and since what s character exists in the tin bonds is concentrated in the bonds to carbon, then despite changes in the number of electronegative atoms (three or four) or their type (Cl or N) there is a constant value of the IS for each type of organotin species.[17]

The *trans* geometry of the hexacoordinated complex cation derived from dimethyltin dichloride is reflected in its QS value—the same as that produced by the equatorial geometry of the pentacoordinated complex anion. The values are somewhat smaller for the complex ions derived from diphenyltin dichloride, and moreover show differences outside experimental error for the separated ions which may arise from crystal-packing considerations. From these values alone (2.88–3.24 ± 0.12 mm/sec) it is difficult to establish the geometries of the ions unambiguously, but given that equivalence of QS values is produced by the dimethyltin combination of *trans*-hexacoordinated cation and equatorial pentacoordinated anion, it would seem highly unlikely that other, different combinations of diphenyltin ion geometries could lead to superimposable Mössbauer spectra as well.[18] The complex ions derived from *n*-butyltin trichloride and tin tetrachloride are all hexacoordinated. However, because of the geometry imposed by the terpyridyl ring system, it is likely that the *n*-butyl group is *trans* to a chlorine atom in both the cation as well as the anion, a situation apparently able to produce field gradient tensors of equivalent magnitude at both tin nuclei.

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(17) Similar similarities are seen for the Fe[57] Mössbauer spectra of ferri- and ferrocyanides [J. F. Duncan and P. W. R. Wigley, *J. Chem. Soc.*, 1120 (1963); N. L. Costa, J. Danon, and R. M. Xavier, *J. Phys. Chem. Solids*, 23 1783 (1962); R. G. Shulman and S. Sugano, *J. Chem. Phys.*, 42, 39 (1965).

(18) A point charge model would predict that $\Delta E_{trans} = 2\Delta E_{cis}$ for octahedral systems [R. R. Berrett and B. W. Fitzsimmons, *Chem. Commun.*, 90 (1966); *J. Chem. Soc., A*, 525 (1967); B. W. Fitzsimmons, N. J. Seeley, and A. W. Smith, *Chem. Commun.*, 390 (1968)].

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An Intermolecular "Memory Effect" in the Formation and Capture of a Potentially Symmetrical Tricyclooctyl Cation[1]

Sir:

In the ring-expansion route to bicyclooctyl[2,3] and bicyclooctenyl[4] cations, the rearrangements pass

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(2) (a) J. A. Berson and P. Reynolds-Warnhoff, *J. Am. Chem. Soc.*, 84, 682 (1962); 86, 595 (1964); (b) J. A. Berson and D. Willner, *ibid.*, 84, 675 (1962); 86, 609 (1964).

through intermediates which, although potentially symmetrical (*e.g.*, 2-bicyclo[2.2.2]octyl cation) or quasi-symmetrical at equilibrium, nevertheless show unsymmetrical behavior. Intermolecular "memory effects"[5] now are shown to occur in the cations derived from optically active tricyclooctyl substrates.[6] The results help in the formulation of the mechanism underlying the exceptionally intricate chemistry of this series.

The products obtained from optically active nortricyclylcarbinyl (1),[7] tricyclo[3.2.1.0²,⁴]octyl (2),[8] and tricyclo[3.2.1.0²,⁷]octyl (3)[9] derivatives in solvolysis and nitrosative deamination are shown in Table I.

The ring expansions of nortricyclylcarbinyl substrates 1 give unrearranged (1) and "*exo*-cyclopropano" (2) products with complete retention (within experimental error) and tricyclic product 3 with partial retention of enantiomeric purity. The configurational relationships given in the structural formulas[7-9] and the data of Table I show that capture of the intermediate leading to 3c or 3d occurs from the same side as that occupied by the departing group in 1a or 1b. This memory effect cannot be a consequence of isomeri-

a, X = OBs; b, X = NH₂; c, X = OAc; d, X = OH
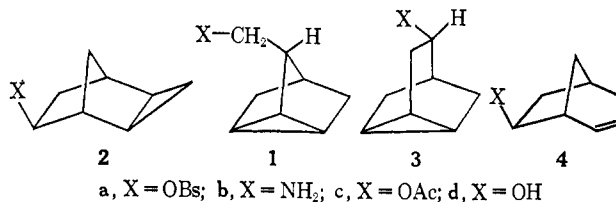
zation of 1a to 3a followed by solvolysis, since 3a gives essentially completely racemic 3c (Table I).[6e] There must be an unsymmetrical intermediate for 3c in addition to the symmetrical ones (6 and/or 7).
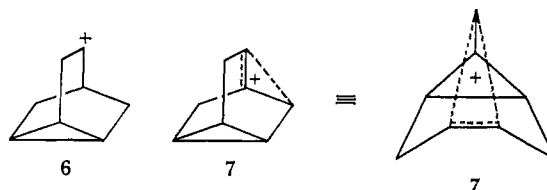
The same unsymmetrical species apparently occurs in the solvolyses of the "*exo*-cyclopropano" compound 2a, which forms primary product 1c with complete retention and tricyclic product 3c with almost exactly the same partial retention of optical purity as that obtained from 1a.

(3) J. A. Berson and M. S. Poonian, *ibid.*, 88, 170 (1966).

(4) J. A. Berson and J. J. Gajewski, *ibid.*, 86, 5020 (1964).

(5) A summary of results on "memory effects" is given by J. A. Berson, *Angew. Chem.*, in press.

(6) For valuable prior studies with the racemic compounds, see (a) R. R. Sauers and J. A. Beisler, *Tetrahedron Letters*, 2181 (1964); (b) R. R. Sauers, J. A. Beisler, and H. Feilich, *J. Org. Chem.*, 32, 569 (1967); (c) A. K. Colter and R. C. Musso, *ibid.*, 30, 2462 (1965); (d) K. B. Wiberg and G. Wenzinger, *ibid.*, 30, 2278 (1965). For parallel studies with certain optically active and isotopically labeled compounds, see (e) J. A. Berson, G. M. Clarke, D. Wege, and R. G. Bergman, *J. Am. Chem. Soc.*, 90, 3238 (1968); (f) J. A. Berson, D. Wege, G. M. Clarke, and R. G. Bergman, *ibid.*, 90, 3240 (1968).

(7) (a) Preparation of the amine from the previously described[7b] optically active *p*-bromobenzenesulfonate gives material with spectral properties identical with those of the racemate. (b) J. A. Berson and R. G. Bergman, *ibid.*, 89, 2569 (1967). (c) Previous correlations[7b] establish configurations and maximum rotations of the 1 series.

(8) (a) The *p*-bromobenzenesulfonate is available from the acetate, prepared by the Simmons–Smith reaction[6d] on optically active *exo*-norbornenyl acetate of known[8b] configuration and maximum rotation. (b) K. Mislow and J. G. Berger, *ibid.*, 84, 1956 (1962).

(9) For absolute configuration and maximum rotation, see ref 6e.

Table I

Starting material[b] and conditions	1 %	1 EP[c]	2 %	2 EP[c]	3 %	3 EP[c]	4 %	4 EP[c]
1, X = OBs; HOAc, NaOAc, 100°	9	95	37	98	15	23	39	0
1, X = OBs; H₂O–dioxane, 100°	36	97	46	103	11	28	7	0
1,[g] X = NH₂; HOAc, NaNO₂	23	96	52	104	14	30	11	0
2, X = OBs; HOAc, NaOAc, 100°	6	101	51	100	15	27	26	0
3, X = OBs; HOAc, NaOAc, 100°	0		0		35	3[d]	65	0
3,[e] X = OBs, H₂O–dioxane, 100°	0		0		58		42	

a In HOAc, X = OAc, NaOAc buffer; in H₂O–dioxane (30:70 v/v), X = OH, pyridine buffer. *b* Absolute configuration as shown. *c* Per cent of the enantiomeric purity of the starting material preserved in this product. Absolute configuration of product as shown. *d* Absolute configuration of product enantiomeric with that of starting material. *e* Optically inactive starting material. *f* About 1–2% of endo-tricyclo-[3.2.1.0²,⁷]oct-8-yl acetate (5) is found in all the acetolyses (see ref 6e). *g* Starting material and products all have configurations enantiomeric to those shown.

It is difficult to ascribe the observed memory effect to ion-pairing phenomena, since the optical purity of the tricyclic product **3** is essentially insensitive to the nature of the solvent or the leaving group (Table I). Furthermore, the original position of the leaving counterion relative to the point of nucleophilic capture to form **3c** (directly adjacent in **1a** and diametrically opposed in **2a**) also is without effect (Table I).[10]

strates of the **2** and **1** structures, respectively, ensure perfect preservation of enantiomeric purity in the **2** and **1** products. Products of the **3** series can be formed optically active from twisted tricyclic cation **10**, but escape to racemic material can occur from **10** via racemic cations **7** and/or **6** or by incompletely stereospecific attack on **10**.

Reversion of **7** and/or **6** to **9** must be slow. Otherwise, solvolysis of **3a** would lead to products **1c** and **2c**,
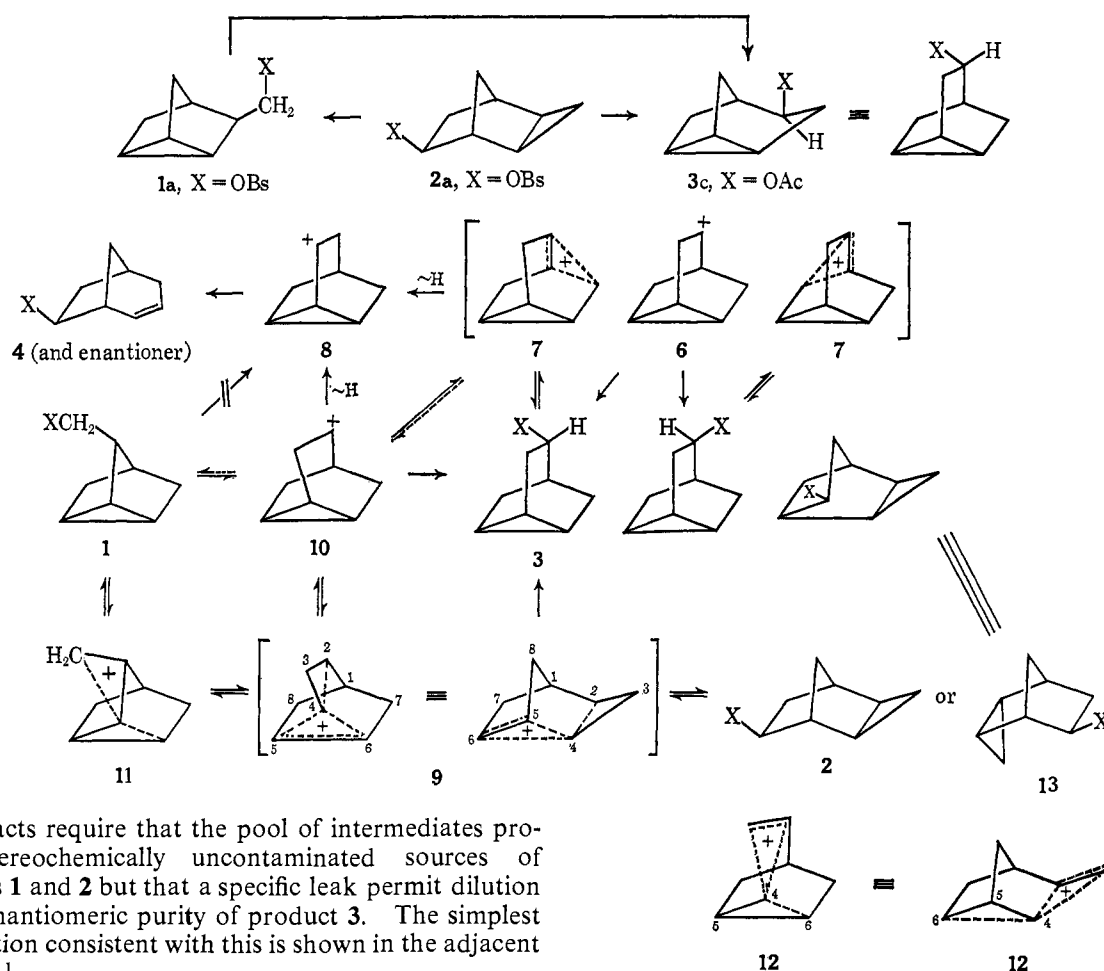
The facts require that the pool of intermediates provide stereochemically uncontaminated sources of products **1** and **2** but that a specific leak permit dilution of the enantiomeric purity of product **3**. The simplest formulation consistent with this is shown in the adjacent scheme.[11]

Optically active cations **9** and **11** derived from sub-

and solvolysis of optically active **1a** or **2a** would give partially racemized **1c** and **2c**, in conflict with the observations of Table I.

(10) Although ion-pair return diverts a portion of **2a** to **1a**,[6b] the rearranged primary bromobenzenesulfonate **1a** is solvolyzed too slowly[6b,d] to be a permissible intermediate in the **2a** → **3c** reaction.

(11) It is now clear[6f] that none of the unsaturated product **4** derived from **1a** or **1b** arises from direct ring expansion to cation **8**. The trans-

annular hydride shift[6e] from **6** and/or **7** leading to a small amount of endo-tricyclo[3.2.1.0²,⁷]oct-8-yl product is not shown.

Optically active **3c** also may result from capture of **9** directly at C-2, but the approximate microscopic reverse of this process, **3a → 9**, does not seem to be important, again since entry into the scheme at **3a** leads only to products **3c** and **4c**, not to **1c** and **2c** (Table I). If escape of some of the cations **9** to racemic intermediates can occur directly and irreversibly (**9 → 7** and/or **6**), cation **10** is superfluous.

The detailed electronic structures of the intermediates **9**, **10**, and **11** are schematic, and this entire pool of optically active cations could be replaced by corresponding sets of classical ions. Rapid equilibration among these (or their replacement by a single nonclassical species, e.g., **12**), however, would predict a product distribution independent of the point of entry into the scheme, in conflict with the results of Table I. In fact, no further economies of representation can be effected, since the data clearly require at least one other intermediate which must be symmetrical (e.g., **6** and/or **7**).

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Preferential Formation of a Symmetrical Rather Than an Unsymmetrical Cyclopropylcarbinyl Cation. Vicinal vs. Transannular Hydride Shift in the Tricyclo[3.2.1.0^{2,7}]oct-4-yl System[1]

Sir:

As part of a study[2] of cations of the nortricyclylcarbinyl–tricyclooctyl series, we have observed that the pronounced preference for transannular rather than vicinal hydride shift seen in norbornyl cations is reversed in tricyclo[3.2.1.0^{2,7}]oct-4-yl cation.

Lithium aluminum hydride reduction of the ketone **1**[3] gives the tricyclic alcohol **2a**, mp 140–141° (lit. mp 124.5–125.5°,[3] 132.5–135°[4]).

Optical activation of the acid phthalate **2c** is achieved by recrystallization of the ephedrine salt. Hydrogenolysis of active alcohol **2a**, [α]D +6.49° (CHCl₃), in acetic acid over platinum oxide gives 2-bicyclo[2.2.2]-octanol (**3a**), mixed with *exo-* and *endo-*2-bicyclo[3.2.1]-octanols. Isolation of **3a** gives material of [α]D +7.84° (CHCl₃). These data combined with the known absolute configuration[5] and approximately known maximum rotation[6] of **3** show that (+)-**2a** has a maximum

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(2) For related papers in this series, 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, D. Wege, G. M. Clarke, and R. G. Bergman, *ibid.*, 90, 3240 (1968).

(3) J. T. Lumb and G. H. Whitham, *Tetrahedron*, 21, 499 (1965). We are indebted to Dr. Whitham for a comparison sample of ketone **1**, which was identical with that prepared in our laboratory.

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

(5) J. A. Berson and D. Willner, *J. Am. Chem. Soc.*, 86, 609 (1964).

(6) Isotopic dilution analyses give 40 ± 4.5[5] and 29.6°.[7] Independent chemical correlations give ≥32[8] and ≥33°.[9]

(7) H. L. Goering and G. Fickes, unpublished; G. Fickes, Ph.D. Thesis, University of Wisconsin, 1965.

rotation of about 24.4–31.7° (CHCl₃) and the absolute configuration indicated.

1	(+)-**2a**, X = OH	(+)-**3a**, X = OH
	b, X = OBs	b, X = OBs
	c, X = OPhth	
	d, X = OAc	
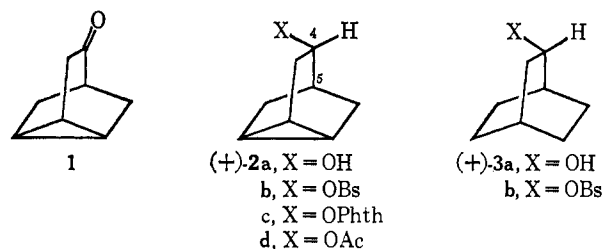
The titrimetrically determined rate constants ($k_t \times 10^4$ sec^{-1}) for acetolysis (NaOAc or KOAc buffer) of **2b** are 0.430 ± 0.005 at 19.90°, 1.67 ± 0.02 at 29.87°, and 6.33 ± 0.16 at 40.16°. The value extrapolated to 25°, 0.871, is ca. ten times that for the 2-bicyclo[2.2.2]-octyl analog **3b**.[7,10] The polarimetric rate constant ($k_\alpha \times 10^4$ sec^{-1}) is 1.38 ± 0.03 at 19.90°, about 3.1k_t; presumably the difference is caused by racemization of **2b** during ion-pair return.[11,12] At least some of this racemization is associated with Wagner–Meerwein rearrangement, since acetolysis of 4-deuterio-**2b** gives **2d** with ~50% of the label at C-4 and ~50% at C-5.[13] The results closely resemble those observed in the *exo*-norbornyl system[11] and are consistent with the formulation of the initial solvolysis intermediate as the symmetrical ion **4**.[14]
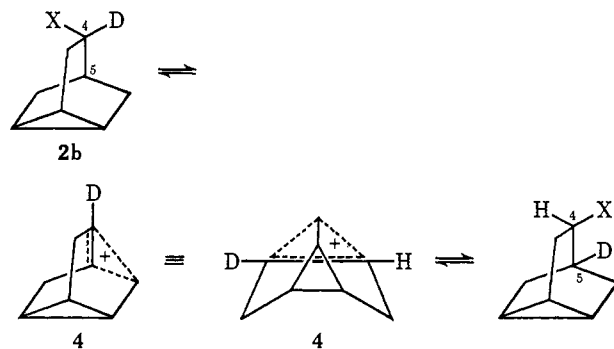

Table I shows that the major products of the solvolysis of **2b** are the closely related pair of alcohols **7a** and **8a** (or acetates **7d** and **8d**). Because of the instability of the tricyclic materials **8a** and **8d**, which readily rearrange to the unsaturated isomers **7a** and **7d**, the yield of substances of the structure **7** and **8** in any run are significant only as their sum. The acetate **7d** isolated from solvolysis of optically active **2b** is completely inactive. The derived ketone (maximum [α]D 883°) also is inactive.

(8) J. A. Berson and N. Kundu, unpublished; N. Kundu, Ph.D Thesis, University of Wisconsin, 1966.

(9) J. A. Berson and E. J. Walsh, Jr., unpublished; E. J. Walsh, Jr., Ph.D. Thesis, University of Wisconsin, 1968.

(10) (a) H. M. Walborsky, M. E. Baum, and A. A. Youssef, *J. Am. Chem. Soc.*, 83, 988 (1961); (b) H. L. Goering and M. F. Sloan, *ibid.*, 83, 1992 (1961), report the value for the *p*-toluenesulfonate.

(11) S. Winstein and D. Trifan, *ibid.*, 74, 1147, 1154 (1952).

(12) S. Winstein and K. C. Schreiber, *ibid.*, 74, 2165 (1952).

(13) This confirms a previous report of a similar labeling experiment.[4]

(14) A minor competing path appears to result in a small amount of direct displacement which gives 2–4% **2d** of inverted configuration in acetolysis. Small amounts of tricyclo[3.2.1.0^{2,7}]oct-3-ene[15] also are found.

(15) (a) W. von E. Doering and W. R. Roth, *Tetrahedron*, 19, 736 (1963); (b) C. A. Grob and J. Hostynek, *Helv. Chim. Acta*, 46, 1676 (1963).