The Stereochemistry of Addition Reactions of Allenes. IV. Stereospecificity of Iodination of 2,3-Pentadiene[1-3]

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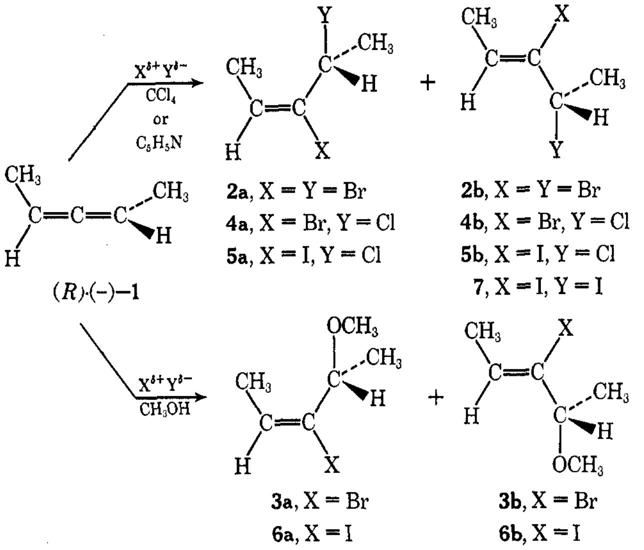
Iodine, iodine bromide, and iodine chloride react with (*R*)-(−)-2,3-pentadiene in methanol to give (−)-*trans*-3-iodo-(4*S*)-methoxy-2-pentene as the major product. The optical purity of the product was found to vary with the nature of the iodinating agent in the order ICl > IBr > I_2. The origin of the apparent low stereospecificity of addition with I_2 in methanol has been traced to the presence of iodide ion produced in the reaction. Optically active 2,3-pentadiene was observed to racemize extensively in the presence of I_2–I^- in diglyme–carbon tetrachloride mixtures. Racemization is attributed to a reaction sequence involving addition of molecular iodine to give *trans*-3,4-diiodo-2-pentene followed by competitive E2 and SN2 reactions of the adduct with I^-. The racemization accompanying SN2 displacement manifests itself in the recovery of partially racemized 2,3-pentadiene and isolation of *trans*-3-iodo-4-methoxy-2-pentene of low optical purity.

There are several aspects of interest concerning electrophilic addition reactions of allenes. The orientation of addition of unsymmetrical reagents indicates the selectivity of the attacking electrophile for attachment to the central or terminal allenic carbon. The monoadducts formed may be cis and trans isomers, depending on the structure of the allene and the electrophile; the isomer distribution reflects the control of the substituents at one double bond on the direction of approach of the electrophile to the other double bond. Also, the stereochemistry of addition to the reacting double bond is important in a study of the reaction mechanism since it provides information as to the possible types of intermediates involved.

We have recently investigated the orientation and stereochemistry of bromine addition to 2,3-pentadiene **1** and have found that a mixture of *cis*- and *trans*-3,4-dibromo-2-pentene, **2a** and **2b**, is formed in carbon tetrachloride. In methanol a mixture of *cis*- and *trans*-3-bromo-4-methoxy-2-pentene, **3a** and **3b**, is formed.[4] The orientation of bromine addition to **1** is therefore similar to that observed with allene[5] and amounts to the attachment of the electrophile to the central carbon and the nucleophile (Br^- or hydroxylic solvent) to the terminal carbon. The major adduct is the trans isomer (Scheme I).

SCHEME I



We have also observed that reaction of bromine with optically active **1** gives optically active adducts **2** in carbon tetrachloride and **3** in methanol.[4] From the configurational relationships between the dissymmetric allene and the asymmetric adducts, the stereochemistry of addition was determined as trans. Similar results were obtained for the reaction of iodine with (−)-**1** in methanol and imply that the adducts in both bromine and iodine addition reactions are formed from dissymmetric reaction intermediates such as bridged bromonium and iodonium ions **8**.

The objectives of the present work were to extend our investigation of electrophilic halogen addition to include other halogens. We report at this time further results on the addition of bromine, bromine chloride, iodine, iodine bromide, and iodine chloride to optically active and inactive 2,3-pentadiene. The work is pertinent to the overall stereospecificity of addition and indicates that, in iodination, the optical purity of the adducts obtained depends significantly on the nature of the iodinating agent.

Results and Discussion

Bromination.—Bromine chloride in carbon tetrachloride reacted rapidly with 1 equiv of **1** at 5° to give 3-bromo-4-chloro-2-pentene **4** as a 28:72 cis–trans mixture. Small amounts (<16%) of the dibromo adduct **2** were also obtained. Under similar conditions, molecular bromine gave a 20:80 cis–trans mixture of **2a** and **2b**. In methanol, both bromine and bromine chloride reacted with **1** to give 3-bromo-4-methoxy-2-pentene **3** as the major product (85%) formed as a 20:80 cis–trans mixture. The minor products (15%) were the corresponding dihalo adducts **2** or **4**. Optically active (*R*)-(−)-**1** gave optically active adducts with bromine and bromine chloride in both carbon tetrachloride and methanol. The observed rotation of the bromo ether **3** was found to be the same, within experimental error, whether prepared from bromine in methanol or bromine chloride in methanol (Table I). We therefore conclude that the stereospecificity of reaction to give **3** is the same for the two electrophiles, Br_2 and BrCl.

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[2] Presented in part at the 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969.

[3] Part III: L. R. Byrd and M. C. Caserio, *J. Amer. Chem. Soc.*, **92**, 5422 (1970).

[4] W. L. Waters, W. S. Linn, and M. C. Caserio, *ibid.*, **90**, 6741 (1968).

[5] H. G. Peer, *Recl. Trav. Chim. Pays-Bas*, **81**, 113 (1962).

TABLE I

OPTICAL ROTATION DATA FOR HALOGENATION OF 2,3-PENTADIENE IN METHANOL

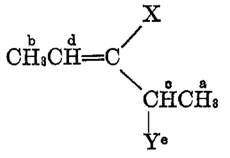
		Halo ether adducts[a]		
1, $[\alpha]_D$	Halogen	cis, %	trans, %	$[\alpha]_D$[b]
−19.8	Br_2	20	80	−11.8
−19.8	BrCl	28	72	−11.1
−15.9	I_2	6	94	−4.1
−19.8	I_2	6	94	−5.5
−19.8	IBr	6	94	−7.8
−19.8	ICl	6	94	−13.4
−19.8	ICl	6	94	−12.5

[a] **3** or **6**. [b] Optical rotation data are corrected for the rotations due to any dihalides **2**, **4**, or **5** present.

Iodination.—Iodine and iodine bromide reacted over a period of several hours with active and inactive **1** in methanol solution to give 6% *cis-* and 94% *trans*-3-iodo-4-methoxy-2-pentene, **6a** and **6b**, respectively. No dihalo adducts were detected in the product mixtures. In contrast, iodine monochloride gave a 6:94 cis–trans mixture of **6** together with 20% *trans*-3-iodo-4-chloro-2-pentene, **5b**. Addition of ICl to **1** in carbon tetrachloride did not proceed cleanly but gave a complex mixture of products that could not be identified satisfactorily. In pyridine, however, ICl reacted smoothly to give the monoadducts, **5a** and **5b**, as the sole products in the ratio of 15:85. The nmr spectral parameters of the adducts prepared in this work are summarized in Table II.

TABLE II

PROTON MAGNETIC RESONANCE DATA FOR ADDUCTS OF 2,3-PENTADIENE

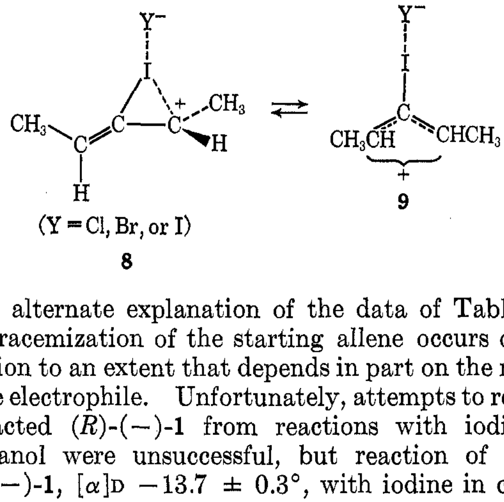


Compd[f]	X	Y	δ_a[a]	δ_b[b]	δ_c[c]	δ_d[d]	δ_e[e]
2a	Br	Br	1.77	1.79	5.12	6.00	
2b	Br	Br	1.80	1.84	4.79	6.22	
3a	Br	OCH_3	1.19	1.72	4.05	6.05	3.14
3b	Br	OCH_3	1.21	1.75	3.62	5.95	3.13
4a	Br	Cl	1.60	1.75	5.00	6.00	
4b	Br	Cl	1.65	1.76	4.65	6.17	
5a	I	Cl	1.49	1.71	4.3	6.0	
5b	I	Cl	1.57	1.74	4.33	6.01	
6a	I	OCH_3	1.17	1.75	3.52	6.43	3.20
6b	I	OCH_3	1.22	1.79	3.31	5.95	3.18
7	I	I	1.73	2.00	5.05	6.18	

[a] (d, 3, J = 6.5 Hz). [b] (d, 3, J = 6 Hz). [c] (m, 1). [d] (m, 1). [e] Y = OCH_3 (s, 3). [f] In CCl_4; chemical shifts in parts per million downfield from internal TMS.

Optically active adducts were obtained from (R)-(−)-**1** and I_2, IBr, and ICl in both methanol and carbon tetrachloride or pyridine. However, the observed rotations of the iodo ether obtained in methanol solution varied significantly with the nature of the iodinating agent (Table I). The data show that the optical rotation and hence optical purity of **6** was greatest when prepared from ICl and least when prepared from I_2. This observation prompted us to investigate the reaction of molecular iodine with **1** in more detail in order to determine the possible cause for the apparent low stereospecificity of addition in methanol.

Racemization Mechanisms.—The iodo ether **6** was found to be optically stable in the presence of excess iodine in methanol, which rules out the possibility of racemization of the product under the reaction conditions. Loss in optical purity must therefore occur prior to the product-forming step. One possible explanation for the variation in the observed rotations of **6** with the iodinating agent is that the stability of the dissymmetric iodonium ion intermediate **8**, which is presumably formed during the reaction, depends on the nature of the associated anion, I^-, Br^-, or Cl^-. Assuming that the anion is not completely dissociated from the cation in **8**, then the nature of this anion might well affect the ease of interconversion of **8** with its symmetrical allylic counterpart **9**. Any product derived from the reaction of **9** with solvent would be expected to be racemic. Precedent for this may be found in the oxymercuration of dissymmetric allenes where the stereospecificity of reaction has been found to vary widely with the nature of the ligand on the mercury electrophile.[6,7] An argument against this, however, is the observation that bromine and bromine chloride show no sensible difference in stereospecificity of their respective reactions with **1** in methanol (Table I). It seems unlikely that the stability of iodonium ions would be dependent on the counter anion, whereas the structurally related bromonium ion would be insensitive to these same anions.



(Y = Cl, Br, or I)

8

9

An alternate explanation of the data of Table I is that racemization of the starting allene occurs during reaction to an extent that depends in part on the nature of the electrophile. Unfortunately, attempts to recover unreacted (R)-(−)-**1** from reactions with iodine in methanol were unsuccessful, but reaction of excess (R)-(−)-**1**, $[\alpha]_D$ −13.7 ± 0.3°, with iodine in carbon tetrachloride led to the recovery of **1** having $[\alpha]_D$ −12.1 ± 0.7°. This represents 12 ± 7% loss in specific rotation over a reaction period of 1.33 hr. In a related experiment, (R)-(−)-**1**, $[\alpha]_D$ −10.7 ± 0.1°, was reacted with iodine in a 3:4 mixture of diglyme and carbon tetrachloride and, when 50% of the allene had been consumed, the remainder was recovered by distillation and found to have $[\alpha]_D$ −10.9 ± 1.0°. We therefore conclude that **1** is not significantly racemized by molecular iodine under the reaction conditions employed.

The product of addition of iodine to **1** in CCl_4 was a moderately stable light brown oil that was identified from its nmr spectrum (Table II) and from its conversion to **6b** on treatment with silver tetrafluoroborate in

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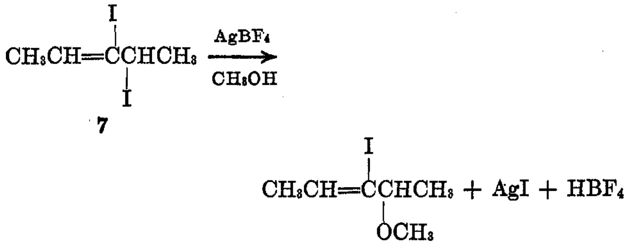
(6) R. D. Bach, *J. Amer. Chem. Soc.*, **91**, 1771 (1969); *Tetrahedron Lett.*, 5841 (1968).

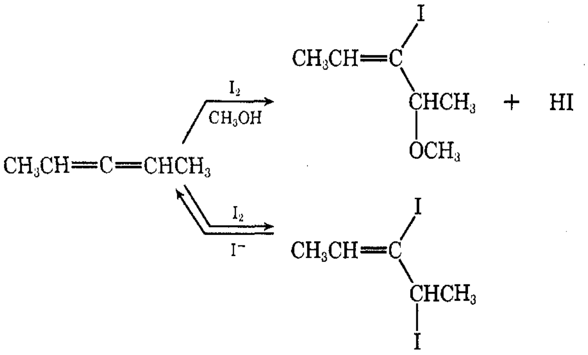
(7) W. S. Linn, W. L. Waters, and M. C. Caserio, *J. Amer. Chem. Soc.*, **92**, 4018 (1970).

methanol as *trans*-3,4-diiodo-2-pentene (**7**). No diiodide formation was detected in the reaction of **1** with iodine in methanol, which is not surprising since the adduct may be expected to be formed reversibly owing to the presence of iodide ions in the reaction mixture (eq 1). Accordingly, treatment of **7** with sodium iodide in a 1:1 mixture of carbon tetrachloride and diglyme led to immediate formation of iodine and 2,3-pentadiene. On standing for long periods of time (3–50 hr), this reaction mixture generated small amounts (2–3%) of 1,3-pentadiene. Since 1,3-pentadiene was not observed until long after the reaction of **7** with iodide was complete, we conclude that its formation is unrelated to the elimination reaction of interest.



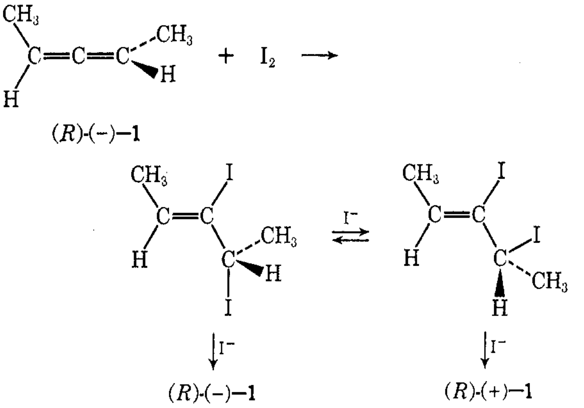
7

6b



(1)

To test the possibility that racemization of **1** might occur by the reversible addition of iodine in the presence of iodide ions, (*R*)-(−)-**1** having $[\alpha]_D$ $-10.7 \pm 0.1°$ was allowed to react with iodine in a 1:1 mixture of diglyme and carbon tetrachloride which was saturated with sodium iodide. The diglyme was necessary to solubilize the sodium iodide. The allene was recovered after 50% conversion to **7** and found to have $[\alpha]_D$ $-6.54 \pm 0.5°$ showing that the presence of iodide ion produced some 39% racemization of **1** within 1.33 hr. Although this result might be interpreted to mean that the iodide-induced elimination of **7** is not completely stereospecific, evidence in support of stereospecific elimination of vicinal dihalides with halide ions is very strong.[8,9] For this reason it seems doubtful that the iodine–iodide induced racemization of **1** stems from nonstereospecific elimination of **7**. A likely explanation for the observed racemization of **1** is shown in the reaction sequence of eq 2. The initial addition of iodine to give **7** and its subsequent E2 elimination to **1** are visualized as stereospecific processes which appear to be nonstereospecific because of a competing SN2 reaction of **7** with iodide ion that leads to the racemization of **7**.

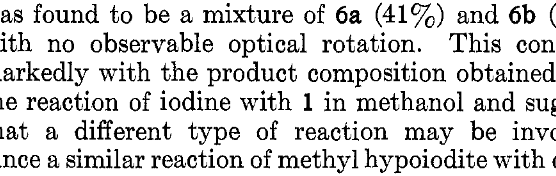


(2)

Conclusions

The observation that the optical purity of the iodo ether **6** varies with the nature of the iodinating agent used in its preparation from **1** can be understood in terms of the relative nucleophilicities of the product ions I⁻, Br⁻, and Cl⁻. In the case of reaction with ICl in methanol, both the iodo ether **6** and the iodochloro adduct **5** are formed *irreversibly* since chloride ion is ineffective in promoting elimination of **5**. Racemization of **1** directly or indirectly by reversible halogen addition is therefore precluded and the optical purity of the iodoether obtained is relatively high. With molecular iodine the iodo ether adduct **6** is formed irreversibly, but the diiodide **7** is formed rapidly and reversibly and is probably racemized to a significant extent by iodide ions in a straightforward displacement reaction. The net result of this is the formation of **6** of low optical purity. Iodine bromide, as expected, represents an intermediate situation since the nucleophilicity of Br⁻ toward halogen and carbon is less than that of I⁻ but greater than that of Cl⁻.

In order to eliminate the attendant racemization by iodide ions in the reaction of **1** with iodine in methanol, addition of methyl hypoiodite to (*R*)-(−)-**1** was attempted (eq 3). The electrophile was prepared as a solution in methanol by the reaction of iodine with silver tetrafluoroborate in methanol. However, the adduct obtained from the reaction of methyl hypoiodite with **1** was found to be a mixture of **6a** (41%) and **6b** (59%) with no observable optical rotation. This contrasts markedly with the product composition obtained from the reaction of iodine with **1** in methanol and suggests that a different type of reaction may be involved. Since a similar reaction of methyl hypoiodite with cyclohexene gave methoxycyclohexane as the major reaction product (60%), the incursion of a free-radical process is strongly implicated even though the reactions were carried out at low temperatures in the dark. In view of this, the results obtained with methyl hypoiodite and **1** cannot be related with any reliability to the comparable reactions of either methanolic iodine, iodine bromide, or iodine chloride with 2,3-pentadiene.



(3)

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[8] D. V. Banthorpe, "Elimination Reactions," E. D. Hughes, Ed., Elsevier, New York, N. Y., 1963.

[9] E. Baciocchi and A. Schiroli, *J. Chem. Soc., B*, 554 (1969).

Since we were unable to show that the optical purity of **6** could be increased if it were prepared from **1** and methanolic iodine in the *absence* of iodide ions, the effect of *added* sodium iodide was studied. Starting with equimolar amounts of iodine and (+)-**1** of rotation $[\alpha]\mathrm{D}$ +23.6° (*c* 75, ether), the iodo ethers **6a** and **6b** obtained in pure methanol had $[\alpha]\mathrm{D}$ +6.3° (*c* 10, ether); in contrast, the iodo ethers obtained in methanol containing a fourfold excess of sodium iodide had *no observable rotation.* This result adds further support to the plausibility of eq 1 and 2 as routes for the racemization of **1**, **6**, and **7**.

Experimental Section

Iodine monochloride (Eastman Kodak) was distilled before use and had bp 97°. Iodine bromide was prepared from molecular iodine and bromine and was obtained as dark brown crystals having mp 40°. Solutions of bromine chloride were prepared by passing chlorine gas into cooled methanol or carbon tetrachloride; 1 equiv of bromine was then added to the solution.[5] The addition of halogens to 2,3-pentadiene in methanol or carbon tetrachloride were carried out as described previously,[4] and the products were analyzed by nmr and glpc. In pyridine (25 ml) equimolar amounts of iodine monochloride and **1** (10 mmol) were stirred at room temperature in the dark for 14 hr, ether (30 ml) was added, and the solution was then washed repeatedly with water followed by extraction with dilute hydrochloric acid. The ether extract was dried, filtered, and evaporated, and the residue analyzed by nmr and glpc.

3,4-Diiodo-2-pentene was prepared by the addition of 1.12 g (16.4 mmol) of **1** as a 40% solution in ether to a solution of 4.17 g (16.4 mmol) of iodine in 100 ml of carbon tetrachloride. The mixture was stirred and maintained at −40° in the dark for 5.5 hr. Unreacted iodine was destroyed with aqueous sodium thiosulfate; the solvents were removed at reduced pressure from the dried organic extract. The nmr spectrum of the crude product was consistent with the structure assigned as *trans*-3,4-diiodo-2-pentene, **7** (Table II). Addition of a slight excess of silver tetrafluoroborate in methanol to **7** gave an immediate precipitate of silver iodide. After neutralization with sodium carbonate the mixture was filtered and the filtrate evaporated. The nmr spectrum of the residue in carbon tetrachloride was identical with that of a known sample of *trans*-3-iodo-4-methoxy-2-pentene, **6b** (Table II).

Optical rotations of the halo ethers **3** and **6** obtained from the addition of halogens to (*R*)-(−)-**1** in methanol solution were corrected for the rotations due to dihalo adducts present in the reaction mixtures. Corrections were necessary only in the case of bromine, bromine chloride, and iodine chloride addition. The assumption was made that the specific rotations of the dihalo adducts were the same when obtained in methanol as in carbon tetrachloride or pyridine.

Racemization of (−)-2,3-Pentadiene.—Reaction of iodine with **1**, $[\alpha]^{25}\mathrm{D}$ −13.7° ± 0.3 (ether), was carried out as described above except that aqueous sodium thiosulfate was added when half of **1** had been consumed. The unreacted allene was recovered from the organic extract by fractional distillation and had $[\alpha]^{25}\mathrm{D}$ −12.1 ± 0.7° (ether). A similar reaction of **1**, $[\alpha]^{25}\mathrm{D}$ −10.7 ± 0.1° (ether), in a mixture of diglyme (3 ml) and carbon tetrachloride (4 ml) led to the recovery of unreacted **1** having $[\alpha]\mathrm{D}$ −10.9 ± 1.0° (ether, CCl_4). Iodine (16.6 mmol) and sodium iodide (1.86 mmol) in 4 ml of diglyme and 4 ml of carbon tetrachloride were added to 1.13 g (16.6 mmol) of **1**, $[\alpha]\mathrm{D}$ −10.7 ± 0.10° (ether), as a 40% solution in ether and the mixture stirred at −42° for 1.33 hr in the dark. Excess iodine was destroyed as before and the unreacted allene recovered by distillation. The specific rotation of recovered **1** was $[\alpha]^{25}\mathrm{D}$ −6.54 ± 0.5° (ether). No 1,3-pentadiene was detected.

2,3-Pentadiene from 3,4-Diiodo-2-pentene.—To 2.5 g (8.3 mmol) of **7** in 1.4 ml of carbon tetrachloride was added 0.11 g (0.7 mmol) of sodium iodide in 1.5 ml of diglyme. The reaction mixture was protected from light throughout the experiment. After 3 hr the iodine was removed by extraction with aqueous sodium thiosulfate, and the organic layer was analyzed by glpc. The major product was 2,3-pentadiene contaminated with up to 3% of 1,3-pentadiene. Analysis of the reaction mixture by glpc immediately following addition of sodium iodide showed 2,3-pentadiene as the only volatile product. On standing for 3 hr or longer, small amounts of 1,3-pentadiene were detected.

Addition of Methyl Hypoiodite to 2,3-Pentadiene.—To 3.26 g (4.8 mmol) of (*R*)-(−)-**1** as a 50% solution in ether, $[\alpha]^{25}\mathrm{D}$ −8.43 ± 0.20°, was added 9.35 g (4.8 mmol) of silver tetrafluoroborate, 4.5 g (4.8 mmol) of sodium carbonate, and 12.19 g (4.8 mmol) of iodine in 50 ml of methanol. After stirring for 18 hr in the dark the reaction was quenched with aqueous sodium thiosulfate and the organic layer repeatedly washed with water, dried, and evaporated. The product had $[\alpha]\mathrm{D}$ 0 ± 1° (CCl_4), and was identified by nmr as a 41:59 mixture of **6a** and **6b**.

Addition of Methyl Hypoiodite to Cyclohexene.[10]—To 3.52 g (9.1 mmol) of silver tetrafluoroborate and 2.3 g (9.1 mmol) of iodine in 75 ml of methanol were added 1.5 g (9.1 mmol) of cyclohexene. The mixture was stirred for 0.5 hr in the dark in the presence of 2.5 g (25 mmol) of calcium carbonate. The product mixture was extracted with ether and water. The ether extract was dried and evaporated and the residue analyzed by glpc and nmr. The products were identified as 60% methoxycyclohexane [(singlet 3.34 ppm, complex 3.0 ppm, complex region 0.8–2.2 ppm downfield from TMS) (CCl_4)] and 35% *trans*-2-iodo-1-methoxycyclohexane [(quartet 4.1 ppm, singlet 3.34 ppm, quartet 3.18 ppm, and complex region 0.8–2.4 ppm, all downfield from TMS) (CCl_4)].

Registry No.—(*R*)-(−)-**1**, 20431-56-5; **2a**, 26889-28-1; **2b**, 26889-29-2; **3a**, 26889-30-5; **3b**, 26889-31-6; **4a**, 26889-32-7; **4b**, 26889-33-8; **5a**, 26889-34-9; **5b**, 26889-35-0; **6a**, 26889-36-1; **6b**, 26889-37-2; **7**, 26889-38-3.

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[10] L. Birckenbach and J. Goubeau, *Ber.*, **65**, 395 (1932).