetrachloride	32.5	25	0.83
Benzene	34.5	25	1.6
Acetone	42.2	25	2.0
Acetone	42.2	47	6.8
N,*N*-Dimethylformamide	43.8	25	2.7

[a] K. Dimroth, C. Reichardt, T. Siepmann, and F. Bohlmann, *Justus Liebigs Ann. Chem.*, **661**, 1 (1963). [b] Calculated by dividing the pseudo-first-order rate constant k_{obsd} by [cyclopentadiene].

There is only a small increase in rate with increasing solvent polarity, comparable to the increase observed in other cycloadditions.[18] Furthermore, doubling the concentration of diene in either benzene or acetone exactly doubles k_{obsd} (*i.e.*, the second-order rate constant, k, of Table I is unchanged). From the rates at two temperatures in acetone, one calculates $\Delta H^{\ddagger} = 10$ kcal/mol and $\Delta S^{\ddagger} = -44$ eu, normal values for a Diels–Alder reaction.[18]

Several attempts were made to determine if the reaction could be catalyzed by Lewis acids, as would be expected for the two-step mechanism. Although most metal halides lead to polymerization of the diene, mercuric chloride does not. Nevertheless, the presence of as much as 1 equiv of $HgCl_2$ in THF has no effect on the rate.

Thus, for cyclopentadiene as the 4-π-electron component, the evidence favors a normal Diels–Alder reaction on the covalent starting material **1a**.

Experimental Section

Instruments.—Analytical glpc was performed on a Perkin-Elmer Model 800 gas chromatograph (flame ionization detector) and utilized the following columns: A, 3 ft × 1/8 in., SE-30 (15%) on Chromosorb P; B, 6 ft × 1/8 in., Carbowax 20M (10%) on Chromosorb P. Quantitative glpc analyses employed the internal standard method; peak areas were measured with a Disc integrator. Preparative glpc was performed on a Varian Aerograph Model 202-1B gas chromatograph (thermal conductivity detector) and utilized the following columns: C, 20 ft × 3/8 in., SE-30 (30%) on Chromosorb P; D, 3 ft × 3/8 in., Carbowax 20M (10%) on Chromosorb W. All nmr spectra were obtained on a Varian Associates A-56/60A spectrometer.

Materials.—Tetrahydrofuran (THF) from Matheson Coleman and Bell was distilled from $LiAlH_4$ and stored over Na ribbon or molecular sieves. *N*,*N*-Dimethylformamide (DMF) from Matheson Coleman and Bell was dried over molecular sieves. Thiophene-free benzene, J. T. Baker Chemical Co., was dried over Na ribbon. Acetone and CCl_4, both ACS reagents from Allied Chemical Co., were used directly without purification. Norbornadiene (Eastman Organic Chemicals), *tert*-butyl alcohol (Matheson Coleman and Bell), $LiAlH_4$ and $CH_3Li(LiBr)$ (both from Alfa Inorganics, Inc.), tri-*n*-butyltin chloride (Aldrich Chemical Co., Inc.), and trichloroacetic acid (Fisher Scientific Co.) were all used directly without further purification.

Cyclopentadiene was obtained by distillation from dicyclopentadiene (Aldrich Chemical Co.). Tri-*n*-butyltin hydride was

(18) (a) S. Seltzer, *Advan. Alicycl. Chem.*, **2**, 1 (1968); (b) J. Sauer, *Angew. Chem., Int. Ed. Engl.*, **6**, 16 (1967); (c) J. E. Baldwin and J. A. Kapecki, *J. Amer. Chem. Soc.*, **92**, 4868 (1970); (d) M. J. S. Dewar and R. S. Pyron, *ibid.*, **92**, 3098 (1970).

prepared by $LiAlH_4$ reduction of tri-*n*-butyltin chloride.[19] Pentachlorocyclopropane was obtained from the reaction of dichlorocarbene with trichloroethylene[20a] and was converted into tetrachlorocyclopropene (**1a**) by established procedures.[20b] Reduction of tetrachlorocyclopropene with tri-*n*-butyltin hydride, according to the method of Breslow, *et al.*,[4b] yielded a mixture of 3-chlorocyclopropene (**11**), 3,3-dichlorocyclopropene (**12**), and 1,3-dichlorocyclopropene (**13**).

Reaction of Cyclopentadiene with 3-Chlorocyclopropene (11), 3,3-Dichlorocyclopropene (12), and 1,3-Dichlorocyclopropene (13).—To 0.6 g of a mixture consisting of 59% **11**, 14% **12**, and 27% **13** in 5 ml of CCl_4 at room temperature was added 2 ml of freshly distilled cyclopentadiene. After the exothermic reaction had subsided, most of the solvent and cyclopentadiene was removed with a rotatory evaporator. Glpc analysis (column B) revealed the presence of two major products and a number of very minor ones. Preparative glpc (column D) led to isolation of the two products which were identified as *endo,anti*-3-chlorotricyclo[3.2.1.$0^{2,4}$]oct-6-ene (**14**) [nmr (CCl_4) δ *ca.* 1.7 (m, 2, H_8), *ca.* 1.8 (m, 2, H_2, H_4), 2.48 (t, 1, J = 1.5 Hz, H_3), 3.03 (m, 2, H_1,H_5), and 5.85 (t, 2, J = 2 Hz, H_6,H_7)] and *endo,anti*-2,3-dichlorotricyclo[3.2.1.$0^{2,4}$]oct-6-ene (**15**) [nmr (CCl_4) δ 1.81 (m, 2, H_8), 2.20 (m, 1, H_4), 2.95 (d, 1, J = 2.5 Hz, H_3), 3.19 (m, 2, H_1,H_5), and 6.01 (m, 2, H_6,H_7)].

Reaction of Norbornadiene with Chlorocarbenoid.—Into a flame-dried flask under argon atmosphere was placed 42 g (0.5 mol) of methylene chloride, 92 g (1.0 mol) of norbornadiene, and 100 ml of dried ether. The flask was cooled in an ice bath while 150 ml of 1.7 *N* methyllithium (lithium bromide) (0.25 mol) was added dropwise over 3 hr; the reaction mixture was stirred at room temperature for an additional 1 hr. The reaction was quenched with 100 ml of water and the ether layer was dried ($MgSO_4$), concentrated (rotary evaporator), and distilled at reduced pressure. The distillate, bp 75–80° (10 mm), was treated with excess silver nitrate in aqueous acetone at 60° for 15 min; the organic layer was separated; and the aqueous layer was extracted with ether. The combined organic phases were dried ($MgSO_4$), concentrated (rotary evaporator), and separated by preparative glpc (column D) giving a component which could not be further fractionated but whose nmr spectrum indicated that it was a mixture of **14** (26%) and *exo,anti*-3-chlorotricyclo-[3.2.1.$0^{2,4}$]oct-6-ene (**16**) (74%) [nmr (CCl_4) δ *ca.* 0.8 and 1.1 (m, 2, H_8), 1.38 (m, 2, H_2, H_4), 3.03 (m, 2, H_1, H_5), 3.68 (t, 1, J = 1.5 Hz, H_3), and 6.45 (t, 2, J = 2 Hz, H_6, H_7).

Reductive Dechlorination[16] of *endo,anti*-3-Chlorotricyclo-[3.2.1.$0^{2,4}$]oct-6-ene (14).—Into a dried flask under argon atmosphere was placed 12 ml of dried THF, 2 ml of *tert*-butyl alcohol, 0.5 g of **14**, and 1.0 g of sodium, and the mixture was refluxed for 8 hr. The contents of the flask were allowed to settle and the supernatant liquid was transferred by syringe to a flask containing 10 ml of water. The original reaction flask was rinsed with ether which was similarly transferred to the second flask. The organic layer was separated, dried ($MgSO_4$), and concentrated (rotary evaporator). Preparative glpc of the residue (column C) gave pure *endo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene (**17**), identical in all respects with the known Diels–Alder adduct of cyclopropene with cyclopentadiene.

General Procedure for Rate Measurements in the Reaction of Tetrachlorocyclopropene (1a) with Cyclopentadiene.—A flask containing 0.710 ml (8.60 mmol) of freshly distilled cyclopentadiene, 0.015 ml of phenylcyclohexane as internal standard, and 3.0 ml of solvent was immersed in a water bath maintained at 25°. Into this solution was rapidly syringed 0.050 ml (0.43 mmol) of tetrachlorocyclopropene (**1a**). Aliquots were removed at selected time intervals through a serum cap and were analyzed by quantitative glpc (column A). Only a small portion (7%) of cyclopentadiene was depleted through dimerization during the course of 1 half-life of the reaction under study. The ratios of the peak areas for product **2a** to standard were determined in each aliquot and the value of (**2a**/standard)$_{final}$ was determined by allowing the reaction to stand at room temperature for several days (corresponding to nearly quantitative conversion of **1a** into **2a**). A plot of log $\{(\mathbf{2a}/\text{standard})_f/[(\mathbf{2a}/\text{standard})_f - (\mathbf{2a}/\text{standard})_i]\}$ *vs.* time yielded a straight line, the slope of which was multiplied by 2.303 and divided by [cyclopentadiene] yielding the second-order rate constants given in Table I. Data from a typical kinetic run are given in Table II. Since analysis of an aliquot taken after only a few seconds showed no product peak, reaction was not occurring either in the injector or on the column. There was no evidence for destruction of the product under these glpc conditions.

TABLE II

KINETIC DATA FROM THE REACTION OF TETRACHLOROCYCLOPROPENE[a] AND CYCLOPENTADIENE[b] IN BENZENE[c] AT 25°

Aliquot	Time, sec	(2a/standard)$_t$[d]
1	1,922	0.18
2	5,820	0.60
3	7,920	0.72
4	10,440	0.96
5	13,430	1.14
6	*Ca.* 4 × 10^5	2.90

[a] 0.43 mmol. [b] 8.60 mmol. [c] 3.0 ml containing 0.015 ml of phenylcyclohexane. [d] Ratio of area of product peak to area of standard peak; injector temperature 125°, column temperature 80°.

In both benzene and acetone as solvents, the rate constant was determined under the same conditions except that twice as much cyclopentadiene was employed. The second-order rate constant was unchanged.

Registry No.—**14**, 29119-61-7; **15**, 29119-62-8; **16**, 29119-63-9.

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