# Molecular Rearrangements. XXIX. Exo/Endo Stereospecificity of Substituted Classical Norbornyl Cations. A Reassessment of "Hot" Carbonium Ions[1,2]

CLAIR J. COLLINS* AND BEN M. BENJAMIN

*Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830*

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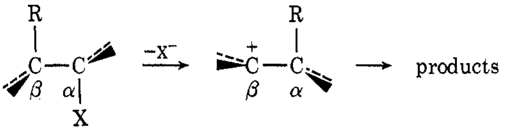
5-*endo*-Hydroxy-5-phenyl-2-*exo*-norbornylamine (**5**), 5-*exo*-hydroxy-5-phenyl-2-*exo*-norbornylamine (**6**), and 5-*exo*-hydroxy-5-phenyl-2-*endo*-norbornylamine (**7**) were treated with sodium nitrite in acetic acid–sodium acetate solution. From the product analyses of the reaction mixture (including glpc and carbon-14 isotope dilution measurements), it is concluded that (1) during reaction of **5** and **6**, ~2% of $S_N2$-like processes take place; (2) the exo/endo stereospecificity for attack on the classical ions formed from **5** and **6** is 160–650:1, whereas the exo/endo stereospecificity for attack on the classical ion E formed from **7** *after* Wagner–Meerwein rearrangement is only 8:1; (3) the production of 2-phenylnorbornane-2,5-*cis,endo*-diol-4-*d* (**8**) in 1.8% yield from 5-phenyl-5-*endo*-hydroxy-2-*endo*-norbornylamine-2-*d* (**7**) means that endo attack upon the *classical* cation E takes place after E has been formed by a Wagner–Meerwein rearrangement, and that **8** is not produced as a consequence of the Hückel–Kern pathway demonstrated in the production of borneol (**19**) from *endo*-fenchylamine (**14**); (4) the concept of a "hot" carbonium ion must now be altered, for, whatever the special character of the cations formed during the amine–nitrous acid reaction, this special character is not lost after Wagner–Meerwein rearrangement; and (5) the different behavior of presumably identical cations when they are produced remotely from different reactants is explained by counterion control in differently oriented ion pairs.

In a preliminary communication[2b] we demonstrated the special character of the cations generated during the amine–nitrous acid reaction by showing that a substituted secondary norbornyl cation can be attacked by solvent from the endo direction even after the cation in question has been formed by Wagner–Meerwein rearrangement. Hückel and Kern[3] had previously demonstrated the same phenomenon with the tertiary cations produced on Wagner–Meerwein rearrangement of the fenchylamines. There can now be no doubt, therefore, that carbonium ions formed on nitrous acid deamination can retain their special character after one[2b] or after several[2a] such Wagner–Meerwein or 6,2-hydride rearrangements,[4] and that they do not necessarily become equivalent to those ions produced on solvolysis of structurally identical compounds (identical, that is, except for leaving group).

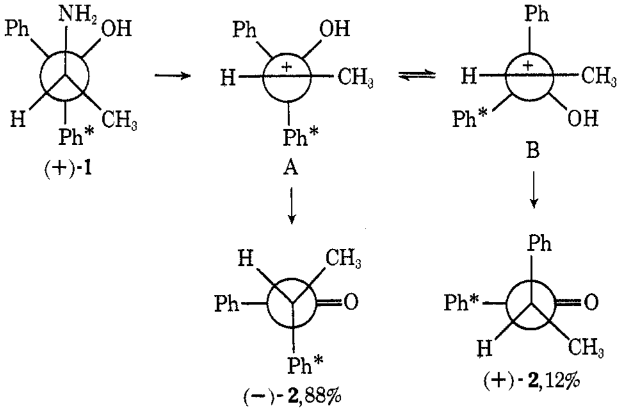
Since the early work[5,6] on the stereochemistry of carbonium ion rearrangements, it has generally been assumed[7–9] that inversion of configuration at the migration terminus ($C_\alpha$) is the predominant (or exclusive) stereochemical result (eq 1) of 1,2 shifts which occur during solvolytic (X = halogen, OTs, OBs, etc.) or amine–nitrous acid (X = $NH_2$) reactions.[10] Although the assumption may be usually valid for 1,2 shifts occurring with solvolyses, it is demonstrably[11–16] untrue for the amine–nitrous acid and other reactions which proceed through decomposition of diazonium ions.[17]



(1)

In an isotopic investigation (with carbon-14) of McKenzie's original example,[5] we demonstrated[11] (Scheme I) that (1) inversion was not the only stereochemical consequence of the deamination of optically active 1,1-diphenyl-2-aminopropanol[18] and (2) whereas

SCHEME I[a]



[a] $C_\alpha$ is the front carbon atom of the Newman projection.

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[1] Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corporation; presented in part at the Symposium on Organic Reaction Mechanisms, Nagoya, Japan, Oct 19, 1971.

[2] (a) Paper XXVIII: C. J. Collins, I. T. Glover, M. D. Eckart, V. F. Raaen, B. M. Benjamin, and B. S. Benjaminov, *J. Amer. Chem. Soc.*, **94**, 899 (1972). (b) A portion of the research described in this paper was reported in preliminary form: C. J. Collins and B. M. Benjamin, *ibid.*, **92**, 3182 (1970).

[3] W. Hückel and H.-J. Kern, *Justus Liebigs Ann. Chem.*, **728**, 49 (1969).

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

[5] (a) A. McKenzie, R. Roger, and G. D. Wills, *J. Chem. Soc.* (*London*), 779 (1926); (b) H. I. Bernstein and F. C. Whitmore, *J. Amer. Chem. Soc.*, **61**, 1324 (1939).

[6] (a) P. D. Bartlett and I. Pöckel, *ibid.*, **59**, 820 (1937); **60**, 1585 (1938). (b) W. Hückel, *Nachr. Ges. Wiss. Gottingen, Math.-Phys. Kl., Fachgruppe* **2**, 59 (1941).

[7] See, for example, R. T. Morrison and R. N. Boyd, "Organic Chemistry," 2nd ed, Allyn and Bacon, Boston, Mass., 1966, p 883; also G. B. Butler and K. D. Berlin, "Fundamentals of Organic Chemistry," Vol. X, Ronald Press, New York, N. Y., 1972, pp 829–830.

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

[9] D. J. Cram and J. E. McCarty, *ibid.*, **79**, 2866 (1957).

[10] See also P. I. Pollak and D. Y. Curtin, *ibid.*, **72**, 961 (1950); D. Y. Curtin, E. E. Harris, and E. K. Meislich, *ibid.*, **74**, 2901 (1952); D. Y. Curtin and E. K. Meislich, *ibid.*, **74**, 5518 (1952); D. Y. Curtin and P. I. Pollak, *ibid.*, **73**, 992 (1951); D. Y. Curtin and E. K. Meislich, *ibid.*, **74**, 5905 (1952).

[11] B. M. Benjamin, H. J. Schaeffer, and C. J. Collins, *ibid.*, **79**, 6160 (1957).

[12] B. M. Benjamin, P. Wilder, Jr., and C. J. Collins, *ibid.*, **83**, 3654 (1961).

[13] B. M. Benjamin and C. J. Collins, *ibid.*, **83**, 3662 (1961).

[14] C. J. Collins, M. M. Staum, and B. M. Benjamin, *J. Org. Chem.*, **27**, 3525 (1962).

[15] C. J. Collins, W. A. Bonner, and C. T. Lester, *J. Amer. Chem. Soc.*, **81**, 466 (1959).

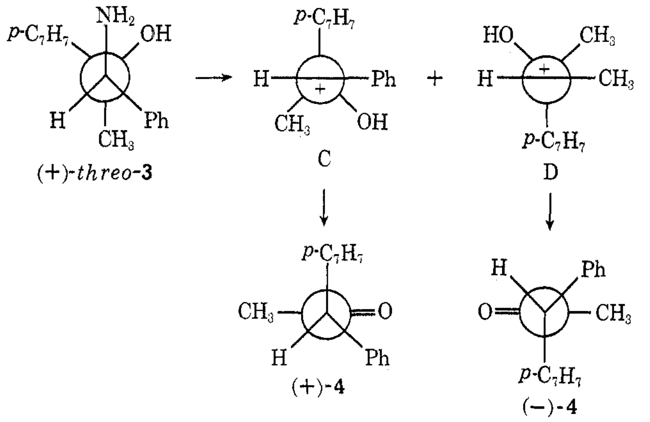
[16] C. J. Collins and B. M. Benjamin, *ibid.*, **85**, 2519 (1963).

[17] C. J. Collins, J. B. Christie, and V. F. Raaen, *ibid.*, **83**, 4267 (1961); C. J. Collins and J. B. Christie, *ibid.*, **82**, 1255 (1960).

[18] This was, in fact, obvious from the Experimental Section of the paper[5a] by McKenzie, Roger, and Wills.

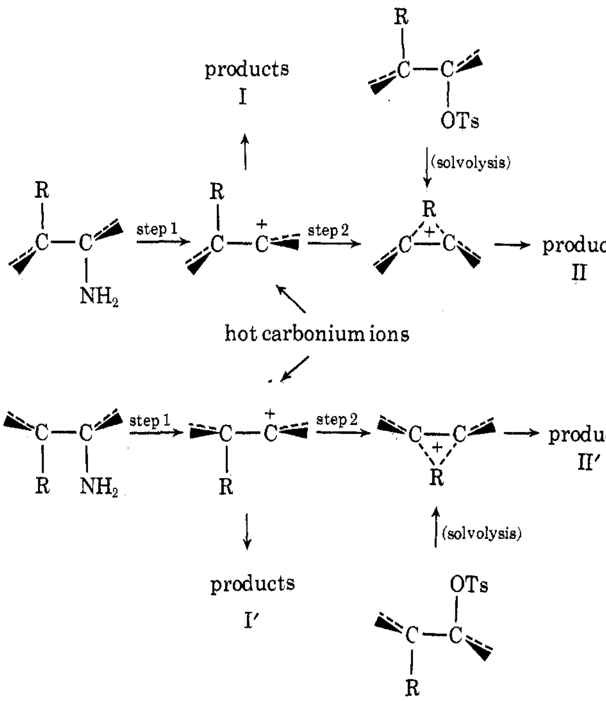
88% of the ketonic product had been formed with migration of the labeled phenyl (Ph*) with inversion of configuration at the migration terminus ($C_\alpha$), 12% had been formed through migration of the unlabeled phenyl (Ph) with retention of configuration at the migration terminus. Later we extended[12-14] these studies to show (Scheme II) that, when aryl migration with retention

SCHEME II



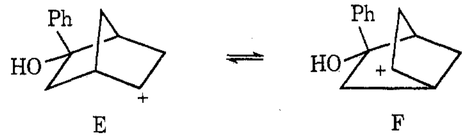
at $C_\alpha$ can take place through a trans transition state,[10] in which the bulky nonmigrating groups are trans one to the other, then *retention can predominate over inversion.* These important observations have not yet been completely appreciated.[7] The foregoing results clearly are in conflict (1) with the assumption[7-9] that inversion at $C_\alpha$ (eq 1) is the exclusive stereochemical result of such 1,2 shifts and (2) with Streitwieser's postulate[8] "that the diazonium ion rather than a carbonium ion is the branching point of the competing reactions" which take place on decomposition of aliphatic diazonium ions.

Some[11-14] of our earlier results are compatible with Winstein's proposal[19] of "hot" carbonium ion formation during amine–nitrous acid reactions. These "hot" carbonium ions were defined[19] as exhibiting no charge delocalization in their highly energetic states, thus explaining the lack of discrimination and multiplicities of products often observed.[4] The "hot" carbonium ion was visualized[19] as losing its excess energy very rapidly,[20] and after one Wagner–Meerwin rearrangement or one hydride shift was believed to become equivalent to those ions formed from solvolytic precursors; this means, for example, that, if a "hot" carbonium ion (as defined)[19,20] intervenes (eq 2) during the amine–nitrous acid reaction, then any rearrangement of atoms in the structure (step 2), whether it be Wagner–Meerwein or hydride shift, allows the ion sufficient time to lose its excess energy ("cool") and become equivalent to the cation formed (eq 2) on solvolysis. Thus, if a bridged ion results from solvolysis, then a bridged ion should result from a structurally related "hot" carbonium ion after a 1,2 shift.



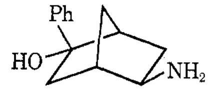
(2)

In our previous paper,[2a] we reported the fates of ions E and F after they were formed indirectly and remotely from precursors which suffered one or more 6,1,2 shifts

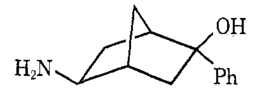


before either E or F could be produced. Using a combination of analytical techniques, including carbon-14- and deuterium-labeling methods, we were able to demonstrate that E and F maintain their classical, open carbonium ion properties even after several successive Wagner–Meerwein rearrangements and 6,1,2-hydride shifts, a result incompatible with the "hot" carbonium ion assumption—at least as originally stated.[19]

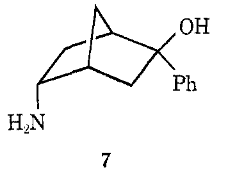
To gain more information on the properties of ions E and F when they are produced in a less circuitous fashion than that employed in our previous studies[2a] we turned our attention to the reaction with nitrous acid of the amines 5-*endo*-hydroxy-5-phenyl-2-*exo*-norbornylamine (**5**), 5-*exo*-hydroxy-5-phenyl-2-*exo*-norbornylamine (**6**), and 5-*exo*-hydroxy-5-phenyl-2-*endo*-norbornylamine (**7**). Compound **5** when subjected to deaminating conditions[2] should lead directly to ion E, whereas **6** and **7** should produce ion F. It was our purpose to determine the stereospecificity for exo *vs.*



**5**



**6**



**7**

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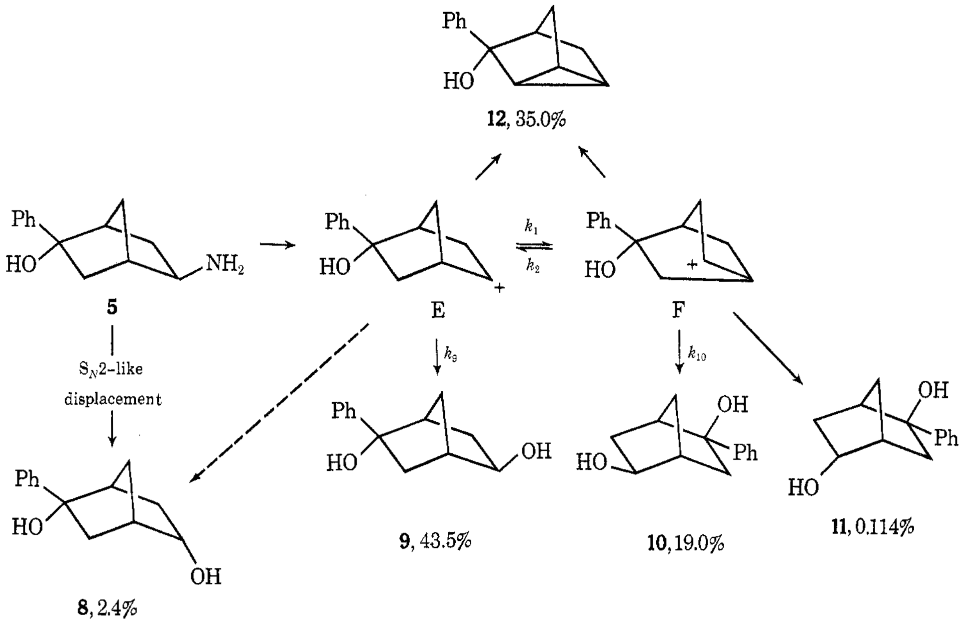
[19] D. Semenow, C. H. Shih, and W. G. Young, *J. Amer. Chem. Soc.*, **80**, 5472 (1958), credit Professor Winstein with proposing a hot carbonium ion intermediate during the amine–nitrous acid reaction.

[20] E. Renk and J. D. Roberts, *ibid.*, **83**, 879 (1961), describe this process in a more colorful fashion by stating "it seems reasonable that any 'hot' allylcarbinyl cations formed by ejection of nitrogen from the corresponding diazonium ions would lose most if not all of their 'sizzle' upon 1,2-shift."

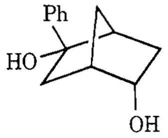
SCHEME III



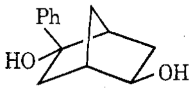
endo attack on both E and F before and after Wagner–Meerwein rearrangement and also to study the effect on this stereospecificity of an exo *vs.* an endo leaving group (**6** *vs.* **7**).

## Method and Results

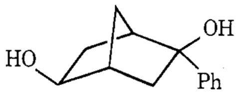
The two exo amines **5** and **6** were prepared from the diols **8** and **11** which, in turn, were prepared by oxidation of **9**[21] and **10**,[21] respectively, with chromic acid followed by reduction of the ketones so obtained with lithium aluminum hydride. The tosylates of **8** and **11** on treatment with sodium azide, followed by reduction, afforded **5** and **6**. Endo amine **7** was prepared from the ketone obtained from **10** by conversion to the corresponding oxime, followed by reduction with lithium aluminum hydride. These three amines were also prepared labeled in their phenyl groups with carbon-14.[2a]



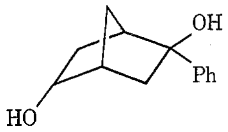
**8**



**9**



**10**



**11**

The amine–nitrous acid reactions in acetic acid–sodium acetate solution were carried out as described previously.[2,17] In addition, one reaction of **5** was carried out using glacial acetic acid as the solvent. All three amines yielded five identifiable products. These were 3-phenyl-3-nortricyclenol (**12**) and the (secondary) monoacetates of the four 2-phenyl-2,5-norbornanediols **8–11**. For simplicity the products are shown in Schemes III–V as the free diols, since the isotope dilution analyses were carried out on product mixtures which had first been treated with lithium aluminum hydride. The products from **5–7** were determined by isotope-dilution methods,[22] and/or by spectral methods, and liquid column chromatography, and the results are given in Table I, together with certain product ratios, whose significance will be discussed later. The results of the deaminations of **5**, **6**, and **7** are also shown graphically in Schemes III, IV, and V, respectively, so that the reactions carried out under like conditions (acetic acid–sodium acetate) can be more easily compared. We showed earlier[20,21] that under the reaction and work-up conditions all products are stable. Finally amine **7** labeled with deuterium in the exo-5 position was prepared and subjected to nitrous acid deamination; the

TABLE I

YIELDS OF PRODUCTS AND PRODUCT RATIOS ON DEAMINATION OF AMINES **5–7**[a]

| | From **5** | | From **6**, | From **7**, |
|---|---|---|---|---|
| Products[b] | HOAc (glacial) | HOAc–NaOAc | HOAc–NaOAc | HOAc–NaOAc |
| | | Yields, % | | |
| **12** | 43.5 | 35.0 | 29.6 | 17.2 |
| **8** | 3.4[c] | 2.4[c] | 0.039[c] | 1.8 |
| **9** | 36.7 | 43.5 | 25.6 | 14.2 |
| **10** | 16.5 | 19.0 | 42.6 | 29.3 |
| **11** | 0.075[c] | 0.114 | 2.2[c] | 34.5 |
| | | Ratios | | |
| **9**:**10** | 2.2:1 | 2.3:1 | 1:1.7 | 1:2.1 |
| **9**:**8** | 10.5:1 | 18:1 | 650:1 | 8:1 |
| **10**:**11** | 220:1 | 166:1 | 19:1 | 1:1.2 |
| **8**:**11** | 45:1 | 21:1 | 1:56 | 1:19 |

[a] Deaminations were performed at ambient temperature. Yields are normalized to 100%. [b] The monoacetates of **8–11** were obtained on deamination, and these were converted to the diols with lithium aluminum hydride. Smaller yields of three other compounds[a] resulting from hydride shift in the ions E and F were obtained. [c] These products were crystallized repeatedly with the addition of the hold-back carrier[23] until the radioactivity contents were constant.

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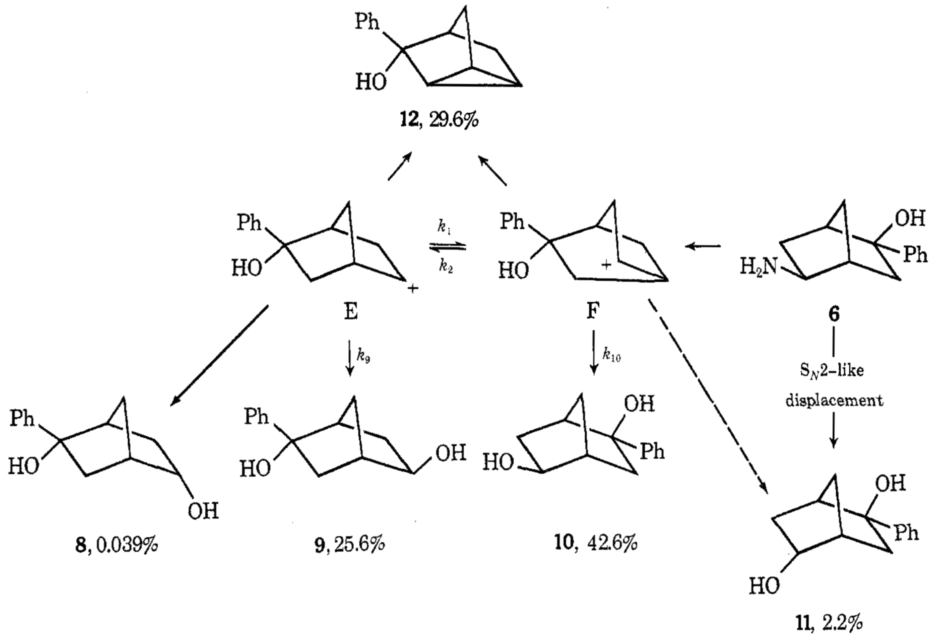
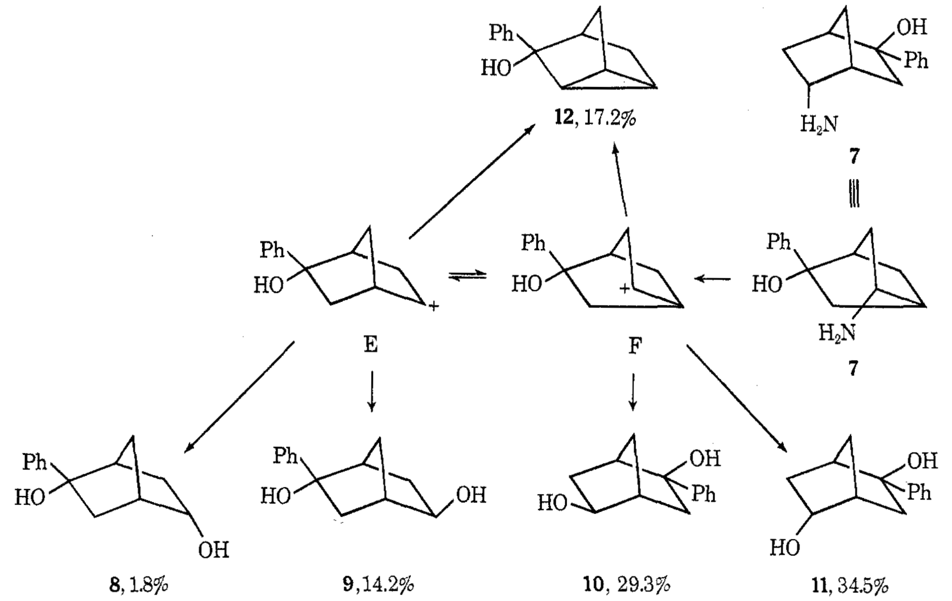
(21) C. J. Collins and B. M. Benjamin, *J. Amer. Chem. Soc.*, **89**, 1652 (1967).

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

SCHEME IV



SCHEME V



deuterium distribution in the 2-*exo*-phenylnorbornane-2,5-*cis,endo*-diol (**8**-*d*) so obtained and isolated was established by nmr.

## Discussion

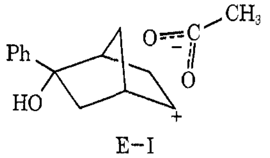
The following conclusions can be drawn from the experiments just discussed.

1.—Both amines **5** and **6** appear to undergo S<sub>N</sub>2 (or S<sub>N</sub>2-like) attack to yield, respectively, the acetates of diols **8** and **11**. Thus **5** yields 2% **8** acetate and **6** yields 2% **11** acetate on nitrous acid deamination in acetic acid-sodium acetate (Schemes III and IV). That these endo products result from S<sub>N</sub>2 processes follows from point 2.

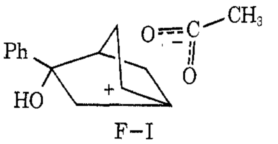
2.—The exo/endo stereospecificity observed for **5** → **8** + **9** (18:1 **9**:**8**) is much greater than the exo/endo stereospecificity observed (166–220:1) for the process **5** → E → F → **10** + **11**. Ion E, after it has been produced by the process **6** → F → E → **8** + **9**, exhibits an exo/endo stereospecificity of 650:1 **9**:**8** much greater than that (18:1) observed when E is produced directly from **5**. These facts lead us to believe that the process **5** → **8** is predominantly S<sub>N</sub>2-like in character (the same argument is valid for the process **6** → **11**).

3.—Since the Wagner–Meerwein pair of cations E ⇌ F produce different ratios of **9**:**10** depending upon their origin from **5** or from **6**, we think they are best written as equilibrating classical ions (E ⇌ F). Thus, neglecting formation of **12** and the minor fractions of endo attack, when E is produced on deamination of **5**, it has a choice of rearrangement to F or collapse with exo counterion to yield the **9** acetate. Since the ratio of **9**:**10** is 2.3:1, E clearly undergoes collapse with counterion before complete equilibrium with F is attained. When F is produced from **6**, it has a similar choice (again neglecting the formation of **12** and small fractions of endo attack). It can collapse with exo counterion to yield the **10** acetate or it can rearrange to E. Ion F obviously collapses with counterion to yield the **10** acetate before it has achieved equilibrium with E, and the ratio of **10**:**9** is 1.7:1.[23]

4.—The exo/endo ratios for attack on ions E and F *after* they have been formed (from **6** and **5**, respectively, Schemes III and IV) through Wagner-Meerwein rearrangement (650:1 **9**:**8**, 165:1 **10**:**11**) are smaller than the ratio (2000:1) for exo/endo attack during acetolysis of 2-*exo*-norbornyl tosylate.[24] Because the counterions formed during reaction of the exo amines **5** and **6** are, we think, [2,17] still exo to the positive charge, as in the ion pairs E-I and F-I, there will be a built-in preference for E-I and F-I to collapse to predominantly

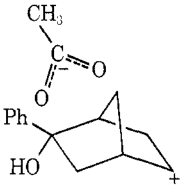


E–I

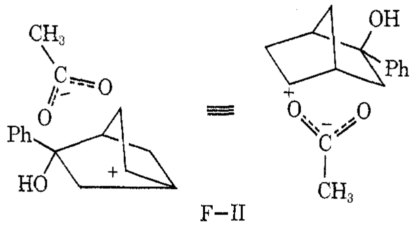


F–I

exo products. For this reason, the aforementioned ratios (165–650:1) are undoubtedly still much too large to be representative of the true exo/endo stereospecificities for the classical ions E and F. We therefore studied the reaction with nitrous acid of the endo amine **7** (Scheme V). Here the ion pairs should be



E–II

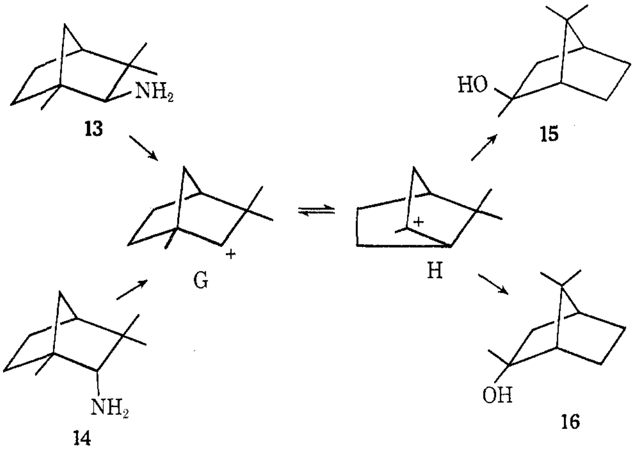


F–II

oriented somewhat as shown in structures E-II and F-II, and the serious bias for collapse to exo products exhibited by E-I and F-I should no longer be present. That ion F—formed directly from **7**—produces more endo product (**11** acetate) than exo (**10** acetate) in the ratio of 1.2:1 is a clear indication of counterion control in the ion pair F-II. After F-II has undergone Wagner-Meerwein rearrangement to E-II, the counterion is no longer in a position to attack directly the site of positive charge, and acetate ions or acetic acid molecules from the solvent should be more nearly under the influence of the steric requirements of E and F as they attack from exo or endo directions. The ratio (8:1) is the lowest yet observed for a substituted, secondary norbornyl cation in the absence of an SNi component and is overwhelming evidence that E has retained its classical character *after* having been formed from F by Wagner-Meerwein rearrangement.[25]

5.—Solvolyses of tertiary 2-norbornyl esters are now generally believed to be limiting [SN1(lim)].[26–31] The Hückel-Kern observation[3] that the *exo-* (**13**) and *endo*-fenchylamine (**14**) yield, among other products, mixtures of *exo-* (**15**) and *endo-α*-fenchene hydrate (**16**) (Scheme VI) provides us with a calibration for the

SCHEME VI



$$\mathbf{13} \longrightarrow 48\%\ \mathbf{15} + 2.8\%\ \mathbf{16}$$

$$\mathbf{14} \longrightarrow 13.5\%\ \mathbf{15} + 1.6\%\ \mathbf{16}$$

stereospecificity of attack on the tertiary *α*-fenchyl cation, H. Here exo attack is undoubtedly hindered somewhat by the *syn*-7-methyl groups, but there seems to be a leaving-group effect in that the endo amine **14** exhibits a lower exo/endo stereospecificity (8.5:1 **15**:**16**) than the exo amine **13**, where the ratio of **15**:**16** is 17.5:1. Comparing stereospecificities for the rearranged ion E from exo amine **6** (650:1 **9**:**8**, Scheme IV), and from endo amine **7** (8:1 **9**:**8**, Scheme V) we see again that the endo leaving group seems to reduce the stereospecificity for exo attack on ion E, just as in the Hückel-Kern[3] case. We believe the explanation just given in paragraph 4 applies to the Hückel-Kern results as well.

6.—Hückel and Kern[3] made another remarkable observation, for on nitrous acid deamination of *endo*-fenchylamine (**14**)—the complete results are shown in Scheme VII—they isolated borneol (**19**) in a yield of 3.5%. The simplest explanation here seems to be a 7,1-7,2-Wagner-Meerwein shift to give the cation K,

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[23] When the tosylates corresponding to the amines **5** and **6** are hydrolyzed, **12** is also produced, but the major products **9** and **10** are formed in a 1.4:1 ratio of **9**:**10** from *both* reactants.[2a] If we assume that ions E and F go to 3-phenyl-3-nortricyclenol (**12**) in the same ratio whether **5** or **6** is the starting material, then for the deaminations of **5** and **6**, respectively (Schemes III and IV), we can derive the following equations.

$$(m_{10}/m_9)_5 = (k_{10}/k_9)[k_1/(k_2 + k_{10})]$$

$$(m_{10}/m_9)_6 = (k_{10}/k_9)[(k_1 + k_9)/k_2]$$

Making the substitutions $(m_{10}/m_9)_5 = 19/43.5$ and $(m_{10}/m_9)_6 = 42.6/25.6$, respectively, and assuming $k_9 = k_{10}$, then we can calculate that the equilibrium constant $k_2/k_1$ for $F \rightleftharpoons E$ is 1.24, in excellent agreement with the value[2a] of 1.4 for the tosylates.

[24] H. C. Brown, J. H. Kawakami, and K. T. Liu, *J. Amer. Chem. Soc.*, **92**, 5536 (1970).

[25] The exo/endo ratio of 8:1 for attack on cation E is well within the range of stereospecificities for attack on secondary norbornyl compounds which have been shown by H. C. Brown and his coworkers to be primarily steric in origin. See, for example, H. C. Brown and K. T. Liu, *J. Amer. Chem. Soc.*, **92**, 200 (1970); H. C. Brown and J. H. Kawakami, *ibid.*, **92**, 201, 1990 (1970); H. C. Brown, J. H. Kawakami, and S. Ikegami, *ibid.*, **92**, 6914 (1970); H. C. Brown and K. T. Liu, *ibid.*, **93**, 7335 (1971), and references cited therein.

[26] S. Winstein, E. Grunwald, and H. W. Jones, *ibid.*, **73**, 2300 (1951).

[27] J. M. Jerkunica, S. Borčić, and D. E. Sunko, *Chem. Commun.*, 1489 (1968).

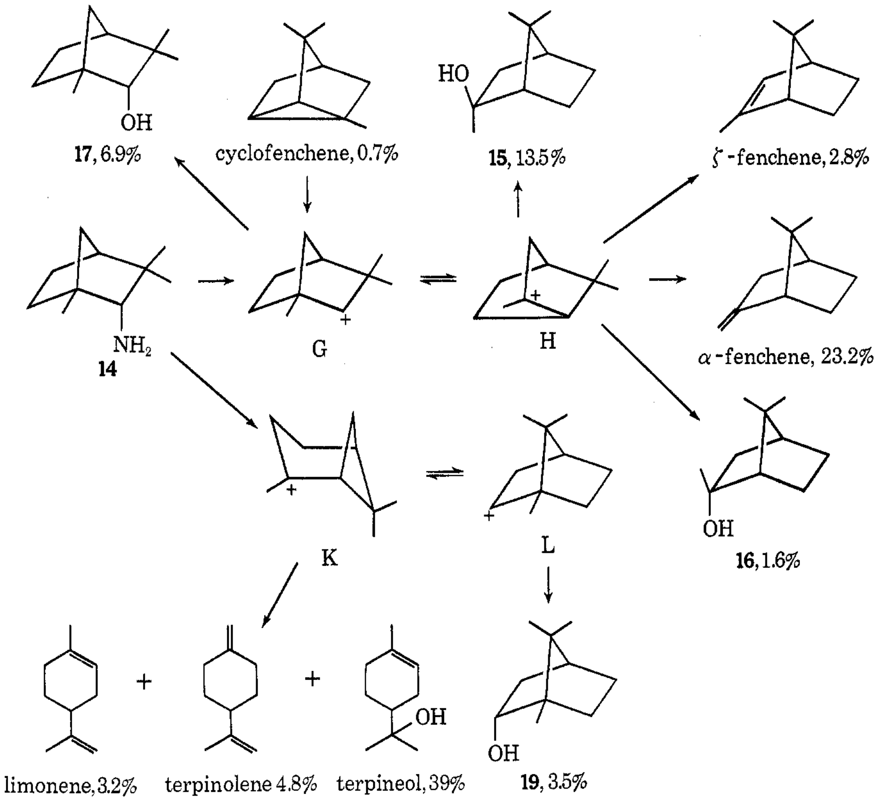
[28] J. P. Schaeffer, M. J. Dagani, and D. S. Weinberg, *J. Amer. Chem. Soc.*, **89**, 6938 (1967).

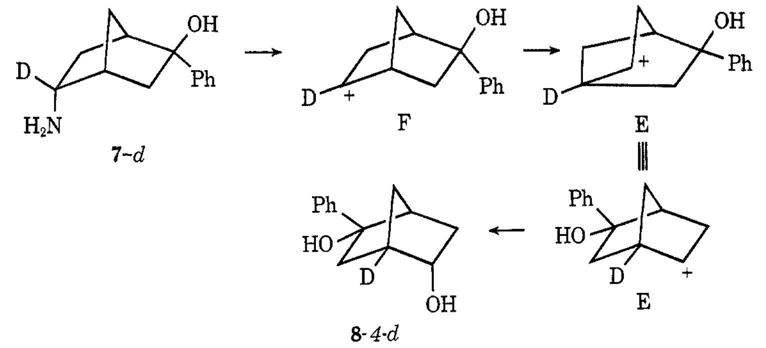
[29] H. C. Brown and S. Ikegami, *ibid.*, **90**, 7122 (1968); H. C. Brown and L.-T. Liu, *ibid.*, **89**, 466 (1967).

[30] J. L. Fry, C. J. Lancelot, L. K. M. Lam, J. M. Harris, R. C. Bingham, D. J. Raber, R. E. Hall, and P. v. R. Schleyer, *ibid.*, **92**, 2538 (1970); J. L. Fry, J. M. Harris, R. C. Bingham, and P. v. R. Schleyer, *ibid.*, **92**, 2540 (1970).

[31] H. L. Goering and J. V. Clevenger, *ibid.*, **94**, 1010 (1972).

SCHEME VII

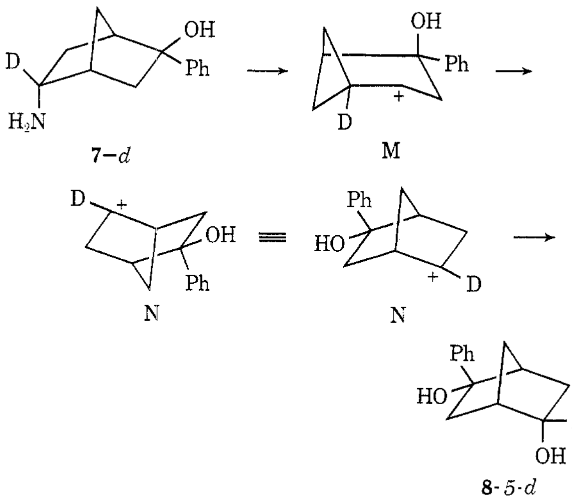




(4)

followed by another Wagner-Meerwein rearrangement to yield cation L, which then goes to borneol (**19**).

The isolation of borneol (**19**) from *endo*-fenchylamine (**14**) opens up the possibility that diol **8** is formed by a similar mechanism during deamination of **7**, as illustrated by eq 3. The two routes can be differentiated by means of deuterium labeling, and this is also shown in eq 3 and 4. The amine-nitrous acid reaction with **7**-*d*, however, led to the usual reaction mixture from which diol **8**-*4-d* was isolated with deuterium only in the 4 bridgehead position, corresponding to the result expected through eq 4 and shown also in Scheme V.



(3)

**7**.—From the foregoing discussion it seems certain that the cations with which we are dealing can be considered to be special in some way. We have no evidence that they are of higher energy than if they had been formed on solvolysis, nor are we aware of any other data which *require* the formation of "hot" carbonium ions during the amine-nitrous acid reaction. "Hot" cations may in fact be unnecessary, for the usual scheme[32] of intimate, solvent-separated, and completely separated ion pairs (eq 5) produced on solvolyses

$$\begin{tikzcd} \mathrm{ROTs} \arrow[r, rightleftharpoons] & \mathrm{R^+OTs^-} \arrow[r, rightleftharpoons] & \mathrm{R^+\|OTs^-} \arrow[r, rightleftharpoons] & \mathrm{R^+ \quad OTs^-} \arrow[d, shift left] \\ & \mathrm{ROAc} & \mathrm{R^+OAc^-} \arrow[l] & \mathrm{R^+\|OAc^-} \arrow[l, rightleftharpoons] \arrow[u, shift left] \end{tikzcd} \qquad (5)$$

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[32] S. Winstein, E. Clippinger, A. H. Fainberg, and G. C. Robinson, *J. Amer. Chem. Soc.*, **76**, 2597 (1954); S. Winstein and A. H. Fainberg, *ibid.*, **80**, 459 (1958); S. Winstein, P. E. Kleindienst, Jr., and G. C. Robinson, *ibid.*, **83**, 885 (1961).

is much different from our picture[4,33] of ion pairing as it occurs during the amine–nitrous acid reaction (eq 6–13). During reaction in aqueous solution the hydroxide ion produced during eq 10 is also the counterion in collapse of the ion pair of eq 12 to carbinol product; that is, part of the leaving group becomes the entering group. When the reaction is carried out in acetic acid-sodium acetate medium, the situation must be somewhat different from that in eq 7–13. Acetyl nitrite is more probably the nitrosating agent,[34] and exchange of acetate for hydroxyl probably takes place before ionization of the diazonium hydroxide (eq 9).[35] Evidence for the latter proposal is to be found in the similarity of the stereochemical and isotopic results during the amine–nitrous acid reaction, in acetic acid-sodium acetate of 1,2,2-triphenylethylamine, and in the thermal decomposition, in the same medium, of *N*-acetyl-*N*-nitroso-1,2,2-triphenylethylamine.[17,36]

$$2HNO_2 \longrightarrow N_2O_3 + H_2O \tag{6}$$

$$N_2O_3 + RNH_2 \longrightarrow RNH_2{}^+NO + NO_2{}^- \tag{7}$$

$$RNH_2{}^+NO \longrightarrow RNHNO + H^+ \tag{8}$$

$$RNHNO \longrightarrow RN{=}NOH \tag{9}$$

$$RN{=}NOH \longrightarrow RN_2{}^+ + OH^- \tag{10}$$

$$RN_2{}^+ + OH^- \longrightarrow R^+ + OH^- + N_2 \tag{11}$$

$$R^+ + OH^- \longrightarrow ROH \tag{12}$$

$$R^+ \longrightarrow \text{other products} \tag{13}$$

## Experimental Section

Pmr spectra were recorded using a Varian A-60 spectrometer. Chemical shifts are reported as $\delta$ values in parts per million downfield from TMS at 0. The chemical shifts are somewhat solvent dependent owing to the anisotropy of the phenyl substituent. Coupling constants are reported in hertz as line separations in cases where those line separations could obviously be measured, and they are not intended to represent computer refined values. Ir spectral data were recorded on a Beckman IR-8 spectrometer. Melting points were taken using a Kofler hot bench. Carbon–hydrogen analyses were performed by Huffman Laboratories, Inc., Wheatridge, Colo., and by Galbraith Laboratories, Inc., Knoxville, Tenn.

**2-*exo*-Phenyl-2-hydroxy-5-norbornanone.**—Chromium trioxide (22 g) was cautiously and slowly added to 250 ml of cold pyridine while stirring. To the yellow complex was added 5 g of diol **9**.[21] The reaction mixture was stirred overnight. It was cooled in an ice–salt bath and 250 ml of cold, concentrated HCl was slowly added. This nearly neutral mixture was continuously extracted with ether for 24 hr. After the ether extracts were dried they were passed through a Norit pad and concentrated. Upon standing for 1 hr crystals formed. Recrystallization from ether containing a little hexane gave a pure product, mp 112°.

*Anal.* Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.39; H, 6.99.

**2-*exo*-Phenylnorbornane-2,5-*endo*-diol** (**8**).—The ketone described above (8.74 g) was treated with 1.5 g of $LiAlH_4$ in ether. The complex was decomposed with water and the ether layer was separated and concentrated. Large crystals formed. They were dissolved in ether and crystallization was allowed to take place again, mp 103°. A total of 6.11 g of pure crystals were obtained. The nmr spectrum (in pyridine) was as follows (in parts per million): hydroxyl hydrogens, 5.81 (2 H), concentration dependent; 5-exo hydrogen, 4.50 (1 H); 3-endo hydrogen, 2.75 (1 H); 3-exo and 6-endo 1 and 4 hydrogens, complex band centered near 2.4 (4 H); 6-exo hydrogen, several components centered near 1.9 (1 H); 7-syn and 7-anti hydrogens, complex pattern centered near 1.45 (2 H). The 5-exo hydrogen gives a broadened signal composed of five partially resolved peaks. The 3-endo hydrogen forms a pair of doublets, $J_{3\text{-endo},3\text{-exo}} = 12.8$ Hz and $J_{3\text{-endo},4} = 2.7$ Hz. The remaining signals are complex. Assignment of signals was aided by the spectrum of the 5-exo deuterated species.

*Anal.* Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.25; H, 7.84.

**2-*endo*-Hydroxy-2-phenyl-5-*exo*-norbornylamine** (**5**).—Diol **8** (8 g) was treated with 9 g of *p*-toluenesulfonyl chloride in 40 ml of pyridine for 21 hr. The mixture was diluted with water and the product was extracted with 4–100-ml portions of ether. The ether extracts were washed successively with cold, diluted HCl and water. After the solution was concentrated, crystals formed, mp 130°. A second crop of crystals was recovered. A total of 14.3 g of pure tosylate was obtained.

*Anal.* Calcd for $C_{20}H_{22}O_4S$: C, 67.01; H, 6.19. Found: C, 66.80; H, 6.05.

A mixture made from 1.4 g of the tosylate from **8**, 1 g of sodium azide, and 10 ml of dimethyl sulfoxide was heated on the steam bath for 1 hr. Water was added and the product was extracted with ether. After the ether was evaporated, an oil remained which could not be caused to crystallize. It gave an nmr signal for the 5-endo hydrogen at 3.49 ppm which was a quartet with the peaks separated by 7.5 and 3.0 Hz ($CDCl_3$ solution). The five aromatic hydrogen signals appeared at 7.3 and the hydroxyl hydrogen signal appeared at 2.32 ppm. A group of signals for four hydrogens appeared between 2.0 and 2.7 and another group of signals for four hydrogens appeared between 1.0 and 1.5 ppm. No signals characteristic of the starting tosylate were detected. A strong absorption was present in the ir spectrum at 2100 $cm^{-1}$ characteristic of azides.

The above azide was reduced with $LiAlH_4$ in ether. The complex was decomposed with water and the ether layer was separated. Upon evaporation of the ether, crystals formed. The compound was recrystallized from ether–hexane mixture, mp 105°.

*Anal.* Calcd for $C_{13}H_{17}NO$: C, 76.80; H, 8.43. Found: C, 76.71; H, 8.26.

**Deamination of 5.**—A sample of amine **5** dissolved in 50 ml of acetic acid was treated with 0.8 g of sodium nitrite. After 20 hr, products were worked up as described for amine **6**. Analysis of the mixture of carbinol products by nmr showed diols **9** and **10** to be present in the ratio of 2.22:1.

To exactly half of the mixture of products from the deamination of 2.1251 g of radioactive amine **5** (30.87 mCi/mol) was added 0.7401 g of nonradioactive diol **8**. After the compounds were converted to the diols by reducing the mixture with $LiAlH_4$, the products were separated by chromatography on alumina. In this way there was obtained 0.369 g of **12** (43.5%), 0.132 g of **10**[21] (15.7%), 0.315 g of **9** (37.3%), and 0.799 g of **8**. Compound **8** was crystallized from ether twice and assayed for carbon-14 content (1.153 mCi/mol). The yield of **8** was therefore 2.59%.

To the second half of deamination product described above was added 0.5760 g of nonradioactive **11**. After the materials were converted to a mixture of carbinols, the products were separated by chromatography. Compound **11** was recovered and crystallized twice from benzene. A few milligrams of **10** were added and the compound was crystallized again, dried, and assayed for carbon-14 content (0.0434 mCi/mol). Therefore the yield of **11** was 0.075%.

In another experiment 3.766 g of radioactive amine **5** (30.87 mCi/mol) was deaminated in 75 ml of acetic acid which was saturated with sodium acetate. The crude mixture of diol products obtained as above was analyzed by nmr. The ratio of **9**:**10** was found to be 2.22:1. To the gross product was added the following materials: 0.1825 g of **11**, 0.2431 g of **8**, 0.1144 g of **10**, and 0.3125 g of **9**. The compounds were separated by chromatography on alumina. The tricyclic alcohol **12** was isolated first (1.074 g, 35.0%). The diols obtained were recrystallized and the following data, millicurie/mole (%), were collected: diol **11**, 0.579 (0.114); diol **8**, 7.240 (2.43); diol **10**, 25.80 (19.0); diol **9**, 25.02 (43.5).

**2-*endo*-Phenyl-2-hydroxy-5-norbornanone.**—To a chromium trioxide–pyridine complex, prepared by cautious addition of 22 g of chromium trioxide to 250 ml of cold pyridine, was added 5 g of diol **10**.[21] The reaction mixture was stirred overnight. It was then cooled using an ice–salt bath and 250 ml of concentrated HCl was slowly added. The mixture was then continuously

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[33] J. H. Ridd, *Quart. Rev. Chem. Soc.*, **15**, 418 (1961).

[34] We are indebted to Professor Theodore Cohen for this suggestion.

[35] See also E. H. White and D. J. Woodcock in "The Chemistry of the Amino Group," Saul Patai, Ed., Interscience, New York, N. Y., 1968, Chapter 8, for discussions of stereochemical retention in such reactions.

[36] C. J. Collins and B. M. Benjamin, *J. Amer. Chem. Soc.*, **85**, 2519 (1963); C. J. Collins, W. A. Bonner, and C. T. Lester, *ibid.*, **81**, 466 (1959).

extracted with ether for 24 hr, at which time no more product could be recovered. Most of the ether was evaporated and the concentrated solution was passed through a Norit pad. Upon addition of hexane to the ether solution, crystallization of the ketone took place, mp 90°.

*Anal.* Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.54; H, 6.99.

**2-*endo*-Phenylnorbornane-2-*exo*,5-*endo*-diol** (11).—The preceding ketone (8.55 g) in ether solution was added to an ether solution of $LiAlH_4$ and the mixture was stirred at ambient temperature for 1 hr. Water was added until the precipitated alumina became grainy. The ether solution was separated by filtration and the alumina was washed thoroughly with fresh ether. When the solution was concentrated the diol crystallized. Recrystallization from ether produced a pure product, mp 109°. The nmr spectrum in pyridine solution is as follows (in parts per million): hydroxyl hydrogens, 6.0 (2 H), concentration dependent; 5 exo hydrogen, 4.38 (1 H); 3-endo hydrogen, 3.28 (1 H); 1-bridgehead, 4-bridgehead, and 7-syn hydrogens, 2.5 (3 H); 3-exo and 6-exo hydrogens, several peaks between 1.3 and 2.2 and partially overlapped by the 7-anti hydrogen, 1.47 (3 H); 6-endo hydrogen, 1.10 (1 H). The coupling constants are $J_{3\text{-endo},3\text{-exo}} = 13.0$, $J_{3\text{-endo},7\text{-anti}} = 2.3$, $J_{6\text{-exo},6\text{-endo}} = 13.3$, $J_{6\text{-endo},7\text{-syn}} = 3.2$, $J_{7\text{-syn},7\text{-anti}} = 8.5$ Hz. Analysis of the spectrum was aided by the spectrum of the 5-exo deuterated species. In the completely protonated form the signal for the 5-exo hydrogen was composed of five poorly resolved components and the signal for the 6-endo hydrogen appeared as a pair of poorly resolved triplets.

*Anal.* Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.35; H, 7.97.

**2-*exo*-Hydroxy-2-phenyl-5-*exo*-norbornylamine** (6).—Pure diol 11 (2.8 g) was dissolved in 15 ml of dry pyridine and 2.8 g of *p*-toluenesulfonyl chloride was added. When the solution was homogeneous, the flask was stoppered and allowed to stand overnight. The contents of the flask were then diluted with 150 ml of water and the aqueous solution was extracted with three 100-ml portions of ether. The ether extracts were washed separately with water, cold dilute HCl, and again with water. After evaporation of the ether, the compound could not be caused to crystallize. Analysis by nmr did not reveal the presence of starting diol. Without further purification the tosylate was placed in a flask with 15 ml of dimethyl sulfoxide and 15 ml of pyridine and 3 g of sodium azide was added. The mixture was heated to 110° for 3 hr. The solution was treated with water and the product was recovered by ether extraction. After the ether extracts were washed with water, the ether was evaporated and an oil remained. It did not crystallize. The nmr spectrum (in $CCl_4$) consisted of a broad triplet for the 5-endo hydrogen at 3.22 and signals for eight other hydrogens between 1.0 and 2.4 ppm. Five aromatic hydrogens appeared at 7.25 ppm. The hydroxyl hydrogen signal was removed by shaking the sample with a drop of $D_2O$. No signals characteristic of the tosylate precursor could be detected. The ir spectrum of the azide contained a strong absorption at 2100 $cm^{-1}$. The crude azide was treated with $LiAlH_4$ in ether solution. The complex was decomposed with water and the supernatant ether layer was removed and concentrated. Benzene was added and the amine crystallized, mp 118°.

*Anal.* Calcd for $C_{13}H_{17}NO$: C, 76.80, H, 8.43. Found: C, 76.83; H, 8.36.

The amine 6 was shown to be free of diol 11 as follows. To 0.2910 g of amine (30.59 mCi/mol) there was added 0.4254 g of nonradioactive diol 11. After the materials were brought into solution the diol was reisolated and found to be nonradioactive.

**Deamination of 6.**—To a solution of 2 g of amine 6 in 100 ml of glacial acetic acid there was added 2 g of solid sodium nitrite over a period of 2 hr. The reaction mixture was then stirred at room temperature for 20 hr and then diluted with water. The products were recovered by ether extraction. After the ether extracts were dried, they were combined, concentrated, and treated with $LiAlH_4$. Isolation of the mixed products was accomplished in the usual way. Integration of the nmr spectrum of the mixture of products showed the presence of diols 10 and 9 in the ratio of 1.67:1.

In another deamination experiment the acetic acid was saturated with anhydrous sodium acetate. The product from 1.569 g of amine 6 was treated with $LiAlH_4$ and the mixture of alcohols was chromatographed on alumina.[21] The following was recovered: 0.350 g of phenylnortricyclanol 12, 0.503 g of diol 10, and 0.303 g of diol 9. In a separate experiment using 1.0111 g of amine 6 labeled in the phenyl group with carbon-14 (30.59 mCi/mol) the deamination product was mixed with 1.1263 g of nonradioactive diol 11. The mixture was treated with $LiAlH_4$ after which 11 was recovered by chromatography on alumina. The diol was crystallized from benzene twice and its radioactivity content was determined. Following this, the sample of 11 was mixed with 40 mg of nonradioactive 12 and 33 mg of nonradioactive 10. It was chromatographed, crystallized, and assayed for carbon-14 content again (0.4349 mCi/mol). This corresponds to a yield of 0.0162 g, 22% of the reaction products. In a similar way the yield of 8 from 6 was found to be 0.039%.

**Carbon-14 Labeled Amines 5 and 6.**—To a solution of 25 g of 5-norbornen-2-ol in 200 ml of acetone cooled in an ice–salt bath there was added slowly 100 ml of cold chromic acid solution, prepared from 26 g of $CrO_3$ and 26 g of sulfuric acid, diluted to 100 ml with water. After stirring for 2 hr at room temperature most of the acetone was evaporated under vacuum. Water was added and the product, 5-norbornen-2-one, was recovered by ether extraction. Crude norbornenone was treated with equimolar amount of Grignard reagent prepared carbon-14-labeled bromobenzene. The complex was decomposed with concentrated ammonium chloride and the product was distilled under vacuum. In several preparations, the yield of 2-*exo*-phenyl-5-norbornen-2-ol[21] was usually <50%. Borohydration of the above phenylnorbornenol was carried out as described for the general reaction.[37] The solvent was composed of 600 ml of tetrahydrofuran and 250 ml of triglyme to prevent precipitation of the intermediate complex. Fractional crystallization of the mixture of products gave 29 g of phenyl-$^{14}C$-labeled 9, mp 163°, and 2-*exo*-phenylnorbornane-2-*endo*,6-*exo*-diol, mp 128°. The conversion of 9 to a mixture of 9 and 10 has been published.[21]

**2-*exo*-Hydroxy-2-phenyl-5-*endo*-norbornylamine** (7).—To a solution of 5 g of 2-*exo*-hydroxy-2-phenyl-5-norbornanone in 50 ml of pyridine was added 5 g of hydroxylamine hydrochloride. After the reaction mixture had been heated on the steam bath for 1 hr, most of the pyridine was evaporated in an air stream. Organic materials were extracted from the pasty mass by triturating it with ether. Crystals of 2-*exo*-hydroxy-2-phenyl-5-norbornanone oxime formed when the ether solution was concentrated. It recrystallized slowly from ether containing a little hexane, mp 128°.

*Anaol* Calcd for $C_{13}H_{15}NO_2$: C, 71.86; H, 6.96. Found: C, 72.09; H, 7.25.

Six grams of the above oxime was added to a solution of 2 g of $LiAlH_4$ in 250 ml of ether and the mixture was heated at reflux temperature for 20 hr. Water was added to decompose the complex and the ether solution was separated and concentrated. Amine was separated from neutral material by extracting it with cold dilute HCl. The acid was neutralized with sodium hydroxide and the amine was extracted with ether. Most of the ether was evaporated after which crystals formed. These crystals were collected on a filter and recrystallized, mp 157°. This compound was thought to be the secondary amine form by ring expansion of the six-membered norbornyl structure. Fractional crystallization from ether–hexane mixtures of the material in the filtrates gave a second compound, mp 81°. It slowly absorbed carbon dioxide when exposed to air.

*Anal.* Calcd for $C_{13}H_{17}NO$: C, 76.80; H, 8.43. Found: C, 76.56; H, 8.30.

Compound 7 containing deuterium in the 5-exo position was prepared by reducing the corresponding oxime with $LiAlD_4$.

**Deamination of 7.**—This amine (2 g) in 50 ml of acetic acid saturated with sodium acetate was deaminated by treating the solution with 2 g of sodium nitrite. The products were isolated and worked up in the same way as described for other deaminations. Chromatography on alumina of the mixture of carbinols gave the following yields of products: 283 mg of phenylnortricyclenol 12, 567 mg of diol 11 from endo attack, 480 mg of diol 10, 233 mg of diol 9. There was also obtained 99 mg of material which consisted in part of a mixture of ~30 mg of 8 and 30 mg of 7-phenylnorbornane-2-*exo*,7-*syn*-diol and some material which was not identified. Positive identification of the constituents of the 99-mg fraction was accomplished by rechromatographing it on alumina and comparing the nmr spectra of the fractions with the spectra of known compounds.

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(37) G. Zweifel and H. C. Brown, *Org. React.*, **13**, 31 (1963).

In another experiment 0.808 g of radioactive amine (59.35 mCi/mol) was deaminated. To the product, as diols, was added 50.0 mg of nonradioactive **8**. The compounds were separated by chromatography on alumina and 633 mg of products were recovered. The last fraction containing **8** was rechromatographed after adding nonradioactive **9** and 7-phenylnorbornane-2-*exo*,7-*syn*-diol as hold-back carrier. Diol **8** was then crystallized and assayed for carbon-14 content (18.78 mCi/mol). This corresponds to a yield of 1.85%.

**Deamination of 7-*exo*-5-*d*.**—Amine **7** containing deuterium in the 5-exo position (9.5 g) was deaminated as described before. After the products had been separated and crystallized, their nmr spectra were then taken to determine the position of the deuterium label. The signal for the 5-exo hydrogen (4.38 ppm, pyridine solution) of 2-*endo*-phenylnorbornane-2-*exo*,5-*endo*-diol (**11**) was absent. Also the signal for the 6-endo hydrogen (1.10 ppm) was collapsed to a pair of doublets.

In the spectrum of 2-*endo*-phenylnorbornane-2-*exo*,5-*exo*-diol (**10**)[21] the signal for the 5-endo hydrogen (3.98 ppm) was missing. Diol **9**, 2-*exo*-phenylnorbornane-2-*endo*,5-*exo*-diol, gave an nmr spectrum[2,21] in which the signal for the 4-bridgehead hydrogen (2.45 ppm) was missing and the signal for the 3-exo hydrogen (2.40 ppm) was collpased to a doublet.

The nmr spectrum of 2-*exo*-phenylnorbornane-2,5-*endo*-diol (**8**) was difficult to analyze. Therefore a sample of **8** weighing 100 mg was mixed with 50 mg of tris(dipivaloylmethane)europium and dissolved in deuteriochloroform. Under these conditions the spectrum was interpreted as follows (in parts per million): secondary hydroxyl hydrogen, 9.52 (br, 1 H); 2 and 6 aromatic hydrogens, 7.95 (m, 2 H); 3, 4, and 5 aromatic hydrogens, 7.45 (m, 3 H); 5-exo and tertiary hydroxyl hydrogens, unresolved, 6.98 (2 H); 3-endo hydrogen, doublet of doublets, 4.47 ($J_{3\text{-endo},3\text{-exo}} = 14.1$, $J_{3\text{-endo},7\text{-anti}} = 2.8$ Hz); the 3-endo hydrogen is partially overlapped by the 6-endo hydrogen, poorly resolved pair of triplets, 4.25 (2 H); 1- and 4-bridgehead hydrogens, unresolved 3.46 (2 H); 3-exo hydrogen, doublet of doublets, 3.03 ($J_{3\text{-exo},3\text{-endo}} = 14.1$, $J_{3\text{-exo},4} = 4.4$ Hz); the 3-exo hydrogen is partially overlapped by components of the 6-exo hydrogen, unresolved, 2.86 (2 H); 7-syn and 7-anti hydrogens, unresolved, 2.29 (2 H). In the spectrum for diol **8** derived from amine 7-*exo*-5-*d*, the signal for the bridgehead hydrogens at 3.46 ppm had an integrated intensity of 1.0. The signal for the 3-exo hydrogen collapsed to a pair of singlets with spacing of 14.1 Hz and the signal for the 5-endo hydrogen was narrower.

**Registry No.**—**5**, 29264-72-0; **6**, 29264-73-1; **7**, 29264-74-2; **7** oxime, 36808-83-0; **8**, 14518-60-6; **8** tosylate, 36808-85-2; **9**, 36808-86-3; **9** (phenyl-$^{14}C$), 36808-87-4; **11**, 36808-88-5; 2-*exo*-phenyl-2-hydroxy-5-norbanone, 36808-89-6; 2-*endo*-phenyl-2-hydroxy-5-norbanone, 36808-90-9.

**Acknowledgment.**—One of us (C. J. C.) wishes to thank Professor Walter Hückel of the University of Tübingen, Germany, for several stimulating and comprehensive discussions, including a review of the material in ref 3 prior to its publication.

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# Sterically Controlled Syntheses of Optically Active Organic Compounds. XVI. Temperature Dependence of Hydrogenolytic Asymmetric Transamination[1]

KAORU HARADA* AND TAKAO YOSHIDA

*Institute for Molecular and Cellular Evolution, Department of Chemistry, University of Miami, Coral Gables, Florida 33134*

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Temperature effects on the hydrogenolytic asymmetric transamination between ethyl pyruvate and optically active amines were studied. Definite temperature effects were observed between −20 and 65°. At relatively low temperature and when the optically active amine had an *R* configuration, the resulting alanine had an *R* configuration. The optical purity of (*R*)-alanine decreased as the reaction temperature increased and the configuration of analine inverted to the *S* configuration at higher temperature. Temperature effects using several optically active amines were studied. Within the context of these results, the possible steric course of the temperature-dependent asymmetric reactions is discussed. The differences of enthalpy of activation ($\Delta\Delta H^{\ddagger}_{S-R}$) and entropy of activation ($\Delta\Delta S^{\ddagger}_{S-R}$) between the formation of *S* amino acid and *R* amino acid were calculated at varying temperature. The results suggest that the entropy factor is very important in the inversion of configuration of the reaction product in the asymmetric synthesis.

Several studies on the hydrogenolytic asymmetric transamination between α-keto acids (or their esters) and optically active amino compounds have been reported.[2-8]

Generally, temperature is one of the most important factors in determining the molecular conformations that are involved in asymmetric syntheses. Some studies of the effect of temperature on asymmetric syntheses have been recorded in the literature.[9-15] In a previous communication,[16] the temperature effect on the hydrogenolytic asymmetric transamination between ethyl pyruvate and optically active amines was reported. This investigation examines further the temperature dependence of hydrogenolytic asymmetric transamination. The optically active amines used were (*S*)-(−)- and (*R*)-(+)-α-methylbenzylamine, (*R*)-(+)-α-ethylbenzylamine, and (*S*)-(−)-α-(1-naphthyl)ethylamine. The reaction temperatures used were in the range of −20 to 65°. The hydrogenation reactions were carried out at 1 atm of hydrogen by using palladium hydroxide on charcoal suspended in absolute alcohol with agitation provided by a magnetic stirrer. One series of the hydrogenation reactions

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