

0.87, *l* 1, chloroform), kindly supplied by Dr. E. J. Walsh, Jr.,<sup>21</sup> gave on oxidation with chromic oxide–pyridine a sample of bicyclo[2.2.2]oct-5-en-2-one of  $[\alpha]_D -65.1^\circ$  (*c* 1.2, *l* 1, chloroform) and hence is about 10% optically pure.<sup>1,7,18,22</sup> The alcohol 17-OH was converted to a *p*-toluenesulfonate 17-OTs<sup>23</sup> in the usual way, and the latter was subjected to acetolysis in the presence of sodium acetate buffer for 24 hr. Conventional work-up and isolation of the tricyclo[3.2.1.0<sup>2,7</sup>]oct-6-*endo*-yl acetate 6-OAc by vpc on column I gave 6-OAc with  $[\alpha]_D +3.46^\circ$  (*c* 5, *l* 1, in chloroform). Lithium aluminum hydride reduction followed by chromic oxide–pyridine oxidation and isolation by vpc on column I gave ketone 16,  $[\alpha]_D +20.6^\circ$  (*c* 1.7, *l* 1, chloroform). Enantiomerically pure material thus has a maximum rotation of about 212°. This figure is subject to the same uncertainty as that for 10-OH.<sup>18</sup> The ketone was homogeneous on column C, and its retention times on columns A and C were identical with that of one of the ketones in the ketone mixture obtained from the acetolysis products of 1-OBs.

**Correlation of Configurations and Optical Rotatory Powers of Tricyclo[3.2.1.0<sup>2,7</sup>]octan-4-ol (1-OH) with those of Bicyclo[2.2.2]octanol (10) and Bicyclo[3.2.1]octan-2-*exo*-ol (12).** A sample (200 mg) of 1-OH,  $[\alpha]_D +6.49^\circ$  (*c* 3.0, *l* 1, chloroform), was dissolved in 2 ml of acetic acid, treated with 150 mg of platinum oxide, and placed in a long-necked flask, which was shaken in a Parr shaker at 40 psi pressure of hydrogen for 27 hr. The solution was neutralized with sodium bicarbonate and extracted with pentane. After having been washed with brine and dried with magnesium sulfate, the pentane extract was evaporated, and the residual material was separated by vpc on column L. (In a separate experiment, the hydrogenation was interrupted before completion, and starting material of undiminished rotation was recovered.) The hydrogenation products were eluted in the order 12-OH, 10-OH, and 11-OH.

The sample consisting largely of bicyclo[2.2.2]octan-2-ol (10-OH) was sublimed and then showed  $[\alpha]_D +7.60^\circ$ ,  $[\alpha]_{388} +21.3^\circ$  (*c* 2.6, *l* 1, chloroform). Capillary vpc on column B showed this sample (called I) to contain 2% bicyclo[3.2.1]octan-2-*exo*-ol (12-OH) and 98% 10-OH. The infrared spectrum was identical with that of an authentic sample.

The vpc fraction of 12-OH was sublimed to remove some column packing material, whereupon it showed  $[\alpha]_D -3.50^\circ$  (*c* 3.1, *l* 1, chloroform). Capillary vpc on column B showed the presence in this sample (called II) of a small amount (~5%) of 10-OH as well as about 4% of an unknown contaminant. For the purposes of the following calculations, it is assumed that the unknown substance is optically inactive.

If the specific rotation of chemically homogeneous 10-OH and 12-OH are called  $\alpha_{10}$  and  $\alpha_{12}$ , the observed specific rotations of samples I and II ( $\alpha_I$  and  $\alpha_{II}$ ) may be represented by eq 1 and 2. Solution of simultaneous eq 1 and 2 gives the values  $\alpha_{10} = +7.84^\circ$

$$\alpha_I = +7.60^\circ = 0.98\alpha_{10} - 0.02\alpha_{12} \quad (1)$$

$$\alpha_{II} = -3.65^\circ = 0.05\alpha_{10} + 0.95\alpha_{12} \quad (2)$$

and  $\alpha_{12} = -4.24^\circ$ . Using the maximum rotation of 17.4° for 12-OH,<sup>19</sup> the optical purity of the 12-OH isolated from hydrogenolysis of 1-OH may be calculated as 24%. Using the maximum rotation of 29.6–40° for 10-OH,<sup>18</sup> the optical purity of the 10-OH isolated from hydrogenolysis of 1-OH may be calculated as 20–26%. This value corresponds to 1-OH of  $[\alpha]_D 6.49^\circ$ , so that enantiomerically pure 1-OH has  $[\alpha]_D 24$ –32° (chloroform).

## Memory Effects in Multiple Carbonium Ion Rearrangements. V. Nucleophilic Capture of an Asymmetric Tricyclooctyl Cationic Intermediate in the Ring Expansion of the Nortricyclylcarbiny System<sup>1,2</sup>

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**Abstract:** A memory effect is observed in the capture of the first ring-expanded cation in reactions of optically active nortricyclylcarbiny derivatives. This nucleophilic capture leads to tricyclo[3.2.1.0<sup>2,7</sup>]oct-4-yl derivatives with partial (*ca.* 30%) survival of the original enantiomeric purity. Configurational correlations show that capture occurs predominantly from the same side as that occupied by the leaving group. The complex series of rearrangements also can be entered from the tricyclo[3.2.1.0<sup>2,4</sup>]oct-6-yl side, with about the same degree of retention of enantiomeric purity. The intermediate responsible for these results cannot be the same as the cation generated in solvolysis of tricyclo[3.2.1.0<sup>2,7</sup>]oct-4-yl derivatives, since that is shown in an accompanying paper to behave quite differently. The nortricyclylcarbiny and tricyclo[3.2.1.0<sup>2,4</sup>]oct-6-yl products are formed with essentially complete preservation of enantiomeric purity. These results require the postulation of at least two cationic intermediates as precursors of the tricyclo[3.2.1.0<sup>2,7</sup>]oct-4-yl products, and taken together with the detailed product distributions and other evidence, they lead to the formulation of the mechanism of the whole set of interconnected processes.

Ring-expansions of norbornylcarbiny derivatives in carbonium ion reactions quite generally produce once-rearranged intermediates that behave unsym-

metrically.<sup>4</sup> In the 2-norbornylcarbiny system, although most of these intermediates 3 and 4 formed from both *endo*<sup>5</sup> and *exo*<sup>6</sup> substrates (1 and 2) suffer further

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(2) For preliminary reports, see (a) J. A. Berson, R. G. Bergman, G. M. Clarke, and D. Wege, *J. Am. Chem. Soc.*, **90**, 3236 (1968); (b) J. A. Berson, G. M. Clarke, D. Wege, and R. G. Bergman, *ibid.*, **90**, 3238 (1968); (c) J. A. Berson, D. Wege, G. M. Clarke, and R. G. Bergman, *ibid.*, **90**, 3240 (1968).

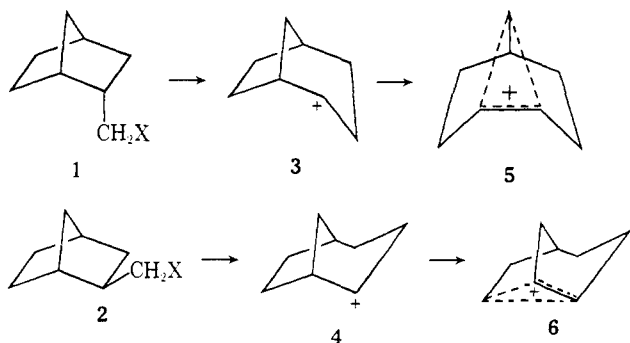
(3) (a) National Institutes of Health Predoctoral Fellow, 1964–1966. (b) Fulbright Research Scholar, 1966–1967. (c) Please address inquiries to this author at Sterling Chemistry Laboratory, Yale University, New Haven, Conn. 06520.

(4) For a review, see J. A. Berson, *Angew. Chem.*, **80**, 765 (1968); *Angew. Chem. Intern. Ed. Engl.*, **7**, 779 (1968).

(5) J. A. Berson and P. Reynolds-Warnhoff, *J. Am. Chem. Soc.*, **84**, 682 (1962); **86**, 595 (1964).

(6) J. A. Berson and D. Willner, *ibid.*, **84**, 675 (1962); **86**, 609 (1964).

bond shift to produce twice-rearranged cations **5** or **6**, there is strong evidence that nucleophiles can capture a portion of the once-rearranged cations. This is partic-

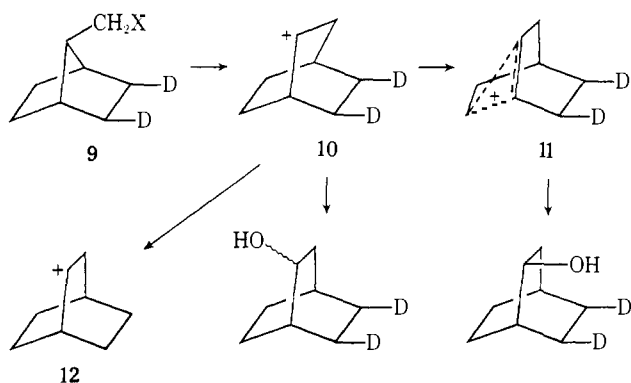


ularly clear in the ring expansion of optically active **1**, where capture of **3**, leading to optically active *endo*- and *exo*-bicyclo[3.2.1]octyl products **7** and **8**,<sup>5</sup> competes with



conformational crossover to **4**<sup>7</sup> and with the second bond shift that forms optically inactive intermediate **5**.

In the 2,3-dideuterio-7-norbornylcarbonyl system<sup>8</sup> **9**, there is some evidence that nucleophilic capture of the once-rearranged cation **10** may occur to a small extent, but most of these species are converted to twice-rearranged cation **11**. The stereochemistry of nucleophilic capture of **10**, an important clue to its nature, is unknown and would be difficult to elucidate, since the small amount of 2-bicyclo[2.2.2]octyl product formed by this path is diluted by a much larger amount formed from the ordinary 2-bicyclo[2.2.2][3.2.1]octyl cation **11**.



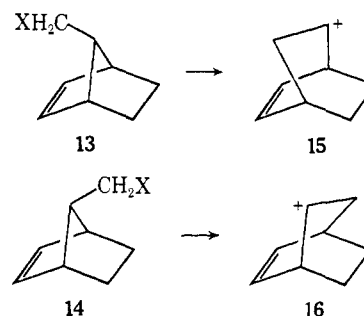
If any nucleophilic capture of the once-rearranged cations **15** and **16** occurs in the ring expansions of the *syn*- and *anti*-norborn-2-enyl-7-carbonyl systems **13** and **14**, it is not enough to be detected by the techniques used.<sup>9</sup>

It would appear that the relative rates of intermolecular nucleophilic capture, crossover (or symmetriza-

(7) Here as elsewhere, structures showing conformationally isomeric or twisted ions are intended as mere mnemonic devices unless specifically designated otherwise.<sup>4</sup>

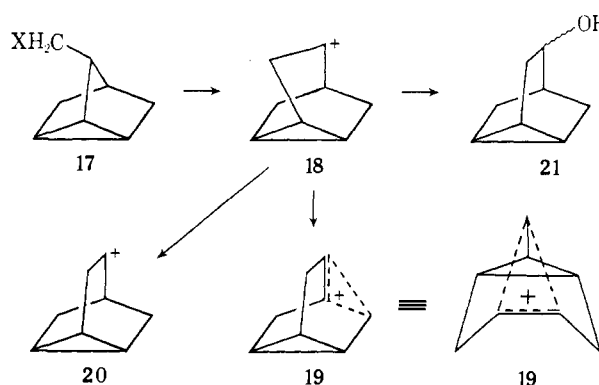
(8) (a) J. A. Berson and M. S. Poonian, *J. Am. Chem. Soc.*, **88**, 170 (1966); (b) J. A. Berson, M. S. Poonian, and W. J. Libbey, *ibid.*, **91**, 5567 (1969).

(9) (a) J. A. Berson and J. J. Gajewski, *ibid.*, **86**, 5020 (1964); (b) J. A. Berson, J. J. Gajewski, and D. S. Donald, *ibid.*, **91**, 5550 (1969).



tion), and intramolecular bond shift are delicately balanced. This makes it difficult to predict whether or not nucleophilic capture can be observed in any specific ring system, but in our view, the examination of such cases is important, since this can provide insights on the structure of the memory-preserving, once-rearranged intermediates.

The present paper reports the nucleophilic capture of such an intermediate in the ring expansion of nortricyclo[3.2.1.0<sup>2,7</sup>]octyl derivatives **17** to the tricyclo[3.2.1.0<sup>2,7</sup>]octyl cation **18**. In practice, this involves the unravelment of a complex skein of relationships among several other carbonium ion systems, but the underlying rationale of the experiment is simple. It is based upon the stereochemical properties of cations of type **18**, which complete a series encompassing **3**, **4**, and **10**.



These once-rearranged cations from the bicyclic ring expansions are converted to other species, either to twice-rearranged cations by bond shift or to conformational isomers,<sup>7</sup> which have the symmetry properties listed in Table I. On formal grounds, there are four

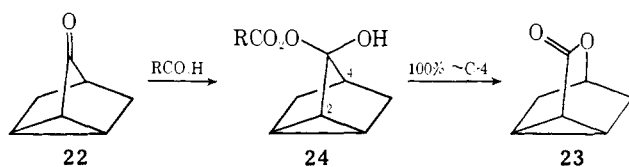
**Table I.** Stereochemical Properties of Cations Derived by Bond Shift and Conformational Change

Starting system	Once-rearr cation	Cation from bond shift	Cation from conform. change
<b>1</b>	<b>3</b>	Symm ( <b>5</b> )	Unsymm ( <b>4</b> )
<b>2</b>	<b>4</b>	Unsymm ( <b>6</b> )	Unsymm ( <b>3</b> )
<b>9</b>	<b>10</b>	Unsymm ( <b>11</b> )	Symm ( <b>12</b> )
<b>17</b>	<b>18</b>	Symm ( <b>19</b> )	Symm ( <b>20</b> )

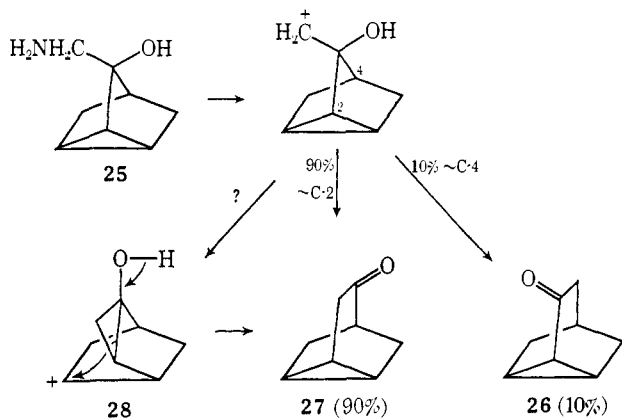
possible combinations of the two properties, symmetry or its absence, taken two at a time. Cations **3**, **4**, and **10** represent three of the combinations and tricyclooctyl cation **18** the fourth. Cation **18** may be looked upon as derived structurally by transannular removal of two hydrogens from any of the other three cations, but it has the unique stereochemical feature that it is the only one of the group that can become symmetrical by *either* bond

shift or conformational change. Therefore, the formation of optically active tricyclooctyl product **21** in the ring expansion of nortricycylcarbinyl substrate **17** would signify that it was the proximate, once-rearranged species **18** that was being trapped, and not the subsequent cations in the scheme, **19** and/or **20**. Moreover, the efficiency and sense of the entrapment could be deduced from the enantiomeric purity and chirality preserved, which could be determined from the optical rotations and relative configurations of product **21** and starting material **17**. The extraction and interpretation of these relationships require a number of pieces of background information. Some of these are described in an accompanying paper,<sup>10</sup> and other studies in the racemic series<sup>11-14</sup> provide valuable guidance. Beyond this, however, the literature of ring expansions of related nortricycylcarbinyl systems contains some puzzling features, and we are concerned first with the question of migratory aptitudes in these reactions.

**Migratory Aptitudes in Ring Expansions of Nortricycyl Derivatives.** Baeyer-Villiger oxidation<sup>15</sup> of nortricyclanone (**22**) gives a lactone (**23**), which must result from cyclopentyl (C-4) migration in the presumed intermediate **24**. This result is in accord with those observed<sup>16</sup> in Baeyer-Villiger rearrangements of several model systems, where cyclopropyl is always a less able migrating group than other *sec*-alkyl groups.



These relative migratory aptitudes are reversed in the nitrosative deamination of the amino alcohol **25**, which gives 10% ketone **26**, resulting from cyclopentyl (C-4) migration, and 90% ketone **27**, resulting from cyclo-



(10) J. A. Berson, D. Wege, G. M. Clarke, and R. G. Bergman, *J. Am. Chem. Soc.*, **91**, 5594 (1969).

(11) R. R. Sauer and J. A. Beisler, *Tetrahedron Letters*, 2181 (1964).

(12) R. R. Sauer, J. A. Beisler, and H. Feilich, *J. Org. Chem.*, **32**, 569 (1967).

(13) A. K. Colter and R. C. Musso, *ibid.*, **30**, 2462 (1965).

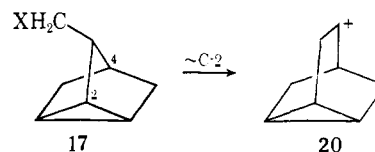
(14) K. B. Wiberg and G. Wenzinger, *ibid.*, **30**, 2278 (1965).

(15) (a) R. R. Sauer, *Tetrahedron Letters*, 1015 (1962). (b) The structure **23** is assigned<sup>15a</sup> from the nmr spectrum in concentrated sulfuric acid. Because of the possibility of rearrangement or selective destruction of the lactone that would result from cyclopropyl (C-2) migration, the extent of the preference for cyclopentyl migration is not firmly established.

(16) R. R. Sauer and R. W. Uebersax, *J. Org. Chem.*, **30**, 3939 (1965).

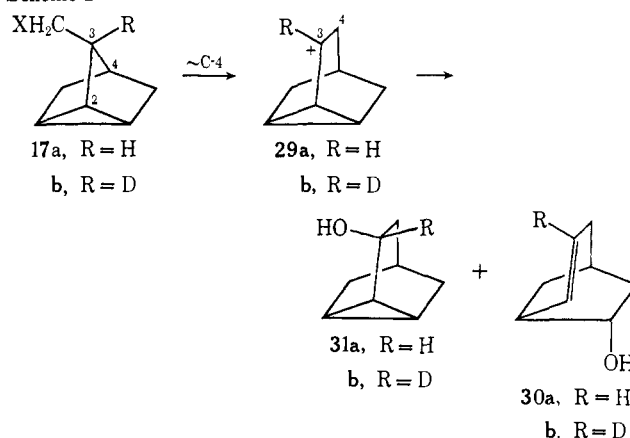
propyl (C-2) migration.<sup>17</sup> An unstable cyclopropanol intermediate, **28**, derived by electrophilic substitution on the cyclopropane ring of **25**, is invoked<sup>17</sup> to rationalize the difference in behavior from the Baeyer-Villiger reaction, but it is not clear why a similar process could not occur in that reaction also. In any case, the predominant over-all structural result in the deamination is presently indistinguishable from net cyclopropyl migration.

The pattern of reactivity becomes still more confusing when one examines the results of solvolytic and deaminative ring expansion of nortricycylcarbinyl derivatives (**17**). These processes produce only small amounts of tricyclo[3.2.1.0<sup>2,7</sup>]oct-4-yl products, resulting from net cyclopropyl (C-2) migration to give cation **20**, but there



are major amounts of products derived from the tricyclo[3.2.1.0<sup>2,7</sup>]oct-3-yl cation (**29**). This species is captured either in the form of the corresponding very sensitive tricyclic product **31** or the closely related unsaturated isomer **33**.<sup>12,14</sup> The most straightforward mechanism imaginable for the **17**  $\rightarrow$  **29** rearrangement involves migration of the cyclopentane ring carbon (C-4) to the methylene side chain, producing the very stable cyclopropylcarbinyl cation **29** directly (Scheme I). If

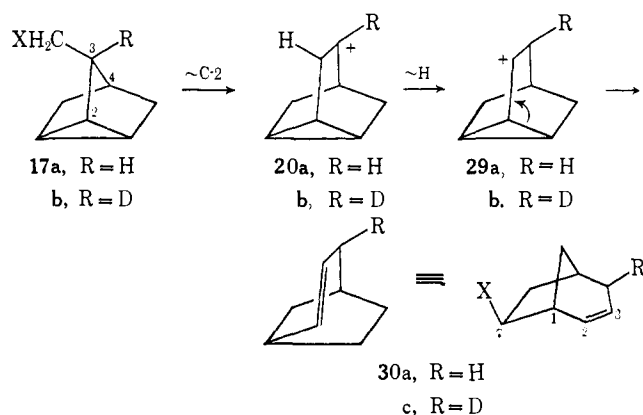
#### Scheme I



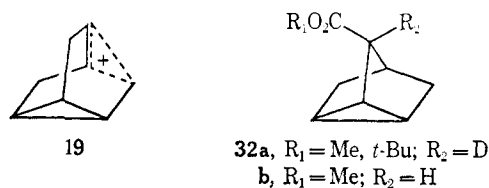
this mechanism is correct, there would appear to be a strange fluctuation in the cyclopropyl/cyclopentyl migratory aptitude ratio, from large in the Baeyer-Villiger oxidation (with oxygen the terminus of migration), to small in the amino alcohol deamination (carbon terminus), to large in the nortricycylcarbinyl ring expansions (carbon terminus). With no obvious rationale for this available, it becomes necessary to consider alternative mechanisms for the rearrangements of nortricycyl compounds of type **17**. In particular, there is the possibility that the formation of cation **29** results not from the direct ring expansion by cyclopentyl (C-4) migration in **17** but instead by a circuitous mechanism in which ring expansion by cyclopropyl (C-2) migration to give cation **20** is followed by hydride shift to **29** (Scheme II). There already are permissive indications on the vicinal hydride shift reaction, since this is an extremely efficient process

(17) J. T. Lumb and G. H. Whitham, *Tetrahedron*, **21**, 499 (1965).

## Scheme II



in cation **20** (or its nonclassical counterpart **19**).<sup>10</sup> Decisive evidence in favor of the circuitous mechanism



(Scheme II) is supplied by a position-labeling experiment. Scheme I predicts that C-3 deuterated starting material **17b** should give unsaturated rearrangement product with vinylic deuterium (**30b**), whereas Scheme II predicts that the deuterium will reside on a saturated carbon (**30c**).

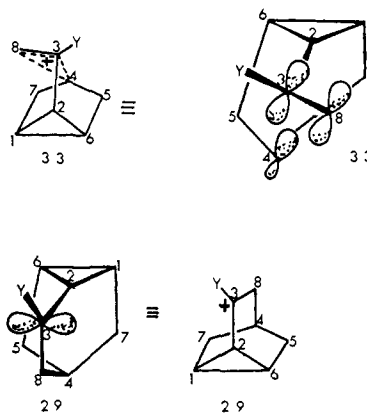
3-Nortricyclylcarbinol-3-*d* (**17b**, X = OH) containing 0.83 D/molecule is formed by lithium aluminum hydride reduction of a mixture of methyl and *t*-butyl esters of 3-nortricyclenecarboxylic-3-*d* acid **32a**, which results from the reaction of methyl 3-nortricyclenecarboxylate **32b** with potassium *t*-butoxide in boiling *t*-butyl alcohol-*O-d*. The location of the deuterium at C-3 follows from the method of synthesis and is confirmed by the nuclear magnetic resonance (nmr) spectrum (solvent CCl<sub>4</sub>), which shows the signal of the carbinol methylene protons as a singlet at  $\delta$  3.34 rather than the doublet characteristic of the undeuterated compound.

Solvolysis of the deuterated *p*-bromobenzenesulfonate (**17b**, X = OBs) in sodium acetate buffered acetic acid gives a mixture (see below) from which, after lithium aluminum hydride reduction and preparative vapor chromatography, the unsaturated alcohol bicyclo[3.2.1]oct-2-en-7-ol **30c** (Scheme II) is isolated. This material contains 0.82 D/molecule, which is 99% of the original label, and its nmr spectrum shows the OH and upfield CH protons as a series of overlapping absorptions of intensity 8. Careful integration of the spectrum (H-2 plus H-3 at  $\delta$  5.2–6.0 *vs.* H-7 at  $\delta$  4.13) shows the presence of  $1.97 \pm 0.04$  vinyl protons. Therefore, not more than 3–4% of the unsaturated alcohol product can be the vinylically deuterated substance **30b** that would result from the direct migration of the cyclopentane ring carbon (C-4) of **17b** (Scheme I); virtually all of the reaction occurs by the cyclopropyl (C-2) migration of Scheme II.

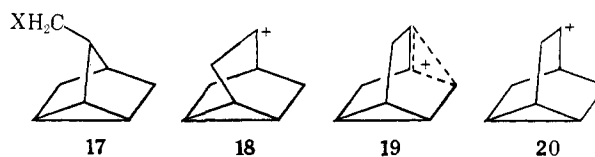
The apparent anomalies in relative migratory aptitudes now disappear, for the labeling experiment shows that *both* rearrangements with carbon termini (the deamination of amino alcohol **25** and the ring expansion

of **17**) have high cyclopropyl/cyclopentyl migration ratios. It is the Baeyer–Villiger reaction, with oxygen as the migration terminus, that is exceptional and prefers cyclopentyl migration, probably because the migrating group is forced to bear a large share of positive charge in the transition state.<sup>18</sup>

The surprising element in the solvolytic ring expansion of **17-OBs** is the migration of the less efficient migrating group (cyclopropyl) to give the less stable ring-expanded tricyclo[3.2.1.0<sup>2,7</sup>]oct-4-yl cation **20**, which only an appended hydride shift finally converts to the more stable tricyclo[3.2.1.0<sup>2,7</sup>]oct-3-yl cation **29** (Scheme II). The mechanism is curiously indirect, since **29** in principle could be generated in one step from **17** by migration of the better migrating group (cyclopentyl), as in Scheme I. A rationale for this behavior in terms of steric inhibition of cyclopropylcarbinyl resonance in the transition state **33** for cyclopentyl migration has been given elsewhere<sup>2</sup> and will not be repeated here.



**An Intermolecular Memory Effect in the Formation and Capture of Tricyclo[3.2.1.0<sup>2,7</sup>]oct-4-yl Cation.** With the path leading to cation **29** now identified as cyclopropyl migration, attention can be redirected to the elucidation of the stereochemistry of capture of the twisted, once-rearranged cation **18**, resulting from ring expansion of the optically active 3-nortricyclylcarbinyl substrates **17**. The literature<sup>11–14</sup> does not provide clear grounds for optimism on the possibility of observing capture of **18** or of its symmetrical counterparts **19** and **20**, since tricyclo[3.2.1.0<sup>2,7</sup>]oct-4-yl acetate (**21-OAc**) when detected<sup>12</sup> at all, is only 8% of the acetolysis product mixture from **17-OBs**. Fortunately, although we observe only slightly larger proportions of **21-OAc** and of the corresponding alcohol **21-OH** in ring expansions of **17** derivatives (Table II), the amount of this product is sufficient to permit spectroscopic identification and



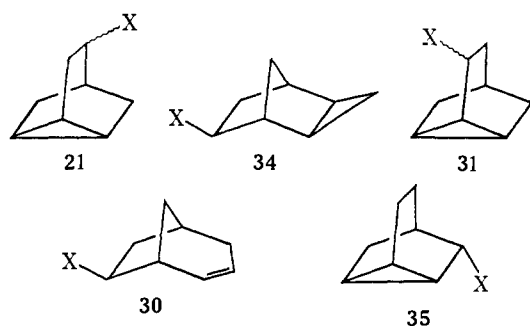
polarimetric examination of samples isolated from the reaction mixture.

(18) For a review, see P. A. S. Smith in "Molecular Rearrangements," Vol. I, P. de Mayo, Ed., Interscience Publishers, New York, N. Y., 1963, pp 577–591.

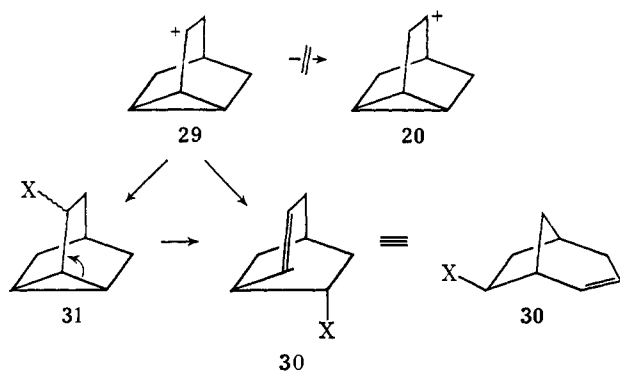
Table II. Product Distributions and Enantiomeric Purities (EP)

Starting material and conditions <sup>a</sup>	Products <sup>a</sup>								
	(+)-17		(+)-34		(+)-21		30		35
	%	EP <sup>b</sup>	%	EP	%	EP	%	EP	%
(+)-17-OBs HOAc, NaOAc 100°	9	94	37	98 <sup>f</sup>	15	27 ± 3 <sup>f</sup>	39	0	Trace
(+)-17-OBs H <sub>2</sub> O, dioxane, py 100°	36	94	46	95	11	32 ± 3	7	0 <sup>c</sup>	<i>g</i>
(-)-17-NH <sub>2</sub> HOAc, NaNO <sub>2</sub> room temp	23	98 <sup>d</sup>	52	103 <sup>d</sup>	14	33 ± 3 <sup>d</sup>	11	0	<i>g</i>
(+)-34-OBs HOAc, 100°	6	100	51	99.5 <sup>i</sup>	15	30 ± 3	26	0 <sup>e</sup>	2 <sup>h</sup>
34-OBs H <sub>2</sub> O, dioxane, py 100°	7	<i>e</i>	71	<i>e</i>	16	<i>e</i>	6	<i>e</i>	<i>g</i>
(+)-21-OBs HOAc, NaOAc, 100°	0		0		35	3-4 <sup>d</sup>	65	0	Trace
21-OBs H <sub>2</sub> O, dioxane, py 100°	0		0		58	<i>e</i>	42	<i>e</i>	<i>g</i>

<sup>a</sup> Absolute configuration shown in text. Signs of rotation refer to acetates. <sup>b</sup> Per cent retention of enantiomeric purity. <sup>c</sup> Assumed. <sup>d</sup> Enantiomeric configuration. <sup>e</sup> Not determined. <sup>f</sup> Average of two separate runs. <sup>g</sup> Not determined. <sup>h</sup> Traces of two other products (0.2 and 0.06%) were present. These may represent transformation products of the hydride-shift product *endo*-tricyclo[3.2.1.0<sup>2,7</sup>]oct-6-yl acetate, since the larger one of them corresponds in retention time to bicyclo[2.2.2]oct-5-en-2-*exo*-yl acetate. <sup>i</sup> By direct comparison of starting acetate and product. The averaged value of Table III was not used here.



The other major products identified in the solvolyses of 17-OBs and in nitrosative deaminations of 17-NH<sub>2</sub> are *exo-exo*-tricyclo[3.2.1.0<sup>2,4</sup>]oct-6-yl (34), *exo*-bicyclo[3.2.1]oct-2-en-6-yl (30), and 3-nortricyclylcarbinyl (17) derivatives (Table II). As is shown elsewhere,<sup>10</sup> products of the tricyclo[3.2.1.0<sup>2,7</sup>]oct-3-yl type (31) are unstable under the conditions of solvolysis and work-up, giving unsaturated bicyclic materials 30 quantitatively. The proportion of 30 therefore represents the amount of tricyclic cation 29 formed, since 29 does not revert to its hydride-shifted isomer 20 under the reaction conditions.<sup>10</sup> The question of whether 29 gives 30 directly or only *via* 31 is immaterial in the present context.


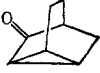


The vapor chromatograms (vpc) of the product mixtures from 17 usually show small peaks that correspond in retention time to *exo*-tricyclo[3.2.1.0<sup>2,7</sup>]oct-8-yl derivatives 35, presumably resulting from transannular shift in cation 19 or 20.<sup>10</sup>

As studies in the racemic series show,<sup>12,14</sup> the four major cation systems involved in these rearrangements lie on interconnected pathways that can be entered by generation of carbonium ions from a substrate of any of the structures 17, 34, or 21. This is borne out in the

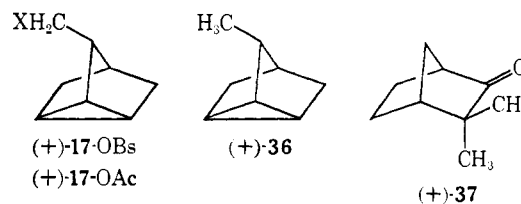
present work and in the companion study,<sup>10</sup> in which entry is effected *via* 17-OBs, 17-NH<sub>2</sub>, 34-OBs, and 21-OBs. A summary of the distribution of products as a function of the mode of entry in our experiments is given in Table II, which also shows the stereochemical results in the optically active series. The basis for the conclusions on the sense and magnitude of retention of enantiomeric purity is the set of configurational correlations now to be described.

Table III. Absolute Configurations<sup>a</sup> and Rotations of Enantiomerically Pure Compounds

Compd	[α] <sub>D</sub> , deg	Solvent	Ref
17-OAc	+46.8	MeOH	<i>a</i>
	+40.1	95% EtOH	<i>b</i>
36	+73.0	95% EtOH	<i>b</i>
38	-54	MeOH	<i>a, c</i>
40	-402	MeOH	<i>a</i>
39	-856	MeOH	<i>a</i>
21-OH	+28 ± 4	Chloroform	<i>a</i>
21-OAc	+22.5 ± 3	Chloroform	<i>a</i>
34-OAc	-9.1	MeOH	<i>a</i>
	+212	Chloroform	<i>d</i>

<sup>a</sup> Present work. <sup>b</sup> Reference 19b. <sup>c</sup> Reference 21. <sup>d</sup> Reference 10. <sup>e</sup> See text for structures.

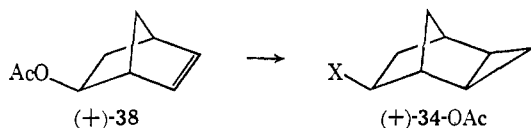
**Configurational Correlations.** The absolute configurations and maximum rotations of 3-nortricyclylcarbinyl acetate and the corresponding *p*-bromobenzenesulfonate 17-OAc and 17-OBs are known from previous correlations with 3-methylnortricyclene (36) which is independently correlated with camphenilone (37).<sup>19</sup> (The signs of rotation refer to the sodium D line unless otherwise indicated.) The amine 17-NH<sub>2</sub> (actu-



(19) (a) J. A. Berson and R. G. Bergman, *J. Am. Chem. Soc.*, **89**, 2569 (1967); (b) J. A. Berson, R. G. Bergman, J. H. Hammons, and A. W. McRowe, *ibid.*, **89**, 2581 (1967).

ally in the enantiomeric series) is prepared from active 3-nortricyclenecarboxylic acid of known<sup>19,20</sup> enantiomeric purity *via* the amide. In the racemic series, the same amine is obtained by this sequence and also from the *p*-bromobenzenesulfonate *via* the phthalimide.

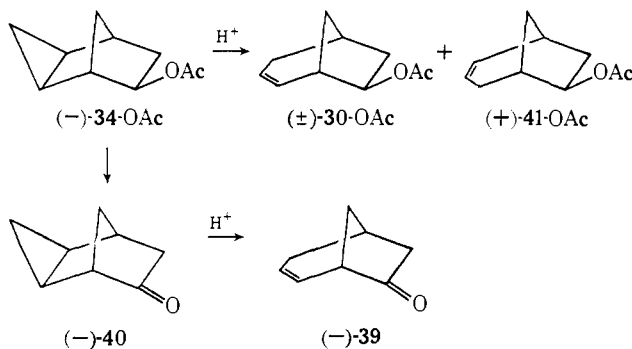
The *exo-exo*-tricyclo[3.2.1.0<sup>2,4</sup>]oct-6-yl series **34** is correlated with *exo*-2-norbornenyl acetate **38** by Simmons-Smith cyclopropanation, a reaction that is modeled on a similar synthesis in the racemic series.<sup>14</sup> The



correlation of **38** with 2-norbornyl acetate,<sup>21</sup> and the maximum rotation (*via* isotopic dilution<sup>22</sup>) and absolute configuration (*via* correlation with camphenilone<sup>20</sup>) of the latter are described in the literature.

Attempts to correlate tricyclic acetate **34-OAc** with unsaturated acetate **30-OAc** by pyrolysis or by acid-catalyzed isomerization lead either to mixtures containing little or none of the desired substance or to fully racemized **30-OAc** (see Experimental Section). Loss of all activity in **30-OAc** occurs even under conditions where the double bond isomer **41-OAc** is obtained active.

The unsaturated acetate **30-OAc** is converted to bicyclic ketone **39**, which in turn is correlated with the tricyclo[3.2.1.0<sup>2,4</sup>]oct-6-yl system *via* tricyclic ketone **40**, the configurational relationship of which to the above described acetate **34-OAc** is established independently.



The conversion of **40** to **39** is effected in poor yield by either boron fluoride etherate or an acidic ion exchange resin. Attempts with other acidic catalysts are unsuccessful. Separation of the desired homoconjugated ketone **39** from side products is difficult, and optical rotation data are available only for a sample 95% pure. This sample of ketone has a detailed optical rotatory dispersion (ord) curve (see Experimental Section) with pronounced and intense Cotton effect maxima. This permits the detection of small amounts of residual optical purity in material obtained from solvolysis products. Even at longer wavelengths, the rotations of enantiomerically pure ketone are very high ( $[\alpha]_{365} 4980^\circ$ ;  $[\alpha]_D 856^\circ$ ).

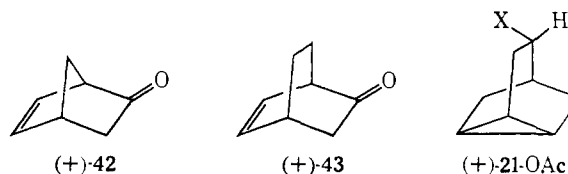
The configurational assignment to (-)-**39**, made on the basis of these chemical transformations, is confirmed by the ord curve, which is virtually enantiomeric with

(20) J. A. Berson, J. S. Walia, A. Remanick, S. Suzuki, P. Reynolds-Warnhoff, and D. Willner, *J. Am. Chem. Soc.*, **83**, 3986 (1961).

(21) K. Mislow and J. G. Berger, *ibid.*, **84**, 1956 (1962).

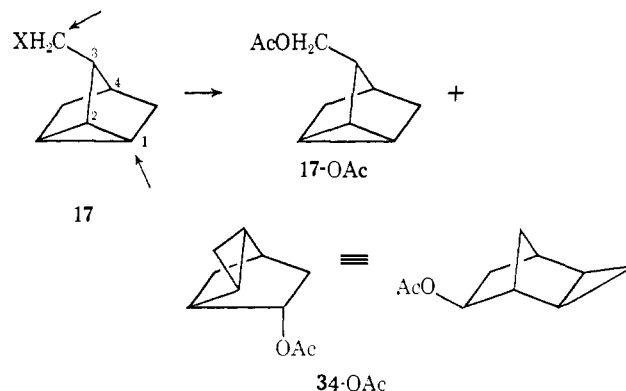
(22) J. A. Berson and S. Suzuki, *ibid.*, **81**, 4088 (1959).

those reported<sup>21</sup> for the two homoconjugated analogs **42** and **43** of the antipodal series.

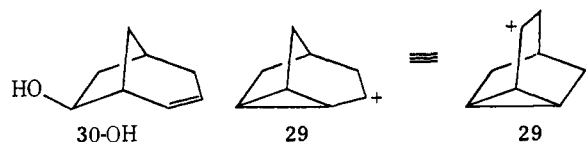


Configurational correlations of the tricyclo[3.2.1.0<sup>2,7</sup>]oct-4-yl series (**21**) are described in the accompanying paper.<sup>10</sup> All of the configurations and maximum rotations are given in Table III. With the exception of the tricyclo[3.2.1.0<sup>2,7</sup>]oct-4-yl derivatives **21**, the magnitudes of rotation all are anchored on 2-norbornanol, the maximum rotation of which is established by isotopic dilution analysis.<sup>22</sup> Because of the common relay, the absolute configurations are not important here, but they are listed for possible future reference.

**Entry by Ring Expansion of 3-Nortricyclylcarbinyll Derivatives (17).** Acetolysis or hydrolysis of 3-nortricyclylcarbinyll *p*-bromobenzenesulfonate (**17-OBs**) and deamination of 3-nortricyclylcarbinyllamine (**17-NH<sub>2</sub>**) give the products shown in Table II. Although there are variations in the distribution of products **17**, **34**, **30**, and **21** as a function of the mode of entry, the stereochemical results are remarkably insensitive. *exo-exo*-Tricyclo[3.2.1.0<sup>2,4</sup>]oct-6-yl product **34** and unrearranged 3-nortricyclylcarbinyll product **17** are always formed with essentially complete retention of enantiomeric purity. The configurational relationships to the starting substrate are those shown in Table II. They imply that the over-all structural change in product formation from **17** reactant results from attack at the carbinyll group to give product **17-OAc** (or **17-OH**) and from attack at C-1 to give product **34-OAc** (or **34-OH**).

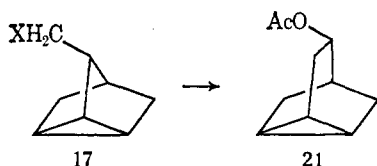


Unsaturated product **30** is isolated optically inactive and can be converted to the corresponding ketone **39**, which shows a very small rotation. This may be caused by an impurity, but if not, the rotation observed corresponds to about 0.2% retention of enantiomeric purity. Since the optically active alcohol **30-OH** or acetate **30-OAc** are not available for control experiments, it is not certain whether this essentially complete racemization represents kinetically controlled capture of a completely symmetrical intermediate (*e.g.*, identical with or derived from cation **29**) or racemization of product **30** after capture (*e.g.*, by the equivalent of Wagner-Meerwein rearrangement, which might also proceed by generation of **29**).



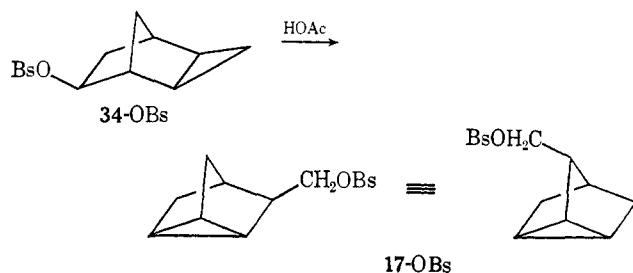
The most striking result is the consistent formation of tricyclo[3.2.1.0<sup>2,7</sup>]oct-4-yl product **21** with partial retention of enantiomeric purity. Because of some looseness in the rotation values of the reference compounds,<sup>10</sup> the absolute values of per cent retention in **21** given in Table II cannot be considered accurate to better than about 2%, but the comparisons within the table are independent of this. There appears to be a slightly greater amount of retention in the hydrolysis of **17-OBs** as compared to its acetolysis, and in deamination of the amine **17-NH<sub>2</sub>**, this trend continues, but the variations are barely outside experimental error. In fact, the rough constancy of the effect over such a wide range of conditions is more significant than the small variations.

The configurational relationships of Table II show that nucleophilic capture of the ring-expanded intermediate to give **21** occurs predominantly from the *same side* as that occupied by the leaving group in **17**. In the acetolysis of **17-OBs**, this result cannot be a consequence of ring expansion accompanied by stereospecific ion-



pair return, **17-OBs** → **21-OBs**, since it is already known that (aside from a small amount of inverted product **21-OAc**) acetolysis of **21-OBs** gives *racemic* **21-OAc**.<sup>10</sup> For reasons discussed below, one also can dismiss a variant of the ion-pair return mechanism which assigns the cause of the asymmetry to the location of the counterion in an ion-pair intermediate. The feeble effects of changes of medium and of leaving group (Table II) argue strongly in favor of an intramolecularly unsymmetrical intermediate as the origin of the memory effect in this reaction.

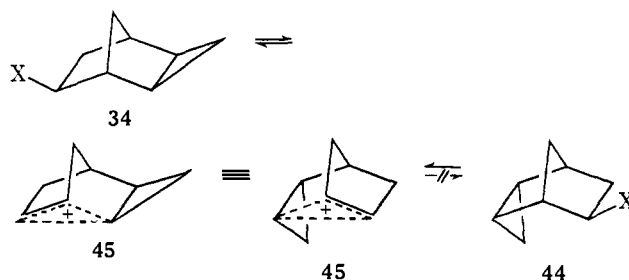
**Entry by Solvolysis of *exo*-Tricyclo[3.2.1.0<sup>2,4</sup>]oct-6-*exo*-yl *p*-Bromobenzenesulfonate (**34-OBs**).** In acetic acid there is a remarkable isomerization (presumably *via* ion-pair intermediates) of **34-OBs** to the much less reactive primary sulfonate **17-OBs**.<sup>14</sup> This competes



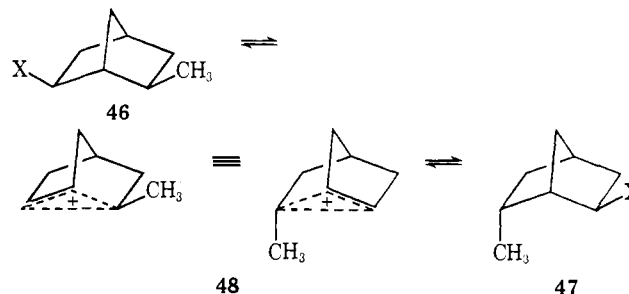
with solvolysis, and about 10% **17-OBs** accumulates during a "complete" solvolysis of **34-OBs**. Fortunately, the rate of acetolysis of **17-OBs** is so slow<sup>14</sup> that it cannot be an intermediate for any significant portion of the acetate products from **34-OBs**. In addition to the ion-pair return product **17-OBs**, solvolysis of **34-**

**OBs** gives some of the corresponding primary acetate **17-OAc**, which is formed with complete retention of enantiomeric purity (Table II). As will become evident, this finding provides an important guide to the over-all mechanism.

It is known from the work of Wiberg and Wenzinger<sup>14</sup> that *endo*-tricyclo[3.2.1.0<sup>2,4</sup>]oct-6-*exo*-yl *p*-bromobenzenesulfonate (**44-OBs**) gives an acetolysis product mixture essentially identical with that of the *exo-exo* isomer **34-OBs**. This is most simply interpreted as an indica-



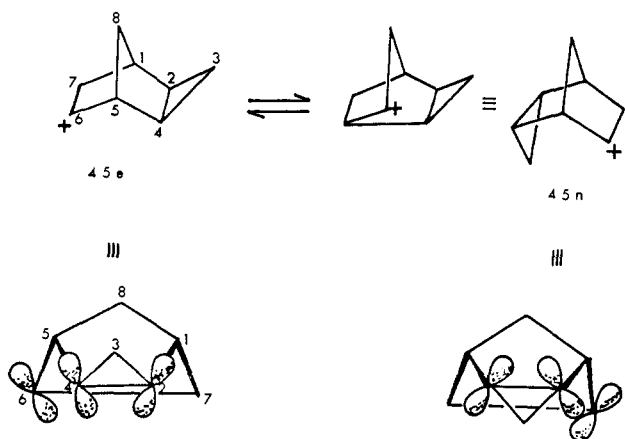
tion of a Wagner–Meerwein relationship between the two systems, which can be connected by a common non-classical ion **45** (or a rapidly interconverting pair of ions). These systems are closely related structurally to the 6-*exo*-methyl- and 6-*endo*-methyl-2-*exo*-norbornyl derivatives **46** and **47**, which are connected by cation **48**. There is, however, a striking difference in the behavior



of the two cations **45** and **48** toward nucleophiles. The 6-methylnorbornyl cation system **48** gives predominantly *exo-exo* product **46**, but there are always significant amounts (10–12%) of *endo-exo* products **47**;<sup>23</sup> the tricyclic cation system **45**, however, is reported<sup>14</sup> to give only *exo-exo* product **34**. With the help of a comparison sample of *endo-exo*-acetate **44-OAc**, kindly supplied by Drs. Wiberg and Wenzinger, we confirm their observation and set an upper limit of 0.4% of this material that can be present and undetected in acetolysis mixtures from **34-OBs** or in the products from the ring expansions of nortricycylcarbinyl substrates **17**. This corresponds to a selectivity ratio of >250 in favor of *exo-exo* product **34-OAc** in the trapping of tricyclic cation **45**, as compared to a ratio of only 8–10 in 6-methylnorbornyl cation **48**. There are no obvious steric grounds for the discrepancy, and we consider two electronic interpretations.

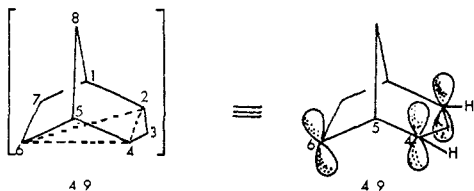
The first starts with the convenient but not obligatory representation of the tricyclic cation **45** as a pair of equilibrating structures, **45e** and **45n**. (The carbon atoms of both structures bear the same numbers.) The *p* orbitals that form the basis set of the cyclopropane C-2–C-4 bond in **45e** are oriented to overlap efficiently with the "endo"-directed lobe of the *p* orbital at C-6. In

(23) J. A. Berson, A. W. McRowe, and R. G. Bergman, *J. Am. Chem. Soc.*, **88**, 1067 (1966); **89**, 2573 (1967).



**45n**, however, the cyclopropane ring orbitals point out and hence away from the p orbital at C-5, making for poor overlap. These orientations or closely approximate ones are those obtaining in the two transition states for nucleophilic capture to give *exo-exo* and *endo-exo* products, respectively, and regardless of whether the cation is truly nonclassical or merely an equilibrating pair, the transition state for *exo-exo* product **34** is favored because of its relationship to the more stable structure **45e**.

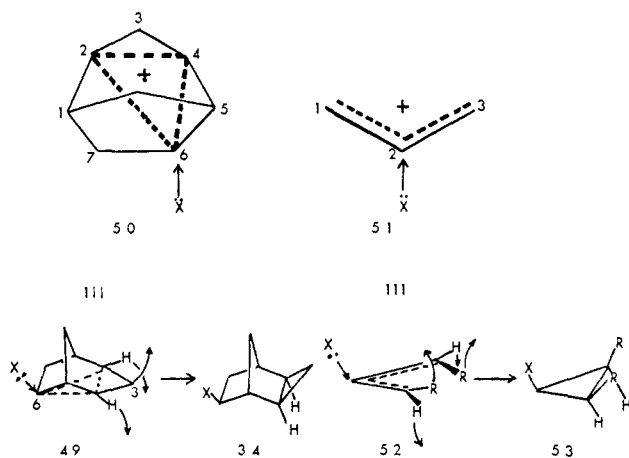
The second and more intriguing possibility considers as an alternative to the cationic intermediate **45** a different species **49**, which is bishomologous and electronically analogous to allyl cation. This "stretched" allylic system differs structurally from **45** by a flattening of the ring system, which puts C-2, C-3, C-4, and the C-2 and C-4 hydrogens of **49** nearly in a plane. There are



other more subtle geometrical differences associated with changes in hybridization, a noteworthy one being some enlargement of the C-2-C-3-C-4 bond angle in **49**. This suggests that the "*exo-cyclopropane*"- (**34**) and "*endo-cyclopropane*"- (**44**) derived systems might interconvert directly by motion of C-3 of cation **49** in an *exo* or an *endo* direction, rather than by the Wagner–Meerwein rearrangement already discussed. This also would provide a conceivable alternative explanation of the highly stereospecific nucleophilic capture to give *exo-exo* product **34**, since reconstitution of a full C-2-C-4 bond and capture by a nucleophile at C-6 (**50**) would correspond electronically to the closure of the C-1-C-3 bond and attack at C-2 of an allyl cation (**51**). The microscopic reverse of **51** (ionization of a cyclopropyl derivative) is a process that should<sup>24,25</sup> and does<sup>25</sup> take place by disrotatory opening of the ring so as to turn the substituents (R) that are *cis* to the leaving group (X) toward the inside of the developing allyl cation. The hypothetical capture–closure process therefore should require the stereochemistry shown as **52** → **53**, which is the exact

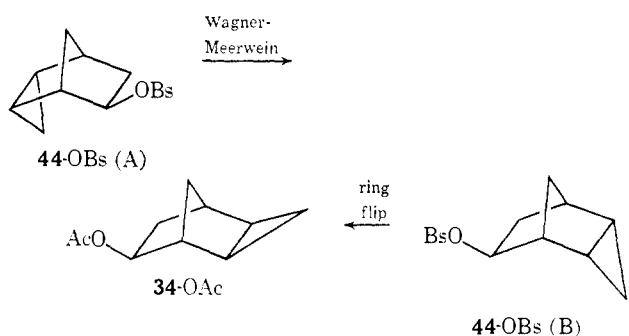
(24) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 397 (1965).

(25) C. H. DePuy, *Accounts Chem. Res.*, **1**, 33 (1968), and references cited therein.



analog of the process **49** → **34**. In this case, the exclusive formation of *exo-exo* product **34** would have quite a different origin from that in the first alternative.

The two interpretations are experimentally distinguishable in principle. If the *exo-exo* and *endo-exo* systems are merely Wagner–Meerwein related, the formation of **34-OAc** from **44-OBs** in the optically active series requires the relative chiralities shown as **34-OAc** and **44-OBs** (A), whereas the reaction through the "loosened ring" intermediate **49** forms *exo-exo* product **34-OAc** from *endo-exo* precursor of the chirality **44-OBs** (B). Although the solution to this direct form of



the problem is not available, the configurational relationships of Table II provide indirect evidence in favor of the Wagner–Meerwein alternative.

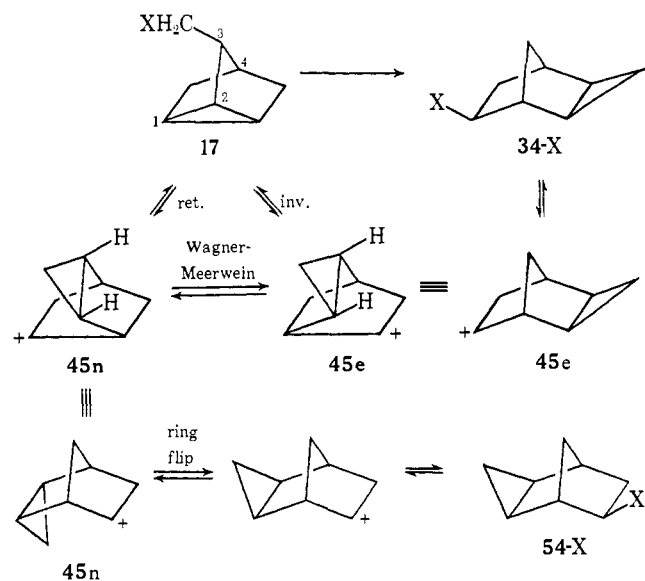
The argument rests on the observations that the ring expansions of optically active nortricycliccarbinyl derivatives **17** give *exo-exo*-tricyclo[3.2.1.0.2<sup>4</sup>]oct-6-yl products **34-X** with complete retention of enantiomeric purity ( $102 \pm 2\%$ ) and with the configurational relationship shown (Table II). The reverse process **34-OBs** → **17-OAc** also is observed (Table II) with the same sense and magnitude of stereospecificity. This is consistent with a mechanism involving electrophilic attack by the CH<sub>2</sub> group of **17** on the cyclopropane ring at C-2 with the perhaps expected<sup>26</sup> retention of configuration to give **45n**, which by Wagner–Meerwein rearrangement is converted to **45e**, the precursor of **34-X**. Electrophilic attack with inversion leads to **45e** also, and in fact, if the Wagner–Meerwein pair **45n** and **45e** represent resonance structures of a nonclassical ion formed di-

(26) (a) S. Winstein, T. G. Traylor, and C. S. Garner, *J. Am. Chem. Soc.*, **77**, 3741 (1955); (b) S. Winstein and T. G. Traylor, *ibid.*, **78**, 2597 (1956); (c) F. R. Jensen, L. D. Whipple, D. K. Wedegaertner, and J. A. Landgrebe, *ibid.*, **81**, 1262 (1959); (d) H. B. Charman, E. D. Hughes, and Sir C. Ingold, *J. Chem. Soc.*, 2523, 2530 (1959); (e) Sir C. Ingold, *Rec. Chem. Progr.*, **25**, 145 (1964); *Helv. Chim. Acta*, **47**, 1191 (1964).

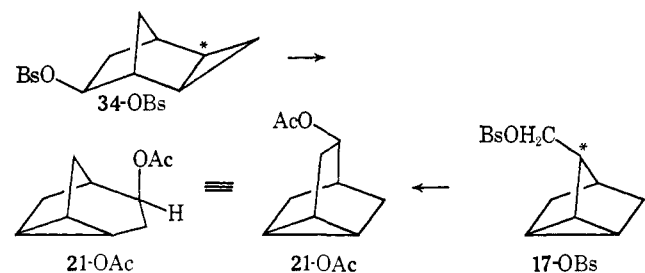


rectly from **17**, the question of inversion *vs.* retention evaporates.

The alternative mechanism involves ring flip in **45n** and ultimate conversion to *exo-exo* product of the antipodal series, **54-X**, no trace of which is observed. The absence of this product shows that the ring flip is of negligible importance in the cations derived from nortricycylcarbiny substrate **17**, and by implication argues strongly against it in the cations derived from *endo-exo*-tricyclo[3.2.1.0<sup>2,4</sup>]oct-6-yl substrate **44**.



The most significant observations on the acetolysis of optically active *exo-exo*-tricyclic substrate **34-OBs** pertain to the configuration and enantiomeric purity of the tricyclo[3.2.1.0<sup>2,7</sup>]oct-4-yl acetate product **21-OAc** (Table II). The predominant stereochemistry is that shown here, and the partial retention of optical purity ( $30 \pm 3\%$ ) is within experimental error the same as that observed ( $27 \pm 3\%$ ) in the acetolytic ring expansion of nortricycylcarbiny *p*-bromobenzenesulfonate (**17-OBs**).



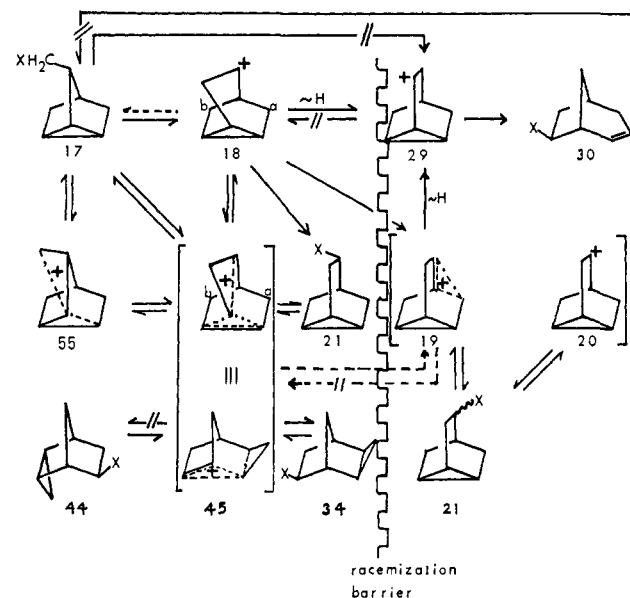
The insensitivity of the memory effect to the nature of the environment or the leaving group in the ring expansions of nortricycylcarbiny derivatives **17-X** described earlier already provides an argument against such environmental factors as counterion "shielding" or counterion-induced asymmetry of the solvent microstructure as the origin of the memory effect. The present observations are even more difficult to reconcile with such hypotheses, for the experiments show that the location of the counterion relative to the point (marked with an asterisk) of nucleophilic capture to form **21-OAc** (directly adjacent in **17-OBs** and diametrically opposed in **34-OBs**) is immaterial. The simplest and most satisfactory explanation involves an unsymmetrical cationic intermediate common to both modes of entry (from **17** or

**34**). This intermediate either reacts with nucleophiles with only partial stereospecificity, or it has available a competing mechanism for conversion to a symmetrical cationic species.

**The Mechanism.** To fit the observations summarized in Table II, the pool of intermediates must provide stereochemically uncontaminated sources of nortricycylcarbiny (**17**) and tricyclo[3.2.1.0<sup>2,4</sup>]oct-6-yl (**34**) products, both of which are formed from either entry with complete preservation of enantiomeric purity, but there must be a "leak" specifically in the path leading to tricyclo[3.2.1.0<sup>2,7</sup>]oct-4-yl (**21**) product, which is formed with partial racemization. The simplest formulation of these requirements is shown in Scheme III.

Substrate of the nortricycylcarbiny structure (**17**) gives optically active cations **18** and **55**, and tricyclo[3.2.1.0<sup>2,4</sup>]oct-6-yl (**34**) substrate gives optically active cation **45**. These three intermediates interconvert without passing through any symmetrical species and thus provide a means by which enantiomeric purity can be preserved completely in the formation of **17**- or **34**-type products from either starting material. The symmetrical intermediates **19**, **20**, and **29** formed elsewhere in the scheme do not revert to species that can be captured to give products **17** or **34** (blocked arrows across the racemization barrier in Scheme III).

Scheme III



The detailed electronic structures of unsymmetrical cations **18**, **55**, and **45** are schematic, and this pool of intermediates could be replaced by corresponding sets of classical ions. However, the data of Table II do not permit rapid interconversion among the optically active intermediates, whatever their structure, for this would predict a product distribution independent of the point of entry (**17** or **34**), in conflict with the observations. In fact, Table II shows that there is a strong predilection for formation of product with the same structure as the substrate. The relevant portion of the data is conveniently summarized in the form of the fraction of the product with the **34** structure formed from **34-OBs** as compared to that from **17-OBs**. (The converse case, involving nortricycylcarbiny (**17**) product from **17-OBs** is less meaningful because of the likelihood of direct displacement in the primary system.) The ratio (**34**

product from **34**-OBs/**34** product from **17**-OBs) has the value 1.4 in acetolysis and 1.5 in aqueous dioxane. These observations cannot be reconciled with rapid interconversion of the intermediates or with a single common intermediate, e.g., **56**.

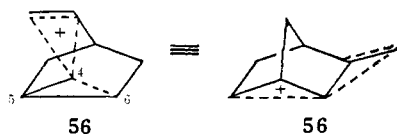


Table II also imposes severe restrictions on interpretations of the memory effect in the ring expansions of nortricycliccarbonyl derivatives (**17**), which lead to the formation of partially racemized tricyclo[3.2.1.0<sup>2,4</sup>]oct-4-yl product **21**. Scheme III incorporates two optically active intermediates from which optically active **21** can arise. The first (**18**) is formed directly in the ring expansion, and its capture to give **21** can occur either before or after symmetrization to **19** or **20**. The competition between capture and symmetrization determines the extent of the memory effect. The second possible intermediate is **45**, which Scheme III shows is formed directly from tricyclo[3.2.1.0<sup>2,4</sup>]oct-6-yl substrate **34** but is separated by at least one other intermediate (**55** or **18**) from nortricycliccarbonyl substrate **17**. The simplest way to account for the observation that the amount of enantiomeric purity in product **21** is the same from **34** substrate as from **17** substrate is with a common intermediate for formation of **21**. Cation **45** can serve this purpose if the ring expansion of **17** is imagined to bypass **18** and go directly to **45** or to go first to **55** and then to **45** (which is the same as making **18** and **45** identical). This simplification requires only that some mechanism exist for conversion of a portion of the **45** cations to symmetrical species, a process that can be depicted as irreversible leakage of **45** across the racemization barrier along the dashed arrow to **19** or **20**. The reverse reaction (**19** or **20** → **45**) clearly is not important, since tricyclo[3.2.1.0<sup>2,4</sup>]oct-6-yl product **34** retains enantiomeric purity completely.

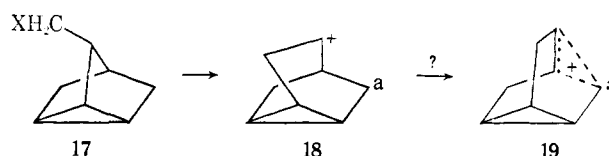
Only one further economy of representation is readily compatible with the experiments. For reasons already given, it is likely that at least two optically active intermediates separate **17** and **34**, and the data require at least one other intermediate, which must be symmetrical, e.g., **19** or **20**. The solvolytic behavior of tricyclo[3.2.1.0<sup>2,4</sup>]oct-4-yl substrates **21**<sup>10</sup> strongly implicates nonclassical ion **19** (or a rapidly equilibrating pair of classical cations **20**), but both are not required.

**Conclusions.** The first intermediate in the ring expansion of nortricycliccarbonyl derivatives **17**-OBs is an unsymmetrical species (**55** or **18**, Scheme III), which is either captured nucleophilically (**18** → **21**) or suffers further change (**55** → **45**) before capture (**45** → **21**). The same unsymmetrical species (**18** or **45**) is generated from tricyclo[3.2.1.0<sup>2,4</sup>]oct-6-yl substrates **34**. The efficiency of the nucleophilic capture step (**45** → **21** or **18** → **21**) relative to symmetrization by bond rearrangement or conformational change (**18** or **45** → **19** and/or **20**) is essentially independent of the leaving group, the medium, or the location of the counterion. Consequently, the unsymmetrical behavior of the intermediate **18** or **45** is most simply interpreted as an intrinsic property of the cation rather than a transient lack of symmetry in its environment. The unsymmetrical structure of the cat-

ionic intermediate is represented for convenience in either conformationally twisted (**18**) or nonclassical (**45**) form, but other representations, involving for example, protonated cyclopropanes or other hydrogen-bridged species may be substituted. We have no basis for a preference among these.

The predominant formation of **21** from **18** is reasonable on steric grounds and from **45** (or other delocalized variants of **18**) on stereoelectronic grounds (attack on the nonclassical bridge with inversion).

It is not yet known whether the unsymmetrical behavior of these intermediates extends to the second bond migration step (**18** → **19** or **45** → **19**). By analogy to many other memory effects,<sup>4</sup> this should manifest itself as a preference for migration of the ring member (a) remote from the leaving group of **17**. Experiments now in progress are designed to answer this question.



### Experimental Section<sup>27</sup>

**3-Nortricycliccarbonyl-3-*d*** (**17b**-OH). Clean potassium metal (1.00 g) was dissolved in *t*-butyl alcohol-*O*-*d*<sup>28</sup> (<1% OH by nmr) with heating and stirring. Methyl 3-nortricyclenecarboxylate (3.03 g) was added and the mixture was heated in a nitrogen atmosphere for 18 hr. About half the solvent was removed by distillation and the residue was cooled and diluted with 5 ml of deuterium oxide. The mixture was extracted twice with pentane, the solution was dried and evaporated, and the residue was distilled bulb to bulb (bath at 60–70°, 10.2 mm) to give 2.52 g of a colorless oil. The nmr spectrum showed a negligible *CHCO*<sub>2</sub>R absorption at  $\delta$  2.34, indicating that deuterium incorporation had occurred. The spectrum also showed *t*-butyl ester absorption at  $\delta$  1.40 and methyl ester absorption at  $\delta$  3.58. Vpc analysis on column A showed the product to consist of 32% methyl ester and 68% *t*-butyl ester. Attempts to separate the mixture by vpc on column J at 170° resulted in selective decomposition of the *t*-butyl ester. Therefore, 1.33 g of the ester mixture was reduced directly with excess lithium aluminum hydride in ether to give 900 mg of **17b**-OH as a clear oil after bulb-to-bulb distillation. The nmr spectrum showed a sharp singlet at  $\delta$  3.34 (2 H, *CHOH*), a slightly broadened singlet at 1.88 (1 H, bridgehead), and complex absorption at 1.57–0.80 (7 H). The OH signal was a broad singlet centered at 3.56. In the spectrum of undeuterated alcohol there is a triplet at 1.68 ( $J = 8$  cps, X part of *A*<sub>2</sub>X due to *CHCH*<sub>2</sub>OH). This absorption was barely visible in the spectrum of deuterated alcohol, and integration suggested the deuterium content in the 3 position to be about 0.9 D/molecule. A falling drop analysis<sup>29</sup> showed 6.90 atom % excess deuterium (0.83 D/molecule).

**Acetolysis of 3-Nortricycliccarbonyl-3-*d* *p*-Bromobenzenesulfonate (17b-OBs).** The above deuterated alcohol **17b**-OH (845 mg, 6.75 mmol) in 10 ml of cold pyridine was treated with 2.00 g (7.8 mmol) of *p*-bromobenzenesulfonyl chloride, and the mixture was kept in the freezer for 18 hr. Work-up by ether extraction gave 2.25 g (97%) of a solid sulfonate **17b**-OBs. A solution of 2.045 g (5.95 mmol) of this material and 555 mg of sodium acetate in 70 ml of acetic acid was heated at 100° for 47 hr. The mixture was worked up in the usual way and the product was distilled bulb to bulb to give 780 mg of a clear oil. Vpc analysis showed the same product distribution as in the acetolysis of undeuterated material **17a**-OBs. The mixture was separated into two fractions on column F at 135°. Fraction 1 which consisted of unsaturated acetate **30c**-OAc and primary acetate **17b**-OAc was reduced to alcohols with lithium

(27) Details of routine experimental techniques are described in the accompanying paper.<sup>10</sup> The vpc column code letters refer to those given there.<sup>10</sup>

(28) E. W. Warnhoff and W. C. Wildman, *J. Am. Chem. Soc.*, **82**, 1472 (1960).

(29) By Mr. J. Nemeth, Urbana, Ill.

aluminum hydride in ether. The alcohols were separated on column H at 130°. Alcohol 30c-OH (ca. 40 mg) was obtained as a waxy solid, >99% pure on capillary column C. Integration of the nmr signal of the vinyl protons at  $\delta$  5.2–6.0 against that of the CHOH proton at 4.13 showed that  $1.97 \pm 0.04$  hydrogens were present in the vinyl positions.

**Correlation of Configuration and Optical Rotatory Power of *exo*-Bicyclo[3.2.1.0<sup>2,4</sup>]oct-6-*exo*-yl Acetate (34-OAc) with Those of Norborn-5-en-2-*exo*-yl Acetate (38).** The procedure of Mislow and Berger<sup>21</sup> for the preparation of optically active 38 was modified slightly. After acetylation of the alcohol mixture obtained by partial asymmetric hydroboration-oxidation of norbornadiene, the mixture of acetates, pyridine, and excess acetic anhydride was poured into ice-water and allowed to stand 0.5 hr. The mixture was then worked up as described<sup>21</sup> except that pentane rather than ether was used for extraction. After removal of the pentane, the residue was distilled through a 15-in. tantalum wire silver-jacketed column, to remove most of the isopinocampheyl acetate. The fractions rich in norbornenyl acetate were then combined and redistilled through a Nester-Faust 24-in. spinning band column. The material obtained in this way was >99.9% pure by capillary vpc on column A, but the optical purity varied from run to run depending upon the conditions used for the hydroboration. In three separate preparations, material with optical purities of 49, 12, and 33% were obtained.

A sample of norbornenyl acetate was purified further by preparative vpc on column N at 187°. Analysis on capillary column A showed this material to be >99.95% homogeneous. It had  $\alpha_D -8.04^\circ$  (neat, *l* 0.5),  $[\alpha]_D -17.8^\circ$  (*c* 5.7, *l* 1, methanol).

Hydrogenation (10% palladium on carbon, 40 psi, 2 hr) gave *exo*-2-norbornyl acetate, >99.9% pure (column A),  $[\alpha]_D -5.67^\circ$  (*c* 10, *l* 1, acetic acid). Based on the value<sup>22</sup>  $[\alpha]_D -17.3 \pm 0.5^\circ$  (in acetic acid) for enantiomerically pure *exo*-2-norbornyl acetate, the above samples of norbornyl and norbornenyl acetates are  $32.8 \pm 1\%$  enantiomerically pure. The rotations of enantiomerically pure norborn-5-en-2-*exo*-yl acetate (38) therefore are  $\alpha_D 49 \pm 1.5^\circ$  (neat, *l* 1) and  $[\alpha]_D 54 \pm 1.7^\circ$  (in methanol). The value for the rotation of the neat material agrees well with that calculated from a sample 97% pure which was reduced to norbornyl acetate.<sup>21</sup>

**Optically Active Tricyclo[3.2.1.0<sup>2,4</sup>]oct-6-yl Acetate (34-OAc).** The Simmons-Smith cyclopropanation was carried out on a sample of crude optically active *exo*-norbornenyl acetate (38) obtained from the same hydroboration run that gave the above material and therefore 32.8% enantiomerically pure. The zinc-copper couple was made from 13 g of zinc, 0.8 g of cupric acetate hydrate, and 20 ml of acetic acid according to the method of LeGoff.<sup>30</sup> The couple was washed with 20 ml of acetic acid and four 40-ml portions of ether and used immediately.

A solution of 1 ml of freshly distilled methylene iodide in 40 ml of ether was added to the couple, and after the initial effervescence had subsided, a mixture of the above sample of norbornenyl acetate (13.5 g) and 32 g of methylene iodide was added at a rate sufficient to maintain gentle reflux. When addition was complete, the mixture was boiled under reflux for 45 hr.

The ether was decanted from the solids, more ether and saturated ammonium chloride solution were added, and after shaking, the ether was again decanted. The solids were washed with more ether, and the combined ether extracts were washed successively with saturated ammonium chloride, dilute ammonium hydroxide, 5% hydrochloric acid, saturated sodium carbonate, and brine. The solution was dried over sodium sulfate and evaporated. Vpc analysis showed this material to consist of about 25% tricyclic acetate 34-OAc mixed with 75% norbornenyl acetate. The tricyclic material was concentrated to about 96% homogeneity by spinning band distillation, and a pure sample (>99.9% homogeneous on column A) was prepared by vpc on column K at 170°. This material showed  $[\alpha]_D -2.78^\circ$  (*c* 8.9, *l* 1, methanol). Enantiomerically pure 34-OAc therefore has  $[\alpha]_D 8.47^\circ$  (methanol).

In earlier runs, samples of norbornenyl acetate of  $\alpha_D -6.56^\circ$  (neat, *l* 1) and  $\alpha_D -24.6^\circ$  (neat, *l* 1) had given 34-OAc with  $[\alpha]_D -1.29^\circ$  and  $[\alpha]_D -4.83^\circ$  (*c* 18, *l* 1, methanol). These give the value  $[\alpha]_D 9.6^\circ$  for enantiomerically pure 34-OAc. We consider this value to be somewhat less reliable because the data were obtained at a time when the very efficient capillary vpc column A was not available. Later work showed the presence of a persistent impurity which only this column could detect. In a more or less

arbitrary manner, we have given the two higher less reliable values equal weight with the lower value and obtain the value  $[\alpha]_D 9.1^\circ$ .

**Acid-Catalyzed Isomerization of Tricyclo[3.2.1.0<sup>2,4</sup>]oct-6-yl Acetate (34-OAc).** To 40 ml of a 0.045 *M* solution of sulfuric acid in glacial acetic acid was added 3.11 g of 34-OAc of  $[\alpha]_D -4.83^\circ$  (*c* 17.7, *l* 1, methanol). The solution was heated at 50° for 24 hr. Following the addition of ice and salt, the mixture was extracted four times with pentane, and the combined pentane fractions were washed with water, sodium bicarbonate solution, and brine. Vpc analysis on column O showed the presence of about 5% starting material, 10% bicyclo[3.2.1]oct-6-en-2-*exo*-yl acetate (30-OAc), 10% of its double bond isomer, bicyclo[3.2.1]oct-3-en-7-*exo*-yl acetate, and the remainder materials (presumably diacetates) of much longer retention times. A preliminary separation of mono- and diacetates was made on a FFAP column (Varian "free fatty acid phase"), 0.25 in.  $\times$  6 ft, at 170°, and the monoacetates were separated on column K at 170°.

Bicyclo[3.2.1]oct-3-en-7-*exo*-yl acetate was obtained >95% pure. The nmr spectrum indicated the presence of olefinic protons, although their integrated intensity was somewhat below the calculated value. The substance had  $[\alpha]_D +45.3^\circ$  (*c* 2, *l* 1, methanol).

The fraction from vpc corresponding to 30-OAc was rechromatographed on column H-1 to give material of 99% homogeneity. The infrared spectrum was identical with that of material isolated from the acetolysis experiments (see below). It was optically inactive (*c* 0.6, *l* 1, methanol).

Hydrogenation of the above sample of tricyclo[3.2.1.0<sup>2,4</sup>]oct-3-en-7-*exo*-yl acetate (20 mg) in 250  $\mu$ l of methanol over a pinch of palladium catalyst was allowed to proceed for 2 days in a Paar shaker. The reaction mixture was centrifuged and the entire supernatant was injected on column H-1. In this way, 15 mg of bicyclo[3.2.1]octan-6-yl acetate was collected. Capillary vpc showed it to be free of the starting material. It showed  $[\alpha]_D -8.31^\circ$ ,  $[\alpha]_{365} -23.1^\circ$  (*c* 1.3, *l* 1, pentane). The infrared spectrum was identical with that of an authentic sample.<sup>31</sup>

Hydrogenation of 20 mg of the above sample of bicyclo[3.2.1]oct-2-en-7-*exo*-yl acetate (30-OAc) gave 15 mg of bicyclo[3.2.1]octan-6-*exo*-yl acetate (>99% homogeneous), which had no observable rotation (*c* 1.5, pentane) at either the 589- or 365- $\mu$ m line. The infrared spectrum and capillary vpc retention time were identical with those of material obtained from the double bond isomer.

(-)-Tricyclo[3.2.1.0<sup>2,4</sup>]octan-6-one (40). A sample of tricyclo[3.2.1.0<sup>2,4</sup>]octan-6-yl acetate (34-OAc),  $[\alpha]_D -1.29^\circ$  (methanol), was reduced with lithium aluminum hydride in the usual manner to give the corresponding alcohol, which was subjected to oxidation with chromic oxide-acetone-sulfuric acid (Jones reagent). The product was distilled to give the crude ketone which was further purified by vpc on column F at 140°. The infrared spectrum showed strong carbonyl absorption at 5.72  $\mu$ . The ketone showed  $[\alpha]_D -61.2^\circ$ ,  $[\alpha]_{365} -376^\circ$  (*c* 2.49, *l* 1, methanol). Its optical rotatory dispersion curve (scaled to enantiomeric purity) is shown in Figure 1.

(-)-Bicyclo[3.2.1]oct-2-en-7-one (39) was formed when a mixture of 1.5 g of the above tricyclic ketone 40, 20 ml of heptane, and 4.0 g of Dowex 50W-X12 cation exchange resin was stirred and heated at 95° for 2 days. The mixture was filtered, the solid material was thoroughly washed with six portions of ether, and the combined ether and heptane solutions were washed with water, 5% hydrochloric acid, and brine. After having been dried over magnesium sulfate, the solution was concentrated by distillation through a Vigreux column to remove ether and then through a tantalum spiral-packed column to remove heptane. The residue was distilled bulb to bulb at 0.2 mm to give 1.25 g of an oil. Vpc showed this material to contain a large number of products, but the retention time of one of the major components corresponded to that of the unsaturated ketone (39). Two successive vpc separations, first on column F and then on a column of 20% UCON 50HB-2000, 12 ft  $\times$  0.25 in., gave the ketone 39 in 95% purity as estimated by capillary vpc. The infrared spectrum was almost identical and the vpc retention time was identical with those of ketone derived from bicyclo[3.2.1]oct-2-en-7-*exo*-ol (30-OH). This sample had  $[\alpha]_D -130^\circ$ ,  $[\alpha]_{365} -757^\circ$  (*c* 0.75, *l* 1, methanol). Since the tricyclic precursor 34-OAc had been prepared from *exo*-norbornenyl acetate 14.7% optically pure, the maximum rotations of ketone 39 are about  $[\alpha]_D 856^\circ$  and  $[\alpha]_{365} 4980^\circ$ . The optical rotatory dispersion curve is shown (scaled to enantiomeric purity) in Figure 2, where similar

(31) H. L. Goering and T. Padmanathan, unpublished results. We are indebted to Professor Goering for spectra of several bicyclo[3.2.1]octan-6-yl derivatives.

(30) E. LeGoff, *J. Org. Chem.*, **29**, 2048 (1964).

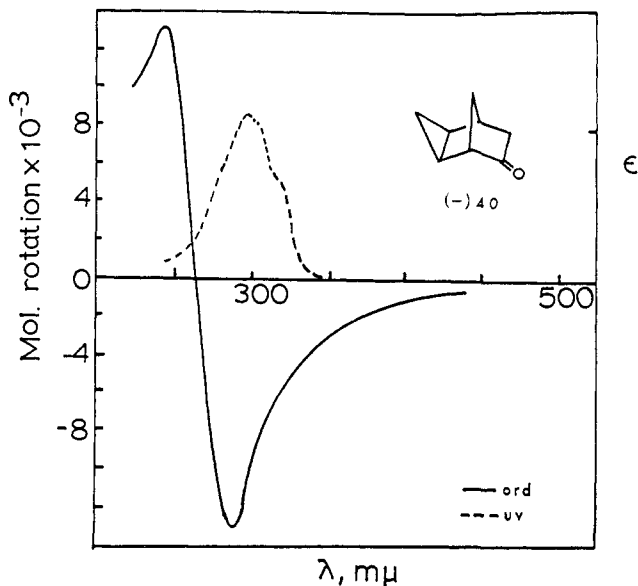


Figure 1. Optical rotatory dispersion (ord) and ultraviolet (uv) spectra of (-)-40 in isoctane solution.

curves for norborn-5-en-2-one and bicyclo[2.2.2]oct-5-en-2-one are shown for comparison.

Acetolysis of (+)-3-Nortricyclylcarbonyl *p*-Bromobenzenesulfonate (17-OBs). A sample of (+)-17-OBs was prepared as previously reported<sup>20</sup> from (+)-methyl 3-nortricyclenecarboxylate of  $[\alpha]_D +15.3^\circ$  (95% ethanol). From the correlations previously established (Table III), this material is 38.2% optically pure. A reference sample of 3-nortricyclylcarbonyl acetate 17-OAc,  $[\alpha]_D +17.9^\circ$  (methanol), had been prepared<sup>19a</sup> by acetylation of the same sample of alcohol 17-OH used to prepare the above sample of 17-OBs.

Two acetolyses of (+)-17-OBs were performed. The first was carried out with 1.91 g of the above sample of (+)-17-OBs dissolved in a solution of 508 mg of sodium acetate in 110 ml of dry acetic acid. After 46 hr at 100°, the mixture was cooled, poured onto ice, salted heavily, and extracted four times with pentane. The pentane extracts were washed with sodium bicarbonate solution and then with brine. After having been dried over magnesium sulfate, the solution was concentrated through a 15-in. silver-jacketed tantalum wire fractionating column. The residue was distilled bulb to bulb to give 1.77 g (92%) of product. The product composition (see below) as shown by capillary vpc analysis did not change when (in a separate run) 2-ml aliquots were removed from the reaction mixture after approximately 25, 75, and 100% reaction and worked up as described. The composition as determined with column A is given in Table II.

Vpc separation on column G at 170° gave tricyclo[3.2.1.0<sup>2,7</sup>]oct-4-yl acetate (21-OAc), >99% homogeneous,  $[\alpha]_D +2.09^\circ$  (*c* 3.48, *l* 1, methanol), 9–11% enantiomerically pure (Table III), or 24–29% of that of the starting material. *exo*-Tricyclo[3.2.1.0<sup>2,7</sup>]oct-6-*exo*-yl acetate (34-OAc), obtained >99.5% homogeneous, had  $[\alpha]_D +3.19^\circ$  (*c* 9, *l* 1, methanol), 35.1% enantiomerically pure (Table III), or 92% of that of the starting material.

In a second run, 4.0 g of (+)-17-OBs gave 1.77 g (92%) of acetates. The mixture was reduced with lithium aluminum hydride to a mixture of alcohols, from which unsaturated alcohol 30-OH was isolated by two successive vpc fractionations on column H-1 at 140°. In this way was obtained 0.171 g of 30-OH, homogeneous on capillary vpc. The nmr spectrum showed a multiplet centered near  $\delta$  5.5 (2 H), a broad signal at 4.1 (1 H), and an overlapping series of absorptions extending from 1.3 to 2.5 (9 H). The sample showed no optical activity. Oxidation with Jones reagent gave a sample of ketone 39 which was obtained 97% pure. It had  $[\alpha]_D +0.60^\circ$ ,  $[\alpha]_{365} +3.88^\circ$  (*c* 7.7, *l* 1, ethanol). These figures correspond to about 99.8% racemization.

The remaining mixture of alcohols from the solvolysis was acetylated and the primary acetate 17-OAc isolated by vpc on column H-1. It showed  $[\alpha]_D +15.7^\circ$  (*c* 1.5, *l* 1, methanol). A vpc on a 250-ft UCON 50HB-2000 capillary column showed the presence of about 6% of the optically inactive acetate 30-OAc. The rotation of the 17-OAc is therefore +16.7°, or 94% of that of 17-OAc with the same enantiomeric purity as the starting material. Except for a

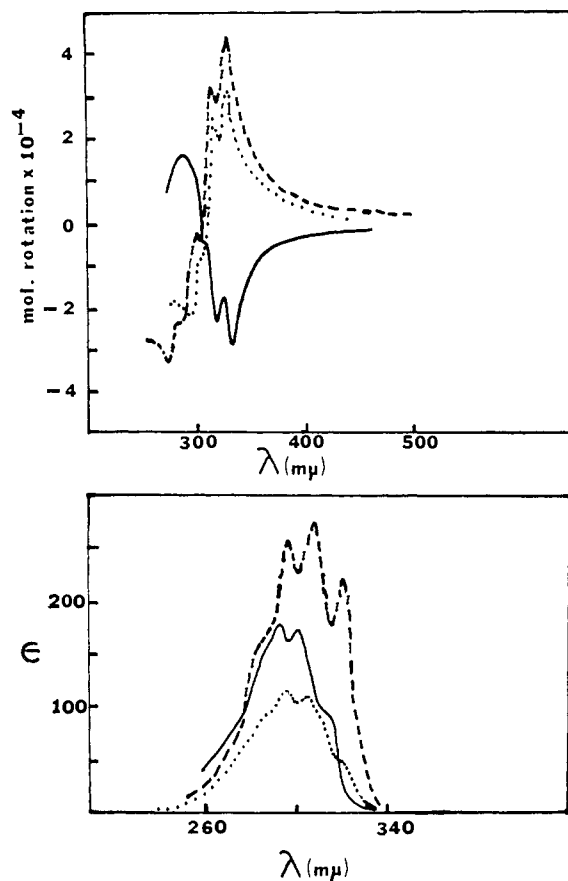


Figure 2. Upper curves: ord spectra of (+)-norborn-5-en-2-one (42, ----),<sup>23</sup> (+)-bicyclo[2.2.2]oct-5-en-2-one (43, ....),<sup>23</sup> and (-)-bicyclo[3.2.1]oct-2-en-7-one (39, —) in isoctane solutions. Lower curves: uv spectra.

small band in the OH region, the infrared spectrum of a sample recovered from the polarimetric solution was the same as that of pure 17-OAc.

The two tricyclic acetates remaining could be separated from each other by successive vpc on columns M and H-1. The first fractionation on column M at 190° effected separation of the acetates but caused a small amount of hydrolysis. The second vpc of each fraction removed the alcohol contaminant that resulted.

In this way there was obtained *exo*-tricyclo[3.2.1.0<sup>2,7</sup>]oct-6-*exo*-yl acetate (34-OAc) of  $[\alpha]_D 3.45^\circ$  (*c* 7.53, *l* 1, methanol) contaminated with 7.8% tricyclo[3.2.1.0<sup>2,7</sup>]oct-4-yl acetate (21-OAc). The 21-OAc fraction contained 4.7% 34-OAc and had  $[\alpha]_D +2.10^\circ$  (*c* 2.9, *l* 1, methanol). These data can be handled by a pair of simultaneous equations to give values for chemically pure 34-OAc and 21-OAc of  $[\alpha]_D +3.56^\circ$  and  $[\alpha]_D +2.02^\circ$ . These are to be compared with the values +3.19 and +2.09° from the first run. Table II reports the mean value for both substances.

Hydrolysis of 17-OBs in Aqueous Dioxane. A solution of 2.25 g of the same sample of 17-OBs, 38.2% enantiomerically pure, and 575 mg of pyridine in 130 ml of 30% water:70% dioxane (*v/v*) was heated at 100° for 28 hr. The product was isolated by pentane extraction and then acetylated with acetic anhydride-pyridine. The composition of the acetate mixture is shown in Table II.

Preparative vpc on column G gave 21-OAc with  $[\alpha]_D +2.62^\circ$  (*c* 2.29, *l* 1, methanol), 34-OAc,  $[\alpha]_D +3.30^\circ$  (*c* 10.2, *l* 1, methanol), and 17-OAc,  $[\alpha]_D +16.7^\circ$  (*c* 3.1, *l* 1, methanol).

Control Experiment on the Optical Stability of Tricyclo[3.2.1.0<sup>2,7</sup>]oct-4-yl Acetate (21-OAc) under Conditions of Acetolysis. A sample of 21-OAc,  $[\alpha]_D +4.93^\circ$  (methanol), was made up to 0.050 *M* in acetic acid containing 0.050 *M* sodium *p*-bromobenzenesulfonate and 0.005 *M* sodium acetate. The solution was heated at 100° for 50 hr, and the acetate was recovered in the usual manner. After bulb-to-bulb distillation, it had  $[\alpha]_D +4.98^\circ$  (methanol).

Acetolysis of Optically Active Tricyclo[3.2.1.0<sup>2,7</sup>]oct-6-yl *p*-Bromobenzenesulfonate (34-OBs). A sample of the above (-)-34-OAc, 32.8% enantiomerically pure, was cleaved with lithium

aluminum hydride and converted to the *p*-bromobenzenesulfonate. This material (5.5 g) was acetylated by dissolving it in 15 ml of dry acetic acid and treating it immediately with a 0.25 *M* solution of sodium acetate in acetic acid (60 ml) which had been preheated to 100°. After 1 hr at 100°, the solution was poured onto ice and extracted with pentane. The material obtained upon work-up was fractionated on column G and rotations measured in methanol after each fraction had been distilled bulb to bulb to give **34-OAc** (homogeneous,  $[\alpha]_D -2.76^\circ$  (*c* 9.4)); **21-OAc** ( $[\alpha]_D -2.14^\circ$  (*c* 2.7), rotation corrected for 7% of **34-OAc** in this fraction). The isolation of primary acetate **17-OAc** required rechromatography on column F to remove an alcoholic impurity. The fraction then consisted of a mixture of two unknown components (2% each), unsaturated acetate (presumably racemic) **30-OAc** (57%), and primary acetate **17-OAc**, 39%. The fraction had  $[\alpha]_D -5.78^\circ$  (*c* 2.78, *l* 1, methanol), from which the rotation  $[\alpha]_D -14.8^\circ$  for the **17-OAc** component can be calculated. This corresponds to 32.8% of enantiomeric purity, or exactly the same value as that of the starting **34-OBs**.

**3-Nortricyclylcarbinyamine (17-NH<sub>2</sub>).** A. A small sample of optically active 3-nortricyclenecarboxylic acid<sup>19a</sup> was converted with diazomethane to the methyl ester, which had  $[\alpha]_D -9.78^\circ$  (*c* 12.5, *l* 1, in 95% ethanol). From the data of Table III, this material is calculated to be 24.4% enantiomerically pure.

A sample of 15.0 g of the above acid was stirred overnight with 100 ml of thionyl chloride. The excess thionyl chloride was evaporated under vacuum, the residue was treated with 25 ml of benzene, and the mixture was evaporated again. The residue was taken up in 75 ml of dry ether and stirred under ammonia gas for 30 min. The mixture was treated with water and extracted with chloroform. After having been dried over magnesium sulfate, the chloroform solution was filtered and evaporated to dryness.

The residual crude amide was taken up in 300 ml of dry ether and treated in small portions with 7.6 g of solid lithium aluminum hydride. The usual work-up gave 8.8 g of liquid amine after bulb-to-bulb distillation.

B. A second preparation of **17-NH<sub>2</sub>** was effected *via* the phthalimide, which was prepared from **17-OBs**, 38.2% enantiomerically pure. A mixture of 1.0 g of **17-OBs**, 0.401 g of anhydrous potassium carbonate, and 0.855 g of freshly recrystallized (absolute ethanol) phthalimide in 20 ml of dimethylformamide was stirred vigorously and boiled under reflux for 10 hr in a nitrogen atmosphere. Water (70 ml) was added, and the precipitated phthalimide was extracted with ether. After having been washed with 2% sodium hydroxide solution and then with water and brine, the extract was dried over magnesium sulfate and evaporated to give 0.689 g (97%) of *N*-nortricyclyl-3-carbonylphthalimide as a white solid. A small amount was recrystallized from methanol for analysis.

*Anal.* Calcd for C<sub>16</sub>H<sub>15</sub>NO<sub>2</sub>: C, 75.87; H, 5.97; N, 5.53. Found: C, 75.88; H, 6.01; N, 5.42.

The remainder of the phthalimide was converted to the amine

by 3 days of boiling with a solution of 7 g of sodium hydroxide in 50 ml of 75% methanol under nitrogen. The amine was isolated by extraction with pentane and distilled bulb to bulb.

**Nitrosative Deamination of 17-NH<sub>2</sub>.** Small samples of amine from both preparative routes were deaminated under identical conditions; they gave the same product mixtures as analyzed by capillary vpc on column B. A preparative scale run was carried out as follows.

An 8.2-g sample of the amine from A, 24.4% optically pure, was dissolved in 100 ml of dry acetic acid, stirred, and treated with 9.0 g of sodium nitrite during 4 hr. The mixture was stirred at room temperature overnight and the sodium nitrite addition was repeated. Water was added and the mixture was extracted three times with pentane. The combined pentane fractions were washed once with 5% hydrochloric acid, then with sodium bicarbonate and brine, and dried over magnesium sulfate. Evaporation and bulb-to-bulb distillation gave 9.2 g (82%) of acetates as a clear oil. A portion of this mixture was separated into two fractions with column K at 180°. Fraction 1 contained unsaturated acetate **30-OAc** and primary acetate **17-OAc**; fraction 2 contained the two tricyclic acetates **21-OAc** and **34-OAc**.

Fraction 1 was cleaved to a mixture of alcohols with lithium aluminum hydride in the usual manner, and a portion of the mixture was subjected to oxidation with Jones reagent. The product was extracted with pentane, washed three times with Tollens reagent, three times with sodium bicarbonate solution, and once with brine. Drying and evaporation left about 80 mg of material, which was distilled bulb to bulb and then purified by vpc on column K. Bicyclo[3.2.1]oct-2-en-7-one (**39**) was obtained 95% pure by capillary vpc and had no observable rotation at either the sodium D or mercury 365-mμ line (*c* 1.40, *l* 1, methanol).

Another portion of the alcohols from reduction of fraction 1 was chromatographed on column H-1 at 140° to separate primary alcohol **17-OH**, which was reacylated and rechromatographed on column H-1 to give **17-OAc** contaminated with 6% of the inactive unsaturated acetate **30-OAc**. The observed rotation of this material was  $[\alpha]_D -10.5^\circ$  (*c* 2.9, *l* 1, methanol), from which the rotation of the **17-OAc** component may be calculated as  $-11.2^\circ$ . This corresponds to an enantiomeric purity of 23.9%, or 98% of that of the starting amine.

Fraction 2 was subjected to a preliminary separation on column M and each subfraction was rechromatographed on column H-1. Tricyclo[3.2.1.0<sup>2,4</sup>]oct-6-yl acetate (**34-OAc**) was obtained contaminated with about 1% tricyclo[3.2.1.0<sup>2,7</sup>]oct-4-yl acetate (**21-OAc**). This sample had  $[\alpha]_D -2.29^\circ$  (*c* 4.15, *l* 1, methanol), which corresponds to 25.2% enantiomeric purity, or 103% of the value of the starting amine. Tricyclo[3.2.1.0<sup>2,7</sup>]oct-4-yl acetate (**21-OAc**) was obtained contaminated with about 10% **34-OAc**. The fraction had  $[\alpha]_D -1.85^\circ$  (*c* 1.19, *l* 1, methanol). The corrected rotation of the **21-OAc** component is  $-1.81^\circ$ , corresponding to 8% enantiomeric purity, or 33% of that of the starting amine.