

thionyl chloride. The excess thionyl chloride was removed *in vacuo* and the acid chloride was distilled b.p. 142–144° (17 mm.) to give 19.3 g. (82%).

The anilide was prepared and after crystallization from methanol had m.p. 172–173°. Oxygen analysis 0.87, 0.87 atom % oxygen-18 calculated for localization in the carbonyl.

***p*-Methoxy-*p'*-nitrobenzoyl Peroxide-Anisoyl Carbonyl-O<sup>18</sup> (III).**—This compound was prepared according to Leffler's procedure. From 17.8 g. (0.105 mole) of anisoyl chloride-CO<sup>18</sup>Cl there was obtained after crystallization from acetone-pentane 3.4 g. (11%) of III, m.p. 108–108.5°.

**Labeled *p*-Nitrobenzoyl-*p*-methoxyphenyl Carbonate (IV).**—The mixed peroxide III, 3.2 g. (0.010 mole), was heated for 1.5 hours under reflux in 50 ml. of purified thionyl chloride.<sup>11</sup> The thionyl chloride was removed *in vacuo* to give a solid which was crystallized from acetone-hexane twice to give 0.70 g. of material which softened at 106° and formed a very viscous melt at 122°. A sample of IV prepared in a trial run softened at 121° and melted 126–128°, after standing for five months this sample melted from 121–127°. A pinkish color had developed in the sample indi-

cating the presence of *p*-methoxyphenol. The infrared spectra of labeled IV and unlabeled IV were identical except for a shoulder at 5.56  $\mu$  in the labeled sample which did not appear in the unlabeled material. We attribute this to *p*-nitrobenzoic anhydride which could be easily formed under the conditions of the reaction. A mixed melting point of labeled IV and unlabeled IV was 120–127°. Oxygen-18 analysis showed 0.65, 0.68 atom % oxygen-18 calculated for localization in one position. On the basis of the acid and anilide the analysis should have been 0.86 atom % oxygen-18.

***p*-Methoxyphenol (V).**—The carbonate IV, 0.50 g. (0.00158 mole), was refluxed for 15 min. with 0.50 g. (0.0125 mole) of sodium hydroxide in 8 ml. of water. The mixture was cooled, acidified to pH 7 and extracted with three 10-ml. portions of ether. The ether was washed with 5 ml. of water and then dried over magnesium sulfate. The ether was evaporated to give 0.16 g. of an oil which crystallized from water to afford 0.09 g. (53%) of *p*-methoxyphenol, m.p. 54–55°, infrared identical with that of an authentic sample of *p*-methoxyphenol. Oxygen-18 analysis 0.19, 0.19 atom % oxygen-18. An authentic sample showed 0.20 atom % oxygen-18.

(11) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., New York, N. Y., 1941, pp. 381.

NEW HAVEN, CONN.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

## Neighboring Carbon and Hydrogen. XXI.<sup>1</sup> *Anti*-7 Derivatives of Norbornene<sup>2</sup> (Bicyclo[2.2.1]heptene) as Homoallylic Systems<sup>3a</sup>

BY S. WINSTEIN AND M. SHATAVSKY<sup>3b</sup>

RECEIVED JULY 7, 1955

The mixture of dibromides obtained from bromine addition to bicycloheptadiene contains an unsaturated component which is very reactive in solvolysis. The solid glycol derived from treatment of the dibromide with aqueous permanganate is no longer unusually reactive in solvolysis. Debromination of the dibromoglycol with zinc-copper couple yields initially a very unreactive monobromoglycol. Further debromination yields *exo-cis*-2,3-dihydroxynorbornane. On the basis of this evidence and the dipole moment of the acetone of the dibromoglycol the unsaturated dibromide is taken to be *exo*-5-*anti*-7-dibromonorbornene. Selective hydrolysis of the more reactive halogen atom of the unsaturated dibromide gives rise to *exo*-5-bromo-*anti*-7-hydroxynorbornene. This bromohydrin yields a toluenesulfonate which is very reactive in acetolysis. Zinc debromination of the bromohydrin and hydrogenation of the *anti*-7-hydroxynorbornene gave rise to 7-hydroxynorbornane, identical with a specimen supplied by R. B. Woodward and C. Norton. The toluenesulfonate of the 7-hydroxynorbornene is twenty-five times as reactive as the *exo*-5-norbornenyl ester and  $2 \times 10^5$  times as reactive as the *endo*-5-norbornenyl derivative. The *anti*-7-norbornenyl system should be classed as a homoallylic one along with others like cholesteryl and 5-norbornenyl. However, it is geometrically quite unique. The full extent of anchimeric assistance to ionization of *anti*-7-norbornenyl *p*-toluenesulfonate may be appreciated from the factor of *ca.*  $10^{11}$  between acetolysis rates of *anti*-7-norbornenyl *p*-toluenesulfonate and its saturated analog which has been studied by Woodward and Norton.

As shown elsewhere,<sup>4</sup> the dibromide from addition of bromine to bicycloheptadiene I contains an unsaturated component which has been concentrated somewhat but not isolated separately. This unsaturated dibromide is unusually reactive in solvolysis by comparison with the saturated dibromonorbornenes also obtained. Similarly,<sup>4</sup> the bromoether obtained on treatment of bicycloheptadiene I with N-bromosuccinimide in methanol also contains a highly reactive unsaturated component. In Table I are given the relative reactivities of the unsaturated dibromide and the unsaturated bromoether relative to *exo*-5-bromonorbornene<sup>4</sup> in 80% alcohol. The dibromide is twenty-three times as reactive, and the bromoether 190 times as reactive, as the *exo*-5-bromonorbornene

even before correction for the rate-retarding polar effect of the second halogen atom<sup>5</sup> or the methoxyl group<sup>5</sup> on solvolysis rate.

TABLE I  
COMPARISON OF REACTIVITY OF SOME DEHYDRONORBORNENYL BROMIDES IN 80% EtOH

Compound	Temp., °C.	<i>k</i> , hr. <sup>-1</sup>	Rel. rate <sup>a</sup> <sub>25°</sub>
XIV	75.0	1.0	1
XV	75.0	1.90 ± 0.02	2
II	24.8	0.043	23
	50.0	1.0	
<i>exo</i> -5-Methoxy- <i>anti</i> -7-norbornene <sup>4</sup>	25.1	0.36	190

<sup>a</sup> Approximated on the basis of identical  $\Delta S^\ddagger$  for the first three compounds.

Considerations of mechanism of halogen addition<sup>4</sup> with or without carbon participation suggested II, III and IV as possible structures of the reactive

(5) *E.g.*, S. Winstein, *et al.*, *THIS JOURNAL*, **70**, 816, 821, 828 (1948); E. Grunwald, *ibid.*, **73**, 5458 (1951).

(1) Paper XX: S. Winstein, M. Shatavsky, C. Norton and R. B. Woodward, *THIS JOURNAL*, **77**, 4183 (1955).

(2) See A. M. Patterson, *Chem. Eng. News*, **30**, 930 (1952), for nomenclature.

(3) (a) Research supported by grants from Julius Hyman and Co., Denver, Colo., and later the Julius Hyman Division of Shell Chemical Co.; (b) deceased, summer, 1954.

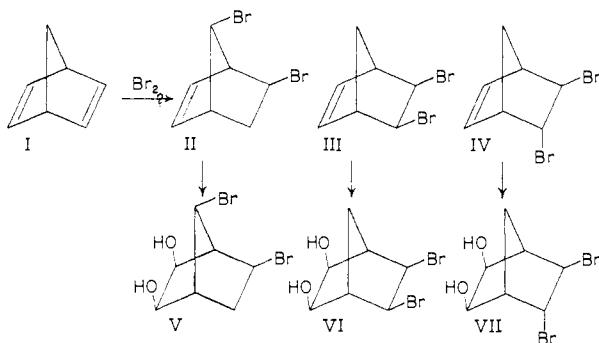
(4) S. Winstein and M. Shatavsky, *Chemistry and Industry*, in press.

TABLE II  
 COMPARISON OF SOLVOLYSIS RATES OF SOME NORBORNYL BROMIDES

Compound	Solvent	Temp., °C.	$k$ , hr. <sup>-1</sup>	Rel. rate $k_2$ , H <sub>2</sub> O, 25°	Rel. rate, <sup>i</sup> $k_1$ , 80% EtOH, 25°
<i>exo</i> -2-Bromo-norbornane <sup>a,b</sup>	80% EtOH	50.0	0.0828		
	80% EtOH	75.0 <sup>c</sup>	1.36		1.0
	80% EtOH	99.9 <sup>e</sup>	10.4		
XII	80% EtOH	75.0	0.021		7.7 × 10 <sup>-3</sup>
	H <sub>2</sub> O	25.0	.0043		
V	H <sub>2</sub> O <sup>d</sup>	25.0	10,400 ± 600 <sup>e</sup>	5.4 × 10 <sup>3</sup>	
	80% EtOH	75.0	0.00236		6.0 × 10 <sup>-4</sup>
IX	H <sub>2</sub> O	50.0	.015		
	H <sub>2</sub> O	75.0	<5 × 10 <sup>-5</sup>		<3 × 10 <sup>-8<sup>k</sup></sup>
<i>trans</i> -2,3-Dibromo-norbornane <sup>g</sup>	H <sub>2</sub> O <sup>f</sup>	25.0	1.94 ± 0.02 <sup>g</sup>	1	
	80% EtOH	99.9	0.042 <sup>h</sup>		1.0 × 10 <sup>-3</sup>
<i>exo</i> -2- <i>syn</i> -7-Di-bromonorbornane <sup>i</sup>	80% EtOH	75.0	.029 <sup>h</sup>		8 × 10 <sup>-3</sup>
	80% EtOH	99.9	.16 <sup>h</sup>		

<sup>a</sup> Data of E. Clippinger.<sup>10</sup> <sup>b</sup> Reported 0.20 hr.<sup>-1</sup> at 55.0°.<sup>11</sup> <sup>c</sup> Extrapolated roughly with  $E^\ddagger = 25.0$  kcal./mole, based on the value<sup>10</sup> of 24.2 kcal./mole in 80% methanol. <sup>d</sup> 0.0110 *M* NaOH. <sup>e</sup> Second-order constant,  $k_2$  hr.<sup>-1</sup> *M*<sup>-1</sup>. <sup>f</sup> 0.0548 *M* NaOH. <sup>g</sup> Sample furnished by H. Kwart<sup>12</sup>; b.p. 74–75° (0.4 mm.),  $n_D^{20}$  1.5710. <sup>h</sup> Rough rate constant based on initial rates. <sup>i</sup> Sample furnished by H. Kwart,<sup>12</sup> b.p. 62–63° (0.4 mm.),  $n_D^{20}$  1.5618. <sup>j</sup> Approximated on the basis of identical  $\Delta S^\ddagger$  for the whole series of compounds. <sup>k</sup> Estimated by comparison with the preceding compound in water.

unsaturated dibromide. The observed solvolysis rate of the unsaturated dibromide was interestingly high for any of these three structures, so that we have followed up this matter by elucidating the structure of the unsaturated dibromide and investigating further the solvolytic behavior of the dibromide and related or derived materials. This work contributes to our knowledge of the anchimeric<sup>6</sup> effects of  $\pi$ -electron-containing substituents<sup>7</sup> in solvolysis.



The first structure proof of the unsaturated dibromide was based on the crystalline dibromoglycol, m.p. 127–128°, which is obtained<sup>4</sup> from the unsaturated dibromide by treatment with dilute potassium permanganate solution. This dibromoglycol yields an acetonide, m.p. 89°, which has been shown in other work<sup>8</sup> to have a dipole moment of 3.64 D. The solvolytic reactivity of the dibromoglycol is shown in Table II, from which it is clear that the dibromoglycol is less reactive in solvolysis than the bromoglycol XII obtained by treatment of *exo*-5-bromonorbornene (XIV) with cold dilute permanganate solution. Thus, the unusually high reactivity associated with the unsaturated dibromide has disappeared on conversion of the olefinic linkage to the glycol grouping.

(6) S. Winstein, C. R. Lindgren, H. Marshall and L. L. Ingraham, *THIS JOURNAL*, **75**, 147 (1953).

(7) *E.g.*, (a) S. Winstein and R. Adams, *ibid.*, **70**, 838 (1948); (b) S. Winstein, H. M. Walborsky and K. Schreiber, *ibid.*, **72**, 5795 (1950); (c) M. Simonetta and S. Winstein, *ibid.*, **76**, 18 (1954).

(8) M. T. Rogers, unpublished work.

Treatment of the dibromoglycol with zinc in alcohol yielded first a monobromoglycol different from the monobromoglycol XII. This new monobromoglycol was uniquely unreactive in solvolysis as is indicated in Table II. On more extended treatment with zinc and alcohol of either the dibromoglycol or the new monobromoglycol there was obtained a completely debrominated glycol which proved to be identical with *exo-cis*-2,3-dihydroxynorbornane (XI), m.p. 140°, which was prepared from treatment of norbornene XIII with cold dilute permanganate solution and which has been reported recently by Kwart and Vosburgh.<sup>9</sup> On the basis of the conversion of the dibromoglycol to the glycol XI, it was concluded that the bicycloheptene carbon skeleton was preserved in the unsaturated dibromide obtained from bicycloheptadiene I.

Considering the possible structures II, III and IV for the unsaturated dibromide, that of the *cis*-dibromide III can be eliminated on the basis of the available evidence. While the dipole moment of the acetonide of the dibromoglycol is permissive<sup>8</sup> for the glycol acetonide VI, the great decrease in reactivity of the unsaturated dibromide on conversion to the glycol might not be expected on the basis of structure III. Also, the dehalogenation of the dibromoglycol, initially to a monobromoglycol different from XII, is not in line with the *cis*-dibromide structure III for the unsaturated dibromide.

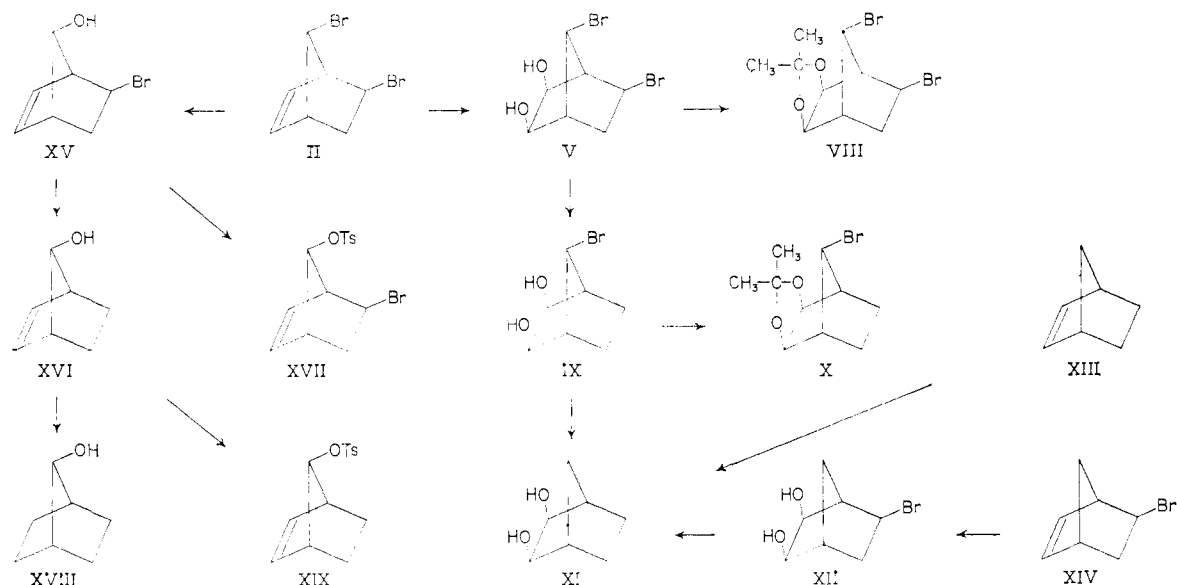
Similarly, the available evidence rules out the *trans*-dibromide structure IV for the unsaturated dibromide. First, the dipole moment of the acetonide of the dibromoglycol is much too high<sup>8</sup> for the acetonide of the dibromoglycol VII. Secondly, the solvolytic reactivity of the dibromoglycol (Table II) is too high for structure VII since it is nearly as reactive as *trans*-2,3-dibromonorbornane. This would correspond to nearly no rate-retarding

(9) H. Kwart and W. G. Vosburgh, *THIS JOURNAL*, **76**, 5400 (1954).

(10) E. Clippinger, Thesis, U.C.L.A., 1955.

(11) J. D. Roberts, W. Bennett and R. Armstrong, *THIS JOURNAL*, **72**, 3329 (1950).

(12) H. W. Kwart and L. Kaplan, *ibid.*, **76**, 4072 (1954).



effect for the glycol hydroxyl groups, whereas they display a substantial rate-retarding effect in *exo*-5-bromo-*exo-cis*-2,3-bicycloheptanediol.

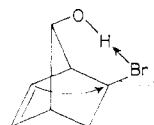
The available evidence supports only structure II for the unsaturated dibromide, namely, *exo*-5-*anti*-7-dibromonorbornene. Such a structure, together with the *exo* configuration for the 5-bromine atom and the *anti* configuration relative to the olefinic linkage for the 7-bromine atom, can be anticipated on mechanistic grounds.<sup>4</sup> Firstly, the dipole moment of the dibromoglycol acetonide V is appropriate for the acetonide of dibromoglycol V. Secondly, structure II for the unsaturated dibromide and therefore V for the dibromoglycol explains the behavior of the dibromoglycol V on zinc debromination. Removal of the *exo*-5-bromine gives the 7-bromoglycol IX, and this, in turn, yields bicycloheptanediol XI on removal of the second less reactive halogen atom. Further, the observations on reactivity receive a satisfactory explanation on the basis of the dibromide structure II for the unsaturated dibromide.

The high reactivity of the unsaturated dibromide II in solvolysis is ascribed to anchimerically assisted ionization of the 7-bromine atom *anti* to the olefinic  $\pi$ -electron cloud. The high reactivity demands the *anti* configuration for the bromine atom since low reactivity is expected for a *syn*-bromine atom. In this connection, Roberts has already mentioned qualitatively that a very low reactivity is associated with a *syn*-chlorine atom in *syn*-7-chloronorbornene.<sup>13</sup> Consistently, we find high reactivity for an *anti*-chlorine atom in the 7-position on the bicycloheptene skeleton in the unsaturated dichloride from bicycloheptadiene I. As is clear from Table III, the unsaturated dichloride exceeds *exo*-5-chloronorbornene in solvolytic reactivity by a factor similar to that which is observed to prevail between the unsaturated dibromide II and *exo*-5-bromonorbornene (XIV) (Table I). Further, it exceeds two other dichlorides<sup>13</sup> in reactivity by at least three to five powers

of ten. On the basis of anchimerically assisted ionization of the 7-bromine atom in the unsaturated dibromide II, it becomes quite clear that the excessively high reactivity should vanish in the absence of the olefinic group. Thus the saturated 2-*exo-syn*-7-dibromonorbornane recently described by Kwart<sup>12</sup> is not more reactive than would be expected from a retarded *exo*-bromide (Table II). Also, the glycol V from the unsaturated dibromide has about the expected reactivity for a dibromide retarded somewhat by the glycol hydroxyl groups (Table II).

The unsaturated dibromide II has been converted to some simpler derivatives which furnish further proof of structure and whose chemistry is also interesting in connection with the homoallylic phenomenon surrounding *anti*-7 derivatives of norbornene. Because of the relatively high reactivity of the 7-bromine relative to the 5-bromine atom in solvolysis, it is possible to solvolyze the unsaturated dibromide II in aqueous acetone to obtain a bromohydrin XV. However, the factor between dibromide II and bromohydrin XV in solvolytic reactivity is approximately only one power of ten<sup>14</sup> (Table I), so successful preparation of the bromohydrin XV depends on careful choice of the stage at which to interrupt the solvolysis of the unsaturated dibromide II. The crystalline bromohydrin XV yields a toluenesulfonate XVII whose reactivity is again

(14) The bromohydrin XV is actually slightly more reactive than the *exo*-5-bromonorbornene instead of slightly less reactive due to the rate-retarding polar effect of an hydroxyl group. At least some of this apparent difference in ionization rates may be due to greater importance of ion pair return<sup>15</sup> in solvolysis of *exo*-5-bromonorbornene than in solvolysis of the bromohydrin XV. However, it seems likely that ionization of bromohydrin XV is facilitated somewhat by hydrogen bonding between the hydroxyl group and the bromine atom.

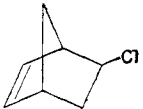
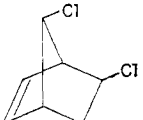
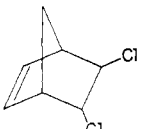
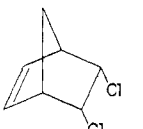


(15) E.g., S. Winstein and K. C. Schreiber, *THIS JOURNAL*, **74**, 2165 (1952); S. Winstein, E. Clippinger, A. H. Fainberg and G. C. Robinson, *Chemistry and Industry*, 664 (1954).

(13) J. D. Roberts, F. O. Johnson and R. A. Carbou, *THIS JOURNAL*, **76**, 5692 (1954).

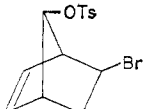
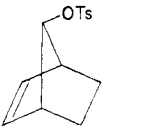
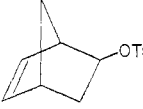
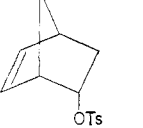
relatively high. As shown in Table IV, the bromohydrin toluenesulfonate XVII is more reactive than *exo*-5-norbornenyl toluenesulfonate in acetolysis even before correction for the rate-retarding bromine atom.

TABLE III  
COMPARISON OF RATES OF SOLVOLYSIS OF SOME DEHYDRO-NORBORNYL CHLORIDES IN 80% EtOH

Compound	Temp., °C.	<i>k</i> , sec. <sup>-1</sup>	Rel. rate <sup>a</sup> 25°
	74.6 99.8	$6.9 \times 10^{-4a}$ $6.9 \times 10^{-5a}$	1
	75.0	$6.4 \times 10^{-5}$	14
	99.9	$1.2 \times 10^{-6}$	$6.3 \times 10^{-3}$
	99.9	$<8.3 \times 10^{-8}$	$<2.2 \times 10^{-4}$

<sup>a</sup> Data of M. Shatavsky.<sup>4</sup> <sup>b</sup> Sample, obtained by chlorine addition to bicycloheptadiene and further purification, 59% unsaturated, was furnished by the Shell Development Co., Denver, Colo. <sup>c</sup> Samples supplied by J. D. Roberts.<sup>18</sup> <sup>d</sup> This sample, obtained by Diels-Alder addition of *cis*-1,2-dichloroethene to cyclopentadiene, was probably contaminated with *cis-exo* material. <sup>e</sup> Approximated on the basis of constant  $\Delta S^\ddagger$  for the series of compounds.

TABLE IV  
COMPARISON OF RATES OF ACETOLYSIS OF SOME DEHYDRO-NORBORNYL *p*-TOLUENESULFONATES AT 25.00°

Compound	<i>k</i> , sec. <sup>-1</sup>	Rel. rate
	$(1.99 \pm 0.02) \times 10^{-3}$	$1 \times 10^4$
	$(3.70 \pm 0.08) \times 10^{-4}$	$2 \times 10^5$
	$1.5 \times 10^{-5a}$	$8 \times 10^3$
	$1.9 \times 10^{-9a}$	1

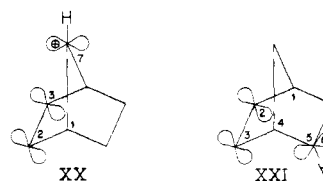
<sup>a</sup> One-third of value for the *p*-bromobenzenesulfonate; data of H. J. Schmid and K. C. Schreiber,<sup>7b,16</sup>

(16) H. J. Schmid, unpublished work.

By successive zinc debromination and hydrogenation it was possible to convert the bromohydrin XV all the way to the saturated 7-norborneol XVIII. This was suggested to us as a further proof of structure by Professor R. B. Woodward since R. B. Woodward and C. Norton at Harvard University had 7-norborneol in hand in an independent study.<sup>1,17</sup> On dehalogenation with zinc and alcohol, bromohydrin XV gave rise to an alcohol XVI *ca.* 90% unsaturated, as shown by quantitative semi-micro hydrogenation. This unsaturated alcohol agreed in m.p. and mixed m.p. with a specimen of 7-hydroxynorborneol which was supplied by R. B. Woodward and C. Norton. The infrared spectra of the two specimens of alcohol agreed well except for some absorption in the 12.4  $\mu$  region by the alcohol XVI from zinc debromination of bromohydrin XV due to slight contamination with nortricyclanol. From hydrogenation of the unsaturated alcohol XVI was obtained alcohol XVIII which proved to be identical in m.p. and in m.p. of the toluenesulfonate derivative with samples supplied by Woodward and Norton.

The toluenesulfonate XIX from the unsaturated alcohol XVI was very reactive in acetolysis. From the data in Table IV, it is clear that the acetolysis rate of the *anti*-7-norbornenyl toluenesulfonate is twenty-five times as reactive as *exo*-5-norbornenyl toluenesulfonate. On the basis of the high reactivities of the toluenesulfonates, the *anti* configuration with respect to the olefinic group is ascribed to the hydroxyl groups in both the bromohydrin XV and the alcohol XVI.

It seems from the present work that the *anti*-7-norbornenyl system should be classed as another homoallylic one along with others such as cholesteryl<sup>7</sup> and 5-norbornenyl.<sup>7</sup> However, the *anti*-7-norbornenyl system is geometrically unique as regards the relation of the cationic center at C-7, in a pre-

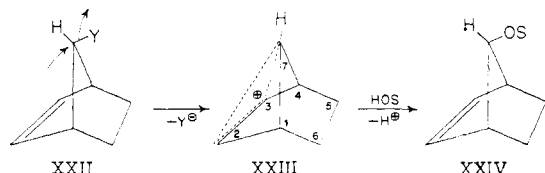


sumed classical 7-norbornenyl cation XX, to the  $\pi$ -electron cloud of the 2,3-olefinic linkage. In the rate of solvolysis, the *anti*-7-norbornenyl halides and toluenesulfonate exceed very substantially the *exo*-5-norbornenyl derivatives. We regard this result as very instructive. While the cationic center at C-7 in a presumed classical 7-norbornenyl cation XX may interact with both C-2 and C-3, the overlap between the vacant *p*-orbital on C-7 and the atomic *p*-orbital on C-2 or C-3 is somewhat further from  $\sigma^{7c}$  than is the case in the analogous presumed classical 5-norbornenyl cation XXI. However, the 2-7 or 3-7 distance in the 7-norbornenyl cation XX is less than the 3-5 distance in the 5-norbornenyl cation XXI. Also, it is not obvious how the net balance between strain and further stabilization in going from the presumed classical cation XX to the actual cation XXIII compares

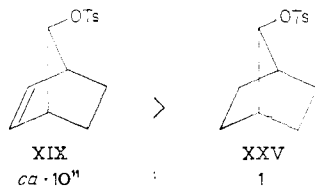
(17) R. B. Woodward and C. Norton, private communication.

with the analogous net balance for the 5-norbornenyl case.

The full extent of the anchimeric assistance to ionization of *anti*-7-norbornenyl derivatives XXII may be appreciated only after noting the extremely low reactivity associated with 7-norbornyl or *syn*-7-norbornenyl derivatives. Thus, 7-norbornyl bromide ionizes in 80% ethanol more slowly than *exo*-2-norbornyl bromide by a factor of at least five powers of ten judging by the behavior of the monobromoglycols IX and XII summarized in Table II. Also, Roberts<sup>13</sup> has mentioned very low solvolytic reactivity for 7-chloronorbornane as well as *syn*-7-chloronorbornene.



The extremely low reactivity toward ionization of the 7-norbornyl system is clearest from the work of Woodward and Norton<sup>1,17</sup> on 7-norbornyl toluenesulfonate (XXV) in the relatively non-nucleophilic acetic acid solvent. Therefore, the extremely large anchimeric assistance provided for ionization of *anti*-7-norbornenyl derivatives XXII becomes clearest by comparison of the rate of acetolysis of *anti*-7-norbornenyl toluenesulfonate (XIX) with Woodward and Norton's value<sup>1,17</sup> for 7-norbornyl toluenesulfonate (XXV). On this basis the comparison is



The present work was interrupted before much scrutiny was made of the products and stereochemistry of solvolysis of *anti*-7-norbornenyl derivatives. The indications from the present work suggest at least a very considerable tendency toward over-all retention of configuration in solvolytic substitution at C-7 in solvolysis of *anti*-7-norbornenyl derivatives XXII. Thus, the unsaturated dibromide II gave, at least very predominantly, the bromohydrin XV, whose toluenesulfonate was very reactive. No other bromohydrin was detected, although the examination was not quantitative. Also, Woodward and Norton have observed<sup>1,17</sup> essentially quantitative formation of the acetate of the original 7-hydroxy-norbornene (XVI) in acetolysis of 7-norbornenyl toluenesulfonate (XIX). The control of stereochemistry of substitution at C-7 in solvolysis of *anti*-7-norbornenyl derivatives XXII by the 2,3- $\pi$ -electron cloud is analogous to that observed at C-3 with cholesteryl derivatives<sup>7</sup> and C-5 with 5-norbornenyl derivatives.<sup>7,16</sup> The cation XXIII from ionization of an *anti*-7-norbornenyl derivative XXII reacts with a nucleophilic reagent or solvent molecule to yield *anti*-7 product XXIV.

It is interesting, but not surprising, that no product from attack of nucleophilic reagent at C-2 or C-3 of the cation XXIII was observed. Such attack, analogous to the predominant attack at C-6<sup>7,18</sup> in the cholesteryl cation or C-2 in the *exo*-5-norbornenyl cation,<sup>7,16</sup> would need to yield a product having both a 3- and a 4-ring fused into a bicycloheptyl skeleton.

### Experimental Part

*exo-cis*-2,3-Dihydroxynorbornane (XI).—To 3.5 g. (0.037 mole) of norbornene dissolved in 350 ml. of 95% ethanol at  $-40$  to  $-60^\circ$  was slowly added dropwise with stirring a solution made up of 5.5 g. (0.035 mole) of potassium permanganate, 5.5 g. of magnesium sulfate and 110 ml. of water. The addition required a half-hour. After the addition, the mixture was allowed to stand a half-hour at  $-40$  to  $-50^\circ$ . Then it was allowed to warm up to  $-10^\circ$ , after which sulfur dioxide was bubbled in. The resulting white mixture was filtered, and the filtrate was evaporated down to ca. 50 ml. This solution was now filtered, and the filtrate was extracted with two 50-ml. portions of methylene chloride. The combined methylene chloride extracts were dried over anhydrous magnesium sulfate a few hours, filtered and the solvent evaporated off using a water aspirator. There resulted 1.8 g. (40%) of white solid, m.p.  $139$ – $140^\circ$  after recrystallization.

*Anal.* Calcd. for  $\text{C}_7\text{H}_{12}\text{O}_2$ : C, 65.59; H, 9.44. Found: C, 65.66; H, 9.46.

*exo-cis*-2,3-Dihydroxy-*exo*-5-bromonorbornane (XII).—A 6.3-g. (0.036 mole) quantity of 70:30 *exo*-dehydronorbornyl, nortricycyl bromide mixture was treated with permanganate solution as in the case of bicycloheptene. The methylene chloride extracts yielded an oily material on evaporation which was extracted with five 20-ml. portions of water at room temperature, leaving a gummy residue. The combined water extracts were filtered and extracted with three 25-ml. portions of methylene chloride. Drying and evaporation of the combined methylene chloride extracts yielded 1.9 g. (36%) of white solid, m.p.  $70$ – $71.5^\circ$  after recrystallization from methylene chloride-petroleum ether and drying for 30 minutes at 1–2 mm.

*Anal.* Calcd. for  $\text{C}_7\text{H}_{11}\text{O}_2\text{Br}$ : C, 40.60; H, 5.36. Found: C, 40.79; H, 5.65.

**Debromination of Bromo-glycols.**—*exo-cis*-2,3-Dihydroxy-*exo*-5-bromonorbornane (XII).—To 3 g. of zinc powder, which was decanted with dilute aqueous cupric sulfate and then washed with two 20-ml. portions of water and one 20-ml. portion of 95% ethanol, was added 25 ml. of 95% ethanol and 0.5 g. (0.0024 mole) of bromoglycol. The stirred mixture was refluxed for two hours and then cooled, after which 5 ml. of saturated aqueous sodium carbonate was added. The mixture was filtered, and most of the solvent was evaporated from the filtrate using an aspirator. The resulting liquid was decanted with two 25-ml. portions of water. The combined water extracts were then extracted with three 25-ml. portions of methylene chloride. The combined methylene chloride extracts were dried over anhydrous magnesium sulfate for three hours, filtered and the solvent was evaporated off using a water aspirator. There resulted 0.14 g. (45%) of white solid, m.p.  $137$ – $138.5^\circ$  after recrystallization from methylene chloride-petroleum ether, m.p.  $138$ – $139^\circ$  on admixture with the glycol from the permanganate oxidation of norbornene.

**Dibromoglycol V.**—The dibromoglycol was treated as above with zinc-copper couple using a 40-minute reflux period and omitting the sodium carbonate in the workup. On a 0.2-mole scale there was obtained a 75% yield of *exo-cis*-2,3-dihydroxy-*anti*-7-bromonorbornane (IX), m.p.  $100$ – $101^\circ$  after recrystallization from methylene chloride-petroleum ether and vacuum drying.

*Anal.* Calcd. for  $\text{C}_7\text{H}_{11}\text{O}_2\text{Br}$ : C, 40.60; H, 5.36. Found: C, 40.86; H, 5.09.

Treatment of the monobromoglycol IX with zinc-copper couple using a 12-day reflux period (eight hours was insufficient) gave, on a 0.004-mole scale, a 40% yield of glycol,

(18) E.g., S. Winstein and A. H. Schlesinger, *THIS JOURNAL*, **70**, 3528 (1948); E. Kosower, unpublished work.

m.p. 139–140°, m.p. 139–140° on admixture with glycol from permanganate oxidation of bicycloheptene.

**Glycol Acetonides.** Dibromo-glycol V.—To 2.2 g. of anhydrous copper sulfate powder in 20 ml. of dry acetone was added 1.17 g. of the dibromoglycol. The mixture was shaken and allowed to stand in a glass stoppered flask for 69 hours. The resulting mixture was then filtered, the solvent was evaporated off using an aspirator, and the resulting oily solid was taken up in 15 ml. of methylene chloride. The solution was washed with 15 ml. of water, and the water portion was extracted with 15 ml. of methylene chloride. The combined methylene chloride solutions were dried over anhydrous potassium carbonate for 36 hours. The solution was then filtered, and the solvent was evaporated off, using an aspirator, to yield 0.9 g. (67%) of solid, m.p. 88.5–89.2° after recrystallization from pentane and 20 minutes drying at 1–2 mm.

*Anal.* Calcd. for  $C_{10}H_{14}O_2Br_2$ : C, 36.84; H, 4.33. Found: C, 37.13; H, 4.52.

***exo-cis*-2,3-Dihydroxy-*anti*-7-bromonorbornane (IX).**—A 3.2-g. quantity of the monobromoglycol IX was converted to the acetonide using a 92-hour reaction period. The reaction mixture was filtered, and the solvent was evaporated off using an aspirator. The resulting solid was taken up in 15 ml. of methylene chloride, and the solution was washed with 15 ml. of water, and then dried over anhydrous potassium carbonate. Evaporation of the solvent yielded 1.0 g. (80%) of a white solid, m.p. 80–81° after recrystallization and drying in vacuum.

*Anal.* Calcd. for  $C_{10}H_{14}O_2Br$ : C, 48.60; H, 6.12. Found: C, 48.51; H, 5.93.

***exo*-5-bromo-*anti*-7-Hydroxynorbornene (XV).**—A 26-g. portion of the dibromide from bromine addition to bicycloheptadiene (23% unsaturated dibromide) was dissolved in 1 l. of 60% acetone, and the solution was kept at 25° for five hours. The reaction mixture was diluted with 2 l. of water and extracted with four 250-ml. portions of methylene chloride. The combined extracts were washed with water and dried over anhydrous magnesium sulfate. Evaporation of the solvent left an oil which was chromatographed on 25 g. of 2:1 silicic acid–Celite.<sup>19</sup>

The chromatographic column was prewashed with 25 ml. of absolute ether, 30 ml. of 1:1 acetone–ether, 25 ml. of absolute ether and 30 ml. of petroleum ether. The oil was put on the column as a solution in petroleum ether, and ca. 80 ml. of petroleum ether was passed through to remove dibromide. Elution with ca. 75 ml. of 1:1 petroleum ether–absolute ether, and evaporation of the solvent yielded 1.8 g. (54%) of material, m.p. 48–49° on crystallization from petroleum ether after decolorizing the solution with Norite.

The chromatography needed to be performed rapidly since the column becomes discolored if the bromohydrin is left on for an extended period.

*Anal.* Calcd. for  $C_7H_8OBr$ : C, 44.47; H, 4.79. Found: C, 44.07; H, 4.97.

For larger batches, it is more convenient to employ 80% acetone because of the limited solubility of the dibromide in the more aqueous medium. For 25 g. of dibromide mixture, 125 ml. of solvent was employed, and a reaction period of five to six hours at 50° was needed. The final product was not as pure as that from the more aqueous medium.

To a 0.9-g. quantity of the bromohydrin in 10 ml. of pyr-

idine was added 1.3 g. of *p*-toluenesulfonyl chloride with cooling, and the reaction mixture was kept in the refrigerator four days. Working up in the usual way yielded 1.3 g. (quantitative yield) of 2-*exo*-bromo-7-*anti*-tosyloxybicyclo-[2,2,1]heptene-5, m.p. 68–69° on recrystallization from petroleum ether, reacting positively to a permanganate test.

*Anal.* Calcd. for  $C_{14}H_{18}O_2SBr$ : C, 48.98; H, 4.40. Found: C, 48.97; H, 4.68.

***anti*-7-Hydroxynorbornene (XVI).**—A 12-g. quantity of zinc dust was decanted with 25 ml. of water, dilute cupric sulfate solution, twice with 25-ml. portions of water, and finally twice with 25-ml. portions of 95% ethanol. A solution of 4.0 g. of *exo*-5-bromo-*anti*-7-hydroxynorbornene in 50 ml. of 95% ethanol was refluxed with the zinc–copper couple with stirring. The resulting cooled reaction mixture was diluted with 750 ml. of water and extracted with four 50-ml. portions of methylene chloride. The combined extracts were dried over anhydrous magnesium sulfate and evaporated to yield 1.2 g. (52%) of solid material, m.p. 114–116° on crystallization from pentane. This material gave a positive test to permanganate. Vacuum sublimation at 5 mm. and room temperature raised the melting point of the bicycloheptenol to 118–119°.

*Anal.* Calcd. for  $C_7H_{10}O$ : C, 76.32; H, 9.15. Found: C, 76.37; H, 9.21.

A crude sample (m.p. 85–90°) of *anti*-7-hydroxynorbornene, furnished by R. B. Woodward and C. Norton, was recrystallized from pentane to yield material of m.p. 116–117°. This did not depress the melting point of the sample, m.p. 114–116°, from zinc debromination of the bromohydrin. Vacuum sublimation at 5 mm. and room temperature of the material, m.p. 116–117°, raised the melting point to 117–118°.

The infrared spectra of the bicycloheptenols from zinc debromination and from Woodward and Norton agreed well except for absorption in the 12.4  $\mu$  region by the bicycloheptenol from zinc debromination due to slight contamination with nortricyclanol.

Conversion of the *anti*-7-hydroxynorbornene to *p*-toluenesulfonate in the usual way in cold pyridine with a reaction time of 24 hours gave a white solid material on crystallization from pentane. This tended to decompose within a few hours on standing at room temperature.

**7-Hydroxynorbornane (XVIII).**—A solution of 0.2744 g. of crude *anti*-7-hydroxynorbornene from debromination of bromohydrin in 25 ml. of methanol absorbed 90% of the theoretical amount of hydrogen over 0.22 g. of 5% palladium-on-barium carbonate. The hydrogen absorption ceased after ten minutes. Under the same conditions nortricyclanol absorbed no hydrogen.

Dilution of the filtered hydrogenation solution with water, extraction of the aqueous solution with three 50-ml. portions of methylene chloride, drying of the combined extracts with magnesium sulfate, and evaporation of the solvent yielded 0.15 g. (54%) of white needles, m.p. 150–151° on crystallization from pentane, m.p. 147.5–149° on admixture with a sample, m.p. 145–148°, furnished by R. B. Woodward and C. Norton. Conversion of some of the alcohol to *p*-toluenesulfonate in the usual fashion gave rise to material, m.p. 54–55°, m.p. 54.5–56° on admixture with a specimen of the toluenesulfonate, m.p. 55–56°, furnished by R. B. Woodward and C. Norton.

*Anal.* Calcd. for  $C_{14}H_{18}O_2S$ : C, 63.13; H, 6.81. Found: C, 63.37; H, 7.00.

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(19) K. N. Trueblood and E. W. Malmberg, *Anal. Chem.*, **21**, 1055 (1949).