on standing salicylalazine crystallized and was filtered to give fluorescent needles (0.42 g, 96%), mp 214–216° (lit.[8] mp 213°); mmp 214–216° with an authentic sample, mp 214–216°, prepared from salicylaldehyde and hydrazine dihydrochloride in water. The ir spectra of the two samples were indistinguishable.

Conversion of 10 to 9. Compound **10** (58 mg) was dissolved in dichloromethane and the red solution was allowed to stand in the air until the color had changed to yellow. The solution was evaporated, and the residue was crystallized from acetic acid to give yellow crystals (44 mg, 78%) of benzil diazine, mp 182–184°; mmp 182–184°.

***N*-Benzylbenzamide (7).** Benzoyl chloride (1.40 g, 0.0100 mol) in dry ether was added to a solution of benzylamine (2.14 g, 0.0200 mol) in dry ether (50 ml). White crystals formed, which were filtered and washed well with ether. The filtrate and washings were evaporated to give a white solid, which was crystallized from benzene to give *N*-benzylbenzamide (1.50 g, 50%), mp 103.5–104° (lit.[3] mp 105–106°).

Benzil Dihydrazone. (12). Benzil dihydrazone was prepared by boiling a solution of benzil and 2 equiv of hydrazine hydrate in 1-propanol under reflux for 60 hr: mp 151.5–152.5° (lit.[9] mp 152–153°); λ_{max} ($CHCl_3$) 2.90, 3.03; 6.19, 6.30 μ; δ ($CDCl_3$) 5.67 (br s, 4 H), 7.2–7.7 (m, 10 H).

Benzil Diazine (9). Benzil dihydrazone (2.38 g, 0.0100 mol) and benzil (4.20 g, 0.0200 mol) were heated under reflux in 1-propanol for 5 hr with a few drops of concentrated hydrochloric acid. A yellow crystalline mass, mp 171–180°, crystallized on cooling. Three crystallizations from glacial acetic acid gave benzil diazine, mp 184–185°.

Acknowledgment. We thank the National Research Council of Canada for support of this work.

Registry No.—**2,** 53555-48-9; **5,** 53555-49-0; **6,** 18076-30-7; **7,** 1485-70-7; **8,** 53555-51-4; **9,** 53555-50-3; **10,** 53555-52-5; **12,** 4702-78-7; sodium methoxide, 124-41-4; benzoyl chloride, 98-88-4; benzylamine, 100-46-9; benzil, 134-81-6; hydrazine, 302-01-2; benzil monohydrazone, 5344-88-7; benzaldehyde, 100-52-7.

References and Notes

(1) For paper II see P. Yates and E. M. Levi, *Can. J. Chem.*, in press.
(2) P. Yates, E. M. Levi, and B. L. Shapiro, *Can. J. Chem.*, **52**, 3343 (1974).
(3) E. Beckmann, *Chem. Ber.*, **23**, 3319 (1890).
(4) In contrast to the autoxidation of **3**,[2] this autoxidation does not appear to be photochemically induced; this is explicable in terms of the pathway proposed for the oxidation of **3**, wherein the photochemical step involves its conversion to an intermediate analogous to **10**.
(5) In the light of our considerations relating to the possible dimerization of **4**,[2] it is of interest to note that **17** could arise by dimerization of **15**.
(6) T. Curtius and K. Thun, *J. Prakt. Chem.*, **44**(2), 161 (1891).
(7) F. Feigl and V. Anger, "Spot Tests in Inorganic Analysis," 6th ed, Elsevier, Amsterdam, 1972, p 338.
(8) H. Cajar, *Chem. Ber.*, **31**, 2803 (1898).
(9) T. Curtius and A. Blumer, *J. Prakt. Chem.*, **52**(2), 117 (1895).

Diazotization of *endo*-7-Aminomethylbicyclo[3.3.1]nonan-3-ols and *endo*-7-Aminomethylbicyclo[3.3.1]non-2-ene[1]

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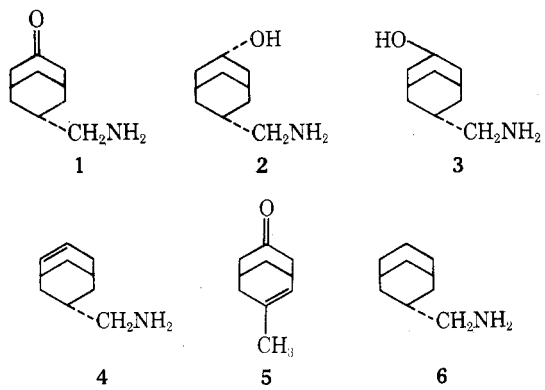
Diazotization of *endo*-7-aminomethylbicyclo[3.3.1]nonan-*exo*-3-ol (**3**) with aqueous nitrous acid produced 3-methylbicyclo[3.3.1]non-2-en-*exo*-7-ol (**7**), *exo*-7-methylbicyclo[3.3.1]nonan-3-one (**8**), and presumably *exo*-8-hydroxybicyclo[4.3.1]dec-2-ene (**9**) as major products. Exposure of *endo*-7-aminomethylbicyclo[3.3.1]nonan-*endo*-3-ol (**2**) to both protic (acetic acid or water) and aprotic (benzene) deamination resulted mainly in formation of 1-methyl-2-oxaadamantane (**19**) and 4-oxahomoadamantane (**20**) in addition to a component tentatively identified as *endo*-8-hydroxybicyclo[4.3.1]dec-3-ene (**21**). Compound **2** yielded *endo*-7-aminomethylbicyclo[3.3.1]non-2-ene (**4**) with dilute sulfuric acid. Deamination of **4** under conditions used for **2** provided 2-adamantanol (**28**) and 2-adamantyl acetate (**29**) as principal products. Elimination, transannular interactions, and apparently ring expansion comprise the dominant reaction routes. **7** gave **8** with sulfuric acid. The preparations of the isomeric 7-methylenebicyclo[3.3.1]nonan-3-ols (**10**) and *endo*-7-methylbicyclo[3.3.1]nonan-3-one (**11**) from reduction of 7-methylenebicyclo[3.3.1]nonan-3-one (**12**) are described. Endo alcohol **10b** provided **19** under acidic conditions. Mechanistic aspects of the investigation are treated.

Previous reports from this laboratory have described the preparation[5] of *endo*-7-aminomethylbicyclo[3.3.1]nonan-3-one (**1**) and its versatility as a precursor to various bicyclo[3.3.1]nonane derivatives.[6] Reduction of **1** with $NaBH_4$ in alcoholic solvents provided the corresponding alcohols,[7] **2** (endo) and **3** (exo). Keeping in mind the possibility for transannular interaction with the hydroxyl and alkenyl moieties, we intended to determine the response of **2** and **3**, as well as the aminoalkene **4**, toward various deaminating systems. Attention was devoted to mechanistic aspects.



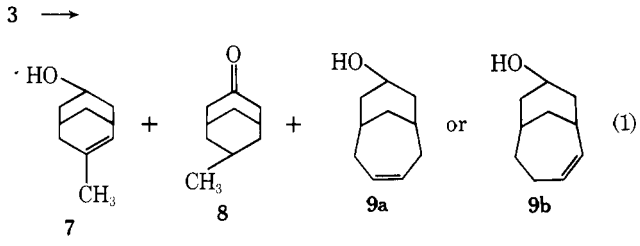
1 **2** **3** **4** **5** **6**

In related studies,[8] diazotization of **1** yielded 4-protoadamantanone and 3-methylbicyclo[3.3.1]non-2-en-7-one (**5**). *endo*-3-Aminomethylbicyclo[3.3.1]nonane (**6**) produced 3-methylbicyclo[3.3.1]non-2-ene, 3-methylenebicyclo[3.3.1]-nonane, *endo*-3-acetoxymethylbicyclo[3.3.1]nonane, and *endo*-3-hydroxymethylbicyclo[3.3.1]nonane.

Results and Discussion

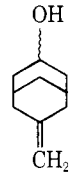
The isomeric amino alcohols **2** and **3** were subjected to deamination in three solvent systems. The major products resulted from elimination and transannular interactions. In addition, there was indication of ring expansion to the bicyclo[4.3.1]decene system.

***endo*-7-Aminomethylbicyclo[3.3.1]nonan-*exo*-3-ol.** When amino alcohol **3** was exposed to sodium nitrite and acetic acid in aqueous solution, the major products were 3-methylbicyclo[3.3.1]non-2-en-*exo*-7-ol (**7**) (50%), *exo*-7-methylbicyclo[3.3.1]nonan-3-one (**8**) (16%), and presumably *exo*-8-hydroxybicyclo[4.3.1]dec-2-ene (**9b**) (12%), eq 1.



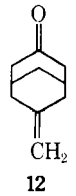
Several uncharacterized minor components (*ca.* 5% of the total) were also present. Structures for **7**, **8**, and **9** were assigned, in part, from spectral and microanalytical data. The nmr spectrum of **7** displayed an allylic methyl group, a multiplet for the alkene proton, and the characteristic seven-line multiplet indicating exo configuration[7] for the hydroxyl moiety.

The infrared spectrum of **8** showed strong carbonyl absorption, and the nmr data contained a doublet for the methyl protons, as well as broad absorption for the methylene protons adjacent to the carbonyl. The exo assignment for the methyl group is based on literature data[9-12] and independent synthesis. A simple preparative method for **8** consisted of exposing **7** to 75% sulfuric acid by analogy to work with lycopodine alkaloids.[13] Presumably, cation **15** (Scheme I) functions as an intermediate. Examples of the conversion of 7-methylenebicyclo[3.3.1]nonan-*exo*-3-ol[9,14] (**10a**) to **8** through the agency of sulfuric acid have been



10a, exo
b, endo

disclosed.[9,10] The stereochemistry was further corroborated by comparison with the endo isomer[11,15] (**11**) of **8** which was obtained by two routes. The first approach consisted of reduction of 7-methylenebicyclo[3.3.1]nonan-3-one[16] (**12**)



12

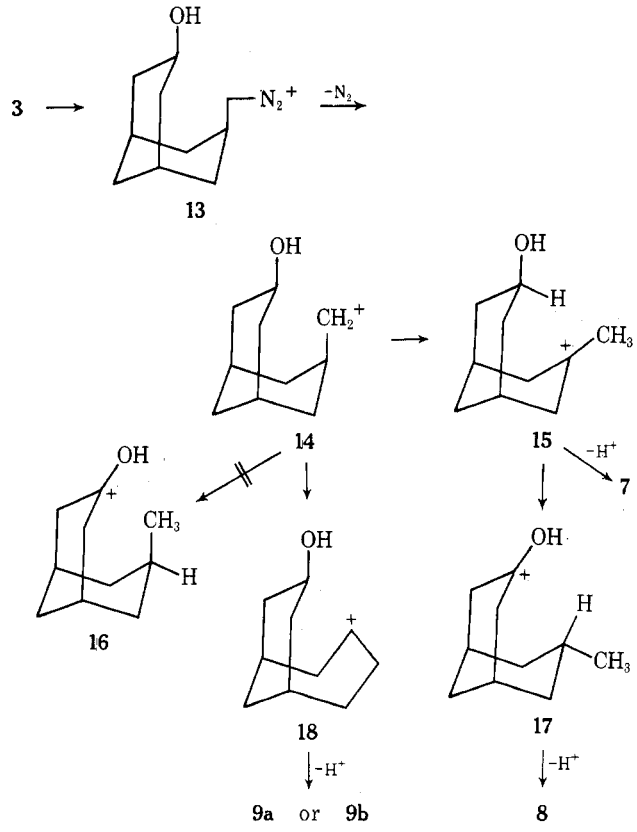
with $LiAlH_4$, followed by acetylation of the isomeric alcohols. After hydrogenation of the mixture of unsaturated acetates, the esters were saponified. Finally, chromic anhydride oxidation provided the desired ketone. A less complex route made use of direct hydrogenation[11,15] of **12** in the presence of platinum oxide. Ketone **11** exhibited spectral (ir and nmr) and physical properties different from those of its isomer **8**. An attempt to use **5**[8] as a precursor for **11** under reducing conditions (H_2–PtO_2) provided unchanged starting material. The reluctance to react can be attributed to the slow rate at which highly alkylated alkenes undergo hydrogenation.[17]

The unsaturated alcohol **9** had informative nmr features consisting of two alkene protons, as well as the seven-line multiplet for the proton α to the exo OH. A multiplet at δ 2.60, assigned to the allylic bridgehead proton, and the relative complexity of the spectrum support the unsymmetrical structure **9b**. The hydroxyl and alkene absorptions in the infrared region were also diagnostic, as was the molecular ion at *m/e* 152 in the mass spectrum. The isomeric alkenol **10a** was ruled out by comparison of the materials. Compound **10a** was prepared by $LiAlH_4$ reduction of **12**.

When isoamyl nitrite in acetic acid or isoamyl nitrite in acetic acid–benzene was used for deamination of **3**, mixtures arose which were difficult to separate by glpc. It appeared, however, that the yield of **8** was greater in these cases.

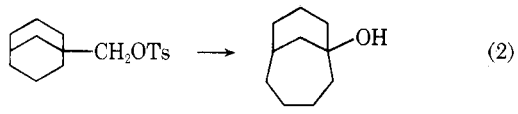
Scheme I outlines reasonable mechanistic pathways for formation of **7**, **8**, and **9** from **3**.

Scheme I



Rearrangement to **15** appears to be the predominant mode of reaction of the initially formed cation **14** (see below). Elimination from **15** comprises the major type of reaction, leading to **7**. Intermediate **15** can undergo further rearrangement by transannular hydride abstraction[10,13] with eventual production of **8** *via* **17**. Transannular hydride abstractions involving bicyclo[3.3.1]nonyl cations have been documented. For example, solvolysis[10] of the tosylate of *exo*-7-methylbicyclo[3.3.1]nonan-*exo*-3-ol provided more than 50% of 3-methylbicyclo[3.3.1]non-2-ene, in addition to *exo*-7-methylbicyclo[3.3.1]non-2-ene from 1,2 elimination. Additional examples are presented in a recent review.[18]

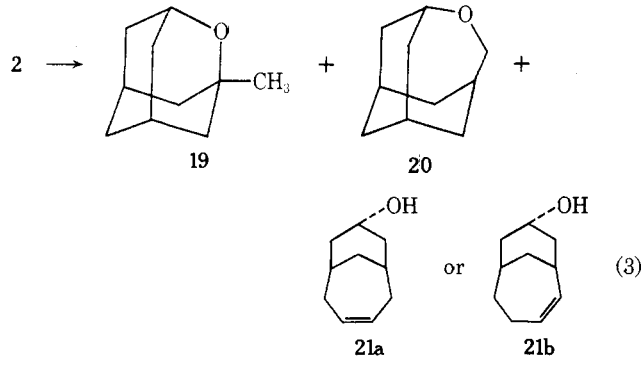
The Demyanov type rearrangement of **14** to **18** provides a rare example of ring expansion from a bicyclo[3.3.1]nonane to a bicyclo[4.3.1]decane. Subsequent elimination of a proton can occur with formation of **9**. A related ring enlargement *via* the (1-bicyclo[3.3.1]nonyl)methyl cation has been reported,[19] eq 2.



(2)

Prior literature that has come to our attention concerning diazotization of amino alcohols generally involved the 1-hydroxy-2-amino types. These compounds undergo ring expansion *via* Tiffeneu–Demyanov rearrangement.[20]

***endo*-7-Aminomethylbicyclo[3.3.1]nonan-*endo*-3-ol.** In the case of the endo alcohol **2**, the major products were 1-methyl-2-oxaadamantane (**19**) and 4-oxahomoadamantane (**20**) in all three systems, eq 3. Identification of **19** and **20** was based on spectral and literature data.[8,21,22]



(3)

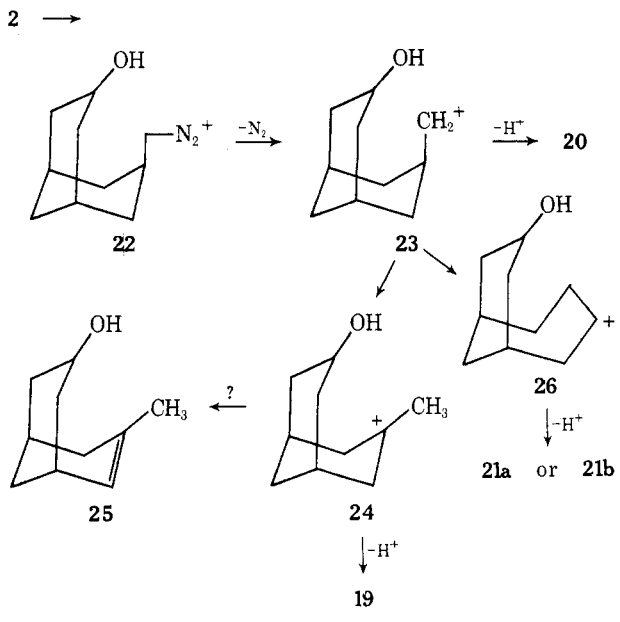
Our studies were carried out with a 95:5 mixture of **2**:**3** since alcohol of this composition (difficult to separate) was readily obtained by $NaBH_4$ reduction[7] of **1**. Upon diazotization with sodium nitrite and acetic acid in aqueous solution at 80–90°, **19** was formed in 36% yield and **20** in 26% yield. A third component (17%) has been tentatively assigned the *endo*-8-hydroxybicyclo[4.3.1]decene structure (most likely **21a**) from its spectral features. Another product (about 7%) appears to be a mixture on the basis of scrutiny by glpc and nmr. About four other components were present, each ~2–3% of the total. At least three of these minor products could arise from the small amount of **3** in the starting material. When **2** was deaminated with isoamyl nitrite in acetic acid at 80–85°, **19** was produced in 55% yield and **20** in 27% yield. Several minor, unidentified components (*ca.* 10% of the total) were also present along with less than 5% of **21**.

With benzene–isoamyl nitrite–acetic acid at reflux, **19** and **20** were again generated as the major products in yields of 23 and 60%, respectively, along with about 5% of **21** and minor components (about 8% of the total).

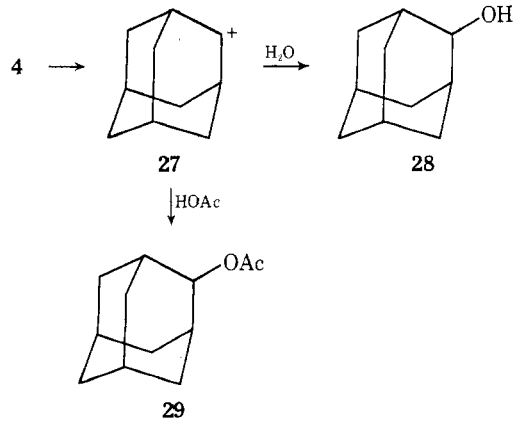
Since elimination leading to olefins is a common occurrence in deamination, it is noteworthy that this type of product was not observed as a major component. In an attempt to synthesize one of the possible hydroxyalkenes, 3-methylenebicyclo[3.3.1]nonan-*endo*-3-ol (**10b**), which might be formed during deamination, compound **12** was reduced with $LiAlH_4$ or $NaBH_4$. Only **19** was detected during glpc analysis of the product. Evidence (nmr) indicated that ring closure did not occur during reduction. Hence, conversion by acidic sites on the solid support may be responsible for some of the **19** isolated by glpc from the diazotization. When a base impregnated column was employed for glpc analysis, it was possible to separate and collect both **10a** and **10b** with very little **19** being formed. When the product mixture from the diazotization of **2** was examined with this column, substantial amounts of **19** were present, providing assurance that **19** is generated during diazotization. The conversion of **10b** to **19** during chromatography on silica gel has been reported,[9] as well as by acid catalysis.[21]

Formation of **19**, **20**, and **21** from **2** can be rationalized according to Scheme II.

Scheme II



Scheme III



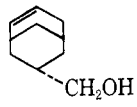
Attack of oxygen by the cation in **23** (see below) would yield **20**. Alternatively, **22** may serve directly as precursor to **20** *via* displacement of molecular nitrogen by the nucleophilic hydroxyl group. Rearrangement of **23** by a 1,2-hydride shift generates the more stable tertiary ion **24**. It is significant that a higher ratio of **20**:**19** is realized when nonpolar benzene serves as the medium. Presumably, the more polar acetic acid and water favor the conversion of **23** to **24**. Cation **23** may also rearrange by a second pathway (see above) to provide the ring-expanded, unsaturated alcohol **21** by way of elimination from **26**.

Transannular reactions in the bicyclo[3.3.1]nonane series are not uncommon. For example, both **5** and **12** produced 1-adamantanol on exposure to H_2/Pd.[8] Reductive cyclization was observed when **1** was hydrogenated in ethanol in the presence of Raney nickel.[7] Other examples are discussed elsewhere.[8,23]

***endo*-7-Aminomethylbicyclo[3.3.1]non-2-ene.** Exposure of amino alcohol **2** to refluxing dilute sulfuric acid resulted in formation of **4** in moderate to good yields. The proposed structure for the aminoalkene is consistent with spectral and microanalytical data. Catalytic hydrogenation produced **6** which was identical with the compound obtained from Wolff–Kishner reduction[6] of **1**. Further characterization of **4** was effected through its benzoyl derivative. Dehydration of alcohols by dilute sulfuric acid is com-

monly employed.[24a] Indeed, too highly concentrated sulfuric acid favors hydration of olefins.[24b]

Amino olefin **4** was subjected to diazotization in the three systems. In all cases, the predominant product resulted from the intermediate 2-adamantyl cation **27.** Deamination of **4** with sodium nitrite and acetic acid in aqueous solution afforded a mixture of three products (Scheme III), the major component being 2-adamantanol (**28**). One of the minor products was 2-adamantyl acetate (**29**), prepared independently by acetylation of **28** with acetyl chloride. The second minor substance, not completely characterized, appears to be an unsaturated alcohol, per-



30

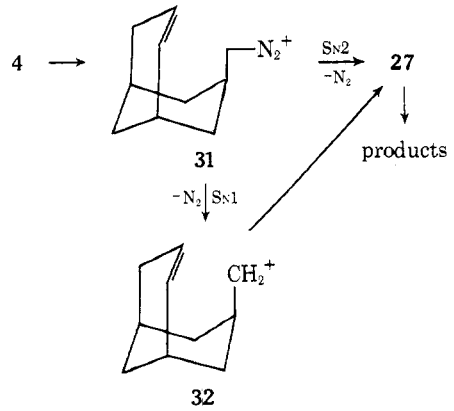
haps **30**[22,38] (or ring expanded product, see above) on the basis of ir and nmr data. Several contaminants were also present in trace amounts in the product mixture. Glpc analysis, in conjunction with authentic materials, pointed to the absence of 1-adamantanol and 4-protoadamantanols.

When diazotization of **4** was carried out in glacial acetic acid containing a small amount of acetic anhydride to ensure anhydrous conditions, the major product was 2-adamantyl acetate (**29**) (75%). Only one principal minor component (*ca.* 10%) was present. Although not identified, it most likely is the acetate of the alcohol which was tentatively assigned structure **30.**

Deamination of **4** was also carried out in benzene solution with isoamyl nitrite and acetic acid. Unlike previous runs in which reaction was immediate and rapid as indicated by nitrogen evolution at room temperature, there was no evidence of diazotization under these conditions. However, heating at reflux produced a mixture of products with **29** representing a major component. The other, unidentified products displayed relatively short retention times in glpc.

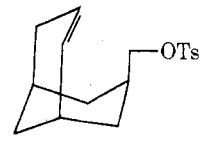
Formation of cation **27** from deamination of **4** might result from either of two paths (Scheme IV). The initially

Scheme IV



formed diazonium ion **31** might lose nitrogen *via* an SN1 type reaction to form the primary cation **32.** Ion **32** then attacks the π system generating the more stable ion **27.** However, it has been reported that diazonium ions do not undergo unimolecular fission to primary carbocations, but rather rearrange by a concerted process[25] (also see Schemes I and II). Alternatively, the π electrons in **31** could assist in the displacement of molecular nitrogen, *via* an SN2 mechanism, to yield **27** directly. The distinction between SN1 and SN2 routes in deamination reactions has been a topic of interest in recent years.[26]

Participation of π electrons in substitution reactions has literature precedent.[27] In a system closely related to our own, the tosylate of *endo*-7-hydroxymethylbicyclo[3.3.1]non-2-ene (**33**) provided mostly **28** in 80% acetone at

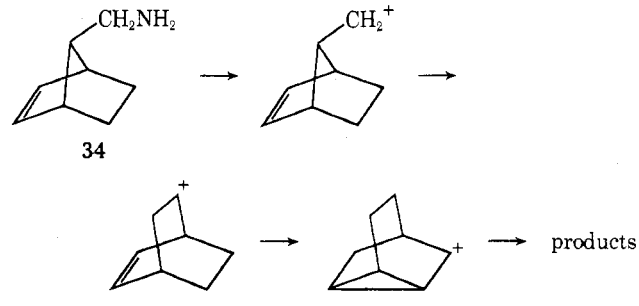


33

25°, along with about 5% of the internal return product, 2-adamantyl tosylate.[28] The rate ratio at 25° for **33** *vs.* its saturated counterpart was 2×20^4. In addition, **30** provided **28** with sulfuric acid.[22]

In deamination of a related compound **34,** involvement of the π electrons with the electrophilic site is not feasible at the initial stage[29] (Scheme V). With the isomeric amine,

Scheme V



the alkene function is unfavorably situated stereochemically for assisting in displacement.[29] Although the type of π participation illustrated in Scheme IV has been proposed in the case of certain diazonium ketones (enol forms), these hypotheses should be regarded as quite speculative.[8,30] Finally, diazotization of *endo*-3-aminobicyclo[3.3.1]nonane gave the 3-endo OH and bicyclonon-2-ene.[31]

Experimental Section

Melting points are uncorrected. Infrared spectra were obtained with Beckman IR-8 and IR-20A and Perkin-Elmer 137 instruments, calibrated with the 1601- cm^{-1} band of polystyrene. Varian T-60 and HA-100 instruments were used to obtain nmr data which are reported in parts per million relative to tetramethylsilane as internal standard. Gas chromatography was carried out with a Varian Aerograph instrument (A-90-P, 1700, or 1800) with the following columns: (A) 15 ft × 0.25 in., 15% Carbowax 20M and 10% NaOH on Chromosorb P (30–60 mesh); (B) 10 ft × 0.25 in., 15% Ucon 50HB2000 and 5% NaOH on Chromosorb W (45–60 mesh); (C) 10 ft × 0.25 in., 20% Carbowax 20M on Chromosorb W (45–60 mesh). Solutions were dried over Na_2SO_4. Microanalyses were performed by the Baron Consulting Co., Orange, Conn. Mass spectral data were obtained with a Hitachi Perkin-Elmer RMU-6E instrument.

The preparations of **2** and **3** have been described[7] previously. The sample of **2** used in diazotization was obtained from **1** and $NaBH_4$ in methanol, and contained 5–7% of **3** by glpc (column A at 225°).

Diazotization of 3. In Water. A mixture of **3** (1.7 g, 10 mmol), water (40 ml), sodium nitrite (0.85 g, 12 mmol), and acetic acid (0.8 ml, 13.5 mmol) was heated at 80–90° for 3 hr. After the cooled solution was extracted with methylene chloride, the organic layer was washed first with 5% sodium bicarbonate, next with water, and then dried. Glpc analysis (column C), with camphor as internal standard, indicated the presence of three major components: **7** (16%), **8** (50%), and **9** (12%]. Pure samples were obtained by preparative glpc followed by sublimation.

8: mp 51.5–53.5° (see below); ir (CCl_4) 1695 cm^{-1} (C=O); nmr

(CCl_4) δ 0.84 (d, 2, CH_3, J = 4–5 Hz); mass spectrum *m/e* 152 (M^+).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.62; H, 10.31.

2,4-Dinitrophenylhydrazone, mp 178.5–180°, from 95% ethanol (see below).

Anal. Calcd for $C_{16}H_{20}N_4O_4$: C, 57.82; H, 6.07; N, 16.86. Found: C, 58.07; H, 5.81; N, 17.02.

7: mp 46–49°; ir (CCl_4) 3350 (OH), 1670 (C—C), 1438, 1377 (CH_3), and 1050 cm^{-1} (C—O); nmr (CCl_4) δ 5.45 (m, 1, HC=C), 3.88 (m, 1, C*H*OH, J_{Ax} = 3–4 Hz, J_{Bx} = 13–14 Hz), 1.60 (s, 3, allylic CH_3); mass spectrum *m/e* 152 (M^+).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.76; H, 10.49.

9: mp 41.5–45.5°; ir (CCl_4) 3570, 3330 (OH), 1650 (C=C), 1040 (C—O), and 714 and 680 cm^{-1}; nmr (CCl_4) δ 5.55 (m, 2, alkene), 3.80 (m, 1, C*H*OH), 3.33 (s, 1, OH), 2.60 (m, 1); mass spectrum *m/e* 152 (M^+).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.63; H, 10.47.

In Acetic Acid. A solution of **3** (2 g, 12 mmol), acetic acid (30 ml), and isoamyl nitrite (2 ml, 15 mmol) was warmed at 60–65° for 3 hr. A greenish color and gas evolution were evident upon mixing. Water (30 ml) was added, and the cooled mixture was extracted with pentane and with benzene. The combined organic extract was washed successively with water, 5% sodium bicarbonate, and water, and then dried. Solvent removal yielded 2.5 g of a yellow oil. Glpc (column C) showed three principal products at least two of which were mixtures and not characterized further. The presence of an acetate was indicated by ir analysis. A positive test with 2,4-dinitrophenylhydrazine pointed to the presence of a ketone, most probably **8**.

exo-**7-Methylbicyclo[3.3.1]nonan-3-one (8 from 7).** Compound **7** (122 mg) was stirred with 4 ml of 75% sulfuric acid for 6 hr at room temperature. The reaction mixture was diluted with water, and then extracted with pentane. Solvent removal afforded the crude product. Glpc analysis (column C) indicated that the conversion of **7** to **8** was essentially quantitative with no by-products. A pure sample was obtained by preparative glpc and subsequent sublimation, mp 54.5–56.5° [lit.[9] mp 57–58°]. The nmr and infrared spectra were identical with those of the ketone isolated from diazotization of **3**; 2,4-dinitrophenylhydrazone, mp 183.5–184.5°, mixture melting point with same derivative of **8** from diazotization of **3**, 182–186°.

endo-**7-Methylbicyclo[3.3.1]nonan-3-one (11 from 12). (1).** Compound **12** (1.33 g) was shaken with 326 mg of PtO_2 in 120 ml of ethyl acetate under 40 psi of hydrogen for 48 hr. The catalyst was removed by filtration, and the solvent was evaporated under reduced pressure to give crude **11** as a yellow solid in greater than 95% yield. Glpc analysis (column C) showed the presence of one very minor impurity as well as the absence of **5**. Preparative glpc and sublimation provided pure **11**, mp 40–42° [lit.[11] mp 42.5–43.5°]; ir (CCl_4) 1706 cm^{-1} (C=O); nmr ($CDCl_3$) δ 0.81 (d, 3, CH_3, J = 6 Hz); mass spectrum *m/e* (rel intensity) 152 (35), 109 (65), 95 (100); 2,4-dinitrophenylhydrazone, mp 170.5–172°, from 95% ethanol.

Anal. Calcd for $C_{16}H_{20}N_4O_4$: C, 57.82; H, 6.07; N, 16.86. Found: C, 57.89; H, 5.95; N, 16.86.

(2). Compound **12** (2.0 g, 13.3 mmol) was reduced with (0.25 g, 6.6 mmol) $LiAlH_4$ in refluxing ether. The crude alcohol mixture was acetylated with acetic anhydride (5 ml)–sodium acetate (3 g)–water (25 ml) by warming on a steam cone for 45 min. Methylene chloride extraction provided 3.3 g of a light yellow liquid. Glpc analysis indicated only partial acetylation. An alternate process was carried out by stirring the crude product with acetyl chloride (7.5 ml)–triethylamine (30–35 ml)–benzene (75 ml) for 1.5 hr at room temperature. Samples of the endo and exo acetates were isolated by glpc. The infrared spectra (CCl_4) confirmed the presence of ester and exocyclic methylene functionalities.

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: (exo) C, 73.96; H, 9.61; (endo) C, 73.99; H, 9.15.

The crude mixture of acetates was hydrogenated at low pressure over 1 g of Pd/C catalyst in 50 ml of methanol. After the catalyst was removed by filtration, the saturated esters in the methanol solution were saponified by heating for 2–3 hr with 40 ml of 5% NaOH. The methanol was evaporated, and the basic solution was extracted with CH_2Cl_2. Drying and solvent removal provided the crude saturated alcohols.

The crude alcohol mixture was oxidized[32] as follows. An oxidizing solution of chromium trioxide (4 g), water (5 ml), acetic acid (12 ml), and concentrated sulfuric acid (3.6 ml) was added dropwise to a solution of the crude alcohols (*ca.* 200 mg) in 10 ml of CH_2Cl_2 and 5 ml of acetic acid until the orange color of the oxidant persisted at room temperature. After 15 ml of water was added, the layers were separated. The aqueous layer was extracted with CH_2Cl_2; the combined CH_2Cl_2 solution was washed with water and then dried. Solvent removal left a yellow oil. Preparative glpc (column C) provided a sample of **11** which proved identical (ir, nmr) with that obtained from the direct catalytic reduction of **12**.

1,3-Dibromoadamantane. A literature procedure[33] was followed with 1-bromoadamantane (100 g), bromine (200 ml), boron tribromide (25 g), and aluminum bromide (0.5 g). The progress of the reaction was monitored by periodic analysis of small aliquots by glpc. Work-up provided 125 g (90%) of the desired product, mp 108–111°, from Skelly B [lit.[34] mp 106–108° (sealed tube)].

12 from 1,3-Dibromoadamantane. A literature method[35] was used with 125 g of 1,3-dibromoadamantane (diglyme as solvent). Work-up led to 41 g (65%) of **12**, mp 159–164° [lit.[35] mp 160–164°]. The product contained traces of diglyme which did not interfere with subsequent reactions.

Attempted Preparation of 11 from 5. A 70-mg sample of **5** was shaken with 108 mg of PtO_2 in 21 ml of ethyl acetate under 40 psi of H_2 for 48 hr. Catalyst and solvent removal left a green colored oil. Glpc analysis (column C) in conjunction with the infrared spectrum indicated the oil to be mainly unreacted **5**.

Diazotization of 2. In Water. A mixture of **2** (2 g, 12 mmol), acetic acid (0.8 ml, 13.5 mmol), water (40 ml), and sodium nitrite (0.85 g, 12 mmol) was heated at 80–90° for 2 hr. The cooled solution was extracted with methylene chloride, and the extract was washed with 10% sodium carbonate and water, and then dried. Solvent removal afforded a yellow oil, 1.8 g. Glpc analysis (column C), 1-adamantanol as internal standard, showed the presence of **19** (36%) and **20** (26%). A minor component (7%) proved to be a mixture upon closer examination. A second component (17%) was tentatively identified as **21**: nmr ($CDCl_3$) δ 5.78 (m, 2, alkene), 3.80 (m, 1, C*H*OH), 2.75 (s, 1, OH, exchangeable with D_2O), 2.4–1.3 (rest of H); ir (CCl_4) 3450, 2995, 1647, 1047, and 707 cm^{-1}; mass spectrum, *m/e* 152 (M^+).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.54; H, 10.27.

Identification of **19** and **20** was accomplished by spectral comparison (ir and nmr) with authentic[36] samples. Several minor contaminants (each 2–3% of the total) were also present.

In Acetic Acid. A solution of **2** (2 g, 12 mmol) and isoamyl nitrite (2 ml, 15 mmol) in acetic acid (30 ml) was kept at 85° for 3 hr. Water (30 ml) was then added, and the cooled solution was extracted with pentane and with benzene. The combined extract was washed with 5% sodium bicarbonate and water, and then dried. Solvent removal afforded 4.2 g of light yellow oil. The product mixture contained appreciable quantities of isoamyl alcohol, isoamyl acetate, and isoamyl nitrite. Glpc analysis (column C), 1-adamantanol as standard, revealed the presence of **19** (55%) and **20** (27%) in addition to four–five minor components (*ca.* 10% of total).

In Benzene. A mixture of **2** (2 g, 12 mmol), acetic acid (0.8 ml, 13.5 mmol), and isoamyl nitrite (2 ml, 15 mmol) in 40 ml of benzene was heated at reflux for 3 hr. The cooled benzene solution was washed with 5% sodium bicarbonate and water, and then dried. Solvent removal afforded 4.4 g of light yellow oil. Isoamyl alcohol, isoamyl acetate, and isoamyl nitrite were present in appreciable quantity. Glpc analysis (column C, 1-adamantanol as internal standard) showed the presence of **19** (23–24%), **20** (60%), and **21** (4–5%) and four–five minor components (*ca.* 10% of total).

Reduction of 12 with $NaBH_4$. A mixture of compound **12** (2.5 g, 16.7 mmol), $NaBH_4$ (0.64 g, 17 mmol), and absolute ethanol (40 ml) was stirred at room temperature for 12 hr. Saline (20%, 5 ml) was added, and the reaction mixture was stirred a few minutes more. The volatile solvents were removed under reduced pressure, and the residue was extracted with CH_2Cl_2. Evaporation of the dried solution gave a crude product, 2.5 g. Glpc analysis (column C, 190°) indicated the presence of **19** and unreacted **12**, identified by their ir and nmr spectra. Glpc analysis (column A) provided **10a** and **10b** which were further purified by sublimation: **10a**, mp 89–90° [lit.[9] mp 93–94°]; **10b**, mp 79–81° [lit.[21] mp 88°]. The infrared and nmr spectral characteristics of the isomeric alcohols were in accord with prior observations.[14]

Compound **12** (0.5 g) was reduced by refluxing with 0.63 g of $LiAlH_4$ in 30 ml of ether for several hours. The reaction mixture was quenched with D_2O and then worked up as described above. The white solid which remained was examined by nmr. None of **19** was contained in the crude product mixture as evidenced by the

lack of the characteristic singlet for the methyl group in **19**. A sample of crude **10b** was subjected to gas chromatography (column C). The nmr spectrum of **19** obtained in this way indicated no incorporation of deuterium into the methyl group during rearrangement on the column, indicating that acidic sites on the solid support are responsible for the conversion of **10b** to **19** during glpc.

***endo*-7-Aminomethylbicyclo[3.3.1]non-2-ene (4 from 2 and 3).** A 75:25 mixture[7] of **2** and **3** (503 mg, 2.9 mmol) was refluxed for 24 hr in 40 ml of 0.1 *M* sulfuric acid. After the solution was made strongly alkaline with 20% sodium hydroxide, the resulting oil was taken up in ether. Solvent removal from the dried solution gave 350 mg, 80% of a light yellow oil which was 95% pure by glpc (column B). An analytical sample of **4** was obtained by preparative glpc: ir (neat) 3345, 3260 (NH_2), 2990 (vinyl CH), 1640 (C=C), and 1600 cm^{-1} (NH_2); nmr ($CDCl_3$) δ 5.68 (m, 2, CH=CH), 2.62 (d, 2, CH_2NH_2), and 1.67 (m, 13, CH, CH_2, and NH_2 exchangeable with D_2O).

Anal. Calcd for $C_{10}H_{17}N$: C, 79.41; H, 11.33; N, 9.26. Found: C, 79.62; H, 11.10; N, 9.01.

Benzamide, mp 135–136°, from cyclohexane: ir (KBr) 3220 (NH), 3050 (aromatic CH), 2990 (vinyl CH), 1635, 1550 (CONH); nmr ($CDCl_3$) δ 7.56 (m, 5, aromatic), 6.77 (m, 1, NH), 5.72 (m, 2, vinyl H), 3.40 (m, 2, CH_2NHCO), and 1.70 (m, 11, CH and CH_2).

Anal. Calcd for $C_{17}H_{21}NO$: C, 79.96; H, 8.29; N, 5.48. Found: C, 79.77; H, 8.26; N, 5.25.

When the above procedure was carried out with 12 g of the mixture of **2** and **3**, 500 ml of 0.1 *M* sulfuric acid, and methylene chloride as extracting solvent, **4** was isolated in 55% yield, bp 64–65° (0.24 mm), bp 42–43° (0.05 mm). Essentially all of the unreacted starting material was recovered by the extraction procedure, and then was separated from **4** by distillation.

6 from 4. A 20-mg sample of **4** in 15 ml of methanol was hydrogenated under 45 psi of hydrogen with 10% palladium on charcoal at room temperature for 2 hr. The catalyst was removed by filtration, and the solvent was evaporated to afford an essentially quantitative yield of **6**. The exact yield could not be determined because of rapid absorption of atomspheric carbon dioxide. Spectral analysis showed the absence of **4**; benzamide, mp 93–95° [lit.[6] mp 93.5–94.5°].

Diazotization of 4. In Water. A solution of sodium nitrite (593 mg, 8.6 mmol) in 2 ml of water was slowly added to a solution of **4** (651 mg, 4.3 mmol) in 10 ml of water containing acetic acid (0.6 ml, 10 mmol). The mixture was then stirred at room temperature for 20 min followed by heating on a steam bath for 30 min. The solid which had separated was taken up in ether. The ether solution was washed with 5% sodium bicarbonate and water, and then dried. Solvent removal gave 632 mg of a yellow solid. Glpc (column C) showed the solid to be 2-adamantanol **28** (90% pure, 87% yield) with minor amounts of 2-adamantyl acetate (**29**) (~5%) and an unsaturated alcohol, perhaps **30** (~5%). Products **28**[37] and **29** were identified by comparison of their infrared spectra to those of authentic samples.

In Acetic Acid. To a solution of 757 mg (5 mmol) of **4** in 10 ml of glacial acetic acid and 2 ml of acetic anhydride was added 690 mg (10 mmol) of sodium nitrite in small portions. The mixture was then stirred at room temperature for 30 min, followed by heating on a steam bath for 30 min. The mixture was diluted with 150 ml of water, and extracted with ether. The ether solution was washed with 5% sodium hydroxide and water, and then dried. Solvent removal afforded 803 mg of a light yellow oil. Glpc analysis (column C) showed the oil to be principally 2-adamantyl acetate **29** (75% yield), along with one unidentified contaminant.

In Benzene. A solution of **4** (765 mg, 5.1 mmol), isoamyl nitrite (610 mg, 5.2 mmol), and acetic acid (0.3 ml, 5.2 mmol) in 20 ml of benzene was refluxed for 1 hr. The solution was then treated with anhydrous potassium carbonate, filtered, and then evaporated to yield 870 mg of a yellow oil. Glpc analysis (column C) showed the oil to be composed of 2-adamantyl acetate **29** (44% yield) and a mixture of low boiling components.

29 from 28. A small sample of **28** and a large excess of acetyl chloride in benzene were warmed on a steam bath for 1 hr. The solution was then washed with water, 5% sodium hydroxide, and again with water. Solvent removal from the dried solution yielded **29**, ~98% pure by glpc. A pure sample of **29** was obtained by preparative glpc: ir (CCl_4) 1710 (C=O), 1235 ($OCOCH_3$), 1040 and 1025 cm^{-1}; nmr (CCl_4) δ 4.84 (br, 1, CHOCO) and 2.2–1.2 (m, 17, CH, CH_2, and $OCOCH_3$).

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Registry No.—2, 50361-66-5; **3,** 50361-68-7; **4,** 53516-37-3; **4** benzamide, 53516-38-4; **7,** 52927-60-3; **8,** 37741-56-3; **8** dinitrophenylhydrazone, 53516-39-5; **9b,** 53516-40-8; **10a** acetate, 53516-41-9; **10b** acetate, 53516-42-0; **11,** 40727-31-9; **11** dinitrophenylhydrazone, 53516-43-1; **12,** 17933-29-8; **21a,** 53516-44-2; **28,** 700-57-2; **29,** 19066-22-9.

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(38) Note added in Proof. Comparison with nmr spectra of authentic material indicates that the compound is not **30.** We are grateful to Professor P. v. R. Schleyer and Professor H. Wynberg for supplying the spectra.