(60.0 mmol) of methyl iodide and 0.84 g (0.12 g-atom) of lithium in 48 ml of ether. To the methyllithium was added dropwise over a period of 15 min a solution of 1.00 g (4.00 mmol) of **19** in 5 ml of ether, and the solution was heated at reflux for 2 hr. The yellow oil obtained upon work-up was heated at reflux with a solution of 0.17 ml of hydrochloric acid in 17 ml of absolute methanol for 2 hr. Ketone **22** (785 mg, 90%) was isolated as previously described for **20**. An analytical sample was obtained by preparative glpc (column B, 164°): $n^{25}D$ 1.5260; ν_{max} 1683, 1663 (split carbonyl), 1599 (conjugated C=C bond), 1379, 1283, 1205, 997, and 840 cm^{-1}; τ 4.64 (m, 1 H), 7.98 (s, 3 H), 8.22 (s, 3 H), 8.77 (s, 3 H), and 9.26 (d, 3 H, J = 6.8 Hz).

Anal. Calcd for $C_{15}H_{22}O$: C, 82.52; H, 10.16. Found: C, 82.21; H, 10.25.

Preparation of 22 from Enol Ether 23. The enol ether **23** (100 mg, 0.38 mmol) in 2 ml of ether was added to a solution of methyllithium prepared from 0.14 g (0.020 g-atom) of lithium and 1.42 g (10.0 mmol) of methyl iodide in 7 ml of ether. The resulting solution was heated at reflux for 4.5 hr, cooled and poured into 10 ml of ice-cold 10% ammonium chloride which was then extracted with ether. The ether solution was washed with water, dried over sodium sulfate, and evaporated to give an oil which shows a band at 3410 cm^{-1} but no carbonyl band in its infrared spectrum. The oil was then heated at 80° under nitrogen for 1.7 hr with a solution of 1.0 ml of methanol, 0.50 ml of water, and 0.015 ml of hydrochloric acid. The reaction mixture was extracted with ether. The ether solution was washed with saturated sodium carbonate and then water, dried over sodium sulfate, and evaporated. The resulting oil was purified by preparative glpc (column D, 171°) to give 45 mg (54%) of **22** which was identical with that obtained by the previous procedure.

4-*epi*-Calarene (25). To a stirred solution of 75 mg (0.073 ml, 1.5 mmol) of 99–100% hydrazine hydrate in 0.20 ml of absolute ethanol at 0–5° was added dropwise over a period of 15 min a solution of 327 mg (1.50 mmol) of **22** in 0.50 ml of absolute ethanol also at 0–5°. The resulting solution was heated at mild reflux under nitrogen for 1.9 hr. Solvent was then thoroughly removed under reduced pressure. To the remaining viscous oil was added 30 mg of powdered potassium hydroxide[30b] and the mixture was heated at 245–255° under nitrogen for 1.8 hr. Glpc analysis (column A, 130°, 200 ml/min) of the resulting yellow oil (300 mg) revealed it to be at least 95% one peak. This peak was collected by preparative glpc (column B, 133°) to give 151 mg (49%) of a colorless oil. An analytical sample was obtained by preparative glpc (column E, 142°). The mass spectrum of this sample showed the parent ion at *m/e* 204.

Anal. Calcd for $C_{15}H_{24}$: C, 88.16; H, 11.84. Found: C, 88.21; H, 11.78.

The nmr spectrum of the product revealed that it was a 3:1 mixture of two compounds. The minor component **26** has nmr absorptions at τ 4.69 (m), 8.66, 8.84, 8.99 (s), 9.04 (d, J = 6–7 Hz), 9.45 (m). The major componen **25** was obtained pure by collecting only the first half of the peak on the above mentioned preparative SE-30 column. The collected material solidified, and three recrystallizations from methanol gave a white solid: mp 60.5–62°; ν_{max} 1667, 1372, 1142, 1126, 1067, 1029, 1014, 976, and 960 cm^{-1}. The nmr spectrum of **25** has a one-proton multiplet at τ 4.69, a three-proton singlet at 8.75, and two singlets at 8.96 and 9.04 which together integrate as 9 protons (C-4 methyl and two geminal methyls). The 100-MHz nmr spectrum shows that these two singlets hide a doublet at τ 9.00 (J = 6.8 Hz). The two cyclopropane protons appear as a multiplet with the major peak at τ 9.61 and other peaks at τ 9.33 and 9.76. The mass spectrum of **25** was essentially identical with that of the mixture of **25** and **26**.

Acknowledgments. We wish to thank the National Institutes of Health for partial support of this research. We are also grateful to the National Science Foundation for providing a traineeship to J. E. S. and funds used in the purchase of the 100-MHz nmr spectrometer.

Molecular Rearrangements. XI.[1] The Synthesis and Neat, Thermal Rearrangement of (+)-(1*R*,3*R*)-2-Chloronorbornene *exo*-Oxide

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Contribution from the Department of Chemistry, Kansas State University, Manhattan, Kansas 66502. *Received March 9, 1970*

Abstract: The synthesis of (+)-(1*R*,3*R*)-2-chloronorbornene *exo*-oxide (**1**) *via* (+)-(1*R*,2*R*)-*exo*-2-norborneol and (−)-(1*R*)-norcamphor is reported. Neat, thermal rearrangement of **1** is found to proceed by >90% chlorine migration to yield (−)-(1*R*,3*R*)-*exo*-3-chloronorcamphor (**2a**), the major rearrangement product. This result together with product stability studies and hydrogen chloride and hydrogen bromide catalyzed rearrangements of this α-chloro epoxide is argued to be supportive evidence for the intermediacy of α-ketocarbonium ion–chloride ion pairs in these rearrangements.

Our results from the neat, thermal rearrangement of the mixture of 1-chloro-*cis*- and -*trans*-4-methylcyclohexene oxide where stereospecific chlorine migration is observed in the formation of *trans*-2-chloro-4-methylcyclohexanone led us to suggest that an α-ketocarbonium ion–chloride ion pair was the intermediate in this molecular rearrangement.[3] The product studies from neat, thermal rearrangement of 2-chloronorbornene *exo*-oxide (**1**),[4] while establishing Wagner–Meerwein rearrangement as a major process, fell short of the desired corroboration of the idea of such ionic intermediates. The major products of neat, thermal rearrangement of **1** are *exo*-3-chloronorcamphor (**2**) and *exo*-2-chloro-7-ketonorbornane (**3**) and the formation of **2** could be explained by either chlorine migration *via* the 3-ketonorborn-2-yl cation–chloride ion pair (**1** → **2a**) or by a hydride shift (**1** → **2b**).[5]

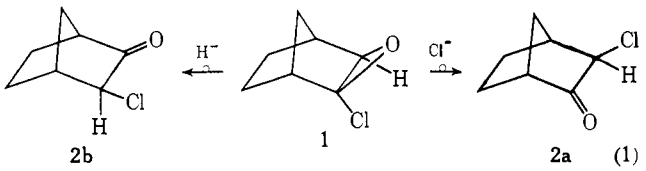
(1) (a) A portion of this work was previously communicated: R. N. McDonald and R. N. Steppel, *J. Amer. Chem. Soc.*, **91**, 782 (1969); (b) for paper X in this series see R. N. McDonald and D. G. Hill, *J. Org. Chem.*, **35**, 2942 (1970).

(2) NDEA Fellow, 1964–1967; NSF Cooperative Fellow, 1967–1968; taken from the Ph.D. Thesis of R. N. Steppel.

(3) R. N. McDonald and T. E. Tabor, *J. Amer. Chem. Soc.*, **89**, 6573 (1967).

(4) R. N. McDonald and T. E. Tabor, *J. Org. Chem.*, **33**, 2934 (1968).

(5) For a flowsheet of some possible pathways and intermediates for the neat, thermal and the hydrogen chloride and acetic acid catalyzed rearrangements of **1** see ref 4.



2b 1 2a (1)

Although most published evidence in the norbornyl system argues against the involvement of 3,2-*endo* hydride shifts[6] even under "favorable conditions,"[6b] the results from the pinacol rearrangement of *endo*-3-phenylbornane-2,3-*exo*,*cis*-diol[7] requires this type of process. Collins and Harding[8a] have recently shown that 3,2-hydride shifts in the norbornyl system under solvolytic conditions occur more easily than previously thought;[6a,8b] whether this involves 3,2-*exo* and/or 3,2-*endo* hydride shifts is as yet unanswered.

As we can see in the pathways leading from **1** to **2** (eq 1), optical activity should be a convenient probe to determine the migrating species since chlorine migration yields one enantiomer of **2**, **2a**, while hydride shifts produce the other enantiomer, **2b**. It should be pointed out that there are two possible modes of hydride shifts to be considered: (1) the 3,2-*endo* hydride shift and (2) multiple hydride shifts involving the 6,2-*endo*,5,6-*exo* and 3,5-*endo* shifts, both of which lead to **2b**. To determine the extent of chloride *vs.* hydride migrations we report here the synthesis and neat, thermal rearrangements of (+)-(1*R*,3*R*)-2-chloronorbornene *exo*-oxide (**1**).

Synthesis of (+)-(1*R*,3*R*)-2-Chloronorbornene *exo*-Oxide (1). Our entry into the synthesis of **1** began with preparation of optically active diisopinocampheylborane (**4**)[9] by the hydroboration of 1-α-pinene with $[\alpha]D^{25}$ −54.9° (*c* 2.0, ethanol).[10] Borane **4** was allowed to hydroborate asymmetrically norbornene. Oxidation with alkaline hydrogen peroxide afforded a mixture of isopinocampheol and *exo*-norborneol which was converted to a mixture of the corresponding acetates by treatment with acetic anhydride and pyridine. Distillation gave optically active *exo*-norbornyl acetate (**5**) in 59% yield.

Lithium aluminum hydride reduction of acetate **5** gave (+)-(1*R*,2*R*)-*exo*-norborneol[12] (**6**) ($[\alpha]D^{27.5}$ +2.78 ± 0.18°, *c* 10.0, $CHCl_3$)[13] in 96% yield. An estimate of the optical purity of **6** can be made from the calculated value determined by Berson and Suzuki[14] of $[\alpha]D$ +2.85–+3.02°, from isotope dilution studies. Using the average of their values, $[\alpha]D$ +2.93, and the maximum deviations in our specific rotation, we conclude that the alcohol **6** so obtained is 88–100% optically pure with a value of 95% optical purity corresponding to the average.

Oxidation of **6** with Jones reagent[15] afforded (−)-(1*R*)-norcamphor[12] (**7**) ($[\alpha]D^{27}$ −18.19 ± 0.27°, *c* 3.07, $CHCl_3$)[13] in 77% yield. The optical purity of **7** was 63% based on the average calculated value for optically pure norcamphor.[12b,16] A similar loss of optical purity was observed in the potassium dichromate–sulfuric acid oxidation of "fully resolved" *exo*-norborneol which gave norcamphor of lower specific rotation than that obtained from less fully resolved *endo*-norborneol.[17] This was ascribed to the faster rate of racemization of *exo*-norborneol in the acidic media prior to oxidation. It was also reported that *exo*-norbornyl acetate can be completely racemized in the presence of *p*-toluenesulfonic acid while *endo*-norbornyl acetate is unaffected.[18] In contrast to this, however, Berson[12a] reported that Oppenauer and Jones oxidations of 1-methyl-*exo*-2-norborneol proceeded without racemization. Also, the use of Sarett's reagent is reported to oxidize *exo*-norborneol to norcamphor without loss of optical purity.[19]

Treatment of **7** with a mixture of phosphorus trichloride and phosphorus pentachloride gave (−)-(1*R*)-2,2-dichloronorbornane (**8**)[20] ($[\alpha]D^{27}$ −9.44 ± 0.37°, *c* 2.097, $CHCl_3$)[13] in 78% yield. To determine whether or not racemization had occurred during this reaction, *gem*-dichloride **8** was hydrolyzed with sodium hydroxide in aqueous methanol. Glpc analysis showed the presence of 2-chloronorbornene and norcamphor in a ratio of 21:79. The norcamphor was isolated by repeated sublimations in 54% yield and was found to have $[\alpha]D^{27}$ −17.83 ± 1.23° (*c* 1.154, $CHCl_3$)[13] showing that no racemization had taken place in the **7** → **8** conversion.

Reaction of **8** with potassium *t*-butoxide in refluxing *t*-butyl alcohol[21] produced (−)-(1*R*)-2-chloronorbornene (**9**) in 88% yield. Epoxidation of **9** with *m*-chloroperbenzoic acid[4] gave (+)-(1*R*,3*R*)-2-chloronorbornene *exo*-oxide (**1**) in a yield of 64%. Neither **9** or **1** were converted to compounds of known optical purity by reactions proven to maintain stereochemical and optical integrity. Although it appears remote, it is unknown whether or not additional losses in optical purity occurred during these last two steps of the synthesis of **1**.

Results of the Neat, Thermal Rearrangement of 1. In order to determine the extent of chlorine migration in the neat, thermal rearrangement of **1**, one of the enantiomers of *exo*-3-chloronorcamphor, **2a** or **2b**, had to be synthesized with known absolute configuration and optical purity. To achieve this, ketone **7** was allowed to react with sulfuryl chloride[4] to give a 79% yield of (−)-

(6) (a) M. Saunders, P. von R. Schleyer, and G. A. Olah, *J. Amer. Chem. Soc.*, **86**, 5680 (1964); (b) J. A. Berson, J. H. Hammons, A. W. McRowe, R. G. Bergman, A. Remanick, and D. Houston *ibid.*, **89**, 2590 (1967); (c) C. J. Collins, Z. K. Cheema, R. G. Werth, and B. M. Benjamin, *ibid.*, **86**, 4913 (1964).

(7) A. W. Bushell and P. Wilder, *ibid.*, **89**, 5721 (1967).

(8) (a) C. J. Collins and C. E. Harding, *ibid.*, **91**, 7194 (1969); (b) G. A. Olah and A. M. White, *ibid.*, **91**, 3956 (1969).

(9) H. C. Brown, N. R. Ayyangar, and G. Zweifel, *ibid.*, **86**, 397 (1964).

(10) This is the largest specific rotation reported for α-pinene, the previous high being $[\alpha]^{20}D$ −54.04° (*c* 4.0, ethanol).[11]

(11) F. H. Thurber and R. C. Thiele, *ibid.*, **53**, 1030 (1931).

(12) The absolute configurations of (−)-*exo*-norborneol and (+)-norcamphor have been assigned as 1*S*,2*S*, and 1*S*, respectively, both by (a) their relationship to terpenes of known absolute configuration (J. A. Berson, J. S. Walia, A. Remanick, S. Suzuki, P. Reynolds-Warnhoff, and D. Willner, *ibid.*, **83**, 3986 (1961)) and (b) by ORD studies (K. Mislow and J. G. Berger, *ibid.*, **84**, 1956 (1962)).

(13) All rotations are averages from at least six (generally ten) readings using a Rudolph Model 80 polarimeter. The error given is the maximum deviation from the average. Most readings centered around the average value. The confidence limits are at the 95% level.

(14) J. A. Berson and S. Suzuki, *J. Amer. Chem. Soc.*, **81**, 4088 (1959).

(15) E. R. H. Jones, K. Bowden, I. M. Heilbron, and B. C. Weedon, *J. Chem. Soc.*, 39 (1946); E. R. H. Jones, A. Bowers, T. G. Halsall, and A. T. Lemin, *ibid.*, 2548 (1953).

(16) J. A. Berson and A. Remanick, *J. Amer. Chem. Soc.*, **86**, 1749 (1964).

(17) S. Winstein and D. Trifan, *ibid.*, **74**, 1154 (1952).

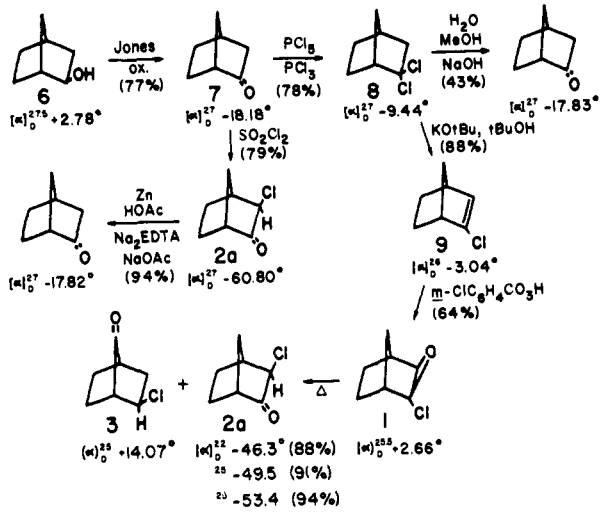
(18) S. Winstein and D. Trifan, *ibid.*, **74**, 1147 (1952).

(19) J. P. Schaefer and D. S. Weinberg, *J. Org. Chem.*, 30, 2635 (1965).

(20) R. L. Bixler and C. Niemann, *ibid.*, 23, 742 (1958).

(21) N. A. LeBel, P. D. Beirne, E. R. Karger, J. C. Powers, and P. M. Subramanian, *J. Amer. Chem. Soc.*, **85**, 3199 (1963).

Scheme I. Synthesis and Neat, Thermal Rearrangement Results from (+)-(1*R*,3*R*)-2-Chlorononbornene *exo*-Oxide (**1**)



(1*R*,3*R*)-*exo*-3-chlorononcamphor (**2a**), the enantiomer corresponding to chlorine migration from rearrangement of **1**. The absolute configuration of **2a** was verified as 1*R*,3*R* from its circular dichroism curve (Figure 1). To show that no racemization occurred in this

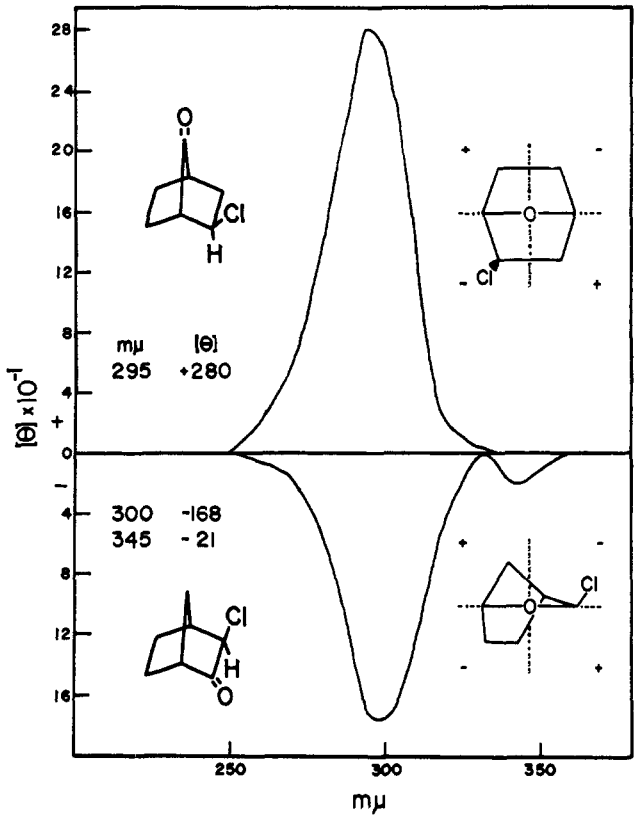


Figure 1. The CD curves of (+)-*exo*-3-chloro-7-ketonorbornane (**3**) (upper) and (−)-*exo*-3-chlorononcamphor (**2**) (lower).

chlorination step, α-chloro ketone **2a** was reduced with zinc in a mixture of acetic acid, sodium acetate, and disodium ethylenediaminetetraacetate to **7**[22] ($[\alpha]D^{27}$ −17.82 ± 1.22°, *c* 1.198, $CHCl_3$).[13] This means that both **7** and **2a** have the same optical purity, 63%.[23]

The neat, thermal rearrangements of **1** were carried out in a distillation flask under a semimicro, platinum spinning band column at 5 mm pressure with a bath temperature of 80°.[4] These rearrangements are very sensitive to a number of factors including the "preparation" of the column (see Experimental Section). The products of three rearrangements were trap-to-trap distilled to remove them from nonvolatile materials. In each case the volatile products correspond to about 30–50% of the weight of the starting material. The major product of rearrangement, *exo*-3-chlorononcamphor (**2**), was separated and collected by glpc from each run and the specific rotations were determined: run 1, $[\alpha]D^{22}$ −46.3 ± 1.1°;[13] run 2, $[\alpha]D^{25}$ −49.5 ± 2.0°;[13] run 3, $[\alpha]D^{25}$ −53.4 ± 1.8°.[13] These average values correspond to 88, 91, and 94% chlorine migration in these three determinations based on $[\alpha]D^{27}$ −60.8° of **2a** as 100%. We hasten to point out that run 2 above may have involved a catalyzed rearrangement since it was complete in an extremely short time, 1 hr. However, the ratio of **2**:**3** from run 2 was the same as observed in other neat, thermal rearrangements of **1**, as were the approximate amounts of the other products. (See below for discussion of HCl and HBr catalyzed rearrangements.)

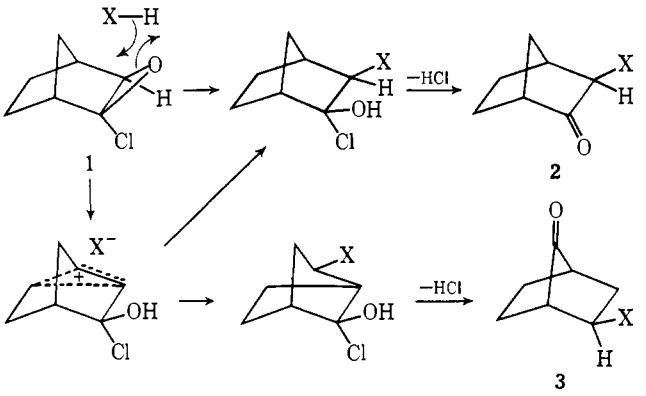
The major process occurring in these rearrangements of **1** is thus established as chlorine migration. It should be noted that these are minimum values since any loss in optical activity in the last two steps in the preparation of **1**, elimination and epoxidation, would increase the amount of chlorine migration.

To ensure the validity of these results, the stabilities of the principal rearrangement products from racemic **1**, *exo*-3-chlorononcamphor (**2**), *exo*-2-chloro-7-ketonorbornane (**3**), *endo*-3-chlorononcamphor (**10**), and 3,3-dichloro-*exo*-2-norborneol (**11**) to thermal and acid-catalyzed conditions were checked. Both **10** and **11** could possibly yield **2**. No change in composition of any of these four compounds was noted after being heated at 80° for 56 hr in tubes sealed at 5 mm pressure or in the presence of 5 mm of hydrogen chloride. α-Chloro ketone **10** (10% by weight) was mixed with racemic **1** and subjected to the conditions for rearrangement. Glpc analysis of the product indicated 20% of **10** was present compared to 2% of **10** in a control rearrangement. The percentage of **2** in this rearrangement had not increased but actually had decreased slightly compared to that of the control.

An acid-catalyzed mechanism had been suggested (ref 1a, footnote 16) for the rearrangement of **1** to **2a** and **3** which is shown below. This prompted us to test this suggestion by investigating the acid-catalyzed, thermal rearrangements of racemic **1** using anhydrous hydrogen chloride and hydrogen bromide. We felt that hydrogen bromide should be a stronger acid and more soluble than hydrogen chloride. The rearrangements were carried out as described above, but with a very slow, continuous bleed of gaseous hydrogen halide being introduced under the surface of the α-chloro epoxide. Surprisingly, although an increased rate of

(22) R. N. McDonald and C. E. Reineke, *J. Org. Chem.*, **32**, 1888 (1967).

(23) An error in this absolute value is of no consequence in determining the per cent chlorine migration since ketone **7** is the common precursor to **1** and **2a**.



rearrangement was observed with hydrogen chloride, the products and their distribution did not change appreciably compared to the uncatalyzed rearrangements.[24]

Under conditions where *exo*-3-bromonorcamphor (**12**) and *exo*-2-bromo-7-ketonorbornane (**13**), the products expected from bromide ion capture, were well separated from the normal products of neat, thermal rearrangement of **1**, glpc analysis of the rearrangement products from three runs employing hydrogen bromide catalysis indicated a maximum of 1.0% of **12** and 1.8% of **13**. The average from three runs was 0.4% of **12** and 0.6% of **13**, and their presence was only ascertained from their retention time comparisons. This evidence not only denies the above suggested pathways but also denies the presence of some other asymmetric intermediates, such as 2-chloro-2-hydroxynortricyclane, in the rearrangement.

The Absolute Configuration of (+)-*exo*-2-Chloro-7-ketonorbornane (3). From the rearrangements of **1** we also isolated the second major rearrangement product **3** in optically active form. Application of the octant rule to this molecule predicted that the circular dichroism curve should be negative for the 1*R*,2*R* configuration of **3**. However, the experimentally determined curve was positive (Figure 1). This indicated that we may have produced the 1*S*,2*S* configuration which is opposite to that expected from mechanistic considerations assuming that no unprecedented processes occur.[4] Several unsuccessful attempts were made[2] to convert **2** and **3** to *exo*-2-chloronorbornane (**14**) for a direct comparison of the signs of the specific rotations of **14** produced from each chloro ketone.

A solution to this problem is available from the report by Snatzke and Eckhardt[25] who found "anti-octant" behavior in the circular dichroism curves of several β-substituted adamantanones when the substituent (included chloride, bromide, iodide, azide, and alkyl carboxylate) is in an axial relationship to the carbonyl group. Models of axial β-chloroadamantanone and **3** demonstrated that the stereopositions of the carbonyl and halogen groups are nearly identical. From this argument we conclude that **3** shows "anti-octant" behavior and that the absolute configurations of (+)-**3** is 1*R*,2*R*.

(24) This point may bear on run 2 of the rearrangement of **1** previously mentioned.

(25) G. Snatzke and G. Eckhardt, *Tetrahedron*, 24, 4543 (1968). We wish to thank Dr. Snatzke for informing us of certain of his data and conclusions prior to publication.

Discussion

The principal reason for carrying out the present study was to seek further information about the nature of the intermediate(s) involved in the epoxide–carbonyl rearrangement of α-chloro epoxides through additional examples. The results for the neat, thermal rearrangement of **1** establish that >90% of the formation of *exo*-3-chloronorcamphor (**2**), the major rearrangement product, involves chlorine migration. Although halogen (fluorine, chlorine, bromine) migration has been observed as the exclusive or predominant process in most thermal, uncatalyzed and many catalyzed rearrangements of α-halo epoxides,[26] the present results and those of the stereospecific formation of *trans*-2-chloro-4-methylcyclohexanone (**15**) from neat, thermal rearrangement of a mixture of 1-chloro-*cis*- (**16**) and -*trans*-4-methylcyclohexene oxide (**17**)[3] appear to be of greatest mechanistic significance.

Let us consider the results from the rearrangements of **1** and of **16** and **17** with the "reasonable" assumption that the same general mechanistic features of rearrangement are present in both systems. In these studies we have found that (1) chlorine is the principal (or exclusive) migrating group, (2) rearrangement is protonic and Lewis acid catalyzed, and (3) carbon–chlorine bond formation is highly stereoselective from **1** and stereospecific from **16** and **17** (*exo vs. endo* and axial *vs.* equatorial, respectively).[27] Both studies equally well dispatch the idea of involvement of three-membered ring chloronium ion since in each study the chlorine must migrate from one face of the molecule in the starting α-chloro epoxide to another in the product(s).

Of major importance from the present research is the conclusion that the 1*R*,3*R* configuration of **1** yields the 1*R*,3*R* and 1*R*,2*R* configurations of **2** and **3**, respectively, the major rearrangement products, which are related to one another by Wagner–Meerwein rearrangement. We believe that these isomers, which are stable to the rearrangement conditions, are formed from a common intermediate and support our previous suggestion of the intermediacy of α-ketocarbonium ion–chloride ion pairs in these rearrangements. In the specific case of the rearrangement of **1** we propose that the 3-keto- and the 7-keto-2-norbornyl cations (or their nonclassical counterpart) are involved. From the lack of significant exchange with bromide ion in the hydrogen bromide catalyzed rearrangements it appears not only that these ion pairs are reasonably tight but that the chlorine migration is intramolecular.[28]

α-Ketocarbonium ions have been recently reported to be intermediates in the acid-catalyzed hydrolyses of secondary α-diazo ketones (A-Se2) while primary α-diazo ketones are hydrolyzed by preequilibrium protonation followed by rate-determining attack by the nucleophile (A-2).[30] The two studies of acid-catalyzed

(26) R. N. McDonald in "Mechanisms of Molecular Migrations," Vol. 3, B. S. Thyagarajan, Ed., Interscience, New York, N. Y., in press.

(27) Although both **2** and its *endo* isomer are formed in the rearrangement of **1** in a ratio of 37.4:4.3 we find no evidence for the formation of *endo*-2-chloro-7-ketonorbornane, the epimer of **3**.

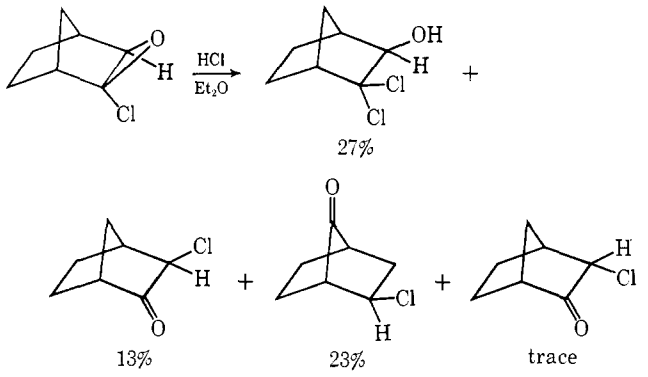
(28) This point of intramolecularity of Cl^- migration has been previously argued for by analogy with the similar rearrangements of enol ester epoxides[3] which have been shown to be intramolecular.[29]

(29) A. L. Draper, W. J. Heilman, W. E. Schaefer, H. J. Shine, and J. N. Shoolery, *J. Org. Chem.*, 27, 2727 (1962). See also footnote 26, ref 3.

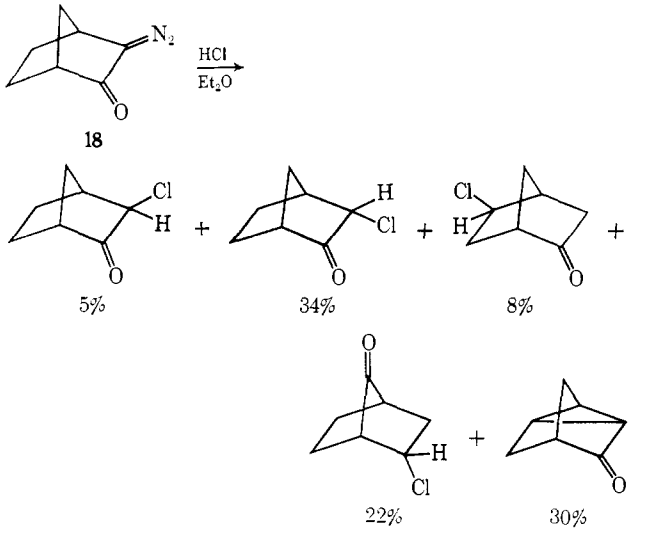
(30) H. Dahn, H. Gold, M. Ballenegger, J. Lenoir, G. Diderich, and R. Malherbe, *Helv. Chim. Acta*, 51, 2065 (1968).

decompositions of α-diazonorcamphor (**18**)[31] differ so greatly in the nature of their products that little can be learned about the structures of the intermediates; product formation appears to be largely dependent on reaction media and conditions. However, it is of interest to note that of the 3-hydroxynorcamphor[31] and 7-keto-2-norborneol[31b] isolated from these catalyzed hydrolyses the *endo* isomers were predominant.

The single set of conditions which appears to be similar in reactions of **1** and **18** involves hydrogen chloride in ether. From racemic **1**[4] the composition of the product from this reaction was



while the distribution of the ketonic products reported from **18**[31b] was



It is obvious that the distributions of the halo ketones from **1** and **18** are very different. This is not too surprising since different approaches to the "same" carbonium ion, *e.g.*, solvolysis of a tosylate and deamination of an amine, can often lead to quite different results which may be a function of the energy of the carbonium ion produced by each approach.[32] Also, the α-ketocarbonium ion generated from α-chloro epoxide **1** will be formed by an *exo*-bond heterolysis while **18** will most probably protonate from the *exo* face and the α-ketocarbonium ion will be produced by *endo* loss of nitrogen; this factor may be important in the energy state of the intermediate cation, or in solvent intervening, as separation of the nitrogen molecule occurs from the *endo*-alkyldiazonium ion (similar to solvent-separated ion pairs).

The major objection to an α-ketocarbonium ion has been expressed as the "obvious" inductive and resonance destabilization of the carbonium ion center by the attached carbonyl group ($C^+—C=O \leftrightarrow C^+—C^+—O^-$), a direct result of the normal polarity of the carbonyl group due to the difference in the electronegativities of carbon and oxygen. However, in an α-ketocarbonium ion the electronegativity comparison does not involve a neutral sp^3 or a more electronegative, neutral sp^2 hybridized carbon (as in saturated or α,β-unsaturated carbonyl compounds) attached to the carbonyl, but an sp^2 hybridized carbon bearing a formal positive charge. This should result in the back-donation of electron density from the carbonyl π system to the carbonium ion center. In support of this postulate, Dr. Wayne Danen has run HMO calculations using a "damped" ω technique for an α-ketocarbonium ion and found a total π energy of 4.336β and a C=C π-bond order of 0.5390. Although admittedly crude when compared to more sophisticated programs, these results indicate stabilization of the carbonium ion center by the carbonyl group.

Experimental Section[33]

(−)-(1*R*,2*R*)-*exo*-Norbornyl Acetate (5).[34] 1-α-Pinene [110.0 g, 0.808 mol; distilled from calcium hydride, bp 153–154°; $[\alpha]^{25}D$ −54.9° (*c* 2.0, ethanol)] (Columbia Chemicals Co., Inc.) was added to a solution of 11.6 g (0.307 mol) of sodium borohydride in 400 ml of diglyme (distilled from calcium hydride). Boron trifluoride etherate (57.4 g, 0.404 mol; bp 122–123°) was added dropwise to the stirred solution at 0°. Stirring was continued for 3.5 hr at 0–5°. A solution of 44.0 g (0.467 mol) of norbornene in 100 ml of dry diglyme was added slowly maintaining the temperature below 7°. The reaction mixture was stirred at 0–5° for an additional 5 hr and then overnight at room temperature. To this mixture 22 ml of 3 *N* sodium hydroxide was added followed by the dropwise addition of 180 ml of 30% hydrogen peroxide with the reaction temperature maintained at 40–45°. After the addition was complete stirring was continued for 2 hr. The reaction mixture was poured into 2 l. of water and extracted with ether. The combined extracts were washed with water and dried over sodium sulfate. The ether was removed by distillation (Vigreux column) and the residue, approximately 200 ml, was treated with 200 ml of dry pyridine and 270 g of acetic anhydride. After standing overnight the reaction mixture was poured onto 2 l. of ice, extracted with ether, and the ether extracts washed with sodium bicarbonate solution and water. After drying (Na_2SO_4), the ether was distilled (36-in. spinning band column) followed by the pyridine (bp 41° (106 mm)) and the digylme (bp 51° (14 mm)). The optically active *exo*-norbornyl acetate (42.5 g, 59%) was distilled at 81–82° (14 mm) (lit.[12] bp 77.0–77.5° (14 mm)). Glpc showed diglyme (2%) as the only impurity which was substantiated from the samples nmr spectrum.

(+)-(1*R*,2*R*)-*exo*-Norborneol (6). A solution of 48.0 g (0.31 mol) of optically active acetate **5** in 100 ml of dry ether was added dropwise to a stirred suspension of 12.1 g of lithium aluminum hydride in 3 l. of ether at room temperature. After the addition was complete the mixture was heated under reflux for 11.5 hr. A 40-ml aliquot was removed, hydrolyzed with ice, and the ether layer dried ($MgSO_4$). Glpc analysis of this sample indicated that the reduction was only 79% complete. An additional 3.0 g of lithium aluminum hydride was added to the original mixture, as was the aliquot, and heating under reflux was continued for 4 hr. An ice–water mixture was added to the mixture in small portions until gas evolution ceased. The majority of the ether layer was

(31) (a) P. Yates and R. J. Crawford, *J. Amer. Chem. Soc.*, **88**, 1561 (1966); (b) M. Hanack and J. Dolde, *Tetrahedron Lett.*, 321 (1966).

(32) E. J. Corey and R. L. Dawson, *J. Amer. Chem. Soc.*, **85**, 1782 (1963).

(33) All melting points were taken on a Kofler hot stage and are corrected. Boiling points are uncorrected. Glpc analyses were performed using an F and M Model 500, temperature programmed, gas chromatograph with thermal conductivity detector.

(34) The procedure reported here was patterned after the asymmetric hydroboration of norbornadiene reported in ref 12b.

decanted and the aqueous layer was acidified with cold, concentrated sulfuric acid. This aqueous layer was then extracted with three 350-ml portions of ether. The combined ether extracts were washed with 5% aqueous sodium bicarbonate, saturated aqueous sodium chloride solution, and dried ($MgSO_4$). The ether was distilled on a Vigreux column and gave 33.5 g (96%) of alcohol **6** after sublimation (50° (6.5 mm)). Glpc analysis showed this product to be pure, mp 126–127° (lit.[12b] mp 125.5–127°), $[\alpha]^{27.5}D$ +2.78 ±0.18° (*c* 10.0, $CHCl_3$).[13]

(−)-(1*R*)-Norcamphor (7). To a solution of 33.1 g (0.295 mol) of (+)-(1*R*:2*R*)-*exo*-norborneol (**6**) in 600 ml of acetone (treated with potassium permanganate and distilled), Jones' reagent[15] was added dropwise until the orange color of the reagent persisted while stirring vigorously and maintaining the temperature between 15 and 25°. This oxidation required approximately 75 ml of the reagent. The reaction mixture was allowed to stir for an additional 15 min and decanted into a separatory funnel containing 200 ml of water. The mixture was shaken vigorously and additional aliquots of water were added until the green chromium salts dissolved. Sodium chloride was added until saturation followed by extraction with three 100-ml portions of ether. The combined extracts were washed with saturated sodium bicarbonate, water, and saturated brine solution, and dried ($MgSO_4$). The solvents were removed by distillation (30-cm Vigreux column) with the last traces removed under reduced pressure leaving a white crystalline product weighing 29.4 g (91%) which showed four components on glpc analysis; norcamphor (94.6%), *exo*-norborneol (0.09%), and two other components totaling 4.5%. Sublimation (50° (20 mm)) gave 24.9 g (77%) of pure (−)-(1*R*)-norcamphor homogeneous to glpc analysis, $[\alpha]^{27}D$ −18.19 ± 0.27° (*c* 3.065, $CHCl_3$),[13] mp 91.0–91.8° (lit.[12a] mp 90–91°).

(−)-(1*R*,3*R*)-*exo*-3-Chloronorcamphor (2a). In a 5-ml flask 2.2 g (0.02 mol) of **7** was heated to 100° and 4.0 g (0.03 mol) of sulfuryl chloride was added dropwise. After heating for 20 min the excess sulfuryl chloride was removed under reduced pressure. Vacuum distillation using a 10-cm Vigreux column afforded 2.30 g (79%) of **2a**, bp 100–102° (10 mm) (lit.[4] bp 85.3° (4.8 mm)). Glpc analysis indicated the sample to be 98.5% pure. A pure sample was glpc collected, $[\alpha]^{27}D$ −60.8 ± 1.6° (*c* 0.816, $CHCl_3$).[13]

Dechlorination of (−)-(1*R*,3*R*)-*exo*-3-Chloronorcamphor (2a). Zinc dust (1.30 g) was added over a period of 5 min to a cold (ice bath) mixture of 1.45 g (0.01 mol) of (−)-(1*R*:3*R*)-*exo*-chloronorcamphor, 3.30 g (0.01 mol) of sodium acetate, 7.5 g (0.02 mol) of disodium ethylenediaminetetraacetate dihydrate, and 14 ml of acetic acid. The mixture was allowed to stir at room temperature for 3 hr and filtered free of unreacted zinc and insoluble salts which were washed with 50 ml of ether. Sodium bicarbonate solution was added to the filtrate until the aqueous layer was basic. The ether was removed and the aqueous layer was continuously extracted with ether. After drying ($MgSO_4$) the ether was removed from the combined extracts by distillation (30-cm Vigreux column). Sublimation gave 1.03 g (93.7%) of (−)-(1*R*)-norcamphor, $[\alpha]^{25}D$ −17.82 ± 1.22° (*c* 1.198, $CHCl_3$)[13] which was >99% pure by glpc.

(−)-(1*R*)-2,2-Dichloronorbornane (8). The procedure employed was essentially that described by Bixler and Niemann.[20] From 8.7 g (79 mmol) of **7**, 18.9 g of phosphorus pentachloride, and 6 ml of phosphorus trichloride, 10.14 g (78%) of dichloride **8** was obtained, bp 74–75° (12 mm) (lit.[20] bp 65–68.1° (12.0–12.4 mm)), $[\alpha]^{27}D$ 9.44 ± 0.37° (*c* 2.097, $CHCl_3$).[13]

Hydrolysis of (−)-(1*R*)-2,2-Dichloronorbornane (8). A solution of 1.59 g (9.6 mmol) of **8**, 0.5 g (12.5 mmol) of sodium hydroxide, 15 ml of methanol, and 10 ml of water was heated under reflux for 13 hr. The acidic reaction mixture was extracted with three 25 ml portions of ether. The combined ether extracts were washed with sodium bicarbonate solution, water, and brine, and dried over magnesium sulfate. Most of the solvent was removed by distillation using a 30-cm Vigreux column. Glpc analysis showed the crude product to consist of 2-chloronorbornene and norcamphorin the ratio of 20.7:79.3, respectively. After further evaporation of solvent, repeated sublimation gave 0.47 g of (−)-(1*R*)-norcamphor (**7**) (54% based on the amount of the *gem*-dichloride converted to the ketone). The optical rotation obtained on a pure sample of **7** so obtained was $[\alpha]^{27}D$ −17.83 ± 1.23° (*c* 1.154, $CHCl_3$).[13]

(−)-(1*R*)-2-Chloronorbornene (9). The procedure used was essentially that described by LeBel for the elimination of hydrogen bromide from *exo,cis*-2,3-dibromonorbornane.[35] From 8.0 g (0.24 g-atom) of potassium dissolved in 150 ml of *t*-butyl alcohol and 16.3 g (99 mmol) of **8** heated under reflux for 40 hr, 11.0 g (88%) of **9** was obtained, bp 72–73° (69 mm), $[\alpha]^{26}D$ −3.40 ± 0.44° (*c* 2.040, $CHCl_3$), which was pure by glpc analysis.

(+)-(1*R*,3*R*)-2-Chloronorbornene *exo*-Oxide (1). The procedure used in the preparation of this compound has been described for the racemic α-chloro epoxide.[4] From 18.18 g (0.144 mol) of **9** and 38.0 g (0.154 mol) of 70% *m*-chloroperbenzoic acid there was obtained 13.33 g (64%) of **1**, bp 41–42° (3.1–3.3 mm), $[\alpha]^{25.5}D$ +2.66 ± 0.17° (*c* 6.442, $CHCl_3$).[13] No extraneous absorptions were present in the nmr spectrum of this compound.

Neat, Thermal Rearrangement of 2-Chloronorbornene *exo*-Oxide and Product Stability Checks. The conditions for neat, thermal rearrangement of 2-chloronorbornene *exo*-oxide in a platinum spinning band distillation column have been described.[4]

Two Vigreux columns were treated with dichromate cleaning solution, ammonium hydroxide, distilled water, and acetone. After air drying, two 10-ml round-bottomed flasks were charged with 1.0 g of 2-chloronorbornene *exo*-oxide and in addition 100 mg of *endo*-3-chloronorcamphor was added to only one flask (sample A, neat epoxide; sample B, epoxide and *endo*-3-chloronorcamphor). The thermal rearrangements were run at a pressure of 5 mm with a bath temperature of 80°. The rearrangements were terminated after 54 hr and the mixtures had turned dark. The columns were rinsed with pentane, the pentane evaporated, and the residues trap-to-trap distilled to give 0.39 and 0.40 g of clear distillate from samples A and B, respectively. Analysis by glpc using a Carbowax 20M column indicated the products (in order of their elution) and their integrated percentages (for samples A and B, respectively) to be as follows: carbon monoxide, 5.6 and 2.3%; cyclohexadiene, 9.7 and 4.1%; unidentified component, 0.3 and 0.1%; 2-chloronorbornene *exo*-oxide, 3.3 and 1.8%; unidentified component, 0.4 and 0.3%; 1-chloro-*syn*-7-hydroxynorbornene, 1.6 and 1.6%; *exo*-3-chloronorcamphor, 46.9 and 42.2%; *exo*-2-chloro-7-ketonorbornane, 28.7 and 27.0%; *endo*-3-chloronorcamphor, 2.0 and 19.9%; and 3,3-dichloro-*exo*-2-norborneol, 0.7 and 1.5%.

Eight glass tubes cleaned in the same manner as the above Vigreux columns were charged with 40–50-mg samples of *exo*-3-chloronorcamphor, *endo*-3-chloronorcamphor, *exo*-2-chloro-7-ketonorbornane, or 3,3-dichloro-*exo*-2-norborneol. The tubes were sealed at a pressure of 5 mm with and without (for each compound) anhydrous hydrogen chloride. The sealed tubes were placed in the 80° bath for 54 hr, allowed to cool to room temperature, and the four tubes which had not been sealed under the 5 mm hydrogen chloride atmosphere were opened carefully and checked with wet indicator paper for hydrogen chloride fumes. All four tubes not sealed with hydrogen chloride gave a negative test for hydrogen chloride. Analysis by glpc (as above) indicated that all of the samples remained unaltered.

Three rearrangements of (+)-(1*R*,3*R*)-2-chloronorbornene *exo*-oxide (**1**) were carried out using the platinum, semimicro spinning band column at 5 mm pressure and a bath temperature of 80°. The amounts of **1** used were 5.0, 3.5, and 1.7 g. The reaction times were 25, 1, and 28 hr and the weights of trap-to-trap distilled products were 2.6, 1.7, and 0.3 g, respectively. The compounds produced and their integrated percentages were as follows for each run, respectively: carbon monoxide (4.6, 6.8, 1.8%); cyclohexadiene (10.3, 15.3, 3.1%); unidentified component (0.9, 1.7, 0.3%); 2-chloronorbornene *exo*-oxide (0.4, 1.7, 1.0%); unidentified component (0.5, 0.3, 0.2%); 1-chloro-*syn*-7-hydroxynorbornane (2.8, 1.6, 2.0%); *exo*-3-chloronorcamphor (45.4, 42.7, 53.5%); *exo*-2-chloro-7-ketonorbornane (27.8, 25.2, 33.5%); *endo*-3-chloronorcamphor (3.3, 2.2, 2.5%); and 3,3-dichloro-*exo*-2-norborneol (4.0, 1.6, 2.0%).

The two major components, (−)-(1*R*:3*R*)-*exo*-3-chloronorcamphor (**2a**) and (+)-(1*R*:2*R*)-*exo*-2-chloro-7-ketonorbornane (**3**), were separated by glpc and collected. The optical rotations of **2a** from the three respective rearrangements were $[\alpha]^{22}D$ −46.3 ± 1.1° (*c* 0.8147, $CHCl_3$),[13] $[\alpha]^{25}D$ −49.5 ± 1.9° (*c* 0.8120 $CHCl_3$),[13] and $[\alpha]^{25}D$ −53.4 ± 1.7° (*c* 0.6894, $CHCl_3$).[13] The optical rotation of **3** obtained from the first run was $[\alpha]^{25}D$ +14.1 ± 1.2° (*c* 0.8282, $CHCl_3$).[13]

Acid-Catalyzed, Thermal Rearrangement of 2-Chloronorbornene *exo*-Oxide. 1. Using Anhydrous Hydrogen Chloride. The first of two runs was carried out in a Vigreux column (treated as above) under the same conditions involved in the neat, thermal rearrangements except that anhydrous hydrogen chloride (contained in a 1-l. glass bulb) was introduced under the surface of the 2-chloronorbornene *exo*-oxide (3.6 g; 0.025 mol) at a rate of approximately

(35) N. A. LeBel, *J. Amer. Chem. Soc.*, **82**, 623 (1960).

1×10^{-6} mol/min which corresponds to approximately 20 bubbles per minute, the rate of hydrogen chloride flow being controlled by a needle valve. After 48 hr the reaction was terminated. Analysis by glpc indicated the presence of the following compounds and their integrated percentages, respectively, in order of their elution: carbon monoxide (2.0%), cyclohexadiene (4.3%), unidentified component (3.5%), 2-chloronorbornene *exo*-oxide (2.3%) 1-chloro-*syn*-7-hydroxynorbornene (3.0%), *exo*-3-chloronorcamphor (49%), *exo*-2-chloro-7-ketonorbornane (29%), *endo*-3-chloronorcamphor (2.3%), and 3,3-dichloro-*exo*-2-norborneol (3.9%).

The second run was made using a semimicro, platinum spinning band column which had been treated with nitric acid, ammonium hydroxide, water, and acetone. After air drying, the rearrangement was carried out as above with 3.6 g (0.025 mol) of 2-chloronorbornene *exo*-oxide. After 96 hr the reaction was terminated. Analysis of the 1.0-g product mixture by glpc indicated the presence of the following compounds and their integrated percentages, respectively, in the order eluted: carbon monoxide (0.6%), cyclohexadiene (1.0%), unidentified component (1.3%), 2-chloronorbornene *exo*-oxide (1.0%), unidentified component (1.3%), 1-chloro-*syn*-7-hydroxynorbornene (2.0%), *exo*-3-chloronorcamphor (52.6%), *exo*-2-chloro-7-ketonorbornane (38%), *endo*-3-chloronorcamphor (2.4%), and 3,3-dichloro-*exo*-2-norborneol (1.0%).

II. Using Anhydrous Hydrogen Bromide. Three rearrangements, the first using a Vigreux column, and the second and third a semimicro spinning band column treated as above, were carried out. The amounts of 2-chloronorbornene *exo*-oxide used were 4.3, 4.0, and 2.5 g. The amounts of distilled product obtained were 1.3, 2.1, and 0.5 g. The reaction times were 96, 105, and 84 hr. The addition of hydrogen bromide was set up in the same manner as in the hydrogen chloride catalyzed rearrangements. The product analyses using glpc were as follows: carbon monoxide (0.8, 1.8, and 0.5%); cyclohexadiene (2.0, 1.6, and 1.2%); unidentified component (2.3, 2.9, and 1.2%); 2-chloronorbornene *exo*-oxide (22.1, 10.3, and 0.9%); unidentified component (0.7, 0.7 and 0.0%); 1-chloro-*syn*-7-hydroxynorbornene (3.5, 3.9, and 1.9%); *exo*-3-chloronorcamphor (33.2, 35.9, and 50.8%); *exo*-2-chloro-7-ketobornane (23.9, 32.6, and 37.7%); *endo*-3-chloronorcamphor (2.9, 3.5, and 2.6%); *exo*-3-bromonorcamphor (0.2, 1.0, and 0.05%); *exo*-2-bromo-7-ketonorbornane (0.1, 1.8, and 0.0%); and 3,3-dichloro-*exo*-2-norborneol (2.3, 2.7, and 2.9%). The amount of *exo*-3-bromonorcamphor for the first and third runs was estimated from large injections and the comparison of the integrated per cent was made with that of 3,3-dichloro-*exo*-2-norborneol. The presence of both bromo ketones is based solely on their glpc retention time comparisons with authentic samples.

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Bridged Polycyclic Compounds. LXIV. The Stereochemistry of Reagent-Promoted 1,3-Eliminations[1]

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Abstract: The *cis*-1,3-dibromide **1**, which has a relatively rigid W conformation **4**, and the *trans*-1,3-dibromide **2**, which has a sickle conformation **5** (or reversed E and N), were treated with various reducing agents to study the formation of γ-elimination product cyclopropane **3** *vs.* that of simple reduction products. With triphenyltin hydride, simple reduction occurred to give **6**. In aprotic solvents **1** and **2** both gave substantial amounts of cyclopropane **3** with a variety of reducing agents. However, with zinc in ethanol, **2** gave quantitative yields of cyclopropane and **1** gave no **2**, but rather the product (**9**) of simple reduction of one halogen followed by ethanolysis. Heavy treatment of the zinc metal by copper sulfate led to a couple, which reduced **1** to give substantial yields of **3**, competing with formation of **9**. The results are discussed briefly in terms of possible conformational requirements for γ-eliminations.

The formation of three-membered rings by 1,3- or γ-eliminations is an important process in organic chemistry.[2] Most such reactions, involving attack on substrates by electron-donating reagents, appear to be two stage. The first stage involves attack by reagent upon substrate to remove the electrofugal group (E) and to give an anionic or anionoid species. In the second step this species decays, by loss of nucleofuge N, to form the three-membered ring. The required stereochemistry at the atom undergoing internal nucleophilic displacement, *i.e.*, where nucleofuge departs, is relatively easy to study. It has been known for some time that inversion is required for such processes as epoxide formation,[3] aziridine formation,[4] for neighboring group reactions involving anchimeric assistance,[5,6] and has been recently demonstrated in several examples of cyclopropane-ring formation.[7,8]

The question of stereochemistry at the atom undergoing electrofugal loss is, in general, a trivial one for two-stage reactions, as long-lived anions or anionoid species have epimerization or rotational opportunities to avoid stereochemical restrictions in most cases.[9]

(1) Paper LXIII: S. J. Cristol, P. R. Whittle, and A. R. Dahl' *J. Org. Chem.*, **35**, 3172 (1970).

(2) For many references, see A. Nickon and N. H. Werstiuk, *J. Amer. Chem. Soc.*, **89**, 3914, 3915, 3917 (1967).

(3) P. D. Bartlett, *ibid.*, **57**, 224 (1935); S. Winstein and H. J. Lucas, *ibid.*, **61**, 1576 (1939).

(4) See, among others, A. Weissberger and H. Bach, *Chem. Ber.*, **64**, 1095 (1931); F. H. Dickey, W. Fickett, and H. J. Lucas, *J. Amer. Chem. Soc.*, **74**, 944 (1952); O. E. Paris and P. E. Fanta, *ibid.*, **74**, 3007 (1952); A. Hassner and C. Heathcock, *J. Org. Chem.*, **29**, 3640 (1964); **30**, 1748 (1965).

(5) In these cases, in general, activation by electron-donating reagents is not required.

(6) S. Winstein, *Bull. Soc. Chim. Fr.*, **18**, C55 (1955).

(7) H. M. Walborsky and C. G. Pitt, *J. Amer. Chem. Soc.*, **84**, 4831 (1962).

(8) (a) S. J. Cristol, J. K. Harrington, and M. S. Singer, *ibid.*, **88**, 1529 (1966); (b) S. J. Cristol and B. B. Jarvis, *ibid.*, **88**, 3095 (1966); (c) *ibid.*, **89**, 401 (1967).

(9) Work described recently[10,11] on the Ramberg–Bäcklund reaction