Studies on the Ionic Addition of Chlorine to Conjugated Dienes

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The compositions of dichloride mixtures obtained from reaction of chlorine under ionic conditions with cyclopentadiene (1), 1,3-cyclohexadiene (2), the 2,4-hexadienes, *cis,cis*-(**3a**), *trans,trans*-(**3b**), *cis,trans*-(**3c**), and the 1,3-pentadienes, *cis*-(**4a**) and *trans*-(**4b**) is reported for several solvents. The stereochemistry of 1,4 addition of chlorine to these dienes is predominantly syn but is generally less stereoselective than is bromine addition. The 1,2 addition of chlorine is generally nonstereospecific except for addition to the 3,4 bond of **4a,b** where attack is 89–95% anti. Appreciable cis 1,2-dichloride is obtained from chlorination of **1** and **2**. The dienes **3a–c** show a preference for anti 1,2 addition only in the less polar solvents, carbon tetrachloride and pentane.

Recently we have reported investigations into the reactions of bromine with conjugated dienes, with our purpose being to determine the stereochemistry of 1,2 and 1,4 additions in such systems.[1a,b] We now wish to report results on the chlorination of these same dienes which will allow comparisons to be made between the mechanisms of reactions of these halogens.[2] The dienes which were chlorinated are cyclopentadiene (1), 1,3-cyclohexadiene (2), the 2,4-hexadienes, *cis,cis*-(**3a**), *trans,trans*-(**3b**), and *cis,trans*-(**3c**), the 1,3-pentadienes, *cis*-(**4a**) and *trans*-(**4b**).

Results and Discussion

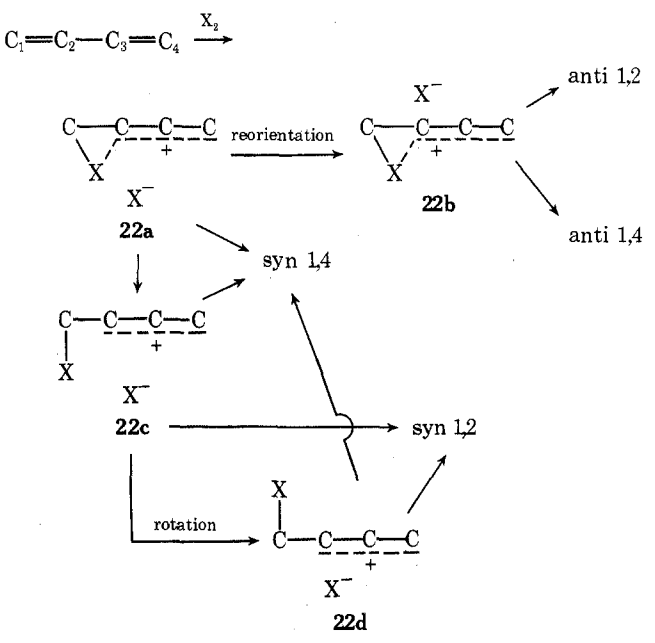
The dichlorides which were obtained from the dienes are identified as follows: from **1**, *cis*-3,4-dichlorocyclopentene (**5**), *trans*-3,4-dichlorocyclopentene (**6**), *cis*-3,5-dichlorocyclopentene (**7**), and *trans*-3,5-dichlorocyclopentene (**8**); from **2**, *cis*-3,4-dichlorocyclohexene (**9**), *trans*-3,4-dichlorocyclohexene (**10**), *cis*-3,6-dichlorocyclohexene (**11**), and *trans*-3,6-dichlorocyclohexene (**12**); from **3a–c**, *erythro*-4,5-dichloro-*cis*-2-hexene (**13**), *threo*-4,5-dichloro-*cis*-2-hexene (**14**), *dl*-2,5-dichloro-*trans*-3-hexene (**15**), *meso*-2,5-dichloro-*trans*-3-hexene (**16**), *threo*-4,5-dichloro-*trans*-2-hexene (**17**), and *erythro*-4,5-dichloro-*trans*-2-hexene (**18**); from **4a,b**, *threo*-3,4-dichloropentene (**19a**), *erythro*-3,4-dichloropentene (**19b**), *cis*-4,5-dichloro-2-pentene (**20a**), *trans*-4,5-dichloro-2-pentene (**20b**), and *trans*-1,4-dichloro-2-pentene (**21**).

Table I shows the composition of mixtures of dichlorides obtained by chlorinating each of the dienes in solvents of differing polarity. Reaction conditions were chosen so as to assure a polar mechanism.[3] Mixtures were analyzed by VPC under conditions which did not permit rearrangement of isomers. In most cases the dichlorides reported were isolated pure and their structures established by NMR or chemical methods.

Table II presents the data of Table I in terms of stereoselectivity in 1,2 and 1,4 addition. Stereochemical results for bromination are included for comparison.

Scheme I presents a mechanism which we believe accounts for results obtained in bromination and chlorination of dienes. According to this mechanism the products from diene addition result from ion pair **22a**. Because of dispersal of charge in the allylic system, the bond between halogen and C_2 is weakened so that an open carbonium ion, **22c**, readily forms allowing for the possibility of front-side attack by the anion with the resultant formation of syn 1,2 product. Syn 1,2-dichloride can also result from the linear dienes by rotation about the C_1–C_2 bond in **22c** to produce **22d**, followed by backside attack by anion.[4] Syn 1,4-dichloride can result by attack of anion on C_4 in either **22a**, **22c**, or **22d**. Formation of anti dichlorides (1,2 or 1,4) can only occur when there is appreciable reorientation in the ion pair **22a** to give **22b**. Attack by anion on C_2 in **22b** yields anti 1,2-dichloride and attack at C_4 yields anti 1,4-dichloride.

Scheme I

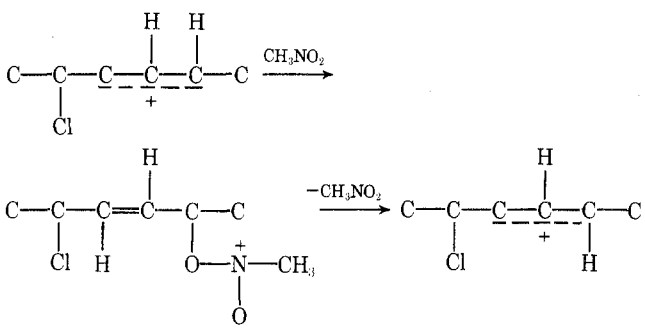


In comparing the results of chlorination with bromination one of the most striking differences is observed with the cyclic dienes, **1** and **2**. Each of these dienes gives appreciable syn 1,2 addition with chlorine. As we have previously stated,[2d] this is evidently explained by the fact that stable allylic carbonium ions are formed from dienes **1** and **2** allowing for ready formation of the open carbonium ion, **22c**. The fact that bromine did not yield detectable syn 1,2-dibromide from dienes **1** and **2** does not necessarily suggest significant differences in the intermediates obtained with bromine and chlorine.[5] Considering the fact that 1,2 bromine addition to the 2,4-hexadienes is nonstereospecific (suggesting weak bridging by bromine), we would anticipate that the intermediate obtained from **1** and **2** with bromine would also be, to a considerable extent, an open carbonium ion. Therefore, absence of syn 1,2 addition with bromine is likely due to the greater steric interaction which would result from syn 1,2 collapse of the ion pair from bromine.[6]

In the less polar solvents (pentane, carbon tetrachloride), the 2,4-hexadienes (**3a–c**) give a 1,2-dichloride adduct which is more than 60% anti[7] suggesting that intermediate **22a** is sufficiently bridged in these systems so that reaction occurs primarily via **22b.** In the more polar solvents (methylene chloride, nitromethane) anti addition occurs less than 50% for **3a** and **3c** and slightly above 50% for **3b.** Bromination of these dienes also produces nonstereospecific 1,2 adduct but the preference for anti addition is substantially higher. One reason for this is that syn addition of bromine probably occurs only via rotation about the C_1–C_2 bond (**22a** to **22d**) rather than by direct syn collapse of open ion **22c,** a route which is possible for the ion pair from chlorine.

An additional comparison between bromine and chlorine relates to addition to the 3,4 bond in the 1,3-pentadienes (**4a,b**) (producing 3,4-dihalides). We have previously observed that bromine addition to the 3,4 bond in **4a,b** occurred 100% anti in contrast to 1,2 addition to the 2,4-hexadienes (**3a–c**), which was not stereospecific.[1] This was explained by noting that the cation from **3a–c** should be more stable (assuming charge dispersal via resonance) than the ion from the 1,3-pentadienes. Chlorine addition to the 3,4 bond in dienes **4a,b** followed the same trend (in comparison to addition to **3a–c**) as bromine addition, although with chlorine a small amount of syn addition was detected (5 and 11% syn addition to **4a** in carbon tetrachloride and methylene chloride, respectively; 5% to **4b** in pentane).

An additional observation concerning the stereochemistry of 1,2 addition which should be mentioned is that chlorination of the cis,cis diene, **3a,** in nitromethane yields significant amounts of 4,5-dichloro-*trans*-2-hexene. In the other solvents isomerization of the cis to the trans bond does not occur. Isomerization of the double bond in nitromethane may be due to the higher polarity of that solvent or perhaps to some specific interaction with nitromethane which would allow for rotation about the 4,5 bond, as shown in the following structures.



A further general observation which can be made is that the amount of 1,4 addition, compared to 1,2 addition, is usually appreciably less for chlorination than bromination.[8] For all runs in Table II the 1,4-dibromide adduct exceeds the 1,2-dibromo adduct. In about one-third of the chlorination runs the main product is the 1,2 adduct, but there are several cases where 1,4 addition is greater for chlorination than bromination. Cyclohexadiene (**2**) shows an especially great contrast between chlorination and bromination, 1,4 addition being highly favored in bromination and 1,2 addition generally favored in chlorination.

A principal interest of our study concerns the stereochemistry of the 1,4 addition. The data in Table II demonstrate that 1,4 chlorine addition occurs primarily by a syn process but that like bromine addition it varies greatly in the degree of stereoselectivity. All of the chlorination runs in Table II with the exception of chlorination of **3b** in methylene chloride show that more than 50% of the 1,4 product is syn. The average of all runs (Table II) is 68% syn 1,4 addition in chlorination compared to 75% in bromination. We have previously attributed the preference for syn 1,4 addition (over anti 1,4 addition) primarily to the specific geometry of the ion pair intermediate (**22a** or **22c**), rather than to some underlying orbital symmetry preference for syn attack.[9] Edmondson[2e] has suggested that if 1,4 addition occurs via a bridged ion (i.e., **22a** or **22b**) the SN2′ process should yield only syn product and that an increase in the amount of anti 1,4 product would be expected with an open carbonium ion (**22c**). Our findings in chlorination and bromination do not appear to be susceptible to such a simple interpretation. In the reactions where there is evidence for the most stable bridging by halogen, i.e., maximum anti stereochemistry in 1,2 addition, we do not necessarily find the highest percentage of syn 1,4 attack. In chlorination of cyclopentadiene the solvent (pentane) showing the highest preference for anti 1,2 addition (69%) shows the lowest preference for syn 1,4 addition (51%). The 2,4-hexadienes (**3a–c**) all show the highest stereospecificity of anti 1,2 addition in pentane (79, 67, and 79%, respectively) but the corresponding percentage of syn 1,4 addition is much lower in pentane than in carbon tetrachloride. Likewise, bromi-

Table I
Chlorination of the Dienes

Diene	Solvent	Dichlorides,[a] %			
		5	**6**	**7**	**8**
1	C_5H_{12}	13	29	29	28
1	CCl_4	27	23	39	11
1	CH_2Cl_2	38	35	18	9
		9	**10**	**11**	**12**
2	C_5H_{12}	15	49	33	3
2	CCl_4	8	22	69	1
2	CH_2Cl_2	14	58	21	7
2	CH_3NO_2	4	59	22	15
		13	**14**	**15**	**16**
3a	C_5H_{12}	15	57	19	9
3a	CCl_4	13	32	49	6
3a	CH_2Cl_2	24	21	31	24
3a	CH_3NO_2	*b*	*b*	36	33
		17	**18**	**15**	**16**
3b	C_5H_{12}	14	28	36	22
3b	CCl_4	13	22	52	13
3b	CH_2Cl_2	21	27	24	28
3b	CH_3NO_2	21	26	29	24
		18	**17**	**16**	**15**
3c[c]	C_5H_{12}	7	27	43	18
3c[c]	CCl_4	9	19	59	11
3c[c]	CH_2Cl_2	23	23	31	22
3c[c]	CH_3NO_2	29	16	31	24
		19	**20**	**21**	
4a	C_5H_{12}	29	20	46	
4a	CCl_4	29	31	40	
4a	CH_2Cl_2	10	47	43	
4a	CH_3NO_2	16	40	44	
4b	C_5H_{12}	10	42	48	
4b	CCl_4	4	47	49	
4b	CH_2Cl_2	2	66	32	
4b	CH_3NO_2	1	67	32	

[a] For dienes **1**, **2**, **3a–c**, the columns of dichlorides (from left to right) represent syn-1,2, anti-1,2, syn-1,4, and anti-1,4 adducts. [b] 1,2 adducts follow (%): **13**, 11; **18**, 10; (**14** + **17**), 10. [c] Additional 1,2 adduct resulting from attack at the trans bond in **3c** is as follows (%): pentane, **13**, 3.1; **14**, 1.7; CCl_4, **13**, 1.4; **14**, 0.9; CH_2Cl_2, (**13** + **14**), 1.4; CH_3NO_2, (**13** + **14**), 0.5.

Table II
Stereoselectivity in Chlorination and Bromination of the Dienes

Diene	Solvent	Chlorination			Bromination[c]		
		1,2 addn, % anti[a]	1,4 addn, % syn[b]	1,4/1,2 addn	1,2 addn % anti	1,4 addn % syn	1,4/1,2 addn
1	C_5H_{12}	69	51	1.4	100	54	1.1
1	CCl_4	46	78	1.0	100	52	1.6
1	CH_2Cl_2	48	67	0.37	100	72	2.8
1	CH_3NO_2				100	58	2.2
2	C_5H_{12}	77	92	0.56	100	83	3.0
2	CCl_4	73	99	2.3	100	96	4.6
2	CH_2Cl_2	81	75	0.39	100	98	4.3
2	CH_3NO_2	94	59	0.59			
3a	C_5H_{12}	79	68	0.39	92	73	1.1
3a	CCl_4	71	89	1.2	79	89	1.9
3a	CH_2Cl_2	47	56	1.2	79	93	4.3
3a	CH_3NO_2	*d*	52	2.2	89	70	1.3
3b	C_5H_{12}	67	62	1.4	88	71	1.4
3b	CCl_4	63	80	1.9	79	79	2.4
3b	CH_2Cl_2	56	46	1.1	85	79	2.7
3b	CH_3NO_2	55	55	1.1	71	62	1.9
3c	C_5H_{12}	79	70	1.6	89	72	1.2
3c	CCl_4	68	84	2.3	77	78	2.2
3c	CH_2Cl_2	50	58	1.1	85	78	2.8
3c	CH_3NO_2	36	56	1.2	78	66	1.4
4a	CCl_4	95		0.67	100		1.3
4a	CH_2Cl_2	89		0.75	100		2.7
4b	C_5H_{12}	95		0.92			

[a] Computed as follows: anti-1,2 adduct/total 1,2 adduct × 100. Anti-1,2 adduct = **6, 10, 14, 18, 17, 19a, 19b** from **1, 2, 3a, 3b, 3c, 4a, 4b**, respectively. For **3c** total 1,2 adduct is for attack at the cis bond only (see footnote *c*, Table I). [b] Computed as follows: syn-1,4 adduct/total 1,4 adduct × 100. Syn-1,4 adduct = **7, 11, 15, 15, 16** from **1, 2, 3a, 3b, 3c**, respectively. [c] See ref 1a, b. [d] See footnote *b*, Table I.

nation of **3a–c** shows the maximum stereospecificity (anti) in 1,2 addition in pentane with a somewhat lower percentage of syn 1,4 addition than in other solvents.

On the other hand, a large preference for syn (over anti) 1,4 attack often accompanies a low stereochemical preference for anti 1,2 attack. For example, in chlorination of cyclopentadiene (**1**) in carbon tetrachloride, 54% of the 1,2-dichloride is syn (formed evidently via an open carbonium ion) but the 1,4 attack is 78% syn. Likewise in chlorination of cyclohexadiene (**2**) in carbon tetrachloride where the maximum syn 1,2 product is obtained, the 1,4-dichloride is 99% syn. We interpret the above results to mean that the bridged ion in these systems can undergo either syn or anti 1,4 attack, and that the reorientation (**22a** → **22b**) necessary for anti 1,2 attack can also lead to anti 1,4 attack. This accounts for the increase in anti 1,4 product which tends to accompany an increase in anti 1,2 product. The preference for syn 1,4 attack is explained by the fact that 1,4 addition results from an intimate ion pair such as **22a** or **22c** and that the anion in such intermediates is present in a geometrical location which favors direct collapse to syn 1,4 product. Therefore, even in the cases where there is evidently an open carbonium ion (e.g., chlorination of **1** in carbon tetrachloride), the 1,4 addition is still largely syn because collapse of the ion pair is faster than reorientation.

The data on halogenation of these dienes reveal that solvents have a striking effect on product ratios. These changes in product ratios which accompany solvent changes for the most part do not seem to be readily explainable from a mechanistic standpoint but some definite trends may be noted. Bromination of dienes **1, 2,** and **3a–c** gave in every case the largest amount of 1,4 addition in methylene chloride. Also, the preference for syn 1,4 product tends to be highest in methylene chloride. Chlorination of these dienes in methylene chloride tends to give opposite results from bromination, i.e., the 1,4:1,2 ratio is lowest in that solvent. The decrease in 1,4 addition is accompanied by a decreased selectivity for syn addition. Chlorination in carbon tetrachloride gives more syn 1,4 addition than any other solvent for each of the dienes studied. The chlorination of cyclohexadiene (**2**) illustrates particularly well the significant differences observed with various solvents. In carbon tetrachloride 69% of the dichloride product is **11** but in methylene chloride, 58% of the product is **10.** Apparently solvents have subtle effects in stabilizing anions or in allowing solvent separation of ion pairs such as **22a.**

Experimental Section

General. Dienes and solvents were obtained commercially in high purity except for cyclopentadiene, which was prepared from its dimer just prior to use. Infrared spectra were obtained on a Beckman IR-10 spectrophotometer. Nuclear magnetic resonance spectra were obtained with Varian A-60, T-60A, and XL-100 instruments. Vapor phase chromatography was done with a Hewlett-Packard 7620A or F & M 1609 flame ionization instruments.

Chlorination Procedure. Chlorinations were done in the dark at −10 ± 2°C. The diene concentrations were 0.02 mole fraction with respect to the solvent. The amount of chlorine was 20–25% of the amount of diene. For example, a typical chlorination to obtain product ratios was done as follows: to 0.10 g (0.0012 mol) of **3c** dissolved in 5.7 ml of CCl_4 (saturated with oxygen gas) was added 0.36 ml of 0.86 *M* chlorine in carbon tetrachloride (0.00031 mol). In another procedure samples of liquid chlorine were vaporized with an oxygen stream into diene solutions. Dichloride product ratios did not differ significantly for the two methods of chlorine addition. Under the chlorination conditions described above cyclohexane was not chlorinated when it was the solvent. At high diene mole fraction (0.5) under nitrogen, detectible amounts of chlorocyclohexane were formed from cyclohexane. We conclude that the chlorination procedure used did not contain a radical component.[3]

Analysis Procedure. Mixtures resulting from chlorination were sampled directly by VPC, using one of the following columns: column A, 2.5% SE-30 on 60–80 Chromosorb W (AW-DMCS), 18 ft × 0.25 in. SS; column B, 2.5% β,β-oxydipropionitrile on 80–100 Chromosorb W (AW-DMCS), 6–14 ft × 0.125 in. SS. VPC analysis of dichloride mixtures is based on corrected peak areas which were established by means of VPC response factors. Response factors were obtained by analysis of known mixtures prepared from pure compounds and the internal standard which was used to obtain yields. The average yields[10] for chlorination in the solvents shown

in Table I for each of the dienes is as follows (%): **1**, 60; **2**, 37; **3a**, 70; **3b**, 71; **3c**, 79; **4a**, 60; **4b**, 56.

Dichlorocyclopentenes (5, 6, 7, 8). VPC analysis on column B (7 ft, 51°) gave retention times (min) of 4.4, 7.4, 20.6, and 22.6 for **6, 8, 5,** and **7**, respectively. Retention times on column A have been reported.[2d] *p*-Chlorobromobenzene was used as an internal standard. Data for the identification of **5, 6, 7,** and **8** have been reported previously.[2d]

Dichlorocyclohexenes (9, 10, 11, 12). VPC (70°) analysis on column A of chlorination mixtures of **2** gave four peaks with retention times of 12.8, 15.0, 16.2, and 18.8 min, assigned to **10, 12, 11,** and **9**, respectively. Bromobenzene was used as an internal standard. Pure samples of **10** and **11** were obtained by spinning-band distillation of chlorination mixtures. Compound **9** was obtained in about 85% purity by spinning-band distillation followed by preparative VPC. Identification of **12** is based on the fact that peak 2 in the chlorination mixtures had a VPC retention time identical with that of **12** prepared independently (below).

Structural assignments for **11** and **12** were made on the basis of preparation from the corresponding 3,6-dibromocyclohexenes by treatment with lithium chloride as reported previously[2d] for **7** and **8**. For example: 0.35 g of *trans*-3,6-dibromocyclohexene[1b] was added to a mixture of 0.62 g of LiCl in 20 ml of Me_2SO. The mixture was stirred at 15° for 15 min, then poured into ice–water and extracted with pentane. Evaporation of the pentane afforded **12**, a solid which melted at 62–63.5° after three recrystallizations from pentane. Compound **11** was obtained by an identical reaction from *cis*-3,6-dibromocyclohexene.[1b] After recrystallization from pentane, **11** had mp 31.5–32.5°.

Structures of **9** and **10** were established by diimide reduction to the dichlorocyclohexanes. For example, 0.25 g of pure **10** was treated with potassium azodicarboxylate in pyridine according to the procedure of Snyder.[11] Unreacted **10** was removed by addition of excess 0.1 *M* potassium permanganate and the product was extracted into pentane and purified by VPC. The product had an identical VPC retention time and ir and NMR spectra with authentic *trans*-1,2-dichlorocyclohexane.[12] By an identical procedure the compound of VPC peak 4 (above) was converted to a product having identical VPC retention time and NMR and ir spectra with authentic *cis*-1,2-dichlorocyclohexane.[13]

NMR analyses also confirmed the structures assigned to the cyclohexadiene dichlorides. All showed three regions of absorptions assignable to vinyl, methine, and methylene hydrogens with integrated intensities of 1:1:2, respectively. Spectra assigned to **11** and **12** showed striking resemblances to the respective isomeric dibromides.[1b] Spectra of **9** and **10** each showed two distinct methine protons and greater multiplicity for the vinyl hydrogen absorptions owing to the lesser degree of symmetry in the structures of **9** and **10**. Summary of NMR data (CCl_4, parts per million downfield from Me_4Si, **10, 11, 12,** 100 MHz; **9,** 60 MHz): **9**, 1.82–2.42 (m, 4, CH_2), 4.08–4.40 (m, 1, CHCl), 4.42–4.70 (m, 1, CHCl), 5.70–5.93 (m, 2, CH=CH); **10**, 1.84–2.56 (m, 4, CH_2), 4.26–4.42 (m, 1, CHCl), 4.42–4.54 (m, 1, CHCl), 5.60–6.02 (m, 2, CH=CH); **11**, 2.08–2.26 (m, 4, CH_2), 4.38–4.60 (m, 2, CHCl), 5.80–5.94 (m, 2, CH=CH); **12**, 1.88–2.57 (m, 4, CH_2), 4.48–4.66 (m, 2, CHCl), 5.86–6.02 (m, 2, CH=CH).

Summary of ir absorptions (cm^{-1}, CCl_4): **9**, 3040, 2960, 2920, 2840, 1640, 1420, 1231, 1205, 1092, 970, 945, 893, 853, 690, 672, 629; **10**, 3040, 2960, 2920, 2900, 2840, 1655, 1442, 1430, 1330, 1240, 1200, 1020, 685, 640, 555; **11**, 3040, 2960, 2900, 1455, 1440, 1390, 1215, 1235, 1190, 980, 885, 700, 620, 483; **12**, 3040, 2960, 1440, 1355, 1260, 1215, 1012, 946, 918, 675, 567.

Dichlorohexenes (13–18). Mixtures of dichlorides produced by chlorination of **3a–c** were analyzed by VPC using columns A and B. Retention times on these columns follow: column A (30°), 31.8, 35.0, 37.8, 37.8, 42.0, and 45.7 min for **13, 18, 17, 14, 16,** and **15**, respectively; column B (14 ft, 50°), 15.6, 16.0, 16.0, 17.6, 24.0, and 28.2 min for **13, 17, 18, 14, 16,** and **15**, respectively. Bromobenzene was used as internal standard.

Pure samples of **15** and **16** were obtained by recrystallization from chlorination mixtures. For example, for preparation of **16**, 2.0 g (0.024 mol) of **3c** in 230 ml of carbon tetrachloride was treated with 34 ml (0.019 mol) of 0.58 *M* chlorine solution (CCl_4). The solvent was removed in vacuo, pentane was added, and the mixture was caused to crystallize by cooling in a dry ice bath. After washing the crystals three times with cold pentane, the solvent was removed and the residue was distilled [bp 80° (35 mm)] to yield 0.64 g of **16** (97% by VPC). By a similar procedure **15** was obtained by starting with chlorination of **3b**.

Structures of **15** and **16** were established[14] by conversion to diepoxyhexanes by a procedure described previously for the corresponding dibromohexenes.[1b] Thus, **16**, obtained as described above, yielded a single diepoxide identical in ir spectrum and VPC retention time with *cis,trans-rac*-(2*R*,3*R*,4*R*,5*S*)-2,3,4,5-diepoxyhexane.[15] Dichloride **15** yielded by the same treatment two compounds having VPC retention times identical with those of *cis,cis-rac*-(2*R*,3*R*,4*R*,5*R*)-diepoxyhexane[15] and *trans,trans-rac*-(2*S*,3*R*,4*R*,5*S*)-2,3,4,5-diepoxyhexane.[15]

The 1,2-dichlorides resulting from chlorination of **3a–c** in CCl_4 were isolated by distillation and VPC collection. The 1,2 adduct isolated from each diene was a mixture of diastereomers having compositions as follows (%): from **3a, 14,** 65, **13,** 35; from **3b, 18,** 66, **17,** 34; from **3c, 17,** 56, **18,** 33, **13,** 7, **14,** 4. The NMR and ir data as well as the crotonaldehyde dichloride derivatives reported below were obtained on the above mixtures of diastereomers.

Assignment of structures to the 1,2 adducts is based on their NMR and ir spectra and on conversion to crotonaldehyde dichlorides by a procedure reported previously for the corresponding 4,5-dibromo-2-hexenes.[1b] Authentic crotonaldehyde dichloride [bp 60–70° (36 mm); reported[16] 58–60° (20 mm)] prepared by chlorination of crotonaldehyde showed two VPC peaks (column A, 38°), peak 1, 13.4 min, 87%, and peak 2, 16.4 min, 13%. The crotonaldehyde dichloride obtained from the 4,5-dichloro-2-hexenes showed identical VPC peaks in ratios as follows:[17] from dichloride of **3a**, peak 1, 48%, peak 2, 52%; from dichloride of **3b**, peak 1, 81%, peak 2, 19%; from dichloride of **3c**, peak 1, 50%, peak 2, 50%. The crotonaldehyde dichloride obtained from the 1,2-dichloride adduct of **3b** was isolated by VPC collection and found to have an ir spectrum identical with that of authentic crotonaldehyde dichloride, ir (CCl_4) O=CH, 2830, 2720; C=O, 1735 cm^{-1}.

The NMR spectra of **13–18** are consistent with the structures assigned. The 1,4 adducts **15** and **16** exhibited one absorption for methyl and one absorption for methine hydrogens whereas 1,2 adducts **13, 14, 17,** and **18** showed two different absorptions for methyl hydrogens. In **13** and **14** the methine hydrogens exhibit different chemical shifts. Spectra (60 MHz, CCl_4) are summarized as follows: (**13, 14**), 1.54 (d, CH_3CHCl of **14**, J = 7.0 Hz), 1.60 (d, CH_3CHCl of **13**, J = 7.0 Hz), 1.76 (d, 3, CH_3CH=CH, J = 5.5 Hz), 4.14 (m, 1, CH_3CHCl), 4.77 (m, 1, CH=CHCHCl), 5.45 (m, 2, CH=CH); **15**, 1.60 (d, 3, CH_3, J = 6.5 Hz), 4.48 (m, 2, CHCl), 5.78 (m, 2, CH=CH); **16**, 1.55 (d, 3, CH_3, J = 6.5 Hz), 4.46 (m, 2, CHCl), 5.68 (m, 2, CH=CH); (**17, 18**), 1.55 (d, CH_3CHCl of **18**, J = 6.5 Hz), 1.51 (d, CH_3CHCl of **17**, J = 6.8 Hz), 1.76 (d, 3, CH_3CH=CH, J = 5.2 Hz), 4.14 (m, 2, CHClCHCl), 5.54 (m, 2, CH=CH).

Summary of ir spectra (cm^{-1}, CCl_4): (**13, 14**), 3020 (C=CH), 1655 (C=C), 780 (cis CH=CH, CS_2), 1445, 1380, 1245, 1200, 850, 650; **15**, 956 (trans CH=CH), 1445, 1375, 1220, 1009, 640; **16**, 953 (trans CH=CH), 1443, 1370, 1200, 1003, 640; (**17, 18**), 3015 (C=CH), 1670 (C=C), 957 (trans CH=CH), 1447, 1380, 1245, 1200, 1181, 1000, 910, 855, 650.

Dichloropentenes (19a–21). Mixtures of dichlorides obtained from **4a,b** were analyzed by VPC using column B (12 ft, 50°). Retention times are 4.8, 5.2, 7.4, 7.4, and 16.4 min for **19a, 19b, 20a, 20b,** and **21**, respectively. Comparative amounts of erythro and threo (**19a, 19b**) isomers produced in reactions were determined by VPC collection and integration of the methyl absorption in the NMR. The fact that the 1,2-dichloride (**20a, 20b**) formed from **4a** or **4b**, respectively, without rearrangement of the double bond was shown by direct NMR measurement of the methylene region (~3.65) for **20a** or **20b** in chlorination mixtures. In VPC analysis of the above mixtures *o*-bromotoluene was used as internal standard.

All of the reported dichloride isomers were isolated by spinning band distillation or VPC collection. Structural assignments are based on NMR and ir spectra. Summary of NMR spectral data (CCl_4, 60 MHz): **19a**, 1.55 (d, 3, CH_3, J_{45} = 6.1 Hz), 4.18 (d of q, 1, $CHClCH_3$, J_{45} = 6.1, J_{34} = 3.8 Hz), 4.50 (dd, 1, CHCH=CH, J_{34} = 3.8, J_{23} = 6.6 Hz), 5.6–5.2 (m, 2, CH=CH_2), 6.04 (ddd, 1, CH=CH_2, J_{23} = 6.6, J' = 8.2, J'' = 18.4 Hz); **19b**, 1.62 (d, 3, CH_3, J_{45} = 6.1 Hz), 3.8–4.5 (m, 2, $CHClCH_3$ and CHCH=CH), 5.15–5.54 (m, 2, CH=CH_2), 5.99 (ddd, 1, CH=CH_2, J = 7.0, J' = 8.0, J'' = 17.2 Hz); **20a**, 1.78 (d, 3, CH_3, J_{12} = 6.5, J_{13} = 1.2 Hz), 3.53 [dd, 1, CH(H), J_{45} = 8.2, $J_{55'}$ = 10.3 Hz], 3.78 [dd, 1, CH(H), $J_{45'}$ = 5.0, $J_{55'}$ = 10.3 Hz), 4.76 (ddd, 1, CHCl, $J_{45'}$ = 5.0, J_{45} = 8.2, J_{34} = 8.0 Hz), 5.43 (dd, 1, CH=CHCCl, J_{23} = 11.0, J_{34} = 8.0, J_{13} = 1.2 Hz), 5.80 (dq, 1, CH=CHCCl, J_{12} = 6.5, J_{23} = 11.0 Hz); **20b**, 1.78 (d, 3, CH_3, J_{12} = 5.4, J_{13} = 1.2 Hz), 3.53 [dd, 1, CH(H), J_{45} = 8.0, $J_{55'}$ = 10.2 Hz], 3.76 [dd, 1, CH(H), $J_{45'}$ = 5.2, $J_{55'}$ = 10.2 Hz], 4.40 (ddd, 1, CHCl, $J_{45'}$ = 5.2, J_{45} = 8.0, J_{34} = 8.0 Hz), 5.32 (dd, 1, CH=CHCHCl, J_{34} = 8.0, J_{23} = 14.4, J_{13} = 1.2 Hz), 5.86 (dq, 1,

CH=CHCHCl, J_{12} = 5.4, J_{23} = 14.4 Hz); **21**, 1.60 (d, 3, CH_3, J_{45} = 6.8 Hz), 4.00 (m, 2, CH_2), 4.42 (m, 1, CHCl), 5.74 (m, 2, CH=CH).

Summary of ir data (cm^{-1}, CCl_4): **19a**, 983 and 930 ($CH=CH_2$), 3090, 2980, 2920, 1445, 1360, 1200, 750, 650 cm^{-1}; **20a**, 720, (CS_2, cis CH=CH), 1665 (C=C), 3040, 2950, 2910, 2860, 1430, 1380, 1310, 1270, 1200, 1170, 960, 920, 680; **20b**, 956 (trans CH=CH), 1670 (C=C), 3040, 2970, 2950, 2910, 2890, 2860, 1425, 1370, 1195, 1170, 670; **21**, 957 (trans CH=CH), 1670 (C=C), 3040, 2970, 2910, 2860, 1440, 1380, 1250, 1215, 1010, 685, 645.

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Registry No.—**1**, 542-92-7; **2**, 592-57-4; **3a**, 6108-61-8; **3b**, 5194-51-4; **3c**, 5194-50-3; **4a**, 1574-41-0; **4b**, 2004-70-8; **5**, 51502-28-4; **6**, 31572-43-7; **7**, 31572-45-9; **8**, 31572-44-8; **9**, 53921-00-9; **10**, 53920-98-2; **11**, 54112-34-4; **12**, 53920-99-3; **13**, 57256-15-2; **14**, 57256-16-3; **15**, 57256-17-4; **16**, 57273-83-3; **17**, 57256-18-5; **18**, 57256-19-6; **19a**, 57256-20-9; **19b**, 53920-93-7; **20a**, 53920-95-9; **20b**, 53920-94-8; **21**, 53920-96-0.

References and Notes

(1) (a) V. L. Heasley, G. E. Heasley, S. K. Taylor, and C. L. Frye, *J. Org. Chem.*, **35**, 2967 (1970); (b) G. E. Heasley, V. L. Heasley, S. L. Manatt, H. A. Day, R. V. Hodges, P. A. Kroon, D. A. Redfield, T. L. Rold, and D. E. Williamson, *ibid.*, **38**, 4109 (1973).

(2) Previous studies on the chlorination of conjugated dienes follow. Butadiene: (a) M. L. Poutsma, *J. Org. Chem.*, **31**, 4167 (1966); (b) V. L. Heasley, G. E. Heasley, R. A. Loghry, and M. R. McConnell, *ibid.*, **37**, 2228 (1972). Isoprene: (c) G. D. Jones, N. B. Tefertiller, C. F. Raley, and J. R. Runyon, *ibid.*, **33**, 2946 (1968). Cyclopentadiene: (d) V. L. Heasley, G. E. Heasley, P. D. Davis, D. M. Ingle, and K. D. Rold, *ibid.*, **39**, 736 (1974). *trans,trans*-2,4-Hexadiene: (e) M. S. Edmondson, *Diss. Abstr.*, 3914 (1971).

(3) For a discussion of competition between radical and ionic mechanisms in chlorination of alkenes, see (a) M. L. Poutsma, *J. Am. Chem. Soc.*, **87**, 2172 (1965); (b) *J. Org. Chem.*, **31**, 4167 (1966).

(4) The attack by chloride ion in **22d** is anti to the chlorine atom already bonded to carbon but the dichlorides formed (both 1,2 and 1,4) from **22d** are the same as those resulting from direct syn addition of both chlorine atoms to the same side of the diene, i.e., they are syn products. For previous discussions of this matter see ref 1b and studies on the bromination of the 1-phenylpropenes [J. H. Rolston and K. Yates, *J. Am. Chem. Soc.*, **91**, 1469 (1969); R. C. Fahey and H. J. Schneider, *ibid.*, **90**, 4429 (1968)].

(5) Although there is evidence (mainly under conditions other than those employed in electrophilic addition) that bromine is a better bridging atom than chlorine [see, e.g., F. Freeman, *Chem. Rev.*, **75**, 454 (1975)], the ability of chlorine to form stable bridged ions in electrophilic addition has been amply demonstrated. Stereospecific anti addition has been observed with a diversity of alkenes such as cyclopentene,[2d] *cis*-2-butene,[3a] and *cis*-di-*tert*-butylethylene: R. C. Fahey, *J. Am. Chem. Soc.*, **88**, 4681 (1966).

(6) For a further discussion see our recent paper on the addition of bromine chloride to **1**: V. L. Heasley, C. N. Griffith, and G. E. Heasley, *J. Org. Chem.*, **40**, 1358 (1975).

(7) Edmondson[2e] reports that essentially equal amounts of anti and syn 1,2-dichloride are obtained from chlorination of **3b** in several solvents. Since our syn:anti 1,4-dichloride ratios and 1,4:1,2 ratios are in good agreement with his, the discrepancy on the ratio of 1,2-dichlorides may be due to the fact that his mixtures of erythro and threo dichlorides were analyzed via diimide reduction to the 2,3-dichlorohexanes. We were able to achieve direct VPC separation of the 1,2-dichlorides and also observed that the NMR spectra of the mixture of 1,2-dichlorides confirmed our VPC analysis.

(8) This trend has been observed for chlorination and bromination of butadiene in several solvents [V. L. Heasley, G. E. Heasley, R. A. Loghry, and M. R. McConnell, *J. Org. Chem.*, **37**, 2228 (1972)]. Chlorination of isoprene[2c] gives more 1,4 than 1,2 addition in most solvents; bromination of isoprene also occurs predominantly 1,4 [V. L. Heasley, C. L. Frye, R. T. Gore, and P. S. Wilday, *ibid.*, **33**, 2342 (1968)].

(9) We assume that attack on a bridged bromonium ion (covalently bonded to both carbon atoms) is essentially a nucleophilic displacement and that opening by attack on the double bond would be an example of the S_N2' mechanism. Although a syn stereochemistry is generally accepted for S_N2', the evidence for this has been questioned [F. G. Bordwell, *Acc. Chem. Res.*, **3**, 281 (1970)]. Liotta [C. L. Liotta, *Tetrahedron Lett.*, 523 (1975)] and Fukui [K. Fukui, *ibid.*, 2427 (1965)] have predicted on theoretical grounds that S_N2' attack should be syn to the leaving group.

(10) The relatively low yields of dichlorides obtained with some of the dienes (particularly with **2**) is probably due to competing substitution reactions. De La Mare and Wong [*Recl. Trav. Chim. Pays-Bas*, **87**, 824 (1968)] have investigated the ionic chlorine substitution reaction which occurs with **4a,b**. We observed that chlorination of **2** in carbon tetrachloride produced benzene (identified by the NMR singlet at δ 7.26) in a mole ratio equal to the dichlorocyclohexenes. Benzene would be obtained by HCl elimination from the allylic substitution product of cyclohexadiene (**2**), 5-chloro-1,3-cyclohexadiene (benzene hydrochloride).

(11) J. W. Hamersma and E. I. Snyder, *J. Org. Chem.*, **30**, 3985 (1965).

(12) M. L. Poutsma, *J. Am. Chem. Soc.*, **87**, 2162 (1965).

(13) N. Isaacs and D. Kirkpatrick, *Tetrahedron Lett.*, 3869 (1972).

(14) Edmondson[2e] proved the structure of the principal 1,4-dichloride of **3b** (**15**) by diimide reduction to *dl*-2,5-dichlorohexane.

(15) G. E. Heasley, R. V. Hodges, and V. L. Heasley, *J. Org. Chem.*, **39**, 1769 (1974).

(16) C. Moureu, M. Murat, and L. Tampier, *Bull. Soc. Chim. Fr.*, **29**, 29 (1921).

(17) Since the major crotonaldehyde dichloride isomer is the same from chlorination of crotonaldehyde and when derived from the chlorination product of **3b** (in CCl_4), the major dichloride from **3b**, **18**, can be assigned the erythro structure on the assumption that chlorine addition to the largely *trans*-crotonaldehyde would be predominantly anti. The chlorination product (in CCl_4) from **3a** yielded a crotonaldehyde dichloride mixture in which the major dichloride was the opposite to that obtained from **3b**, so it follows that the major dichloride (**14**) of **3a** (CCl_4) is threo. Additional evidence for assignment of erythro and threo structures was obtained by converting the chlorination product of **4a** to crotonaldehyde dichlorides. The crotonaldehyde dichloride obtained in major amount (>95%) had a VPC retention time identical with that of the major crotonaldehyde dichloride derived from **3a**. Thus the assignment of the threo structure to **14** follows if the nearly stereospecific addition to the 3,4 bond in **4a** (and **4b**) is assumed to be anti.

New Precursors for Arylcarbenes. Photocycloelimination Reactions of Cyclic Carbonates[1,2]

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Cyclic arylpinacol carbonates undergo photoinduced [5 → 2 + 2 + 1] cycloeliminations to give arylcarbenes. The carbonates studied include benzopinacol carbonate, *meso*- and *dl*-hydrobenzoin carbonates, and the *dl*- and *meso*-α,α'-dimethylhydrobenzoin carbonates. Arylcarbenes formed by photolysis of these substrates react in methanol to give methyl ethers and the properties of phenylcarbene obtained from the *meso*- and *dl*-hydrobenzoin carbonates are found to be virtually identical with those obtained from conventional precursors such as *trans*-2,3-diphenyloxiranes and phenyldiazomethane; i.e., the secondary to primary insertion selectivity in pentane and the stereospecificity in the addition to *cis*-2-butene are the same.

It has become increasingly apparent that both thermal and photocycloelimination reactions, like the reverse reactions of cycloaddition, have broad synthetic utility.[4,5,6] We have recently described the [5 → 2 + 2 + 1] photocycloelimination of pinacol sulfites[4] and as part of our continuing research program in this area have investigated the chemi-