Strong evidence exists in the literature[4,7] to support the thermal ring opening reaction of I and other *gem*-dihalocyclopropanes.[3]

Experimental Section[8]

The dihalocarbene adducts were generally prepared by a procedure similar to those described earlier.[9-11] The procedure for the thermal ring-opening reaction of substituted *gem*-dihalocyclopropanes in the presence of morpholine is similar to that described in a previous paper.[1] The preparation of III has not been described before and is briefly given below.

6-Bromo-2-chlorobicyclo[3.1.0]hexane (III).—To a cooled (0–10°) flask containing 27.2 g (0.40 mol) of cyclopentene, 150 ml of pentane, and 33.6 g (0.30 mol) of potassium *t*-butoxide was added dropwise 41.70 g (0.20 mol) of dibromochloromethane (Dow). After the addition the reaction was stirred for 2–3 hr at room temperature, water was added, and the organic layer was separated, washed, dried, and concentrated. The residue upon vacuum distillation yielded 65% III, bp 53° (2.0 mm), n^{25}_{D} 1.5257–1.5298. The analysis and spectral data is described in Table I.

Tables I and II describe the details of the thermal ring-opening reaction of 6,6-dihalobicyclo[3.1.0]hexanes with morpholine at 128°.

Registry No.—Morpholine, 110-91-8; I, 2568-36-7; II, 23595-96-2; IIIα, 23595-97-3; IIIβ, 23595-98-4; IV, 23595-99-5; V, 23596-00-1.

Acknowledgment.—The author wishes to express his appreciation to Professor Daniel Swern of Temple University, Philadelphia, Pa., for his generous help in obtaining all of the nmr spectra.

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(7) L. Gatlin, R. E. Glick, and P. S. Skell, *Tetrahedron*, **21**, 1345 (1965).

(8) (a) The elemental analyses were obtained by Dr. Stephen M. Nagy, Belmont, Mass. (b) Melting and boiling points are uncorrected. The nmr spectra (neat) were recorded on a Varian A-60A spectrometer and the δ values are in parts per million from tetramethylsilane.

(9) W. von E. Doering and A. K. Hoffman, *J. Amer. Chem. Soc.*, **76**, 6162 (1954).

(10) P. S. Skell and A. Y. Garner, *ibid.*, **78**, 3409 (1956).

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Reactions of Chlorine and Iodobenzene Dichloride with Cyclodecenes[1]

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Additions to medium-ring olefins have led to data of considerable significance for reaction mechanisms.[3,4] Both vicinal and transannular addition products have been obtained, and transannular processes may dominate the overall reaction.[3,4] Halogen additions to olefins have received much attention and have been shown to proceed by both cationic and radical pathways,[5] but few halogen additions to medium-ring cycloalkenes have been reported.

Bromine adds to *cis*-cyclodecene in carbon tetrachloride at −10° to form both *trans*-1,2-dibromocyclodecane (10% yield) and *cis*-1,6-dibromocyclodecane (40% yield), as well as other components in a complex mixture.[4d,e] Only the transannular product, *trans*-1,6-dibromocyclodecane, has been identified in the product mixture obtained from *trans*-cyclodecene under the same conditions.[4d] Both bromine[6] and chlorine[4a,7] add normally to *cis*-cyclooctene to produce *trans*-1,2-dihalocyclooctanes.

We report here an investigation of the reactions of chlorine and of idobenzene dichloride,[8] both under ionic and radical conditions,[5,8] with the isomeric cyclodecenes. Product-distribution data have been obtained and are summarized in Table I.

The production of a single, vicinal addition product in the reaction of *cis*-cyclodecene with chlorine, under both ionic and radical conditions, contrasts surprisingly with the predominant formation of the transannular addition product when bromine[4d,e] or iodobenzene dichloride is the reactant. Although we do not yet have enough energy data to have predicted these results with any confidence, the precise course of these halogen additions undoubtedly depends on a delicate balance of energy requirements among competing pathways. The energy requirements for product formation from a 2-chlorocyclodecyl intermediate (cation or radical) and chlorine is lower than that for reaction of the intermediate with iodobenzene dichloride (or bromine) and for transannular hydrogen shift. With iodobenzene dichloride or bromine as reactant, transannular hydrogen shift in the intermediate is favored over direct product formation.[9]

No vicinal dichloride was obtained from *trans*-cyclodecene reacting with either chlorine or iodobenzene dichloride. The greater internal strain in the *trans*-cyclodecene compared with the *cis* isomer may be wholly responsible for the occurrence of transannular hydrogen shifts, but geometry may be an important factor, also. Examination of a Dreiding molecular model of *trans*-cyclodecene indicates that one side of the C=C π cloud is effectively blocked by the chain of methylene groups in the ring, and, without severe conformational change, the initially formed intermediate would not be likely to form vicinal product by *anti* addition. The large amount of 3-chloro-1-cyclodecene formed from *trans*-cyclodecene, compared with that from *cis*-cyclodecene, probably is related in a similar fashion to the conformations of the olefins.

Dechlorination of the *trans*-1,2-dichlorocyclodecane

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(1) (a) Based on the Ph.D. Dissertation of D. B. S., Louisiana State University, 1969. The financial assistance from the Charles E. Coates Memorial Fund, donated by George H. Coates, for preparation of the Ph.D. Dissertation of D. B. S. is gratefully acknowledged. (b) Presented in part at the Southeastern Regional Meeting of the American Chemical Society, Tallahassee, Fla., Dec 1968, paper number 39.

(2) National Aeronautics and Space Administration Trainee, 1964–1966.

(3) For reviews of medium ring chemistry, including some additions to olefins, see (a) V. Prelog and J. G. Traynham, in "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 9; (b) A. C. Cope, M. M. Martin, and M. A. McKervey, *Quart. Rev.* (London), **20**, 148 (1966).

(4) (a) J. G. Traynham and T. M. Couvillon, *J. Amer. Chem. Soc.*, **89**, 3205 (1967); (b) M. Fisch and G. Ourisson, *Chem. Commun.*, 407 (1965); (c) J. G. Traynham, G. F. Franzen, G. A. Knesel, and D. J. Northington, Jr., *J. Org. Chem.*, **32**, 3285 (1967); (d) J. Sicher, J. Zavada, and M. Svoboda, *Collect. Czech. Chem. Commun.*, **27**, 1927 (1962); (e) M. Havel, M. Svoboda, and J. Sicher, *ibid.*, **34**, 340 (1969). (We acknowledge with gratitude the receipt of a prepublication copy of this paper from Professor Sicher.)

(5) M. L. Poutsma, *J. Amer. Chem. Soc.*, **87**, 2161 (1965).

(6) A. C. Cope and G. W. Wood, *ibid.*, **79**, 3885 (1957).

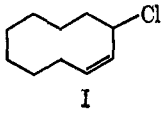
(7) (a) E. A. Forbes, B. R. Gofton, R. P. Goughton, and E. S. Waight, *J. Chem. Soc.*, 4711 (1957); P. W. Havinga, *Rec. Trav. Chim. Pays-Bas*, **81**, 1053 (1962).

(8) D. D. Tanner and G. C. Gidley, *J. Org. Chem.*, **33**, 38 (1968).

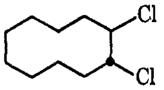
(9) A substantial difference in the composition of the dihalocyclopentane product mixtures formed from bromine and chlorine additions to bicyclo[2.1.0]pentane has been reported: R. T. LaLonde, *J. Amer. Chem. Soc.*, **87**, 4217 (1965).

TABLE I

PRODUCT CONVERSIONS FROM CHLORINATIONS OF CYCLODECENES[a]



I



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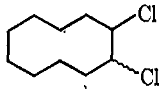
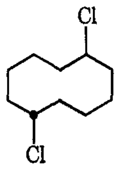
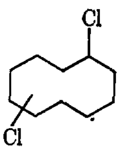


III[b]



IV



V[c]

				Vicinal		Transannular	
Cyclodecene	Reagent	Condition[d]	I	II	III	IV	V
cis	Cl_2	Ionic	13	63			
cis	Cl_2	Radical	22	29			
trans	Cl_2	Ionic	39			5	13
trans	Cl_2	Radical	43			9	9
cis	$C_6H_5ICl_2$	Ionic	10		8		24
cis	$C_6H_5ICl_2$	Radical	6				45
trans	$C_6H_5ICl_2$	Ionic	46			10	3
trans	$C_6H_5ICl_2$	Radical	31				32

[a] Per cent. Based on starting cyclodecene, some of which was not converted into products and was removed with solvent during rotary evaporation. [b] Vicinal dichloride identified from nmr spectrum of mixture; probably *trans*, but stereochemistry not established. [c] One or more transannular dichlorides (1,4-, 1,5-, and/or 1,6-), identified from nmr spectrum. [d] Conditions for chlorination, ionic or radical; see Experimental Section for details.

product with zinc dust in refluxing ethanol gave a mixture of cyclodecenes (78% *trans* and 22% *cis*).[10a] Both *anti*[10b] and *syn*[4e] eliminations of bromine by zinc dust have been reported; in the 10-membered ring, *syn* elimination appears to be the preferred process for both debromination and dechlorination. It is important to note that vicinal chlorine addition to *cis*-cyclodecene (no zinc or zinc chloride) is an *anti* process (*trans*-1,2-dichloride), but zinc- and iodide-promoted dechlorinations of the dichloride are predominantly *syn*.

Experimental Section

For gas chromatography, a Beckman Model GC-5 instrument equipped with a thermal conductivity detector and a 12 ft × 1/8 in. column packed with 5% Carbowax 20M on 60–80 mesh Chromosorb P was used. Nuclear magnetic resonance (nmr) data were obtained with Varian Model A-60A and HA-100 instruments with the assistance of Mr. W. Wegner, and chemical shifts are reported in parts per million relative to tetramethylsilane internal reference (negative sign indicates downfield). Infrared (ir) spectra were recorded on a Perkin-Elmer Model 137 instrument. Melting points were obtained with a Thomas-Hoover apparatus and are uncorrected. Element microanalyses were performed by Mr. R. Seab in these laboratories and are reported as the average of three determinations.

Molecular Chlorine Additions.—For 10 min, oxygen (for ionic conditions)[5] or nitrogen (for radical conditions)[6] was admitted through a sintered-glass dispersion tube and bubbled vigorously into a solution of cyclodecene[11] (0.05 mol) in carbon tetrachloride (100 ml) in a 38 × 200 mm test tube. For the radical reaction, the solution was irradiated with a clear 150-W light placed 4 in. from the test tube. The gas flow (O_2 or N_2) was maintained while chlorine gas (0.05 mol; Matheson, 99.5% purity), which had been passed through concentrated sulfuric acid, was bubbled into the solution. Hydrogen chloride was evolved during the reaction.[12] After the chlorine flow had been discontinued, the flow of O_2 or N_2 was continued for 30 min longer to sweep out any remaining HCl and Cl_2. The solvent and unreacted cyclodecene were removed by rotary evaporation, and the product mixture was distilled at reduced pressure. The distillate fractions were examined by ir and nmr techniques and were identified as 3-chloro-1-cyclodecene, *trans*-1,2-dichlorocyclodecane, *trans*-1,6-dichlorocyclodecane, and other nonvicinal dichlorocyclodecanes.[13] Table I summarizes the product distribution data.

In a representative experiment, distillation of the product mixture obtained from *cis*-cyclodecene gave two fractions, A [bp 51–55° (0.15 mm), 1.09 g], and B [bp 71–83° (0.15 mm), 6.55 g]. Element analyses (within 0.3% of calculated values for C and H) and nmr spectra revealed that fraction A was essentially pure 3-chloro-1-cyclodecene (13% yield) and fraction B was essentially pure *trans*-1,2-dichlorocyclodecane (63% yield). In like fashion, distillation of the product mixture from *trans*-cyclodecene gave two fractions, C [bp 35–38° (0.10 mm), 3.40 g], identified as 3-chloro-1-cyclodecene (39% yield), and D [bp 63–66° (0.10 mm), 2.00 g], which partially crystallized on standing. The solid (0.56 g) was recrystallized from hexane: mp 101–103°. It was subsequently identified by element analysis, nmr spectrum, and derivitization as *trans*-1,6-dichlorocyclodecane (IV, 5% yield). The liquid portion of D (1.44 g) gave an nmr spectrum with an A:B:X proton ratio of 8:8:2, indicative of transannular dichlorides.[4a] Thin layer chromatography with hexane solvent on silica gel plates activated at 120° immediately before use revealed two components in the liquid fraction in a ratio of 9:1.

Reaction of chlorine with *trans*-cyclodecene (but not with *cis*-cyclodecene) formed 0.5 g of a white, flocculent solid, which crystallized from chloroform–methanol to give colorless needles not melting below 330°. *Anal.* Found: C, 65.00; H, 11.05.

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[10] (a) Dechlorination of *trans*-1,2-dichlorocyclodecane with potassium iodide in refluxing Cellosolve (50 hr, 88% conversion) produced a mixture of 90% *trans*- and 10% *cis*-cyclodecene (T. M. Couvillon, Ph.D. Dissertation, Louisiana State University, 1966, p 82). In the cyclohexane system, elimination of bromine by potassium iodide has been shown to be more stereoselective (*anti*) than elimination by zinc dust.[10b] (b) C. L. Stevens and J. A. Valicenti, *J. Amer. Chem. Soc.*, **87**, 838 (1965).

[11] *cis*- and *trans*-cyclodecene were prepared as described by J. G. Traynham, D. B. Stone, and J. L. Couvillion, *J. Org. Chem.*, **32**, 510 (1967). Reevaluation of the stereoselective dehydrochlorinations of chlorocyclodecane revealed that the predominant olefin comprises 93–94% of the product mixture.

[12] The exit gas reacted with aqueous silver nitrate to form a white precipitate and turned wet blue litmus paper red, but it did not affect wet starch–iodide paper.

[13] (a) Vicinal and nonvicinal dichlorides are readily distinguished from each other by the ratio of signals for $ClCCH_2$ and for $CH_2CH_2CH_2$ in the nmr spectrum of the product.[4a] (b) No evidence for the presence of any other chlorocyclodecenes was obtained, and the nmr spectra appear to exclude isomers of I within the detection limits of the nmr spectrometer. (c) The products do not interconvert readily. Under the conditions of these experiments, neither Cl_2 nor HCl added to 3-chloro-1-cyclodecene. Dichlorocyclodecanes decomposed during attempted gas chromatography, but they appeared to be stable to the chlorination reaction conditions.

This solid is insoluble in benzene, carbon tetrachloride, and chloroform and is assumed to be a low molecular weight polymer containing chlorine.

Ionic Reaction of Iodobenzene Dichloride[8] with Cyclodecenes.—For 10 min oxygen was admitted through a sintered-glass dispersion tube and bubbled into a solution of cyclodecene (0.05 mol) in carbon tetrachloride (30 ml), iodobenzene dichloride (0.05 mol) was added to the solution, and the oxygen flow was continued until the insoluble iodobenzene dichloride had disappeared (approximately 36 hr). Hydrogen chloride was evolved during the reaction. The solvent was removed by rotary evaporation, the product mixture was distilled at reduced pressure, and the distillate fractions were examined by ir and nmr techniques. Table I summarizes the product distribution data. Some of the distillate fractions were mixtures; a low-boiling fraction contained isomeric chloroiodobenzenes[8] as well as 3-chloro-1-cyclodecene, and the dichlorocyclodecane fraction from *cis*-cyclodecene was a mixture of vicinal and transannular dichlorides.[13] These mixtures were not separated satisfactorily, but they were readily analyzed by nmr spectroscopy.

Radical Reaction of Iodobenzene Dichloride[8] with Cyclodecenes.—A mixture of cyclodecene (0.05 mol), carbon tetrachloride (30 ml), and iodobenzene dichloride (0.05 mol), contained in a 100-ml round-bottom flask, was degassed by a freeze–thaw method to eliminate molecular oxygen. The flask was sealed, and the mixture was stirred with a magnetic stirrer at room temperature until the iodobenzene dichloride had disappeared (5 hr). Hydrogen chloride was evolved when the flask was opened. The mixture was worked up as described above for the ionic reaction with iodobenzene dichloride. The nmr spectrum of the dichlorocyclodecane fraction indicated that only transannular dichlorides were present.[13]

Reaction with *trans*-cyclodecene (but not with *cis*-cyclodecene) led to the formation of 1.3 g of a white, flocculant solid, which recrystallized from chloroform–methanol as needles which did not melt below 330°. This solid was not examined further.

Product Identification. **3-Chloro-1-cyclodecene** distilled at 51–55° (0.15 mm): nmr ($DCCl_3$) −5.50 (2 H, C=CH), −4.21 (1 H, HCCl), −2.05 (4 H, CH_2CCl and $CH_2C{=}C$), and −1.43 (10 H, $CH_2CH_2CH_2$), all multiplets. *Anal.* Calcd for $C_{10}H_{17}Cl$: C, 69.55; H, 9.92. Found: C, 69.42; H, 10.02. The stereochemistry of the C=C was not determined.

The addition product identified as ***trans*-1,2-dichlorocyclodecane**, bp 68–72° (0.17 mm), gave an nmr spectrum ($DCCl_3$) consistent only with a 1,2 isomer:[4a] −4.36 (2 H, HCCl), −2.08 (4 H, HCCCl), and −1.57 (12 H, $CH_2CH_2CH_2$), all multiplets. The signal at −4.36 was a broad, complex one from which coupling constants could not be discerned, even with decoupling experiments. Partial dehalogenation of a sample of the dichloride with zinc dust in refluxing ethanol, and partial dehydrochlorination by potassium *t*-butoxide in dimethyl sulfoxide solution (room temperature), produced olefin (78% *trans*- and 22% *cis*-cyclodecene from zinc reaction; 1-chloro-1-cyclodecene from potassium *t*-butoxide reaction) and left dichloride whose nmr spectrum was unchanged from that of the starting material. Since the isomeric *cis*- and *trans*-1,2-dichlorocyclodecanes are expected to undergo these elimination reactions at different rates, these results are taken to be strong evidence that a single 1,2-dichloride was formed in the addition reaction. Since ***cis*-1,2-dichlorocyclodecane** (synthesized by refluxing a mixture of *cis*-diol, excess thionyl chloride, and dioxane[14]) is a solid [mp 84.5–86.5°; nmr ($DCCl_3$) −4.96 (HCCl)], the addition product is *trans*-1,2-dichlorocyclodecane.

***trans*-1,6-Dichlorocyclodecane** (mp 101–103°) crystallized from a distillation fraction [bp 63–66° (0.10 mm)] from some of the chlorine additions. The nmr spectrum ($DCCl_3$) reveals an A:B:X proton ratio of 8:8:2, consistent with a 1,4-, 1,5-, or 1,6-dichloride structure.[4a] A portion of the dichloride was converted into *trans*-1,6-bis(phenylthio)cyclodecane,[4d] mp 101–103° (mixture of *trans*-1,6-dichloro- and *trans*-1,6-bis(phenylthio)cyclodecanes, mp <93°).

Registry No.—*cis*-Cyclodecene, 935-31-9; *trans*-cyclodecene, 2198-20-1; chlorine, 7782-50-5; iodobenzene dichloride, 932-72-9.

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[14] D. J. Cram, *J. Amer. Chem. Soc.*, **75**, 332 (1953).

Reactions of Phosphorus Azides with Activated Alkynes[1]

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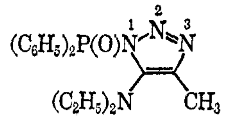
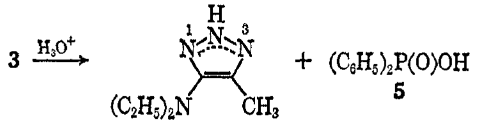
Phosphorus azides are known to add to a variety of substituted alkenes,[4–9] but there appears to be no record of studies on the reactions with alkynes, although a few condensations of some alkynes with aryl and alkyl azides have been summarized.[9,10] We wish to report that **1a** and the ynamine **2a** react in boiling benzene to yield crystalline **3** (49%). Infrared (P→O at 8.1 μ) and nmr analyses (Table I) support the structure. Rapid hydrolytic cleavage occurred with **3** upon exposure to the atmosphere to give the triazole **4** and diphenylphosphinic acid (**5**). Acid hydrolysis gives **4** and **5** in near-quantitative yield. The broadness of the signal for the proton on nitrogen in the nmr spectrum ($CDCl_3$) of **4** suggests tautomers with the hydrogen on N-1 and N-3. Although isomers **3** and **6** are possible from reaction of **1a** and **2a**, evidence favors **3**. Several types of molecular models indicate a strong probability of nonbonded interaction between the $(C_6H_5)_2P(O)$ and $(C_2H_5)_2N$ groups in **3** and between the $(C_6H_5)_2P(O)$ and CH_3 groups in **6**, respectively. Restricted rotation around the P–N and C_6H_5–P bonds in **3** and **6** might

$R_2P(O)N_3$
1a, $R = C_6H_5$
b, $R = C_2H_5O$

$R'C{\equiv}CR''$
2a, $R' = (C_2H_5)_2N$; $R'' = CH_3$
b, $R' = C_2H_5O$; $R'' = H$



3



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[1] We gratefully acknowledge support from the Public Health Service, Cancer Institute, Grant CA 07202-07.

[2] Research Associate, 1968–1970.

[3] Predoctoral Candidate, 1969–present.

[4] K. D. Berlin and L. A. Wilson, *Chem. Ind.* (London), 1522 (1965).

[5] K. D. Berlin and L. A. Wilson, *Chem. Commun.*, 280 (1965).

[6] K. D. Berlin and M. A. R. Khayat, *Tetrahedron*, **22**, 975 (1966); **22**, 987 (1966).

[7] K. D. Berlin, L. A. Wilson, and L. M. Raff, *ibid.*, **23**, 965 (1967).

[8] K. D. Berlin and R. Ranganathan, *ibid.*, **25**, 793 (1969).

[9] F. R. Benson and W. L. Savell, *Chem. Rev.*, **46**, 1 (1950).

[10] R. Huisgen, R. Knorr, L. Möbius, and G. Szeimies, *Chem. Ber.*, **98**, 4014 (1965).