stirred slurry of 250 mg of lithium aluminum hydride in 20 ml of ether was added dropwise 250 mg of **2** in 15 ml of ether. The resulting mixture was stirred at room temperature for 2 hr. Hydrolysis was effected by addition of aqueous HCl. The layers were separated and the aqueous layer was extracted with ether. The ether extract was washed with water and dried, and the solvent was removed by distillation to give 250 mg of a crude mixture of *trans*- and *cis*-3-vinylcyclohexanols identical with the material obtained from photolysis of **2** in cyclohexane. Glpc analysis indicated that the two isomers were present in ratio of 10:90.

Photolysis of 1 and 3 at 2537 Å. The following samples were prepared in quartz test tubes and irradiated at 2537 Å in a Rayonet reactor using a merry-go-round: (a) 10.4 mg of **1** (98%, no **3**) in 1.04 ml of cyclohexane, and (b) 13.0 mg of **3** (96% + 4% **1**) in 1.30 ml of cyclohexane. After 15 min, glpc analysis revealed that 17% of **3** had been converted to **2**, while only 3% of **1** had been converted to **2**. Conversion of **3** to **1** was also more rapid than the conversion to **1** to **3**. The difference in per cent of **2** in these reactions increased until it reached 25% (1 hr), after which time **2** decreased as the per cent of **3** reached the same level in both samples.

Acid-Catalyzed Reaction of 3. A solution of 25 mg of **3** and 3 mg of *p*-toluenesulfonic acid in 2 ml of benzene was allowed to stand for 4 days at 25°. Glpc indicated a decrease of ~20% in the amount of **3** present, but no increase in **1**.

Pyrolysis of 3. A solution of 15 mg of **3** in 1 ml of xylene was heated in reflux for 1 hr. No **2** was observed by glpc, but **1** increased relative to **3**. Quantitative glpc revealed that the increase in **1**, as well as the increase in a higher retention time product, resulted from transformation of **3** both to these compounds and to products not detectable by glpc (presumably polymers). The loss of **3** was divided about evenly between these two processes.

Registry No. 1, 31598-70-6; **2**, 1740-63-2; **3**, 43101-33-3; 4-cyclooctenol, 4277-34-3; 4-vinylcyclohexene, 100-40-3; 3-cyclohexen-1-yl methyl ketone, 7353-76-6; 4-vinylcyclohexanone, 1740-64-3; *trans*-3-vinylcyclohexanol, 43101-34-4; *cis*-3-vinylcyclohexanol, 43101-35-5.

References and Notes

(1) (a) Supported by a research grant from the NSF. (b) Alfred P. Sloan Fellow, 1968–1970; John Simon Guggenheim Fellow, 1970–1971. (c) NDEA Title IV Fellow, 1965–1968; NSF Trainee, 1968–1969. (d) PRF Predoctoral Fellow, 1968–1969.

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Deamination of 1-Adamantylamine

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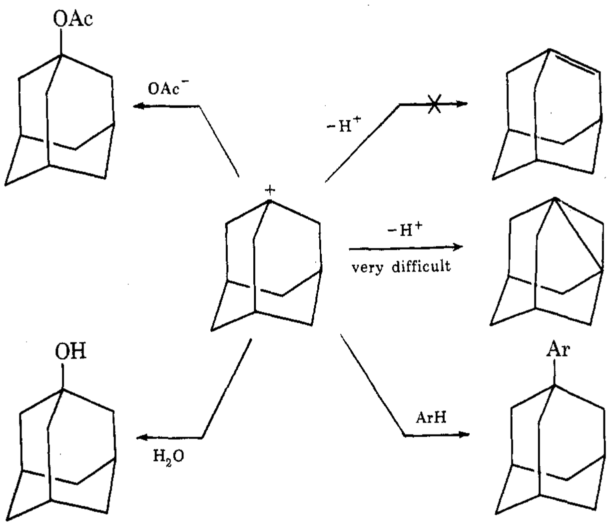
Kazanskii has reported[1] that the deamination of 1-adamantylamine by nitrous acid affords 1-adamantanol and adamantane in 20 and 80% yields, respectively. The adamantane must arise by hydride abstraction, and the necessary stoichiometry of such a process, with adamantane derivatives as the only possible hydride sources, makes the high yield of adamantane surprising. However, intermolecular hydride shifts are known for other adamantane systems[2-4] and therefore this reaction is of mechanistic interest. Accordingly, we decided to examine in detail the deamination of adamantylamines.

Two types of deamination reactions were studied: "normal," with aqueous acid and sodium nitrite;[5] and aprotic, employing isoamyl nitrite and 1 equiv of acetic acid.[6] The product analyses are contained in Table I.

Within our limits of detection (0.1%) no adamantane is formed under any conditions; the only products are 1-adamantanol and 1-adamantyl acetate. We must conclude that intermolecular hydride transfer is not an important reaction pathway in deamination, and therefore that the earlier results[1] are in error. This conclusion is strengthened by our observation that adamantane is not found even when deamination is carried out in the presence of the excellent hydride source, triphenylmethane (Table I).

In examining the literature on aprotic deaminations of alkylamines, one is struck by the minimal amount of alkylation of the aromatic solvents. Typically, only 0.5–2.5% of alkylbenzene is produced, the major products being alkene and cyclopropanes resulting from elimination and rearrangement, and alcohols or acetates.[6,7] Because the 1-adamantyl cation cannot lose a proton (Bredt's rule), and because incorporation of a cyclopropyl ring into the adamantane skeleton can be accomplished only with difficulty,[8] one might expect adamantylamine to yield significantly more alkylbenzenes than other alkylamines.



However, when the aprotic deamination of 1-adamantylamine is carried out in benzene solution, no phenyladamantane at all is detected among the products. When anisole is present, a trace (*ca.* 0.2%) of *p*-anisyladamantane is found. In each case, the only significant products are 1-adamantanol and 1-adamantyl acetate.

Friedman has suggested[9] that a tight diazonium ion-acetate ion pair is the principal intermediate in aprotic deamination in nonpolar solvents. The formation of a tight ion pair would seem to be the best explanation for our results also, with the difference that the cation is more likely the 1-adamantyl ion, because of the known ease of formation of this species.[10,11] We further suggest that the molecule of water formed along with the diazonium ion remains associated with the ion pair. Such an association is consistent with the formation of large amounts of alcohol in the absence of other intermolecular products,

Table I
Deamination Products of 1-Adamantylamine[a]

Run	Reactants	Product composition, %[b]			
		AdH	1-AdOH	1-AdOAc	1-AdAr
1	1-$AdNH_2$, $NaNO_2$ AcOH, H_2O, 5°	0.0 ± 0.1	75.0 ± 0.5	25.0 ± 0.5	
2	1-$AdNH_2$, $NaNO_2$ AcOH, H_2O, 85°	0.0 ± 0.1	70.7 ± 0.5	29.3 ± 0.5	
3	1-$AdNH_2$, $NaNO_2$ AcOH, H_2O, 85°	0.0 ± 0.1	97.0 ± 1.0	3.0 ± 1.0	
4	1-$AdNH_2$, $NaNO_2$ HCl, H_2O, 85°	0.0 ± 0.1	100.0		
5	1-$AdNH_2$, AcOH *i*-AmONO, C_6H_6	0.0 ± 0.1	41.0 ± 0.5	59.0 ± 0.5	0.0 ± 0.1
6	1-$AdNH_2$, AcOH *i*-AmONO, $PhOCH_3$	0.0 ± 0.1	44.3 ± 0.2	55.7 ± 0.2	0.2 ± 0.1
7	1-$AdNH_2$, *i*-AmONO $PhOCH_3$	0.0 ± 0.1	100.0[c]		0.0 ± 0.1
8	1-$AdNH_2$, *i*-AmONO AcOH, Ph_3CH, CCl_4	0.0 ± 0.1	37.5 ± 0.5	62.5 ± 0.5	

[a] Ad = 1-adamantyl; OAc = $OCOCH_3$; Ar = C_6H_5 or *p*-$C_6H_4OCH_3$; AcOH = CH_3COOH; *i*-Am = *i*-C_5H_{11}. [b] See Experimental Section for analytical details. [c] Formed in 24% yield; 76% 1-$AdNH_2$ recovered.

for the collapse of the "solvated" ion pair to alcohol and acetate certainly should be more rapid than its dissociation in the low dielectric aromatic solvents.

In the aqueous systems, the tight ion pair likely is in equilibrium with a solvent-separated one, from which the alcohol product is formed.

Experimental Section

Analytical Procedure. The reaction product (crude, isolated as below) was dissolved in a minimum volume of ether or methylene chloride and analyzed by gas chromatography. The instrument employed was a Perkin-Elmer Model 810 gas chromatograph equipped with dual 12 ft × 0.125 in. columns packed with 10% DC-550 silicone oil on Chromosorb W HMDS, and a flame ionization detector. Helium was the carrier gas, and analyses were conducted at an oven temperature of 195°. Authentic samples were used for peak identification by both absolute retention time and peak enhancement. All peak areas were measured with a planimeter. All percentages reported in Table I are the average of at least three measurements on each of three separate chromatograms.

General Procedure for Deamination. Run 1. A mixture of 2.5 g (0.0165 mol) of 1-adamantylamine, 40 ml of glacial acetic acid, and 10 ml of water was placed in a three-neck flask equipped with a thermometer, a mechanical stirrer, and an addition funnel. The mixture was cooled to 5°, and a solution of 1.26 g (0.0182 mol) of sodium nitrite in 5 ml of water was added dropwise. The resulting mixture was allowed to warm to room temperature and then heated gently until nitrogen evolution ceased. After neutralization with dilute sodium hydroxide, the solution was extracted several times with ether. The combined ether extracts were washed with water and brine and dried over magnesium sulfate. The solution was then concentrated to about 5 ml by careful distillation, and the concentrate was analyzed.

Run 2. The general procedure was followed save that the entire reaction was run at 85°.

Run 3. Conditions for this run were identical with those reported by Kazanskii.[1] A mixture of 2.50 g (0.0165 mol) of 1-adamantylamine, 1.75 ml (0.0307 mol) of glacial acetic acid, and 15 ml of water was placed in a flask. Over 45 min 1.375 g (0.020 mol) of sodium nitrite in 5 ml of water was added. The reaction mixture was heated on the steam bath for 45 min, and the products were isolated as in run 1.

Run 4. The procedure of run 3 was followed, except that 2.5 ml of concentrated hydrochloric acid replaced the acetic acid.

General Procedure for Aprotic Deamination. Run 5. Into a three-neck flask equipped with a mechanical stirrer, a reflux condenser, and an addition funnel were placed 2.513 g (0.0165 mol) of 1-adamantylamine, 0.922 g (0.0165 mol) of glacial acetic acid, and 40 ml of benzene. To this heterogeneous mixture was added dropwise at room temperature a solution of 2.134 g (0.0182 mol) of isoamyl nitrite in 10 ml of benzene. Addition was complete in 45 min. The reaction mixture was heated at reflux on a steam bath for 3 hr. After cooling, it was washed in turn with saturated sodium bicarbonate solution, water, and brine, and dried over magnesium sulfate. The dried extracts were concentrated to about 5 ml by careful distillation, and the concentrate was analyzed.

Run 6. The procedure of run 5 was followed with anisole in place of benzene.

Run 7. The procedure of run 5 was followed, omitting the glacial acetic acid.

Run 8. The procedure of run 5 was followed, employing carbon tetrachloride as the solvent. Triphenylmethane (4.446 g, 0.0182 mol) was added at the beginning of the process.

Registry No. 1-Adamantylamine, 768-94-5.

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A New Synthesis of β,γ-Unsaturated Aldehyde Derivatives. Acid-Catalyzed Rearrangements of 1-Alkylidene-2-alkoxycyclopropanes[1]

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In earlier work the facile synthesis of 1-alkylidene-2-alkoxycyclopropanes (1) by the generation of unsaturated carbenes from *N*-nitrosooxazolidones (2) in the presence of vinyl ethers (3) has been described.[3] The ready availability of such compounds made a study of their chemical reactivity of interest.