small sample was separated by g.c. and the infrared spectrum was similar to that of authentic 9.[11a] A phenylurethan was prepared and recrystallized from pentane, m.p. 133–136° (lit.[11a] 136.7–137°), m.m.p. with the phenylurethan of 8 119–121°.

Reactions with Tetraethylammonium Acetate. exo-Bicyclo-[2.2.2]oct-5-ene-2-yl Tosylate (2b).—To a cold (−10°) stirred solution of 205 mg. (1.04 mmoles) of tetraethylammonium acetate monohydrate[30] in 0.6 ml. of dry acetone was added 250 mg. (0.90 mmole) of exo-tosylate 2b in 0.6 ml. of dry acetone. The solution was allowed to warm to room temperature and, after stirring for 2 hr. at this temperature, the solution was stirred at reflux for an additional 2 hr. Upon cooling, the reaction mixture was added to 75 ml. of water and the product was extracted with two 25-ml. portions of ethyl ether followed by a 25-ml. portion of pentane. The combined extracts were thoroughly washed with saturated sodium bicarbonate solution and then with water.

(30) J. Steigman and L. P. Hammett, J. Am. Chem. Soc., 59, 2536 (1937).

The dried ether–pentane solution was concentrated by distillation to give 146 mg. of high boiling residue which was shown to consist of a mixture of 46% 5c, 32% 7c, 10% 2d, and 12% 10 by gas chromatography on column B.

endo-Bicyclo[2.2.2]oct-5-en-2-yl Tosylate (3, R = Ts).—endo-Tosylate 3 (R = Ts; 184 mg., 0.66 mmole) was added to a stirred solution of 469 mg. (2.38 mmoles) of tetraethylammonium acetate monohydrate in 1.5 ml. of dry acetone. The solution was then stirred at gentle reflux for 30 hr. and, after a similar work-up to that described above, 86 mg. of crude acetates was obtained; g.c. analysis shows the presence of 22% 2d and 78% axial-bicyclo[3.2.1]oct-3-en-2-yl acetate.

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The Stereochemistry of Elimination Reactions. The 2,3-Dihalonorbornanes[1,2]

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RECEIVED JUNE 19, 1963

The kinetics of dehydrohalogenation of the three isomeric 2,3-dibromonorbornanes, endo-cis-2-bromo-3-chloronorbornane and exo-2-bromo-endo-3-chloronorbornane, have been examined with sodium pentoxide as the base. The trans- and endo-cis-dibromides were also studied with potassium t-amyloxide. Hydrogen exchange was not detected when the 2,3-dideuterated analogs of the trans- and endo-cis-dibromides were subjected to conditions of partial elimination. Kinetic isotope effects were measured at 126.7° for the endo-cis-dibromide and 96.3° for the trans-dibromide and the observed values (k_H/k_D = 3.4 and 3.6, respectively) are considered too large for a two-step mechanism. Both chlorobromides afford nearly exclusively 2-chloro-2-norbornene upon reaction with potassium t-butoxide. From reactivity considerations, product studies, and the results of isotopic substitution, elimination reactions of 2,3-dihalonorbornanes are considered to follow a concerted, though probably not synchronous, pathway.

Recently, DePuy and co-workers have suggested that a plot of the rate of bimolecular elimination vs. the dihedral angle will show maxima at both 0 and 180° and a minimum at 90°.[5] This generalization was based on observations that the base-promoted cis eliminations of a series of trans-2-arylcyclopentyl tosylates were of a concerted nature, and that k_{trans}/k_{cis} in the arylcyclopentyl system is only about 14. In addition, the observed favoring of cis over trans dehydrochlorination in bridged bicyclic dichlorides[6,7] was interpreted in terms of this proposal.

We have been of the opinion that, as a general rule, cis coplanar E2 reactions will be faster than trans noncoplanar bimolecular eliminations. As the result of another study, we had available the three isomeric 2,3-dibromonorbornanes.[8] A detailed kinetic analysis of the dehydrobromination of these isomers was considered of interest for several reasons. Among these were: (1) a determination of whether coplanar cis and noncoplanar trans eliminations in this series followed similar mechanisms, (2) a comparison of the activation parameters with those reported for concerted trans E2 reactions of simple dihaloethylenes, and (3) a comparison of trans-eliminations from exo-cis- and endo-cis-dihalides.

In the course of these studies, kinetic and product analyses of the dehydrohalogenation of the endo-cis-and exo-2-bromo-endo-3-chloronorbornanes were made,

(5) C. H. DePuy, R. D. Thurn, and G. F. Morris, J. Am. Chem. Soc., 84, 1314 (1962).
(6) S. J. Cristol and E. F. Hoegger, ibid., 79, 3438 (1957).
(7) S. J. Cristol and N. L. Hause, ibid., 74, 2193 (1952).
(8) N. A. LeBel, ibid., 82, 623 (1960).

as well as a study of the hydrogen–deuterium isotope effect and exchange phenomena for the endo-cis- and trans-dibromides.

I, X = Y = Br   IV, X = Y = Br   V, X = Y = Br
II, X = Br, Y = Cl   VI, X = Cl, Y = Br
III, X = Y = Cl   VII, X = Y = Cl
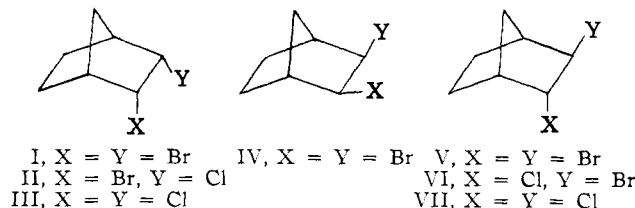
Results

The synthesis of the three dibromides I, IV, and V has been described previously.[8] In the earlier work, the structures of the cis-dibromides were based on dipole moment evidence and the fact that the exo-cis isomer would be expected from the free radical addition of hydrogen bromide to 2-bromo-2-norbornene. Recently, we had obtained a great deal of additional data which require that the dibromide of m.p. 60.5–61.5° be assigned the endo-cis structure I, and the lower melting isomer must have structure IV. The 2,3-dideuterated analogs of I and V were prepared in an analogous manner employing sym-dibromodideuterioethylene. The free radical addition of hydrogen bromide to 2-chloro-2-norbornene afforded mixtures of endo-cis-2-bromo-3-chloronorbornane (II) and exo-2-bromo-endo-3-chloronorbornane (VI) in the ratio 3:7, and the isomers were separated by distillation. The structures were assigned by analogy,[8] and are consistent with the nuclear magnetic resonance spectra.[9]

In order to allow a direct comparison with the data that Cristol and Hoegger obtained for the dichlorides III and VII,[6] the dehydrobrominations of dihalides I, II, IV, V, and VI were studied at several different

(9) The n.m.r. analysis of the 2,3-dihalonorbornanes will be discussed in a later manuscript.

temperatures in pentanol solution employing sodium 1-pentoxide as the base. The reactions were cleanly second order and were usually followed to at least 80% completion.

The product from the dibromides has been reported to be exclusively 2-bromo-2-norbornene.[8] Studies with potassium t-butoxide showed that both bromochlorides II and VI underwent elimination of the elements of *hydrogen bromide* to give primarily 2-chloro-2-norbornene (Table I).

TABLE I
PRODUCTS OF THE DEHYDROHALOGENATION OF II AND VI WITH POTASSIUM t-BUTOXIDE IN t-BUTYL ALCOHOL

Compound	2-Chloro-2-norbornene,[a] %	2-Bromo-2-norbornene,[a] %
cis-Chlorobromide (II)	95.7	4.3
trans-Chlorobromide (VI)	98.7	1.3
35.5% II, 65.5% VI	98.6	1.4
Mixture of vinyl halides[b]	96.2	3.8

[a] Determined by gas chromatography; accuracy estimated to be ±0.5%. [b] A synthetic mixture consisting of 96.5% by weight of 2-chloro-2-norbornene and 3.5% of 2-bromo-2-norbornene.

Kinetic data are tabulated in the Experimental section, and Table II summarizes the pertinent data and activation parameters.

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

Compd.	$k' \times 10^4$,[a] l. mole^{-1} sec.$^{-1}$	Rel. rate	$\Delta H^{\ddagger}$, kcal. mole^{-1}	$\Delta S^{\ddagger}$, e.u.
IV	1.1	1.0	26.2	−8.8
III	0.03[b]	0.02	30.3[b]	−5.4[b]
I	3.0	2.8	25.9	−7.5
II	1.04	0.95	24.4	−13.9
V	94.5	85.9	26.4	+0.7
VI	30.3	27.6	25.3	−4.7
VII	1.75[b]	1.6	30.9[b]	+4.4[b]

[a] Interpolated. [b] Calculated from the data of ref. 5.

Exchange studies were carried out with the 2,3-dideuterated analogs of I and V, and the results are given in Table III. It is to be noted that recovery of starting material after partial reaction and analysis for deuterium content indicated no exchange.[10]

TABLE III
HYDROGEN–DEUTERIUM EXCHANGE STUDIES

Compound	Atoms D in starting material	Temp., °C.	Base/solvent	Reacn., %	Atoms D recovd.
I, 2,3-d_2	1.915	119.7	NaOAm/AmOH	37	1.924
V, 2,3-d_2	1.89	102.3	NaOAm/AmOH	56	1.85
	1.903	55.7	KOt-Bu/t-BuOH	31.4	1.930
	1.930	55.7	KOt-Bu/t-BuOH	49.4	1.937

Exchange experiments with *trans*-2,3-dibromonorbornane-2,3-d_2 employing sodium pentoxide–pentanol as the medium indicated a small amount of exchange of hydrogen for deuterium. We attribute this result to the difficulty of purifying the unreacted dihalide starting material, and subsequently employed the t-butoxide–t-butyl alcohol system for this study.

One final point can be emphasized. Gas chromatography analysis of the unreacted *endo-cis*- and *trans*-dideuterated dihalides recovered from the exchange studies indicated *no isomerization*.

(10) The estimated error in deuterium analysis is ±1% relative. The data in Table III, after correction for isotope effects due to partially deuterated species, are within experimental error of the values expected for no exchange.

We chose also to study the dehydrobromination of isomers I and V employing sodium t-amyloxide in t-amyl alcohol. A summary of pertinent kinetic data is given in Table IV.

TABLE IV
KINETIC DATA FOR THE DEHYDROBROMINATION OF *endo-cis* AND *trans*-2,3-DIBROMONORBORNANE WITH SODIUM t-AMYLOXIDE

Compd.	$k_{110}°' \times 10^4$,[a] l. mole^{-1} sec.$^{-1}$	$k_{50}°' \times 10^4$,[a] l. mole^{-1} sec.$^{-1}$	$\Delta H^{\ddagger}$, kcal./mole	$\Delta S^{\ddagger}$, e.u.
I	1.86[a]	0.11[a]	20.2	−19
V	27.9	8.15	21.1	−11

[a] Extrapolated.

Kinetic isotope effects were determined for the dehydrobrominations of the *endo-cis*- (I) and *trans*- (V) dibromides with sodium pentoxide. The observed second-order rate constant for I-2,3-d_2 at 126.7° was found to be 4.12 ± 0.02 l./mole/sec. This value was corrected for the amount of hydrogen species present—assuming that the hydrogen containing impurity was exclusively the monodeuterated species—by application of the equation

$$k_{obsd.} = (\% \text{ dideuterated cmpd.}) k_D + 1/2 (\% \text{ monodeuterated cmpd.})(k_H + k_D)$$

A value of k_D for I of 3.91×10^{-4} l./mole/sec. was obtained and, together with the interpolated k_H, led to an isotope effect of $k_H/k_D = 3.4 \pm 0.1$ at 126.7°. In the same manner, the $k_{obsd.}$ for V-2,3-d_2 (7.45 ± 0.03 l./mole/sec.) afforded an average $k_D = 7.04 \times 10^{-4}$ l./mole/sec. at 96.3°. With the simplifying assumptions that the monodeuterated *trans* impurity has equal amounts of hydrogen in the *exo* and *endo* positions, and that the isotope effect is the same for *exo-cis*- and *endo-cis*-dehydrobromination of V, k_H/k_D (av.) = 3.6 ± 0.1 at 96.3°.

Discussion

The results of dehydrohalogenation clearly confirm the noted preference[6] for *cis*-elimination over *trans*-elimination in the 2,3-dihalonorbornanes. At 110°, this ratio amounts to factors of 31, 29, and 67 for the dibromides, chlorobromides, and dichlorides, respectively. *cis*-Dehydrobromination is also favored over *trans*-dehydrobromination with the stronger base t-amyloxide; the factors are 71 and 15 at 50° and 110°, respectively. An examination of the enthalpies and entropies of activation from Table II suggests that these parameters vary in the *same direction* and by approximately the same magnitude in the series dibromide:bromochloride:dichloride regardless of whether a *trans*- or a *cis*-elimination course is followed. This trend indicates that both elimination processes proceed *via* the same (or very similar) mechanistic course(s). In contrast, an analysis of the activation energies for base-catalyzed dehydrohalogenations of the isomeric dihaloethylenes led to the suggestion that *trans*-elimination takes place by a one-step, concerted process and that *cis*-elimination follows an E1CB course.[11]

This similarity of mechanism for the *trans*- and *cis*-eliminations had been advanced earlier on the basis of studies with III, VII, and *exo*-2-p-toluenesulfonyl-*endo*-3-chloronorbornane.[6] These authors suggested a carbanion mechanism (E1CB) rather than a concerted process. It is our contention that the data described above can allow a choice between these possibilities and that concerted dehydrohalogenations best fit the evidence.

Although one cannot *a priori* state that activation enthalpies would vary according to the sequence diBr > Br–Cl > diCl if a carbanion mechanism were operating, whereas the inverse order would be expected for a

(11) S. I. Miller and R. M. Noyes, *J. Am. Chem. Soc.*, **74**, 629 (1952).

concerted process, some evidence to this effect is available in the literature. For example, trans-1,2-dichloroethylene (cis-elimination, E1CB) shows a lower activation energy for dehydrohalogenation than does the trans-dibromide.[11] With the 2,3-dihalonorbornanes (cis or trans), the dibromides undergo elimination at a faster rate than the dichlorides because favorable energetics more than offset a slightly less positive entropy of activation. A more convincing argument can be made by comparing the kinetic data from the dihalonorbornanes with that from the dehydrohalogenations of simple 1,2-dihalides which undergo elimination by concerted processes. From careful studies with cis-1,2-dihalocyclohexanes[12] and with β-haloethyl bromides,[13] the following trends can be noted: (1) the bromochlorides suffer elimination of the elements of hydrogen bromide; (2) activation enthalpies and entropies are similar for 1,2-dibromides and 1,2-chlorobromides, with the latter having slightly lower rate constants; (3) 1,2-dichlorides undergo much slower elimination because of enthalpy differences despite somewhat more favorable activation entropies. Although the solvent–base compositions are different, these trends are also evident with the dihalonorbornanes. To be sure, these reactivity comparisons cannot prove a general concerted mechanism, but they appear to be more than coincidental.

Relative rates of elimination reactions that proceed via a carbanion mechanism with proton abstraction as the rate-determining step must depend both upon the acidity of the β-hydrogen and the steric hindrance associated with its transfer to base. In the 2,3-dihalonorbornanes, the trans isomers would present more hindrance to base attack than would the endo-cis isomers and accordingly cis-elimination might be expected to proceed more slowly. The opposite is consistently observed and this is more in keeping with a one-step mechanism.

Some additional support for the concerted elimination viewpoint is given by the isotopic studies. No hydrogen exchange was detected when the dideuterated analogs of I and V were subjected to conditions of partial elimination, and no isomerization of starting material took place. The stereochemical argument alone cannot define the concerted nature of the elimination reaction,[14] nor can the lack of deuterium exchange of a reactant.[6,15] However, the failure to detect exchange is a necessary criterion and is established.

The hydrogen–deuterium isotope effect represents more compelling support. The values of k_H/k_D of 3.4 for I and 3.6 for V are very similar, despite the fact that trans-elimination is taking place in the former and cis-elimination in the latter. These ratios are among the highest observed for simple β-eliminations, and are of a magnitude expected for a concerted process.[16,17] A carbanion process would result in a lower hydrogen isotope effect since the hydrogen atom should be more than half-transferred to the base at the transition state. The β-phenylethyl halide system is generally considered a good model for the concerted E2 reaction, with the transition state lying slightly to the carbanion-side of the "central" state.[17] Extrapolation of data available for the dehydrobromination of β-phenylethyl bromide[18] with sodium ethoxide in ethanol leads to an estimate of

$k_H/k_D = 3.6$ at 127°. Since the effects of β-phenyl and β-bromo substituents on the nature of the transition states of E2 eliminations should be roughly equivalent,[17] the similarities in isotope effects are consistent with a concerted process for the 2,3-dibromonorbornanes as well. The kinetic isotope effects are also similar in magnitude to that for the Hofmann elimination of ethyltrimethylammonium ion[19]; this reaction is generally considered to follow a concerted, though not synchronous, pathway.

Another compelling argument in favor of a one-step mechanism for the dehydrohalogenation of the 2,3-dihalonorbornanes is the observed dependence of the leaving group upon the products of elimination from the bromochlorides II and VI (Table I). Both cis and trans isomers afford primarily 2-chloro-2-norbornene. If a two-step process (E1CB) were occurring, the rate-determining step would be carbanion formation and the leaving group would be expected to have very little, if any, effect on the rate. Such appears to be the case for the eliminations of trans-2-chlorocyclohexyl phenyl sulfone and trans-2-tosyloxycyclohexyl phenyl sulfone which show nearly identical rates, whereas cyclohexyl tosylate undergoes concerted E2 elimination much more rapidly than does cyclohexyl chloride.[20] If the compounds II and VI underwent elimination via an E1CB mechanism, one would necessarily predict predominant carbanion formation on the carbon atom bearing the bromine substituent, with subsequent rapid elimination of chloride ion. This prediction follows from the large amount of experimental evidence from studies of polyhaloalkanes to the effect that α-halogen substituents promote carbanion formation in the order I > Br > Cl > F.[21] The effect will be even more pronounced if it is accepted that β-halogens facilitate carbanion formation in the order Cl > Br > I. The fact that dehydrobromination predominates with II and VI is completely consistent with the fact that bromide is a better leaving group than chloride in concerted E2 eliminations.

The further observation that the bromochlorides react somewhat more slowly than the corresponding dibromides (even when the latter are corrected for a statistical factor of 2) can be rationalized on the basis of the greater stability of the olefin (2-bromo-2-norbornene vs. 2-chloro-2-norbornene) being formed in the transition state.[18] This is consistent with a concerted process having some double bond character in the transition state.

The preference for cis-elimination is still maintained with t-amyloxide as the base. At 110°, k_{cis}/k_{trans} is 15 and at 50° it is about 74. The much higher rates are undoubtedly associated with the greater base strength of the t-alkoxide, and this effect is prevalent in most concerted E2 reactions.

Two further points should be considered. trans-Dehydrobromination is three times faster from the endo-cis-dibromide I than from the exo-cis-isomer IV. This result must be due to the greater accessibility of the exo-hydrogens in I, and is consistent with other observations of hydrogen transfer reactions in norbornane systems.[22] Another possibility is that the more-hindered endo-halogen atoms in I are subject to steric assistance to departure in the transition state of the concerted elimination reaction. It is also tempting to conclude that the trans-dibromide undergoes exo-cis elimination faster than endo-cis-elimination.

(12) H. L. Goering and H. H. Espy, J. Am. Chem. Soc., **78**, 1454 (1956).

(13) J. Hine and P. B. Langford, ibid., **78**, 5002 (1956).

(14) D. J. Cram, D. A. Scott, and W. D. Nielsen, ibid., **83**, 3696 (1961).

(15) J. Hine, R. Wiesboeck, and O. B. Ramsey, ibid., **83**, 1222 (1961).

(16) F. H. Westheimer, Chem. Rev., **61**, 265 (1961).

(17) For a general treatment of bimolecular β-elimination reactions, see J. F. Bunnett, Angew. Chem. Intern. Ed. Engl., **1**, 225 (1962).

(18) W. H. Saunders, Jr., and D. H. Edison, J. Am. Chem. Soc., **82**, 138 (1960).

(19) V. J. Shiner, Jr., and M. L. Smith, ibid., **80**, 4095 (1958).

(20) H. L. Goering, D. I. Relyea, and K. L. Howe, ibid., **79**, 2502 (1957).

(21) J. Hine, R. Wiesboeck, and R. G. Ghirardelli, ibid., **83**, 1219 (1961), and references cited therein.

(22) Private communication from Prof. H. Shecter.

An α-elimination followed by hydrogen or halide migration is a distinct possibility in these cases. We do not consider that this mode of reaction is important with the 2,3-dihalonorbornanes because (1) we have been unable to detect the presence of 3-halonortricylenes in the products (even by effecting the elimination with potassium *t*-butoxide in dimethyl sulfoxide), and (2) the kinetic isotope effect is much larger than that observed in concerted α-dehydrohalogenations of haloforms.[23]

The evidence presented above supports the premise that E2 reactions of 1,2-dihalides follow a concerted pathway with varying degrees of C–H and C–X bond breaking depending upon the dihedral angle and the structure of the olefinic product. The fact that structural features preventing the H and X leaving groups from becoming *trans* and coplanar does not, at this time, seem a valid criterion for necessitating a carbanion mechanism. The *trans* coplanar elimination process may best approach the synchronous concerted mechanism.

Experimental

Starting Materials.—The 2,3-dibromonorbornanes were prepared by hydrogenation of the corresponding Diels–Alder adducts of dibromoethylene and cyclopentadiene. The *endo-cis* compound I was purified by recrystallization from methanol; m.p. 60.5–61.5° (lit.[8] m.p. 60.4–61.3°). Careful fractionation of *trans*-2,3-dibromonorbornane by means of a spinning-band column afforded a product having b.p. 55° (0.4 mm.), $n^{23.5}$D 1.5564 (lit.[8] b.p. 63–64° at 0.4 mm. n^{25}D 1.5560). The dibromide was found to be homogeneous by gas chromatography on a column packed with 25% by weight silicone gum rubber on firebrick at 185°, 7 p.s.i.g. helium pressure. The *exo-cis*-dibromide IV was recrystallized from methanol and had a melting point of 55.0–55.6° (lit.[8] m.p. 55.3–55.6°).

sym-Tetrabromodideuterioethane.—A modification of the reported procedure[24,25] was employed for the preparation of dideuterioacetylene. Granular calcium carbide (62 g., dried for 36 hr. at 180° and 1 mm.) was placed in a 500-ml. flask fitted with a stirrer, addition funnel, and an outlet tube which was connected to a series of traps, containing 160 g. and 100 g. of liquid bromine, respectively. Another trap, cooled by Dry Ice–acetone, was included immediately before the traps containing bromine. The system was flushed with dry nitrogen for about 30 min., during which time the system was flame-dried. Deuterium oxide (23.5 g., 99.95% purity) was added dropwise to the calcium carbide with ice-bath cooling. The acetylene which passed through the bromine caused a temperature rise which required moderate cooling of the traps occasionally. When all the deuterium oxide had been added, the ice-bath was replaced by an oil-bath and the calcium carbide was heated gradually. After completion of acetylene evolution the system was dismantled and the contents of the traps were combined and distilled. The residual liquid was washed with aqueous sodium bisulfite solution. Subsequent drying and distillation gave 151.5 g. (b.p. 76–78° at 0.7 mm., 74–75% based on deuterium oxide) of pure *sym*-tetrabromodideuterioethane, n^{25}D 1.6359 (lit.[26] b.p. 114° at 1 mm., n^{20}D 1.6379). Infrared analysis showed an intense C–D stretching band at 4.5 μ and practically no C–H absorption.

1,2-Dibromo-1,2-dideuterioethylene.—A solution of 167.5 g. (0.48 mole) of *sym*-tetrabromodideuterioethane in 250 ml. of ethanol was added dropwise with stirring to a suspension of 31.4 g. (0.48 mole) of granular zinc in 125 ml. of ethanol. After refluxing for an additional 15 hr., the mixture was cooled and 800 ml. of water was added. The organic layer was separated. The aqueous layer was filtered and the filtrate was extracted with pentane. The extracts were combined with the original layer and the solution was dried. The pentane was removed and the residue was distilled to give 40.5 g. (45%) of *sym*-dideuteriodibromoethylene, b.p. 107–110°, n^{25}D 1.5392 (lit.[27] b.p. 108–110°, n^{25}D 1.5420).

Diels–Alder Addition of sym-Dibromodideuterioethylene to Cyclopentadiene.—A mixture of 35.6 g. (0.19 mole) of *sym*-dibromodideuterioethylene and 12.5 g. (0.19 mole) of freshly distilled cyclopentadiene was placed in the glass liner of a stain-

less steel vessel under 400 p.s.i.g. nitrogen pressure. The reaction mixture was heated at 180–190° for 8–10 hr. The dark colored product was distilled from a Claisen flask to give 18.08 g. (37.0%) of product, b.p. 45–95° (0.5 mm.), which contained 3.7 g. of crystalline material. The solid was separated and was washed with pentane. The mother liquors and washings were redistilled through a tantalum spiral column affording 6.84 g. (14.2%) of liquid dibromide fractions, b.p. 48–62° (0.4 mm.), n^{25}D 1.5568–1.5700, and an additional 1 g. of solid. The crystalline product was recrystallized from methanol to yield a total of 3.40 g. of *endo-cis*-5,6-dibromo-2-norbornene-*exo*-5,6-d_2, m.p. 116–117° (lit.[8] m.p. 116.5–117.5°).

Careful fractionation of the liquid dibromide mixture gave 4.01 g. of *trans*-5,6-dibromonorbornene-5,6-d_2, b.p. 52–62° (1.0–0.8 mm.), $n^{24.5}$D 1.5620–1.5650 (lit.[8] b.p. 57–58° at 0.8 mm., n^{25}D 1.5660). Gas chromatography on the silicone column at 185° indicated that the product was homogeneous.

trans-2,3-Dibromonorbornane-2,3-d_2.—A solution of 3.9 g. (0.015 mole) of the *trans* adduct in 50 ml. of ethyl acetate was hydrogenated as described previously. Distillation through a spinning-band column gave two fractions; total yield 2.60 g. (67%). The second fraction consisted of 1.97 g. of *trans*-2,3-dibromonorbornane-2,3-d_2, b.p. 55° (0.5 mm.), n^{23}D 1.5548 (lit.[8] b.p. 63–64° at 0.4 mm., n^{25}D 1.5560).

Fraction II was found to be homogeneous when analyzed by gas chromatography (silicone column at 185°).

endo-cis-2,3-Dibromonorbornane-exo-2,3-d_2.—Hydrogenation of 2.08 g. (0.008 mole) of *endo-cis* isomer and recrystallization from methyl alcohol furnished 1.47 g. (70.2%) of *endo-cis*-2,3-dibromonorbornane-*exo*-2,3-d_2, m.p. 61–62° (lit.[8] m.p. 60.4–61.3°).

2,2-Dichloronorbornane.—The method employed was essentially that of Bixler and Nieman.[28] From 90.2 g. (0.82 mole) of norcamphor dissolved in 60 ml. of phosphorus trichloride and 193.4 g. (0.93 mole) of phosphorus pentachloride there was obtained 92.5 g. (68.4%) of 2,2-dichloronorbornane, b.p. 58–60° (6.0 mm.) (lit.[28] b.p. 65–68.1° at 12.0–12.4 mm.). The product was a low melting solid and was used without further purification.

2-Chloro-2-norbornene.—The dehydrohalogenation of 2,2-dichloronorbornane was carried out in the manner reported[8] except that the product was taken up in hexane. From 41.3 g. (0.25 mole) of 2,2-dichloronorbornane there was obtained upon distillation a negligible forerun; a major fraction of 14.93 g. (46.4%) of 2-chloro-2-norbornene, b.p. 47–49° (18 mm.), n^{25}D 1.4876 (lit.[29] b.p. 64–66° at 52 mm., n^{25}D 1.4875); and 4.7 g. of a higher boiling residue. The 2-chloro-2-norbornene was shown to be homogeneous by gas chromatography.

Free Radical Addition of Hydrogen Bromide to 2-Chloro-2-norbornene.—In a 400-ml. reaction vessel fitted with a gas inlet tube, a Hanau S-81 quartz immersion lamp, and a condenser protected with a drying tube there was added 10.0 g. (0.078 mole) of 2-chloro-2-norbornene in 400 ml. of dry olefin-free pentane. The mixture was flushed for 15 min. with dry nitrogen. The reaction vessel was placed in a cooling bath and was saturated with anhydrous hydrogen bromide. With the hydrogen bromide bubbling at a gentle rate, the solution was irradiated for a total of 25 min. in 5-min. intervals, followed by 2 min. during which the lamp was turned off. The reaction vessel was again flushed with nitrogen to remove most of the hydrogen bromide and the pentane solution was washed successively with 50 ml. of water, 50 ml. of 10% sodium carbonate solution, and 50 ml. of water. The pentane solution was dried over magnesium sulfate. A small sample was withdrawn, concentrated, and analyzed by gas chromatography. The chromatogram showed that the reaction was complete (no vinyl chloride) and yielded only two products in the ratio of 70:30. The major compound was assigned the 2-*exo*-bromo-3-*endo*-chloronorbornane(VI) structure and the minor product as *endo-cis*-2-bromo-3-chloronorbornane (II).

The pentane was removed by distillation and the residual liquid was distilled to give 13.34 g. of a mixture of *cis*- and *trans*-chlorobromides, b.p. 78–84° (6 mm.). There was obtained from the residue 0.85 g. of pure *cis*-chlorobromide; total yield 14.19 g. (87.2%).

The liquid was fractionated at 2 mm. to give the fractions

Fraction	B.p., °C.	Wt., g.	% trans	% cis
I	54–55	6.80	99	..
II	55–65	2.46	68.8	31.2
III	65–71	1.26	4.9	95.1
IV	71–72	1.62	1.2	98.8

An analytical sample of *trans*-2-*exo*-bromo-3-*endo*-chloronorbornane had b.p. 80–80.5 (6 mm.), n^{25}D 1.5289.

(23) J. Hine and P. B. Langford, *J. Am. Chem. Soc.*, **79**, 5497 (1957).

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(25) R. G. O'Meara and J. B. Clemmer, *Chem. Abstr.*, **23**, 1598 (1929).

(26) I. Heilbron, "Dictionary of Organic Compounds," Vol. IV, Oxford University Press, New York, N. Y., 1953, p. 415.

(27) C. S. Hodgman, "Handbook of Chemistry and Physics," 39th Ed., Chemical Rubber Publishing Company, Cleveland, O., 1958, p. 933.

(28) R. L. Bixler and C. Nieman, *J. Org. Chem.*, **23**, 742 (1958).

(29) J. D. Roberts, F. O. Johnson, and R. A. Carboni, *J. Am. Chem. Soc.*, **76**, 5692 (1954).

Anal. Calcd. for $C_7H_{10}BrCl$: C, 40.14; H, 4.81; Br, 38.14; Cl, 16.92; total halogen as Cl, 33.84. Found: C, 40.25; H, 4.97; total halogen as Cl, 33.81.

An analytical sample of the *endo-cis*-2-bromo-3-chloronorbornane had b.p. 71–72° (2 mm.) and solidified as a low melting solid.

Anal. Calcd. for $C_7H_{10}BrCl$: C, 40.14; H, 4.81. Found: C, 40.07; H, 4.91.

It was found that the intermediate fractions could be further purified by freezing out the *cis* isomer from a pentane solution cooled with a Dry Ice–acetone bath.

Upon gas chromatographic analysis (silicone) at a column temperature of 154° the *trans* isomer had a retention time of 9.25 min., while that of the *cis* isomer was 15.75 min.

Product Studies on the Dehydrohalogenation of the Chlorobromides.—Three 0.5-g. (0.0024 mole) samples of the chlorobromides were dehydrohalogenated using 1.0 g. (0.026 mole) of potassium in 25 ml. of *t*-butyl alcohol. The reaction was refluxed for 12 hr., 30 ml. of water was added, and the aqueous solution was extracted with four 50-ml. portions of pentane. Each pentane layer was back extracted with three 25-ml. portions of water. The pentane solutions were combined and concentrated on a steam bath to about 20 ml. and then dried over magnesium sulfate. The reaction mixtures were analyzed by gas chromatography (see Table I).

At a column temperature of 149°, 2-chloro-2-norbornene and 2-bromo-2-norbornene had retention times of 14.0 and 21.75 min., respectively.

Sodium 1-Pentoxide in 1-Pentanol.—1-Pentanol was distilled from sodium and the fraction boiling at 134–135° was collected. To 1 l. was added the required amount of clean sodium (cut into small pieces) and the solution was stored in the dark in a polyethylene bottle with an Ascarite protecting tube. The solution was standardized with standard potassium acid phthalate just prior to use.

Sodium *t*-Amyloxide in *t*-Amyl Alcohol.—*t*-Amyl alcohol was refluxed over metallic sodium and was distilled. The fraction boiling at 101–102° was collected and the appropriate amount of sodium was added. The mixture was refluxed overnight under a nitrogen atmosphere. The solution was filtered through a sintered glass funnel in a drybox, and standardized before use.

Potassium *t*-Butoxide in *t*-Butyl Alcohol.—*t*-Butyl alcohol was dried with potassium and distilled. The fraction boiling at 81–82.5° was used. The base was prepared and stored as described above.

Kinetic Measurements.—An accurately weighed sample (about 0.2 to 1.2 g.) of compound was placed in a volumetric flask. Standard base solution was added and the time was noted. Aliquots varying from 5 to 10 ml. were pipetted into clean, dry Pyrex tubes which were sealed immediately. The tubes were immersed simultaneously in a constant temperature oil bath (see Table V), the temperatures being recorded with a National Bureau of Standards calibrated thermometer. The time of immersion was noted. Samples were withdrawn at definite intervals and were quenched in a Dry Ice–acetone bath. The contents were transferred to a flask or beaker containing an excess of approximately 8 N nitric acid. The halide was determined by the Volhard method. Calculations of the rate constants were made graphically by a plot of t *vs.* $\log \left[(b/a)[(a-x)/(b-x)]\right]$ and the slopes were obtained by the method of least squares. In general, good second-order plots were observed to at least 80% reaction. In certain cases, particularly with the *endo-cis*-dibromide at the higher temperatures, the points showed a slight downward trend. In these cases, the rate constants were calculated from points up to about 60% reaction. All rate constants were corrected for solvent expansion. The factors employed at the various temperatures were obtained from the data of Zander.[30] The kinetic data are summarized in Tables V and VI.

A plot of $\log k_r/T$ *vs.* $1/T$ afforded the thermodynamic quantities from the slope and intercept determined by the method of least squares.[31] Interpolated rate constants were obtained from the expression

$$\Delta F^{\pm} = 4.575 \times 10^{-3} T_1 \log \left(\frac{2.084 \times 10^{10} T_1}{k_{T_1}} \right)$$

Exchange Studies. A. *endo-cis*-**2,3-Dibromonorbornane-2,3-**d_2.—To 100 ml. of 0.5016 N solution of sodium pentoxide in pentanol, 1.3772 g. (0.0053 mole) of the dibromide was added. From this solution, 3 aliquots of 30 ml. each were placed into combustion tubes, sealed, and immersed in constant temperature oil bath at 119.7 ± 0.015°. The tubes were withdrawn at different time intervals and quenched in Dry Ice–acetone. After removal of the pentane and pentanol, the residue was distilled yielding recovered *endo-cis*-2,3-dibromonorbornane-*exo*-2,3-d_2

(30) A. Zander, *Ann.*, **224**, 56 (1884).

(31) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., 1961, p. 99.

Table V

RATE CONSTANTS FOR ELIMINATIONS OF 2,3-DIHALONORBORNANES WITH SODIUM 1-PENTOXIDE IN 1-PENTANOL

Compd.	Init. concn. of cmpd., moles/l. × 10²	Init. concn. of base, moles/l.	T, °C., ±0.05°	$k' \times 10^4$,ᵃ l./mole-sec.	Av. k'
IV	2.454	0.3300	123.2	3.40	3.67 ± 0.27
	2.401	.3957	123.2	3.98	
	2.390	.3314	113.0	1.52	1.47 ± 0.06
	2.498	.3957	113.0	1.41	
	3.881	.2982	110.0	0.98	0.98
	3.303	.3430	101.9	.57	0.57 ± 0.01
	2.947	.5170	101.9	.58	
	4.192	.3790	95.0	.22	0.22
	2.042	.3430	86.7	.11	0.11
I	4.032	.3957	122.5	9.28	9.28
	4.150	.3285	111.5	3.65	3.70 ± 0.05
	4.095	.4030	111.5	3.75	
	2.259	.5071	107.1	2.25	2.31 ± 0.05
	2.733	.4917	107.1	2.36	
	4.048	.5251	101.6	1.38	1.38 ± 0.03
	4.102	.5251	101.6	1.34ᵇ	
	4.084	.3430	101.9	1.42ᵇ	
	3.755	.5170	86.8	0.31	0.31 ± 0.003
	3.943	.3430	86.8	.30	
	4.218	.5170	66.1	.033	0.033 ± 0.0002
	4.278	.3430	66.1	.033	
II	2.233	.1493	146.1	15.7	15.3 ± 0.4
	1.709	.1493	146.1	14.9	
	2.549	.1502	127.1	3.61	3.64 ± 0.02
	2.595	.1502	127.1	3.66	
V	4.115	.3314	111.7	105.0	105.0
	3.752	.3880	97.3	27.7	28.4 ± 0.7
	4.170	.3105	97.3	29.2	
	3.757	.5170	86.8	9.58	9.77 ± 0.19
	4.096	.3430	86.8	9.96	
	3.837	.5170	66.1	0.904	0.903 ± 0.001
	3.665	.3430	66.1	0.902	
VI	2.543	.1526	106.9	20.2	20.6 ± 0.3
	2.379	.1502	106.9	20.7	
	3.526	.1502	106.9	21.0	
	3.947	.1468	96.7	7.66	7.49 ± 0.18
	4.802	.1502	96.7	7.22	
	3.603	.1508	96.7	7.59	
	2.888	.1508	96.7	7.38	
	2.459	.1125	96.7	7.62	
	3.333	.1502	86.8	2.68	2.80 ± 0.1
	2.822	.1502	86.8	2.93	
	2.652	.4529	86.8	2.89	
	2.653	.4529	86.8	2.72	

ᵃ Observed k corrected for solvent expansion.   ᵇ Calculated from the slope to 60% reaction.

which was recrystallized from methanol (m.p. 61–62°, lit.[8] 60.4–61.3°).

B. *trans*-**2,3-Dibromonorbornane-2,3-**d_2.—A solution of 1.7158 g. (0.0066 mole) of the dibromide was dissolved in 100 ml. of 0.5525 N solution of sodium pentoxide in pentanol. The mixture was placed in a combustion tube, sealed, and immersed in a bath at a constant temperature of 102.3°. After 40 min., the reaction was quenched and worked up as before. The residue was purified by distillation using a spinning-band column. The distillate, b.p. 50° (0.3 mm.) (lit.[8] b.p. 63–64° at 0.4 mm.), was further purified by gas chromatography on a silicone column at 185°.

Dibromide (7.9096 g., 0.0309 mole) was dissolved in 50 ml. of 0.7645 N potassium *t*-butoxide in *t*-butyl alcohol. The solution (45 ml.) was sealed in a combustion tube and immersed in a bath at 55.65 ± 0.02° and after 33 min., quenched, worked up, and analyzed as described above. The recovered starting material was further subjected to a similar treatment for 42.5 min. and again the products were purified and analyzed.

TABLE VI

RATE CONSTANTS FOR THE DEHYDROBROMINATION OF THE 2,3-DIBROMONORBORANES WITH SODIUM t-AMYLOXIDE IN t-AMYL ALCOHOL

Init. concn., moles/1. × 10²	Init. concn. of base, mole/1.	T, °C. ±0.05°	$k \times 10^4$, 1./mole/sec.	Av. k × 10⁴
endo-cis-2,3-Dibromonorbornane (I)				
3.412	0.4903	96.5	6.35	
2.562	.4903	96.5	6.28	6.15 ± 0.2
2.587	.4894	96.5	5.82	
3.472	.3293	106.8	13.17	
2.524	.3263	106.8	13.27	13.12 ± 0.1
2.669	.3263	106.8	12.91	
trans-2,3-Dibromonorbornane (V)				
4.07	0.3068	56.07	14.42	
3.64	.3068	56.07	14.95	14.47 ± 0.3
2.96	.2954	56.07	14.04	
3.340	.2918	45.89	5.06	
3.187	.2918	45.89	5.43	5.17 ± 0.2
3.661	.2774	45.89	5.02	

The analysis for deuterium content[32] of starting material and recovered material are given in Table III.

Assuming that the proton containing species is monodeuterated, the following expressions are derived

$$(-d[D]/dt) = k_D[D][B]; \quad (-d[H]/dt) = 1/2k_D[H][B] + 1/2k_H[H][B]$$

where [H] = concn. of monodeuterated species and [D] = concn. of dideuterated species. Dividing and integrating, one can obtain

$$\log (H_0/H) = [(k_H + k_D)/2k_D]\log (D_0/D) \quad (1)$$

From eq. 1 and the observed deuterium analysis it is possible to show that the amount of enrichment in deuterium content is con-

(32) Deuterium analyses are by J. Nemeth, Noyes Chemical Laboratory, Urbana, Ill., and are reported to be 1% relative with scattering to 2% relative.

sistent—within the limit of analysis—with the expected isotope effect, and corresponds to essentially no exchange.

Kinetic Isotope Effects.—From the kinetic data given in Table VII for the deuterated compounds, k_D (obsd.) was measured. Corrections for the amount of monodeuterated (assumed) contaminant can be made from eq. 2 and 3.

$$(d[Br]/dt) = k_D[D][B] + 1/2k_D[H][B] + 1/2k_H[H][B] \quad (2)$$
$$k_{obsd.} = k_D[D] + 1/2k_D[H] + 1/2k_H[H] = k_D[D] + 1/2[H](k_D + k_H) \quad (3)$$

TABLE VII

RATE CONSTANTS FOR THE DEHYDROBROMINATION OF THE DIDEUTERATED 2,3-DIBROMONORBORNANES WITH SODIUM 1-PENTOXIDE IN 1-PENTANOL

Compd.	Concn., moles/1. × 10²	Concn. base, mole/1.	T, °C. ±0.03°	$k'_D \times 10^4$, 1./mole/sec.	Av. k'
I-2,3-d_2	2.630	0.1123	126.7	4.09	4.12 ± 0.03
(1.91D)	1.820	.1123	126.7	4.14	
V-2,3-d_2	3.322	.4688	96.3	7.43	7.45 ± 0.02
(1.90D)	2.612	.4688	96.3	7.46	

An isotope effect at 123° was determined for *endo-cis*-2,3-dibromonorbornane (I) by allowing a sample of a known mixture of undeuterated I and monodeuterated I (prepared by the addition of DBr to 2-bromo-2-norbornene) to react to partial completion. Unreacted starting material was recovered as described above and was analyzed for deuterium content. The % reaction was determined by Volhard titration. The following data were recorded.

Atom, % D		Concn. base. mole/1.	Concn. cmpd., moles/1. × 10³	Reacn., %	k_H/k_D
Start	Recovd.				
4.20	4.77	0.4683	3.51	40.7	3.81 ± 0.6
4.20	5.02	0.4683	3.51	51.6	4.04 ± 0.6

The value for the isotope effect may be calculated from eq. 4.

$$\log (H_0/H) = [2k_H/k_H + k_D)](\log D_0/D) \quad (4)$$

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT DEPARTMENT, UNION CARBIDE CHEMICALS CO., SOUTH CHARLESTON 3, W. VA.]

Free-Radical Additions to Norbornadiene

BY DAVID J. TRECKER AND JOSEPH P. HENRY

Addition of a number of addends with low chain-transfer constants to norbornadiene,[1] under free-radical conditions, leads to the corresponding nortricyclene[2] derivatives as the sole 1:1 adducts. Addition of thiophenol, a reagent with a high chain-transfer constant, gives rise to 5-norbornen-2-yl phenyl sulfide, the unrearranged adduct, as well as the nortricyclene derivative. The propensity of the 6-norbornen 2-yl radical (III) to rearrange to the 5-nortricyclyl radical (IV) is related to measured chain-transfer constants. Competitive addition of the trichloromethyl radical to a mixture of norbornadiene and norbornene demonstrates that the effect of the second double bond is strictly an additive one. No lowering of energy by means of a homoconjugative transition state (V) is indicated. Dipole moment studies of 3-dichloromethylene-5-chloronortricyclene indicate that the 5-chloro position is *exo* to the methylene bridge. This strongly suggests that chlorine abstraction by the 3-trichloromethyl-5-nortricyclyl radical is governed by steric considerations.

Introduction

Reactions involving homoconjugative addition of reactive intermediates to bicyclic olefins have received considerable attention in recent years.[3-8] With interest focused primarily on the nature of the ionic intermediates, investigators have studied rearrangements

resulting from addition of numerous addends[9] to norbornadiene. These rearrangements[10,11] lead to 2,7-disubstituted-5-norbornenes and 3,5-disubstituted nortricyclenes and have been rationalized in terms of intermediates which may be conveniently represented by I and II.[3]

While ionic additions of this sort have been exhaustively investigated, analogous free-radical reactions

(1) Bicyclo[2.2.1]hepta-2,5-diene.

(2) Tricyclo[2.2.1.0²,⁶]heptane.

(3) S. Winstein and M. Shatavsky, *J. Am. Chem. Soc.*, **78**, 592 (1956); *Chem. Ind.* (London), 56 (1956).

(4) L. Schmerling, J. P. Luvisi, and R. W. Welch, *J. Am. Chem. Soc.*, **78**, 2819 (1956); H. Bluestone, S. B. Soloway, J. Hyman, and R. E. Lidov, U. S. Patents 2,730,548 (Jan. 10, 1956), 2,738,356 (March 13, 1956), 2,782-238 (Feb. 19, 1957).

(5) G. T. Youngblood, C. D. Trivette, Jr., and P. Wilder, Jr., *J. Org. Chem.*, **23**, 684 (1958).

(6) N. A. Milas and P. P. Otto, *ibid.*, **25**, 2225 (1960).

(7) R. P. Arganbright and W. F. Yates, *ibid.*, **27**, 1205 (1962).

(8) J. B. Miller, *ibid.*, **26**, 4905 (1961).

(9) Among the reagents which have been added to norbornadiene are bromine,[3,4] chlorine,[3,7] hydrogen bromide,[4-5] hydrogen chloride,[5] *p*-toluenesulfonyl chloride,[2] mercuric acetate,[2] *t*-butyl hydroperoxide (acidcatalyzed),[5] water,[5] methanol,[5] performic acid (acid-catalyzed),[5] and nitrosyl chloride.[8]

(10) Ionic rearrangements of this sort are reviewed by P. D. Bartlett in H. Gilman, "Organic Chemistry," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1953, pp. 63-70.

(11) P. von R. Schleyer, *J. Am. Chem. Soc.*, **80**, 1700 (1958), and references therein.