Molecular Rearrangements. XXVIII. Nitrous Acid Deamination of 3-*exo*-Phenyl-3-hydroxy- and 3-*endo*-Phenyl-3-hydroxy-2-*endo*-norbornylamines[1a,1b,2,3]

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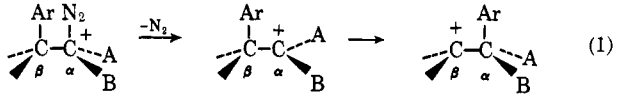
Abstract: The title compounds, labeled both with deuterium and with carbon-14, have been subjected to nitrous acid deamination in acetic acid–sodium acetate solution. The yields of products have been determined by gpc, by isotope dilution, by liquid column chromatography, or by all three methods. The mechanistic implications of the data—namely that the "memory effects" can be explained by counterion control and that the classical carbonium ion intermediates survive several 1,2 shifts—are discussed in detail. It is concluded either that "hot" carbonium ions are not necessary to explain the results, or that they must be redefined.

In earlier studies[4] of the reactions of primary aliphatic amines and α-amino alcohols with nitrous acid, we presented both isotopic and stereochemical evidence for classical, open carbonium ion intermediates, some of which can maintain configuration because of restricted rotation about the central C–C$^+$ bond and a preferred direction of attack by entering group.[5] Since we repeatedly demonstrated[4c,4f,4g,4i] that 1,2-aryl shifts during amine–nitrous acid reactions can occur with retention of configuration at the migration terminus, then at least for the reactions studied, Streitwieser's proposal[6] "that the diazonium ion rather than a carbonium ion is the branching point of the competing reactions" cannot be correct. This conclusion follows because the nitrogen must already have left the migration terminus (C_α) if migration with retention of configuration (eq 1) is to take place.

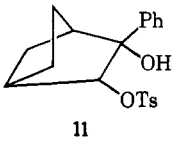


(1)

Winstein's suggestion[7] that a "hot" carbonium ion might be formed during the amine–nitrous acid reaction is not so easy to accept or reject on the basis of our earlier[4,5] work. The "hot" carbonium ion was pictured[7] as having been produced without anchimeric assistance, and to have undergone no charge delocalization. It should thus be highly energetic, and react in a nondiscriminatory fashion, as observed,[5–7] to yield a multiplicity of products (by comparison with the corresponding solvolyses). By definition,[7] then, "hot" carbonium ions should have "lost most if not all of their sizzle"[8] after a single hydride shift or Wagner–Meerwein rearrangement.

It thus seemed important to determine whether the unusual behavior associated with carbonium ions formed during the amine–nitrous acid reaction could be maintained after one or more Wagner–Meerwein rearrangements or 6,1,2-hydride shifts. If so, then almost certainly the so-called "hot" carbonium ions—at least as defined[7,8]—could not be responsible for this unusual behavior. Conversely, if the unusual behavior is associated only with the initially formed carbonium ion, and all ions produced subsequent to a single 6,2 shift exhibit behavior consistent with that observed on solvolysis, then the intervention of a "hot" carbonium ion could be considered possible.

We therefore undertook an exhaustive study of the amine–nitrous acid deamination of the two reactants 3-*exo*-phenyl-3-hydroxy-2-*endo*-bicyclo[2.2.1]heptylamine (**1**) and 3-*endo*-phenyl-3-hydroxy-2-*endo*-bicyclo[2.2.1]heptylamine (**2**), which are related mechanistically through the carbonium ion cycle A–F, as shown in Scheme I. These two amines were chosen for study because it should be possible to compare their behavior with that of 3-*endo*-phenyl-3-hydroxy-2-*exo*-bicyclo[2.2.1]heptyl tosylate (**11**), whose hydrolysis, together



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(1) (a) Research sponsored by the U. S. Atomic Energy Commission under contract with Union Carbide Corporation; presented in part at the Symposium on Organic Reaction Mechanisms, Nagoya, Japan, Oct 19, 1971; (b) a portion of this work is taken from the Ph.D. Dissertation of Michael D. Eckart, University of Tennessee, Knoxville, Tenn.; (c) AEC Postdoctoral Fellow, 1963–1965; (d) Predoctoral Fellow, Oak Ridge Associated Universities, 1966–1968; (e) ORAU Research Participant from the Rose-Hulman Institute of Technology, Terre Haute, Ind., Summer 1966, and visiting scientist, Summer 1967.

(2) Paper XXVII: C. J. Collins and C. E. Harding, *Justus Liebigs Ann. Chem.*, **745**, 124 (1971).

(3) Preliminary communications of this work are: (a) C. J. Collins, V. F. Raaen, B. M. Benjamin, and I. T. Glover, *J. Amer. Chem. Soc.*, **89**, 3940, 5314 (1967); (b) C. J. Collins, V. F. Raaen, and M. D. Eckart, *ibid.*, **92**, 1787 (1970); (c) C. J. Collins and B. M. Benjamin, *ibid.*, **92**, 3182, 3183 (1970); (d) V. F. Raaen, B. M. Benjamin, and C. J. Collins, *Tetrahedron Lett.*, 2613 (1971).

(4) (a) B. M. Benjamin and C. J. Collins, *J. Amer. Chem. Soc.*, **78**, 4952 (1956); (b) W. A. Bonner and C. J. Collins, *ibid.*, **78**, 5587 (1956); (c) B. M. Benjamin, H. J. Schaeffer, and C. J. Collins, *ibid.*, **79**, 6160 (1957); (d) V. F. Raaen and C. J. Collins, *ibid.*, **80**, 1409 (1958); (e) C. J. Collins, W. A. Bonner, and C. T. Lester, *ibid.*, **81**, 466 (1959); (f) B. M. Benjamin, P. Wilder, and C. J. Collins, *ibid.*, **83**, 3654 (1961); (g) B. M. Benjamin and C. J. Collins, *ibid.*, **83**, 3662 (1961); (h) C. J. Collins, J. B. Christie, and V. F. Raaen, *ibid.*, **83**, 4267 (1961); (i) C. J. Collins, M. M. Staum, and B. M. Benjamin, *J. Org. Chem.*, **27**, 3525 (1962); (j) C. J. Collins and B. M. Benjamin, *J. Amer. Chem. Soc.*, **85**, 2519 (1963).

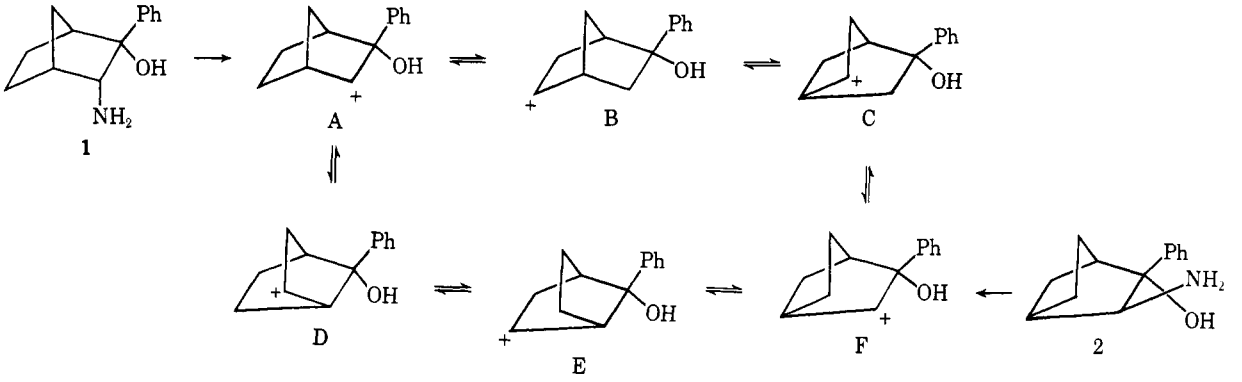
(5) C. J. Collins, *Accounts Chem. Res.*, **4**, 315 (1971).

(6) A. Streitwieser, Jr., and W. D. Schaeffer, *J. Amer. Chem. Soc.*, **79**, 2888 (1957); A. Streitwieser, Jr., *J. Org. Chem.*, **22**, 861 (1957).

(7) D. Semenow, C. H. Shih, and W. G. Young (*J. Amer. Chem. Soc.*, **80**, 5472 (1958)) credit Professor Winstein with the proposal.

(8) E. Renk and J. D. Roberts, *ibid.*, **83**, 878 (1961).

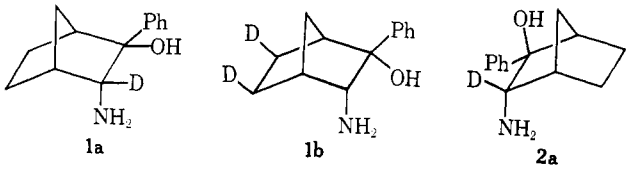
Scheme I



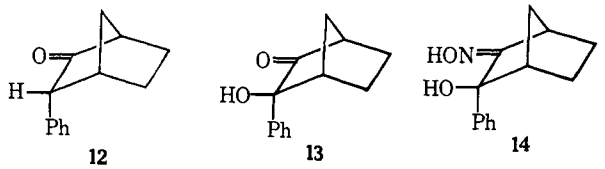
with two of its deuterium-labeled isotope position isomers, we studied previously.[9] As can be seen from the orientation of structure **11**, it should produce, on hydrolysis, a nonclassical ion[9] corresponding to the Wagner–Meerwein pair E ⇌ F.

Method and Results

Amine **1** and its deuterium-containing isotope position isomers **1a** and **1b** were prepared as described



previously.[10] Amine **2** and its isotope position isomer **2a** were synthesized starting from 3-*endo*-phenyl-2-bicyclo[2.2.1]heptanone (**12**), which was converted to **13**



deuteride. The synthetic procedures, nmr spectra, and carbon and hydrogen analyses all confirm the structures assigned to **1**, **1a**, **1b**, **2**, and **2a**. In addition, the amines **1** and **2** were prepared labeled with carbon-14 in the phenyl groups. The syntheses were identical with those for the nonradioactive compounds except that bromobenzene-$^{14}C^{12}$ was employed during the Grignard reactions.

Deamination of **1** and **2** in acetic acid–sodium acetate at room temperature yielded a variety of products, and these are shown in Schemes II and III. The diols were produced as the monoacetates, but for simplicity are shown in Schemes II and III as the free diols (**3**, **4**, **5**, **6**, **9**, and **10**). Certain of the compounds (**8**, **9**, and **10**) produced on deamination of **1** were not observed in the reaction products from the deamination of **2**. The monoacetates of the diols were identified, and their yields were determined by analytical gpc techniques (see Experimental Section), but on a macroscopic scale we were unable to separate and characterize them. The oil isolated on working up the deamination product was, therefore, treated with lithium aluminum hydride, and the resultant mixture could then be satisfactorily separated into its components by liquid column chromatography on alumina. The yields of the deacetylated

Table I. Percentage Yields of Products Obtained on Deamination of **1** and **2**

Products	Amine 1				Amine 2	
	Liquid elution method[a]		Gpc[b,c] method	Isotope[a] dilution method	Gpc[b] method	Isotope[a] dilution method
3	4.0[c]	4.8[d]	5.5[d]	4.3 ± 0.01[c]	6.3	6.3 ± 0.02[c]
4	3.0	3.6	3.0[e]	2.7 ± 0.01[c]	1.7[e]	3.7 ± 0.02[c]
5	20.8	23.5	22.1		29.2	
6	4.8	5.7	9.7		37.2	
7	6.4	7.6	8.1		22.3	
8	18.8	22.2	18.4		0.4	Trace?
9	18.9	22.2	22.3			Trace?
10	8.8	10.4	10.4		0	

[a] Performed on reaction mixture which had been treated with lithium aluminum hydride. [b] Performed on original reaction mixture. [c] The figures in this column are the actual yields. The error given is the duplicability of the radioactivity assays. [d] These yields are normalized to 100%. [e] Decomposed on column.

in poor yield by the Biltz reaction,[11] and thence to the oxime **14** which could be converted to **2** or **2a**, respectively, by reduction with lithium aluminum hydride or

products were then compared with the yields of the corresponding acetates (**8** was determined as the free ketone by gpc, but as the carbinol on alumina, whereas **7** was unaffected by treatment with lithium aluminum hydride). These data are recorded in Table I, and as

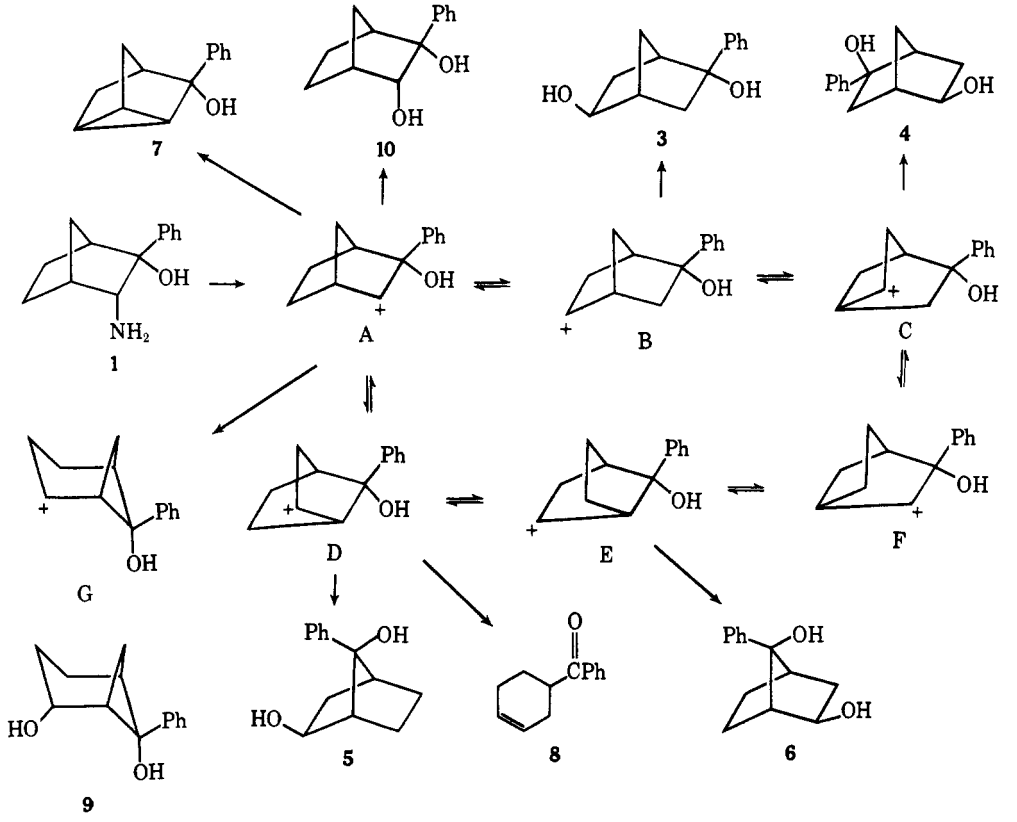
(9) C. J. Collins and B. M. Benjamin, *J. Amer. Chem. Soc.*, **89**, 6565 (1967).

(10) C. J. Collins, B. M. Benjamin, V. F. Raaen, I. T. Glover, and M. D. Eckart, *Justus Liebigs Ann. Chem.*, **739**, 7 (1970).

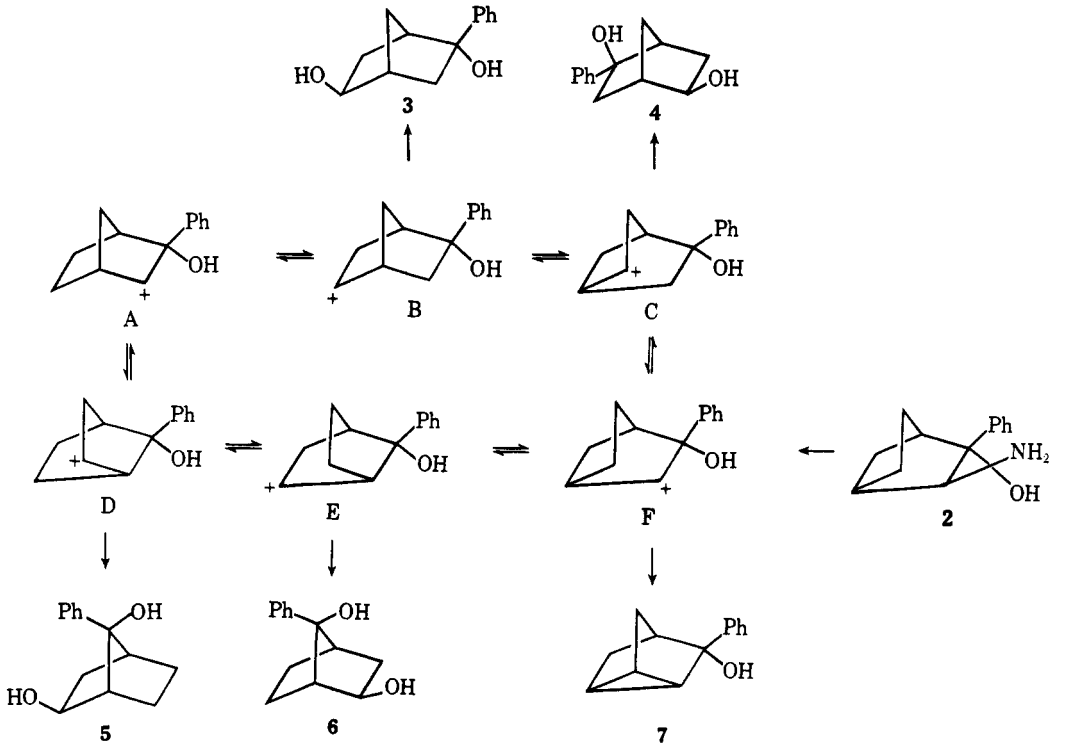
(11) H. Biltz, *Ber.*, **32**, 650 (1899).

(12) C. J. Collins and W. A. Bonner, *J. Amer. Chem. Soc.*, **77**, 97 (1955).

Scheme II



Scheme III



can be seen, the results of the two different methods are in excellent agreement.

In addition, for reasons which will become apparent in the Discussion, we carefully determined the yields of the two minor components **3** and **4** by the isotope-dilution method[13] (**1** and **2** were prepared with phenyl-^{14}C labels), and these results are also recorded in Table I.

(13) V. F. Raaen, G. A. Ropp, and H. P. Raaen, "Carbon-14," McGraw-Hill, New York, N. Y., 1968, Chapter 2.

Compounds **3–7** were described[9] by us previously, and are compounds isolated on the hydrolysis of **11**. Products **8** and **9** have also been described.[10] 2-*exo*-Phenylbicyclo[2.2.1]heptyl-2,3-*cis*-*endo*-diol (**10**) was identified by independent synthesis from norcamphorquinone by (1) treatment with 1 mol of phenyllithium followed by (2) reduction with lithium aluminum hydride. In this manner we obtained a mixture of two diols from which **10** was isolated.

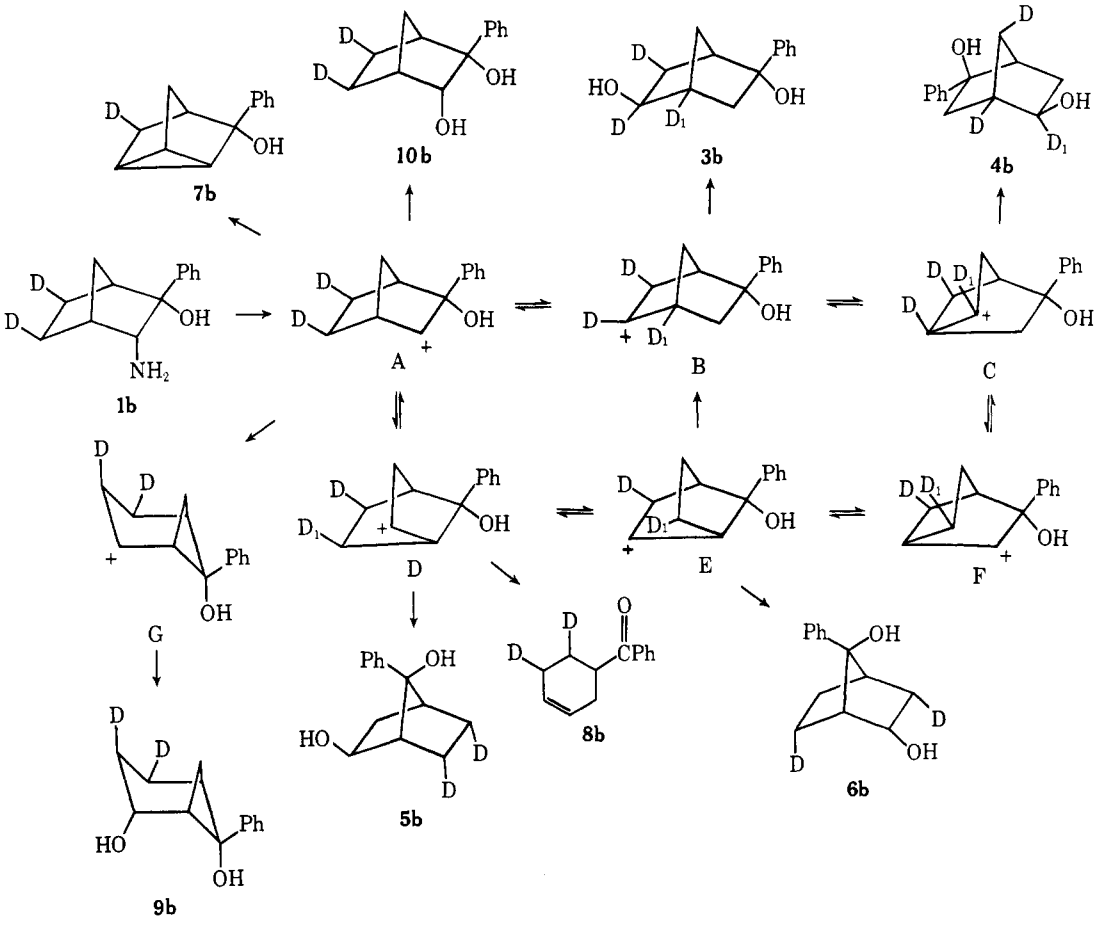
Table II. Percentage Yields and Deuterium Distributions in **3a** and **4a** from Deaminations of **1a** and **2a**

Reactant	Product 3a		Product 4a	
	Yield, %[a]	D'[b]	Yield, %[a]	D'[b]
1	4.25 ± 0.01	0.11 ± 0.025	2.7 ± 0.01	0.175 ± 0.016
2	6.3 ± 0.02	0.145 ± 0.025	3.7 ± 0.02	0.23 ± 0.016

[a] The ± values are the reproducibilities of the carbon-14 assays. [b] The ± values are estimated standard deviations.

The products **3b**–**10b** obtained upon deamination of **1b** were all isolated, and the positions of their deuterium atoms (or atom in the case of **7b**) were determined by nmr spectroscopy. The deuterium assignments are as shown in Scheme IV. Our experiments describing how the predicted positions. In Scheme V we give the presumed mechanism for production of **3a** and **4a**. Since the other products behaved as expected, they are not shown in Scheme V. In Scheme V the positions designated D' signify where the deuterium goes in **3a** and **4a**

Scheme IV



we excluded ion E as a precursor of ketone **8b** have previously been described.[10] The deuterium atoms labeled D_1 in Scheme IV signify that a portion of the original *exo*-6 deuterium of **1b** proceeds to products **3b** and **4b** *via* the counterclockwise route. Since diols **3b** and **4b** were formed in low yields (see, for example, Table II), the amount of recycling B → A or C → F was too small to measure. Only in **3b** and **4b**, therefore, was it possible to measure the contributions of both clockwise and counterclockwise pathways. We were interested in establishing the ratio D_1:D (C_4:C_5) for both **3b** and **4b**, but the error in our determinations appeared to be too high to allow us to say with certainty that this ratio was different in the two diols. From the results obtained, however, it appeared that D_1 (**4b**) was about 12% and D_1 (**3b**) was about 6% of the total deuterium content of C_4 and C_5. We therefore repeated the deamination experiments with **1a** and **2a**, respectively. The products all contained deuterium in by counterclockwise routes from *either* **1a** or **2a**. The per cent D' in C_3 for both **3a** and **4a** from both reactants was determined by nmr spectroscopy and the results are given in Table II, together with the yields of **3** and **4** as determined by the carbon-14 isotope-dilution method.[13]

Discussion

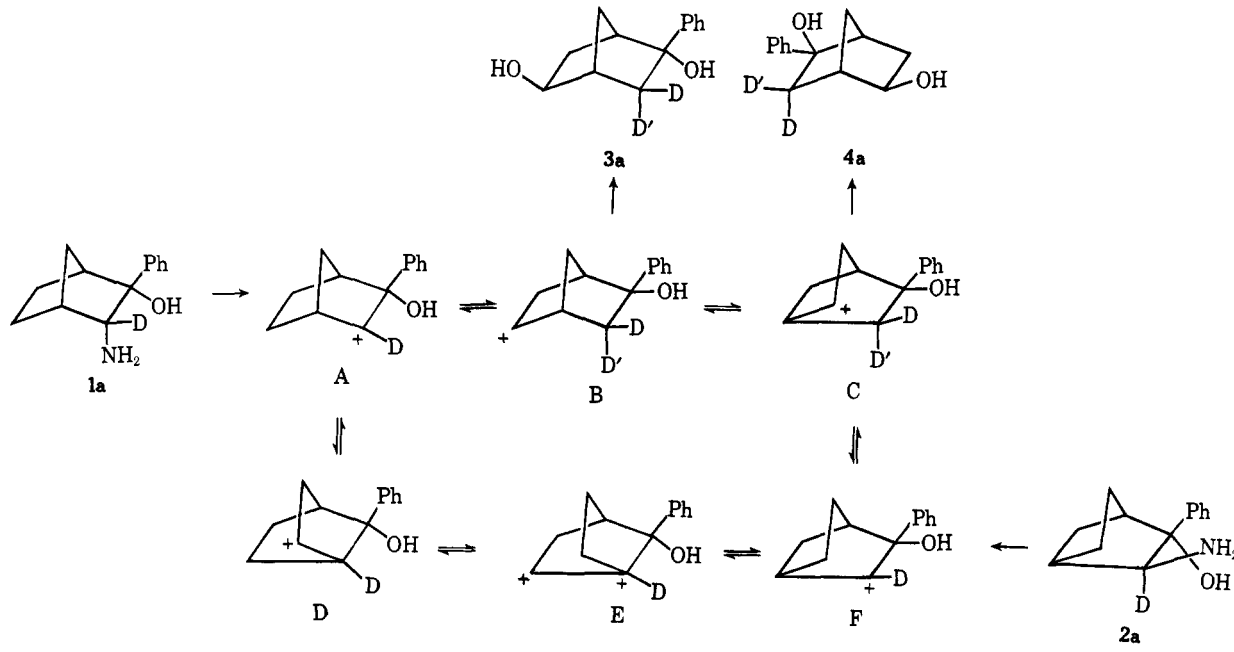
Several important conclusions follow from the results just presented.

(1) The reaction of amine **1** with nitrous acid yields three products (**8**, **9**, and **10**, Scheme II) not previously encountered[9] on hydrolysis of **11**. The *cis*-diol **9**, formed by a 7,1–7,2 Wagner–Meerwein rearrangement, is unprecedented in solvolytic reactions,[14,15] and can be

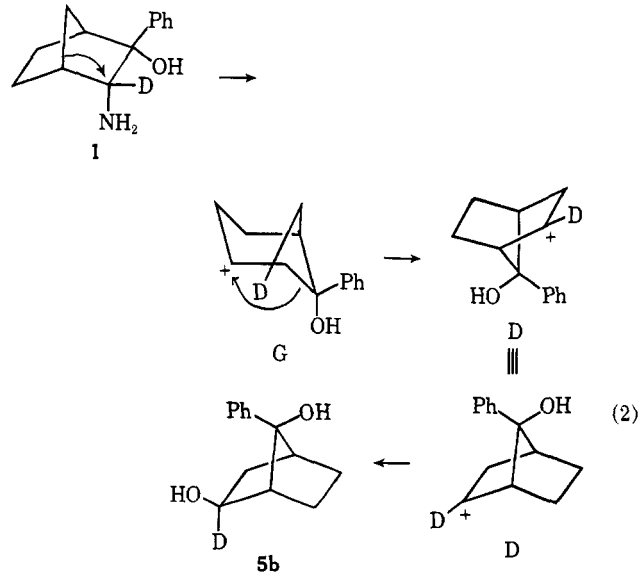
(14) P. Yates and R. J. Crawford (*J. Amer. Chem. Soc.*, **88**, 1561 (1966)) were the first to observe such a rearrangement on decomposition of 3-diazonorcamphor.

(15) W. Kirmse, G. Arend, and R. Siegfried, *Angew. Chem., Int. Ed. Engl.*, **9**, 165 (1970).

Scheme V



conceived of either as arising through a concerted process (**1** → G directly), or as being formed through the classical carbonium ion A (**1** → A → G). The Δ^3-cyclohexenyl phenyl ketone (**8**) could conceivably arise from ions G, D, or E (or from all of them). We have previously reported,[10] however, on the basis of deuterium tracer experiments, that **8** arises predominantly from ion D, with only a trace being formed from ion G. We can also rule out any measurable contribution from the pathway G → D → **8**, since any D formed in this manner from **1a** (eq 2) should lead also to diol **5b** with



(2)

an endo-deuterium. However, nmr analysis of the isolated signal (quartet, 3.4–3.5 ppm) for the 2-endo proton in the sample isolated on deamination of **1a** showed no detectable fraction of **5b** to be present.[16]

(2) Although, by definition,[7] the process **1** → A → G → **9** (or **1** → G → **9**), being unknown in solvolysis, is of the type pictured for a "hot" carbonium ion, the formation of Δ^3-cyclohexenyl phenyl ketone (**8**) is not, for A, if it is "hot" should lose its excess energy (or "sizzle," according to Roberts[8]) on Wagner–Meerwein rearrangement to D.[17] The yields of the two products **8** and **5** from the amines **1** and **2** are shown in Scheme VI. Both products are obtained from **1** in approximately equal amounts (18.5% **8** and 22% **5**, respectively). From **2**, however, only **5** was observed in 29% yield (the 0.4% of **8** originally reported[3b] could not be confirmed with isotope-dilution analysis; see Table I). It is, of course, possible that D produced from **1**, having undergone a single 1,2 shift, still possesses some excess vibrational energy[17] and thus suffers ring cleavage to **8**, whereas D from **2**, having undergone a Wagner–Meerwein *plus* a hydrogen shift, is now normal, and reacts with acetate to yield **5** without ring opening to **8**. Another possibility, based upon counterion control,[18–23] is that amine **1** produces the ion-pair D-I, and that amine **2** yields the ion-pair D-II, the counterion in each case maintaining the same relative position occupied by the amino group in the starting amine.[24] Ion pair D-I, formed after deamination of **1**, is not conveniently situated for collapse to **5** acetate, and the entering

(16) The scheme shown in eq 2 has a precedent in the work of W. Hückel and H. J. Kern, *Justus Liebigs Ann. Chem.*, **728**, 49 (1969), who isolated borneol (3.5% yield) upon the nitrous acid deamination of 2-*endo*-fenchylamine.

(17) For a dissenting view, see the Discussion in the paper by E. J. Corey and R. L. Dawson, *J. Amer. Chem. Soc.*, **85**, 1782 (1963), who say (p 1784), "In general, it is not possible to predict whether excess vibrational energy, gained during exothermic decomposition, would be lost to surrounding molecules before rearrangement can occur."

(18) H. Kwart, in collaboration with us [H. Kwart, E. N. Givens and C. J. Collins, *ibid.*, **90**, 7162 (1968); *ibid.*, **91**, 5532 (1969)] and independently [H. Kwart and J. L. Irvine, *ibid.*, **91**, 5541 (1969); H. Kwart and P. S. Strilko, *Chem. Commun.*, 767 (1967)], has repeatedly emphasized the importance of solvation factors and counterion effects in controlling stereospecificity.

(19) R. Huisgen and H. Reimlinger, *Justus Liebigs Ann. Chem.*, **599**, 161, 183 (1956); R. Huisgen and Ch. Rüchardt (*ibid.*, **601**, 21 (1956)) have proposed the intervention of oriented ion pairs in the thermal decomposition of *N*-nitroso-*N*-acylamines.

(20) M. Silver (*J. Amer. Chem. Soc.*, **83**, 3482 (1961)) discusses specific solvation of the cation during the amine–nitrous acid reaction.

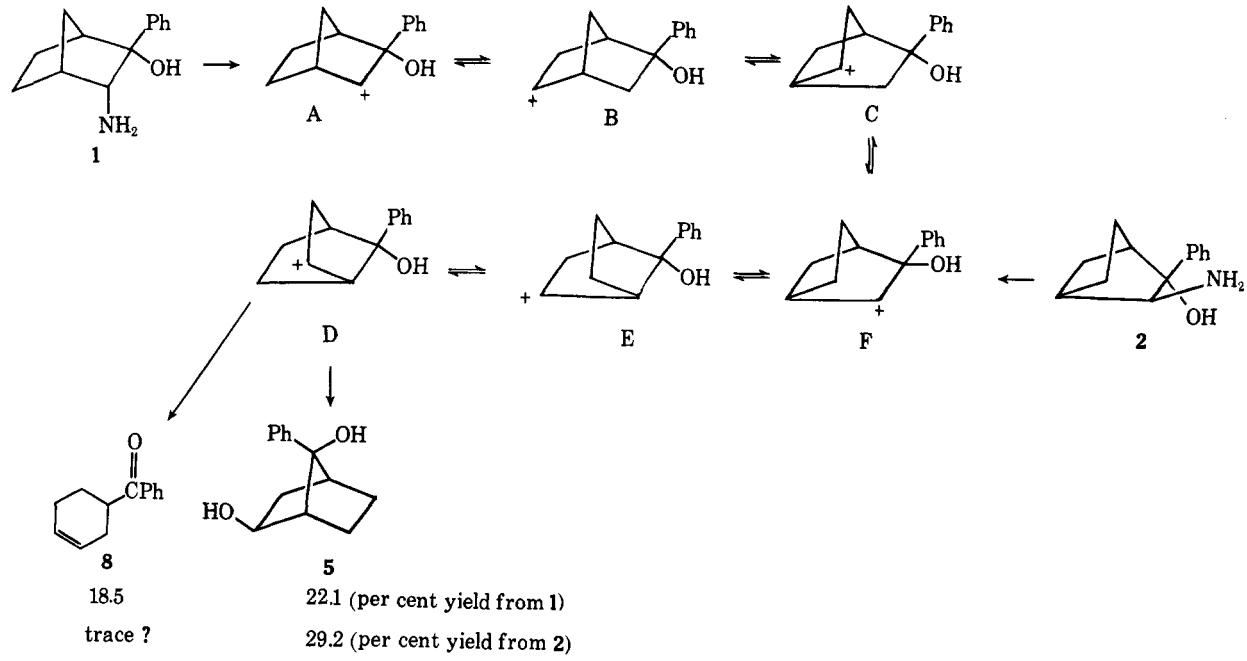
(21) T. E. Cohen and E. Jankowski, *ibid.*, **86**, 4217 (1964); R. A. Moss, *J. Org. Chem.*, **31**, 1032 (1966).

(22) R. A. Moss and S. M. Lane, *J. Amer. Chem. Soc.*, **89**, 5655 (1967); R. A. Moss and D. W. Reger, *ibid.*, **91**, 7539 (1969).

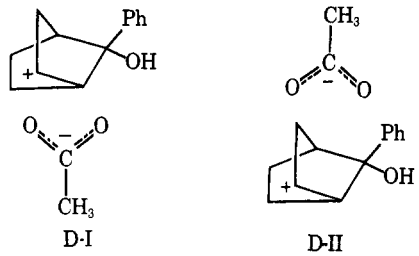
(23) E. H. White in "The Chemistry of the Amino Group," S. Patai, Ed., Interscience, New York, N. Y., 1968, Chapter 8.

(24) The initial steps of the mechanism of the nitrous acid deamination of primary aliphatic amines are well known [J. H. Ridd, *Quart.*

Scheme VI



group must come in from the solvent before it can successfully attack the positive charge on the cation.[3b] Thus ring opening [D-I → **8**] can compete with nucleophilic attack [D-I → **5** acetate]. The situation for D-II, formed from **2** after Wagner–Meerwein and hydride shift, however, is much different. Here the cation and anion are admirably oriented for collapse to **5** acetate, and if our proposal is correct, they must do so to the complete exclusion of ring cleavage to **8**, which cannot now compete with a nucleophilic attack by the counterion. The relatively high (10%) yield of **10** acetate could also be a result of counterion control. The ion pair formed on decomposition of the diazonium acetate produced from **1** should be well oriented for collapse to **10** acetate before rearrangement of cation A can occur.



(3) The products isolated (Scheme III) on nitrous acid deamination of amine **2** are unexceptional in that they are exactly those isolated upon hydrolysis of the tosylate **11**. There was no evidence for exo or endo attack on ion F, nor did we find evidence for 7,1–7,2 Wagner–Meerwein shift. Of the Wagner–Meerwein pairs A ⇌ D, E ⇌ F, and B ⇌ C, only the latter produced both products to be expected from such a pair. Thus, it is only by a comparison of the yields and properties of **3** and **4** from both reactants that we are able to draw conclusions concerning the nature of the ions B ⇌ C. First, consider the ratio of the yields of the two diol acetates (of **3** and **4**) formed from the Wagner–Meerwein pair B ⇌ C (Tables I and II). From the isotope-dilution experiments, the ratio **3**:**4** from amine **1** is 1.6, and from amine **2** it is 1.7 (identical within experimental error). This ratio (1.6–1.7) is not too different from that observed (1.4, see Scheme VII and the Experimental Section) on hydrolysis of the tosylates **15** and **16**. In the latter case the results are consistent with the interpretation that B and C are the nonclassical ion B ↔ C, or at least that the equilibrating ions B ⇌ C have reached their equilibrium point. In the deaminations[3c] of the amines **17** and **18** (Scheme VIII) the capture ratios for B and C clearly indicate that B and C have not yet reached equilibrium, for **17** yields more **3** than **4** (2.2:1), whereas **18** produces more **4** than **3** (1.7:1). Returning now to Schemes II and III (and Table II) we see that **3** and **4** are formed in the same ratio (1.6–1.7) from either **1** or **2**. It is thus tempting to conclude that B and C, having been remotely formed from both reactants, and requiring at least a hydride shift during their trips from A and F, respectively, have now lost their excess vibrational energy, and in contrast to the "hot" classical ions formed from **17** and **18**, are now "cool" nonclassical ions (B ↔ C), similar to those formed on hydrolysis of the tosylate **16** and **17** (Scheme VII). Such a conclusion, however, is false, as can be seen (Table II and Scheme V) from the deuterium distributions in **3a** and **4a** obtained on deamination of the deuterated *endo*-amines **1a** and **2a**. These results show that *both* **1a** and **2a** proceed to the Wagner–Meerwein pair B ⇌ C *predominantly* in clockwise directions (Scheme V); that is to say, both amines prefer to ap-

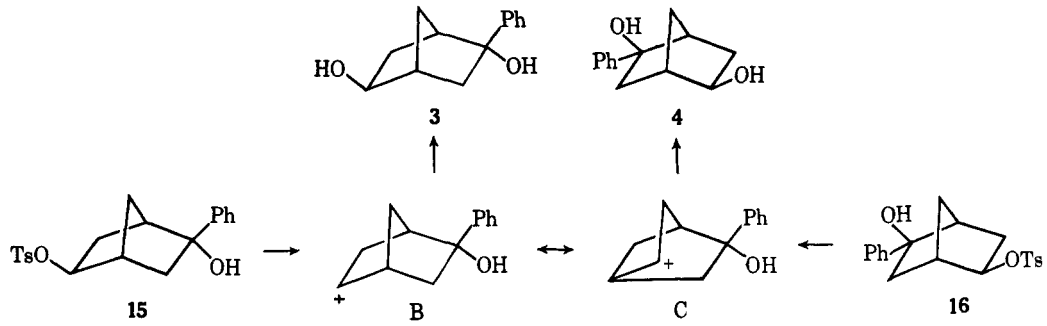
Rev., Chem. Soc., **15**, 418 (1961)], and for the solvent acetic acid–sodium acetate would be written as follows

$$RNH_2 \xrightarrow{HNO_2} RNHNO \longrightarrow RN{=}NOH \longrightarrow$$

$$RN{=}NOCOCH_3 \longrightarrow \left[\overset{+}{R}N_2 \ \overset{-}{O}Ac\right] \xrightarrow{-N_2} \underset{\text{ion pair}}{\left[R^+ \ \overset{-}{O}Ac\right]}$$

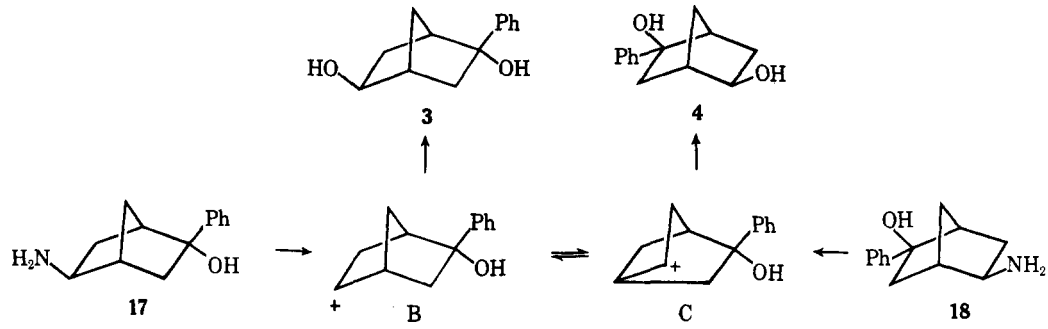
It is reasonable to expect that the ion pairs formed on reaction of **1** and **2** with nitrous acid should exhibit different cation–anion orientations, and that these orientations should survive one or more 1,2 shifts, as symbolized in D-I and D-II. (For evidence for this statement see ref 4h.)

Scheme VII



ratio 3:4 from both **15** and **16** is 1.4:1

Scheme VIII

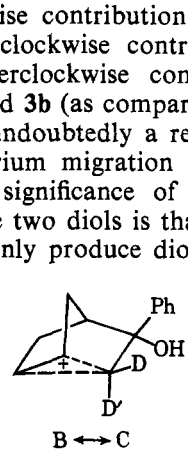


ratio 3:4 from **17** is 2.2:1

ratio 3:4 from **18** is 1:1.7

proach the equilibrium B $\rightleftharpoons$ C from the "B side." This means that even product **4a**, which is only one hydride shift (**2a** → F → C → **4a**) removed from reactant **2a**, is produced 77% by the long route [**2a** → F → E → D → A → B → C → **4a**] and only 23% of the shorter, more direct route. Thus, the identical capture ratio [3:4 $\cong$ 1.65] of A and B from both reactants cannot be used as a criterion for nonclassical character of the cation pair B $\rightleftharpoons$ C.

(4) The most important observation recorded in Table II, however, is that the fraction D′/(D′ + D) is not the same for diol **3a** as for diol **4a**. This observation was made for the deaminations *both* of **1a** and of **2a**, and supports the preliminary results (see previous discussion) for the deuterium distribution in **4b** (about 12% counterclockwise contribution from **1b**) and **3b** (about 6% counterclockwise contribution from **1b**). The smaller counterclockwise contributions to the production of **4b** and **3b** (as compared with **4a**) (18%) and **3a** (11%) are undoubtedly a result of an isotope effect during deuterium migration (ion D → ion E, Scheme IV). The significance of the inequality of D′/(D′ + D) in the two diols is that the nonclassical ion B ↔ C could only produce diols **3a** and **4a** with



identical fractions of D′, whereas classical ions B $\rightleftharpoons$ C *which have not yet reached their equilibrium point* are consistent with the fractions actually observed. This means that even after **2a** has proceeded through the long (clockwise) route to B through a Wagner–Meerwein rearrangement and a hydride shift (four 1,2 shifts in all), the ion B has survived as a classical ion. For an explanation of this point see Appendix A.

(5) All of the foregoing conclusions were based on the assumption that "classical," "nonclassical," and "hot" carbonium ions possess the properties usually ascribed[7,8,25] to them. We recognize that this assumption is not necessarily valid, yet these concepts are part of the scientific folklore of physical organic chemistry, and must be reckoned with in discussing the amine–nitrous acid reaction. A good example of the dangers inherent in arbitrary distinctions between classical and nonclassical carbonium ions has recently been provided.[26] Further, the original definition[7,8] of the "hot" carbonium ion presumably formed on nitrous acid deaminations of primary aliphatic amines has been challenged[17] and, in fact, so little is known of this mysterious "hot" cation that defining it is not easy. If we accept Corey's argument,[17] then the six cations represented in Schemes I–IV are classical because they are "hot" and can survive several rearrangements. Certainly Skell's observation[27] that the carbonium ions produced on deoxidation in strongly basic medium undergo rapid and successive rearrangements is consistent with Corey's view.[17] Hückel[28] had repeatedly called attention to the inconsistencies inherent in attempts to describe *dynamic* processes in terms of static cationic intermediates through a sort of slow motion view ("Zeitlupenbetrachtungen").

Finally we wish to comment on the extremely favorable circumstances relating to the mechanism of deam-

(25) P. D. Bartlett, "Nonclassical Ions," W. A. Benjamin, New York, N. Y., 1965.
(26) L. Radom, J. A. Pople, V. Buss, and P. von R. Schleyer, *J. Amer. Chem. Soc.*, **93**, 1813 (1971).
(27) P. S. Skell and I. Starer, *ibid.*, **81**, 4117 (1959); **82**, 2971 (1960).
(28) W. Hückel, *J. Prakt Chem.*, **32**, 320 (1966), and personal communications.

ination of the amines **1** and **2** which permitted the investigation of products **3** and **4** and the resulting conclusions. It is precisely because **3** and **4** are minor constituents in both deaminations that we were able to carry out this study, for apparently the processes A → B and F → C are the slowest in the entire cycle. It is this fact which effectively prevents an experimentally measurable recycling of material from **1** and **2** after it reaches the stage of ions B and C.

Experimental Section

Preparation of the Amines 1, 1a, and 1b. The preparation of 3-*exo*-phenyl-3-hydroxy-2-*endo*-norbornylamine (**1**) and the deuterium-containing isotope-position isomer **1b** has been described previously.[10] The synthesis of **1a** differed from that of **1** only in that during the last step, reduction of 3-*exo*-phenyl-3-hydroxy-2-norbornanone oxime, lithium aluminum deuteride was substituted for lithium aluminum hydride.

2-*exo*-Hydroxy-2-phenyl-3-norbornanone (13). The ketol was prepared by the Biltz[11] oxidation of 2-*endo*-phenyl-3-norbornanone (**12**). In a typical procedure, 10 g of ketone was added to a solution of 15 g of concentrated (70.8%) nitric acid in 60 ml of glacial acetic acid. The mixture was heated, with stirring, until a vigorous exothermic reaction began at 85°. Temperature excursions above 95° were prevented by cooling the reaction vessel in an ice bath. After cooling (1 hr) to room temperature the oxidation products were poured on ice and extracted with ether; the ether layer was washed with saturated sodium bicarbonate solution, and was dried over magnesium sulfate. The combined oxidation products from 40 g of ketone were chromatographed on alumina (2.5 × 100 cm column). Initial elution with hexane removed a small amount of unreacted ketone together with an unidentified solid; further elution with benzene–hexane (1:1, v/v) removed the desired ketol. Crystallization of the ketol fraction from ether–hexane (1:4) afforded 21 g (48%), mp 70–72°.

2-*exo*-Hydroxy-2-phenyl-3-norbornanone Oxime (14). Hydroxylamine hydrochloride (20 g) was added to a solution of 21 g of 2-*exo*-hydroxy-2-phenyl-3-norbornanone in 60 ml of pyridine. The solution was heated (100–110°), with stirring, for 30 min. An additional 12 g of hydroxylamine hydrochloride was added and heating was continued for 1 hr. The mixture was permitted to stand overnight and was then added to ice and water. The chilled mixture was extracted with several portions of ether; the pyridine was removed from the ether by extraction with cold, dilute hydrochloric acid solution (~2 *N*). Care was taken to ensure that the oxime was kept below 0° and free of excess hydrochloric acid. The ether layer was washed with sodium bicarbonate solution, dried over magnesium sulfate, filtered, and evaporated. The residue was crystallized from chloroform–hexane to give 19.3 g (85%) of the oxime, mp 129–131°. Part of the nmr spectrum (pyridine solution) of the carefully purified sample of the oxime showed an isolated signal, a 7-Hz wide singlet, at 3.92 ppm. Other samples of the oxime which had been crystallized only once or twice showed a small additional signal at 3.80 ppm. This signal belonged to the *exo*-phenyl epimer of the oxime and this fact was confirmed by isotope dilution experiments.

A sample of the *endo*-phenyl oxime labeled in the phenyl group with carbon-14, 0.5824 g, 3.18 mCi/mol, was mixed with 2.013 g of the nonradioactive *exo*-phenyl oxime. The mixture was treated with lithium aluminum hydride in ether and the resultant amines were isolated. After several crystallizations from ether–hexane mixtures, 3-*exo*-phenyl-3-hydroxy-2-*endo*-norbornylamine was isolated and had a constant melting point of 93° and a radioactive assay of 0.0521 mCi/mol. Therefore, the *endo*-phenyl oxime was contaminated with 5.75% of the *exo*-phenyl epimer.

3-*exo*-Hydroxy-3-phenyl-2-*endo*-norbornylamine (2). To the oxime (19.3 g), dissolved in 500 ml of ether, was added 12 g (0.32 mol) of lithium aluminum hydride. The solution was heated, with stirring, at reflux for 2 days. An additional portion (5 g, 0.13 mol) of lithium aluminum hydride was added, followed by continued heating at reflux for 1 hr. Ether was then removed by heating the reaction vessel at 70° on a hot water bath; the temperature was maintained for 1 hr after most of the ether had been removed. The flask was then cooled, 300 ml of ether was added, and stirring was resumed to break up the pasty mass. The reduction complex was decomposed by the slow addition of 17 ml of water, 12 ml of 20% sodium hydroxide solution, and 75 ml of water. The ether layer was separated and the aqueous layer was extracted with six 50-ml portions of ether. The combined ether layers were dried over magnesium sulfate, filtered, and evaporated to give 16.5 g (88%) of the amine. The free amine was crystallized from cold ether, mp 79–80°. The nmr spectrum in carbon tetrachloride is as follows: aromatic hydrogens, 7.0–7.4 (5 H); 2-exo hydrogen, 3.10 (1 H); amino and hydroxyl hydrogens, 2.7 (concentration dependent, 3 H); 4-bridgehead hydrogen, 2.27 (1 H); 7-syn hydrogen, 2.04 (doublet, $J \sim 10$ Hz, 1 H); 1-bridgehead hydrogen, 1.78 (1 H); 7-anti, 5- and 6-exo, 5- and 6-endo hydrogens, 0.8–1.6 (5 H).

3-*endo*-Hydroxy-3-phenyl-2-*endo*-norbornylamine-2-*d* (1a). In order to simplify the nmr analyses **1a** was synthesized with deuterium not only in the exo-2 position, but also in the exo-5 and anti-7 positions. To avoid confusion during the Discussion, however, only the exo-2 deuterium was specified. 5-Norbornen-2-ol (20 g, 0.18 mol) was added to a mixture of 28 ml of tetrahydrofuran, 11 ml of deuterium oxide, and 1 g of 5% palladium on carbon, and deuterium gas was introduced into the flask. Deuteration required approximately 20 hr under ambient conditions. Deuterium was generated electrolytically from a deuterium oxide solution that contained deuteriosulfuric acid. The deuterated alcohol was oxidized to 2-norbornanone-*5,6-exo-d*$_2$ with chromic acid–acetone reagent.[29] From this point through the synthesis of 3-*endo*-hydroxy-3-phenyl-norbornanone-*6-exo,7-anti-d*$_2$ 2-oxime, the procedures used were the same as for the undeuterated series of compounds. Integration of the nmr spectrum showed the compounds to be 75% deuterated in the positions indicated. The oxime was recrystallized from chloroform–hexane to provide an analytical sample, mp 129–131° dec.

Anal. Calcd for $C_{13}H_{13}D_2NO_2$: C, 71.22; H, 6.85; N, 6.39. Found: C, 71.25; H, 6.73; N, 6.28.

The oxime was reduced with lithium aluminum deuteride in the manner described for the reduction of the undeuterated oxime. Failure to use the rigorous conditions described always resulted in greatly diminished yields. The overall yield from 5-norbornen-2-ol (300 g) to deuterated amine (17 g) was 3%. A satisfactory carbon–hydrogen analysis could not be obtained because the amine absorbed carbon dioxide from the air. The nmr spectrum in carbon tetrachloride solution is as follows: aromatic hydrogens, 7.0–7.4 (5.00 H); 2-*exo*-hydrogen, signal totally absent; amino and hydroxyl hydrogens, 2.7 (2.98 H); 4-bridgehead hydrogen, 2.27 (1.01 H); 7-syn hydrogen, 2.04 (1.00 H); 1-bridgehead hydrogen, 1.78 (0.99 H); remaining hydrogens, 0.8–1.6 (3.26 H). Assignment of signals is partly based on the following information: the signal for the 4-bridgehead hydrogen is considerably sharpened in the deuterated compound which is expected when there is no exo hydrogen for coupling. No signal appears for the 2-exo hydrogen, deuterium having been introduced by lithium aluminum deuteride reduction of the corresponding oxime. The signal for the 7-syn hydrogen is collapsed to a broad singlet. In the highest field signals, 76% deuteration is apparently in agreement with the nmr analysis of precursor compounds prepared by catalytic deuteration.

Deamination of 1. In a typical experiment the amine **1** or its deuterated counterparts **1a** and **1b** were deaminated in sodium acetate–acetic acid solution as described previously.[10] The mixture of products was placed on an alumina column[9] from which Δ^3-cyclohexenyl phenyl ketone was removed by eluting it with benzene. The remaining products were recovered by eluting the column with methanol. After evaporating the solvents the materials were treated with lithium aluminum hydride and the deacetylated products were separated by careful chromatography on a freshly prepared alumina column. Alternatively, after deamination, the entire yield of mixed products was reduced with lithium aluminum hydride and then separated by column chromatography. In this case the first compound to be eluted, using benzene solvent, was Δ^3-cyclohexenylphenylcarbinol. The other compounds were recovered from the column by gradually increasing the polarity of the solvent first with ether, then with methanol. After the final elution with the methanol–ether mixture, the alumina was removed from the glass column and treated with water. The mass was washed well with ether from which was recovered **10**, 2-*exo*-phenylnorbornane-2,3-*cis*,*endo*-diol, mp 80–82°. The nmr spectrum was as follows (in CCl_4 solution): aromatic hydrogens, 7.0–7.5 (5 H); hydroxyl hydrogens, 4.2 (concentration dependent, 2 H); 3-exo hydrogen, 3.71 (doublet, $J \sim 4.5$ Hz, 1 H). The remaining eight hydrogen signals between 0.8 and 2.8 ppm were not assigned.

(29) K. Wiberg, "Oxidation in Organic Chemistry," Academic Press, New York, N. Y., 1965, Part A.

Compound **10a** from **3a** did not have a signal for the 3-exo hydrogen. Compound **10** was identical with a sample of **10** prepared independently from norcamphorquinone[30] (9.30 g in 200 ml of ethyl ether) and phenyllithium (from 11.8 g of bromobenzene and 1.04 g of lithium metal and 200 ml of ethyl ether). The ether solution of phenyllithium was added to the norcamphorquinone under a nitrogen atmosphere over a 1-hr period. The mixture was then treated with 100 ml of ammonium chloride solution, extracted with ether, dried over $MgSO_4$, and taken to dryness. The residue was taken up in the minimum volume of benzene and subjected to chromatography on a column of Al_2O_3 (Fisher 80–200 mesh) using benzene–hexane (1:1 and then 3:1). The eluent, on evaporation, yielded an ether-soluble oil (8.03 g) plus a white solid. The oil was not further purified, but 7.25 g of it in 50 ml of ether was reduced directly with lithium aluminum hydride (3.5 g in 50 ml of ether). After allowing the mixture to stir for 3 days, it was treated with 3.5 g of H_2O, followed by 0.75 ml of 20% aqueous sodium hydroxide solution and then by 3.5 g of H_2O. After stirring, the ether was decanted from the sludge and taken to dryness (5.32-g yield). The oil was placed on a column of Fluorosil with the minimum volume of benzene, then developed with hexane, yielding a few milligrams of a white solid. The eluent solvent was then changed to a 1:1 mixture of hexane–benzene, then to benzene. At this point about 2 g of 2-*exo*-phenylnorbornane-2,3-*cis*-*endo*-diol (**10**) was collected. On recrystallization from hexane 1.5 g of **10** was obtained, mp 80–82°.

The nmr spectra of the two samples of **10** were identical.

Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.08; H, 7.85.

The 1.5 g of **10** above was treated with sulfuric acid according to the procedure used[31] for the rearrangement of 2-phenylnorbornane-2,3-*cis*-*exo*-diol. The product, produced quantitatively, was 3-*endo*-phenylnorbornanone-2, indistinguishable from an authentic[31] sample.

Nmr Analysis of Deamination Products. The nmr spectrum of 3-phenyl-3-nortricyclenol (**7**) has been described.[9] The signals for the C-5 hydrogens appear at 1.07 ppm and the signals for the C-1, C-2, and C-6 hydrogens appear at 1.23 ppm. Compound **7** derived from **1b** showed a signal with a relative strength for three hydrogens at 1.23 ppm while the signal at 1.07 had a relative strength for one hydrogen. Amine **1a** gave **7** which had a signal at 1.23 ppm with relative strength for only two hydrogens.

A description of the nmr spectrum of ketone **8** and its deuterated analogs derived from amines **1a** and **1b** appeared previously.[10]

The fate of the deuterium labels in **3** and **4** was determined by careful integration of the nmr spectra of the deuterated and nondeuterated forms. Spectra for compounds **3** and **4** have been reproduced in earlier publications.[6d,e] In the undeuterated diol **4**, the hydrogens at C-3 gave signals centered at δ 2.07 ppm (pyridine solvent), which overlap the multiplet for the anti-7 proton. The integrated intensity of the three signals is 3.00 ± 0.02. In the product **4a** from either **1a** or **2a** the same set of signals has an integrated intensity of 2.00 ± 0.03 indicating that all the deuterium is located at those positions. Similar measurements on other products of deamination of **1a** and **2a** showed no loss of deuterium. Oxidation of **4a** to the 5-ketone followed by reduction to the 2-*exo*,-5-*endo*-diol[3d] allowed us to isolate the signal for the 3-endo proton since it is deshielded by the 5-*endo*-hydroxyl group and appears at δ 3.25 ppm. The 3-endo proton signal of **4a**, starting from **1a**, had an integrated intensity of 0.11 ± 0.03, and starting from **2a** the same signal had an intensity of 0.175 ± 0.017. A sample of 2-*endo*-phenylnorbornane-2-*exo*,5-*endo*-diol derived from 3-*exo*-hydroxy-3-phenyl-2-*endo*-norbornylamine-*2,5-exo-7-anti-d*$_3$ gave a spectrum which has a small, sharp, easily detected signal for the 3-endo hydrogen. Spin coupling constants affecting the 3-endo hydrogen are collapsed because of the presence of deuterium in the 3-exo and 7-anti positions. The third deuterium present in the 6-exo position causes the signal for the 5-exo hydrogen at 4.36 ppm to appear as a broadened 1–2–1 type triplet with spacings of about 3.8 Hz. The signal for the 3-exo proton of **4a** appears at 2.0 ppm and is overlapped by components of other signals.

Diol **3** without deuterium gives a quartet for the 3-exo proton at δ 2.4 ppm (pyridine solvent) and is overlapped by the signal for the C-4 bridgehead proton. The integrated intensity is 2.00 ± 0.03. Integration of the same set of signals for the deuterated glycols **9a** gave the value 1.89 ± 0.04 starting from **1a** and 1.855 ± 0.04 starting from **2a**. These data were confirmed by oxidation of **3a** with pyridine–chromium trioxide to 2-*exo*-phenyl-2-*endo*-hydroxy-5-norbornanone[3d] whose 3-exo hydrogen is at δ 2.6 ppm (pyridine) and is also overlapped by the signal from the C-4 bridgehead hydrogen. Integration of the spectrum for the ketone derived from **3a** confirmed the above data.

The errors for each determination were taken as the extreme limits of repeated integrals, no single determination being outside these limits. Several samples were prepared for each compound whose nmr spectrum was analyzed. For comparison of integrals, we used

$$\sigma_z^2 = \left(\sigma_x \frac{\delta_z}{\delta_x}\right)^2 + \left(\sigma_y \frac{\delta_z}{\delta_y}\right)^2$$

where σ_x and σ_y are the errors in observations x and y, and σ_z is the error in the quotient.

We have additional support for the data in the table. The amine 5,6-di-*exo*-d_2-**1b** was also deaminated and the diols **3** and **4** derived therefrom were isolated (M. D. Eckart, unpublished work). The results indicated that about 12% of **4** and about 6% of **3** were formed by counterclockwise routes. There is no reason why these results should coincide exactly with the first line of Table I, for during deamination of 5,6-di-*exo*-d_2-**1b**, there is migration of deuterium at the D ⇌ E stage, superimposing an isotope effect on the mechanism.

Diol **5a**, separated from the product mixture from deamination of **1a**, showed an nmr signal (in deuteriochloroform) of intensity for only one hydrogen at 2.4 ppm which is the region assigned to the bridgehead hydrogens.[6e] Similarly, compound **6a** showed the presence of only one bridgehead hydrogen signal.

Solvolysis of 2-*exo*-Phenyl-2-hydroxy-5-*exo*-norbornyl Tosylate (15). A sample of diol **3**, 2.88 g, was dissolved in 50 ml of pyridine and 2.8 g of *p*-toluenesulfonyl chloride was added. The mixture was stirred overnight and then poured into 500 g of ice and water. The product was extracted with five 100-ml portions of ether. The ether extracts were washed successively with cold dilute hydrochloric acid and combined. The ether was evaporated using a rotary evaporator while being careful to avoid heating the residue over 35°. The compound could not be induced to crystallize. It decomposed if heated above 40° or was allowed to stand for 2 days at room temperature. The nmr spectrum in $CDCl_3$ showed the expected aromatic pattern for the tosylate ether. The signal for 5-exo hydrogen appeared at 4.7 ppm. No signal appeared between 3 and 4 ppm for the 5-exo hydrogen of the unesterified diol. The freshly prepared tosylate was dissolved in 100 ml of acetone and 100 ml of water containing 2 g of K_2CO_3 was added. The reaction vessel was sealed and heated for 8 hr on the steam bath. The acetone was then evaporated and the products were recovered by ether extraction. Integration of the nmr spectrum of the mixed products showed the ratio of **3** to **4** to be 1.4:1. The signals for the 5-exo hydrogen diols appeared well separated at about 4.3 and 3.9 ppm, respectively, and were easily distinguished. The hydrolysis products were also analyzed by chromatography on alumina and the following yields were obtained: **7**, 7.45%; **5**, 2.46%; **3**, 36.70%; **4**, 51.70%; **6**, 1.73%.

Solvolysis of 2-*endo*-Phenyl-2-hydroxy-5-*exo*-norbornyl Tosylate (16). Compound **16** was prepared from 2.08 g of diol **3** and 2 g of *p*-toluenesulfonyl chloride. The product was worked up in a manner similar to that for compound **15**. The ester could not be induced to crystallize. Complete esterification was proved by the absence of a nmr signal for the free diol at 3.9 ppm. The ester could not be induced to crystallize and it was hydrolyzed without further purification. The hydrolysis products were isolated in the usual way and the nmr spectrum was recorded for the crude mixed products. Integration of the signals at 4.3 and 3.9 ppm showed the ratio of diols **3** and **4** to be 1.4:1. The same ratio was obtained by chromatographic separation.

Determination of the Yields of 3, 4, and 9 from Deamination of 1 and 2. Amine **1** was synthesized as described above with the exception that the phenyl group contained carbon-14, 6.428 mCi/mol. Deamination of 20.86 mmol of the amine (as the hydrochloride) was carried out in 117 g of acetic acid containing 16 g of sodium acetate. Before isolation of the products, the following nonradioactive carriers were added: 0.2235 g of **3**, 0.1274 g of **4**, and 0.3283 g of **9**. After thorough mixing the products were recovered and subjected to chromatographic separation to reisolate **3**, **4**, and **9**. These compounds were purified by crystallization and their carbon-14 assays were as follows: **3**, 2.876 mCi/mol; **4**, 3.049 mCi/mol;

(30) K. Alder, H. K. Schäfer, H. Esser, H. Krieger, and R. Reubke, *Justus Liebigs Ann. Chem.*, **593**, 23 (1955).

(31) C. J. Collins, Z. K. Cheema, R. G. Werth, and B. M. Benjamin, *J. Amer. Chem. Soc.*, **86**, 4913 (1964).

9, 4.727 mCi/mol. The yields were 4.25, 2.70, and 21.43%, respectively.

Amine **2** (as the nonradioactive hydrochloride), 18.04 mmol, was deaminated in 100 g of acetic acid containing 14 g of sodium acetate. The following radioactive materials were then added: **3**, 0.2500 g, 0.3125 mCi/mol; **4**, 0.1500 g, 0.3007 mCi/mol. When reisolated the diols gave carbon-14 assays as follows: **3**, 0.1615 mCi/mol; **4**, 0.1574 mCi/mol. The yields of **3** and **4** were 6.34 and 3.2%, respectively. Although 0.2500 g of radioactive **9** was added to the deamination mixture, it could not be reisolated because the yield of **9** is very low.

Appendix A, for Scheme V

Consider (Scheme IX) the two nonclassical ions (B ↔ C)$_c$ formed from the amine **1a** by the clockwise route (Scheme V), and (B ↔ C)$_{cc}$ formed from the amine **1a** by the counterclockwise route. Cations (B ↔ C)$_c$ and (B ↔ C)$_{cc}$ both should yield products **3a** and **4a** in the same ratio [**3a**:**4a** = x:(1 − x)]. If the relative concentrations of (B ↔ C)$_c$ and (B ↔ C)$_{cc}$ are y and (1 − y) respectively, then the fraction of D′ in [**3a**]$_c$ + [**3a**]$_{cc}$ is

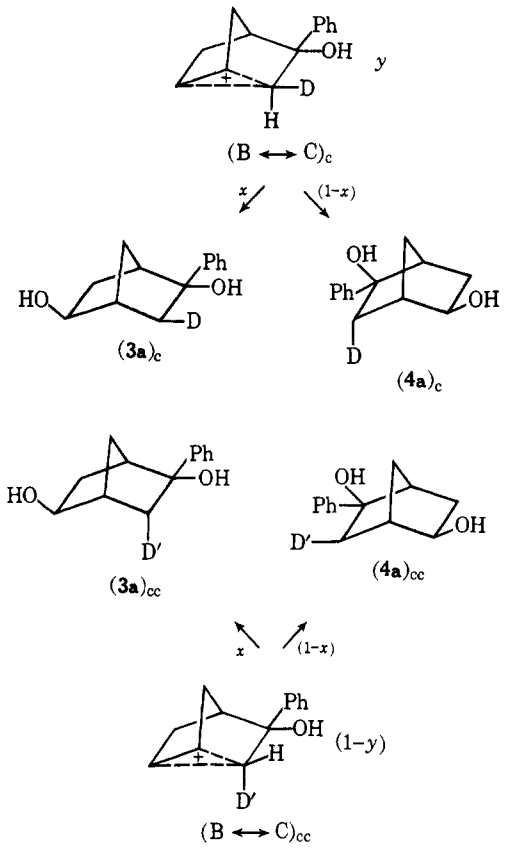
$$\left(\frac{D'}{D' + D}\right)_3 = \frac{x(1 - y)}{xy + x(1 - y)} = 1 - y$$

and the fraction of D′ in (**4**)$_c$ + (**4**)$_{cc}$ is

$$\left(\frac{D'}{D' + D}\right)_4 = \frac{(1 - y)(1 - x)}{y(1 - x) + (1 - y)(1 - x)} = 1 - y$$

Thus, nonclassical ions (B ↔ C)$_c$ and (B ↔ C)$_{cc}$ yield **3a** and **4a** with identical distributions of deuterium. If (B ⇌ C)$_c$ and (B ⇌ C)$_{cc}$, however, are classical ions *which have not yet reached their equilibrium concentrations*, then the ratio of the two ions formed by the clockwise route (B:C)$_c$ will be different than the ratio of the ions formed by the counterclockwise route (B:C)$_{cc}$, and the deuterium distributions in **3a** and **4a** should be different.

Scheme IX



Molecular Geometry. III. The Structure of Racemic 7-Chloro-1,3-5-trimethyl-5*H*-pyrimido[5,4-*b*][1,4]benzothiazine-2,4(1*H*,3*H*)-dione, a Stable Sulfonium Ylide

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Abstract: The crystal and molecular structure of racemic 7-chloro-1,3,5-trimethyl-5*H*-pyrimido[5,4-*b*][1,4]-benzothiazine-2,4(1*H*,3*H*)-dione (I) has been determined using single-crystal X-ray diffraction techniques. The crystals are monoclinic in the space group $P2_1/n$ (C_{2h}^5) with four molecules in a unit cell of dimensions a = 12.514 (5), b = 8.029 (2), c = 13.730 (5) Å, and β = 99.61 (1)°. Least-squares refinement of the structure led to a final value of the conventional R factor of 0.059 for the 1699 data having $F_o^2 \geq 3\sigma(F_o^2)$. The charge delocalized representation (Ia) is estimated to contribute 85% to the overall bonding in this sulfonium ylide.

The nature of the bonding in sulfonium ylides has been elucidated by chemical studies.[2-5] Several reviews of the literature are available.[6-8]

The resolution of sulfonium salts into optically active components ruled out a planar bonding arrangement

(1) Part II in this series: John P. Schaefer and Karen Walthers, *Tetrahedron*, **27**, 5289 (1971). This work represents a portion of the dissertation of L. L. Reed presented to the Graduate College of the University of Arizona in partial fulfillment of the requirements for the Ph.D. degree.

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(3) A. Hochrainer and W. Silhan, *Monatsh. Chem.*, **97**, 1477 (1966).

(4) H. Nozaki, D. Tunemoto, Z. Morita, K. Nakamura, K. Watanabe, M. Takaku, and K. Kondo, *Tetrahedron*, **23**, 4279 (1967).

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(8) H. König, *Fortschr. Chem. Forsch.*, **9**, 487 (1968).