The dinitrophenylhydrazone had mp 152–154° (EtOAc–EtOH–H_2O).

2,4,4-Trimethylcyclohexanone[12] was prepared by the general procedure of Ritchie and Taylor:[11] yield 79%; bp 76–77° (15 mm); $n^{22}D$ 1.4481; ir 1718 (C=O), 1390, 1370 cm^{-1} (*gem*-CH_3); nmr ($CDCl_3$) δ 1.23 (s, 3), 1.01 (s, 6), 0.95 (d, 3, J = 7 Hz).

The dinitrophenylhydrazone had mp 150–151° (ethanol) (lit.[12] mp 149–150°).

1-Acetoxy-2,4,4-trimethylcyclohexene (5) was prepared following the general procedure of House, *et al.*:[4] yield 90%; bp 92.5–93.5° (15 mm); $n^{22}D$ 1.4514; ir 1760 (C=O), 1715 (C=C), 1390, 1370 cm^{-1} (*gem*-CH_3); nmr ($CDCl_3$) δ 2.12 (s, 3), 0.98 (s, 6).

Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.5; H, 10.0. Found: C, 72.4; H, 9.9.

1,2-Bis(chloromethyl)benzene[13] **(3).** Phthalyl alcohol (6.9 g, 0.05 mol) and triphenylphosphine (27.0 g, 0.103 mol) were refluxed in 200 ml of dry carbon tetrachloride for 22 hr.[14] The reaction mixture was cooled to 0° and poured into petroleum ether (400 ml, bp 40–60°) to complete the precipitation of triphenylphosphine oxide. Filtration, evaporation, and distillation gave pure 1,2-bis(chloromethyl)benzene: yield 5.2 g (61%); bp 55–56° (0.3 mm); mp 55–56° (lit.[11] mp 54–55°); nmr ($CDCl_3$) δ 7.34 (s, 4), 4.74 (s, 4).

cis-**But-2-ene-1,4-diol**[15] was prepared by hydrogenation of but-2-yne-1,4-diol (20.0 g) in 300 ml of pyridine (5% Pd on $BaSO_4$, 1.0 g)[5] in 88% yield.

General Cycloalkylation Procedure. Methyllithium in ether (21 mmol) was added to 50 ml of dimethoxyethane (DME) and the bulk of the ether was removed under reduced pressure. The enol acetate (10 mmol) in 5 ml of DME was added dropwise to the methyllithium solution containing a white precipitate (0°, slow N_2 stream, magnetic stirring). After 15 min the reaction mixture was heated to 60° to dissolve the lithium *tert*-butoxide. The dichloride (10 mmol) in 5 ml of DME was added in one lot. After *ca.* 5 min the reaction was complete (vpc and nmr; prolonged reaction time did not affect the yield significantly) and the reaction mixture was poured into an ice-cooled mixture of 5% sodium bicarbonate solution (100 ml) and pentane (50 ml). The water phase was extracted with pentane (2 × 50 ml), the combined pentane extracts were dried (Na_2SO_4), and the solvent was evaporated to yield the crude reaction product.

1,8,8-Trimethylfuro[3,4-*c*]bicyclo[4.3.1]decan-10-one (1) was prepared from **5** and **6**. The crude reaction product (yield >95%) was practically pure **1** (nmr, ir). Sublimation *in vacuo* gave an analytical sample: mp 108–110°; ir (KBr) 3125, 3100 (furan), 1697 (C=O), 1393, 1378 (*gem*-CH_3), 878 cm^{-1} (furan); nmr ($CDCl_3$) δ 7.30 (s, 2), 1.27 (s, 3), 0.98 (s, 3), 0.92 (s, 3); mass spectrum m/e 232 (M^+).

Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.6; H, 8.7. Found: C, 77.5; H, 8.7.

1-Methyl-3,4-benzobicyclo[4.3.1]decan-10-one (4) was prepared from **2** and **3**. The crude reaction product (yield >95%) was almost pure **4** (nmr). Distillation gave a colorless oil which crystallized on cooling: yield 65%; bp 110–112° (0.4 mm); mp 64–65.5°; $n^{21}D$ 1.5555; ir 3030 (aromatic CH), 1708 (C=O), 750 cm^{-1}; nmr ($CDCl_3$) δ 7.06 (s, 4), 1.08 (s, 3); mass spectrum m/e 214 (M^+).

Anal. Calcd for $C_{15}H_{18}O$: C, 84.1; H, 8.5 Found: C, 84.1; H, 8.5.

1,8,8-Trimethylbicyclo[4.3.1]dec-3-en-10-one (8) was prepared from **5** and **7**. The crude reaction product was chromatographed on silica (50 g) with methylene chloride as eluent to give **8** in 35% yield: $n^{25}D$ 1.4913; ir 1706 cm^{-1} (C=O); nmr ($CDCl_3$) δ 5.93–5.70 (m, 2), 3.10–2.55 (m, 1, J = 4.4 Hz), 1.20 (s, 3), 0.93 (s, 3), 0.87 (s, 3); mass spectrum m/e 192 (M^+).

Anal. Calcd for $C_{13}H_{20}O$: C, 81.2; H, 10.5. Found: C, 80.9; H, 10.3.

1-Methylbicyclo[4.3.1]dec-3-en-10-one (9) was prepared from **2** and **7**. The crude reaction product was chromatographed on silica (50 g) with methylene chloride as eluent to give **9** in 34% yeild: bp 59–60° (0.4 mm); $n^{26}D$ 1.4998; ir 1710 cm^{-1} (C=O); nmr ($CDCl_3$) δ 5.92–5.67 (m, 2), 1.11 (s, 3); mass spectrum m/e 164 (M^+).

Anal. Calcd for $C_{17}H_{20}N_4O_4$ (dinitrophenylhydrazone): C, 59.3; H, 5.9; N, 16.3. Found: C, 59.6; H, 5.8; N, 16.2.

The dinitrophenylhydrazone had mp 177–179° (EtOAc–EtOH–H_2O).

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Registry No.—1, 50388-42-6; **2,** 1196-73-2; **3,** 612-12-4; **4,** 50388-44-8; **5,** 50388-45-9; **6,** 6372-18-5; **7,** 1476-11-5; **8,** 50388-48-2; **9,** 50388-49-3; **9** 2,4-dinitrophenylhydrazone, 50388-50-6; 2-methoxycarbonyl-4,4-dimethylcyclohexanone, 50388-51-7; 2-methoxycarbonyl-4,4-dimethylcyclohexanone 2,4-dinitrophenylhydrazone, 50388-52-8; 2-methoxycarbonyl-2,4,4-trimethylcyclohexanone, 50388-53-9; 2-methoxycarbonyl-2,4,4-trimethylcyclohexanone 2,4-dinitrophenylhydrazone, 50388-54-0; 2,4,4-trimethylcyclohexanone, 2230-70-8; phthalyl alcohol, 612-14-6; *cis*-but-2-ene-1,4-diol, 6117-80-2; but-2-yne-1,4-diol, 110-65-6.

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Addition of Chlorine to 1,3-Butadiene with Antimony Pentachloride

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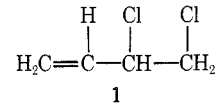
The reaction of $SbCl_5$ with simple olefins was reported recently.[1] The reaction yielded vicinal dichloroalkanes by a cis addition, as evidenced by the formation of *cis*-1,2-dichlorocyclohexane from cyclohexene, presumably by a concerted pathway.

We report here on the reaction of $SbCl_5$ and 1,3-butadiene (BDN) to produce dichlorobutene (DCB) isomers. This reaction is strongly stereoselective toward the formation of **2** when compared to the reaction of molecular



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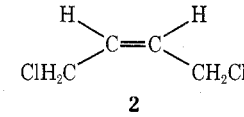

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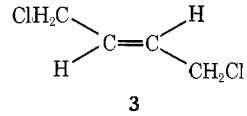

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chlorine and butadiene under similar conditions. The latter reaction has been studied previously,[2] and data indicate only trace quantities of **2**. These data have been confirmed by our work, using conditions and apparatus com-

Table I
$SbCl_5$ + BDN Reactions[a]

Run No.	Solvent	Reaction temp, °C Low	Reaction temp, °C High	DCB isomers,[b] % 1	2	3	Remarks
1	CH_2Cl_2	−26	−5	38.3	23.5	38.2	Mole fraction BDN = 0.5 ($SbCl_5$ added neat).
2	CH_2Cl_2	−19	−10	23.8	40.9	35.3	Run as in footnote *a* except shielded from ambient light in lab.
3	CH_2Cl_2	−19	−13	26.3	37.9	35.8	Run as in footnote *a*.
4	CH_2Cl_2	−22	−12	25.6	23.6	50.8	Reverse addition mode. BDN added to $SbCl_5$ solution.
5	CH_2Cl_2	−26	−13	35.1	40.1	24.8	Concentration of both reactants was about $1/2$ that in footnote *a*.
6	CCl_4	−8	−1	33.0	33.5	33.5	Temperature was higher to avoid freezing CCl_4. Run as in footnote *a*.
7	$CHCl_3$	−20	−11	38.4	26.5	35.1	Run as in footnote *a*.

[a] General reaction conditions were 0.1 mol of BDN + 0.5 mol of solvent (mole fraction BDN = 0.17) with a solution of 50% by volume $SbCl_5$ in same solvent added dropwise until 0.02 mol of $SbCl_5$ had been added. Equipment was not shielded from ambient light in lab. System was under dry N_2 and essentially anhydrous. [b] Area per cent by gc normalized to DCB. Results were reported at 20% theoretical BDN conversion. Samples taken at lower conversions during each experiment did not show significant variation.

Table II
Cl_2 + BDN Reaction in CH_2Cl_2[a]

Mole ratio of Cl_2/BDN	Reaction temp, °C Low	Reaction temp, °C High	DCB isomers,[b] % 1	2	3
0.085	−21	−12	54.3	0.4	45.3
0.17	−20	−15	53.5	0.7	45.8
0.22	−20	−12	53.8	0.8	45.4

[a] General reaction conditions were 0.1 mol of BDN + 0.5 mol of CH_2Cl_2, with Cl_2 bubbled into solution in stepwise fashion and snap samples taken with gc syringe. [b] For comparison, vapor-phase reaction of BDN + Cl_2 at about 150° produces approximately 36% of **1**, 17% of **2**, and 47% of **3**. See also P. M. Colling, *Diss. Abstr.*, **24**, 3977 (1964).

Table III
Cl_2 + BDN Reaction in Various Solvents

Solvent	DCB isomers,[a] % 1	2	3
$CHCl_3$	61.0	0.7	38.3
CCl_4	42.4	0.7	56.9
CH_3OH	61.6	0.0	38.4
CH_3CN	50.7	0.0	49.3
$CHCl_2CHCl_2$	57.1		42.9
CH_3CCl_3	48.2	0.6	51.2
dl-$CH_2ClCHClCHClCH_2Cl$	47.0	0.8	52.2

[a] General reaction conditions same as in Table II, footnote *a*.

parable to those used for study of the $SbCl_5$ reaction.[3] Earlier work has shown that liquid-phase reaction of Cl_2 and butadiene in a wide variety of solvents has no significant effect on the relative amount of **2** produced.[4]

Data for the current study are presented in Tables I–V. In view of equilibrium data, product isomer ratios appear to be kinetically controlled. A possible intermediate for the formation of **2** is suggested in Figure 1. Conductivity data imply that $SbCl_5$ does not have significant ionic character in the solvents employed (*i.e.*, $SbCl_4^+$ and $SbCl_6^-$ are insignificant). Monomeric $SbCl_5$, as a trigonal bipyramid, could interact with cisoid butadiene and result in transfer of two chlorine atoms to the diene in which the addition occurs antarafacially, *e.g.*, trans to the butadiene molecular plane. The orbital symmetry of the intermediate for the antarafacial 1,4 addition to butadiene (*i.e.*, participation of the highest occupied molecular orbital in butadiene) is similar to the orbital symmetry for a concerted suprafacial, or cis 1,2 addition to cyclohexene. Suprafacial 1,4 addition would be symmetry forbidden. In-

Table IV
Dichlorobutene Isomer Equilibrium Data

Compd	Equil at 60°, %	Equil at 105°, %
1	17	24
2	6	8
3	77	68

Table V
Conductivity of $SbCl_5$ Solutions (μmhos)

	Solvent	Soln, 50% by volume
CH_2Cl_2	1.10	1.25
CCl_4	0.00	0.10
$CHCl_3$		0.10

volvement of various combinations of axial and equatorial bonds of $SbCl_5$ may be invoked to obtain reasonably good intermediate stereochemistry, employing a very simple approximation using covalent radii[5] (Figure 2). For example, axial–equatorial participation may be reasonable for a concerted suprafacial 1,2 addition to form **1**, equatorial–equatorial for a concerted antarafacial 1,4 addition to cisoid butadiene to form **2**, and axial–axial for formation of **3**.

To substantiate this mechanism $SbCl_5$ was treated with *trans,trans*-2,4-hexadiene. The addition of molecular chlorine to this diene has been studied in detail[6] and closely resembles the addition of molecular chlorine to butadiene. However, repeated attempts to add chlorine to the hexadiene by means of $SbCl_5$ led to complete formation of polymeric substances.

Dependency of isomer ratio on the solvent employed, order of reactant mixing, and reactant concentration was observed. All solvents tested showed an overwhelming preference for **2** compared to the Cl_2 and butadiene reaction. CH_2Cl_2 gave the highest selectivity under the same reaction conditions. Order of reactant mixing appears important, since reversing the addition mode (*i.e.*, addition of butadiene to $SbCl_5$ solution) while maintaining other reaction conditions essentially the same reduced the concentration of **2** by almost a factor of 2 while showing an increase in **3** (run 4). It is believed that this change in isomer ratio is not due to preferential overchlorination of the dichlorobutene isomers. The increase of **3** may be caused by its formation by an intermolecular mechanism which would be favored in the presence of excess $SbCl_5$ encountered in the reverse addition mode.

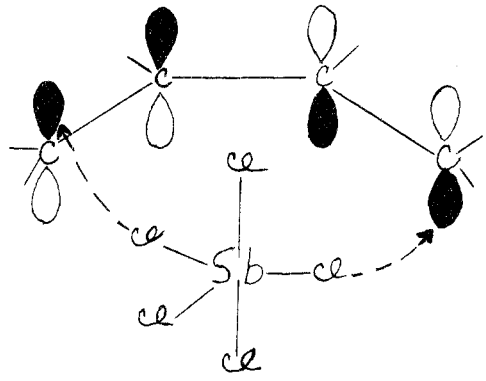

Figure 1. Intermediate for the formation of *cis*-1,4-dichlorobutene-2.

Two experiments point to reactant concentration as possible factor in isomer selectivity. The experiment in which the butadiene concentration was relatively high (mole fraction = 0.5) and $SbCl_5$ was added neat indicated relatively low **2**. Another experiment in which the concentration of both reactants were reduced by a factor of 2 relative to normal conditions in Table I had no significant effect on **2**, but the relative amount of **1** increased at the expense of **3**. In both cases, where chlorination occurred in the presence of relatively high concentrations of $SbCl_5$ (*i.e.*, neat $SbCl_5$ addition and reverse mixing of reactants), the isomer selectivity toward **2** was reduced.

The reaction mixture is stable toward isomerization. A sample remained at ambient lab conditions for 4 days with no significant change in the dichlorobutene isomer ratio. The presence of ambient light in the lab had no significant effect. The existence of the dichlorobutene isomers in the reaction mixture was determined by gc retention times relative to known isomer mixtures and verified semiquantitatively by nmr [multiplets at 3.6 and 4.0 ppm characteristic of terminal and allylic CH_2Cl groups in **1** and (**2** + **3**), respectively]. Experiments were performed to demonstrate that alteration of the dichlorobutene isomer ratio does not occur either in the gc or by prolonged exposure to $SbCl_3$, a likely reaction product. The reaction product from one of the chlorinations in CH_2Cl_2 was mixed at the 50% level with a solution of known dichlorobutene isomer ratio and analyzed by gc with no significant difference observed. This virtually eliminated the possibility of isomerization catalysis by an unidentified reaction product. Solutions of known isomer ratio were dissolved in $SbCl_3$ + CH_2Cl_2 solutions in proportions comparable to those encountered in the chlorination experiments, allowed to stand at room temperature for several hours, and analyzed by gc. No significant change in isomer ratio was observed.

Experimental Section

Solvents employed were of Spectrograde quality. CH_2Cl_2 was supplied by Fischer Scientific Co., $CHCl_3$ and CCl_4 by Matheson Coleman and Bell, as was 1,3-butadiene, instrument grade lecture bottle. $SbCl_5$ was supplied by Alpha Inorganic.

Karl Fischer reagent titration, employed to measure the amount of water in 1,3-butadiene and solvents, yielded the following: butadiene, <10 ppm; CH_2Cl_2, 39 ppm; CCl_4, 27 ppm; and $CHCl_3$, 330 ppm. Gc analysis was as follows: butadiene, 99.97%; CH_2Cl_2, 99.9%; CCl_4, 98.8%; and $CHCl_3$, 99.0% purity. The reaction system was maintained anhydrous by purging and blanketing with nitrogen having a water content of less than 0.001% by weight.

Conductivity data (Table V) clearly indicate that $SbCl_5$ was essentially anhydrous.

The dichlorobutene isomer equilibrium data[7] (Table IV) were obtained from the following starting mixtures: **1**, 0%; **2**, 5%; **3**, 95%; and from **1**, 95%; **2** and **3** combined 1%; impurities, mainly dichlorobutanes, 4%.

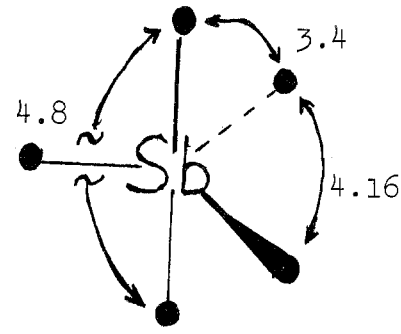

Figure 2. Approximate molecular dimensions of $SbCl_5$.

Registry No.—Chlorine, 7782-50-5; 1,3-butadiene, 106-99-0; antimony pentachloride, 7647-18-9; *cis*-1,4-dichlorobutene-2, 1476-11-5.

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Solvolysis of Xanthenyl and Fluorenyl Ion Pairs in 1,2-Dimethoxyethane

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An ostensibly routine attempt to prepare the xanthenylmethylamine derivative **4** from the corresponding amide **1** by hydride reduction in hot 1,2-dimethoxyethane (DME) led instead to an 83% yield of 9,9-dimethylxanthene (**2**),