[Contribution from the Department of Chemistry, Wayne State University, Detroit 2, Mich.]

# The Mechanism of Elimination Reactions. II.[1] Kinetic Preference for *exo-cis* Bimolecular Eliminations with *trans*-2,3-Dihalonorbornanes

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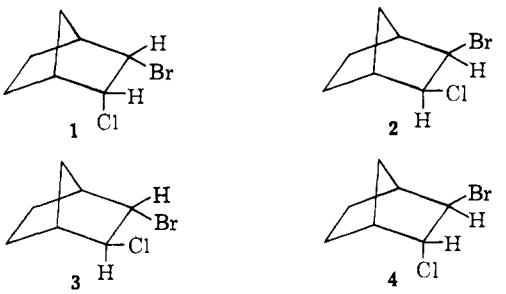
By application of a combination of kinetic and product analyses and specific deuterium labeling, *trans*-2,3-dihalonorbornanes have been shown to undergo nearly exclusive *exo-cis* bimolecular dehydrohalogenations. This influence is sufficient to cause the preferential elimination of hydrogen chloride rather than hydrogen bromide in the E2 reaction of *endo*-2-bromo-*exo*-3-chloronorbornane. The result is attributed to a steric effect, and the mechanism is considered to involve a concerted pathway with considerable carbanion character.

The superiority in rate of bromide over chloride as the leaving group in concerted, bimolecular β-elimination reactions is generally accepted. For those studies in which product analyses have been made, dehydrohalogenations of vicinal bromochlorides usually give vinyl chlorides in predominant amounts.[3,4] Systematic studies of E2 reactions[5] have resulted in the recognition that orientation and the usual stereoelectronic preference for *trans* elimination may be altered by steric factors[6] and geometrical considerations.[1,7,8] Recently, an example of a favored *cis* elimination over *trans* elimination has been documented with cyclohexyl derivatives; the results are interpreted in terms of a carbanion process with steric hindrance to proton abstraction responsible for the relative reactivities.[9] We wish to report evidence for the favored *exo-cis* (relative to *endo-cis*) *bimolecular* eliminations of norbornyl derivatives, that this effect is probably steric in origin, and that the usual preferential E2 elimination of hydrogen bromide over hydrogen chloride may even be altered. Pertinent to the arguments presented is the fact that such conclusions could have only been tenuous had they been obtained with 2-monosubstituted norbornanes because of complications arising from competing unimolecular processes with the *exo* isomers.[9a] With the 2,3-dihalonorbornanes E1 and Sn side reactions are suppressed.

## Results

Diels–Alder addition of 1-bromo-2-chloroethylene and cyclopentadiene afforded a mixture of the four isomeric 5-bromo-6-chloro-2-norbornenes. Careful fractionation allowed isolation of the two *cis* isomers in pure form. Hydrogenation gave *endo-cis*- and *exo-cis*-2-bromo-3-chloronorbornane, **1** and **2**, respectively. Compound **1** had been obtained previously by another route,[1] and its structure was confirmed by gas chromatographic behavior and spectral comparisons. The structure assigned to **2** was consistent with its n.m.r. spectrum.[10] The two *trans*-adducts could not be separated and were not resolved by gas chromatography. Hydrogenation gave a mixture of *endo*-2-bromo-*exo*-3-chloronorbornane (**3**) and *exo*-2-bromo-*endo*-3-chloronorbornane (**4**). Isomer **4** was available in pure form.[1] The n.m.r. spectrum of the mixture clearly showed the presence of two isomers, and planimetry indicated 51 ± 2% of **3** and 49 ± 2% of **4**.




Product studies for the dehydrohalogenation of the isomers **1**–**4** have been carried out under several different sets of conditions, and the results are summarized in Table I. These data show that three of the bromo-

Table I

Products of Dehydrohalogenation of the 2-Bromo-3-chloronorbornanes

| Compound | Conditions[a] | 2-Chloro-2-norbornene,[b] % | 2-Bromo-2-norbornene,[b] % |
|---|---|---|---|
| 1 | A | 95.7[c] | 4.3[c] |
| | B | 94.4 | 5.6 |
| 2 | C | 93.7 | 6.3 |
| | B | 91.0 | 9.0 |
| 4 | A | 98.7[c] | 1.3[c] |
| | B | 98.6 | 1.4 |
| | D | 97.5 | 2.5 |
| | E | 98.5 | 1.5 |
| 51% **3**, 49% **4**[c] | B | 48 | 52 |
| | C | 51.5[d] | 48.5[d] |
| | D | 48.8 | 51.2 |
| | E | 48.3 | 51.7 |

[a] A = potassium *t*-butoxide in *t*-butyl alcohol at reflux; B = sodium ethoxide in ethanol at 96° (sealed tube); C = potassium *t*-butoxide in *t*-butyl alcohol at 96° (sealed tube); D = sodium propoxide in 1-propanol at 86° (sealed tube); E = sodium propoxide in 1-propanol at 106°. [b] Determined by gas chromatography; accuracy = ±0.5%. [c] Determined by integration of n.m.r. spectrum; accuracy ±2.0%. [d] Average of two runs. [e] Data of ref. 1.

(1) Paper I: *J. Am. Chem. Soc.*, **85**, 3199 (1963).

(2) (a) Alfred P. Sloan Foundation Fellow, 1961–1965. (b) National Science Foundation Cooperative Graduate Fellow, 1962–1964.

(3) J. Hine and P. B. Langford, *J. Am. Chem. Soc.*, **78**, 5002 (1956).

(4) H. L. Goering and H. H. Espy, *ibid.*, **78**, 1454 (1956).

(5) Recent comprehensive reviews of bimolecular β-elimination reactions are given in (a) J. F. Bunnett, *Angew. Chem. Intern. Ed. Eng.*, **1**, 225 (1962); (b) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp. 186–206; (c) D. V. Banthorpe in "Reaction Mechanisms in Organic Chemistry," Vol. 2, "Elimination Reactions," American Elsevier Publishing Co., Inc., New York, N. Y., 1963.

(6) The effect of steric hindrance upon orientation is summarized in ref. 5b and pertinent literature citations are given. Another viewpoint, which is not nearly so divergent as the protagonists seem to suggest, requires a minimum threshold of structural complexity before steric effects can become dominant in controlling orientation, and the case is best presented in ref. 5c.

(7) S. J. Cristol and E. F. Hoegger, *J. Am. Chem. Soc.*, **79**, 3438 (1957); S. J. Cristol and N. L. Hause, *ibid.*, **74**, 2193 (1952), and references cited.

(8) C. H. DePuy, R. D. Thurn, and G. F. Morris, *ibid.*, **84**, 1314 (1962).

(9) F. G. Bordwell, R. L. Arnold, and J. B. Biranowski, *J. Org. Chem.*, **28**, 2496 (1963).

(9a) Note Added in Proof.—A preferred *exo-cis* bimolecular elimination from *exo*-2-norbornyl bromide has now been reported: H. Kwart, T. Takeshita, and J. L. Nyce, *J. Am. Chem. Soc.*, **86**, 2606 (1964). No data are yet available describing the relative rate of *endo-cis* elimination from *endo*-2-norbornyl compounds.

(10) The n.m.r. spectra of dihalonorbornanes and norbornenes will be the subject of a forthcoming manuscript.

chlorides (**1**, **2**, and **4**) suffer >91% elimination of hydrogen bromide, but that the remaining isomer **3** shows 99% elimination of hydrogen chloride. The mixture of **3** and **4** was partially dehydrohalogenated, and the recovered starting material showed substantial enrichment in **3**. With sodium ethoxide at 96°, recovered starting material indicated 25 ± 2% of **4** and 75 ± 2% of **3** after 42.6% reaction. On the other hand, a similar reaction containing 1 *M* lithium bromide was run, and recovered material after 44% reaction showed 23 ± 2% of **4** and 77 ± 2% of **3**.

Kinetic analyses were carried out for the dehydrohalogenation of compounds **1**, **2**, and **3** with sodium pentoxide–pentanol as the base–solvent combination, and the data are given in Table II with similar data for the isomer **4**.

TABLE II

RATE CONSTANTS, RELATIVE RATES, AND ACTIVATION PARAMETERS FOR THE DEHYDROHALOGENATIONS OF THE 2-BROMO-3-CHLORONORBORNANES WITH SODIUM PENTOXIDE AT 110°

| Compound | Av. $k' \times 10^4$, l./mole-sec. | Rel. rate | $\Delta H^*$, kcal./mole | $\Delta S^*$ |
|---|---|---|---|---|
| 1 | 0.74[a,c] | 3.1 | 26.4 | −9.2 |
| 2 | 0.24[a] | 1.0 | 26.2 | −11.9 |
| 3 | 4.05[b] | 17 | 25.3 | −8.4 |
| 4 | 27.2[c] | 113 | 26.0 | −2.7 |

[a] Extrapolated or interpolated from the data at other temperatures as given in the Experimental section. [b] Obtained by measurements with the mixture of **3** and **4**. The method of analysis is given in the Experimental section. [c] Data of ref. 1.

The results given in Tables I and II made it appear certain that *exo-cis* elimination should be general for most *trans*-1,2-dihalonorbornanes. Confirmation of this proposal for the dibromo and dichloro analogs requires isotopic substitution. We have utilized a combination of specific deuterium labeling and kinetic measurements to confirm that *trans*-2,3-dibromonorbornane (**5**) must also undergo nearly exclusive *exo-cis* elimination.

2-Bromo-3-deuterio-2-norbornene was obtained by dehydrobromination of the 2,3-dibromo-2,3-dideuterionorbornanes.[1] Light-catalyzed addition of hydrogen bromide[1,11] afforded a mixture of *trans*-2,3-dibromonorbornane-*endo*-2-*d* (**6**) and *endo-cis*-2,3-dibromonorbornane-*exo*-2-*d* (**8**). On the other hand, the addition of deuterium bromide to 2-bromo-2-norbornene gave a mixture of *trans*-2,3-dibromonorbornane-*exo*-2-*d* (**7**) and **8**. Pure samples of **6** and **7** were separated, and the assigned structures were confirmed by n.m.r. analysis. Kinetic data for the base-catalyzed elimination studies are given in Table III.

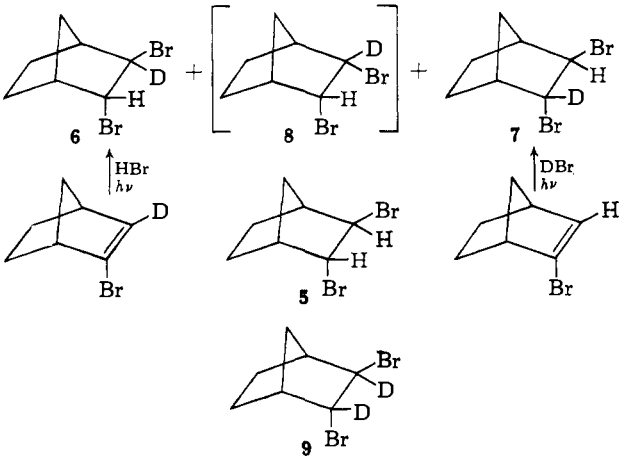



TABLE III

RATE CONSTANTS FOR THE DEHYDROBROMINATION OF DEUTERIUM-SUBSTITUTED 2,3-DIBROMONORBORNANES WITH SODIUM PENTOXIDE IN PENTANOL

| Compound | D-label | Temp., °C. | No. of runs | Av. $k' \times 10^4$, l./mole-sec. |
|---|---|---|---|---|
| 5 | None | 86.60 ± 0.03 | 2 | 8.12 ± 0.12 |
| 6[a] | *endo* | 86.60 ± .03 | 3 | 7.96 ± .07 |
| 7 | *exo* | 96.28 ± .03 | 2 | 7.36 ± .11 |
| 9 | *exo-endo* | 96.28 ± .03 | 2 | 7.04 ± .2[b] |

[a] Analysis by n.m.r. showed approximately 12% contamination by **5**. [b] Data of ref. 1.

## Discussion

There seems no doubt that *trans*-2,3-dihalonorbornanes undergo predominant *exo-cis* dehydrohalogenation. The data given in Table III demonstrate that *trans*-2,3-dibromonorbornane (**5**) and its *endo*-2-monodeuterated analog **6** give the same rate constant for dehydrobromination; thus, *endo*-deuterium substitution has little, if any,[12] effect on the rate. On the other hand, both *trans*-2,3-dibromonorbornane-2,3-$d_2$ (**9**) and the *exo*-monodeuterated analog **7** also dehydrohalogenate at nearly identical rates; the rate constants are approximately $^1/_{3.5}$ as large as those of **5** and **6** because of the primary isotope effect.[1] Obviously, *exo*-deuterium substitution alone is sufficient to account for the kinetic isotope effect in the dehydrobromination of *trans*-2,3-dibromonorbornane. Both of the *trans*-bromochlorides **3** and **4** also react *via* an *exo-cis* elimination pathway as given by the product studies of Table I.

The only reasonable explanation available to explain the noted preference would seem to be steric hindrance to *endo-cis* elimination. Arguments invoking E1 character to the transition states would not seem valid, since competing solvolysis reactions are unimportant under the reaction conditions employed. Moreover, *trans* eliminations from the *cis*-dihalides are considered to proceed *via* a mechanism similar to that of the *cis* eliminations,[1] yet the *endo-cis* isomers (*cf.* **1** and *endo-cis*-2,3-dibromonorbornane) dehydrohalogenate faster than do the *exo-cis* compounds (*cf.* **2** and *exo-cis*-2,3-dibromonorbornane). Stereoelectronic factors (*e.g.*, coplanar *cis* geometry) would seem to be very similar for both *exo* and *endo* modes of *cis* elimination. It appears, therefore, that proton removal from the *exo* direction represents the favorable steric pathway for these reactions.

A most significant observation which must result from this preferred *exo-cis* elimination is that *endo*-2-bromo-*exo*-3-chloronorbornane (**3**) affords mainly 2-bromo-2-norbornene upon treatment with sodium hydroxide. To our knowledge, this represents the first recorded example of a kinetic preference for elimination of hydrogen chloride rather than hydrogen bromide in a bimolecular dehydrohalogenation reaction. From comparative kinetic data, it can be estimated that *exo-cis* elimination from *trans*-2,3-dihalonorbornanes is more

(11) N. A. LeBel, *J. Am. Chem. Soc.*, **82**, 623 (1960).

(12) The results are not considered sufficiently accurate to permit the quantitative estimation of small secondary isotope effects, if such might exist in E2 reactions.

favorable than *endo-cis* elimination by a *minimum* of 2.2 kcal./mole in free energy of activation.

With the availability of kinetic and product results for the dehydrohalogenation of nine different 2,3-dihalonorbornanes,[1,7] additional comments concerning the mechanism of the reaction are in order. A case has been made in support of a concerted, bimolecular pathway with a considerable degree of carbanion character for these reactions. The arguments included a discussion of activation parameters, the isotope effect, lack of hydrogen–deuterium exchange, and product studies. Of the four isomeric bromochlorides **1**–**4**, three show predominant dehydrobromination (**1**, **2**, and **4**). A comparison of activation parameters for dehydrohalogenation of these isomers with those of the analogous dibromides shows that, for each pair, the dibromide reacts faster because of activation entropy factors. The order and magnitude of this difference is the same for the less constrained 1,2-dihaloethanes[3] and *cis*-1,2-dihalocyclohexanes[4] which probably follow a *trans* coplanar elimination pathway.

The relative rate data for dehydrohalogenation of **3** and **4** may even provide more compelling support for the concerted process. Since each isomer undergoes *exo-cis* elimination, a concerted elimination mechanism would seem to require that **4** (loss of HBr) be faster than **3** (loss of HCl) as was observed. On the other hand, if a carbanion process were operative for *both* isomers, **3** (formation of anion $\alpha$ to Br, $\beta$ to Cl) should be favored in rate *provided that* the leaving group has little effect. Additional data on this latter point are required. In examples where the carbanion mechanism is suspected, differences in rate of elimination with various leaving groups become smaller, but no evidence has yet been presented to show that loss of the normally poorer leaving group can become dominant.[13,14]

The activation parameters recorded for dehydrochlorination of **3** are intriguing. Replacement of chlorine in the bromochlorides by bromine (dibromides) generally does not significantly change the activation enthalpy and raises the activation entropy by about 2 e.u. It would not be imprudent to expect the activation parameters for dehydrochlorination of **3** to be very similar to those for *trans*-2,3-dichloronorbornane ($\Delta H^*$ = 30.9 kcal./mole, $\Delta S^*$ = +4.4 e.u.).[7] However, the observed values (Table II) showed a difference of about −6 kcal./mole in $\Delta H^*$ and −12.8 e.u. in $\Delta S^*$. We interpret this surprising reversal as representing a shift in the E2 mechanism further toward the carbanion extreme, or a shift to an E1cB mechanism. Added lithium bromide has no effect in increasing the relative rate of dehydrohalogenation of **3**. Studies of isotopic exchange with **3** are under way.

## Experimental

**Starting Materials.**—The compounds *trans*-2,3-dibromonorbornane (**5**), *trans*-2,3-dibromonorbornane-*exo*-2*d* (**7**) and -*endo*-2-*d* (**6**), and *exo*-2-bromo-*endo*-3-chloronorbornane (**4**) were prepared as described previously.[1,11] Identity and purity were established by g.c. on a column consisting of 10% w./w. of Polyglycol E 20,000 on 35/80 mesh Chromosorb P, comparison of physical properties and infrared spectra, and by n.m.r. analysis.

**1-Bromo-2-chloroethylene.**—The preparation employed was that of Sabanejeff.[15] From 453.6 g. (1.52 moles) of antimony pentachloride and 278.9 g. (1.5 moles) of 1,2-dibromoethylene, there was obtained 323.3 g. of a mixture of 1,1-dibromo-2,2-dichloroethane and 1,2-dibromo-1,2-dichloroethane, b.p. 85–90° (12 mm.), $n^{25}$D 1.5622. The mixture was added dropwise to 82.4 g. (1.26 moles) of zinc in 250 ml. of ethanol at such a rate to maintain reflux. After the addition, the mixture was stirred for an additional 3 hr. One liter of water was added and the organic layer was separated. The aqueous layer was extracted with two 250-ml. portions of pentane. The pentane extracts were combined with the original layer, washed with three 250-ml. portions of water, and dried. The pentane was removed and the 1,2-dihaloethylenes were fractionated with a spinning-band column. There was collected 11.4 g., b.p. 48–75°, and 62.8 g. of 1-bromo-2-chloroethylene, b.p. 75–83°, $n^{25}$D 1.4872 (lit.[15] b.p. 80–83°; lit.[16] pure *trans*, b.p. 72.5–75.4°, $n^{15}$D 1.4998; pure *cis*, b.p. 84.6°, $n^{15}$D 1.4982). Analysis by g.c. showed this fraction to be a mixture of about 19% *trans* and 81% *cis* isomers. The over-all yield was 29.6% based on 1,2-dibromoethylene.

**Diels–Alder Addition of 1-Bromo-2-chloroethylene to Cyclopentadiene.**—A mixture of 156.1 g. (1.10 moles) of the isomeric 1-bromo-2-chloroethylene and 48.5 g. (0.73 mole) of freshly distilled cyclopentadiene was heated in five sealed glass tubes at 190–195° for 5 hr. Distillation gave a forerun, 84.7 g. (mostly unreacted halide), a mixture of liquid and solid, b.p. 49–100° (1.6 mm.), and 37.5 g. of a high-boiling residue. The solid (21.5 g.) was removed by filtration, and the filtrate was fractionated on a spinning-band column at 1.8 mm. to give the fractions

| Fraction | Temp., °C. | Wt., g. | Composition, %[a] *trans* | *exo-cis* | *endo-cis* | Unidentified |
|---|---|---|---|---|---|---|
| 1 | 53–54 | 8.89 | 96.8 | | | 3.2 |
| 2 | 55–58 | 1.31 | 87.1 | 7.3 | | 5.6 |
| 3 | 58–65 | 1.33 | 42.3 | 44.9 | Trace | 12.8 |
| 4 | 65–67 | 3.05 | 2.7 | 86.9 | 3.8 | 6.6 |
| 5 | 67–68 | 4.07 | Trace | 93.6 | 3.6 | 2.8 |
| 6 | 68–70 | 2.56 | | 66.0[b] | 34.0 | Trace |

[a] By g.c. [b] Analysis by g.c. of the supernatent liquid.

From fraction 6, the column and the pot residue, there was obtained an additional 4.86 g. of the solid adduct. Analysis by g.c. indicated a product balance of 11.13 g. of the *trans* adducts, 8.84 g. of the *exo-cis* adduct, and 27.46 g. of the *endo-cis* adduct (total of 47.43 g., 31.5% based on cyclopentadiene).

***exo-cis*-5-Bromo-6-chloro-2-norbornene.**—Fractions 3, 4, and the supernatant from fraction 6 were combined and refractionated. A middle cut of 1.44 g., b.p. 65–66° (1.8 mm.), $n^{25}$D 1.5525, was shown to be 98% *exo-cis*-5-bromo-6-chloro-2-norbornene by g.c.

*Anal.* Calcd. for $C_7H_8BrCl$: C, 40.52; H, 3.89; total halogen as Cl, 34.18. Found: C, 40.76; H, 3.80; total halogen as Cl, 34.58.

***exo-cis*-2-Bromo-3-chloronorbornane (2).**—Hydrogenation of 0.97 g. (4.67 mmoles) of the *exo-cis* adduct using 107 mg. of prereduced platinum oxide in ethyl acetate afforded 0.89 g. (91%) of *exo-cis*-2-bromo-3-chloronorbornane (**2**), b.p. 63–64° (1 mm.), $n^{25}$D 1.5383. On standing, the compound solidified as a low melting solid.

*Anal.* Calcd. for $C_7H_{10}BrCl$: C, 40.14; H, 4.81; total halogen as Cl, 33.84. Found: C, 40.40; H, 4.84; total halogen as Cl, 34.05.

***endo-cis*-5-Bromo-6-chloro-2-norbornene.**—Four grams of the solid adduct was recrystallized twice from methanol and dried *in vacuo* to give 3.55 g. of *endo-cis*-5-bromo-6-chloro-2-norbornene, m.p. 91–92°; g.c. showed no contamination by other isomers.

*Anal.* Calcd. for $C_7H_8BrCl$: C, 40.52; H, 3.89; total halogen as Cl, 34.18. Found: C, 40.81; H, 3.97; total halogen as Cl, 33.96.

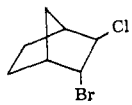
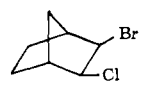
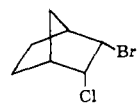
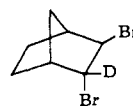
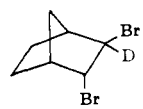
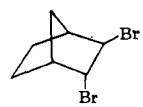
***endo-cis*-2-Bromo-3-chloronorbornane (1).**—Two grams (9.64 mmoles) of the solid adduct was hydrogenated as described above. The product, 1.87 g. (93%), was distilled, b.p. 61–62° (1 mm.), and was identical in all respects with the *endo-cis* isomer obtained by the free-radical addition of hydrogen bromide to 2-chloro-2-norbornene.[1]

**The *trans* Adducts.**—Fraction 1 was redistilled, b.p. 54–55° (1.4 mm.), $n^{25}$D 1.5375, and showed only one peak on g.c. The n.m.r. spectrum,[10] however, clearly indicated the presence of two *trans* isomers in a ratio of 1:1.

(13) H. L. Goering, D. I. Relyea, and K. L. Howe, *J. Am. Chem. Soc.*, **79**, 2502 (1957).
(14) J. Hine, R. Wiesboeck, and O. B. Ramsay, *ibid.*, **83**, 1222 (1961).
(15) A. Sabanejeff, *Ann.*, **216**, 241 (1883).
(16) H. van de Walle, *Bull. soc. chim. Belges*, **28**, 369 (1914).

TABLE IV

RATE CONSTANTS FOR DEHYDROHALOGENATION OF 2,3-DIHALONORBORNANES WITH SODIUM PENTOXIDE IN PENTANOL

| | Init. concn. of compd., moles/l. × 10² | Init. concn. of base, mole/l. | T, °C. ±0.05 | k′ × 10⁴, l./mole-sec. | Av. k′ |
|---|---|---|---|---|---|
|  | 1.512 | 0.8940 | 86.6 | 0.439 | |
| | 1.038 | .2833 | 86.6 | .410 | 0.428 ± 0.018 |
| | 1.378 | .8960 | 86.6 | .436 | |
| | 1.138 | .2857 | 96.7 | 1.20 | |
| | 1.089 | .2857 | 96.7 | 1.21 | 1.21 ± 0.01 |
| | 1.388 | .2833 | 96.7 | 1.22 | |
| | 1.084 | .1456 | 107.0 | 3.02 | |
| | 1.297 | .1456 | 107.0 | 2.91 | 3.01 ± 0.10 |
| | 0.885 | .1456 | 107.0 | 3.09 | |
|  | 1.840 | .9180 | 107.0 | 0.176 | |
| | 1.462 | .9180 | 107.0 | .174 | 0.179 ± 0.09[a] |
| | 1.915 | .9180 | 107.0 | .188 | |
| | 2.292 | .2398 | 127.3 | 1.04 | |
| | 1.754 | .2398 | 127.3 | 0.993 | 1.01 ± 0.03[a] |
| | 1.674 | .2398 | 127.3 | 0.993 | |
| | 1.998 | .0877 | 146.2 | 5.04 | |
| | 1.877 | .0877 | 146.2 | 5.00 | 5.09 ± 0.15[a] |
| | 2.612 | .0877 | 146.2 | 5.24 | |
|  | 2.284 | .4570 | 107.1 | 0.548 | |
| | 2.091 | .4570 | 107.1 | .530 | 0.545 ± 0.015 |
| | 2.420 | .4570 | 107.1 | .556 | |
|  | 1.679 | .4080 | 96.3 | 7.47 | 7.36 ± 0.11 |
| | 2.277 | .4080 | 96.3 | 7.25 | |
|  | 1.246 | .4013 | 86.6 | 7.86 | |
| | 2.873 | .2802 | 86.6 | 8.06 | 7.96 ± 0.07 |
| | 2.671 | .2786 | 86.6 | 7.96 | |
|  | 3.351 | .4080 | 86.6 | 8.24 | 8.12 ± 0.12 |
| | 3.826 | .4080 | 86.6 | 8.01 | |

[a] Calculated on the basis of 95% purity as indicated by g.c. analysis.

*Anal.* Calcd. for $C_7H_8BrCl$: C, 40.52; H, 3.89; total halogen as Cl, 34.18. Found: C, 40.83; H, 4.05; total halogen as Cl, 34.12.

**Hydrogenation of the *trans* Adducts.**—Two grams (9.64 mmoles) of the *trans* adduct was hydrogenated with platinum oxide in ethyl acetate. There was isolated 1.77 g. (87.6%) of a compound, b.p. 55–56° (1.8 mm.), $n^{25}D$ 1.5273, which showed a g.c. retention time identical with that of *exo*-2-bromo-*endo*-3-chloronorbornane (**4**), obtained by the radical addition of hydrogen bromide to 2-chloro-2-norbornene.[1] However, the n.m.r. spectrum showed two *trans* isomers in the ratio 1:1.

At 178°, the retention times of the unsaturated *trans*, *exo-cis*, and *endo-cis* adducts were 6.3, 12.55, and 17.6 min., respectively; while the corresponding saturated analogs had retention times of 7.1, 16.2, and 18.3 min., respectively.

**Kinetic Measurements.**—The kinetic procedure followed was essentially that described previously.[1] Calculations of rate constants and activation parameters were done graphically, and slopes and intercept were obtained by the method of least squares. Typical kinetic results are shown in Table IV. The rate constants for dehydrohalogenation of the mixture of the *trans*-chlorobromides **3** and **4** were obtained by titration of total halide produced with time. By appropriate substitution of the known rate constants for dehydrohalogenation of **4** in the kinetic equation, rate constants for **3** could be interpolated.

TABLE V

TYPICAL DETERMINATION OF RATE CONSTANT OF 2-*endo*-BROMO-3-*exo*-CHLORONORBORNANE AT 96.7°

| t, min. | $X_T$, moles/l. × 10² | $X_D$, moles/l. × 10² | $X_E$, mole/l. × 10² |
|---|---|---|---|
| 5 | 0.113 | 0.077 | 0.036 |
| 10 | .237 | .150 | .087 |
| 15 | .308 | .218 | .090 |
| 30 | .545 | .400 | .145 |
| 60 | .955 | .680 | .275 |
| 120 | 1.397 | 1.020 | .377 |
| 180 | 1.675 | 1.195 | .480 |
| 240 | 1.818 | 1.287 | .531 |
| 360 | 2.105 | 1.358 | .747 |
| 480 | 2.290 | 1.378 | .912 |

$X_T$ = total halogen titrated

$X_D$ = halogen calculated from rate constant of 2-*exo*-bromo-3-*endo*-chloronorbornane at 96.7°

$X_E = X_T - X_D$; halogen from 2-*endo*-bromo-3-*exo*-chloronorbornane

The rate constant is calculated from slope of line obtained from plotting $t$ *vs.* $\log (b/a)[(a - X_E)/(b - X_T)]$. For Table V, $a$ = initial concentration of 2-*endo*-bromo-3-*exo*-chloronorbornane = $1.388 \times 10^{-2}$ mole/l., $b$ = initial concentration of base = 0.2833 mole/l., $k' = 1.22 \times 10^{-4}$ l. mole$^{-1}$ sec.$^{-1}$. For Table VI, $a$ = initial concentration of 2-*endo*-bromo-3-*exo*-chloronorbornane = $2.594 \times 10^{-2}$ mole/l., $b$ = initial concentration of base = 0.1456 mole/l., $k' = 2.91 \times 10^{-4}$ l. mole$^{-1}$ sec.$^{-1}$.

TABLE VI

TYPICAL DETERMINATION OF RATE CONSTANT OF 2-*endo*-BROMO-3-*exo*-CHLORONORBORNANE AT 107.0°

| t, min. | $X_T$, moles/l. × 10² | $X_D$, moles/l. × 10² | $X_E$, mole/l. × 10² |
|---|---|---|---|
| 3 | 0.131 | 0.068 | 0.063 |
| 15 | .386 | .290 | .096 |
| 30 | .666 | .508 | .158 |
| 60 | 1.123 | .813 | .310 |
| 90 | 1.368 | .993 | .375 |
| 120 | 1.578 | 1.106 | .472 |
| 180 | 1.763 | 1.220 | .543 |
| 240 | 1.912 | 1.267 | .645 |
| 360 | 2.105 | 1.292 | .813 |
| 480 | 2.245 | 1.297 | .948 |

**Product Studies for the Dehydrohalogenation of the Bromochlorides.**—The procedure employed was essentially identical for all product studies summarized in Table I. Weighed samples of the chlorobromides **1**–**4** (0.10–0.15 g.) were dissolved in 10 ml. of the appropriate base–solvent solutions (0.3 *N*) in tubes. The tubes were sealed and heated at the prescribed temperatures for a period equivalent to at least ten half-lives. Water was added, and the aqueous phase was extracted with four 50-ml. portions of pentane. The pentane extracts were backwashed with water. The combined aqueous layer and water washing were diluted to volume, and the extent of reaction was determined by Volhard titration. In most cases, reaction was at least 98% complete. The pentane extract was dried and concentrated, and the vinyl halides were analyzed by g.c. at 96° (Table I).

The runs in which the reaction was carried to partial completion (mixture of **3** and **4**) were carried out in much the same manner, except that a calculated quantity of base was employed. Recovered starting materials were purified by distillation and were analyzed by planimetry of the n.m.r. spectra.

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