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$_2$O, 5°	0.0 ± 0.1	75.0 ± 0.5	25.0 ± 0.5	
2	1-AdNH$_2$, NaNO$_2$ AcOH, H$_2$O, 85°	0.0 ± 0.1	70.7 ± 0.5	29.3 ± 0.5	
3	1-AdNH$_2$, NaNO$_2$ AcOH, H$_2$O, 85°	0.0 ± 0.1	97.0 ± 1.0	3.0 ± 1.0	
4	1-AdNH$_2$, NaNO$_2$ HCl, H$_2$O, 85°	0.0 ± 0.1	100.0		
5	1-AdNH$_2$, AcOH *i*-AmONO, C$_6$H$_6$	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$_3$CH, CCl$_4$	0.0 ± 0.1	37.5 ± 0.5	62.5 ± 0.5	

[a] Ad = 1-adamantyl; OAc = OCOCH$_3$; Ar = C$_6$H$_5$ or *p*-C$_6$H$_4$OCH$_3$; AcOH = CH$_3$COOH; *i*-Am = *i*-C$_5$H$_{11}$. [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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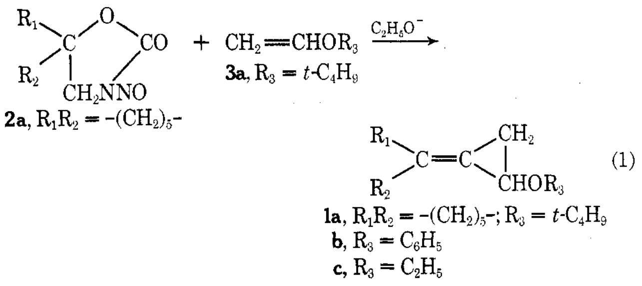
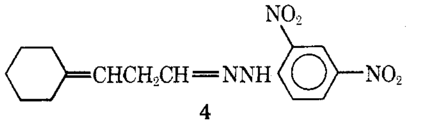
In earlier work the facile synthesis of 1-alkylidene-2-alkoxycyclopropanes (1) by the generation of unsaturated carbenes from *N*-nitrosooxazolidones (2) in the presence of vinyl ethers (3) has been described.[3] The ready availability of such compounds made a study of their chemical reactivity of interest.



The synthesis of 1-cyclohexylidene-2-*tert*-butoxycyclopropane (**1a**) in 67% yield was accomplished before the improved method of generation of unsaturated carbenes[4] had been studied. The yields of **1b** and **1c** were 44 and 24%, respectively, but no attempts were made to maximize these yields.

On treatment of **1a** with 2,4-dinitrophenylhydrazine reagent[5] at room temperature an almost quantitative yield of the yellow 2,4-dinitrophenylhydrazone of 3-cyclohexylidenepropanal (4) was obtained. This compound rearranged easily to the red 2,4-dinitrophenylhydrazone of 3-cyclohexyl-2-propenal (5) on recrystallization from alcohol. However, if precautions were taken to wash out all acid with carbonate, 4 could be recrystallized unchanged. All attempts to obtain 3-cyclohexylidenepropanal failed, as this aldehyde is evidently so labile that tarry materials are rapidly produced even in the cold under a variety of acidic conditions.



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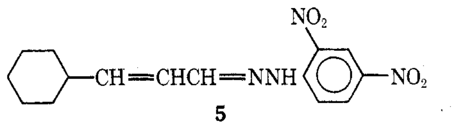

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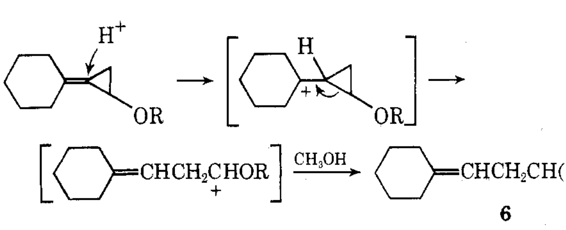
On treatment of a methanolic solution of **1a** with a cation exchange resin at room temperature, the dimethyl acetal of 3-cyclohexylidenepropanal (6) was produced in high yield. The fact that a mixed acetal was not found stems from acid-catalyzed ketal exchange with the excess methanol. A likely mechanism is shown in Scheme I. This reaction is unique in that the acetal of a β,γ-unsaturated aldehyde is produced in one step from a readily available intermediate.

Scheme I



Experimental Section

***N*-Nitroso-1-oxa-3-azaspiro[4.5]decan-2-one (2a).** This compound was prepared as described[6] when needed.

1-Cyclohexylidene-2-*tert*-butoxycyclopropane (1a). To a solution at room temperature of 10.0 g of **2a** in 100 ml of freshly distilled *tert*-butyl vinyl ether,[7] bp 78.5–79.5°, was added 5.5 g of lithium ethoxide ethanolate[8] in one portion. The temperature rose rapidly to 72° and the theoretical amount of nitrogen was collected during the first 10 min. After the reaction mixture was washed with a small amount of dilute acid and saturated salt solution, the organic layer was passed through a cone of anhydrous magnesium sulfate. The filtrate on distillation through a spinning band column yielded 6.97 g (66%) of **1a**: bp 92.8–93.1° (7.0 mm); ir (neat) 5.61 μ (for a double bond exocyclic to a cyclopropane[9]); nmr [$(CH_3)_4Si$ 10.0, CCl_4] τ 6.44 (unresolved triplet, 1, $CHOC_4H_9$), 7.75 (m, 4, allylic cyclohexyl H), 8.43 [m, 6, -$(CH_2)_3$-], 8.77 [s, 9, $(CH_3)_3C$-], and 8.94 (m, 2, cyclopropyl CH_2). This experiment was the best of six varying runs.

Anal.[10,11] Calcd for $C_{13}H_{22}O$: C, 80.4; H, 11.4. Found: C, 80.3; H, 11.4.

1-Cyclohexylidene-2-phenoxycyclopropane (1b). In one similar run involving 10.0 g of **2a**, 75 ml of freshly distilled phenyl vinyl ether.[7] and 5.5 g of lithium ethoxide ethanolate[8] the temperature rose to 78°. After a similar work-up there was isolated 5.1 g (44%) of **1b**, bp 112–113° (0.4 mm), mp 44.0–45.2°. The analytical sample,[11] mp 43.5–45.0°, was obtained after recrystallization from methanol and vacuum sublimation.

Anal.[12] Calcd for $C_{15}H_{18}O$: C, 84.1; H, 8.5. Found: C, 83.8; H, 8.3.

1-Cyclohexylidene-2-ethoxycyclopropane (1c). In a similar run in which ethyl vinyl ether[7] was used a 24% yield of **1c**, bp 69.0–71.5° (2.5 mm),[11] was obtained.

Anal.[10] Calcd for $C_{11}H_{18}O$: C, 79.5; H, 10.9. Found: C, 79.3; H, 11.1.

3-Cyclohexylidenepropanal Dimethyl Acetal (6). A mixture of 4.0 g of **1a** in 50 ml of dry methanol and 15 g of Dowex 50W-4, a cation exchange resin, was stirred at room temperature for 20 hr. After filtration of the resin, most of the methanol was removed under reduced pressure and the residue was dissolved in ether and treated with 10% sodium bicarbonate. After a conventional work-up, distillation afforded 2.90 g (77%) of **6**,[11] bp 92.5–95.0° (6.5 mm).

Anal.[10] Calcd for $C_{11}H_{20}O_2$: C, 71.7; H, 11.0. Found: C, 71.6; H, 11.1.

3-Cyclohexylidenepropanal 2,4-Dinitrophenylhydrazone (4). On mixing 0.80 g of **1a** and 20 ml of 2,4-dinitrophenylhydrazine reagent,[5] a yellow precipitate formed rapidly. This solid was collected after 5 min and washed with cold alcohol. On drying 1.28 g (97%) of crude **4**, mp 120–125° dec, was obtained. This material darkened in the melting point capillary before melting. A solution of this yellow solid in ethyl acetate was washed with 10% sodium bicarbonate. The resulting yellow 2,4-DNPH derivative, **4**, uv λ_{max} 360 mμ (ϵ 24,500),[13] melted at 131.5–134.0° without darkening prior to melting.[11] If the original yellow solid, **4**, was recrystallized from hot ethanol without the alkaline wash a red 2,4-DNPH derivative, **5**, mp 206.0–207.5°, uv λ_{max} 379 mμ (ϵ 28,300),[13] was obtained.[11]

Anal. Calcd for $C_{15}H_{18}N_4O_4$: N, 17.6. Found (**4**):[10] N, 17.6. Found (**5**):[12] N, 17.7.

Similar results were obtained with **1b** and **1c**.

Registry No. **1a,** 37150-71-3; **1b,** 37150-69-9; **1c,** 37150-70-2; **2a,** 20498-55-9; **3a,** 926-02-3; **3b,** 766-94-9; **3c,** 109-92-2; **4,** 42880-51-3; **5,** 6556-91-8; **6,** 42880-53-5.

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