# The Effect of Structural Rigidity on the Photoreduction of Imines[1]

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Upon irradiation in 2-propanol, $\Delta^{1,9}$-octahydroquinoline (1) gives *trans*-decahydroquinoline, 2-methyl-$\Delta^1$-piperideine (2) gives 2-methylpiperidine, *N*-isopropylidenepropylamine (7) gives *N*-propyl-2-aminopropane, and 2-phenyl-$\Delta^1$-pyrroline (8) gives 2,2′-diphenyl-2,2′-bipyrrolidine (9). Comparative photolyses of 2 and 7 and 8 and *N*-benzylidenecyclohexylamine (10) show that cyclic imines 2 and 8 do not show enhanced reactivity toward photochemical hydrogen abstraction reactions when compared with acyclic analogs. It is concluded that the low reactivity of the carbon–nitrogen double bond toward photochemical hydrogen abstraction reactions is not due only to rapid radiationless decay by twisting about the carbon–nitrogen bond.

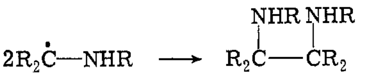
Among the most common reactions of compounds containing the carbonyl chromophore, upon irradiation in solvents containing readily abstractable hydrogens, is photoreduction.[2] Although the photochemical reactions of compounds containing a carbon–nitrogen double bond have received less attention than those containing a carbon–oxygen double bond, reactions analogous to the photoreduction of the carbonyl group have been observed.[3-5] While a mechanism similar to that postulated for ketone photoreduction can be written for imines (Scheme I), the actual mechanism has been demonstrated[3,4] not to involve an excited state of the imine at all. Instead, a carbonyl compound (as added sensitizer, from hydrolysis of the imine, or as a photogenerated species), after being excited to its triplet state, abstracts a hydrogen atom to produce a ketyl radical (Scheme II). This radical then transfers a hydrogen atom to the imine to generate an $\alpha$-aminoalkyl radical (eq 9). Products are then produced as shown in eq 4 and 5.

### Scheme I

$$R_2C{=}NR \xrightarrow{h\nu} R_2C{=}NR^* \qquad (1)$$

$$R_2C{=}NR^* + CH_3CH_2OH \longrightarrow R_2\dot{C}{-}NHR + CH_3\dot{C}HOH \qquad (2)$$

$$R_2C{=}NR^* \longrightarrow R_2C{=}NR \qquad (3)$$



$$2R_2\dot{C}{-}NHR \longrightarrow R_2\overset{NHR}{\overset{|}{C}}{-}\overset{NHR}{\overset{|}{C}}R_2 \qquad (4)$$

$$2R_2\dot{C}{-}NHR \longrightarrow R_2CHNHR + R_2C{=}NR \qquad (5)$$

### Scheme II

$$R_2C{=}NR + H_2O \rightleftarrows R_2CO + H_2NR \qquad (6)$$

$$R_2CO \longrightarrow R_2CO^* \qquad (7)$$

$$R_2CO^* + CH_3CH_2OH \longrightarrow R_2\dot{C}OH + CH_3\dot{C}HOH \qquad (8)$$

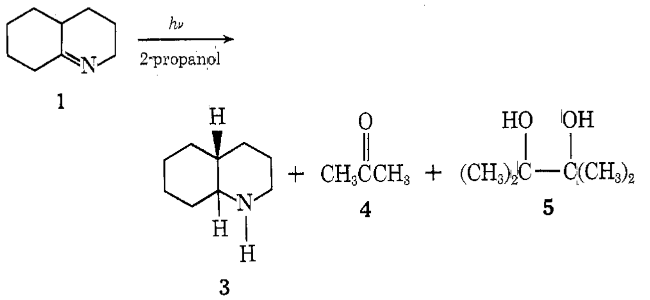
$$R_2\dot{C}OH + R_2C{=}NR \longrightarrow R_2CO + R_2\dot{C}NHR \qquad (9)$$

There are several possible reasons for the low reactivity of excited imines toward hydrogen abstraction reactions. First, the rate of hydrogen abstractions by the excited imine (eq 2) may be slow, as postulated by Fischer.[3] Alternatively, it may be that the rate of radiationless decay of the excited imine (eq 3) is much faster than hydrogen abstraction (eq 2). Padwa and coworkers[4,6,7] have postulated the latter explanation and have further suggested that twisting about the carbon–nitrogen double bond is responsible for this rapid radiationless decay. The result of such twisting, syn–anti isomerization, is a known photochemical reaction of the carbon–nitrogen double bond,[8-11] lending support to this decay mechanism.

We report here our investigations of photochemical reductions of some cyclic imines in 2-propanol. The incorporation of the carbon–nitrogen double bond into a ring system should prevent twisting as a deactivation mechanism and might therefore allow observation of photoprocesses normally obscured by syn–anti isomerization.

## Results and Discussion

Our initial studies focused on $\Delta^{1,9}$-octahydroquinoline (1)[12] and 2-methyl-$\Delta^1$-piperideine (2).[13] Upon irradiation in reagent 2-propanol, 1 produced *trans*-decahydroquinoline (3) in 98% yield, acetone (4), and 2,3-dimethyl-2,3-butanediol (5). No *cis*-decahydroquinoline was detected by GC analysis of the photolysis solution. Under similar conditions, 2 produced 2-methylpiperidine (6) in 72% yield, along with 4 and 5. In addition, small amounts of several unidentified products, with longer GC retention times, were observed. The production of acetone in the photolysis suggested that this compound might be acting as a chemical sensitizer[3,4] for the reaction. That this was indeed the case was confirmed by several experiments. The disappearance of 2 accelerated as the reaction proceeded. Thus in one experiment, ca. 16% of 2 had reacted after 30 min of irradiation and ca. 50% had reacted after 60 min. This is attributed to increasing chemical sensitization by acetone as its concentration increased throughout the course of the reaction. Addition of a large molar excess of acetone drastically accelerated the rate of reduction. Finally, we found the reagent 2-propanol contained ca. 0.002 *M* acetone impurity. By careful purification it was possible to decrease the acetone concentration to less than $10^{-4}$ *M*. Upon comparative irradiation in the purified and in reagent 2-propanol, 6 was produced more rapidly in the latter solvent (see Table I).



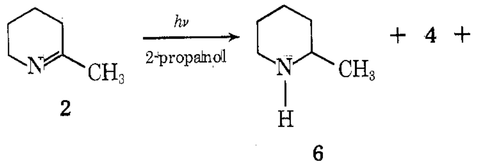
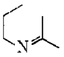
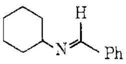


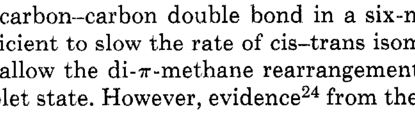
**Table I**
**Amounts of Photolysis Products**

| Compd | Run[a] | Acetone concn, *M* | Photoproduct, mmol |
|---|---|---|---|
| **2** | A | $<10^{-4}$ | 0.033 |
| **2** | A | 0.002 | 0.088 |
| <br>**7** | A | $<10^{-4}$ | 0.202 |
| **8** | B | $<10^{-4}$ | 0.125 |
| <br>**10** | B | $<10^{-4}$ | 0.122 |

[a] In each run, samples of imine in 2-propanol were irradiated in parallel and concentrations were adjusted to ensure equal light absorption at the beginning of the run.

It was felt that the best evidence for the effect of twisting on the decay processes of imines could be obtained from a comparison of the relative quantum yields of photoreduction of a cyclic imine and an acyclic model. *N*-Isopropylidenepropylamine[14] (**7**) was chosen as an acyclic model for **2**. Upon irradiation in 2-propanol, **7** produced *N*-propyl-2-aminopropane in 88% yield. When **2** and **7** were irradiated in parallel, **7** was found to react faster than **2** (Table I). However, **7** was observed to undergo substantial hydrolysis to acetone and 1-aminopropane owing to traces[15] of water in the photolysis solvent. Thus, chemical sensitization by acetone probably accounts for the enhanced rate of reaction of **7**.

To avoid the problem of chemical sensitization by traces of acetone, the photochemical behavior of 2-phenyl-$\Delta^1$-pyrroline[17,18] (**8**) was investigated. Upon irradiation in 2-propanol, **8** produced 2,2′-diphenyl-2,2′-bipyrrolidine[19] (**9**) in 87% yield. The identity of **9** was established by comparison of its melting point and spectral properties with those of a sample prepared by the aluminum amalgam[20] reduction of **8**. Comparison with an acyclic model compound, *N*-benzylidenecyclohexylamine (**10**), previously studied by Padwa and coworkers,[4] does not show an enhanced reactivity toward photoreduction for **8**[21] (Table I).



**8** **9**

These results indicate that imines with the carbon–nitrogen double bond in a five- or six-membered ring, like acyclic imines, are much less reactive toward photochemical hydrogen abstraction than are carbonyl compounds. Evidence[23] from alkene photochemistry indicates that confinement of a carbon–carbon double bond in a six-membered ring is sufficient to slow the rate of cis–trans isomerization enough to allow the di-π-methane rearrangement to occur via the triplet state. However, evidence[24] from the ionic addition of alchols to cyclic alkenes upon irradiation indicates that cyclohexenes are able to twist enough for this reaction to occur, while cyclopentenes are unable to attain a sufficient degree of twisting. Thus, while the evidence is somewhat inconclusive on the ability of **2** to undergo radiationless decay by twisting, **8** is unable to twist to a significant degree. Therefore, the low reactivity of **8** must be due to factors other than rapid radiationless decay by twisting. Other possible explanations for this low reactivity include a slow rate of hydrogen abstraction (eq 2), or other rapid decay processes.

Finally, it is interesting to note that the α-aminoalkyl radicals derived from **1**, **2**, and **7** undergo disproportionation (eq 5), while the radical derived from **8** couples instead (eq 4). This is in accord with results observed with carbon radicals, which have demonstrated that delocalization of the unpaired electron favors coupling over disproportionation.[25]

## Experimental Section[26]

$\Delta^{1,9}$-Octahydroquinoline (**1**),[12] $\lambda_{max}$ (2-propanol) 244 nm (ε 230), 2-methyl-$\Delta^1$-piperideine (**2**),[13] $\lambda_{max}$ (2-propanol) 237 nm (ε 180), *N*-isopropylidenepropylamine (**7**),[14] $\lambda_{max}$ (2-propanol) 235 nm (ε 210), 2-phenyl-$\Delta^1$-pyrroline (**8**),[17] $\lambda_{max}$ (2-propanol) 242 nm (ε 15,600), benzaldehyde *N*-cyclohexylimine (**10**)[4], $\lambda_{max}$ (2-propanol) 244 nm (ε 17,600), and *N,N′*-dicyclohexyl-1,2-diphenyl-1,2-diaminoethane[20] were prepared by literature procedures.

***N*-Propyl-2-aminopropane.** This secondary amine was prepared by a variation of the procedure of Norton et al.[14] A solution of 9.9 g (0.10 mol) of **7** and 0.18 g of platinum oxide in 50 ml of anhydrous methanol was hydrogenated in a Parr hydrogenator at an initial pressure of 38 psi. After 15 min no further pressure drop was evident. The reaction was stopped after 40 min and the catalyst removed by filtration. The solvent was removed by distillation through a 12-in. Vigreux column and the residue was distilled through a 4-in., helices-packed column to give 4.4 g (44%) of amine, bp 89–90° (ca. 630 mm).

**2,2′-Diphenyl-2,2′-bipyrrolidine (9).** The general procedure of Jaunin[20] was used. To a solution of 1.00 g (0.0069 mol) of **8** in 150 ml of ether was added 0.38 g (0.014 mol) of aluminum foil, 0.031 g of mercuric chloride,[27] and 1 ml of water. After stirring overnight, the solids were removed by filtration and the solvent was removed in vacuo. The residue was recrystallized from ethanol–water to give 0.42 g (41%) of **9**:[19] mp 130–131°; NMR ($CCl_4$) τ 3.07 (s, 10 H, aromatics), 6.8–8.8 (series of overlapping multiplets, 14 H); ir ($CCl_4$) 3400, 3300, 3070, 2980, 1445, 1320, 1095, 1065, 1030 $cm^{-1}$; $\lambda_{max}$ (2-propanol) 252 nm (ε 480), 258 (490), 264 (380), and 269 (shoulder, 240). Anal. Calcd for $C_{20}H_{24}N_2$: C, 82.14; H, 8.27; N, 9.58. Found: C, 82.21; H, 8.13; N, 9.60.

**Purification of 2-Propanol for Photolysis.** Reagent 2-propanol was found by GC and uv analysis to contain ca. $2 \times 10^{-3}$ *M* acetone. After reflux over sodium borohydride followed by distillation from calcium hydride with a 14-in., helices-packed column, less than $1 \times 10^{-4}$ *M* acetone was detectable.

**Preparative Photolysis of $\Delta^{1,9}$-Octahydroquinoline (1).** A solution of 1.02 g (0.00745 mol) of **1** in 300 ml of 2-propanol was purged with nitrogen and irradiated through quartz with a Hanovia 450-W high-pressure mercury lamp for 4 hr. Analysis by GC (6 ft × 0.125 in., 10% UCW-982 silicone gum rubber on 60/80 Chromosorb W at 120°) showed the reaction to be completed at this point. Distillation yielded 1.01 g (98%) of photoproduct, bp 76–78° (6 mm). The photoproduct was identified as **3** by comparison of its ir and NMR spectrum and GC retention time with those of an authentic sample. None of the cis isomer was detectable by GC.

**Preparative Photolysis of 2-Methyl-$\Delta^1$-piperideine (2).** A solution of 3.0 g (0.031 mol) of **2** in 525 ml of reagent 2-propanol was purged with nitrogen and irradiated through quartz with a Hanovia 450-W high-pressure mercury lamp. Ice-bath cooling was used to maintain the temperature of the solution at 10–20°. After 8 hr of irradiation, GC analysis (UCW column described above, temperature-programmed run, 76–100°), with aniline as internal standard, showed that 90% of **2** had reacted to produce 1.96 g (72%) of **6**, 1.9 g of **5**, and ca. 12% of four unidentified components. The solution was concentrated and **6** and **5** were identified by isolation by preparative GC (5 ft × 0.25 in., 3% silicone gum rubber SE-30 at 80°) and comparison of their NMR and ir spectra with those of authentic samples.

**Preparative Photolysis of 2-Phenyl-$\Delta^1$-pyrroline (8).** A solution of 2.0 g (0.014 mol) of **8** in 95% ethanol was purged with nitrogen and irradiated through quartz with a Hanovia 450-W high-pressure mercury lamp for 90 hr. The solvent was removed at reduced pressure and the residue crystallized upon standing. Upon recrystallization from ethanol, a solid, mp 130–131°, was obtained and identified as **9** by comparison of its NMR and ir spectra and melting point with those of an independently synthesized sample.

**General Procedure for Analytical Photolyses.** In each run, 15 ml of ca. 0.03 *M* solutions of imine in 2-propanol (concentrations were adjusted so that the amount of light absorbed initially was approximately the same for each tube in comparative runs) were placed in quartz photolysis tubes and purged with nitrogen. Tubes were then irradiated with a Hanovia 450-W high-pressure mercury lamp, using a "merry-go-round" apparatus to ensure equal amounts of light incident on each tube. Analysis was conducted by GC using aniline as internal standard for **2** and **7** (UCW column described above at 90°) and naphthalene as internal standard for **8** and **10** (UCW column described above, temperature-programmed run, 150–250°).

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**Registry No.**—**1**, 1074-06-2; **2**, 1462-92-6; **3**, 767-92-0; **5**, 76-09-5; **6**, 109-05-7; **7**, 22023-64-9; **8**, 700-91-4; **9**, 54276-78-7; **10**, 2211-66-7; *N*-propyl-2-aminopropane, 21968-17-2.

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(15) If an equilibrium constant of 1 is assumed for the reaction acetone + *N*-propylamine ⇄ imine + water, the presence of only 0.01% water would cause approximately 10% hydrolysis of a 0.03 *M* solution of imine.[16]

(16) A. LeBris, G. Lefebvre, and F. Coussemant, *Bull. Soc. Chim. Fr.*, 1366 (1964), have reported an equilibrium constant of 2 for the reaction of acetone and isopropylamine.

(17) D. F. Starr, H. Bulbrook, and R. M. Hixon, *J. Am. Chem. Soc.*, **54**, 3971 (1932). See S. J. Love and J. A. Moore, *J. Org. Chem.*, **33**, 2361 (1968), for the correct structural assignment for this compound.

(18) Owing to the large extinction coefficient of **8**, the small amount of acetone present in the purified 2-propanol will not absorb an appreciable amount of light.

(19) Presumably **9** was formed as a mixture of meso and *dl* isomers. After recrystallization a sharp-melting product was obtained. No attempts were made to determine which isomer was isolated.

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(21) No hydrolysis of **10** was detected under our reaction conditions. It was expected that **10** would be much more stable to hydrolysis than was **7**, since the equilibrium constant should be much larger.[22]

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(26) Boiling points and melting points are uncorrected. Nuclear magnetic resonance spectra were obtained on a Varian Model EM-360 spectrometer. Ultraviolet spectra were obtained on a Beckman Acta V spectrophotometer. Infrared spectra were obtained on a Perkin-Elmer Model 710A spectrophotometer. Gas-liquid partition chromatograms were obtained on a Hewlett-Packard Model 5750 chromatograph. Elemental analyses were obtained from Spang Microanalytical Laboratory, Ann Arbor, Mich.

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# Synthesis of 2-Substituted 8,9-Dehydroadamantanes[1]

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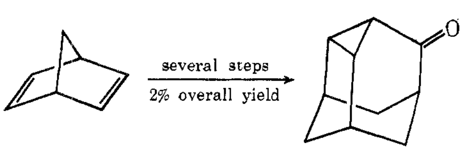
Acetone-sensitized photoisomerization of 2-protoadamantenone gives 8,9-dehydro-2-adamantanone (**1**). Several new 2-substituted 8,9-dehydroadamantanes have been prepared from **1**. A general route for the introduction of alkyl substituents at the C-8 bridgehead of **1** has been devised and is illustrated by the synthesis of 8-methyl-8,9-dehydro-2-adamantanone.

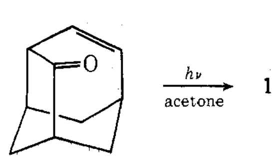
In view of the considerable interest in the properties and chemistry of adamantane derivatives,[2] it is striking that 8,9-dehydro-2-adamantanone (**1**), a structurally rigid conjugated cyclopropyl ketone which contains a plane of symmetry and is potentially of significant synthetic utility, has received only modest attention.[3–8] It would appear that this has been the case because it simply has not been convenient to employ **1** in synthesis. The only reported preparation of **1** involves a multistep reaction sequence which converts norbornadiene to **1** in an overall yield of 2%.[3] We now wish to report (a) an alternative and improved procedure for the synthesis of **1**, (b) the preparation of several 2-substituted 8,9-dehydroadamantanes from **1**, and (c) a synthetic route for introducing alkyl substituents at C-8 of **1**.



**1**

## Results and Discussion

It is well established that the triplet-sensitized photorearrangement of a β,γ-unsaturated ketone can lead to a formal [1,2] shift of the acyl group and the formation of an isomeric conjugated cyclopropyl ketone (the oxa-di-π-methane photorearrangement).[9] Thus, by analogy, **1** should be accessible by the photoisomerization of 2-protoadamantenone (**2**). The availability of **2**[10] led us to examine its photochemistry. Irradiation of a nitrogen-purged 0.5% solution of **2** [$\lambda_{max}$(EtOH) 296 nm (ε 230)] in acetone through a Pyrex filter with a Hanovia L 450-W lamp proceeds smoothly to give **1**.[11] Under these conditions **1** [$\lambda_{max}$(EtOH) 277 nm (ε 40)] undergoes slow photodecomposition, but this reaction does not effectively compete with the photo-



**2**