isomeric adduct from the carbene addition to durene.

Decomposition in Naphthalene. In the manner of the foregoing experiment, 50 g of recrystallized naphthalene and 0.522 g of 1 gave rise to 1.26 g of white crystalline material, which showed three components by TLC.

The crude mixture was dissolved in a minimal mount of benzene and chromatographed on a column packed with 50 g of alumina (100–200 mesh). The column was eluted with benzene, and each fraction was examined by TLC after concentration, and ones of similar composition were combined. The first fractions amounted to 600 mg of naphthalene; the second fraction, 420 mg (58%), mp 195–198 °C, was identified by NMR (Table I) as **7-(1,4-diphenyl-1,2,3-triazol-5-yl)-2,3-benzonorcaradiene (11a)**. Two crystallizations from absolute ethanol gave an analytically pure sample: mp 203–204.5 °C; mass spectrum, *m/e* 361. Anal. ($C_{25}H_{19}N_3$) C, H, N.

The third fraction (240 mg, 41;), mp 192–196 °C, was assigned the structure **7-(1,4-diphenyl-1,2,3-triazol-5-yl)-3,4-benzocycloheptatriene (11b)**, based on the NMR spectrum (Table I). A portion of this material was purified on a 2-mm preparative silica TLC plate by elution with a benzene/ethyl acetate (20:1) mixture; **11b** was removed from the silica gel by extracting with ethyl acetate, and the extract was concentrated under aspirator vacuum, whereupon **11b** crystallized, mp 196–201 °C. Two recrystallizations from absolute ethanol gave an analytically pure sample: mp 201–202 °C; mass spectrum, *m/e* 361. Anal. ($C_{25}H_{19}N_3$) C, H, N.

A sample of **11a** was fused and kept at 210 °C for 15 min; on cooling, it was unchanged except for a tint of yellow. Heating at 210 °C for an additional 10 min brought about no change, but further heating caused darkening and evident decomposition.

Decomposition in Thiophene. Thermolysis of 0.522 g (0.002 mol) of 1 in 70 mL of freshly distilled thiophene gave a yellow solution, which was filtered to remove a small amount of 1,4-diphenyl-1,2,3-triazole-5-carboxaldehyde azine.[15] The excess thiophene was removed by vacuum distillation (0.1 mm) at room temperature, leaving a viscous yellow oil, which was triturated with three 25-mL portions of petroleum ether (bp 30–60 °C). The combined extracts were refrigerated, whereupon 405 mg (60%) of a white, crystalline solid, mp 177–185 °C, precipitated. On the basis of the NMR spectrum (Table I), the adduct was identified as **6-(1,4-diphenyl-1,2,3-triazol-5-yl)-2-thiabicyclo[3.1.0]hex-3-ene (12)**. The spectrum was unchanged when a solution of **12** in $CDCl_3$ was heated at 107 °C for 12 h in a sealed tube. Two recrystallizations from an ethanol/petroleum ether (bp 30–60 °C) mixture yielded analytically pure material, mp 191–192 °C. Anal. ($C_{19}H_{15}N_3S$) C, H, N, S.

Thermal Rearrangement of Norcaradiene (10a). A sealed tube containing 50 mg of analytically pure **10a** in $CDCl_3$ (1% Me_4Si) was placed in a vapor bath of refluxing isoamyl alcohol (bp 130 °C). At periodic intervals the tube was removed, cooled to room temperature, and examined spectroscopically (NMR). After heating at this temperature for 24 h, no subsequent changes were observed. On the basis of the ^1H NMR spectrum, the original solute had been isomerized entirely to 1,3,5,6-tetramethyl-2-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene (**19**): NMR ($CDCl_3$) δ 7.72 (m, 2 H), 7.30 (m, 8 H), 6.15 (s, 1 H), 2.30 (s, 2 H), 1.90 (s, 3 H), 1.75 (s, 3 H), 1.65 (s, 3 H), 1.61 (s, 3 H).

Registry No. **1**, 15764-89-3; **2**, 75918-84-2; **3a**, 87185-25-9; **3b**, 87185-27-1; **4a**, 87185-26-0; **4b**, 87185-28-2; **5a**, 87185-30-6; **5b**, 87185-29-3; **6**, 87185-31-7; **7**, 87185-32-8; **8**, 87185-33-9; **10a**, 87185-34-0; **10b**, 87185-35-1; **11a**, 87185-36-2; **11b**, 87185-37-3; **12**, 87185-38-4; **18**, 87185-39-5; **19**, 87189-84-2; 1,3,5-MeNCD, 87185-40-8; CHT, 544-25-2; 1-MeCHT, 3045-88-3; 3,4-CHT, 78968-78-2; 2,4-CHT, 71457-57-3; 1,4-CHT, 66729-58-6; *p*-cymene, 99-87-6; *p*-*tert*-betyltoluene, 98-51-1; *p*-diisopropylbenzene, 100-18-5; durene, 95-93-2; naphthalene, 91-20-3; thiophene, 110-02-1; *p*-di-*tert*-butylbenzene, 1012-72-2; (1,4-diphenyl-1*H*-1,2,3-triazol-5-yl)methylene, 63296-69-5; benzene, 71-43-2; toluene, 108-88-3; *o*-xylene, 95-47-6; *m*-xylene, 108-38-3; *p*-xylene, 106-42-3; mesitylene, 108-67-8; *p*-ethyltoluene, 622-96-8.

Involvement of Neighboring Chlorine in the Exchange Reactions of Iodine Monochloride and Vicinal Organic Iodochlorides

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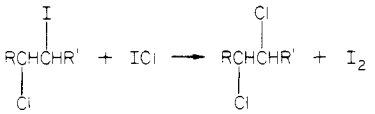
The reaction of vicinal organic iodochlorides and ICl in CCl_4 at 25 °C forms vicinal organic dichlorides and iodine. The rate law for this exchange reaction of ICl and 2-chloro-3-iodo-2,3-dimethylbutane is overall third order: second order in ICl and first order in iodochloride with a value of $k_3 = 7.2 \pm 0.9$ M^{-2} s^{-1}. Stereospecific exchange occurs in the reaction of ICl and *erythro*- and *threo*-2-chloro-3-iodobutane. Thus the erythro isomer forms only *meso*-2,3-dichlorobutane while the threo isomers form only the *dl* dichloride. Nonstereospecific exchange occurs in the reaction of ICl and *erythro*- and *threo*-1-chloro-2-iodo-1-phenylpropane. The data support a mechanism involving a cationic intermediate. In addition, the chlorine atom is involved in the reaction prior to the product-determining step.

Iodine monochloride (ICl) has been known for years to react with organic iodides to form an organic chloride and iodine.[1] We have found that a similar exchange reaction occurs between ICl and vicinal organic iodochlorides to form iodine and vicinal organic dichlorides according to the eq 1. In this paper, we present evidence that these



(1)

two exchange reactions are similar in that they have the same stoichiometry and follow the same rate law. However, in the reaction of vicinal organic iodochlorides, the chlorine atom is involved in the reaction prior to the product-determining step.

Table I. Rate Data for the Exchange Reaction of ICl and 2-Chloro-3-iodo-2,3-dimethylbutane in CCl_4 at 25 °C

(*vic*-iodochloride)$_0$, M	$(ICl)_0$, M	k_{app}, M^{-1} s^{-1}	k_3, M^{-2} s^{-1}
0.034 89	0.004 41	0.249 ± 0.003	7.14
0.034 89	0.001 60	0.201 ± 0.003	5.75
0.017 00	0.002 59	0.139 ± 0.001	8.17
0.017 44	0.001 60	0.123 ± 0.001	7.05
0.006 98	0.001 60	0.0549 ± 0.0004	7.87

[a] Average 7.2 ± 0.9.

(1) (a) Geuther, A. *Justus Liebigs Ann. Chem.* **1862**, *123*, 124. (b) Friedel, C. *Ibid.* **1865**, *135*, 206.

0022-3263/83/1948-4010$01.50/0

Table II. Stereochemistry of the Exchange Reaction of ICl with 2-Chloro-3-iodobutanes and 1-Chloro-2-iodo-1-phenylpropanes in CCl_4 at 25 °C

starting compd	config	concn, M	$(ICl)_0$, M	% erythro (meso) dichloride	% threo (*dl*) dichloride
$CH_3CHICHClCH_3$	erythro	0.059	0.14	100	0
		0.059	0.21	100	0
$CH_3CHICHClCH_3$	threo	0.059	0.12	0	100
		0.059	0.18	0	100
$C_6H_5CHClCHICH_3$	erythro	0.042	0.062	87	13
		0.042	0.12	89	11
$C_6H_5CHClCHICH_3$	threo	0.055	0.062	45	55
		0.055	0.12	50	50

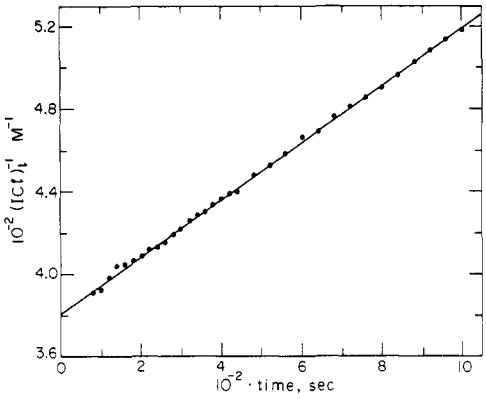
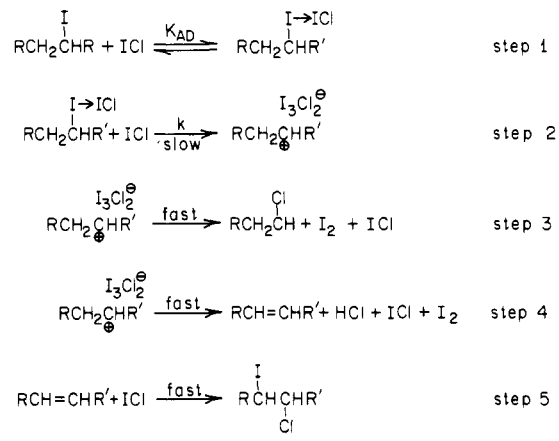


Figure 1. Experimental data for one typical run for ICl and 2-chloro-3-iodo-2,3-dimethylbutane.

Scheme I



Results

The rate of reaction of ICl and 2-chloro-3-iodo-2,3-dimethylbutane was determined at 25 °C in CCl_4. In all runs the organic iodochloride was present in excess. The change in concentration of ICl with time was determined directly from spectroscopic analysis performed at 462 and 518 nm. The experimental data fit a rate law that is second order in ICl. The experimental data for one typical run are shown in Figure 1. The values of the pseudo-second-order rate constant k_{app} are listed in Table I. Values of k_{app}/(iodochloride)$_0$ are relatively constant, giving an overall third-order rate constant, k_3, of 7.2 ± 0.9 M^{-2} s^{-1}. An overall third-order rate law, first order in iodochloride and second order in ICl, was established by Keefer and Andrews[2] for the reaction of ICl and a number of organic iodides.

The stereochemistries of the dichlorides formed by the reaction of ICl and the erythro and threo stereoisomers[3] of 2-chloro-3-iodobutanes and 1-chloro-2-iodo-1-phenylpropanes at 25 °C in CCl_4 are given in Table II. The dichlorides are formed with retention of configuration by the reaction of ICl and the 2-chloro-3-iodobutanes. In contrast, reaction of ICl and the 1-chloro-2-iodo-1-phenyl propanes forms mixtures of the two stereoisomers. The products of the reaction of ICl and 2-chloro-3-iodobutanes were analyzed by gas–liquid phase chromatography. Authentic samples of the products were prepared by the chlorination of *cis*- and *trans*-2-butene in CCl_4. This reaction is known to form the 2,3-dichlorobutanes in an antistereospecific manner.[5] The products of the reaction of ICl and the 1-chloro-2-iodo-1-phenylpropanes were analyzed by ^1H NMR. The use of ^1H NMR to distinguish between the erythro and threo stereoisomers of 1,2-dihalo-1-phenylpropanes is well established.[6]

Discussion

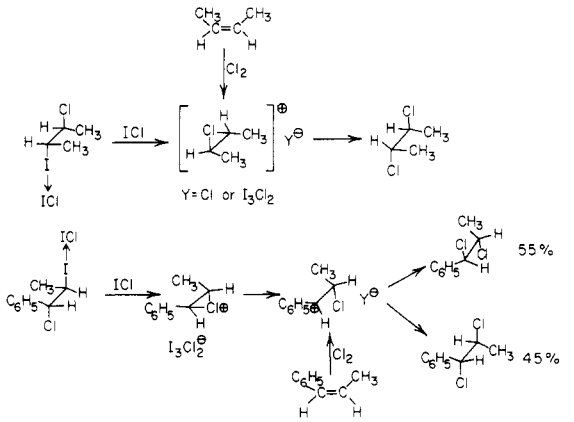
The mechanism of the exchange reaction between alkyl iodides and ICl is believed to occur by the ionic mechanism shown in Scheme I.[2,7] The first step of this mechanism is the reversible formation of a molecular complex between an alkyl iodide and ICl. The existence of such 1:1 molecular complexes between alkyl halides and I_2 are well documented.[8,9] The second and rate-determining step is the attack of ICl on the 1:1 molecular complex. This reaction generates a cationic intermediate that is the common precursor to both the normal exchange (step 3) and elimination–readdition reactions (steps 4 and 5). The tendency of the intermediate to react by one or all of steps 3–5 determines the overall stoichiometry of the process. Thus if the intermediate reacts by only step 3, the ratio $A = (ICl)_0 - (ICl)_t/(I_2)_t$ equals 1. If only step 4 and 5 are involved in product formation, A equals 2. Under the conditions of the kinetic experiments of the reaction of ICl and 2-chloro-3-iodo-2,3-dimethylbutane, A values calculated between various data points for each of the kinetic runs gave an A value of 1.0 ± 0.1. This indicates that normal exchange was occurring with not more than a 10% contribution from the elimination–readdition pathway.

Under conditions where $(RCH_2CHIR')_0 > (ICl)_0$[10] the rate law consistent with the mechanism is given by eq 2.

$$\frac{-d(ICl)_t}{dt} = \frac{kK_{AD}(RCH_2CHIR')_0(ICl)_t^2}{[1 + K_{AD}(RCH_2CHIR')_0]^2} = k_{app}(ICl)_t^2 \quad (2)$$

(2) Keefer, R. M.; Andrews, L. J. *J. Am. Chem. Soc.* **1953**, *75*, 543.
(3) The terms erythro and threo are defined as follows. Anti addition of a reagent to an (*E*)-alkene forms the erythro product. Anti addition of a reagent to a (*Z*)-alkene forms the threo product. The use of the terms pref and parf in place of erythro and threo has recently been suggested.[4]
(4) Carey, F. A.; Kuehne, M. E. *J. Org. Chem.* **1982**, *47*, 3811.
(5) Poutsma, M. L.; Katch, J. L. *J. Am. Chem. Soc.* **1971**, *89*, 6595.
(6) Schmid, G. H. *Can. J. Chem.* **1968**, *46*, 3415.
(7) Britten-Kelly, M. R.; Goosen, A.; Scheffer, A. *J. S. Afr. Chem. Inst.* **1975**, *28*, 224.
(8) Thiele, J.; Peter, W. *Ber.* **1905**, *38*, 2842.
(9) Keefer, R. M.; Andrews, L. J. *J. Am. Chem. Soc.* **1952**, *74*, 1891.
(10) $(X)_t$ denotes the total stoichiometric concentration of species X in solution at time t (seconds) in moles/liter.

Scheme II



If the value of $K_{AD}(RCH_2CHIR') \ll 1$, then the rate law becomes that shown in eq 3. Our data for the reaction

$$-d(ICl)_t/dt = k_3(RCH_2CHIR')_0(ICl)_t^2 \quad (3)$$

of ICl and 2-chloro-3-iodo-2,3-dimethylbutane are in accord with the rate law given by eq 3.

Our data agree well with the previous work of Keefer and Andrews,[2,11] who measured the rates of the reactions of ICl and a number of organic halides. For the reaction of benzyl iodide and benzyl bromide, the rate law in eq 3 is obeyed. In contrast, the values of $k_{app}/(\text{alkyl halide})_0$ for the reactions of isopropyl iodide and *tert*-butyl bromide decrease markedly with increasing $(\text{alkyl halide})_0$. Thus the reactions of these alkyl halides obey the rate law in eq 2. Our data suggests that the exchange reaction of ICl and 2-chloro-3-iodo-2,3-dimethylbutane occurs by the mechanism in Scheme I. Based on the rate law, the value of K_{AD}, the equilibrium constant for the formation of the molecular complex, is small.

The products of the reaction of ICl and the erythro and threo isomers of 2-chloro-3-iodobutane and 1-chloro-2-iodo-1-phenylpropane provide information about the stereochemistry of this exchange reaction. Stereospecific exchange occurs in the reaction of ICl and the 2-chloro-3-iodobutanes. The erythro (or threo) iodochloride forms only the meso (or *dl*) dichloride. This results suggests that the neighboring chlorine atom participates in the reaction to form a chloronium ion as shown in Scheme II. In this way, replacement of iodine by chlorine occurs with retention of configuration.

In the reaction of ICl and the 1-chloro-2-iodo-1-phenylpropanes, nonstereospecific exchange was found. Such a result can also be explained by neighboring chlorine participation prior to the product-determining step. But in this case, participation leads to migration of the chlorine atom from carbon 1 to 2 to form a highly unsymmetrical chloronium ion or weakly constrained carbonium ion intermediate as shown in Scheme II.

The proposed involvement of cationic intermediates with varying degrees of chloronium-ion-like character is strongly supported by comparisons with the corresponding additions of chlorine to the *E* and *Z* isomers of 2-butene[5] and 1-phenylpropene[12] in CCl_4. The antistereospecific addition of chlorine to the 2-butenes parallels the stereospecific exchange reaction of iodine monochloride with the 2-chloro-3-iodobutanes. Moreover, the addition of chlorine to (*Z*)-1-phenylpropene gives a product distribution identical within experimental error to that of the exchange reaction of *threo*-1-chloro-2-iodo-1-phenylpropane (55% threo, 45% erythro). Also the stereoselectivity observed in the addition of chlorine to (*E*)-1-phenylpropene (70% erythro adduct) again closely parallels that for the exchange reaction of *erythro*-1-chloro-2-iodo-1-phenylpropane (88% erythro adduct).

Our data support the view that neighboring chlorine participates in the exchange reaction of ICl and vicinal organic iodochloride prior to the product-determining step. However, our data do not support chlorine assistance in the breaking of the carbon–iodine bond in the rate-determining step. This is evident from a comparison of the rate of exchange of *tert*-butyl iodide and 2-chloro-3-iodo-2,3-dimethylbutane. Keefer and Andrews[11] found that "a solution made up to contain 0.160 M *tert*-butyl iodide and 4.77×10^{-3} M ICl produces the maximum quantity of I_2 within 2 min after its preparation". This reaction occurred too rapidly to permit Keefer and Andrews to study the reaction kinetics. Since the exchange reaction of 2-chloro-3-iodo-2,3-dimethylbutane can be easily measured by standard methods, it is clear that the chlorine atom has a rate-retarding effect. This is consistent with data of Winstein,[13] who found that chlorine retards rates of solvolysis by a factor of up to 10^{-3} when compared to hydrogen. Thus, in the exchange reaction of vicinal organic iodochlorides, chlorine participation lags behind carbon–iodine bond breaking in the rate-determining transition state.

In summary, the reaction of ICl and organic vicinal iodochlorides occurs by the same ionic mechanism as simple organic halides. The added feature of the reaction of organic vicinal iodochlorides is participation by chlorine prior to the product-determining step.

Experimental Section

All boiling and melting points are uncorrected. GLC analysis was carried out by using a Varian Aerograph Series 2740 analytical instrument equipped with an FID. Proton magnetic resonance spectra were recorded on a Varian T-60 or HA-100 spectrometer in $CDCl_3$ containing $(CH_3)_4Si$ as an internal standard. ACS grade CCl_4, CH_2Cl_2, and CH_3CN were used without further purification. (*E*)- and (*Z*)-1-phenylpropene, (*E*)- and (*Z*)-2-butene, and 2,3-dimethyl-2-butene were obtained commercially and used without further purification. Iodine monochloride was purified by fractional crystallization from the melt, discarding the remaining liquid portion.[14]

***erythro*-1-Chloro-2-iodo-1-phenylpropane** was prepared by adding with stirring a solution of 0.445 g (1.7 mmol) of *erythro*-2-iodo-1-phenyl-1-propanol in 2 mL of CH_2Cl_2 to a cold (ice bath) solution of 0.50 g (4.2 mmol) of thionyl chloride in 7 mL of CH_2Cl_2. After the addition, the reaction mixture was stirred for 1 h at ice temperature and for 4 h at room temperature. The reaction mixture was transferred to a separatory funnel and washed successively with 5% aqueous $NaHCO_3$, 5% aqueous $NaHSO_3$, and saturated NaCl solutions. The CH_2Cl_2 layer was dried over anhydrous K_2CO_3 and filtered, and solvent was removed at reduced pressure. The crude product was recrystallized from pentane to give the product: 0.4 g (1.4 mmol, 83% yield); mp 49.5–50.5 °C; NMR δ 2.12 (d, J = 6.5 Hz, 3 H), 4.50 (dq, J = 6.5, 9.0 Hz, 1 H), 4.99 (d, J = 9.0 Hz, 1 H), 7.31 (s, 5 H). Anal. Calcd for $C_9H_{10}ICl$: C, 38.53; H, 3.59. Found: C, 38.62; H, 3.65.

***erythro*-2-Iodo-1-phenyl-1-propanol** was prepared by adding 17.0 g (0.0670 mol) of finely ground iodine in several portions over 5–10 min to a vigorous stirred solution of 7.5 g (0.0670 mol) of (*E*)-1-phenylpropene and 9.0 g (0.0416 mol) of yellow mercuric oxide in 100 mL of 80% aqueous acetonitrile at room temperature. After an additional 10–15 min the reaction mixture was filtered by suction to remove the red mercuric iodide by using a small amount of acetonitrile as a rinse solution. The filtrate was poured into a separatory funnel containing a fivefold excess of water and

(11) Keefer, R. M.; Andrews, L. J. *J. Am. Chem. Soc.* **1954**, *76*, 253.
(12) Fahey, R. C.; Schubert, C. *J. Am. Chem. Soc.* **1965**, *87*, 5172.
(13) Winstein, S.; Grunuwald, E. *J. Am. Chem. Soc.* **1948**, *70*, 828.
(14) Calder, G. V.; Giauque, W. F. *J. Phys. Chem.* **1965**, *69*, 2443.

a pinch of $NaHSO_3$. The contents were shaken, and the oil layer was removed. The oil was dissolved in ether, clarified over Norit, and filtered, and the ether was removed at reduced pressure to give 15.4 g (0.0586 mol, 92% yield) of a clear oil. The oil was used without further purification to prepare *erythro*-1-chloro-2-iodo-1-phenylpropane: NMR δ 1.72 (d, J = 7 Hz, 3 H), 4.45 (dq, J = 4.0, 7.0 Hz, 1 H), 4.86 (d, J = 4.40 Hz, 1 H), 7.29 (s, 5 H); irradiation of the δ 1.72 doublet collapsed the δ 4.45 (dq) into a doublet (J = 4.0 Hz).

***threo*-1-Chloro-2-iodo-1-phenylpropane** was prepared in 78% yield by the same method as the erythro isomer but by using *threo*-2-iodo-1-phenyl-1-propanol: bp 92 °C (0.3 mmHg); NMR δ 1.87 (d, J = 7.0 Hz, 3 H), 4.56 (dq, J = 6.0, 7.0 Hz, 1 H), 4.96 (d, J = 6.0 Hz, 1 H), 7.33 (s, 5 H); irradiation of the δ 1.87 doublet collapsed the δ 4.56 multiplet into a doublet (J = 6.0 Hz). Anal. Calcd for $C_9H_{10}ICl$: C, 38.53; H, 3.59. Found: C, 38.46; H, 3.75.

***threo*-2-Iodo-1-phenyl-1-propanol** was prepared in 78% yield by the same method as the erythro isomer but by using (*Z*)-1-phenylpropene as the starting alkene. Recrystallization from pentane gave a white solid: mp 37–38 °C; NMR δ 1.78 (d, J = 6.5 Hz, 3 H), 4.37 (m, 2 H), 7.31 (s, 5 H); irradiation of the δ 1.78 doublet formed a singlet at δ 4.37 indicating that the two methine protons have equivalent chemical shifts. Anal. Calcd for $C_9H_{11}IO$: C, 41.26; H, 4.20. Found: C, 41.01; H, 4.32.

***erythro*-2-Chloro-3-iodobutane** was prepared by adding a solution of 2.54 g (15.6 mmol) of ICl in 10 mL of CH_2Cl_2 dropwise to a vigorously stirred solution of 1.14 g (16.5 mmol) of (*E*)-2-butene in 25 mL of CH_2Cl_2. The reaction was carried out at room temperature, and the reaction vessel was shielded from light by covering it with aluminum foil. After several minutes of stirring, the reaction mixture was transferred to a separatory funnel and washed with 5% aqueous $NaHSO_3$ solution, water, and saturated NaCl solution. The CH_2Cl_2 layer was dried over anhydrous Na_2CO_3 and filtered, and CH_2Cl_2 was removed at reduced pressure. Distillation gave the product: 2.20 g (10.1 mmol, 65% yield); bp 35–37 °C (5 mmHg) [lit.[15] bp 34.8–35.3 °C (5 mmHg)]; NMR δ 1.66 (d, J = 6.5 Hz, 3 H), 1.98 (d, J = 6.5 Hz, 3 H), 4.03 (qu, J = 6.54 Hz, 1 H), 4.23 (qu, J = 6.5 Hz, 1 H).

***threo*-2-Chloro-3-iodobutane** was prepared in 73% yield by the same method as the erythro isomer but by using (*Z*)-2-butene as the starting alkene: bp 35–37 °C (5 mmHg) [lit.[15] bp 33.2–33.5 °C (4 mmHg)]; NMR δ 1.59 (d, J = 6.5 Hz, 3 H), 1.89 (d, J = 6.5 Hz, 3 H), 4.04 (dq, J = 3.0, 6.5 Hz, 1 H), 4.43 (dq, J = 3.0, 6.5 Hz, 1 H).

2-Chloro-3-iodo-2,3-dimethylbutane was prepared by the same method as *erythro*-2-chloro-3-iodobutane but by using 2,3-dimethyl-2-butene as the starting alkene: bp 66–65 °C dec; NMR δ 2.13 (s, 6 H), 1.89 (s, 6 H). Anal. Calcd for $C_6H_{12}ICl$: C, 29.24; H, 4.86. Found: C, 29.35; H, 4.95.

Product Analysis of Exchange Reaction. The following general procedure was used in all cases. A solution of ICl in CCl_4 (0.070–021 M) was added to a solution of the organic vicinyl iodochloride also in CCl_4 (0.042–0.059 M). The reaction mixture was protected from light and placed in a thermostated bath at 25 °C for 20 h. The reaction mixture was then washed with a 5% aqueous $NaHSO_3$ solution, water, and a saturated NaCl solution. The CCl_4 layer was dried over anhydrous Na_2CO_3 and filtered, and CCl_4 was removed at reduced pressure. The products of the reaction of ICl and the 2-chloro-3-iodobutanes were analyzed by GLC on a 2 m × 6 mm 30% Carbowax 20M on Chromosorb P (60/80 mesh) column. The retention times at a flow rate of 96 mL/min and 56 °C are as follows: *meso*-2,3-dichlorobutane, 4.5 min; *dl*-2,3-dichlorobutane, 5.0 min. The products of the reaction of ICl and the 1-chloro-2-iodo-1-phenylpropanes were analyzed by NMR. The methyl protons of the threo isomer of 1,2-dichloro-1-phenylpropane are upfield relative to those of the erythro isomer.[6]

Kinetics of the Exchange Reaction of ICl and 2-Chloro-3-iodo-2,3-dimethylbutane. Separate solutions of ICl in CCl_4 and 2-chloro-3-iodo-2,3-dimethylbutane in CCl_4 were equilibrated at 25 °C in a thermostated bath. Equal volumes of the two preequilibrated solutions were rapidly mixed, and a sample was transferred immediately to a 1.0-cm quartz UV cell placed in the thermostated cell compartment of the spectrometer. The reactions were followed to about 25% completion. The above procedure was then repeated in order to obtain absorbance–time curves at the two wavelengths, 462 and 518 nm, for each set of solutions. Values of absorbances of the solution at zero reaction time were obtained by extrapolation of the absorbance–time curves to zero time. The values of $(ICl)_t$ were calculated according to eq 4. Published values[16] were used for $\epsilon_{I_2}^{518}$ and $\epsilon_{I_2}^{462}$.

$$(ICl)_t = (ICl)_0[Abs_t^{518}\cdot\epsilon_{I_2}^{462} - Abs_t^{462}\cdot\epsilon_{I_2}^{518}]/[Abs_0^{518}\cdot\epsilon_{I_2}^{462} - Abs_0^{462}\cdot\epsilon_{I_2}^{518}] \quad (4)$$

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Registry No. ICl, 7790-99-0; *erythro*-$CH_3CHICHClCH_3$, 39160-00-4; *threo*-$CH_3CHICHClCH_3$, 39159-99-4; *erythro*-$C_6H_5CHClCHICH_3$, 87261-44-7; *threo*-$C_6H_5CHClCHICH_3$, 87261-45-8; 2-chloro-3-iodo-2,3-dimethylbutane, 87261-43-6; *erythro*-2-iodo-1-phenyl-1-propanol, 87261-46-9; *threo*-2-iodo-1-phenyl-1-propanol, 87261-47-0.

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Configurational Stability of a Cyclopropyl Grignard Reagent Containing a Metalated 2-Hydroxymethyl Group[1]

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Mixtures of *cis*- and *trans*-2-bromo-3-(hydroxymethyl)-1,1-dimethylcyclopropane were treated with methylmagnesium bromide to metalate the hydroxyl groups and then with magnesium to form metalated Grignard reagents. The compositions of products obtained upon hydrolysis with D_2O indicated that the metalated Grignard reagents in refluxing diethyl ether did not undergo signficant cis–trans isomerization. This work provides an example of the configurational stability of a cyclopropyl Grignard reagent with a secondary rather than a tertiary α-carbon. Because of these results with cyclopropyl Grignard reagents containing a metalated hydroxyl group, prior observations on additions of allylic Grignard reagents to 3-(hydroxymethyl)cyclopropenes only of products resulting from a cis relationship of magnesium and hydroxymethyl must be due to the stereochemistry of the addition process rather than to a subsequent isomerization.

In an earlier study, we investigated reactions of allylic Grignard reagents (in excess) with 3-(hydroxymethyl)-cyclopropenes (1).[2] That study was part of a program to determine the stereochemical relationships between the

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