Diazotization of *endo*-7-Aminomethylbicyclo[3.3.1]nonan-3-one and *endo*-3-Aminomethylbicyclo[3.3.1]nonane[1]

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Diazotization of *endo*-7-aminomethylbicyclo[3.3.1]nonan-3-one (**1**) under various conditions was investigated. In a protic medium (acetic acid), 3-methylbicyclo[3.3.1]non-2-en-7-one (**3**) was the only major product. With an aprotic system (benzene), 4-protoadamantanone (**4**) was the principal product, accompanied by **3**. *endo*-3-Aminomethylbicyclo[3.3.1]nonane (**2**) was diazotized under the same sets of conditions yielding (a) elimination products, 3-methylbicyclo[3.3.1]non-2-ene (**5**) and 3-methylenebicyclo[3.3.1]nonane (**6**); and (b) substitution products, 3-acetoxymethylbicyclo[3.3.1]nonane (**7**) and 3-hydroxymethylbicyclo[3.3.1]nonane (**8**). Catalytic hydrogenation of **3** resulted in reductive cyclization to 1-adamantanol in excellent yield. Sodium borohydride reduction of **3** furnished 3-methyl-7-hydroxybicyclo[3.3.1]non-2-ene (**9**), which was converted to 1-methyl-2-oxaadamantane (**10**) on exposure to a Lewis acid catalyst or hydrogen and palladium. The stereochemical and mechanistic aspects of the various transformations are treated.

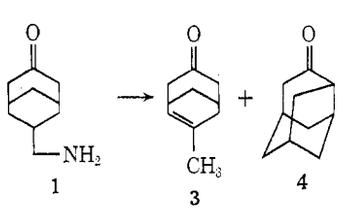
In prior work from this laboratory, rearrangement of 1-*N*,*N*-dichloroaminoadamantane with aluminum chloride, followed by exposure to hydrochloric acid, yielded *endo*-7-aminomethylbicyclo[3.3.1]nonan-3-one (**1**).[3] Wolff–Kishner reduction of **1** gave high yields of *endo*-3-aminomethylbicyclo[3.3.1]nonane (**2**).[4] The objective of the present study was to investigate the response of these amines to diazotization conditions, and to elucidate the mechanistic features. In addition, the chemical behavior of some of the novel products was examined.

Important advances in the chemistry of aliphatic deamination *via* diazotization have been made in recent years. The aspects of synthetic utility and mechanism have been reviewed.[5-9]

Results and Discussion

Synthetic Aspects.—Amines **1** and **2** were deaminated by two procedures. Procedure I entailed aprotic diazotization in benzene with an equivalent amount of acetic acid and a slight excess of isoamyl nitrile.[10] Procedure II involved reaction with isoamyl nitrite in acetic acid.

Under aprotic conditions, **1** gave principally 4-protoadamantanone (**4**) (67% yield), together with 3-methylbicyclo[3.3.1]non-2-en-7-one (**3**) (20% yield) and two minor products (unidentified ketones), eq 1



1 3 4 (1)

(Table I). Compound **4** was identified by comparison of ir and nmr spectra with those of the authentic material,[11-13] formation of the 2,4-dinitrophenylhydrazone derivative,[11,12] and Wolff-Kishner reduction to 4-protoadamantane.[14] Compound **3**, a colorless liquid, was characterized by the presence of a carbonyl band in the ir spectrum and an endocyclic double bond (δ 5.5, 1 H, indistinct doublet split by the bridgehead proton) and an allylic methyl (δ 1.6, 3 H, singlet) group in the nmr spectrum. Microanalyses were consistent with the proposed structure. Chemical identification was carried out by Wolff–Kishner reduction to 3-methylbicyclo[3.3.1]non-2-ene (**5**), which was also synthesized by an alternate route.[4] Under protic conditions, **1** gave **3** as the only major product (48% yield) with traces of **4** and unidentified ketones.

TABLE I

DIAZOTIZATION OF **1**[a]

Solvent	Products, % yield—**4**	**3**
C_6H_6	67	20
CH_3CO_2H	Trace	48
CH_3OH	*b, c*	*b, c*
n-C_6H_{14}[d]	65	15
o-$C_6H_4Cl_2$[e]	72	16
m-$C_6H_4(OCH_3)_2$	70	15
HCO_2H[f]	*b, g*	*b, g*
p-$ClC_6H_4CO_2H$[h]	69	9

[a] Amine, 0.01 mol; isoamyl nitrite, 0.011 mol; acetic acid, 0.01 mol; solvent, 20 ml; 80°; 1 hr; unless otherwise indicated. [b] Tar and a small quantity of viscous liquid containing traces of **3** and **4**. [c] Recovered amine, 60%. [d] Slow reaction; acetate salt of **1** is quite insoluble. [e] Gas evolution began at room temperature; fast reaction. [f] Acetic acid omitted. [g] Recovered amine, 54%. [h] Benzene solvent, acetic acid omitted.

Diazotization of amine **2** under either protic or aprotic conditions gave 3-methylbicyclo[3.3.1]non-2-ene (**5**), 3-methylenebicyclo[3.3.1]nonane (**6**), 3-acetoxymethylbicyclo[3.3.1]nonane (**7**), and 3-hydroxymethylbicyclo[3.3.1]nonane (**8**), eq 2 (Table II). Compounds **5** and **6** were identified by comparison with authentic samples.[4] Structural assignment for **7** was based on the ir spectrum (ester absorption) and

(1) Chemistry of Adamantanes and Related Compounds. VII; for the preceding publication in the series see ref 4; preliminary communication, J.-H. Liu and P. Kovacic, *Chem. Commun.*, 564 (1972).
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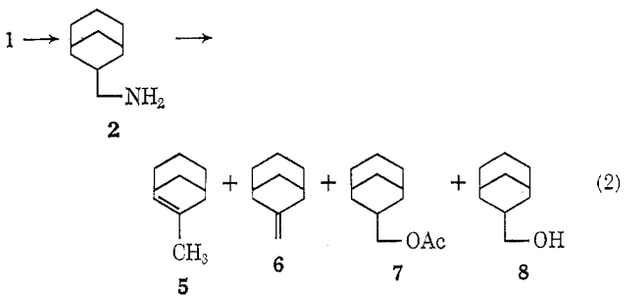


(2)

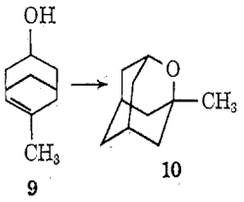
TABLE II
DIAZOTIZATION OF 2[a]

Solvent	Products, % yield 5	6	7	8
C_6H_6	21	15	35	4
CH_3CO_2H	29	6	28	5
CH_3OH[b]		No reaction		
CH_3CO_2H[b]		No reaction		
H_2O[c]		No reaction		

[a] Amine, 0.01 mol; isoamyl nitrite, 0.011 mol; acetic acid, 0.01 mol; solvent, 20 ml; 80°; 1 hr; unless otherwise indicated. [b] HCl salt of 2 was used. [c] H_2SO_4 (0.03 mol) in place of CH_3CO_2H; isomayl nitrite was replaced by 0.01 mol of sodium nitrite.

nmr spectrum (acetyl group at δ 2.1 and methylene doublet, J = 4 Hz, at δ 3.9). However, there were extraneous bands at δ 1.5–1.6, apparently arising from an impurity (about 10%), probably an isomeric material which did not separate during glpc. Rearrangement followed by combination with a nucleophile is a frequent occurrence in such reactions.[5,8] Information concerning the nature of **8** was obtained from the ir spectrum and comparison with the alcohol derived from hydrolysis of **7**. The nmr spectrum of **8** from diazotization exhibited extraneous bands, similar to those found for **7**, indicating the presence of a minor impurity (not separable in glpc). Independent syntheses of **7** and **8** were devised. Compound **6**, obtained by Hofmann degradation of **2**,[4] was converted to **8** *via* hydroboration and subsequent oxidation with hydrogen peroxide.[15] This alcohol displayed the same ir spectrum and glpc retention time as did that from diazotization. The nmr spectra were essentially identical except for absorption bands from the impurity in the diazotization product. Microanalysis provided data in agreement with theory. Esterification of **8** (from hydroboration) yielded acetate **7**. Glpc retention time and the ir spectrum corresponded to those of **7** from hydrolysis of **8** from diazotization. Nmr and microanalytical data were also used in identification.

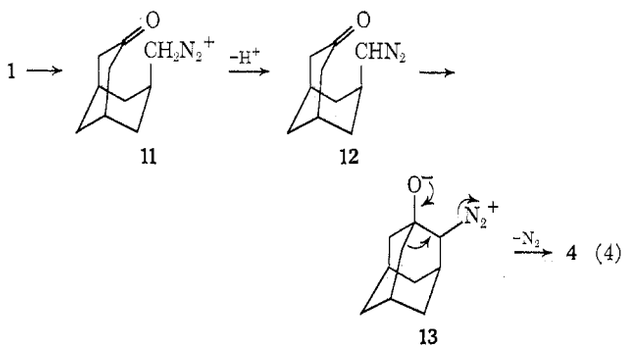
Hydrogenation of **3** in absolute ethanol with palladium on charcoal gave 1-adamantanol (91% yield). In contrast, sodium borohydride reduction generated 3-methyl-7-hydroxybicyclo[3.3.1]non-2-ene (**9**) in good yield. In addition to the ir spectrum for **9**, nmr data were particularly informative, showing an endocyclic olefinic proton (δ 5.85, 1 H, indistinct doublet), a proton adjacent to the hydroxyl group (δ 3.95), an allylic methyl group (δ 1.65), and an exchangeable proton (δ 2.9, singlet). Compound **9** was converted to 1-methyl-2-oxaadamantane (**10**) by exposure to formic acid at reflux, by hydrogenation with palladium on charcoal, or by treatment with acetic anhydride and zinc chloride, eq 3. Characterization of **10**, prepared by an alternate route, is described elsewhere.[4]



(3)

Stereochemistry.—The parent hydrocarbon, bicyclo[3.3.1]nonane, is known to exist in the chair–chair conformation,[16,17] despite some steric interaction of the hydrogens at C-3 and C-7. Monosubstitution at the C-3 or C-7 position may change the stereochemistry. Thus, an exo substituent maintains the original conformation, whereas an endo one results in conversion to the chair–boat form.[16,18–20] However, these two conformers are in rapid equilibrium at room temperature.[20] The aminomethyl groups in **1** and **2** are present in the endo configuration,[4] as well as hydroxymethyl and acetoxymethyl in **8** and **7**, respectively. Since **6** would be expected to prefer a chair–chair conformation, hydroboration should result in addition from the less hindered site,[21] also giving rise to the endo forms of **7** and **8**. We gave the endo assignment to the hydroxyl in **9** based on nmr splitting patterns, making use of pertinent literature data.[19,20,22,23] Further support was provided by analogy to hydride reduction of related ketones in the bicyclo[3.3.1]nonane series.[22]

Reaction Mechanisms.—Several pathways appear reasonable for conversion of **1** to **4**. One possibility is outlined in eq 4.



(4)

Formation of diazoalkanes from primary diazonium ions has been described.[5–8,24,25] **12** to **4** has analogy in the well-known intermolecular reaction of ketones

(15) H. C. Brown and G. Zweifel, *J. Amer. Chem. Soc.*, **83**, 2544 (1961).

(16) G. L. Buchanan, "Topics in Carbocyclic Chemistry," Vol. I, D. Lloyd, Ed., Plenum Press, New York, N. Y., 1969, p 199.

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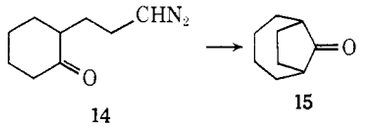
with diazoalkanes,[26] and particularly in the intramolecular example[27] depicted in eq 5. Our mechanistic

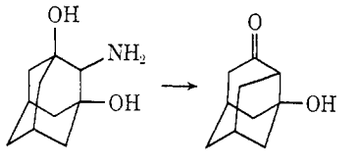


(5)

14 15

scheme is in accord with that proposed by Gutsche[27] and coworkers for **14** to **15**.

The intermediacy of **13** derives support from the observation that diazotization[11] of **16** gives **17**, eq 6.



(6)

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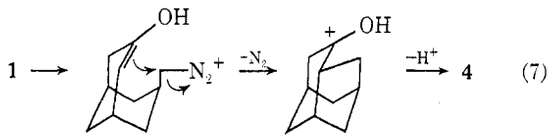
Other skeletal rearrangements of adamantanes to protoadamantanes have been noted by various investigators.[11,28-30]

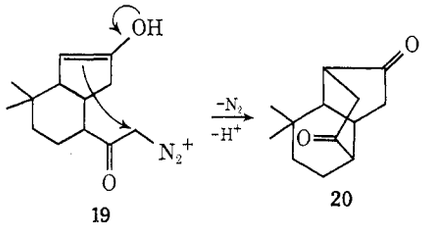
An alternative mechanistic possibility is shown in eq 7. A structure (**19**), strikingly similar to **18**, was



(7)

18

invoked[31] by Miyano and Dorn to account for an analogous interaction, eq 8. However, we feel that

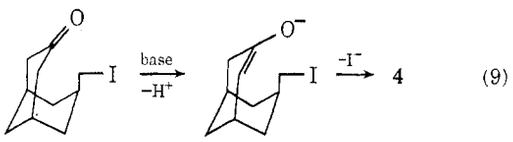


(8)

19 20

this pathway is much less likely since enol content in monoketones is extremely low.[32,33]

Mention should also be made of another route reported for the synthesis of **4**, involving exposure of the iodo ketone **21** to base.[12,13] The reaction may entail SN2 displacement of halide by enolate anion **22**, eq 9. If so, the process bears resemblance to that described in eq 7.

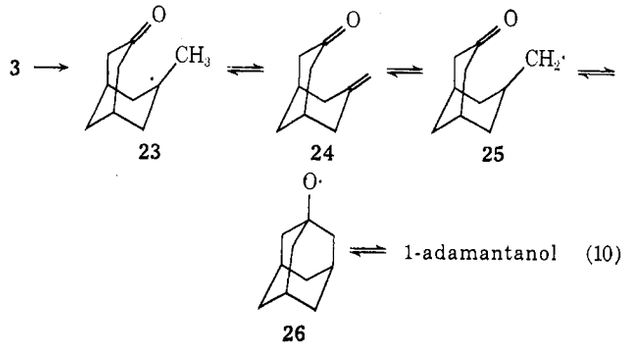


(9)

21 22

Compound **3** would result from hydride shift followed by proton elimination. The rearrangement–elimination pathway appears to be favored under protic conditions.[8]

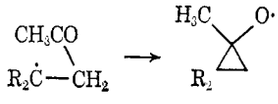
Attention will now be devoted to the ring closures observed for **3** and **9**. Transannular reactions in cyclic systems represent an interesting area of stereochemistry.[34] In relation to the present work, a number of examples are recorded in which a bicyclo[3.3.1]nonane is converted to an adamantane derivative.[16,35-37] Equation 10 furnishes a mechanistic rationale for



23 24 25 26

(10)

reductive cyclization of **3** to 1-adamantanol on hydrogenation with palladium on charcoal. Since alkene isomerization[38,39] can occur under these conditions, it is reasonable to postulate the existence of intermediates such as **23**, **24**, and **25**. In fact, 7-methylenebicyclo[3.3.1]nonan-3-one (**24**) was converted to 1-adamantanol almost quantitatively on exposure to the same reducing environment. Species **23** and **25** may be present as adsorbed forms on the catalyst. Alternatively, hydrogen atom attack on carbonyl oxygen may be involved at some stage. Generally, an olefinic bond is more susceptible to hydrogenation than the carbonyl group.[40a] The situation is complicated by the fact that the rate of reduction of the alkene linkage decreases with increasing substitution (three alkyl groups in the present case).[40b] Starting material **3** was recovered when hydrogen was omitted, indicating that catalyst alone is incapable of effecting isomerization. A transformation analogous to eq 10 is set forth in eq 11.[41] Conversion of **25**



(11)

to **26**, as well as eq 11, represents the reverse of β fission of alkoxy radicals.

Another case of ring closure was observed in the conversion of **9** to **10** under Lewis acid conditions or on contact with H_2/Pd, eq 3. The cation **27** is a reasonable intermediate when acid catalysis is employed.

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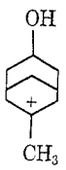

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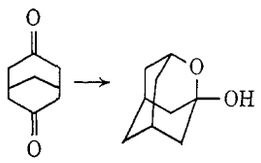
The radical counterpart of **27** may play a similar role during catalytic hydrogenation. A related overall result was obtained during hydrogenation of **28** in the presence of Raney nickel,[42] eq 12.



(12)

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Transannular ring closures of alcohols to tricyclic ethers have also been effected by lead tetraacetate[20,43a] or irradiation in the presence of mercuric oxide–iodine.[20] For example, bicyclo[3.3.1]nonan-3-ol served as precursor to oxaadamantane.[20]

Reaction conditions, mostly solvent, were altered in attempts to throw additional light on the course of reaction. In the diazotization of **1** (Table I), polarity of solvent was varied widely (acetic acid, benzene, and hexane). It has been pointed out that the extent of diazoalkane formation should increase in an aprotic medium.[8,25b] Changing the solvent from polar acetic acid to nonpolar benzene greatly increased the yield of **4**, in accord with the postulate set forth in eq 4. We are unable to predict which form, keto or enol, of **1** would be favored by a decrease in solvent polarity, and hence cannot judge the result in relation to eq 7. Whether the solvent was benzene or hexane made little difference in composition of the product mixture. Reaction rate (based on gas evolution) in hexane was considerably slower than in benzene, presumably a reflection of solubility or solvation factors.

Among other variables, the effect of alteration in the Lewis base character of the aromatic solvent (*o*-dichlorobenzene, benzene, and *m*-dimethoxybenzene) was explored. There was no significant change in the ratio of **3**:**4**. Rough approximations based on gas evolution gave the indicated influence on reaction rate, $o\text{-}C_6H_4Cl_2 > C_6H_6 \sim m\text{-}C_6H_4(OCH_3)_2$. The consequences of variation in acidity of the medium were also determined. When *p*-chlorobenzoic acid, a stronger acid, was substituted for acetic acid, the yield of **4** remained constant, whereas the amount of **3** decreased somewhat. With an additional increase in acidity (formic acid), little product was formed and most of the starting material was recovered, presumably owing to essentially complete protonation of the amine.

Table II summarizes data from additional scrutiny of diazotization involving **2**. Only elimination (**5** and **6**) and substitution (**7** and **8**) products were found. In benzene or acetic acid, the ratio of the two pathways was essentially the same, 36:39 and 35:33, respectively. The increase in yield of **5** in acetic acid appears to reflect the favorable effect of a polar solvent on ionic rearrangements.[8] However, some olefinic product may be derived from thermolysis involving *tert*-acetate impurity present in **7**.[43b] In both systems, acetate product (**7**) predominated over alcohol (**8**). This may be a consequence of the existence of tight ion pairs[9] (acetate anion) in the diazotization medium, in addition to the order of nucleophilicity,[44] $AcO^- > H_2O$.

Experimental Section

Materials and Analytical Procedures.—Benzene (thiophene-free, Mallinckrodt), isoamyl nitrite (Aldrich), 1-adamantanol (Aldrich), and glacial acetic acid (Du Pont, 99.7%) were used as received. Amino ketone **1**[3] and amine **2**[4] were synthesized according to literature procedures. Ir spectra were obtained with a Beckman IR-8 spectrophotometer (calibrated with the 1601.8-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 (δ) (in $CDCl_3$ unless otherwise indicated) relative to tetramethylsilane as internal standard. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn., and Micro-Tech Laboratories, Skokie, Ill. Glpc was conducted on a Varian Aerograph 1800 instrument with a 10 ft × 0.25 in. column, 15% Carbowax 20M on Chromosorb W (45/60 mesh). The yields were calculated by determining the weights of the glpc peak areas, and by weighing the individual collected products (total loss of 5–10% compared to injected weight). Melting points and boiling points are uncorrected.

Diazotization of 1. Procedure I.[10]—A mixture of **1** (1.67 g, 0.01 mol), benzene (20 ml), acetic acid (0.8 g, 0.01 mol), and isoamyl nitrite (1.4 g, 0.011 mol) was placed in a flask equipped with a condenser and drying tube. The mixture was heated at 80° for 1 hr. Gas evolution immediately occurred and gradually subsided. The homogeneous solution was cooled and washed in succession with water, 5% sodium carbonate, and water, then dried and freed of benzene. Glpc analysis of the light yellow oil (2 g) (isothermal at 180°, 100 ml/min) revealed the presence of 4-protoadamantanone (**4**) (67% yield) and **3** (20% yield).

Compound **4**, mp 206.5–207.5° (sealed tube), lit. mp 205–208°,[11] 210–212°,[12] 212–214°,[13] was identified by comparison of ir and nmr spectra with those of the authentic material. The 2,4-dinitrophenylhydrazone (bright orange, mp 194–195°, lit. mp 193–194.5°,[11] 195–196°[12]) was obtained after three crystallizations from ethanol–chloroform. Wolff–Kishner reduction of **4** gave protoadamantane in 65% yield, mp 210–212° (sealed tube) (lit.[14] mp 210.5–212°).

Procedure II.—A mixture of **1** (5.8 g, 34.5 mmol), acetic acid (60 ml), and isoamyl nitrite (9.7 g, 83 mmol) was heated at 80° for 1 hr. Gas was rapidly evolved at room temperature. Water (200 ml) was added to the cooled solution, followed by extraction with Skelly F. The organic layer was washed in succession with water, dilute base, and water, dried, and freed of solvent. The crude product (5.5 g) on distillation provided **3**, colorless liquid (2.5 g, 48% yield): bp 138–140° (17 mm); ir (neat) 2970, 2850, 1710, 1420, 1380, 1370, 1350, 1300, 1230, 1170, 1100, 1055, 910, and 835 cm^{-1}; nmr δ 5.5 (indefinite d, 1 H), 2.9–1.9 (m, 10 H), 1.6 (s, 3 H).

Anal. Calcd for $C_{10}H_{14}O$: C, 79.96; H, 9.39. Found: C, 79.87; H, 9.53.

Chemical confirmation of the structure of **3** was obtained by Wolff–Kishner reduction to **5**, which was identical to authentic material.[4]

Hydrogenation of 3 to 1-Adamantanol.—Compound **3** (0.6 g, 4 mmol) was hydrogenated overnight at room temperature in 50 ml of absolute ethanol with 10% palladium on charcoal (0.3 g) in a Parr apparatus. After filtration, removal of solvent afforded 1-adamantanol (0.55 g, 91% yield) as a white solid, identified by comparison with commercial material. In a control experiment, in which hydrogen was replaced by nitrogen, glpc after work-up indicated that starting material was recovered unchanged.

(42) H. Stetter, P. Tacke, and J. Gärtner, *Chem. Ber.*, **97**, 3480 (1964).

(43) (a) P. Brun, M. Pally, and B. Waegell, *Tetrahedron Lett.*, 331 (1970). (b) We are grateful to a referee for mentioning this possibility.

(44) J. March, "Advanced Organic Chemistry: Reactions, Mechanisms, and Structures," McGraw-Hill, New York, N. Y., 1968, p 289.

Hydrogenation of 24 to 1-Adamantanol.—7-Methylenebicyclo-[3.3.1]nonan-3-one[45] (0.5 g, 3.3 mmol) was hydrogenated, and the product was isolated as described for **3**. 1-Adamantanol (0.5 g, 98% yield) was obtained.

***endo*-3-Methyl-7-hydroxybicyclo[3.3.1]non-2-ene (9).**—A mixture of **3** (0.75 g, 5 mmol), absolute ethanol (150 ml), and sodium borohydride (0.76 g, 20 mmol) was stirred at room temperature overnight. Water was added, and the product was extracted with chloroform. Evaporation of solvent from the dried solution provided **9** (0.4 g, 50% yield by glpc analysis): mp 32.5–33°; ir (CCl_4) 3580, 2950, 1430, 1380, 1350, 1300, 1200, 1110, 1070, 1060, 760, and 930 cm^{-1}; nmr δ 5.85 (indefinite d, 1 H), 3.95 (m, 1 H),[19,20,22,23] 2.9 (s, 1 H, exchangeable with D_2O), 2.5–1.5 (m, 13 H, sharp s at 1.65).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 79.04; H, 10.47.

1-Methyl-2-oxaadamantane (10). Procedure A.—A product mixture containing **9** (principal component, 0.15 g, 1 mmol) was heated at 100° in formic acid (3 ml) for 8 hr. After the mixture was cooled, ether (20 ml) and water (20 ml) were added. The organic layer was washed with 5% sodium carbonate and then water, dried, and freed of solvent. Glpc analysis indicated that the main product was **10** (0.13 g, 88% yield) whose spectral data were identical with previously reported values.[4]

Procedure B.—Compound **9** (0.288 g, 1.88 mmol) was hydrogenated as described for the hydrogenation of **3**. An 82% yield (0.23 g) of **10** was obtained.

Procedure C.—In an attempt to synthesize the acetyl derivative,[46] a mixture of **9** (2 g), acetic anhydride (25 ml), and zinc chloride (2 g) was heated at 95–105° for 1 hr. The cooled solution was quenched with ice water and extracted with ether. The ether layer, after being stirred overnight with 10% sodium bicarbonate, was separated, washed with water, dried, and freed of solvent. A dark brown liquid (1 g) was obtained which contained **10** as the major component (glpc).

Diazotization of 2.—Diazotization of **2** under various conditions was performed as described in the case of **1**, yielding **5**, **6**, **7**, and **8**. Compounds **5** and **6** were identified by comparison with authentic samples.[4] Compound **7** was identified by comparison with authentic material (*vide infra*). The ir spectra and glpc retention times were essentially identical. However, the nmr spectrum of the diazotization product indicated the presence of an impurity (about 10%, nmr absorption at δ 1.5–1.6). Compound **8** was identified by comparison with authentic material (*vide infra*). The ir spectra and glpc retention times were essentially identical (more thorough investigation was not carried out because of the paucity of material).

3-Hydroxymethylbicyclo[3.3.1]nonane (8) from 6.—Hydroboration[15] of **6** (1.3 g, 9.6 mmol) gave 1.1 g of liquid product. Glpc analysis indicated that **8** (0.91 g, 62% yield) was the principal component: ir (neat) 3420–3350, 2900, 2860, 1460, 1110, 1080, 1040, 1020, and 990 cm^{-1}; nmr δ 3.5 (d, 2 H, J = 4 Hz), 2.3–1.8 (m, 16 H, one exchangeable with D_2O).

Anal. Calcd for $C_{10}H_{18}O$: C, 77.86; H, 11.76. Found: C, 77.58; H, 12.01.

8 from 7.—Acetate **7**, obtained from diazotization of **2**, was hydrolyzed with 20% sodium hydroxide. The ir spectrum and glpc retention time of the product were essentially identical with those of the alcohol obtained from hydroboration of **6**. However, the nmr spectrum showed the presence of an impurity (about 10%, absorption at δ 1.5–1.6.

3-Acetoxymethylbicyclo[3.3.1]nonane (7) from 8.—A mixture of **8** (0.83 g, 5.4 mmol, obtained from **6**), zinc chloride (1 g, 7.3 mmol), and acetic anhydride (12.5 g) was stirred at 105° for 1 hr, then cooled, quenched with ice water, and extracted with ether.[46] The ether solution was stirred with 5% sodium carbonate for 5 hr at room temperature. After the ether layer was separated, washed with water, dried, and freed of solvent, crude **7** was obtained (1.1 g). Glpc analysis indicated 90% purity (92% yield). Product from glpc collection showed ir (neat) 2950, 2880, 1760, 1470, 1360, 1220, 1110, 1080, 1030, 980, and 885 cm^{-1}; nmr δ 3.9 (d, 2 H, J = 4 Hz), 2.1 (s, 3 H), 2.1–0.9 (m, 15 H).

Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.44; H, 10.26. Found: C, 73.67; H, 10.43.

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Registry No.—**1**, 34650-78-7; **2**, 37445-20-8; **3**, 38339-46-7; **6**, 19437-17-3; **7**, 41189-05-3; **8**, 19490-36-9; **9**, 41189-07-5; **10**, 6508-22-1; isoamyl nitrite, 110-46-3.

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Thermal and Photochemical Reactions of Some Bicyclic Aziridine Enol Ethers[1a]

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Acid–base-catalyzed, thermal, and photochemical rearrangements of some bicyclic aziridine enol ethers are described. For example, 6-phenyl-2,4-bis(benzhydrylidene)-3,5-dioxa-1-azabicyclo[4.1.0]heptane (**3a**), an azirine–ketene adduct, rearranges on alumina to give dioxazepine **4**, which undergoes a further transformation to yield lactone **6**. The latter is converted to the isomeric 1,3 diketone **8** on treatment with alcoholic base. On the other hand, thermolysis of **3a** at 140–150° gives the seven-membered ring diether **15a**, an isomer of **4**, and lactone **16a**, an isomer of **6**. Dioxazepine **15a** rearranges to **16a** on further heating while **15c** leads to the five-membered lactone **19c**. Photolysis of **3a** at 310 nm results in the formation of a mixture of compounds from which **15a** and **16a** are isolated. Further photolysis of **15a** affords **16a**. These results are discussed. The mechanistic pathway for both pyrolysis and photolysis involves R–O cleavage of a cyclic enol ether C=C—O—R followed by O–C or C–C ring closure with rearrangement of R.

Imines have been shown to react with ketenes to yield 1:1 and/or 1:2 adducts of structures of type **1** and **2**, respectively.[2] In contrast, we have found that a number of 1-azirines react with diphenylketene to give 1:2 cycloadducts that possess the dioxa-1-azabicycloheptane structure **3**.[3]

One interesting feature of this novel heterocyclic system is that it contains a variety of functional groups. Of special interest would be the comparison of the thermal and photolytic behavior of this fused three-

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