to 0°, and deoxygenated by evacuating to 5 cm and filling with nitrogen seven times. The solution was refluxed for 67 hr; at the end of that time it was clear and colorless. The solution was stripped to 200 ml and washed with three 200-ml portions of sodium bicarbonate. The solution was then dried over magnesium sulfate and the remaining chloroform removed to give 67.5 g of a slightly yellow oil. This material (35.7 g) was distilled (2.5 mm) to give five fractions: 1.21 g, bp 30–90°; 6.69 g, bp 90–100°; 7.38 g, bp 100–120°; 8.92 g, bp 120–125°; and 5.75 g of orange residue. Fraction 1 was recovered 1-ethylcyclohexene; fractions 3, 4, and 5 all showed aromatic absorbtion in the infrared and nmr. Fraction 2, bp 90–100°, was examined by vpc (20 ft × 0.25 in. Dow 11 column at 140°, flow rate 70 cc/min) to give peaks at 21.0 and 22.8 min with relative areas of 1:1.8. Both materials were collected from repeated injections. The sample of shortest retention time was found to still be a mixture of the two original materials by reinjection. This material showed olefinic absorption in the infrared and nmr and was not further investigated.

The sample of longest retention time (22.8 min) was homogeneous (>99%) on reinjection: infrared 2990 (s), 2900 (s), 1450 (s), 1380 (m), 1200 (w), 1040 (m), 1030 (w), 950 (m), 930 (m), 910 (m), and 765 (s) cm^{-1}; nmr τ 7.6 (multiplet, 2 H), 7.9–8.9. (multiplet, 10 H), and 9.1 (triplet, J = 7 Hz, 3 H). This material did not give a precipitate with ethanolic silver nitrate in 2 hr at room temperature and was assigned as 1-ethyl-2-trichloromethylcyclohexane (IV).

Anal. Calcd for $C_9H_{15}Cl_3$: C, 47.08; H, 6.59; Cl, 47.33. Found: C, 47.17; H, 6.38; Cl, 46.15.

1-Ethyl-2-trichloromethylcyclohexane (0.135 g) was dissolved in 95% ethanolic potassium hydroxide solution. The mixture immediately became cloudy. After 15 min at room temperature, the solution was worked up by extraction to give 0.071 g of a clear, colorless liquid. The infrared spectrum of this material showed a moderately strong band at 1617 cm^{-1}. The nmr showed a multiplet at τ 7.3 (3.3 H), a multiplet at 7.6–8.8 (7.7 H), and a triplet (J = 7 Hz) at 9.1 (3 H). The dehydrohalogenation product did not react with ethanolic silver nitrate solution after 12 hr at room temperature.

Addition of Bromotrichloromethane to 1-Octene. The photoaddition of bromotrichloromethane to 1-octene gave 1,1,1-trichloro-3-bromononane, bp 98–100° (0.9 mm) (lit.[32] bp 99–102° (0.6 mm)), in 80% yield. Dehydrohalogenation of this material, as described for the hexene adduct, gave 70% of 1,1,1-trichlorononene-2, bp 76–79° (0.9 mm), n^{23}D 1.4750 (lit.[32] bp 70–75° (0.6 mm), n^{26}D 1.4758). A detailed nmr analysis of this material showed it to be solely the *trans* isomer.

Molecular Orbital Calculations. An extended Hückel program[25] supplied by the Quantum Chemistry Program, Indiana University, was modified for use on an IBM 7074 computer. The program as used could handle a maximum of six hydrogens and six first-row elements in one molecule. The following parameters were used in the calculations: K in Wolfsberg–Helmholtz approximation,[24] 1.5; C–H bond length, 1.10 Å; C–C bond length, 1.54 Å; C=C bond length, 1.34 Å; Slater exponent for carbon, 1.625; H_{ii}2s, 21.40 eV; H_{ii}2p, 11.40 eV.

In reporting the results of these calculations, the geometry of the system is given in Table VII together with the sum of all energy levels below the radical orbital, E_c (the energy of the corresponding carbonium ion), E_r (the energy of the radical orbital), and E_t (the total energy of the radical).

Acknowledgment. This work was supported by the National Science Foundation GP-2024, and is a portion of the Ph.D. Thesis of R. M. Kopchik, University of Rochester, 1967. We thank L. D. Colebrook for his help with the nmr data.

(32) M. S. Kharasch, O. Reinmuth, and W. H. Urry, *J. Amer. Chem. Soc.*, **69**, 1105 (1947).

The Stereochemistry of Addition Reactions of Allenes. I. Methoxymercuration and Halogenation of 1,3-Dimethylallene[1,2]

William L. Waters, William S. Linn, and Marjorie C. Caserio

Contribution from the Department of Chemistry, University of California, Irvine, California 92664. *Received June 6, 1968*

Abstract: A procedure for the partial resolution of 1,3-dimethylallene by asymmetric hydroboration is described. The (−) enantiomer is assigned the *R* configuration. The stereochemistry of electrophilic addition of mercuric acetate in methanol to optically active 1,3-dimethylallene has been determined by relating the configuration of the dissymmetric allene to the configuration of the major asymmetric adduct. Similarly, the orientation and stereochemistry of halogen addition to (−)-1,3-dimethylallene in carbon tetrachloride, ether, and methanol have been studied. The results of this work establish that oxymercuration and halogenation of 1,3-dimethylallene under the conditions studied are stereospecific *trans* additions. These reactions and their stereochemistry are discussed with reference to the types of intermediate cations that may participate.

The mechanisms of addition reactions of allenic compounds are interestingly complex because of the numbers of different types of reaction intermediates that can in principle be involved. For example, addition of an electrophilic reagent (X$^+$) to an allene could generate a vinyl cation (A), a nonplanar allylic cation (B), or a bridged ion (C), depending on whether initial attack by the electrophile occurs at the terminal carbon, the central carbon, or at both (eq 1).

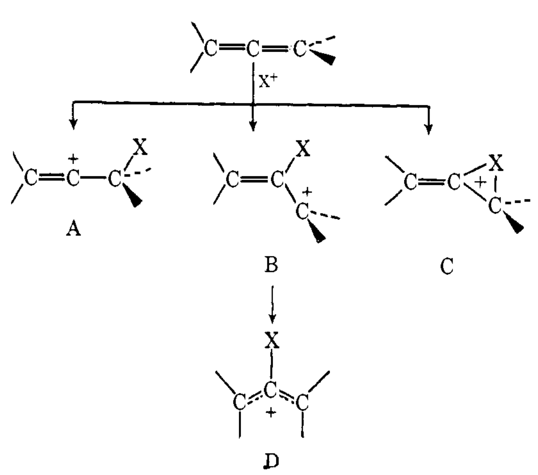
The possibility exists that these intermediates may interconvert and, in particular, the cation B may undergo rapid bond rotation to give the planar resonance-stabilized allylic ion D. The situation becomes even more diverse if the geminal substitutents at the terminal allenic carbons are different, as in 1,3-disubstituted allenes, since there are now two directions of approach of the reagent X$^+$ and hence two stereochemically different sets of ions to consider as possible intermediates.

Some information as to the types of intermediates involved can be inferred from studies of the orientation of addition of unsymmetrical reagents to allenes and, in fact, most of the reported studies of electrophilic,

---

(1) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work (PRF-2357-A1, 4).

(2) Presented in part at the 154th and 155th National Meetings of the American Chemical Society, Chicago, Ill., Sept 1967, and San Francisco, Calif., April 1968.



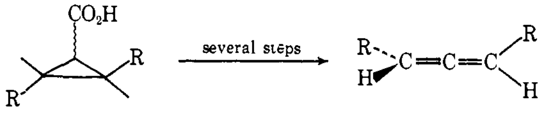
(1)

nucleophilic, and free-radical additions have dwelt mainly on the orientation of the reagent about the double bond undergoing attack.[3] Relatively little is known, however, of the factors that determine the stereochemical orientation about the double bond remaining in the monoadduct, and even less is known of the stereochemistry of addition to the reacting double bond. The objective of the present work was to investigate the above-mentioned stereochemical features of certain electrophilic addition reactions of allenes in order to probe further into the natures of the intermediates involved. Thus the stereochemistry of addition to the reacting double bond can, in principle, be determined if the starting allene is optically active and of known configuration, and an asymmetric center of known or easily established configuration is generated in the adduct. Once the stereochemistry and stereospecificity of addition is established, it is possible to infer whether the products are derived from symmetrical or unsymmetrical intermediates.

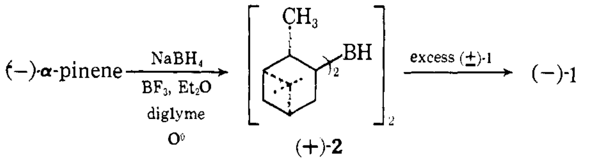
Since it is essential to know the configurations of both the dissymmetric allene and the adducts in order to establish the stereochemistry of addition, we chose to first study those reactions that give products whose configurations may be readily established. The particular reactions described in this paper include methoxymercuration, bromination, and iodination of (−)-1,3-dimethylallene (2,3-pentadiene), **1**. The first part of the paper reports the resolution and absolute configuration of **1**, and the second part describes the orientation and stereochemistry of electrophilic addition reactions to **1**.

I. Resolution and Absolute Configuration of 1,3-Dimethylallene[4]

The difficulties of resolution of dissymmetric allene hydrocarbons are well known, and, until recently, no general method for their synthesis was available. The situation is summarized in a recent paper by Jones and coworkers,[5] who also describe a useful and general method for the synthesis of optically active 1,3-disubstituted allenes from the corresponding optically active *trans*-2,3-disubstituted cyclopropanecarboxylic acids. The method involves several synthetic steps and leads to allenes of undetermined optical purities.



We have developed a simple and potentially general method for the partial resolution of 1,3-disubstituted allene hydrocarbons based on the method of asymmetric hydroboration developed by Brown and coworkers.[6] These workers have shown that *in situ* hydroboration of (−)-α-pinene with diborane in diglyme leads to the precipitation of (+)-*sym*-tetraisopinocampheyldiborane,[6b] which has proved to be a highly stereoselective hydroborating agent of unhindered *cis*-alkenes and can be used to prepare certain optically active alcohols and alkenes in high optical purity.[6c] Utilizing this reagent for the hydroboration of excess 1,3-dimethylallene, we anticipated that the recoverable allene would be enriched in one enantiomer, and this was confirmed by experiment (eq 2).



(2)

In a typical run, a suspension of (+)-**2** in diglyme was prepared from (−)-α-pinene, $[\alpha]_D$ −55.3° ($CHCl_3$), and diborane (formed *in situ* from sodium borohydride and boron trifluoride etherate); a twofold excess of racemic **1** was then added to the reaction mixture maintained at 0°. After 2–3 hr, the unreacted allene was recovered and fractionally distilled giving allene of specific rotation $[\alpha]_D \sim -17°$ (ether). The level of asymmetric induction varied somewhat with the particular reaction conditions, as summarized in Table I, and the lowest

Table I. Specific Rotations in the Partial Resolution of 1,3-Disubstituted Allenes by Asymmetric Hydroboration

α-Pinene, mol	BH_3, mol	RCH═C═CHR Amt, mol	RCH═C═CHR $[\alpha]_D$,[a] deg	Time,[b] hr
0.225[c]	0.113[d]	0.225[e]	−21.0	3
0.149[c]	0.075[d]	0.147[e]	−18.7	3
0.100[c]	0.050[d]	0.100[e]	−43.8	4
0.086[f]	0.043[d]	0.086[e]	+4.4	1.5
0.149[c]	0.075[d]	0.149[e]	−17.7	3
0.026[c,g]	0.013[d]	0.026[e]		3
0.163[c]	0.081[h]	0.147[e]	−7.8	
0.139[c]	0.069[h]	0.139[e]	−7.6	2.5
0.012[c]	0.006[h]	0.012[i]	−180	3

[a] In ether. [b] Optimum yields (up to 100% of recoverable allene) were achieved in 3 hr. [c] (−)-α-Pinene, $[\alpha]^{24}_D$ −55.3° (*c* 8, $CHCl_3$). [d] Based on a 4:3 mol ratio of $BF_3 \cdot Et_2O$ to $NaBH_3$ in diglyme as solvent. [e] $CH_3CH{=}C{=}CHCH_3$ containing some diethyl ether. [f] (+)-α-Pinene, $[\alpha]^{23}_D$ +40.8° (*c* 3, CCl_4). [g] **1** (7.4 mmol) were consumed and 4.0 mmol of (−)-α-pinene were recovered. [h] In THF. [i] $C_6H_5CH{=}C{=}CHC_6H_5$.

---

(3) For recent comprehensive reviews on the chemistry of allenes see (a) D. R. Taylor, *Chem. Rev.*, **67**, 317 (1967); (b) M. V. Mavrov and V. F. Kucherov, *Russ. Chem. Rev.*, **36**, 233 (1967); (c) A. A. Petrov and A. V. Fedorova, *ibid.*, **33**, 1 (1964).

(4) For preliminary communication of this work, see W. L. Waters and M. C. Caserio, *Tetrahedron Letters*, in press.

(5) J. M. Walbrick, J. W. Wilson, Jr., and W. M. Jones, *J. Am. Chem. Soc.*, **90** 2895 (1968).

(6) (a) H. C. Brown, N. R. Ayyangar, and G. Zweifel, *ibid.*, **86**, 1071 (1964); (b) G. Zweifel and H. C. Brown, *ibid.*, **86**, 393 (1964); (c) H. C. Brown, N. R. Ayyangar, and G. Zweifel, *ibid.*, **86**, 397 (1964); (d) G. Zweifel, N. R. Ayyangar, T. Munekata, and H. C. Brown, *ibid.*, **86**, 1076 (1964); (e) H. C. Brown and G. J. Klender, *Inorg. Chem.*, **1**, 204 (1962).

levels of activity, [α]D −7.6°, were obtained on hydroboration of **1** with a borane mixture prepared from (−)-α-pinene and BH_3 in tetrahydrofuran.[7]

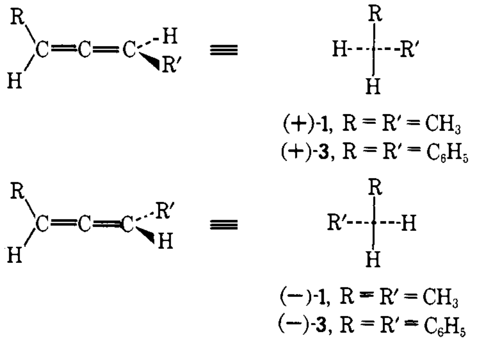
The single advantage of this method of partial resolution of allenes is its simplicity. In one step, a level of asymmetric induction is achieved that compares favorably with that obtained by the synthesis developed by Jones and coworkers.[5]

It was of basic importance to our work on the stereochemistry of additions to allenes to establish the absolute configuration of (−)-**1**. This could in principle be deduced from the configuration of the transition state for asymmetric hydroboration if this were known with any certainty. A mechanism of asymmetric induction in hydroborations with active **2** has been described,[8] and other less rigorous transition-state models of hydroboration have been proposed by Brown, *et al.*,[6a–d] and by Streitwieser, *et al.*[9] However, none of these models satisfactorily accounts for the course of asymmetric induction observed with *trans* or hindered alkenes. In such cases, the reaction appears to be mechanistically complex.[6a] Displacement of α-pinene is observed in amounts suggestive that **2** is not directly involved in hydroboration of the alkene but undergoes a slow dissociation to α-pinene and triisopinocampheyldiborane, which subsequently reacts with the alkene.[7] In the hydroboration of **1** with a suspension of **2** in diglyme, displacement of α-pinene was indeed observed in amount corresponding to one-half the molar equivalent of allene consumed. The reaction is therefore complex and appears to involve more than one type of asymmetric borane. Hence, we abandoned attempts to predict the configuration of (−)-**1** from transition-state models of hydroboration.

Despite our inability to formulate a precise description of the transition states that lead to asymmetric induction, we consider that it is reasonable to assume they are similar for structurally related compounds. We will assume, then, that the stereoselectivity developed in the transition states of hydroboration of **1** is the same as that developed in the hydroboration of the structurally related compound, 1,3-diphenylallene, **3**. Under comparable reaction conditions, therefore, the configuration of the enantiomer enriched in recovered **1** is expected to be the same as that enriched in recovered **3**. Hydroboration of excess racemic **3** with a borane mixture prepared from (−)-α-pinene and BH_3 in tetrahydrofuran (see Table I) led to the recovery of optically active **3** of rotation [α]^{26}D −180° ($CHCl_3$), the configuration of which is known to be *R*.[10] We conclude, therefore, that (−)-**1**, obtained by asymmetric hydroboration under the same conditions, also has the *R* configuration.[11]

According to Lowe,[12] the absolute configuration of allenes can be predicted from Brewster's rules[13] relating the sign of rotation with the handedness or chirality of the screw pattern of polarizability. Thus by viewing a dissymmetric allene along its orthogonal axes such that the more polarizable substitutent in the *vertical* axis is uppermost and toward the viewer, then, if the more polarizable substituent in the *horizontal* axis is to the *right*, the screw pattern of polarizability is clockwise and the enantiomer will be *dextrorotatory;* if it is to the *left*, the screw pattern of polarizability is anticlockwise and the enantiomer will be *levorotatory* (see Scheme I). Applying this simple rule to 1,3-dimethylallene, we conclude that (−)-**1** has the *R* configuration, in agreement with our assignment based on transition state arguments.

Scheme I



(+)-**1**, R = R′ = CH_3
(+)-**3**, R = R′ = C_6H_5

(−)-**1**, R = R′ = CH_3
(−)-**3**, R = R′ = C_6H_5

Brewster[14] has also predicted that (−)-**1** has the *R* configuration based on a helical model of optical activity, and he has calculated the rotation of optically pure (*R*)-(−)-**1** to be [α]D −174° (EtOH). This means that 1,3-dimethylallene of rotation [α]D −15.9° (ether) obtainable by asymmetric hydroboration is calculated to be about 9% optically pure. Rotation data reported in subsequent sections of this paper indicate fair agreement with Brewster's calculation for the optical rotation of **1**.

II. Methoxymercuration of (−)-1,3-Dimethylallene

Oxymercuration of allene hydrocarbons has been studied recently by two groups of workers.[15,16] Waters and Kiefer[15] have shown that addition of mercuric acetate in methanol to 1,3-dimethylallene gives in high yield an 83:17 mixture of *trans*- and *cis*-3-acetoxymercuri-4-methoxy-2-pentenes, **4** and **5**. These authors suggest that the reaction involves the preequilibrium formation of σ-bonded mercurinium ions, **6** and **7**, which, in the rate-determining step, collapse to products by a *trans*-rearward attack of solvent at the methyl-substituted carbon (Scheme II). This mechanism is consistent with that proposed for the oxymercuration of monoalkenes,[17,18] and accounts for the preferential

---

(7) The reduced stereoselectivity observed in tetrahydrofuran is probably the result of the greater solubility and degree of dissociation of **2** in tetrahydrofuran compared to that in diglyme (*cf.* ref 6e). Dissociation of **2** leads to α-pinene and triisopinocampheyldiborane, and the latter has been observed to be less stereoselective in the hydroboration of *trans*-alkenes,[6a] presumably because it offers a less-hindered reaction environment.

(8) D. R. Brown, S. F. A. Kettle, J. McKenna, and J. M. McKenna, *Chem. Commun.*, 667 (1967).

(9) A. Streitwieser, Jr., L. Verbit, and R. Bittman, *J. Org. Chem.*, **32**, 1530 (1967).

(10) S. F. Mason and G. W. Vane, *Tetrahedron Letters*, 1593 (1965)

(11) The absolute configuration of 1,3-dimethylallene has been independently established by W. M. Jones and J. M. Walbrick, *ibid.*, in press.

(12) G. Lowe, *Chem. Commun.*, 411 (1965).

(13) J. H. Brewster, *J. Am. Chem. Soc.*, **81**, 5475 (1959).

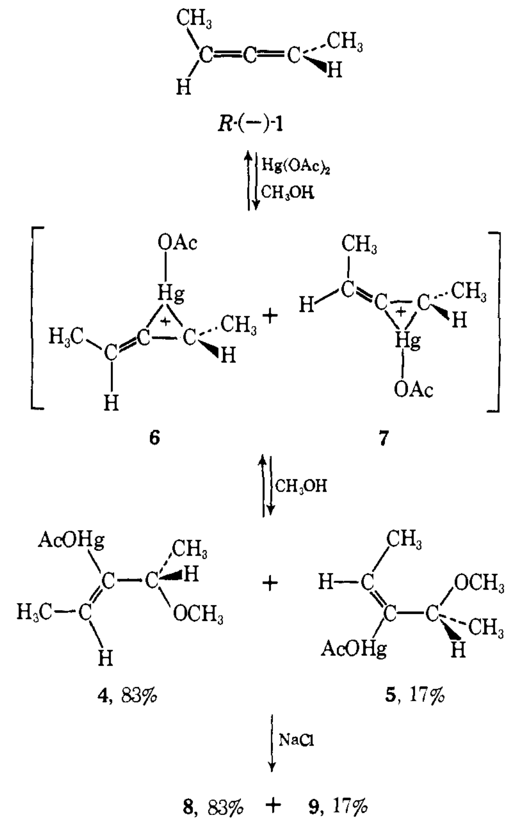
(14) J. H. Brewster in "Topics in Stereochemistry," Vol. 2, N. L. Allinger and E. L. Eliel, Ed., John Wiley & Sons, Inc., New York, N. Y., 1967.

(15) W. L. Waters and E. F. Kiefer, *J. Am. Chem. Soc.*, **89**, 6261 (1967).

(16) R. K. Sharma, B. A. Shoulders, and P. D. Gardner, *J. Org. Chem.*, **32**, 241 (1967).

(17) (a) J. Chatt, *Chem. Rev.*, **48**, 7 (1951); (b) N. S. Zefirov, *Russ. Chem. Rev.*, **34**, 527 (1965); (c) T. G. Traylor and A. W. Baker, *J. Am. Chem. Soc.*, **85**, 2746 (1963); (d) T. G. Traylor, *ibid.*, **86**, 244 (1964); (e) H. C. Brown, J. H. Kawakami, and S. Ikegami, *ibid.*, **89**, 1525 (1967); (f) V. I. Sokolov, Y. A. Yustynyuk, and A. O. Reutov, *Dokl.*

Scheme II



formation of the *trans* isomer **4**. Thus approach of the nucleophile *trans* to the mercury bridge is expected to be less sterically hindered by the substituents at the vinyl terminus in **6** than in **7**, and the *trans* product **4** would, therefore, be formed at the faster rate.

This mechanism requires that reaction be a stereospecific *trans* addition, but it cannot be assumed *a priori* that this is the case. *cis* oxymercuration of allenes is not unknown,[17c,d,h,i] and one cannot exclude the possibility that allylic ions analogous to D (eq 1) may intervene. We therefore investigated the stereochemistry of the reaction using optically active **1**.

Results

Reaction of mercuric acetate with (*R*)-(−)-**1**, $[\alpha]_D$ −15.9° (ether), in methanol solution gave the expected 83:17 mixture of **4** and **5**. This mixture was converted to the corresponding *trans*- and *cis*-3-chloromercuri-4-methoxy-2-pentenes, **8** and **9**, by treatment with aqueous sodium chloride. The specific rotation of the mercurichloride mixture was $[\alpha]_D$ −4.3° ($CHCl_3$). Recrystallization from hexane led to enrichment in the *trans* isomer **8** (95%), $[\alpha]_D$ −3.4° ($CHCl_3$). A summary of the optical rotation data from several such experiments is given in Table II.

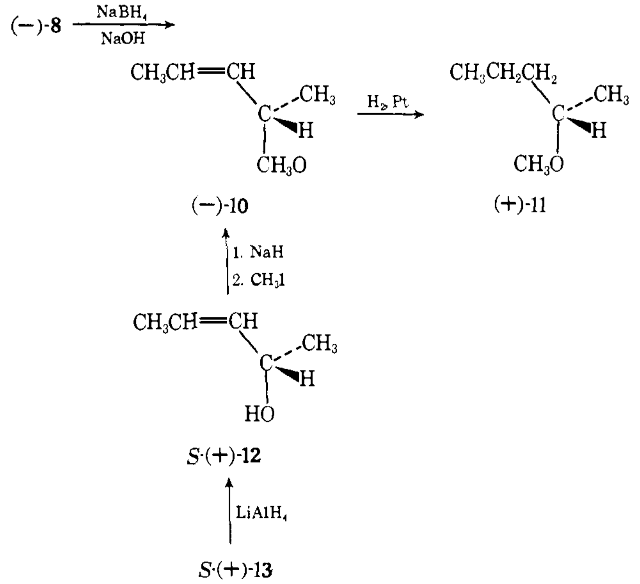
Table II. Optical Rotation Data for Products of Methoxymercuration of Optically Active 1,3-Dimethylallene

1^a	$[\alpha]^{22-26}_D$	−15.9	−43.8	+4.4	−17.7	−7.8
8^b	$[\alpha]^{22-26}_D$	-3.4^c	-10.6^d	$+1.2^d$	-4.3^c	-2.2^c

[a] In ether. [b] 95 ± 2% **8**. [c] In $CHCl_3$. [d] In C_6H_6.

In order to establish the over-all stereochemistry of addition, it was necessary to determine the configuration at the asymmetric center of the adducts. This was achieved in the case of the major product by the sequence of reactions shown in Scheme III. Reduction of **8** (95% pure), $[\alpha]_D$ −3.4° ($CHCl_3$), with sodium borohydride gave (−)-4-methoxy-2-pentene, **10**, as a *cis–trans* mixture containing 82% of the *trans* isomer,[19,20] $[\alpha]_D$ −5.3° (ether). Hydrogenation of (−)-**10** in ethanol over a platinum catalyst gave 2-methoxypentane, **11**, $[\alpha]_D$ +1.2° ($CHCl_3$).

Scheme III



The configuration of *trans*-(−)-**10** is assigned as *S* by reason of its formation from *trans*-(*S*)-(+)-3-penten-2-ol (**12**),[21a] the configuration of which has been related to (*S*)-(+)-lactic acid.[21b] Accordingly, the *S* configuration may also be assigned to (−)-**8**. However, since we were unsure of the effect of approximately 18% of *cis*-**10** on the rotation of predominantly *trans*-**10**, we felt it desirable to extend the configurational assignments to the saturated ether **11**. We therefore carried out a series of transformations to obtain optically active **11** starting with the acid phthalate of *trans*-(*S*)-(+)-3-penten-2-ol,[22] $[\alpha]_D$ +22.0° ($CHCl_3$), which is estimated to be 58% optically pure.[23] Reduction of the (+)-acid phthalate **13** with lithium aluminum hydride gave **12**, which, on methylation, gave *trans*-(−)-**10**, $[\alpha]_D$ −54.2° ($CHCl_3$), as previously observed by Hill, Kenyon, and

---

Akad. Nauk SSSR, **173**, 356 (1967); (g) J. Halpern and H. B. Tinker, *J. Am. Chem. Soc.*, **89**, 6427 (1967); (h) A. Factor and T. G. Traylor, *J. Org. Chem.*, **33**, 2607 (1968); (i) T. T. Tidwell and T. G. Traylor, *ibid.*, **33**, 2614 (1968).

(18) M. M. Kreevoy, G. Stokker, R. A. Kretchner, and A. K. Ahmed, *ibid.*, **28**, 3184 (1963); M. M. Kreevoy and M. A. Turner, *ibid.*, **30**, 373 (1965); K. Ichikawa, K. Nishimura, and S. Takayama, *ibid.*, **30**, 1593 (1965).

(19) Although the configuration at the asymmetric center is presumably unaffected by the transformation **8** to **10**, replacement of the HgCl group is evidently not completely stereospecific. This result is not without precedent since some racemization has been shown to occur in the reduction of *exo-cis*-2-hydroxy-3-chloromercurinorbornane with sodium borodeuteride (see ref 20). Also, borohydride reductions of both *cis*- and *trans*-4-methylcyclohexylmercuric chlorides are nonstereospecific (T. G. Traylor, private communication).

(20) F. G. Bordwell and M. L. Douglass, *J. Am. Chem. Soc.*, **88**, 993 (1966).

(21) (a) H. W. J. Hill, J. Kenyon, and H. Phillips, *J. Chem. Soc.*, 576 (1936); (b) P. A. Levene and H. L. Haller, *J. Biol. Chem.*, **81**, 703 (1929).

(22) *trans*-(+)-3-Penten-2-ol, **12**, is derived from the (+)-acid phthalate, **13**. See footnote 18 in H. L. Goering and W. I. Kimoto, *J. Am. Chem. Soc.*, **87**, 1748 (1965).

(23) H. L. Goering, M. M. Pombo, and K. D. McMichael, *ibid.*, **85**, 965 (1963).

Phillips.[21a] Catalytic hydrogenation of *trans*-(−)-**10** gave (+)-**11**, [α]D +9.9° ($CHCl_3$). Thus (*S*)-(+)-**12** is related to (+)-**11**, and hence to (−)-**8**.

Conclusions

The observation that (*S*)-(−)-**8** is derived from (*R*)-(−)-**1** allows the conclusion that *oxymercuration of 1,3-dimethylallene in methanol proceeds by trans addition*, at least with respect to formation of the major product. 1,3-Dimethylallene behaves, therefore, like normal alkenes, which generally give products of *trans* oxymercuration,[17] and we accordingly favor the mechanism of Scheme II showing the intervention of σ-bridged mercurinium ions **6** and **7**.

Since we were unable to isolate a pure sample of the minor *cis* adduct **9** (or **5**) free of the *trans* adduct, we could not directly determine its configuration. We assume, however, that it is similarly formed from **1** by *trans* addition, in which case the configuration at the asymmetric center should be *opposite* to that in (−)-**8**, namely *R*.

If it is assumed that conversion of the acid phthalate **13** of 58% optical purity to the saturated ether (+)-**11**, and conversion of (−)-**1** to (+)-**11**, occur with no loss in optical purity, we estimate that the optical purity of **1** of rotation [α]D −15.9° is 7%, in fair agreement with the value of 9% based on Brewster's calculated value for the rotation of optically pure **1**.[14] Our estimate is probably low for the reason that purification of the adduct **8** by recrystallization may well have resulted in optical fractionation with enrichment in the racemic form.[24] Alternatively, the argument may be stated in reverse. That is, assuming that **1**, [α]D −15.9°, is 9% optically pure, then the rotation of the saturated ether **11** should be +1.7° if all steps in the transformations **1** to **11** and **13** to **11** are 100% stereospecific, in fair agreement with the observed rotation of +1.2°. Since the major uncertainty is the stereospecificity of the oxymercuration step, this may be regarded as evidence that oxymercuration is indeed highly stereospecific.

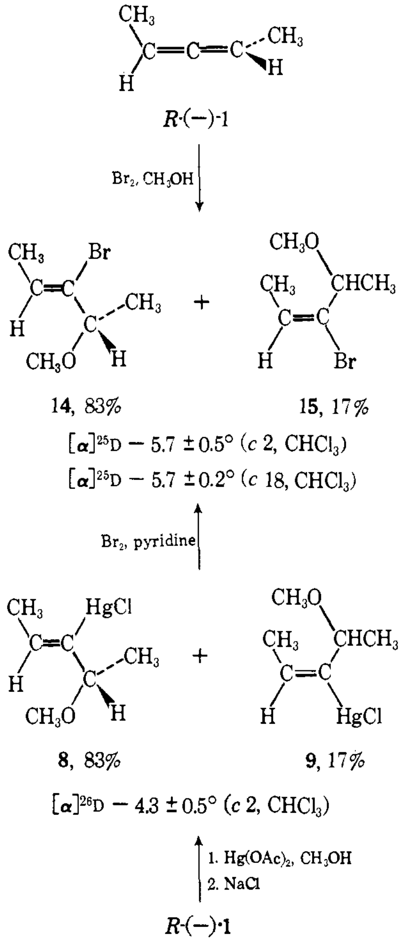
Halogenation of (−)-1,3-Dimethylallene. Halogen addition to unsymmetrically substituted allenes has been studied mainly with respect to the orientation of addition. The products of kinetic control are usually monoadducts in which the more highly substituted double bond is attacked, but subsequent rearrangement to more stable products is frequently observed.[25]

An investigation was recently reported by Jacobs, *et al.*,[26] of the addition of bromine to optically active 2,2-dimethyl-3,4-hexadien-1-ol. Since the reaction led to inactive product, these authors have concluded that a symmetrical intermediate (or transition state) is involved. In contrast, bromination of optically active phenylallenecarboxylic acids has been shown to give optically active bromolactones in high stereospecificity.[27]

As far as we know, there are no published studies on the stereochemistry of halogen addition to simple allene hydrocarbons. There is even a sparsity of orientational data. For example, the bromination of 1,3-dimethylallene was investigated some years ago by Acree and Laforge,[28a] who reported that, in methanol solution, a mixture of dibromo- and methoxybromopentenes were formed but the orientation and configuration about the double bond were not established.[28b] We therefore undertook to examine this and related reactions more fully in order to determine the product distributions and the over-all stereochemistry of addition.

Bromination in Methanol. Reaction of **1** with a dilute solution of bromine in methanol produced an 83:17 mixture of *trans*- and *cis*-3-bromo-4-methoxy-2-pentenes, **14** and **15**, and about 5% of the corresponding dibromides **16** and **17**, the exact amount depending on the bromine concentration. The structures of the bromomethoxy products were established by their identity with the products formed from reaction of bromine with an 83:17 *trans–cis* mixture of mercurichlorides **8** and **9** obtained by methoxymercuration of **1** (Scheme IV).

Scheme IV



Bromination of optically active **1**, [α]D −15.9° (ether), in methanol gave optically active methoxy bromides, **14** and **15**, [α]D −5.7° ($CHCl_3$). The configurations at the asymmetric centers of **14** and **15** were related to those of **8** and **9** by the reaction sequence of

---

[24] We are grateful to Professor James H. Brewster for kindly pointing this out to us.

[25] A. V. Fedorova and A. A. Petrov, *J. Gen. Chem. USSR*, 31, 3273 (1961).

[26] T. L. Jacobs, R. Macomber, and D. Zunker, *J. Am. Chem. Soc.*, **89**, 7001 (1967).

[27] K. Shingu, S. Hagishita, and M. Nakagawa, *Tetrahedron Letters*, 4371 (1967).

[28] (a) F. Acree, Jr., and F. B. LaForge, *J. Org. Chem.*, **5**, 430 (1940). (b) The addition of bromine to 1,3-dimethylallene is reported to give *cis*-3,4-dibromo-2-pentene as the major product [*cf.* D. C. Duffey, J. P. Minyard, and R. H. Lane, *J. Org. Chem.*, 31, 3865 (1966)]. On the basis of our results, we conclude that the configuration of the major adduct was incorrectly assigned.

Scheme IV. Thus methoxymercuration of **1**, $[\alpha]_D$ $-15.9°$ (ether), followed by treatment with aqueous sodium chloride gave an 83:17 mixture of **8** and **9**, $[\alpha]_D$ $-4.3°$ ($CHCl_3$), which in turn gave an 83:17 mixture of **14** and **15**, $[\alpha]_D$ $-5.7°$ ($CHCl_3$), on treatment with bromine in pyridine.

A number of conclusions may be made from this data. First, the orientation of methoxybromination of **1** is essentially the same as that observed in methoxymercuration; nucleophilic attack occurs exclusively at the methyl-substituted carbon, and the major product is the *trans* isomer. Second, the observation that the sign and magnitude of optical rotation of the methoxy bromide mixture is the same, within experimental error, whether obtained from (−)-**1** directly by bromination in methanol or indirectly by oxymercuration indicates that both bromination and oxymercuration have the same stereochemistry and similar stereospecificities. We conclude, therefore, that *bromination of* **1** *in methanol is a stereospecific trans addition.* In Scheme IV, these configurational relationships are specified for the major product only, although it is assumed that the asymmetric configuration of the minor product **15** is *opposite* to that of the major product **14**.

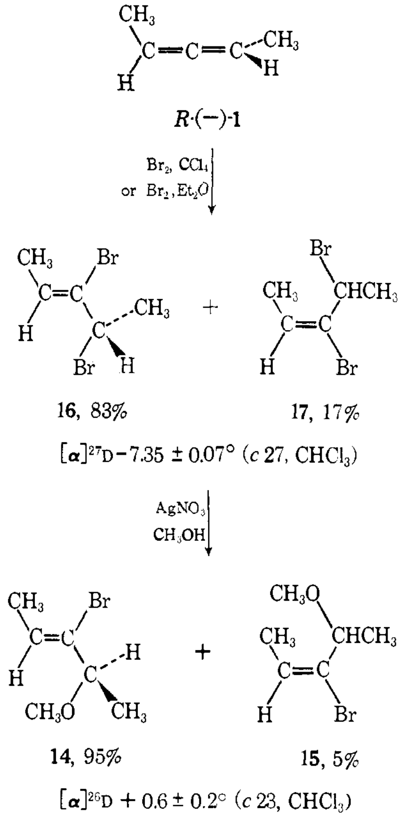
The stereospecificity observed in the bromination of **1** precludes dominant intervention of planar allylic ions in this case, and we accordingly formulate the reaction as proceeding through bridged bromonium ions of type C (eq 1, X = Br) which collapse to products by *trans* attack of the nucleophile at the methyl-substituted carbon.

Bromination in Inert Solvents. Reaction of **1** in either carbon tetrachloride or diethyl ether gave an 83:17 mixture of *trans*- and *cis*-3,4-dibromo-2-pentenes, **16** and **17**. Their structures were established by their conversion to the corresponding methoxy bromides, **14** and **15**, on reaction with silver nitrate in methanol (Scheme V). Bromination of (−)-**1**, $[\alpha]_D$ $-15.9°$ (ether), in carbon tetrachloride produced optically active **16** and **17**, $[\alpha]_D$ $-7.35°$ ($CHCl_3$).

While it seems only reasonable that the dibromides are formed by a stereospecific *trans* addition analogous to methoxy bromide formation, we sought to confirm this by relating the configurations of the dibromides to compounds of established configuration. We first attempted to regenerate the parent allene by stereospecific *trans* debromination with iodide ion. This reaction, however, gave only 1,3-pentadiene. We then attempted to convert the dibromide mixture to the methoxy bromides **14** and **15** by S_N2 displacement of allylic bromine with sodium methoxide in dimethyl sulfoxide. Instead, this reaction led to elimination and formation of 1-penten-3-yne. Finally, we succeeded in converting **16** and **17** to **14** and **15** by reaction with silver nitrate in methanol (Scheme V). However, an 83:17 *trans–cis* mixture of **16** and **17**, $[\alpha]_D$ $-7.35°$, gave a 95:5 *trans–cis* mixture of **14** and **15**, $[\alpha]_D$ $+0.6°$. ($CHCl_3$). Some geometric rearrangement has therefore occurred, and the small net positive rotation indicates the configuration of **14** is *opposite* to that obtained in the direct bromination of **1** in methanol.

This result means that the two-step conversion of (−)-**1** to (+)-**14** proceeds with a *low* degree of stereospecificity either by *cis* addition of bromine followed by an S_N1-type displacement with net retention or by *trans* addition of bromine followed by S_N1 displacement with *net inversion.* The latter alternative is preferred by analogy with the observed *trans* bromination of **1** in methanol and the fact that S_N1 solvolyses of allylic halides generally proceed with rearrangement and extensive racemization with net inversion.[29] The stereochemistry of bromine addition shown in Scheme V is therefore depicted as *trans.*

Scheme V

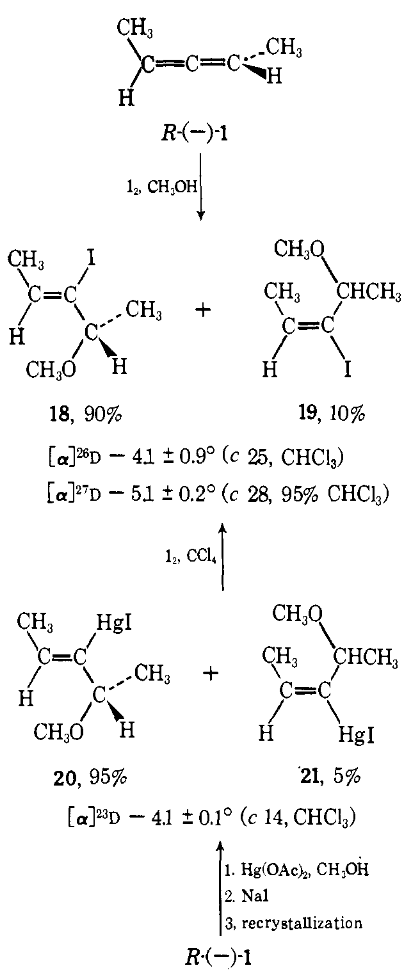


The methanolysis of **16** and **17** deserves one further comment. The stereochemical outcome of this reaction (*i.e.*, extensive racemization with net inversion, and geometric rearrangement) implies that planar allylic ions of type D (eq 1, X = Br) are more likely intermediates than the bridged bromonium ions of type C (X = Br). Participation of the neighboring vinyl bromine is not then important in the silver-assisted methanolysis of the dibromides.

Iodination. Iodine reacted very slowly with **1** in carbon tetrachloride solution, and the product, which is presumably a diiodide, was unstable and was not isolated. In methanol, however, iodine reacted with **1** at a reasonable rate and gave a *trans–cis* mixture of 3-iodo-4-methoxy-2-pentenes, **18** and **19**, in the ratio of 90:10. The structures of these adducts were established by their independent formation from a *trans–cis* mixture of 4-methoxy-3-iodomercuri-2-pentenes **20** and **21**, by displacement of the HgI group with iodine in carbon tetrachloride (Scheme VI). The orientation of methoxyiodination of **1** is, therefore, the same as that observed in oxymercuration and bromination, although the amount of *trans* adduct formed is slightly greater.

[29] (a) P. B. D. de la Mare in "Molecular Rearrangements, P. de Mayo, Ed., Interscience Publishers, New York, N. Y., 1963, Chapter 2, p 27. (b) R. H. DeWolfe and W. G. Young, *Chem. Rev.*, **56**, 753 (1956).

Scheme VI



Reaction of (−)-**1**, $[\alpha]_D$ −15.9° (ether), with iodine in methanol gave a 90:10 *trans–cis* mixture of optically active adducts **18** and **19**, $[\alpha]_D$ −4.1° ($CHCl_3$). Similarly, a 95:5 mixture of the mercurials **20** and **21**, $[\alpha]_D$ −4.2° ($CHCl_3$), gave a 95:5 mixture of **18** and **19**, $[\alpha]_D$ −5.1° ($CHCl_3$), on reaction with iodine in carbon tetrachloride. This sequence of reactions establishes the configuration of the major product **18** as *S*, and its formation from (*R*)-(−)-**1** necessitates that the iodination reaction proceed by a stereospecific *trans* addition.

Iodination in methanol must to a significant extent, therefore, involve asymmetric intermediates, and we conclude that these are probably the bridged iodonium ions of type C (eq 1, X = I). The over-all orientation, *cis–trans* isomer distribution and stereochemistry of addition is, therefore, very similar to that observed in oxymercuration and bromination.

Experimental Section

All optical rotations were measured with a Zeiss polarimeter reading to 0.01°. Nmr spectra were recorded with a Varian A-60A spectrometer, and chemical shifts are reported in parts per million downfield from internal TMS. All product percentages were determined by nmr integration data and are reliable to ±2%. Melting points were taken in sealed capillaries and are uncorrected.

1,3-Dimethylallene (1) was prepared in 53% yield by the reaction of methyllithium with carbon tetrabromide in the presence of a mixture of *cis*- and *trans*-2-butenes. This method, first developed by Untch, Martin, and Castellucci,[30a] gives substantially better yields than the two-step allene synthesis *via* dihalocyclopropanes reported earlier.[30b–d] Fractional distillation of the crude product in diethyl ether gave a main fraction, bp 36–48°, containing 35% by weight of **1** in ether. This solution was used in subsequent reactions without further enrichment.

1,3-Diphenylallene (3) was prepared from 1,3-diphenyl-1-chloro-2-propanone by the method of Craig and Moyle.[31] The white, crystalline product, mp 51–52° (lit. mp 49–51°,[32] 52–56° [33]), was obtained in low yield (<20%) from a mixture of the *cis*- and *trans*-enol phosphates and appeared to be unstable when exposed to air and light for short periods.

Asymmetric hydroboration of 1 was carried out essentially by the method of Brown and coworkers.[6] Boron trifluoride etherate (16.1 g, 0.113 mol) in 16 ml of diglyme (purified by distillation from $LiAlH_4$) was added slowly to a stirred solution of (−)-α-pinene (30.45 g, 0.225 mol), $[\alpha]^{26}_D$ −55.3 ± 0.2° (*c* 8, $CHCl_3$), and sodium borohydride (0.088 mol, 4% excess of theoretical) in 85 ml of diglyme at 0°. After 4 hr, racemic **1** (15.3 g, 0.225 mol) as a 30% solution in ether was added to the stirred borane mixture at 0°. After a further 3 hr of stirring at 0°, the volatile components were removed by evaporation at 25° and 5 mm pressure. The distillate was mostly ether and **1** with some unreacted α-pinene. Fractional distillation gave **1** (7.77 g, 100% recovery of theoretical excess) in ether, $[\alpha]^{23}_D$ −21.0 ± 0.3° (*c* 20, Et_2O). A summary of the results of several runs is given in Table I. Good yields of recovered **1** were obtained when the above mentioned excess of sodium borohydride was used.

Asymmetric hydroboration of **1** (9.45 g, 0.139 mol) in 30 ml of ether with a borane mixture prepared from 19.0 g (0.139 mol) of (−)-α-pinene and 69.5 ml of 1 *M* BH_3 in THF was performed as described above for *in situ* hydroboration in diglyme, and gave 2.95 g (62.5%) of **1**, $[\alpha]^{22}_D$ −7.6 ± 0.2° (*c* 4, Et_2O).

Asymmetric hydroboration of **3** (0.0121 mol) in THF with a borane mixture prepared from 6 ml of 1 *M* BH_3 in THF and 1.64 g (0.012 mol) of (−)-α-pinene gave, after evaporation of the solvent and unreacted α-pinene, a residue which was purified by chromatography over silica gel. Using 16 g of silica gel per gram of crude product in hexane, and a 12-in. column, 0.5 in. i.d., **3** was eluted pure with 500 ml of hexane. Recovered **3** had $[\alpha]^{26}_D$ −180 ± 2° (*c* 0.4, $CHCl_3$).

Oxymercuration of 1,3-Dimethylallene. Mercuric acetate (25.8 g, 0.081 mol) was stirred in 25 ml of anhydrous methanol until dissolved. (*R*)-(−)-1,3-Dimethylallene (5.5 g, 0.081 mol), $[\alpha]_D$ −15.9 ± 0.3° (*c* 8, Et_2O), in ether was added with stirring. After 3 min a test for mercuric ion was negative.[15] Sodium carbonate (10.6 g, 0.1 mol) was then added to neutralize acetic acid and the methanol was removed by evaporation at reduced pressure. An aqueous solution of sodium chloride (5.85 g, 0.1 mol) was then shaken with the alkylmercuric acetate and the resultant mercurichlorides (25.2 g, 93%), **8** and **9** were separated by filtration. Nmr analysis[15] established the product composition as 83% **8** and 17% **9**. The mixture had $[\alpha]^{26}_D$ −4.6 ± 0.1° (*c* 9, $CHCl_3$). Recrystallization from hexane gave as a first crop 12.48 g (0.037 mol) of a mixture containing 95% **8** and 5% **9**, $[\alpha]^{23}_D$ −3.4 ± 0.1° (*c* 10, $CHCl_3$).

Reaction of 4-Methoxy-3-chloromercuri-2-pentene with Sodium Borohydride. 4-Methoxy-2-pentene. To a stirred solution of **8** containing 5% of **9** (12.4 g, 0.037 mol, $[\alpha]^{23}_D$ −3.4° (*c* 10, $CHCl_3$)), in 25 ml of aqueous 0.5 *M* sodium hydroxide at 0° was slowly added 40 ml of a 1 *M* solution of sodium borohydride, 0.5 *M* in sodium hydroxide. The reaction mixture was then stirred an additional 15 min and extracted with ether. The ether extract was dried over magnesium sulfate, filtered, and evaporated at reduced pressure. The distillate was trapped at −78° and fractionally distilled to give 2.16 g (59%) of 4-methoxy-2-pentene, $[\alpha]^{23}_D$ −5.3 ± 0.1° (*c* 33, Et_2O), which, by nmr, was identified as an 82:18 *trans–cis* mixture. The residue from the flash evaporation was found to contain appreciable amounts of the dialkylmercurial corresponding to **8**. Formation of dialkylmercurials in borohydride reductions has been observed previously.[20]

Bromination of 1,3-Dimethylallene in Methanol. To 100 mg of **1** in 200 ml of methanol was added 1 equiv of bromine in 20 ml of methanol. At room temperature, the color of bromine disap-

---

[30] (a) K. G. Untch, D. J. Martin, and N. T. Castellucci, *J. Org. Chem.*, **30**, 3572 (1965); (b) W. von E. Doering and A. K. Hoffman, *J. Am. Chem. Soc.*, **76**, 6162 (1954); (c) W. von E. Doering and P. M. LaFlamme, *Tetrahedron*, **2**, 75 (1958); (d) L. Skattebøl, *Tetrahedron Letters*, 167 (1961); *Acta Chem. Scand.*, **17**, 1683 (1963).

[31] J. C. Craig and M. Moyle, *J. Chem. Soc.*, 3712 (1963).

[32] T. L. Jacobs and D. Danker, *J. Org. Chem.*, **22**, 1424 (1957).

[33] W. M. Jones, J. W. Wilson, Jr., and F. B. Tutwiler, *J. Am. Chem. Soc.*, **85**, 3309 (1963).

peared rapidly. After 5 min, the reaction mixture was neutralized with 1 equiv of sodium carbonate. The methanol was removed by evaporation at reduced pressure, and the residual oil (300 mg) was extracted with ether, dried, evaporated, and analyzed by nmr. The product was identified in this way as a 5:1 mixture of *trans*- and *cis*-3-bromo-4-methoxy-2-pentenes, **14** and **15**, with about 5% of the corresponding 3,4-dibromo-2-pentenes, **16** and **17**. The nmr spectrum of the major product **14** in carbon tetrachloride showed two one-proton quartets at 5.95 and 3.62 ppm, a three-proton singlet at 3.13 ppm, and two three-proton doublets at 1.75 and 1.21 ppm. The spectrum of the minor product **15** showed corresponding resonances at 6.05, 4.05, 3.14, 1.72, and 1.19 ppm, respectively.

Bromination of 14.7 mmol of (*R*)-(−)-**1**, $[\alpha]^{22}\text{D}$ −15.9° (*c* 7, ether), in 200 ml of methanol with 14.7 mmol of bromine in 20 ml of methanol under the conditions described for the racemic allene afforded a 5:1 mixture of optically active **14** and **15**, $[\alpha]^{25}\text{D}$ −5.7 ± 0.50° (*c* 2, $CHCl_3$). This latter rotational value was obtained by subtracting from the total observed rotation the theoretical amount of observed rotation due to the dibromides **16** and **17**. This was possible by knowing the concentration (nmr) of the dibromides and their specific rotation (see below).

Bromination of *trans*-3-Chloromercuri-4-methoxy-2-pentene in Pyridine.[34] Bromine (10 mmol) and an equal amount of the 83:17 *trans–cis* mixture of **8** and **9** in 25 ml of pyridine solution were stirred at room temperature for 5 min. Ether (30 ml) was added and the solution washed repeatedly with water. The ether extract was dried, filtered, and evaporated. The nmr spectrum of the residual oil in carbon tetrachloride showed it to be an 83:17 mixture of *trans*- and *cis*-3-bromo-4-methoxy-2-pentenes, **14** and **15**. The spectrum was identical in all respects with that of the major products of bromination of **1** in dilute methanol solution.

Bromination of 5 mmol of optically active **8** and **9**, $[\alpha]^{26}\text{D}$ −4.3 ± 0.5° (*c* 2, $CHCl_3$), as described above for racemic material, gave optically active **14** and **15**, $[\alpha]^{25}\text{D}$ −5.7 ± 0.2° (*c* 18, $CHCl_3$).

Bromination of 1,3-Dimethylallene in Carbon Tetrachloride. Bromination was repeated on the same scale in carbon tetrachloride, and the reaction was worked up as before. The nmr spectrum of the products in carbon tetrachloride or chloroform solutions showed the presence of an 83:17 mixture of *trans*- and *cis*-3,4-dibromo-2-pentenes, **16** and **17**. The spectrum showed two chemically shifted sets of two methyl doublets and two single-proton quartets. In carbon tetrachloride, chemical shifts determined for the major (*trans*) compound **16** were 6.22, 4.79, 1.84, and 1.80 ppm; corresponding shifts for the minor (*cis*) product **17** were 6.00, 5.12, 1.79, and 1.77 ppm. The same results were obtained on bromination of **1** in ether.[28b]

Bromination of (−)-1,3-dimethylallene, $[\alpha]^{22}\text{D}$ −15.9 ± 0.2° (*c* 7, ether), in ether on the same scale as above yielded an 83:17 mixture of *trans*- and *cis*-3,4-dibromo-2-pentenes, $[\alpha]^{27}\text{D}$ −7.35 ± 0.07° (*c* 27, $CHCl_3$).

Debromination of 3,4-Dibromo-2-pentene with Iodide Ion. A 5:1 mixture of *trans*- and *cis*-3,4-dibromo-2-pentenes (0.01 mol) was dissolved in 10 ml of ethylene glycol and added slowly to a tenfold excess of sodium iodide dissolved in 50 ml of ethylene glycol at 70°. The reaction mixture darkened and was stirred an additional 1 hr at 70°. The mixture was distilled at 10 mm, and the volatile components were trapped at −78°. The only volatile product found by glpc and nmr analysis was 1,3-pentadiene (*ca.* 60% of theoretical).

Reaction of 3,4-Dibromo-2-pentene with Methoxide Ion. A 5:1 mixture of *trans*- and *cis*-3,4-dibromo-2-pentenes (0.01 mol) in 15 ml of dimethyl sulfoxide was slowly added to 0.1 mol of sodium methoxide in 40 ml of dimethyl sulfoxide at 70°. After stirring for 1 hr, the mixture was poured into 200 ml of water. The organic layer was extracted with 50 ml of ether, and washed seven times with 200-ml portions of saturated ammonium chloride solution, dried, filtered, and evaporated at 10 mm. No products were retained in the distillation flask. The distillate, which was trapped at −78°, was analyzed by glpc and found to contain one compound besides ether. Separation of this compound from ether was achieved by preparative glpc using a 0.25 in. × 15 ft SE 30 column at 50°. Infrared and nmr analysis (three-proton multiplet centered at 5.33 ppm and three-proton doublet at 1.88 ppm, *J* = 1.5 cps), established the product as 1-penten-3-yne.

Reaction of 3,4-Dibromo-2-pentene with Silver Nitrate in Methanol. A 5:1 mixture of *trans*- and *cis*-3,4-dibromo-2-pentenes (0.01 mol) in 10 ml of methanol was slowly added to 0.015 mol of silver nitrate in 40 ml of refluxing methanol. Immediate precipitation of silver bromide occurred. Stirring was continued for a further 5 min, then 0.01 mol of sodium carbonate was added. After 5 min, the mixture was filtered, dried, and the methanol evaporated at 27° (15 mm). Glpc showed only methanol present in the distillate while nmr analysis of the residual oil showed it to be a 95:5 mixture of **14** and **15** together with about 15% of a third compound which is probably the nitrate ester of 3-bromo-4-hydroxy-2-pentene.[35] This by-product was completely removed by repeated washing of an ether solution of the products with water. On repeating the reaction, it was observed that the amount of nitrate ester could be increased with increasing silver nitrate concentration.

The reaction was repeated on the same scale as described above using a 5:1 mixture of optically active **16** and **17**, $[\alpha]^{27}\text{D}$ −7.35 ± 0.07° (*c* 27, $CHCl_3$).

The 95:5 product mixture of **14** and **15** had a specific rotation, $[\alpha]^{26}\text{D}$ +0.9 ± 0.2° (*c* 11, $CHCl_3$). The reaction was repeated at 27°. The product ratio was unchanged and the specific rotation was not measureably different, $[\alpha]^{25}\text{D}$ +0.6 ± 0.2° (*c* 23, $CHCl_3$).

Iodination of 1,3-Dimethylallene in Methanol. Iodine (1.86 g, 0.00735 mol) in 30 ml of methanol was added to **1** (0.5 g, 0.00735 mol) dissolved in 20 ml of methanol. The reaction mixture was stirred rapidly at room temperature for 18 hr in a flask covered with aluminum foil to exclude light. During the reaction, the purple color of the solution slowly faded to light brown. Sodium carbonate (1 equiv) was then added and the product isolated as described previously for bromination. The product was colored, and attempts at removing the color with thiosulfate failed. The nmr spectrum of the resultant oil (0.862 g, 0.004 mol) showed the presence of two compounds in a 9:1 ratio. In chloroform, the major product showed two single-proton quartets at 5.95 and 3.31 ppm, a three-proton singlet at 3.18 ppm and two three-proton doublets at 1.79 and 1.22 ppm. This compound was shown to be *trans*-3-iodo-4-methoxy-2-pentene, **18**, by its identity with the product of iodination of *trans*-3-iodomercuri-4-methoxy-2-pentene, **20**. The minor product **19** gave a similar nmr spectrum but with chemical shifts of 6.43, 3.52, 3.20, 1.75, and 1.17 ppm. No resonances corresponding to a diiodide adduct could be detected. The two sets of vinyl quartets exhibited unequal allylic coupling (*J* ≅ 1.5 and 1.0 cps), the larger being assigned to the *cis* isomer.

Iodination of (−)-1,3-dimethylallene, $[\alpha]^{22}\text{D}$ −15.9° (*c* 7, ether), in methanol was repeated on the same scale as above. The 9:1 mixture of **18** and **19** had $[\alpha]^{26}\text{D}$ −4.1 ± 0.9° (*c* 25, $CHCl_3$).

***trans*-3-Iodomercuri-4-methoxy-2-pentene** was prepared optically active by addition of 0.478 g (0.0070 mol) of (−)-1,3-dimethylallene, $[\alpha]^{22}\text{D}$ −15.9° (*c* 7, ether), to 2.2 g (0.0070 mol) of mercuric acetate in 30 ml of methanol followed by addition of 1.5 g (0.01 mol) of aqueous sodium iodide. After one recrystallization from *n*-hexane, the products were identified by nmr to be a 95:5 mixture of *trans*- and *cis*-3-iodomercuri-4-methoxy-2-pentenes, **20** and **21**, $[\alpha]^{25}\text{D}$ −4.2 ± 0.1° (*c* 14, $CHCl_3$). In chloroform, the *trans* isomer **20** showed two single-proton quartets at 6.53 and 4.18 ppm, a three-proton singlet at 3.23 ppm and two three-proton doublets at 1.98 and 1.28 ppm. The *cis* isomer **21** showed a similar spectrum with resonances at 5.59, 4.63, 3.28, 1.77, and 1.24 ppm. Both quartets and doublets produced by each compound suffered a 17 ± 2% loss of area when their integration was compared to that for the methoxy singlets. This observation is in accord with ^{199}Hg–^{1}H spin-spin coupling phenomena noted elsewhere.[15]

Iodination of *trans*-3-Iodomercuri-4-methoxy-2-pentene in Carbon Tetrachloride. A 95:5 mixture of optically active **20** and **21** (1.5 g, 0.0035 mol), $[\alpha]^{25}\text{D}$ −4.2°, was stirred at room temperature for 24 hr with 0.89 g (0.0035 mol) of iodine in 30 ml of carbon tetrachloride. The slightly purple solution was then decanted from the red precipitate of mercuric iodide, and the solvent evaporated at reduced pressure. The oil was then dissolved in 50 ml of ether and washed twice with saturated sodium thiosulfate solution. The colorless organic layer was then separated and dried over anhydrous magnesium sulfate. The ether was stripped and the residual oil (0.552 g) dissolved in chloroform. Nmr analysis identified the product as a 95:5 mixture of *trans*- and *cis*-3-iodo-4-methoxy-2-pentenes, $[\alpha]^{27}\text{D}$ −5.1 ± 0.2° (*c* 28, $CHCl_3$), the nmr spectrum of

---

[34] The authors are indebted to F. Jensen for suggesting this solvent system which appears to promote only ionic bromination of the mercurial [*cf.* F. R. Jensen and L. H. Gale, *J. Am. Chem. Soc.*, **82**, 148 (1960)]. Our experience with other solvents such as carbon tetrachloride and benzene is that appreciable alteration of the original 83:17 *trans*:*cis* ratio of the alkylmercuric chloride occurs during formation of the vinyl bromide.

[35] S. Oae and C. A. VanderWerf, *J. Am. Chem. Soc.*, 75, 2724 (1953).

which was identical in all respects with that obtained by methanolic iodination of **1** (see above).

trans-**4-Methoxy-2-pentene.** Sodium hydride (5.29 g, 0.126 mol) as a 56% by weight suspension in mineral oil was first washed with dry ether and then covered with 50 ml of dry ether. To the stirred hydride suspension was slowly added 9.0 g (0.105 mol) of *trans*-3-penten-2-ol[36] with cooling. When evolution of hydrogen ceased, methyl iodide (17.9 g, 0.126 mol) was added and the mixture stirred at room temperature for 24 hr. After dropwise addition of water to destroy excess hydride, the mixture was extracted with water and ether. The ether extract was dried over magnesium sulfate and filtered. The ether was distilled off through a 9-in. column packed with metal helices. The residue was distilled through the same column giving 4.27 g (0.043 mol, 43%) of *trans*-4-methoxy-2-pentene, **10**, bp 89–91° (lit.[21a] bp 90°). The nmr spectrum in carbon tetrachloride showed a two-proton multiplet centered at 5.7 ppm, a one-proton multiplet centered at 3.5 ppm, a three-proton singlet at 3.32 ppm, and two three-proton doublets at 1.75 and 1.13 ppm.

Optically active **10** was obtained in the following manner. *trans*-3-Penten-2-ol was converted into the acid phthalate ester and resolved *via* the brucine salt according to the method of Hill, Kenyon, and Phillips.[21a] The (+)-acid phthalate ester, $[\alpha]^{22}\text{D}$ +22.2 ± 0.2° (*c* 4, $CHCl_3$), which is estimated to be 58% optically pure,[23] was reduced with lithium aluminum hydride in ether to give (+)-*trans*-3-penten-2-ol. Treatment of this alcohol with sodium hydride and methyl iodide as described for the racemic alcohol gave (−)-4-methoxy-2-pentene, $[\alpha]^{23}\text{D}$ −54.2° (*c* 3, $CHCl_3$).

2-Methoxypentane. The procedure and apparatus used to effect catalytic hydrogenation of 4-methoxy-2-pentene to 2-methoxypentane was that described by Brown and Brown.[37] In the reaction flask (B) was placed 35 ml of ethanol, 1 ml of 5% chloroplatinic acid, and 1 g of activated charcoal. In the generator flask (A) was placed 10 ml of 1.0 *M* sodium borohydride, 1 *M* in sodium hydroxide. The system was purged with nitrogen. Basic sodium borohydride solution (5 ml, 1 *M*) in ethanol and 0.7 ml of glacial acetic acid were injected separately into B while the contents were stirred magnetically. Concentrated hydrochloric acid (10 ml) was injected into A which effectively replaced nitrogen with a hydrogen atmosphere. Into B was injected 3.0 g of 4-methoxy-2-pentene. As hydrogen was absorbed, sodium borohydride solution was automatically drawn into A as required. After about 10 hr the theoretical amount of borohydride solution had been consumed. The contents of B were filtered into 50 ml of 5% sodium carbonate solution and extracted with 50 ml of ether. The ether extract was washed repeatedly with water, dried, and distilled. Distillation through a 9-in. column packed with metal helices gave, after removal of the solvent, 1.38 g of 2-methoxypentane, **11**, bp 88–89°. The nmr spectrum of this product showed *no* vinyl resonances. The O-methyl singlet was superimposed on the one-proton methine resonance at 3.4 ppm; a methyl doublet was evident at 1.12 ppm, and the remaining signals were complex multiplets in the region 0.7–1.6 ppm.

Catalytic hydrogenation (by the procedure described above) of (−)-**10**, $[\alpha]\text{D}$ −54.2° (*c* 3, $CHCl_3$), obtained by methylation of (+)-*trans*-3-penten-2-ol, gave (+)-**11**, $[\alpha]\text{D}$ +9.9° (*c* 5, $CHCl_3$). Catalytic hydrogenation of an 82:18 *trans–cis* mixture of (−)-**10**, $[\alpha]^{23}\text{D}$ −5.33° (*c* 33, Et_2O), obtained by borohydride reduction of (−)-**8**, gave (+)-**11**, $[\alpha]^{24}\text{D}$ +1.2° (*c* 11, $CHCl_3$).

---

[36] E. R. Coburn, "Organic Syntheses," Coll. Vol. III, John Wiley & Sons, Inc., New York, N. Y., 1955, p 696.

[37] C. A. Brown and H. C. Brown, *J. Org. Chem.*, 31, 3989 (1966).

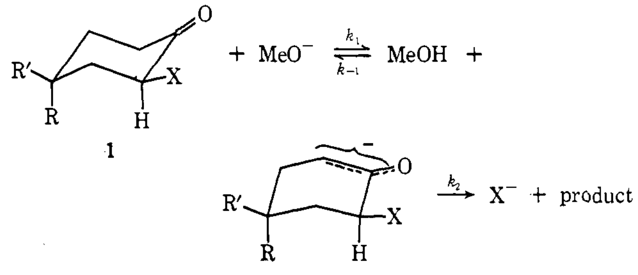
Lack of Steric Hindrance and of Stereoelectronic Control in Proton Removal from 4,4-Disubstituted Cyclohexanones

F. G. Bordwell and Richard G. Scamehorn[1]

Contribution from the Department of Chemistry, Northwestern University, Evanston, Illinois 60201. *Received April 13, 1968*

Abstract: Comparison of the rates of base-catalyzed deuterium exchange at the α positions of 4,4-diphenyl-, 4-methyl-4-phenyl-, and 4,4-dimethylcyclohexanones with that of cyclohexanone itself failed to reveal steric hindrance to proton abstraction by the 4-axial substituents. Since the original evidence for stereoelectronic control in proton abstraction is based on the assumption that the steric effect of a 4-axial substituent is substantial, these results cast doubt on the importance of this factor.

The kinetic data presented in an earlier paper[2] revealed a sizable rate retardation for Favorskii reactions of 2-chloro-4,4-disubstituted cyclohexanones relative to 2-chlorocyclohexanone itself. From studies of deuterium exchange and Br/Cl leaving group effects it was concluded that the reactions proceeded by loss of halide ion from an enolate ion rather than by a concerted 1,3 elimination of a hydrogen and a halogen atom.



1

2

The rate retardation was found to be associated with the presence of the axial group, since the rate for 2-chloro-4-phenylcyclohexanone was not retarded. Two explanations for this axial effect are possible: (a) the axial group interferes in some way with the loss of X^- (k_2 and k_{obsd}) will then decrease relative to 2-chlorocyclohexanone), or (b) the axial group causes a shift in the equilibrium resulting in a lower concentration of enolate ion (k_{obsd} will then decrease since $k_{obsd} = K_{eq}k_2$). Shift of the **1** ⇄ **2** equilibrium away from **2** conceivably could result from a decrease in k_1 caused by steric hindrance to removal of the C-6 axial proton from **1**. In fact, it has been suggested that a similarly

---

[1] National Institutes of Health Predoctoral Fellow, 1966–1968.

[2] F. G. Bordwell, R. R. Frame, R. G. Scamehorn, J. G. Strong, and S. Meyerson, *J. Amer. Chem. Soc.*, 89, 6704 (1967).