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Rearrangements in Carbonium Ion-Type Reactions of C¹⁴-Labeled Norbornyl Derivatives^{1,2}

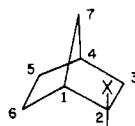
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The extents of isotope-position rearrangement have been determined in solvolyses of *exo*- and *endo*-norbornyl-2,3-C¹⁴ *p*-bromobenzenesulfonates and nitrous acid reactions of *exo*- and *endo*-norbornyl-3-C¹⁴-amines. The bridged "norbornonium" ion proposed by Winstein and Trifan as the intermediate in cationic reactions of norbornyl derivatives does not suffice to account for the C¹⁴-distributions in the reaction products. The formation of norbornyl derivatives with C¹⁴ in the 5- and 6-positions along with the observed percentages of rearrangement require 1,3-type hydride shifts which may occur by way of a "nortricyclonium" ion or its equivalent. The extent of rearrangement was found to increase in the solvolytic reactions as nucleophilic character of the solvent decreased. The rearrangement in the amine-nitrous acid reactions was relatively independent of solvent. More rearrangement was observed when the starting norbornyl derivatives had the *exo*-configuration. Possible interpretations of the experimental results are presented.

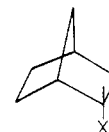
Introduction

Carbonium ion-type reactions of *exo*- and *endo*-norbornyl derivatives (I and II, respectively) have been found to have unusual stereochemical and kinetic characteristics. Solvolyses of the chlorides⁴ (Ia, IIa) and *p*-bromobenzenesulfonates⁵ (Ib, IIb) as well as the reaction of the amines⁶ (Ic, IIc) with nitrous acid yield exclusively substitution products with the *exo*-configuration (I), irrespective of the configuration of the starting material. The solvolysis rates of the *endo* compounds (II) approximate those of the corresponding cyclohexane derivatives,⁷ while those of the *exo* compounds (I) are up to 350 times greater.^{4,5,7} Of particular significance is the observation⁵ that solvolysis of optically active *exo*-norbornyl *p*-bromobenzenesulfonate



EXO-

I



ENDO-

II

Ia, X = Cl	IIa, X = Cl
Ib, X = -SO ₂ C ₆ H ₄ Br	IIb, X = -SO ₂ C ₆ H ₄ Br
Ic, X = -NH ₂	IIc, X = -NH ₂
Id, X = -OAc	IId, X = -OAc
Ie, X = -OH	IIe, X = -OH
If, X = -NO ₂	IIIf, X = -NO ₂

gives only racemic *exo*-norbornyl derivatives. The *endo* derivatives solvolyze with predominant racemization although a small fraction (~8%) of the optical activity survives, the amount being rather solvent dependent.

Winstein⁵ has demonstrated that all of the above experimental results may be accounted for by assuming intermediate formation of the non-classical "norbornonium"⁸ cation (III) analogous to that previously suggested for the conversion of camphene

(8) The present use of this and similar names stems from our feeling that non-classical carbonium ion intermediates of this general type are best designated as "onium" ions to indicate their relationship to ethylenonium, ethyleneacetoxonium, etc., intermediates. While names like "norbornonium," "nortricyclonium" or "tricyclobutonium" (for the ion postulated earlier, J. D. Roberts and R. H. Mazur, *ibid.*, **73**, 3542 (1951)) do not represent an extension of the system used for "ethylene-onium" intermediates, they seem justifiable on the basis of the fairly loose general usage of the -onium suffix as well as from the descriptive and euphonic advantages.

(1) Preliminary reports of this work were given at the Symposium on Reaction Mechanisms at the 75th Anniversary Meeting of the American Chemical Society, September 7, 1951, and by J. D. Roberts and C. C. Lee, *THIS JOURNAL*, **73**, 5009 (1951).

(2) Supported in part by the joint program of the Office of Naval Research and the U. S. Atomic Energy Commission.

(3) Gates and Crellin Laboratories, California Institute of Technology, Pasadena 4, California.

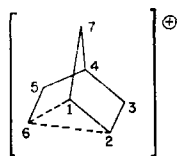
(4) J. D. Roberts, L. Urbanek and R. Armstrong, *THIS JOURNAL*, **71**, 3049 (1949); J. D. Roberts, W. Bennett and R. Armstrong, *ibid.*, **72**, 3329 (1950). See also J. D. Roberts and W. Bennett, *ibid.*, **76**, 4623 (1954).

(5) S. Winstein and D. Trifan, *ibid.*, **71**, 2953 (1949); *ibid.*, **74**, 1147, 1154 (1952).

(6) (a) K. Alder and G. Stein, *Ann.*, **514**, 211 (1934); (b) G. Komppa and S. Beckmann, *ibid.*, **512**, 172 (1934).

(7) S. Winstein, B. K. Morse, E. Grunwald, H. W. Jones, J. Corse, D. S. Trifan and H. Marshall, *THIS JOURNAL*, **74**, 1127 (1952).

hydrochloride to isobornyl chloride.⁹ III has a plane of symmetry (defined by C-4,5,6 and the mid-point of the 1,2-bond) and can be expected to be formed from *exo*-norbornyl derivatives with substantial "driving force" in the ionization process.^{4,5,7}

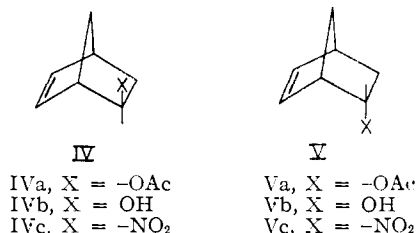


III

It has been pointed out¹⁰ that III does not uniquely account for the stereochemical and kinetic results with norbornyl systems. Indeed, several other cationic intermediates could explain the observed behavior although these are not as well supported by analogies from other systems as is III. In the present investigation, more definite information as to the nature of the intermediate was sought through study of carbonium ion-type reactions of C¹⁴-labeled *exo*- and *endo*-norbornyl derivatives.

Synthetic and Degradative Procedures

Synthesis of norbornyl-2,3-C¹⁴ *p*-bromobenzenesulfonates started from barium carbide-C¹⁴. Acetylene-1,2-C¹⁴ generated from the carbide was converted to vinyl-1,2-C¹⁴ acetate by treatment with acetic acid and mercuric phosphate.¹¹ The Diels-Alder reaction between vinyl-1,2-C¹⁴ acetate and cyclopentadiene¹² afforded a mixture of *exo*- and *endo*-dehydronorbornyl-2,3-C¹⁴ acetates (IVa and



Va, respectively). Hydrogenation of the Diels-Alder adduct gave a mixture of norbornyl-2,3-C¹⁴ acetates (Id, IId) which with lithium aluminum hydride⁵ afforded a mixture of norborneols (Ie, Iie). The product with *p*-bromobenzenesulfonyl chloride in pyridine¹³ yielded a *p*-bromobenzenesulfonate mixture (Ib, Iib). The solvolysis rate curve of the sulfonate ester mixture in 75% acetone-25% water indicated the presence of 19% of the reactive *exo*-isomer (essentially completely solvolyzed in 30 minutes at 45°) in agreement with Winstein and Trifan.⁵ The pure *endo* isomer (Iib) was readily obtained by selective solvolysis of the *exo* isomer in the mixture.

(9) T. P. Nevell, E. de Salas and C. L. Wilson, *J. Chem. Soc.*, 1188 (1939).

(10) J. D. Roberts, R. E. McMahon and J. S. Hine, *THIS JOURNAL*, **72**, 4237 (1950).

(11) (a) G. O. Morrison and T. P. G. Shaw, *Trans. Electrochem. Soc.*, **63**, 425 (1933); (b) B. S. Groth and S. B. H. Johanson, U. S. Patent 2,376,964 (May 29, 1945); *C. A.*, **39**, 3303 (1945).

(12) K. Alder and H. F. Rickert, *Ann.*, **543**, 1 (1939).

(13) R. S. Tipson, *J. Org. Chem.*, **9**, 235 (1944).

A norborneol-2,3-C¹⁴ mixture enriched in the *exo* isomer (Ie) was obtained from the lithium aluminum hydride product by a stereochemical equilibration procedure based on that of Doering and Aschner.¹⁴ Analysis of the mixture by the solvolysis rate curve of its *p*-bromobenzenesulfonate indicated the presence of 70% of the *exo* isomer. The large difference in rate⁵ between the *exo*- and *endo*-norbornyl *p*-bromobenzenesulfonates permitted use of the sulfonate ester mixture in place of the pure *exo* isomer for product isolations since the initial rapid solvolysis was almost entirely due to the *exo* material and the unreacted *endo* ester could be readily separated from the reaction products.

To prepare *exo*- and *endo*-norbornyl-3-C¹⁴-amine, formaldehyde-C¹⁴ was converted to 2-nitroethanol-1-C¹⁴ with nitromethane in high dilution by a procedure similar to that used by Hays, *et al.*¹⁵ The 2-nitroethanol-1-C¹⁴ was dehydrated to 2-nitroethylene with phthalic anhydride.¹⁶ The product was found to add readily to cyclopentadiene in ether at room temperature¹⁷ and afforded 5-nitronorbornene-6-C¹⁴ (IVc, Vc) in excellent yield. No suitable procedure was found for determination of the ratio of *endo* to *exo* isomers formed in this Diels-Alder addition nor were the isomers obtained pure. The unsaturated character of the nitro group would be expected to lead to a high degree of stereospecificity in the addition of nitroethylene to cyclopentadiene¹⁸ so that the *endo* isomer might be expected to predominate to the extent of >90%. In the absence of more specific information, the product will be designated as *endo*-5-nitronorbornene-6-C¹⁴ (Vc).

Hydrogenation of Vc afforded *endo*-2-nitronorbornane-3-C¹⁴ (Iif) which on reduction with iron and hydrochloric acid was converted to *endo*-norbornyl-3-C¹⁴-amine (Iic). The *exo* isomer (Ic) was obtained by isomerization of Iif with triethylamine and reduction. Pure Ic (>90% *exo*) was afforded by fractional crystallization of the acetylated reduction product. The yields of acetyl derivative indicated the isomerization product of Iif to have the composition 70-80% If and 30-20% Iif.

Solvolysis of the labeled norbornyl *p*-bromobenzenesulfonates in 75% acetone-25% water, acetic acid and formic acid yielded *exo*-norborneol, *exo*-norbornyl acetate and *exo*-norbornyl formate, respectively, as previously reported.⁵ The infrared spectrum of the product of the aqueous norbornylamine-nitrous acid reaction indicated it to be *exo*-norborneol contaminated with 2-5% of norcamphor. The latter substance might have been formed by an α -elimination from norbornyl nitrite (or nitrate).¹⁹ Deamination of the norbornylamines in acetic acid gave *exo*-norbornyl acetate. The esters were cleaved to *exo*-norborneol with lithium aluminum hydride for degradation.

(14) W. v. E. Doering and T. E. Aschner, *THIS JOURNAL*, **71**, 838 (1949).

(15) J. T. Hays, G. F. Hager, H. M. Engelmann and H. M. Spurlin, *ibid.*, **73**, 5369 (1951).

(16) G. D. Buckley and C. W. Scaife, *J. Chem. Soc.*, 1471 (1947).

(17) Previously run at 105-115° for 8 hours by K. Alder, H. F. Rickert and E. Windemuth, *Ber.*, **71**, 2451 (1938).

(18) M. C. Kloetzel in R. Adams, "Organic Reactions," Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1948, pp. 10-12.

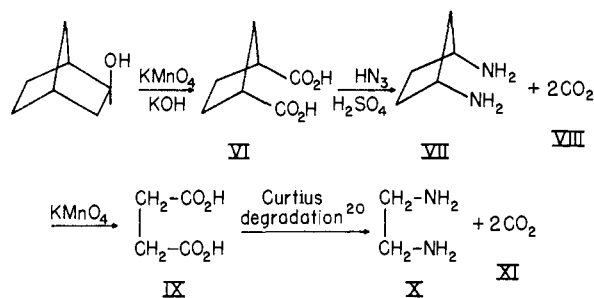
(19) J. W. Baker and D. M. Easty, *J. Chem. Soc.*, 1193 (1952).

TABLE I
 RADIOACTIVITY ANALYSES OF DEGRADATION PRODUCTS OF *exo*-NORBORNYL DERIVATIVES FROM SOLVOLYSES OF NORBORNYL-2,3-C¹⁴ *p*-BROMOBENZENESULFONATES

Exp.	Reactant	Config.	Solvent	Temp., °C.	Acid Meas. act. ^c	V1 ^a Cor. act. ^d	Diamine Meas. act. ^e	VII ^b Cor. act. ^d	BaCO ₃ Meas. act. ^e	VIII Cor. act. ^d	Rearr. %
A	Norborneol mixture from Diels-Alder synthesis (blank)	<i>endo-exo</i> ^g	362	876	0.5	1	1226	847	0.1
B	Norborneol mixture from stereochemical equilibration (blank)	<i>exo-endo</i> ^f	489	1181	4.4	7	1615	1115	0.6
C	Sulfonate ester ^g	<i>exo</i> ^h	75% acetone-25% water	45	586	1417	444	767	815	563	54.1
D	Sulfonate ester ^g	<i>endo</i>	75% acetone-25% water	Reflux	470	1138	361	623	759	525	54.8
E	Sulfonate ester ^g	<i>exo</i> ^h	HOAc	45	650	1571	397	684	1160	800	43.6
F	Sulfonate ester ^g	<i>endo</i>	HOAc	Reflux	593	1433	376	650	1007	696	45.3
G	Sulfonate ester from norborneol stereochemical equilibration product ^g	<i>exo-endo</i> ^f	HCOOH	45	496	1199	416	718	671	464	60.0
H	Sulfonate ester from norborneol equilibration product ^g	<i>exo-endo</i> ^f	HCOOH	Reflux	663	1603	522	900	924	638	56.3
I	Sulfonate ester ^g	<i>endo</i>	HCOOH	Reflux	510	1232	398	688	744	514	55.8
J	Sulfonate ester from norborneol mixture obtained from Diels-Alder synthesis	<i>endo-exo</i> ^g	HOAc	Reflux	622	1505	488	840	892	616	55.8
K	Sulfonate ester from product J	<i>exo</i>	HOAc	Reflux	658	1590	582	1000	798	550	63.0
L	Sulfonate ester from product K	<i>exo</i>	HOAc	Reflux	312	753	293	505	362	242	67.1
M	Sulfonate ester from product H	<i>exo</i>	HOAc	Reflux	223	539	209	361	221	153	67.0
N	Norbornyl formate (30.8% rearranged)	<i>exo</i>	HCOOH ⁱ	45 ^j	629	1520	242	418	1465	1011	27.5 (0.0) ^k
O	Norbornyl formate (30.8% rearranged)	<i>exo</i>	HCOOH ⁱ	Reflux ^l	669	1617	402	693	1319	910	42.8 (17) ^k
P	Norbornyl acetate from norborneol equilibration	<i>exo-endo</i> ^f	HOAc ^m	Reflux ⁿ	662	1600	24	42	2168	1500	2.6

^a *cis*-Cyclopentane-1,3-dicarboxylic acid. ^b *cis*-Cyclopentane-1,3-diamine as the stannous chloride derivative. ^c Measured C¹⁴-activities in counts/min., determined using a windowless methane-filled counter ("Nucleometer"), of "infinitely thick" barium carbonate samples with a cross-sectional area of 2.90 cm.² prepared as described by J. D. Roberts, W. Bennett, E. W. Holroyd and C. H. Fugitt, *Anal. Chem.*, **20**, 904 (1948). The activities are corrected for background and have standard deviations of less than 3% or ± 5 counts/min., whichever is larger. ^d C¹⁴-activities in dis./min./mg. of barium carbonate corrected for self-absorption and dilution by non-labeled carbon atoms as described by J. D. Roberts, R. E. McMahon and J. S. Hine, *THIS JOURNAL*, **72**, 4237 (1950). ^e Approximately 81% *endo* and 19% *exo*. ^f Approximately 70% *exo* and 30% *endo*. ^g C¹⁴-Activities given in duplicate represent either parallel solvolyses or separate combustions on the products of a single solvolysis reaction. ^h Selective solvolysis of *exo* isomer in a mixture of ~70% *exo*- and ~30% *endo*-norbornyl-2,3-C¹⁴ *p*-bromobenzenesulfonates. ⁱ Solution contained 0.46 *M* sodium *p*-toluenesulfonate and 0.46 *M* sodium formate. ^j The reaction time was 0.33 hr. ^k Corrected for rearrangement in starting material. ^l The reaction time was 20 hr. ^m Solution contained 0.37 *M* potassium *p*-toluenesulfonate and 0.41 *M* potassium acetate. ⁿ The reaction time was 20 hr.

The degradation scheme for location of the C¹⁴ in the *exo*-norborneol samples follows.



The radioactivity of VI represents that of the norborneol, while VII contains the C¹⁴ which migrated from its original location at the 2,3-positions. Consequently, the figures (activity of VII/activity of VI) $\times 100$ are designated as "% rearrangement."

(20) A. A. Benson and J. A. Bassham, *THIS JOURNAL*, **70**, 3939 (1948).

The carbon dioxide VIII, isolated as barium carbonate, provides a check on the % rearrangement but was not used in the calculations since values for C¹⁴-activities of barium carbonate samples from the Schmidt reaction by our procedures are always 3-5% low. The remainder of the degradation scheme was carried through for several selected cases to provide a more exact picture of the C¹⁴-distribution. The difference in activity between VII and IX gave the activity of the 7-position. X represents the 5,6-positions of the starting material and the carbon dioxide (XI) activity is derived from that of the 1,4-carbons.

Experimental Results

Data for the % rearrangement in the solvolyses of *exo*- and *endo*-norbornyl *p*-bromobenzenesulfonates in 75% acetone-25% water, glacial acetic acid and anhydrous formic acid are presented in Table I. Corresponding figures for the reactions of *exo*- and *endo*-norbornylamines with nitrous acid in water and acetic acid are given in Table II. The results of the complete degradations are shown in Table III.

TABLE II
RADIOACTIVITY ANALYSES OF *exo*-NORBORNEOL FROM REACTIONS OF *exo*- AND *endo*-NORBORNYL-3-C¹⁴-AMINES WITH NITROUS ACID

Config. of amine	Solvent	Temp., °C.	C ¹⁴ -Activities ^a			
			Acid VI ^b	Di-amine VII ^c	BaCO ₃ VIII	Rearr., %
<i>endo</i> ^d	0.1905	0.000	0.1714	0.0
<i>endo</i>	HBF ₄ -H ₂ O	25	.3706	.1711	.1716	46.2
<i>endo</i>	HOAc	25	.0432	.0180	.0232	41.6
		25	.1470	.0659	.0795	44.9
<i>endo</i>	HOAc	90-100	.0505	.0222	.0263	43.9
<i>exo</i>	HBF ₄ -H ₂ O	25	.0648	.0330	.0281	50.9
<i>exo</i>	HOAc	25	.0766	.0176	.0178	48.0
<i>exo-endo</i> ^e	HBF ₄ -H ₂ O	25	.4039	.2105	.1804	52.1

^a Activities in microcuries/millimole ($\mu\text{c.}/\text{mmole}$) determined by the vibrating reed electrometer method as described by O. K. Neville, THIS JOURNAL, 70, 3499 (1948). ^b *cis*-Cyclopentane-1,3-dicarboxylic acid. ^c *cis*-Cyclopentane-1,3-diamine as the dibenzoyl derivative. ^d Blank degradation on amine. ^e Approximately 70-80% *exo*-amine.

extents of rearrangement corresponded to those which would obtain at equilibrium under the solvolysis conditions, several repetitive reactions were run. Acetolysis of a predominantly *endo*-norbornyl *p*-bromobenzenesulfonate yielded an acetate which was 56% rearranged. Conversion of the acetate (*exo*) to the sulfonate ester and further solvolysis gave a material which was 63% rearranged. A further repetition yielded 67% rearranged acetate. An attempt to further rearrange an *exo*-norbornyl formate, made by solvolysis in refluxing formic acid which showed 69% rearrangement, through conversion to the *p*-bromobenzenesulfonate and solvolysis in acetic acid resulted in no significant change. It appears that the equilibrium extent of rearrangement under these conditions is around 67-70%.

Discussion

In the absence of evidence to the contrary, it will

TABLE III
RADIOACTIVITY ANALYSES OF DEGRADATION PRODUCTS

Reaction	Acid VI ^a	Diamine VII ^b	BaCO ₃ VIII	Acid IX ^c	Diamine X ^d	BaCO ₃ XI
<i>exo</i> -Norbornyl <i>p</i> -bromobenzenesulfonate in HOAc at 45°	Meas. act. ^e	496	416, 244 ^g	671	197, 136 ^g	109
	Cor. act. ^f	1199	718, 422 ^g		271, 188 ^g	75
	% of total (100)		60	39	38	15
Sulfonate ester from norborneol mixture ^h obtained from Diels-Alder synthesis in formic acid at reflux	Meas. act. ^e	2376	2284	2613	2083	2334
	Cor. act. ^f	5740	3940	1805	2880	1610
	% total act. (100)		68.7	31.5	50.2	28.1
<i>exo-endo</i> -Amine mixture ⁱ with HO-NO in HBF ₄ -H ₂ O	Meas. act. ^j	0.4039	0.2105 ^k	0.1804	0.02377 ^l
	% of total act. (100)		52.1	44.7	5.9

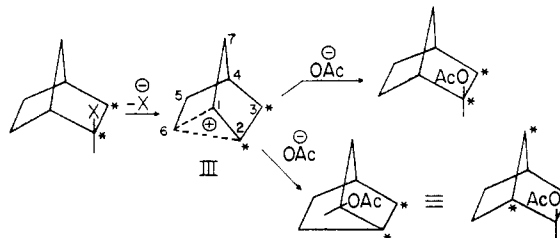
^a *cis*-Cyclopentane-1,3-dicarboxylic acid. ^b *cis*-Cyclopentane-1,3-diamine as stannous chloride derivative. ^c Succinic acid. ^d Ethylenediamine as dihydrobromide. ^e See footnote (c) of Table I. ^f See footnote (d) of Table I. ^g Lower activity figures are for the material which was carried through the complete degradation sequence. ^h Approximately 81% *endo* and 19% *exo*. ⁱ Approximately 70-80% *exo*-amine. ^j See footnote (a) of Table II. ^k As dibenzoyl derivative. ^l As di-*p*-bromophenacyl succinate.

A consistent feature of the rearrangement pattern is a 5-10% difference in % rearrangement between the *endo* and *exo* series. It is probable that the difference is due to some direct displacement of the leaving group by solvent which would lead to unrearranged product with the *exo*-configuration. This conclusion is strongly supported by the observation of Winstein and Trifan⁵ that the acetolysis of *endo*-norbornyl *p*-bromobenzenesulfonate yields 7-8% of optically active *exo*-norbornyl acetate while the *exo*-sulfonate ester gives only racemic *exo*-acetate.

The substantially greater rearrangement on solvolysis of norbornyl *p*-bromobenzenesulfonate in refluxing formic acid as compared with formic acid at 45° is clearly due to further rearrangement of the first-formed *exo*-norbornyl formate at the higher temperature. A blank run with 31% rearranged *exo*-norbornyl formate in refluxing formic acid for 20 hours yielded 43% rearranged ester. No corresponding rearrangement was detected at 45°, nor was labeled *exo*-norbornyl acetate altered when heated to reflux with acetic acid. Winstein and Trifan⁵ have noted that optically active *exo*-norbornyl acetate is not racemized in similar conditions.

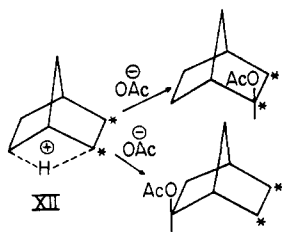
In order to determine how closely the observed

be assumed that the only mechanistic difference between the solvolyses of *exo*- and *endo*-norbornyl *p*-bromobenzenesulfonates is the previously reported⁵ direct replacement reaction which takes place with the *endo* isomer, and, consequently, that the part of the reaction which leads to rearrangement is independent of the configuration of the starting materials. It should be clear that the observed extents of rearrangement, along with the substantial C¹⁴-activity in the 5- and 6-positions of the solvolysis product, cannot be accounted for on the assumption that the only carbonium ion intermediate is the norbornonium cation III. With

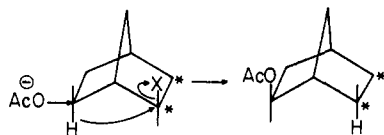


III, the probability of reaction at the 1- and 2-positions is equal (neglecting the isotope effect) and thus a maximum of 50% rearrangement would

be predicted, with no possibility of isotope-position rearrangement to the 5- and 6-positions. Indeed, no combination of the customary 1,2-alkyl or 1,2-hydrogen shifts can lead to 5,6-labeled norbornyl derivatives if the unstable 1-norbornyl cation is excluded as an intermediate. The only reasonable mode of formation of 5,6-labeled products is by way of 2,6-hydrogen migrations and the present work offers convincing evidence that "1,3-type" hydrogen migrations will proceed in favorable circumstances.²¹ Hydrogen migration might take place *via* a non-classical hydrogen-bridge cation



such as XII which could account for the formation of a product with C¹⁴ at the 5- and 6-positions, but *direct* formation of this intermediate, alone or in competition with III, could not lead to more than 50% rearrangement. Although the extent of rearrangement and formation of products with C¹⁴ at the 5- and 6-positions can be rationalized by some contribution of a concerted attack at the 6-position with concomitant hydride shift as shown in the following equation, such eventualities is ruled out by the finding of Winstein and Trifan⁵ that the product is completely racemized.

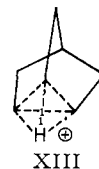


Any intermediate or intermediates which would tend to lead to a statistical distribution of the C¹⁴ over the entire norbornyl carbon skeleton may be excluded by the following argument. If the C¹⁴ were distributed evenly over the norbornyl skeleton, 71.5% rearrangement would be observed. Although this figure is equal within experimental error to the observed equilibrium distribution (see above) there is strong circumstantial evidence that no C¹⁴ is present at the 4-position. Total degradation (see Table III) reveals that, under near-equilibrium conditions, the activity of the 7-position is within experimental error equal to the sum of the activities of the 1- and 4-positions. If *all* the carbon atoms were becoming "scrambled" in the rearrangement process, the activity at the 7-position would be just one-half the sum of the activities at the 1- and 4-positions. The only reasonable interpretation of the near-equilibrium C¹⁴-distribution is that an intermediate or intermediates are involved which tend to spread the C¹⁴ initially at position 2 over positions 1, 2 and 6 and the activity

(21) See also W. A. Mosher and J. C. Cox, Jr., *THIS JOURNAL*, **72**, 3701 (1950); W. v. E. Doering and A. P. Wolf, Abstracts of the XII International Congress of Pure and Applied Chemistry, 1950, p. 437.

at position 3 over positions 3, 5 and 7.²² In this event, the activity at C-7 would be equal to the sum of the activities of C-1 and C-4 as observed. The finding that rearrangement is not complete in a given solvolysis reaction militates against the postulation of a single cationic intermediate, and supports the suggestion of two or more intermediates being formed either simultaneously or consecutively.

All of the experimental results which have been so far obtained can be accommodated if it is assumed that important roles in the rearrangement processes are played by both intermediates III and the non-classical "nortricyclonium" ion XIII (or its equivalent). XIII has a 3-fold symmetry axis and, acting



alone, it would be expected to react with solvent at the 1-, 2- and 6-positions with equal probability thus leading to 66.7% rearrangement. The C¹⁴ distributions actually observed for most of the "single-pass" reactions are intermediate for what would be expected from III or XIII. For example, the C¹⁴-distribution in the carbon skeleton of the acetolysis product of *exo*-norbornyl *p*-bromobenzenesulfonate (Ib) can be calculated within experimental error if it is assumed that 45% of the reaction proceeds *via* XIII and 55% by III (see Fig. 1).

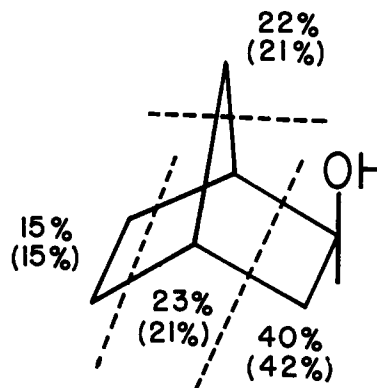
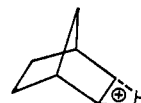


Fig. 1.—Comparison of calculated²² (in parentheses) and found C¹⁴-distributions in solvolysis of *exo*-norbornyl-2,3-C¹⁴ *p*-bromobenzenesulfonate in acetic acid assuming 45% of the reaction proceeds *via* XIII and 55% *via* III.

The fact that the percentages of the rearrangement observed in the solvolyses in aqueous acetone are less than those in acetic acid suggests that III is the initial intermediate^{1,5} and that XIII is formed

(22) The observed near-equilibrium distribution rules out any 2,3-hydrogen shift which would be associated with such an intermediate as



shown [M. J. S. Dewar, *Ann. Reports (Chem. Soc.)*, 121 (1951)1, since cations of this type in combination with III and XIII would lead to "scrambling" of all of the atoms.

from it in a subsequent step. The aqueous solvent is more nucleophilic than acetic acid and III would then have a shorter lifetime and a smaller opportunity to rearrange to XIII. The rearrangement data (Table I) indicate that XIII is involved to the extent of 27% in the solvolysis of Ib in aqueous acetone.

The "nortricyclonium" ion (XIII) is interesting as the equivalent of the historically important but frequently discredited cyclopropane mechanism for Wagner-Meerwein rearrangements.²³ A possible formulation of XIII which is analogous to Walsh's²⁴ model of the cyclopropane ring and recent molecular orbital models for boron hydrides²⁵ is shown in Fig. 2. Here, the proton may be considered to be embedded in a molecular orbital containing two electrons and formed by the overlap of three sp^2 orbitals protruding from 1-, 2- and 6-positions.

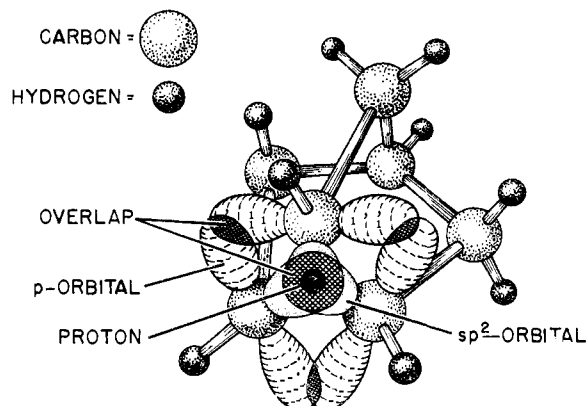
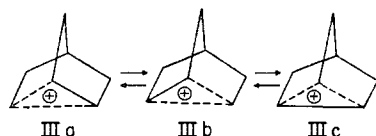


Fig. 2.—Possible atomic orbital representation of "nortricyclonium" ion (XIII) formulated with the aid of Prof. M. J. S. Dewar.

Winstein²⁶ has suggested an alternative representation of the hydride shifts here associated with XIII, which involves equilibration of three ions of type III (IIIa–IIIc). In this formulation, the interconversions are written as proceeding by way of



hydride shifts from the 6- to 2- to 1-positions through intermediates like XII. The consequences of this hypothesis are very much the same as those expected for XIII, and we have been unable to arrive at any experimental method of distinguishing between these formulations. The essential point of difference is a rather subtle one, namely, whether XIII is a true intermediate, that is, occupies a "valley" in the potential energy diagram for the reaction, or is merely a transition state in the

(23) For some examples of the utility of the cyclopropane formulation in accounting for the products of Wagner-Meerwein rearrangements with terpenes see L. Ruzicka, *Helv. Chim. Acta*, **1**, 110 (1918). See also, J. L. Simonsen and L. N. Owen, "The Terpenes," Vol. 11, 2nd Ed., Cambridge University Press, London, 1949, pp. 156-165.

(24) A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949).

(25) H. C. Longuet-Higgins, *J. chim. phys.*, **46**, 268 (1949).

(26) See also, P. D. Bartlett in H. Gilman, "Organic Chemistry," Vol. 111, John Wiley and Sons, Inc., New York, N. Y., 1953, pp. 68-69.

interconversion of IIIa–IIIb–IIIc. Certainly, XIII is the more economical representation.

There are some interesting differences between the rearrangements associated with the solvolyses of the sulfonate esters and the reactions of the amines with nitrous acid. In the deamination processes, the percentage of rearrangement is comparatively insensitive to differences in configuration or reaction medium. Thus, the spread in the extent of rearrangement between the *exo* and *endo* isomers is comparatively slight, and acetic acid as a solvent actually leads to slightly less rearrangement than is observed in aqueous fluoboric acid. Furthermore, ion XIII appears to be less important in the amine-nitrous acid reactions than in the solvolysis processes. Whereas XIII accounts for nearly half of the reaction path in acetolysis of the *exo*-norbornyl sulfonate, it is probably not involved to an extent of greater than 20% in the amine-nitrous acid reaction.²⁷

There are several possible explanations of the differences between the solvolysis and amine-nitrous acid reactions.²⁸ The 5-12% smaller extent of rearrangement in the deamination reaction may be partially due to (1) an unlikely non-rearranging formation of norcamphor, (2) energy differences between the carbonium ions obtained in deamination and solvolysis processes or, (3) "internal return" isomerization. The insensitivity of the rearrangements to ionizing power of the solvent in the amine-nitrous acid reactions observed in this and other²⁹ work as well as the lack of selectivity in migration-aptitude studies³⁰ with β,β -diarylethylamines suggest that carbonium ions obtained by decomposition of alkyldiazonium ions are of high energy relative to those obtained in solvolysis. This is to be expected from the high energy of formation of nitrogen from the diazonium ions and should result with less need for assistance from solvent and neighboring groups in cation formation. It seems possible that part of the greater proportion of direct replacement found in the amine-nitrous acid reaction may arise from direct formation of a small amount of "classical" norbornyl cation which could react with solvent before rearranging to the more stable isomers III and XIII.³¹ An important

(27) The percentage of participation of XIII (or its equivalent) may be calculated from the data in Table III and the following considerations. If XIII were the only intermediate, the C¹⁴-activity at the 5-position (represented by diamine X) would be 33.3% of the activity of the norborneol. Therefore the fraction of the reaction which proceeds via XIII (or its equivalent) is three times the percentage activity of X. Degradation of the *exo*-norborneol from the reaction of the norbornyl-3-C¹⁴-amine with nitrous acid was carried only to succinic acid IX, since the product should be labeled with C¹⁴ only at the 2-, 5- and 7-positions. Therefore, the carboxyl groups of IX should contain no C¹⁴-activity and the total activity of IX would be equal to that of the diamine X. The participation of intermediate XIII is easily calculated from the activity of IX to be about 18%.

(28) A minor source of discrepancy would be an isotope effect in reactions at the 2-position of the doubly labeled norbornyl derivatives used in the solvolysis processes. The labeled position (3) of the amines is away from the immediate reaction site so that practically no isotope effect would be expected. It seems unlikely that isotope effects should introduce deviations much greater than our experimental error.

(29) J. D. Roberts and C. M. Regan, *THIS JOURNAL*, **75**, 2069 (1953).

(30) L. S. Ciereszko and J. G. Burr, Jr., *ibid.*, **74**, 5431 (1952).

(31) This possibility could be tested experimentally since any amount of the reaction proceeding by such a path would lead to optically active norborneol if one started with optically active *exo*-norbornylamine.

difference between the solvolyses and amine-nitrous acid reactions is the "internal return" process demonstrated by Winstein and Trifan⁵ in the solvolysis of *exo*-norbornyl *p*-bromobenzenesulfonate. The observation that the optically active sulfonate ester is racemized more rapidly than it is solvolyzed led to the conclusion that the reaction proceeded through an internally compensated ion-pair consisting of the cation III and *p*-bromobenzenesulfonate anion. This ion-pair could react with solvent to give the solvated cation III or could collapse to give racemized sulfonate ester. Any given molecule of sulfonate ester could thus arrive at the ion-pair stage several times before reacting irreversibly with solvent to give cation III and subsequently the solvolysis product. Clearly, we are not dealing with a strictly irreversible carbonium ion process in the solvolysis reactions and the possibility of some rearrangement at the ion-pair stage must be considered. Presumably, the ion-pair is more stable and longer-lived than a simple carbonium ion and this fact provides some chance for rearrangement, perhaps by conversion to an isomeric ion-pair corresponding to structure XIII. On the other hand, the decomposition of the norbornyldiazonium ion is likely to be a completely irreversible process. The "internal return" phenomenon should be absent and less rearrangement expected.

Acknowledgment.—We are greatly indebted to Professor S. Winstein of the University of California at Los Angeles for discussions and much valuable information regarding the solvolysis of norbornyl *p*-bromobenzenesulfonates well in advance of publication. Several discussions with Professor M. J. S. Dewar have been very helpful.

Experimental

Vinyl-1,2-C¹⁴ Acetate.—Acetylene-C¹⁴ was generated by addition of water under reduced pressure to barium carbide³² containing 1 mc. of C¹⁴ in a 100-ml. round-bottomed reaction flask fitted with a dropping funnel and connected in series with a Dry Ice trap and two liquid nitrogen traps. The reaction mixture was boiled gently for 10 minutes, frozen in Dry Ice and the system evacuated to 1.0 mm.

Mercuric oxide (0.30 g.) was heated with 4.0 ml. of glacial acetic acid and 1.0 ml. of acetic anhydride in a 1-l. flask until all of the solid dissolved. Five milliliters of a 5% solution of 1:1 phosphorus pentoxide-sirupy phosphoric acid in glacial acetic acid was added whereby mercuric phosphate precipitated. The mixture was frozen in a Dry Ice bath, the flask was evacuated to 0.05 mm. and attached to the vacuum system. The acetylene was allowed to vaporize into the flask and the system brought to atmospheric pressure by flushing with inactive acetylene.

The reaction flask was shaken overnight, during which time the pressure fell to 60 mm. The product was removed with a pipet, mixed with 1.0 g. of anhydrous potassium acetate and distilled through a semi-micro column. The yield of vinyl-1,2-C¹⁴ acetate, b.p. 72–74°, was 2.73 g. (71% based on 1 l. of acetylene). The distillation residue was mixed with about 5 g. of inactive vinyl acetate and distilled to scavenge out any remaining labeled product. A further 10 ml. of the mercuric phosphate-acetic acid mixture was added to the reaction flask which was then cooled with liquid nitrogen, evacuated, warmed to room temperature, and the system filled with inactive acetylene at atmospheric pressure. The flask was again shaken overnight and the product isolated as before. The reaction flask was washed with inactive vinyl acetate which was then used to scavenge the distillation residue. The yield of radioactive vinyl ace-

tate was not determined, but was at least 40% based on barium carbide-C¹⁴.

Dehydronorbornyl-2,3-C¹⁴ acetate was prepared by heating 14 g. of cyclopentadiene and 21 g. of labeled vinyl acetate in a sealed tube at 200° for 10 hours. There was obtained 10.5 g. of unreacted vinyl acetate and 13.5 g. (73%, based on unrecovered vinyl acetate) of dehydronorbornyl-2,3-C¹⁴ acetate, b.p. 82–83° (17 mm.), *n*_D²⁰ 1.4667. Several subsequent reactions were carried out using the recovered labeled vinyl acetate. Radioactivity assays of the adducts indicated an over-all C¹⁴-yield of 25% based on barium carbide.

Norbornyl-2,3-C¹⁴ acetate was obtained in 97% yield by low-pressure hydrogenation of dehydronorbornyl-2,3-C¹⁴ acetate at room temperature over platinum oxide in ethyl acetate. The product had b.p. 69° (6 mm.), *n*_D²⁰ 1.4578.

Norborneol-2,3-C¹⁴ was produced by cleavage of norbornyl-2,3-C¹⁴ acetate with lithium aluminum hydride in ether in 90% yield.

Partial Isomerization of *endo*- to *exo*-Norborneol.—A mixture of 15 g. of norborneol-2,3-C¹⁴, 0.30 g. of fluorenone and 0.15 g. of sodium in 35 ml. of toluene was heated under reflux for 48 hours. Most of the toluene was removed under reduced pressure and the residue washed into a sublimation tube with methanol. Removal of the methanol followed by sublimation yielded 13.2 g. (88%) of isomerization product which was found to contain 74% of the *exo* isomer by analysis of the solvolysis rate curve of its *p*-bromobenzenesulfonate in 75% acetone–25% water.

Norbornyl-2,3-C¹⁴ *p*-bromobenzenesulfonates were prepared by the general method of Tipson.¹² The reaction between the alcohols and *p*-bromobenzenesulfonyl chloride was allowed to proceed for two days at 0°. The extractions and washings of the product were carried out at 0° to minimize hydrolysis. Recrystallization from ether-pentane mixtures gave 80–85% yields of the mixed *exo-endo*-norbornyl *p*-bromobenzenesulfonates. The product from pure *exo*-norborneol had m.p. 60° (lit.⁵ 55.7–57.0°) while that from pure *endo*-norborneol had m.p. 62–63° (lit.⁵ 60.0–61.7°).

Selective Solvolysis of the Mixed Sulfonates in 75% Acetone.—A solution (about 7% by weight) of *endo*- and *exo*-sulfonate ester mixture in 75% acetone–25% water (by volume) was heated at 45° for one-half hour. Under these conditions the *exo* isomer was essentially completely solvolyzed while the *endo* isomer was practically unreacted (the first-order solvolysis rate constants at 45 ± 0.1° are 7.8 × 10⁻⁶ sec.⁻¹ and 2.41 × 10⁻⁸ sec.⁻¹ for the *endo*- and *exo*-norbornyl *p*-bromobenzenesulfonates, respectively). Titration of the liberated *p*-bromobenzenesulfonic acid with sodium hydroxide gave the *exo* content of the mixture. The unreacted *endo*-sulfonate ester was recovered by neutralization of the reaction mixture with sodium hydroxide solution and extraction with alcohol-free ether. The extract was dried over magnesium sulfate, concentrated, and pentane added to precipitate the *endo*-sulfonate ester. The filtrate was evaporated to dryness and the residue sublimed to yield *exo*-norborneol, m.p. 127–128°, in 60–65% yields based on reacted *exo*-sulfonate. The recovery of the unreacted *endo*-sulfonate was nearly quantitative.

Solvolysis of *endo*-Norbornyl-2,3-C¹⁴ *p*-Bromobenzenesulfonate in 75% Acetone–25% Water.—A solution of 4.97 g. of *endo*-norbornyl-2,3-C¹⁴ *p*-bromobenzenesulfonate in 75 ml. of 75% acetone–25% water (by volume) was refluxed for 48 hours. The products were isolated as described above. Sublimation of the residue from the ether extraction yielded 0.91 g. (54%) of *exo*-norborneol, m.p. 127–128°, phenylurethan, m.p. 145–146°.

Solvolysis of *exo*-Norbornyl-2,3-C¹⁴ *p*-Bromobenzenesulfonate in Acetic Acid.—A solution of 7.9 g. of the mixed norbornyl-2,3-C¹⁴ *p*-bromobenzenesulfonates from the isomerization reaction described above, 2.5 g. of potassium acetate (10% excess) and 50 ml. of glacial acetic acid was heated at 45° for 20 minutes. Most of the acetic acid was removed under reduced pressure at 45°. The residue was diluted with ice-water, basified with cold sodium hydroxide solution, and extracted with alcohol-free ether. The extract was dried and concentrated to a few ml. Addition of pentane caused the unreacted *endo*-sulfonate ester (2.1 g., 27%) to crystallize. Fractional distillation of the mother liquors yielded 1.6 g. (44%) of *exo*-norbornyl acetate, b.p. 60–61° (5 mm.).

Solvolysis of *endo*-Norbornyl-2,3-C¹⁴ *p*-Bromobenzenesulfonate in Acetic Acid.—The procedure for solvolysis of

(32) Obtained from Tracerlab, Inc., on allocation from the United States Atomic Energy Commission.

the *exo*-sulfonate ester was followed except that the reaction mixture was heated under reflux for 20 hours. From 4.97 g. of *endo*-norbornyl-2,3- C^{14} *p*-bromobenzenesulfonate was obtained 1.53 g. (66%) of *exo*-norbornyl acetate.

Solvolytic of Norbornyl-2,3- C^{14} *p*-Bromobenzenesulfonates in Formic Acid.—A solution of 6.8 g. of the mixed norbornyl-2,3- C^{14} *p*-bromobenzenesulfonates from the isomerization reaction described above and 1.4 g. of sodium formate in 40 ml. of anhydrous formic acid (98–100% reagent grade distilled from Drierite) was heated at 45° for 20 minutes. The resulting solution was worked up as described for the acetic acid solvolyses. The yield of *exo*-norbornyl formate, b.p. 79–80° (25 mm.), was 1.9 g. (66%). No unreacted *endo*-sulfonate ester could be recovered.

In other experiments, using mixed or pure *endo*-sulfonate esters, the reaction mixtures were refluxed for 20 hours. *exo*-Norbornyl formate was obtained in 70–75% yields.

2-Nitroethanol-1- C^{14} .—The procedure for the preparation of this compound was a modification of that described by Hayes, *et al.*,¹⁵ and employed the apparatus shown in Fig. 3. The boiler was charged with 100 g. of redistilled nitromethane, 40 g. of dioxane and 1.5 ml. of 10% citric acid solution. The system was then evacuated to 175 mm., the boiler heated with an oil-bath at 120–130° and the stirrer started. A solution of 1.27 mc. of formaldehyde- C^{14} (0.133 mmole in about 4.5 ml. of water)³³ was mixed with 12 g. of ordinary 36% formaldehyde, 16 g. of dioxane and 0.4 ml. of 10% sodium hydroxide solution; the last 10 ml. of the diluent mixture was used to wash the solution into the dropping funnel. The basic formaldehyde solution was added dropwise over a two-hour period to the refluxing nitromethane in the reaction tube. Finally, a mixture of 4 g. of 36% formaldehyde solution, 4 g. of dioxane and 0.1 ml. of 10% sodium hydroxide solution was added over 20 minutes; refluxing was then continued for an additional 15 minutes. The yellow solution in the boiler was filtered and the solvent removed under reduced pressure. The residue was washed into a 100-ml. distillation flask with 6.0 g. of inactive nitroethanol in two portions. The material was then distilled under reduced pressure taking, as 2-nitroethanol, the fraction of b.p. 59–63° (1.0 mm.). The residue was scavenged three times with a total of 13.0 g. of inactive 2-nitroethanol. The total yield of 2-nitroethanol-1- C^{14} was 29.0 g. (58% after making allowance for the material used as carrier). Radioactivity assay indicated a C^{14} -yield of 45% based on the reported activity of the formaldehyde- C^{14} .

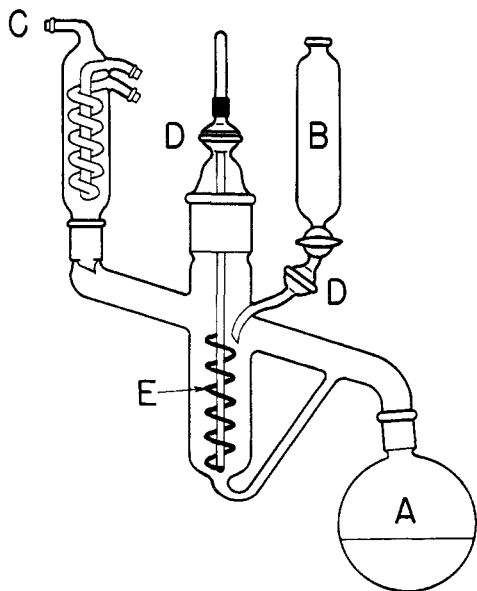


Fig. 3.—Apparatus for formaldehyde- C^{14} -nitromethane reaction; A, nitromethane boiler; B, formaldehyde- C^{14} solution; C, vacuum connection; D, ball joints; E, heavy wire spiral stirrer.

(33) Obtained on allocation from the Los Alamos Scientific Laboratories of the United States Atomic Energy Commission.

Nitroethylene-2- C^{14} was prepared from 2-nitroethanol-1- C^{14} substantially as previously described.¹⁶ In order to minimize polymerization of the nitroethylene by water formed in the dehydration reaction, the product was condensed in an ice-cooled receiver containing a few grams of anhydrous calcium chloride. In a typical experiment, the dehydration product from 40 g. of 2-nitroethanol-1- C^{14} and 90 g. of phthalic anhydride was filtered from the calcium chloride and a small amount of polymer, the residue washed several times with dry ether and the combined filtrates dried over fresh calcium chloride. The resulting ethereal solution of nitroethylene-2- C^{14} was used directly in the next synthetic step.

***endo*-5-Nitronorbornene-6- C^{14} .**—The ethereal solution (about 50 ml.) of nitroethylene-2- C^{14} from the above preparation was added with stirring over 1.5 hours to a solution of 30 g. of freshly distilled, dried cyclopentadiene and dissolved in 75 ml. of dry ether. The reaction mixture warmed to the refluxing temperature during the addition and was then allowed to stand overnight. After removal of the ether and excess cyclopentadiene, distillation of the residue through a short vacuum-jacketed Vigreux column afforded 37.0 g. (61% based on 2-nitroethanol) of almost colorless *endo*-5-nitronorbornene-6- C^{14} ; b.p. 74–77° (4.3 mm.). The product was semi-solid at room temperature.

***endo*-2-Nitronorbornane-3- C^{14} .**—A mixture of 26.5 g. of *endo*-5-nitronorbornene-6- C^{14} , 150 ml. of glacial acetic acid and 0.2 g. of platinum oxide was shaken with hydrogen at two atmospheres. The uptake of hydrogen was rapid and several pauses for cooling of the reaction mixture were necessary. Hydrogen absorption practically ceased after the quantity calculated for one double bond was taken up. The catalyst was removed by filtration and most of the acetic acid distilled under reduced pressure. The residue was taken up in 50 ml. of ether and washed with 25 ml. of water. It was then dried over magnesium sulfate, the ether removed, and the residue sublimed. The yield of colorless, solid *endo*-2-nitronorbornane-3- C^{14} was 21.7 g. (81%). The m.p. of the product was not very well-defined even after repeated sublimation. Most of the material melted from 64–67°.

Anal. Calcd. for $C_7H_{11}NO_2$: C, 59.55; H, 7.86. Found: C, 59.84; H, 8.13.

Isomerization of *endo*-2-Nitronorbornane-3- C^{14} .—A mixture of 32 g. of *endo*-2-nitronorbornane-3- C^{14} and 1.6 g. of triethylamine was heated on a steam-bath overnight. The material was taken up in 100 ml. of pentane and shaken with 50 ml. of 20% acetic acid containing 10 g. of urea.³⁴ The pentane solution was dried over Drierite, the pentane removed and the residue distilled under reduced pressure. The yield of a colorless liquid mixture of *exo*- and *endo*-2-nitronorbornane-3- C^{14} was 31.0 g. (97%); b.p. 78° (4 mm.).

***endo*-Norbornylamine-3- C^{14} .**—To a mixture of 35 ml. of water, 35 ml. of dioxane and 10 ml. of concentrated hydrochloric acid was added 30 g. of 20-mesh iron filings. When the gas evolution ceased, there was added 21 g. of 2-nitronorbornane-3- C^{14} and the mixture refluxed for two days. Several milliliters of hydrochloric acid was added and the mixture steam distilled until 75 ml. of distillate was collected. The residue in the flask was basified with sodium hydroxide solution and an additional 125 ml. of steam distillate collected. The second distillate was extracted three times with ether and the combined extracts dried over potassium carbonate. Removal of the ether through a short column left a colorless liquid residue which on sublimation yielded 11.5 g. (70%) of a hygroscopic white solid which softened at 43° and melted mostly in the range 53–59°. The acetyl derivative of the product had m.p. 123–126°. After repeated recrystallizations from ligroin (b.p. 90–100°), the m.p. was 125–126° (lit.³⁵ m.p. 124°).

***exo*-Norbornylamine-3- C^{14} .**—Reduction of 31 g. of the isomerized 2-nitronorbornane-3- C^{14} described above with iron and hydrochloric acid was performed as in the preceding experiment. The dried ethereal solution of the amine was diluted to 31 ml. with dry ether and added over one-half hour with stirring to 22 g. of acetic anhydride dissolved in 300 ml. of dry ether. The mixture was refluxed for 1 hour, washed with 10% potassium carbonate solution and dried over anhydrous potassium carbonate.

The ethereal solution was concentrated on a steam-bath

(34) Recommended for the regeneration of nitroparaffins from their salts by N. Kornblum and G. E. Graham, *THIS JOURNAL*, **73**, 4041 (1951).

until solid appeared and then allowed to cool. Recrystallization of the first crop of solid gave 5.4 g. of acetyl derivative, m.p. 140–141°. Further systematic crystallization of the material from the mother liquors from ether and later from heptane–ethyl acetate mixtures yielded a total of 11.4 g. of acetyl derivative having m.p. 140–141° (lit.^{6a} m.p. 139°). Repeated recrystallizations of a small sample gave a product of m.p. 141–142.4°.

Regeneration of the amine was effected by heating 11.0 g. of the acetyl derivative with 100 ml. of 10% sulfuric acid under reflux for 24 hours. The reaction mixture was basified with sodium hydroxide solution and extracted with five 40-ml. portions of ether. The extracts were dried over potassium carbonate, and the ether removed through a short column. Distillation of the residue yielded 6.3 g. (79%) of *exo*-norbornylamine-3-C¹⁴ as a colorless liquid, b.p. 78° (55 mm.), which solidified when stored in a refrigerator.

Diazotization of Norbornylamines in Aqueous Fluoboric Acid.—Essentially the same procedure was used for all of the experiments and only a typical reaction with *endo*-norbornylamine-3-C¹⁴ will be described. A mixture of 3.4 g. of the amine and 10 ml. of water was neutralized with 2 *N* fluoboric acid and then an extra equivalent of acid was added. The mixture, which contained some precipitated amine fluoborate, was stirred with a magnetic stirrer and a solution of 2.4 g. (10% excess) of sodium nitrite in 10 ml. of water was added over a period of one hour. The whole was allowed to stand for two days at room temperature and then extracted five times with ether. The combined extracts were dried over magnesium sulfate, the ether removed and the yellow semi-solid residue steam distilled from 20% sodium hydroxide solution. The solid in the receiver was separated by decantation. The residual aqueous phase was saturated with sodium chloride and extracted with ether. The ether extract was combined with the solid and dried over magnesium sulfate. The ether was removed and the residue sublimed. The yield of *exo*-norborneol, m.p. 117–121° (lit., 127–128°, 127.8–128.5°)⁶ was 2.6 g. (77%). The infrared spectrum of the crude norborneol indicated the presence of a few per cent. of norcamphor.

Diazotization of Norbornylamines in Glacial Acetic Acid.—The following procedure is typical. *endo*-Norbornylamine-3-C¹⁴ (6.0 g.) was dissolved in 40 ml. of glacial acetic acid. The solution was stirred with a magnetic stirrer, and 6.0 g. of solid sodium nitrite added portionwise over one hour. The mixture was then allowed to stand overnight at the end of which time was added a final 1.5 g. of sodium nitrite (making a total of two equivalents). Water (15 ml.) was added and the mixture was then poured into 150 ml. of cold 20% sodium hydroxide solution. The whole was extracted with five 40-ml. portions of pentane and the combined extracts washed with 1 *N* hydrochloric acid to remove any unreacted amine (generally less than 10%). The pentane solution was dried over Drierite and the pentane removed through a short column. Fractionation of the residue afforded 4.0 g. (50%) of *exo*-norbornyl acetate, b.p. 77–79° (15 mm.).

An analogous procedure was employed for the reaction at 90–100°. A three-necked flask heated in an oil-bath and fitted with a reflux condenser and a solid addition tube was used. A total of four equivalents of sodium nitrite was added and the yield of *exo*-norbornyl acetate was 60%.

***cis*-Cyclopentane-1,3-dicarboxylic Acid.**—To a solution of 1.0 g. of norborneol in 5 ml. of pentane were added 4.0 g. of solid potassium permanganate and 40 ml. of cold 20% potassium hydroxide solution. During the reaction, the flask was cooled in an ice-bath and stirred with a magnetic stirrer. After 1–3 hours, sulfur dioxide was bubbled through the reaction mixture to remove the excess permanganate and manganese dioxide. The whole was extracted with eight 25-ml. portions of ether. The combined extracts were dried over magnesium sulfate and concentrated on a steam-cone to about 10 ml. The balance of the solvent was removed under reduced pressure at room temperature. The solid residue (a dark, intractable sirup resulted when the evaporation was not performed carefully) was dissolved in alcohol-free ether and filtered through a layer of charcoal supported on a sintered glass funnel. Addition of pentane to the filtrate caused the *cis*-cyclopentane-1,3-dicarboxylic acid to crystallize. The product had m.p. 120–121° (lit.³⁵

119–120.6°). Occasionally, it was necessary to recrystallize the product once or twice to obtain pure material. The yields generally ranged from 40–70%.

Decarboxylation of *cis*-Cyclopentane-1,3-dicarboxylic Acid.—In a 100-ml. flask equipped with a magnetic stirrer and a 2-hole stopper carrying a dropping funnel and a gas outlet tube were placed 0.5 g. of *cis*-cyclopentane-1,3-dicarboxylic acid and a solution of 10 mmoles (50% excess) of hydrazoic acid in 10 ml. of alcohol-free chloroform. The gas outlet was connected to a gas-washing bottle containing saturated barium hydroxide solution. The mixture was stirred and 1.5 ml. of concentrated sulfuric acid added dropwise under slight nitrogen pressure. After all of the acid had been added, nitrogen was passed slowly through dropping funnel to sweep the evolved carbon dioxide into the gas-washing bottle. After the initial reaction subsided, the mixture was heated at 40–45°. The total reaction time was 1–2 hours and in the middle of this period an additional 5 mmoles of hydrazoic acid in 5 ml. of chloroform was added to ensure complete reaction.

The barium carbonate was separated by filtration, washed repeatedly with boiled distilled water, and then digested in boiling distilled water overnight. The precipitate was collected, washed well with boiled distilled water and after a final washing with acetone, dried at 100° at 1 mm. for 2–3 hours. The yields of purified barium carbonate ranged from 70–80%.

The material in the reaction flask was chilled in ice and diluted with 30 ml. of water. The chloroform layer was separated and washed with water. The combined aqueous extracts were basified and distilled into 5 ml. of 2 *N* hydrochloric acid. When the distillation flask was dry, the residue was cooled and 30 ml. of water added. The distillation was again carried to dryness, water was added and the process repeated. The combined distillates were evaporated to dryness in a stream of air on a steam-cone. *cis*-Cyclopentane-1,3-diamine dihydrochloride was obtained as a hygroscopic yellow powder in 70–90% yields.

In some of the work the diamine was converted to the stannous chloride complex³⁶ for radioactivity assay by the following procedure. A solution of 0.35 g. of *cis*-cyclopentane-1,3-diamine dihydrochloride in 2.0 ml. of water was mixed with 1.1 g. (2 equiv.) of stannous chloride dihydrate in 2.0 ml. of water. The whole was heated on a steam-bath for five minutes and then cooled in ice. Crystallization of the stannous chloride complex was initiated by scratching, and the resulting long needles were collected by suction filtration and air-dried. The yield was 0.88 g., m.p. 145–146°.

Anal. Calcd. for C₅H₁₄N₂Cl₆Sn₂·H₂O: C, 10.52; H, 2.83; N, 4.92. Found: C, 10.26; H, 2.90; N, 4.95.

When these reaction conditions were not used, partially hydrated material of indefinite m.p. (about 170°) often was obtained. The reported melting point of the monohydrate is 172°.³⁶ The dibenzoyl derivative of the diamine was more readily obtainable in analytically pure form and so was used in the later stages of the work for characterization and radioactivity assay of the diamine. The dibenzoyl derivative was obtained by shaking 0.1 g. of *cis*-cyclopentane-1,3-diamine dihydrochloride with 0.4 g. of benzoyl chloride and 10 ml. of 10% sodium hydroxide solution until the odor of benzoyl chloride disappeared. The solid was separated by filtration, washed with water and recrystallized from an ethanol–water mixture. The yield of purified dibenzoyl derivative as colorless plates of m.p. 213–215° was 70–90 mg.

Anal. Calcd. for C₁₉H₂₀O₂N₂: C, 74.00; H, 6.54. Found: C, 74.11; H, 6.49.

Oxidation of *cis*-Cyclopentane-1,3-diamine Dihydrochloride.—To a solution of 0.85 g. of *cis*-cyclopentane-1,3-diamine dihydrochloride in 68 ml. of water was added 6.8 g. of potassium permanganate. The mixture was heated under reflux for 15 minutes and then cooled. The manganese dioxide was collected by filtration and washed thoroughly with water. The filtrates were acidified with hydrochloric acid and decolorized with sulfur dioxide. The resulting solution was extracted continuously with alcohol-free ether for two days. The extract was dried over magnesium sulfate, evaporated to near dryness under reduced pressure at room temperature, and the resulting precipitate of succinic

(35) S. F. Birch, W. J. Oldham and R. A. Johnson, *J. Chem. Soc.*, 818 (1947).

(36) O. Diels, J. H. Blom and W. Koll, *Ann.*, **443**, 242 (1925).

acid collected by filtration. The yield was 0.080 g., m.p. 180–185°. Recrystallization from water afforded 0.045 g. of material with m.p. 188–189°. The melting point of the product was not depressed by admixture with an authentic sample. In some instances, the succinic acid was converted to the corresponding di-*p*-bromophenacyl ester which after recrystallization from dioxane–ethanol had m.p. 213–214° (lit.³⁷ m.p. 211°).

(37) W. L. Judefund and E. E. Reid, *THIS JOURNAL*, **42**, 1043 (1920).

Degradation of succinic acid was achieved by the procedure previously described.²⁰ The ethylenediamine was converted to the dihydrobromide, colorless plates from alcohol, for radioactive assay. Since the product did not melt but decomposed, the purity was verified by analysis.

Anal. Calcd. for C₂H₁₀N₂Br₂: C, 10.81; H, 4.50; N, 12.61; Br, 72.07. Found: C, 10.91; H, 4.67; N, 12.90; Br, 72.00.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

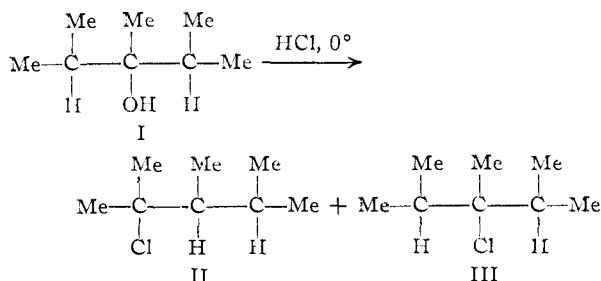
Structure of the Chlorides from 2,2,3-Trimethyl-3-pentanol and 2,3,3-Trimethyl-2-pentanol; Steric Effects as a Factor in the Rearrangements of Highly Branched Carbonium Ions¹

BY HERBERT C. BROWN AND RACHEL BRITTON KORNBLUM²

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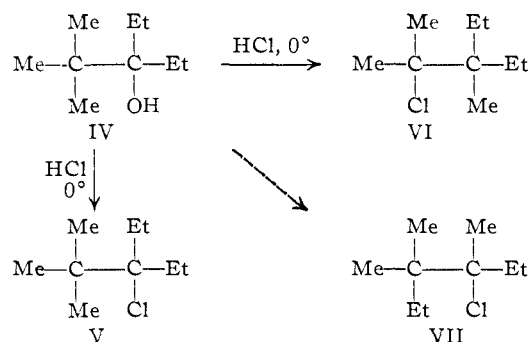
Treatment of 2,2,3-trimethyl-3-pentanol with hydrogen chloride at 0° leads to the formation of 3-chloro-2,2,3-trimethylpentane. Similarly, 2,3,3-trimethyl-2-pentanol yields the corresponding tertiary chloride. In both cases the products were established from rate of hydrolysis data and melting points to be essentially pure compounds, free of detectable amounts of any rearranged chlorides. The assignment of structures to the two chlorides was confirmed by photochemical chlorination of the 2,2,3- and 2,3,3-trimethylpentanes and comparison of the rates of hydrolysis of the tertiary chlorides formed in these chlorinations with the corresponding data for the chlorides obtained from the alcohols. The conversion of these tertiary alcohols into their chlorides without rearrangement contrasts strongly with the ready rearrangement observed in the reaction of 2,2-dimethyl-3-ethyl-3-pentanol with hydrogen chloride. It is suggested that the presence of the two ethyl groups in the latter compound results in a geometrical arrangement which blocks approach to either face of the planar carbonium ion. Such steric hindrance to substitution reactions of highly branched carbonium ions may be an important structural requirement for ready rearrangements in highly branched structures. If this interpretation is valid, it suggests that rearrangements in the reactions of highly branched tertiary alcohols and related derivatives may take place in the carbonium ions after their formation rather than by a synchronous ionization–rearrangement process. The available evidence leads to the conclusion that simple carbonium ions, without special features, are best represented in their classical forms. There is, at present, no evidence available to indicate that the direct formation of bridged ionic intermediates is of importance in the reactions of simple aliphatic derivatives containing bulky substituents.

Treatment of 2,3,4-trimethyl-3-pentanol (I) with hydrogen chloride at 0° leads to the formation of a product which contains two different tertiary chlorides, as shown by an analysis of the solvolysis data.³ These two chlorides were identified as 2-chloro-2,3,4-trimethylpentane (II) and 3-chloro-2,3,4-trimethylpentane (III) by chlorinating the parent hydrocarbon and analyzing the solvolysis data for the tertiary chlorides in the reaction mixture.⁴ The reaction evidently involves a hydride ion shift in the carbonium ion presumably formed in the reaction.⁵



Similarly, treatment of 2,2-dimethyl-3-ethyl-3-pentanol (IV) with hydrogen chloride leads to the

formation of a product which, from solvolysis data, contains at least two different tertiary chlorides⁴ (V, VI). Unfortunately, we encountered difficulties in attempting to establish the structures of these products.⁶ It appeared that these difficulties might be the result of the formation of a third chloride (VII) arising from a double alkyl group shift in the carbonium ion intermediate.



In order to eliminate this possible complication we decided to undertake a study of the reaction of 2,2,3-trimethyl-3-pentanol (VIII) with hydrogen chloride. In the course of this study we encountered unusual results which made it desirable to extend the study to the isomeric alcohol, 2,3,3-trimethyl-2-pentanol (IX). These compounds possess the obvious advantage that each should form only a single rearranged tertiary chloride (XI, X) in addition to the unrearranged isomer (X, XI).

(6) R. S. Fletcher, Ph.D. Thesis, Purdue University.

(1) Chemical Effects of Steric Strains. XI.

(2) Based upon a thesis submitted by Rachel Britton Kornblum in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) H. C. Brown and R. S. Fletcher, *THIS JOURNAL*, **71**, 1845 (1949).

(4) H. C. Brown and R. S. Fletcher, *ibid.*, **73**, 1317 (1951).

(5) F. C. Whitmore, *ibid.*, **54**, 3274 (1932), and numerous subsequent papers in *THIS JOURNAL*.