# Syntheses and Nitrous Acid Deaminations of *anti-* and *syn*-7-Norbornenylamine[1]

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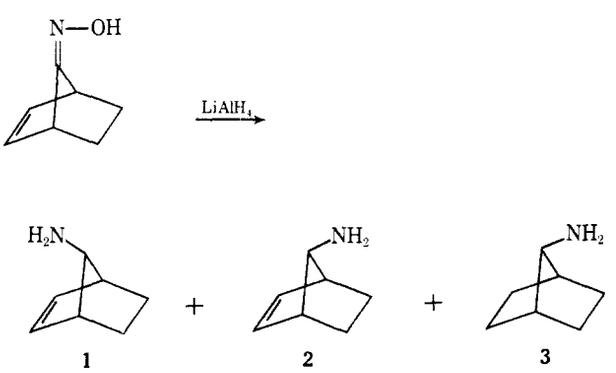
*anti-* and *syn*-7-norbornenylamines (**2** and **1**) and *anti*-9-benzonorbornenylamine (**20**) were synthesized. Nitrous acid deaminations of **2** and **20** proceeded with retention of configuration yielding *anti*-7-norbornenol and *anti*-9-benzonorbornenol, respectively. The same reaction with **1** gave bicyclo[3.2.0]hept-2-en-4-ol derivatives with complete rearrangement.

The product distribution and the extent of racemization observed in the deaminations of optically active *endo-* and *exo*-2-norbornylamines have been extensively investigated and discussed in comparison with the related results obtained in the solvolyses of sulfonate esters of the corresponding alcohols.[2-4] The solvolytic reactivity of 7-norbornenyl halides or sulfonate esters and related compounds has also received considerable interest.[5-8] However, to the best of our knowledge, no one has reported a study of the deamination of 7-norbornenylamines. Accordingly, we undertook the synthesis of *anti-* and *syn*-7-norbornenylamines and *anti*-7-benzonorbornenylamine and a study of their deamination reactions.

## Results

**Synthesis of *syn*-7-Norbornenylamine (1).**—At the outset, the lithium aluminum hydride reduction of the oxime of norbornen-7-one[9,10] appeared to be a convenient method for the synthesis of 7-norbornenylamines. However, by vpc this reaction was shown to produce **1**, *anti*-7-norbornenylamine (**2**), and the saturated 7-norbornylamine (**3**)[11] in a ratio of 1:89:10, and the isolation of these products in pure states was difficult. Therefore, we gave up the use of this reaction and carried out the synthesis outlined in Chart I.




Norbornene (**4**) was allowed to stand with ethyl azidoformate in *n*-pentane at room temperature to give an oily triazoline derivative (**5**). When **5** was allowed to stand in methanol, an exothermic reaction occurred with the evolution of nitrogen gas. Ethyl 2,3-*exo*-aziridino[2.3]norbornane-1′-carboxylate (**6**) was formed.[12] The infrared spectrum of **6** showed an ester absorption, but no N—H and C=N band. It was found that the thermal decomposition of **5** in a nonpolar solvent, *e.g.*, toluene, was not suitable for the preparation of **6** because of the formation of a byproduct (probably 2-carbethoxyiminonorbornane).[13] Alkaline hydrolysis of **6** afforded 2,3-*exo*-aziridino[2.3]-norbornane (**7**), whose structure was established by the nmr[14] and infrared spectra (see the Experimental Section) and by catalytic reduction to the known *exo*-2-norbornylamine.[2,3a] A reaction of **6** with dry hydrogen bromide gas in pentane led to the formation of a rearranged bromide **8**. Since **8** was unstable on standing at room temperature, immediate treatment with sodium methoxide in methanol was carried out to prepare *syn*-7-N-carbomethoxyaminonorbornene (**9**) with the elimination of hydrogen bromide and with simultaneous ester exchange. The nmr peaks of two vinyl protons in **9** appearing as a multiplet at $\tau$ 4.02 was consistent with the *syn* configuration of 7-N-carbomethoxyamino group.[15] Hydrolysis of **9** with potassium hydroxide in aqueous methanol afforded the crude olefinic amine **1**. For purification, it was immediately converted into *syn*-7-acetamidonorbornene (**10**) by treatment with acetic anhydride in pyridine. Careful elution chromatography on Florisil gave the pure **10**, which was shown to be homogeneous on capillary vpc analysis (45-m Golay column BDS). The pure sample of **1** was obtained from the purified **10** by basic hydrolysis and stored as its hydrochloric salt. The over-all yield from ethyl azidoformate was 13%. The structure was supported by the nmr spectrum as shown in Experimental Section. The catalytic hydrogenation of **10** and its epimer **19** described later gave the same saturated compound, 7-acetamidonorbornane (**11**),[16] which was identified by mixture melting point and comparison of its infrared spectra with that of an authentic sample prepared by catalytic reduction of the mixture of **1**, **2**, and **3** (obtained in turn from lithium aluminum hydride

(1) Part XV of a series on bicyclic systems. Part XIV: H. Tanida and H. Ishitobi, *J. Am. Chem. Soc.*, **88**, 3663 (1966).

(2) E. J. Corey, J. Casanova, Jr., P. A. Vatakencherry, and R. Winter, *ibid.*, **85**, 169 (1963).

(3) (a) J. A. Berson and A. Remanick, *ibid.*, **86**, 1749 (1964); (b) J. A. Berson and D. A. Ben-Efrain, *ibid.*, **81**, 4094 (1959).

(4) S. Winstein, E. Clippinger, R. Howe, and E. Volgelfanger, *ibid.*, **87**, 376 (1965), and references cited therein.

(5) H. C. Brown and H. M. Bell, *ibid.*, **85**, 2324 (1963), and references cited therein.

(6) S. Winstein, A. H. Lewin, and K. C. Pande, *ibid.*, **85**, 2324 (1963), and references cited therein.

(7) H. Tanida, T. Tsuji, and H. Ishitobi, *ibid.*, **86**, 4904 (1964).

(8) H. Tanida, T. Tsuji, and T. Irie, *ibid.*, **88**, 864 (1966).

(9) P. G. Gassman and P. G. Pape, *Tetrahedron Letters*, 9 (1963).

(10) R. K. Bly and R. S. Bly, *J. Org. Chem.*, **28**, 3165 (1963).

(11) For the mechanism of lithium aluminum hydride double-bond reductions in the 7-substituted norbornadiene and *syn*-7-substituted norbornenes, see B. Franzus and E. I. Snyder, *J. Am. Chem. Soc.*, **87**, 3423 (1965).

(12) The numbering used in this paper is shown in the charts.

(13) The formation of an anil derivative of this kind has often been observed in the thermolysis of triazoline derivatives. For example, (a) K. Alder and G. Stein, *Ann.*, **501**, 1 (1933); (b) A. C. Oehlschlager, P. Tillman, and L. H. Zalkow, *Chem. Commun.*, 596 (1965).

(14) For the detailed nmr study of aziridine derivatives, see K. Tori, K. Kitahonoki, Y. Takano, H. Tanida, and T. Tsuji, *Tetrahedron Letters*, 869 (1965).

(15) E. I. Snyder and B. Franzus, *J. Am. Chem. Soc.*, **86**, 1166 (1964).

(16) L. H. Zalkow and A. C. Oehlschlager [*J. Org. Chem.*, **28**, 3303 (1963)] prepared **11** through a different route and reported the same properties.

CHART I

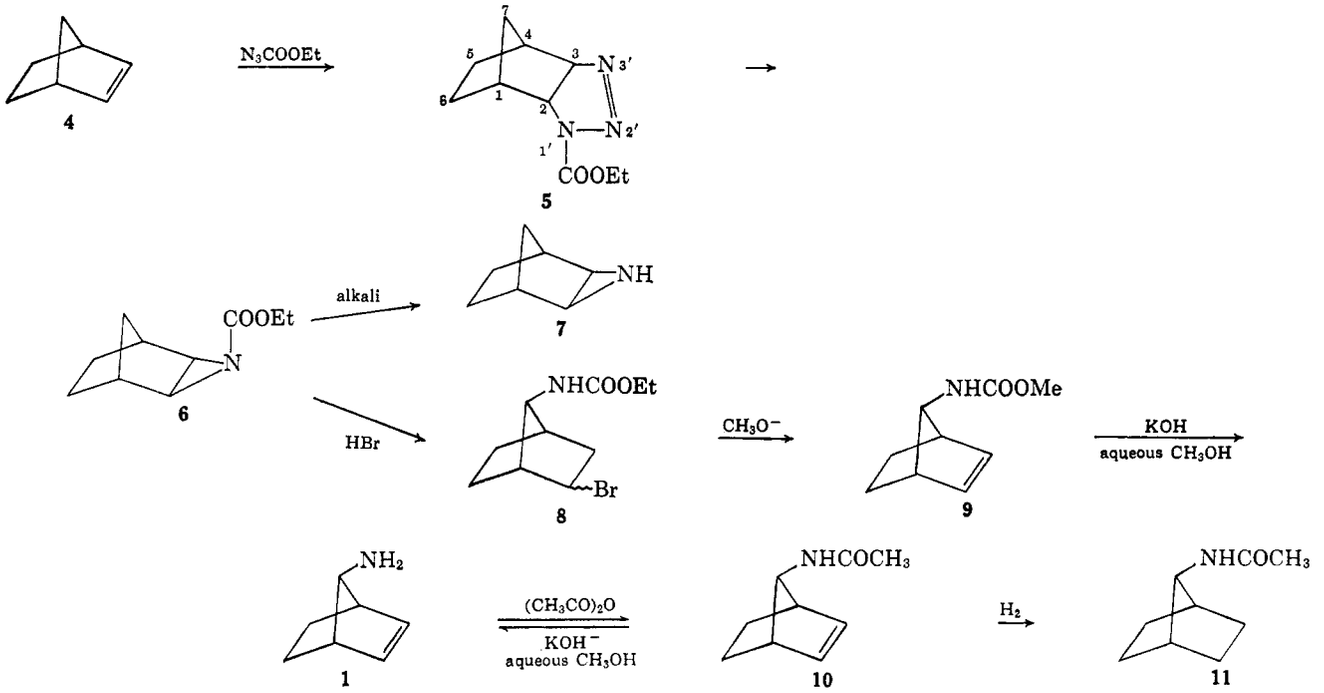
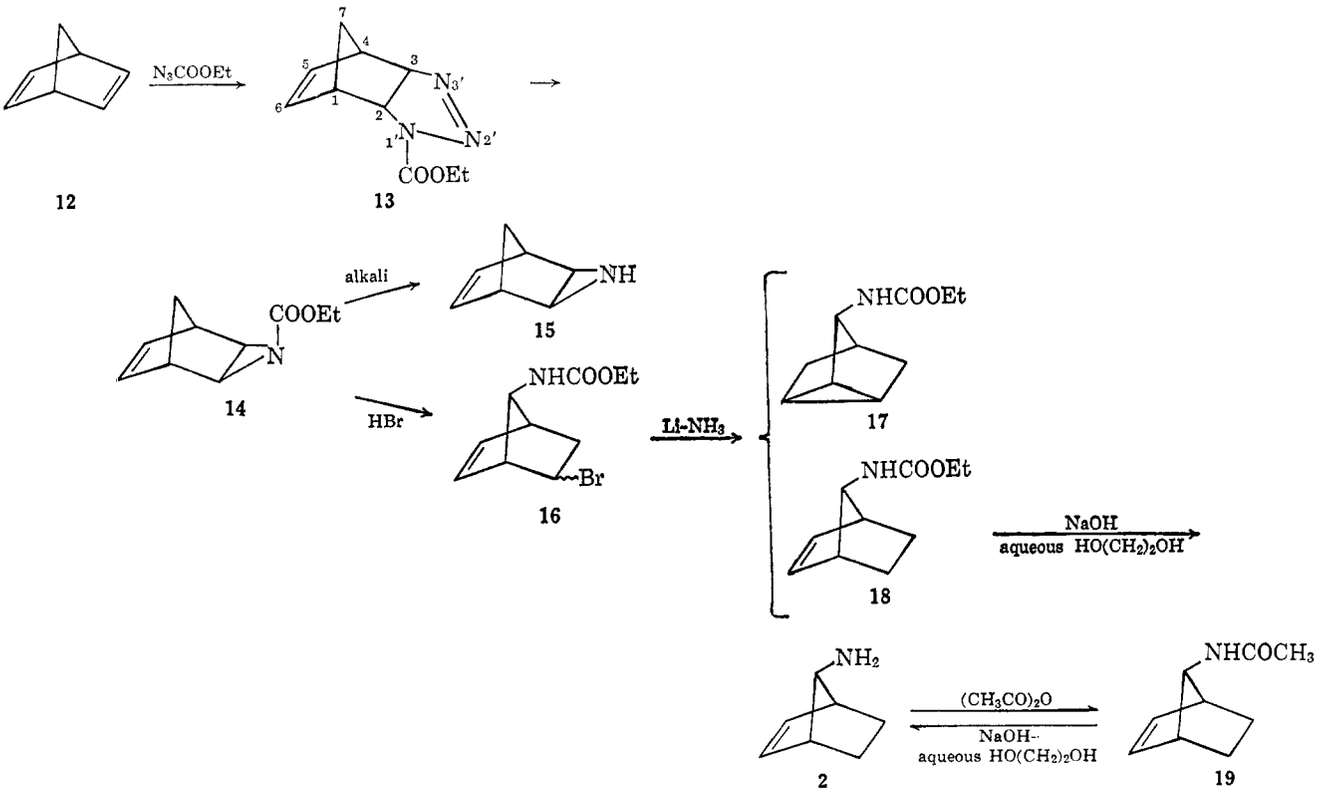



CHART II



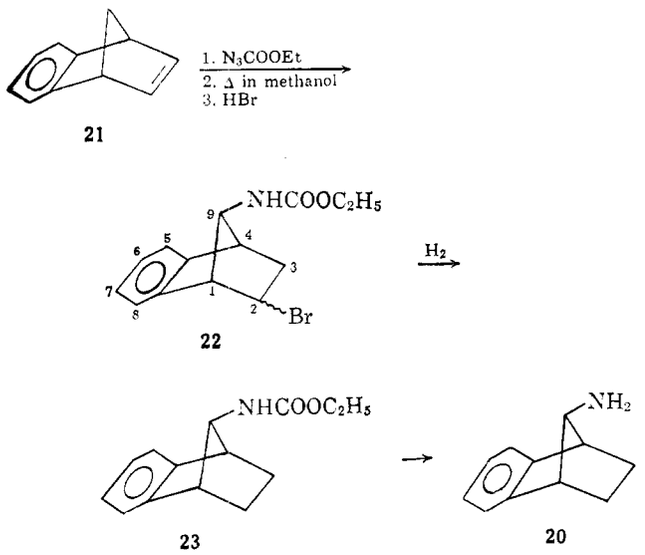

reduction of 7-oxyiminonorbornene, followed by acetylation).

**Synthesis of *anti*-7-Norbornenylamine** (2).—Reaction of norbornadiene (**12**) with ethyl azidoformate gave the triazoline derivative **13**, which was converted into the N-carbethoxyaziridine derivative **14** by treatment with methanol and then into 2,3-*exo*-aziridino-[2.3]norborn-5-ene (**15**) by hydrolysis. The structure of **15** was confirmed by nmr[14] and infrared spectra (see the Experimental Section). Treatment of **14** with hydrogen bromide at room temperature yielded only a dark brown tar. At −50° and upon neutralization of the reaction mixture with isopropylamine before work-up, however, 2-bromo-*anti*-7-N-carbethoxyaminonorbornene (**16**) was successfully obtained. Because of its labile nature, **16** was immediately treated with lithium–liquid ammonia to give the two kinds of debrominated compounds, 3-N-carbethoxyaminonortricyclene (**17**) and *anti*-7-N-carbethoxyaminonorbornene (**18**), in a ratio of 2.5:1 on vpc analysis. The characteristic nature of norbornene derivatives to form silver nitrate complex was used to separate **17** and **18**.

The structure of **17** was assigned by the absorption bands at 803 and 810 $cm^{-1}$ owing to cyclopropyl CH[17] and the absence of an olefinic band in the infrared spectrum. The olefinic carbamate **18** regenerated by the decomposition of the silver nitrate complex with ammonia was subjected to drastic hydrolysis (boiling aqueous ethylene glycol containing sodium hydroxide)[18] to yield crude *anti*-7-aminonorbornene (**2**) which, for purification, was converted into the acetate **19** as performed in the case of *syn* isomer **1**. (See Chart II.) Hydrolysis of the thus purified **19** gave the pure sample of **2**. The nmr spectrum was entirely consistent with the structure of **2** (see the Experimental Section). The difference of coupling between the C-7 protons of **1** (doublet of triplets) and **2** (triplet) supported the view of a stereospecific coupling suggested by Snyder and Franzus.[15] The over-all yield was 2% from ethyl azidoformate.

**Synthesis of *anti*-9-benzonorbornenylamine (20)** was achieved by a reaction route similar to that used for the preparation of **1**. Addition of azidoformate to benzonorbornadiene (**21**), followed by thermal de-

CHART III




composition of the thus-formed triazoline derivative in methanol, and followed then by Wagner–Meerwein rearrangement *via* treatment with hydrogen bromide, gave 2-bromo-*anti*-9-N-carbethoxyaminobenzonorbornene (**22**). Catalytic reduction followed by hydrolysis with sodium hydroxide–boiling aqueous ethylene glycol afforded **20** (Chart III). The exclusive formation of *anti*-9-benzonorbornenol[7] from the deamination of **20** as described later proved the structure.

**Deaminations.**—The nitrous acid deaminations of **1** and its hydrochlorides were carried out in acetic acid. Examination and isolation of products were performed by vpc. An internal standard added before running the vpc analysis made possible the calculation of absolute yields. The structures were established by retention time analysis and comparison of the infrared spectra with those of the authentic samples prepared by independent routes. As presented in Table I,

(17) J. D. Roberts, E. R. Trumbull, Jr., W. Bennett, and R. Armstrong, *J. Am. Chem. Soc.*, **72**, 3116 (1950).

(18) It was quite different from the facile hydrolysis observed in **9**, presumably owing to the steric interference of the ethano bridge of **18**.

TABLE I

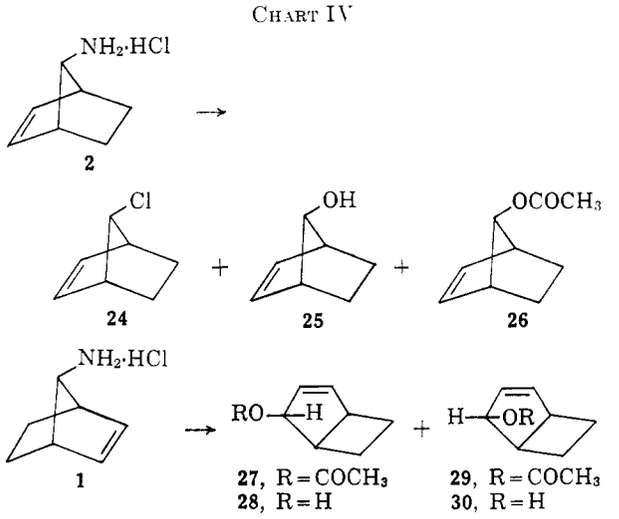
DEAMINATION OF *anti*-7-NORBORNENYLAMINE (**2**) IN ACETIC ACID–WATER AT 20.0 ± 0.1°[a]

| Material | Mole % of $CH_3COOH$ | Total yield, % | Products ratio, % 24 | 25 | 26 |
|---|---|---|---|---|---|
| **2**·HCl | 100 | 72.0 | 22.3 | 55.6 | 22.1 |
| | 75 | 69.8 | 10.4 | 75.1 | 14.5 |
| | 50 | 68.8 | 6.2 | 85.3 | 8.5 |
| | 27 | 64.3 | 0 | 100 | 0 |
| | 10 | 61.8 | 0 | 100 | 0 |
| **2** | 100 | 75.3 | 0 | 76.9 | 23.1 |
| | 75 | 75.3 | ... | 80.3 | 19.7 |
| | 50 | 78.2 | ... | 96.2 | 3.8 |
| | 27 | 78.2 | ... | 100 | 0 |

[a] Four molar equivalents of sodium nitrite to amine was used.

the deamination of **2**·HCl produced *anti*-7-norbornenyl chloride (**24**), *anti*-7-norbornenol (**25**), and *anti*-7-norbornenyl acetate (**26**). The same reaction of the free amine **2** yielded only the two compounds, **25** and **26**. The absence of other possible products, such as *syn*-7-norbornenol and its acetate (products with inversion) and bicyclo[3.2.0]hept-2-en-4-ol and 3-nortricyclenol and their acetates (products with rearrangement), in amounts greater than 0.2% was demonstrated by capillary vpc analysis. Hydrolysis of the deamination products of **2**·HCl with lithium aluminum hydride gave only **24** and **25**, further catalytic reduction of which yielded the corresponding saturated 7-chloronorbornane and 7-norbornanol. No *endo*- and *exo*-

CHART IV



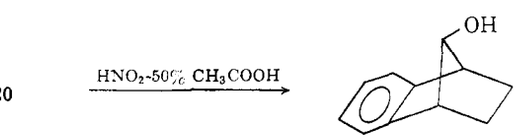

norbornanol could be detected. This suggested that no tricyclo[4.1.0.$0^{3,7}$]heptan-2-yl derivatives[19] were formed under the deamination conditions employed here. Accordingly, it can be concluded that the deamination of **2** proceeded with complete retention of configuration. (See Chart IV.)

The deamination of **1**–HCl was carried out in glacial acetic acid. Vpc analysis indicated the formation of four products, *anti*-bicyclo[3.2.0]hept-2-en-4-ol (**28**) and its acetate (**27**) and *syn*-bicyclo[3.2.0]hept-2-en-4-ol (**30**) and its acetate (**29**), in the ratio of 24:72:1:3 and in a total yield of 91.3%. For identification, an

(19) This information is important, since the formation of these kinds of tricyclic products was reported in the solvolyses of *anti*-7-norbornenyl halide and *p*-bromobenzenesulfonate. See ref 8 and references cited therein.

authentic sample of **28** was prepared by hydrolysis of *syn*-7-norbornenyl *p*-toluenesulfonate.[20] The Oppenauer oxidation of **28** followed by lithium aluminum hydride reduction yielded a mixture of **30** and **28** in a ratio of 75:25. Those methods are essentially the same as those used by Winstein for the synthesis of the saturated analogs, the bicyclo[3.2.0]heptan-2-ol derivatives.[20b] Treatment of the mixture of deamination products with methylmagnesium iodide or lithium aluminum hydride led to a mixture of two kinds of alcohols in a ratio of 96:4, the main one of which was identified as **28** by comparison of the infrared spectrum and mixture melting points of the phenylurethan, derived therefrom, with an authentic sample.[20a] The minor alcohol was identified as **30** by retention time analysis of itself and its acetate. However, isolation was not achieved because of the small amount. The absence of other possible products such as the inverted **25**, the retained *syn*-7-norbornenol, and nortricyclenol produced with a hydride shift in amounts greater than 0.2% was demonstrated by vpc analysis. However, a control experiment showed that treatment of **28** with acetic acid brought about the epimerization with acetylation. Therefore, the above product ratios do not represent complete kinetic control.

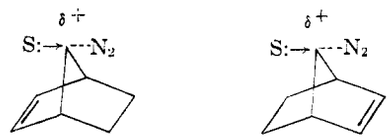
Deamination of **20** in 50% aqueous acetic acid yielded predominantly *anti*-9-benzonorbornenol[8] with a minor amount of its acetate. Therefore, as far as the stereochemical course is concerned, no important information other than that in the deamination of **2** was obtained.



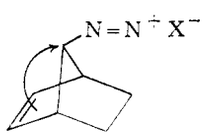

## Discussion

The pertinent features of our results are perhaps the following three. (1) The deamination of the *anti*-amine **2** proceeded with complete retention of configuration. An apparent parity of configuration between the products from the deamination and those from hydrolysis of *anti*-7-norbornenyl *p*-toluenesulfonate[6] was observed, although at the present time some questions have been proposed as to whether the retention in the hydrolysis products represents complete kinetic control.[5,8] (2) The unusually high yield of the intramolecular products (**24** and **25**) in the diazonium ion decomposition of **2**, when compared with the results obtained from the deaminations of *endo*- and *exo*-2-norbornylamines is particularly significant. Berson and Remanick[3a] observed the values 16:80 and 10:87 as the ratios of alcohol to acetate produced in the deaminations of *endo*- and *exo*-2-norbornylamines, respectively. The deamination of **2** or **2**·HCl in glacial acetic acid yielded the intramolecular products (**24** + **25**) and the intermolecular product **26** in the ratio of *ca.* 78:22. (3) The reaction of the *syn*-amine **1** proceeded with complete rearrangement into the bicyclo[3.2.0]heptene system.

The possibility that the alkyldiazonium ion decomposition takes place in a concerted manner with the aid of solvent participation should be excluded from all the present results, as far as it suggests an SN2 displacement of the diazonium ion by solvent with inversion of configuration.[21]




It is generally agreed that, because the driving force for the decomposition of an alkyldiazonium ion is the exothermic elimination of a stable nitrogen molecule, the activation energy is much smaller than that in the solvolysis of halides or sulfonate esters and thus transition state should resemble the reactant.[22-24] On the basis of this, two diverse views have been proposed concerning the role of neighboring group participation in the transition state of deamination. One view has suggested that help from neighboring groups is neither necessary nor possible for such a small positive charge as developed on the carbon in the transition state of deamination.[23,22b] In the other, rather extreme view suggested by Streitwieser,[21,22b] it has been emphasized that a rearranging group in the deamination provides not only anchimeric assistance, *i.e.*, a *push* for a leaving group, but also that it is being *pulled* over by the positive field being generated with splitting off of nitrogen; participation by neighboring groups is pronounced. The greatest participation by the double bond was observed in the solvolysis of 7-norbornyl derivatives.[25] Thus, it may be considered that the present results provide an exceptionally favorable case for the second view. The retention of configuration in the deamination of **2** can be explained by the 2,3-$\pi$-bond participation as in the solvolysis of *anti*-7-norbornenyl derivatives,[26] provided one can assume that the $\pi$ electrons considerably participate in the dissociation of the C–N bond at a stage wherein the positive charge is still mainly on the nitrogen. However, we would like to emphasize that this stereospecific result is not only a feature in the solvolysis but also in the deamination. It markedly contrasts with the results in the carbonium ion reactions of 2-norbornyl derivatives. That is, the solvolysis of *exo*-2-norbornyl *p*-toluenesulfonate proceeds with complete retention of configuration,[4] while the deamination of *exo*-2-norbornylamine gives a 2% yield of the *endo* products.[3]




(20) (a) S. Winstein and E. T. Stafford, *J. Am. Chem. Soc.*, **79**, 505 (1957); (b) S. Winstein, F. Gadient, E. T. Stafford, and P. E. Klinedinst, Jr., *ibid.*, **80**, 5895 (1958).

(21) (a) A. Streitwieser, Jr., *J. Org. Chem.*, **22**, 861 (1957); (b) A. Streitwieser, Jr., and W. D. Schaffer, *J. Am. Chem. Soc.*, **79**, 2888 (1957).

(22) (a) H. Ridd, *Quart. Rev.* (London), **15**, 418 (1961); (b) H. Zollinger, "Azo and Diazo Chemistry, Aliphatic and Aromatic Compounds," Interscience Publishers, Inc., New York, N. Y., 1961, pp 93–101, 123–136.

(23) R. Huisgen and C. Rüchardt, *Ann.*, **601**, 1, 21 (1956).

(24) G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).

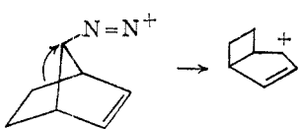
(25) *E.g.*, J. A. Berson, "Molecular Rearrangements," Part 1, P. D. Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 2, p 195.

(26) S. Winstein, M. Shatavsky, C. J. Norton, and R. B. Woodward, *J. Am. Chem. Soc.*, **77**, 4183 (1955).

Alternatively, it is possible to explain the retention of configuration, without assuming neighboring group participation, in terms of a cyclic SNi transition state in the diazonium ion pairs[27] or *via* an SN2 process with frontal attack.[22b,28,29] It appears to us that no

example of inversion of configuration in the reactions of 7-norbornenyl derivatives has been reported.[30] If, owing to the increasing strain with rehybridization of $C_7$ to $sp^2$, the structure of the transition state is largely equivalent to that of the $sp^3$-hybridized atom present initially and a planar $sp^2$ configuration is difficultly achieved, the exclusive contribution of the frontal attack does not seem unreasonable.

In the decomposition of *syn*-diazonium ion, the formation of a stabilized intermediate allylic bicyclo[3.2.0]-hept-2-enyl cation provides a strong driving force for the ring cleavage.[20a]



## Experimental Section

All melting points were taken in sealed capillaries and were corrected. Unless stated otherwise, infrared spectra were determined using a Nippon Bunko IR-S spectrometer in carbon tetrachloride and carbon disulfide. Nmr spectra[31] were determined at 60 Mc with a Varian A-60 spectrometer using tetramethylsilane as internal standard in deuteriochloroform or carbon tetrachloride. Vpc analysis was carried out on a Hitachi-Perkin-Elmer gas chromatograph F-6, using helium as a carrier gas. Preparative gas chromatography was performed on a Shimazu gas chromatograph Model GC-1B.

**Addition of Ethyl Azidoformate to Norbornenes. Ethyl 2,3-*exo*-*v*-Triazolino[2.3]norbornane-1′-carboxylate (5).**—A solution of 47.4 g of norbornene (**4**) and 43.5 g of ethyl azidoformate in 200 ml of pentane was allowed to stand for 5 days under ice cooling until a strong infrared band at 2160 $cm^{-1}$ characteristic of azido group disappeared. On removing the excess of norbornene under reduced pressure, 75.7 g (96%) of oily **5** was obtained: $\nu_{max}^{film}$ 2955, 1720, 1418, 1142, 970, 892, and 763 $cm^{-1}$.

**Ethyl 2,3-*exo*-*v*-triazolino[2.3]norborn-5-ene-1′-carboxylate (13)**, colorless prisms, mp 66–67°, and **ethyl 2,3-*exo*-*v*-triazolino[2.3]-benzonorbornene-1′-carboxylate (31)**, colorless prisms, mp 94°, were similarly prepared from norbornadine (**12**) and benzonorbornadiene, respectively.

For **13**, $\nu_{max}^{CCl_4}$ was 2980, 1713, 1413, 1142, 963, 907, 883, 760, and 705 $cm^{-1}$.

*Anal.* Calcd for $C_{10}H_{13}N_3O_2$: C, 57.96; H, 6.32; N, 20.28. Found: C, 57.90; H, 6.36; N, 20.39.

For **31**, $\nu_{max}^{CCl_4}$ was 2990, 1723, 1418, and 1143 $cm^{-1}$.

*Anal.* Calcd for $C_{14}H_{15}N_3O_2$: C, 65.35; H, 5.88; N, 16.33. Found: C, 65.57; H, 5.92; N, 16.62.

**Decomposition of Triazoline Derivatives in Methanol.**—When 75.7 g of **5** was added into 250 ml of absolute methanol and warmed to 40°, the violent evolution of nitrogen gas was observed. After the evolution of gas ceased, the solution was concentrated under vacuum and distilled at 75–76° (23 mm) to obtain 56.7 g (87%) of **ethyl 2,3-*exo*-aziridino[2.3]norbornane-1′-carboxylate (6)**: $n^{25.5}D$ 1.4833 [lit.[32] bp 99–100° (24 mm), $n^{25}D$ 1.4841]; $\nu_{max}^{film}$ 2930, 1710, 1380, 1300, 1260, 1185, and 1095 $cm^{-1}$.

*Anal.* Calcd for $C_{10}H_{15}NO_2$: C, 66.27; H, 8.34; N, 7.73. Found: C, 66.16; H, 8.45; N, 7.73.

The similar decomposition of **13** and **31** afforded the following compounds. **Ethyl 2,3-*exo*-aziridino[2.3]norborn-5-ene-1′-carboxylate (14)** was obtained in 60% yield: bp 80–82° (4 mm); $n^{25.5}D$ 1.5060; $\nu_{max}^{film}$ 2990, 1720, 1375, 1295, 1282, and 1230 $cm^{-1}$.

*Anal.* Calcd for $C_{10}H_{13}NO_2$: C, 67.02; H, 7.31; N, 7.82. Found: C, 67.16; H, 7.62; N, 8.08.

**Ethyl 2,3-*exo*-aziridino[2.3]benzonorbornene-1′-carboxylate (32)** was found in 97% yield: bp 130° (4 mm); $\nu_{max}^{film}$ 2990, 1726, 1375, 1280, 1215, 1190, 1165, 1100, 1025, 830, 757, and 740 $cm^{-1}$.

*Anal.* Calcd for $C_{14}H_{15}NO_2$: C, 73.34; H, 6.59; N, 6.11. Found: C, 73.08; H, 6.66; N, 6.17.

**Preparations of Aziridine Derivatives (7, 15, and 33).**—A solution of 6.3 g of **6** and 3.9 g of potassium hydroxide in 200 ml of ethanol was refluxed for 4 hr. After the ethanol was evaporated under reduced pressure, the mixture was diluted with water and extracted with ether. The ether layer was dried over potassium carbonate and concentrated under a stream of nitrogen gas. The residue was sublimed at 80° (10 mm) to yield 2.40 g (63%) of a waxy solid **7**, which quickly forms the carbonate on exposure to atmosphere. Compound **7** had $\nu_{max}^{CCl_4}$ 3280, 2920, 2840, 1460, 1445, 1355, 1335, 1295, 1208, 1188, 1140, 1118, 1090, 1015, 965, 945, 930, 918, 875, and 840 $cm^{-1}$. The oxalate of **7**, mp 138–139°, was analyzed.

*Anal.* Calcd for $C_9H_{13}NO_4$ (oxalate): C, 54.26; H, 6.58; N, 7.03. Found: C, 54.43; H, 6.66; N, 6.93.

In the same way **14** afforded **15** in 60% yield: bp 120–130° (bath temperature; 2 mm), which decomposes in atmosphere (attempts to prepare a salt of **15** with organic acid have failed); $\nu_{max}^{CCl_4}$ 3110, 3040, 2980, 1445, 1350, 1328, 1270, 1185, 1126, 1115, 1060, 998, 960, 890, and 847 $cm^{-1}$.

Similarly, **2,3-*exo*-aziridino[2.3]benzonorbornene (33)**, mp 95–96° (pentane), was obtained from **32** in 75% yield: $\nu_{max}^{CCl_4}$ 3290, 2970, 1310, 1265, 1190, 1165, 1110, 1046, 990, 940, 880, and 840 $cm^{-1}$.

*Anal.* Calcd for $C_{11}H_{11}N$: C, 84.04; H, 7.05; N, 8.91. Found: C, 84.25; H, 7.14; N, 8.96.

***syn*-7-N-Carbomethoxyaminonorbornene (9).**—Hydrogen bromide gas generated from a reaction of 79.3 g of bromine with tetralin was introduced into a solution of 57.2 g of **6** in 570 ml of pentane with stirring at room temperature during 5 hr. After removal of the solvent, the residue was dissolved in ether, washed with aqueous sodium carbonate, and dried over sodium sulfate. Evaporation of the solvent afforded 68.1 g of crude **8** (82% yield) which gradually decomposes on standing at room temperature to give a dark brown liquid, and therefore, it was immediately subjected to the following elimination reaction. To a sodium methoxide solution, which was prepared by dissolving 21.6 g of sodium metal in 310 ml of methanol, 24.6 g of **8** was added; this was boiled for 4.5 hr. After removal of the solvent, the residue was dissolved in ether, washed with water, and dried over sodium sulfate. The ether solution was evaporated and distilled at 90–103° (5 mm) to give 9.7 g (62%) of **9**, $n^{29}D$ 1.4902.

*Anal.* Calcd for $C_9H_{13}NO_2$: C, 64.65; H, 7.84; N, 8.38. Found: C, 64.35; H, 8.03; N, 8.30.

Vpc trace showed the presence of 10% impurity: $\nu_{max}^{CCl_4}$ 3430, 3060, 2940, 2850, 1735, 1508, 1360, 1225, 1116, 1059, and 713 $cm^{-1}$ (*cis* double bond).

***syn*-7-Acetamidonorbornene (10).**—A solution of 8.5 g of **9** in 130 ml of 30% aqueous methanol containing 28.6 g of potassium hydroxide was refluxed for 17 hr and then the methanol was removed by distillation under atmospheric pressure. Since the distilled methanol contained some amounts of the desired amine **1**, 1 ml of acetic acid was added to the distillate which was evaporated to dryness leaving 1-$CH_3COOH$ salt. Treatment of the salt with aqueous alkali recovered **1**. The reaction mixture concentrated by the distillation of methanol was dissolved in ether, washed with saturated sodium chloride solution, and combined with the above **1**. The ether solution was dried over potassium carbonate and evaporated, and the residue was distilled to give 3.4 g (61%) of crude **1** at 68–71° (40 mm). The crude **1** (1 g) was acetylated by treatment with 1.9 g of acetic anhydride in 10

(27) P. S. Bailey and J. G. Burr, Jr., *J. Am. Chem. Soc.*, **75**, 2951 (1953), and ref 22a.

(28) R. Huisgen and H. Reimlinger, *Ann.*, **599**, 161 (1956).

(29) (a) J. A. Mills, *J. Chem. Soc.*, 260 (1953); (b) T. Cohen and E. Jankowski, *J. Am. Chem. Soc.*, **86**, 4217 (1964).

(30) Refer to the Introduction in, H. Tanida and Y. Hata, *J. Org. Chem.*, **20**, 977 (1965).

(31) For the description of peaks, s = singlet, d = doublet, m = multiplet, dt = doublets of triplets, and so on.

(32) P. Schneiner, *J. Org. Chem.*, **30**, 7 (1965).

ml of pyridine to give 1.1 g of **10**. Elution chromatography on Florisil using ether–petroleum ether (bp 40–50°) followed by recrystallization from hexane gave 730 mg of pure **10** as colorless needles, mp 92.5°. Capillary vpc on a 45-m Golay column BDS showed that these needles were homogeneous.

*Anal.* Calcd for $C_9H_{19}NO$: C, 71.49; H, 8.67; N, 9.26. Found: C, 71.27; H, 8.87; N, 9.18.

Nmr spectroscopy ($CDCl_3$) showed two vinyl H (dt) at $\tau$ 4.00, one C-7H (d) at 6.15, two bridgehead H (m) at 7.20, three $CH_3CO$ (s) at 8.12, two C-5,6 *exo* H (m) at ~8.2, and two C-5,6 *endo* H (qui) at ~9.1; $\nu_{max}^{CCl_4}$ 3453, 3042, 2940, 2842, 1681, 1497, and 718 $cm^{-1}$.

***syn*-7-Norbornenylamine (1).**—The pure **1** was obtained as an oil, $n^{28}D$ 1.5062, from the pure **10** using a similar procedure to the alkaline hydrolysis of **9**. Product **1**·HCl was recrystallized from ether–methanol to give colorless needles: mp >250°; $\nu_{max}^{CCl_4}$ 3451, 3390, 3060, 2940, 2800, 1610, 1337, 1280, 1130, 865, and 715 $cm^{-1}$;[33,34] $\lambda_{max}^{methanol}$ 194 m$\mu$ ($\epsilon$ 5400); nmr ($CDCl_3$) two vinyl H at $\tau$ 4.02 (dt, long-range spin coupling with *anti* C-7H), one C-7H at 7.07 (tt), two C-1,4H at 7.39 (sex), two C-2,3-*exo*-H at ~8.3 (m), and two C-2,3 *endo*-H at ~9.1 (m).

*Anal.* Calcd for $C_7H_{12}ClN$ (hydrochloride): C, 57.72; H, 8.31; N, 9.62. Found: C, 57.95; H, 8.46; N, 9.93.

**5-Bromo-*anti*-7-N-carbethoxyaminonorbornene (16).**—A solution of 107. 9 g of **14** in 950 ml of pentane was cooled at −50° in an acetone–Dry Ice bath. Dry hydrogen bromide gas generated from 241 g of bromine and tetralin was bubbled with stirring into the solution during 6 hr. The solution gradually became whitely turbid. After additional stirring for 0.5 hr, 48 g of isopropylamine in 240 ml of ether was added to the solution below −30°, and then the acetone–Dry Ice bath was removed. Subsequently, 190 ml of saturated aqueous potassium carbonate was added with efficient stirring to the reaction mixture for 1 min and extracted with ether, and the ether solution was washed with aqueous sodium chloride and dried over sodium sulfate. Evaporation of the solvent gave 146.6 g (94%) of crude **16**. Since **16** was unstable, further treatment was carried out without purification.

***anti*-7-N-Carbethoxyaminonorbornene (18).**—Compound **16** (146 g) in 100 ml of ether was added over 0.5 hr at −50° to a stirred solution of 31.4 g of lithium metal in 2.2 l. of liquid ammonia. After stirring for 2 hr, the blue solution was successively treated with 69.3 g of ethanol and 161 g of powdered ammonium chloride, and the remaining ammonia was evaporated by warming. The residue was dissolved in water and extracted with ether, and the ether solution was dried over potassium carbonate. Evaporation of the solvent and distillation at 70–125° (3 mm) gave 62.5 g of an oil, which was dissolved in 100 ml of pentane and extracted three times with 30 ml of 2 *N* aqueous silver nitrate. The combined silver nitrate solution was treated with an excess of concentrated aqueous ammonia and extracted with ether, and the ether solution was washed with water. Drying and evaporation of the solvent gave 32.0 g of an oil, which was distilled at 91–95° (2 mm) to give 18.5 g (18%) of **18**. The analytical sample, $n^{24}D$ 1.4892, was obtained after further distillation and vpc of the sample indicated a slight contamination of 3-N-carbethoxyaminonortricyclene: $\nu_{max}^{film}$ 3420, 3040, 2940, 2840, 1730, 1330, 1220, 1058, 775, and 713 (*cis* double bond) $cm^{-1}$; nmr ($CDCl_3$) two vinyl H (t) at $\tau$ 4.0, one C-7H (d) at 6.59, and two bridgehead H (m) at 7.30.

*Anal.* Calcd for $C_{10}H_{15}NO_2$: C, 66.27; H, 8.34; N, 7.73. Found: C, 66.08; H, 8.50; N, 7.66.

The pentane layer treated with the silver nitrate solution was dried over sodium sulfate and evaporated to give 50.5 g (50%) of **17**, which was recrystallized from pentane to afford colorless needles: mp 62–63° (lit.[36] mp 64°); $\nu_{max}^{CS_2}$ 3440, 3042, 2920, 2840, 1727, 1210, 1060, 1055, 810, and 803 $cm^{-1}$. The nmr spectrum in $CDCl_3$ indicated no vinyl hydrogen.

*Anal.* Calcd for $C_{10}H_{15}NO_2$: C, 66.27; H, 8.34; N, 7.73. Found: C, 66.44; H, 8.33; N, 7.58.

***anti*-7-Acetamidonorbornene (19).**—The carbamate **18** (18.5 g) was dissolved in 120 ml of 30% aqueous ethylene glycol containing 20.4 g of sodium hydroxide, and refluxed for 3.5 hr. The reaction mixture was diluted with pentane, washed with aqueous sodium chloride, and dried over potassium carbonate. Evaporation of the solvent and distillation under nitrogen atmosphere gave 5.8 g of **2** boiling at 78–87° (70 mm). Acetylation of **2** with 10.2 g of acetic anhydride in 20 ml of pyridine afforded 7.4 g of crude **19**. Elution chromatography on Florisil using ether–petroleum ether gave 3.5 g (23%) of pure **19**, mp 123.5° (colorless needles from hexane). Capillary vpc on a 45-m Golay BDS column showed that this material was homogeneous.

*Anal.* Calcd for $C_9H_{13}NO$: C, 71.49; H, 8.67; N, 9.26. Found: C, 71.30; H, 8.73; N, 8.98.

Nmr spectroscopy ($CDCl_3$) showed two vinyl H (t) at $\tau$ 3.98, one C-7H (d) at 6.40, two bridgehead H (m) at 7.30, three $CH_3CO$ (s) at 8.05, two C-5,6 *exo* H (m) at ~8.3, and two C-5,6 *endo* H (m) at ~8.9; $\nu_{max}^{CCl_4}$ 3458, 3040, 2920, 2842, 1690, 1500, 1460, 1370, 1328, 1260, 1127, and 710 $cm^{-1}$.

***anti*-7-Norbornenylamine (2).**—The pure sample of **2** was obtained as a waxy solid by alkaline hydrolysis of the purified **19** in aqueous ethylene glycol and stored as its hydrochloride: mp >250°; $\lambda_{max}^{CH_3OH}$ 187 m$\mu$ ($\epsilon$ 10,900); nmr ($CDCl_3$) two vinyl H at $\tau$ 3.98 (t), one C-7H at 7.23 (m), two C-1,4 H at 7.62 (sex), two C-2,3 *exo*-H at ~8.3 (m), and two C-2,3 *endo*-H at ~ 9.0 (m).

*Anal.* Calcd for $C_7H_{12}ClN$ (hydrochloride): C, 57.72; H, 8.31; N, 9.62. Found: C, 57.93; H, 8.50; N, 9.59.

**7-Acetamidonorbornane (11)** was obtained as colorless needles in quantitative yield by catalytic reduction of **10** or **19** with palladium on charcoal in methanol, mp 129.5–130° (lit.[16] mp 130°).

**2-Bromo-*anti*-9-N-carbethoxyaminobenzonorbornene (22)** was prepared from **32** in 60% yield according to a similar procedure used for the preparation of **9**. Compound (**22**) had bp 130–133° (0.01–0.02 mm); mp 82.0–82.5° (colorless needles from methanol); $\nu_{max}^{CCl_4}$ 3380 (NH), 2940, 1720, 1495, 1230, and 1058 $cm^{-1}$; nmr ($CDCl_3$) four aromatic H ($A_2B_2$, m) at $\tau$ 2.82, one C-2 H (d) at 6.14, one C-9 H (d) at 6.22, one C-1 H (t) at 6.43, one C-4 H (m) at 6.58, one C-3 *exo* H (AB type dt) at 7.60, and one C-3 *endo* H (AB type dd) at 7.80.

*Anal.* Calcd for $C_{14}H_{16}BrNO_2$: C, 54.20; H, 5.20; N, 4.51. Found: C, 54.12; H, 5.26; N, 4.70.

***anti*-9-N-Carbethoxyaminobenzonorbornene (23).**—Compound **22** (2.5 g) was hydrogenated over palladium on charcoal in 150 ml of ethanol containing 660 mg of sodium acetate. The usual work-up afforded 1.36 g (73%) of **23**: bp 124–126° (0.2 mm); mp 67–68° (hexane); $\nu_{max}^{CCl_4}$ 3420, 2930, 1730, 1500, 1220, and 1057 $cm^{-1}$.

*Anal.* Calcd for $C_{14}H_{17}NO_2$: C, 72.70; H, 7.41; N, 6.06. Found: C, 72.82; H, 7.63; N, 6.05.

***anti*-9-Aminobenzonorbornene (20). A.**—A solution of 5.0 g of **23** and 4.3 g of potassium hydroxide in 40 ml of 25% aqueous ethylene glycol was refluxed for 3.5 hr. The reaction mixture was extracted with pentane, and the pentane layer was washed with water, dried over potassium carbonate, and evaporated under a nitrogen atmosphere. Distillation of the residue gave 2.4 g (70%) of **20**: bp 88–92° (1 mm); nmr ($CDCl_3$) four aromatic H ($A_2B_2$ m) at $\tau$ 2.94, one C-9 H (m) at 6.83, two bridgehead H (m) at 7.02, two C-2,3 *exo* H (m) at 8.06, and two C-2,3 *endo* H (m) at 8.86; $\nu_{max}^{CCl_4}$ 3412, 2940, 2842, 1612, 1462, and 1413 $cm^{-1}$. The hydrochloride had a melting point of >240°.

*Anal.* Calcd for $C_{11}H_{14}ClN$ (hydrochloride): C, 67,51; H, 7.21; N, 7.16. Found: C, 67.57; H, 7.22; N, 7.41.

**B.**—A solution of 1.5 g of 2,3-*exo*-aziridino[2.3]benzonorbornene (**33**) in 30 ml of methanol was added dropwise to a solution of 4.8 g of 48% aqueous hydrogen bromide in 30 ml of methanol at room temperature, and stirred for 2 hr. After removal of the solvent, the solution was made alkaline with 10% aqueous sodium hydroxide and extracted with ether. After drying over potassium carbonate, distillation gave 2.0 g of a bromide boiling at 118–124° (2 mm), which was, in turn, hydrogenated over palladium on charcoal in the presence of sodium acetate to afford 1.0 g (66%) of **20**.

**Lithium Aluminum Hydride Reduction of 7-Oxyiminonorbornene.**—A mixture of 17.9 g of 7-norbornenone, 12.7 g of hydroxylamine hydrochloride, and 15.2 g of sodium acetate in 500 ml of 70% aqueous methanol was allowed to stand overnight at room temperature. The reaction mixture was concentrated and

(33) The absorption maxima of NH stretching bands appears at 3390 and 3451 $cm^{-1}$ for **1** and at 3406 $cm^{-1}$ for **2**.[34] A number of typical examples of an internal interaction between a hydroxy group and $\pi$ electrons of a double bond have been provided by *syn*-7-norbornenol and related compounds because of their suitably fixed molecular geometry.[7,35] Little information is available concerning a similar interaction owing to an amino group and a double bond. Thus, the bands in **1** will be a typical example.

(34) Determined with a Perkin-Elmer Model 12C spectrograph, LiF prism, 20-mm cell.

(35) P. von R. Schleyer, D. S. Trifan, and R. Bacski, *J. Am. Chem. Soc.*, **80**, 6691 (1958).

(36) G. Müller and R. Merten, *Chem. Ber.*, **98**, 1097 (1965).

extracted with ether. The ether layer was washed with water and dried over sodium sulfate. Evaporation of the solvent and distillation at 70–73° (3 mm) afforded 16.5 g of an oil, which showed no carbonyl band in the infrared spectrum. The oil was treated with 10.2 g of lithium aluminum hydride in 400 ml of anhydrous ether under gentle reflux for 14 hr. The usual work-up followed by distillation at 80–90° (70 mm) gave 10.6 g of a basic oil, which was acetylated with acetic anhydride to give 5.7 g of mixture of amides. Capillary vpc on a 45-m Golay column BDS indicated it to be a mixture of **10**, **11**, and **19** in the ratio 1:10:89.

**Deamination of the *anti*-Amine 2. A. Identification of Products.**—A solution of 1.65 g of **2**·HCl in 22 ml of glacial acetic acid was maintained at 20 ± 0.1° with stirring while 1.56 g of solid sodium nitrite was added in numerous small portions over 30 min. The mixture was stirred for additional 5 hr and then allowed to stand overnight at room temperature. An additional 390 mg of sodium nitrite was added and stirring was continued for 1 hr more at 20°. The reaction mixture was poured onto crushed ice, treated with 40% aqueous sodium hydroxide, and saturated with sodium chloride. The oil which separated was extracted with three 40-ml portions of ether. The ether solution was dried over sodium sulfate and evaporated to dryness by slow distillation through a fractionating column leaving 1.10 g of an oil. Vpc analysis of the oil was carried out using two kinds of capillary columns (45-m Ucon LB-550-X and 45-m Apiezon L, at a flow pressure of 1.3 kg/cm² of helium as a carrier gas) and showed three well-resolved peaks which were identified as **24**, **25**, and **26**. The retention times on the Ucon column of 130° and on the Apiezon column of 90° were, for **24**, 10.3 and 8.1; for **25**, 20.0 and 7.9; for **26**, 18.8 and 13.1 min, respectively. Control expeiments demonstrated the absence of *syn*-7-norbornenol, bicyclo[3.2.0]hept-2-en-4-ol and its acetate, and 3-nortricyclenol and its acetate in amounts greater than 0.2% in the deamination products. The infrared spectrum of the above residue in $CCl_4$ differed from the mixture of authentic samples of **24**, **25**, and **26**, by two strong absorptions at 1625 and 1278 $cm^{-1}$ which were assigned to a nitrate not emerged on vpc.[37]

A small portion (100 mg) of the mixture was treated with 50 mg of lithium aluminum hydride in 20 ml of anhydrous ether. Capillary vpc analysis on the reduction product showed it to be a mixture of **24** and **25**. The further catalytic reduction over palladium on charcoal gave 7-chloronorbornane and 7-norbornanol which emerged, respectively, at 12- and 21-min retention times on a 45-m Ucon LB-550-X capillary column at 130° and with a flow pressure of 1.3 kg/cm² of helium; *endo*- and *exo*-2-norbornanol could not be detected. Isolation of the deamination products was carried out by preparative vpc on 2 m × 21 mm polyethylene glycol succinate column (10% on Chromosorb W) at 106° and with a flow rate of 600 ml/min. The retention times of **24**, **26**, and **25** were 4.5, 14, and 21 min, respectively. Each fraction collected was identified by comparison of infrared spectra with those of the authentic samples independently prepared.

**B. Quantitative Products Distribution.**—The sample of 135 mg of **2**·HCl was weighed in a 10-ml volumetric flask and filled to 10 ml with glacial acetic acid. Aliquots (2-ml portions of the acetic acid solution) were diluted with weighed amounts of water in varying ratios. Each of the aliquots was treated with 25 mg of sodium nitrite at 20 ± 0.1°, and allowed to stand for 4 hr. An additional 25 mg of sodium nitrite was added and maintained at 20 ± 0.1° for 2 hr more. The reaction mixture was poured into cooled 10% aqueous sodium hydroxide, saturated with sodium chloride, and subjected to the continuous extraction with 10 ml of ether for 0.5 hr. A weighed amount of *p*-cymene as an internal reference was added to the ether solution. This solution was examined by vpc analysis on 2 m × 3 mm stainless steel column packed with diethylene glycol succinate (5% on Chromosorb W) at 70° and with a flow pressure of 1.0 kg/cm² The retention times of **24**, **25**, **26**, and *p*-cymene were 2.5, 18.8, 11.6, and 4.4 min, respectively.

Quantitative distribution of the products was determined using the calibration curves made as follows. A weighed amount of *p*-cymene was added to the hexane solutions containing **24**, **25**, and **26** in varying, but accurately weighed ratios, and the mixtures were examined by vpc. Calibration curves were made by plotting the weight ratio of each of components to *p*-cymene *vs.* the ratio of the corresponding peak areas. Control experiments showed that the above procedure caused no epimerization of 7-norbornenols and their acetates. Table I listed the data thus determined, and the errors in the absolute magnitude of the figures are within ±1.5%.

**Deamination of the *syn*-Amine 1.**—A solution of 2.16 g of **1**·HCl in 29 ml of glacial acetic acid was maintained at 20 ± 0.1°, treated with 3.54 g of sodium nitrite, and worked up as in the deamination of **2**·HCl. The residual oil (1.74 g) was distilled at 80–85° (20 mm) to give 1.32 g of colorless oil. The infrared spectrum in $CCl_4$ showed a strong acetate band and a hydroxyl band around 3500 $cm^{-1}$. Vpc on a 45-m Ucon LB-550-X capillary column showed four well-resolved peaks. The product was hydrolyzed by methylmagnesium iodide in the usual manner. Vpc analysis of the thus obtained alcohol boiling at 103° (bath temperature; 26 mm) showed two peaks in the relative areas of 25:1 whose retention times were identical with those of **28** and **30**. The absence of other possible products mentioned in the text was established. The infrared spectrum of the alcohol mixture was identical with that of **28**, in which the contamination of **30** was too small to be detected. The products distribution described in the text was determined by the same procedure as in the case of **2**-HCl using tetralin as an internal standard. On a Ucon LB-550-X capillary column at 130°, **28**, **30**, **29**, and **27** emerged at the retention times of 21.5, 23.6, 25.8, and 27.2 min, respectively.

**Materials for Identification and Vpc Analysis.**—The preparations of **24**,[27] 7-chloronorbornane,[30] **25**,[38,39] **26**,[17] 3-nortricyclenol,[40] *syn*-7-norbornenol,[20a] and **28**[20a] were carried out according to the known methods.

*exo*-2-Norbornanol, mp 127–128° (lit.[41] mp 127.6–128.5°), was prepared by hydroboration of norbornene, and its *endo* isomer, mp 148–149.5° (lit.[42] mp 152.0–153.0°), by lithium aluminum hydride reduction of norcamphor. Acetylation of **28** with acetic anhydride in pyridine gave **27**, bp 92° (28 mm), $n^{20}D$ 1.4701.

*Anal.* Calcd for $C_9H_{12}O_2$: C, 71.02; H, 7.95. Found: C, 70.91; H, 8.01.

***syn*-Bicyclo[3.2.0]hept-2-en-4-ol (30).**—A solution of 160 mg of **28**, 182 mg of benzoquinone, and 716 mg of aluminum *t*-butoxide in 13 ml of benzene was boiled with stirring for 41 hr. The reaction mixture was cooled and washed with 10% aqueous hydrochloric acid, and then with 5% aqueous sodium hydroxide. After drying over sodium sulfate, evaporation of the solvent gave 69 mg of brown oil (bicyclo[3.2.0]hep-2-en-4-one). The oil was dissolved in 5 ml of anhydrous ether and treated with 12 mg of lithium aluminum hydride. After the usual work-up, an oil was distilled at 120–140° (bath temperature, 26 mm). This oil was analyzed with a 3 mm × 2 m diethylene glycol polyester column (5% on Chromosorb W) at 80° and with a 45-m Ucon LB-550-X capillary column at 140°, with a flow pressure of 1.3 kg/cm² of helium. The analysis with the two kinds of column showed that the oil was a mixture of 75% *syn*-**30**, and 25% *anti*-**28**. The retention time of the main **30** was identical with that of the minor alcohol derived from the deamination of **1**. Compound **30** showed $\nu_{max}^{film}$ 3360, 3040, 2920, 2850, 1460, 1102, 1072, 1058, 1030, 792, and 746 $cm^{-1}$.

**Deamination of 20.**—The deamination of **20** was carried out in 50% aqueous acetic acid. The infrared spectrum and vpc of the crude product indicated the formation of *anti*-9-benzonorbornenol with a small amount of its acetate. Recrystallization from hexane gave the pure alcohol in 85% yield, which was confirmed by mixture melting point and comparision of infrared spectrum with an authentic sample.[7]

(37) In the case of deamination of 2-norbornylamines, the very minor formation of a norbornyl nitrate was observed. However, it was reported that the minor side products of this kind did not affect the product distribution determined in this study. See ref 3.

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