Michael E. Landis and John C. Mitchell*

Department of Chemistry, Southern Illinois University, Edwardsville, Illinois 62026

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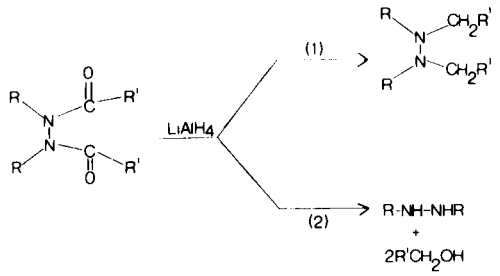
Reaction of a series of four-membered ring hydrazides (1,2-diaroyl-1,2-diazetidines) with lithium aluminum hydride at 80° results in reductive saturation of both carbonyl groups affording 1,2-diaryl-1,2-diazetidines in modest yield. Reactions at 22° result in reductive fragmentation at one carbonyl moiety, producing a monoaroyl-1,2-diazetidine as the exclusive product. A mechanism similar to that postulated for the temperature-dependent reduction of amides by lithium aluminum hydride is proposed for the reduction of these 1,2-diazetidines.

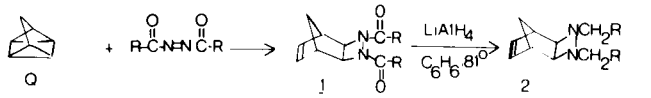
J. Heterocyclic Chem., **16**, 1637 (1979).

The reduction of cyclic (1,2) and acylic (3-5) hydrazides with lithium aluminum hydride is well known. Two reaction pathways, involving either reductive saturation (equation 1) or cleavage (equation 2) have been identified, and temperature and substituent effects on these competitive



modes have been reported (6,7). The suitability of this reduction to highly-strained cyclic hydrazines, in particular those in four-membered rings, is unknown. We now report on mechanistic pathways involved in the reduction of a series of these 1,2-diazetidines with lithium aluminum hydride.

Fused-ring diaroyl-1,2-diazetidines **1** were prepared by cycloadditions of quadricyclane Q with diaroyldiazines as previously described (8). Reduction of **1a-c** with lithium aluminum hydride in refluxing benzene produced saturated 1,2-diazetidines **2a,b,c** in 28%, 35%, and 89%



a. R = C_6H_5-

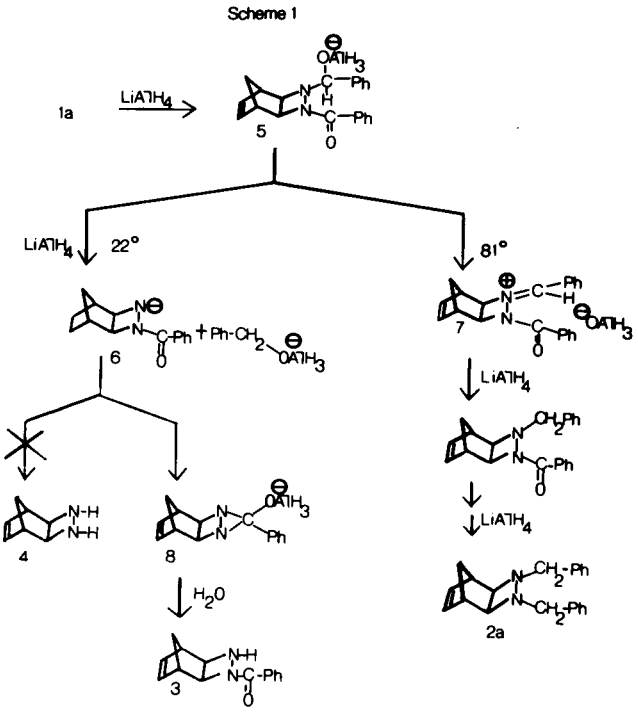
b. R = p-CH_3O-C_6H_4-

c. R = p-CF_3-C_6H_4-

yields, respectively. For **1a** at room temperature, the formation of **2a** was completely suppressed, and the dominant product (isolated in 55% yield) is monoaroyl hydrazide **3** (*and benzyl alcohol*). Little or no unsubstituted hydrazine **4** was observed.

These results are consistent with a mechanism as shown in Scheme I. Addition of lithium aluminum hydride to **1a** gives an *O*-aluminate complex **5** that reductively cleaves to benzyl alcohol and **6** at 22°, while cleavage to imine **7** dominates at 81°. This trend favoring imine-formation with increasing temperature is consistent with trends reported for tertiary amides (9). Continued reduction of **7** ultimately affords saturated 1,2-diazetidine **2a**. That hydrazine **4** is unobserved in the reduction at 22° indicates the resistance of mono-aroyl hydrazide **6** to further reductive cleavage. The absence of further fragmentation of **6** may be attributable to its existence as aluminate complex **8**, that regenerates **3** upon hydrolysis.

Scheme I



EXPERIMENTAL

All ^1H and ^{19}F nmr spectra were recorded on a Varian T-60 nmr spectrometer with ^1H chemical shifts reported in parts per million (δ) relative

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to tetramethylsilane and with ^{19}F chemical shifts reported in parts per million (∅) relative to fluorotrichloromethane. All ir spectra were recorded on a Perkin-Elmer 710B infrared spectrometer, and mass spectra were recorded on a Varian MAT-111 gc-mass spectrometer. Melting points are uncorrected. 3,4-Diaroyl-3,4-diazatricyclo[4.2.1.$0^{2,5}$]non-7-enes **1a-c** were prepared by cycloadditions of diaroyldiazines with quadricyclane as previously described (8).

Preparation of 3,4-Diaryl-3,4-diazatricyclo[4.2.1.$0^{2,4}$]non-7-enes (**2a-c**).

Nine and one tenth mmoles of the appropriate diazetidine **1a,b,** or **c** was added portionwise over 15 minutes to a refluxing slurry of 79 mmoles of lithium aluminum hydride in 75 ml. of benzene. After refluxing for an additional 2 hour, excess hydride was destroyed with saturated aqueous ammonium chloride. The solution was decanted and dried over magnesium sulfate; solvent was removed at reduced pressure. Saturated diazetidines **2a-c** can be purified by chromatography on alumina with methylene chloride as eluent (**2a-c** elute as pale yellow bands).

For 3,4-dibenzyl-3,4-diazatricyclo[4.2.1.$0^{2,5}$]non-7-ene **2a** (28%), m.p. 74-6°c)C; nmr (deuteriochloroform): 7.26-7.49 δ (m, 10H), 5.90 δ (broad s, 2H), 3.98 δ (d, 2H, J = 13 Hz), 3.70 δ (d, 2H, J = 13 Hz), 3.39 δ (s, 2H), 2.79 δ (broad s, 2H), 2.68 δ (d, 1H, J = 8 Hz), 1.58 δ (d, 1H, J = 8 Hz); ir (potassium bromide): no NH or C=O.

Anal. Calcd. for $C_{21}H_{22}N_2$: C, 83.40; H, 7.33; N, 9.26. Found: C, 83.15; H, 7.21; N, 9.28.

3,4-Di-(*p*-methoxybenzyl)3,4-diazatriccyclo-[4.2.1.$0^{2,5}$]non-7-ene (**2b**).

This compound was obtained in 35% yield, m.p. 71-73°; nmr (deuteriochloroform): 7.28 δ (d, 4H, J = 12 Hz), 6.82 δ (d, 4H, J = 12 Hz), 5.80 δ (broad s, 2H), 3.85 δ (d, 2 H, J = 12 Hz), 3.74 δ (s, 6H), 3.55 δ (d, 2H, J = 12 Hz), 3.38 δ (s, 2H), 2.83 δ (broad s, 2H), 2.63 δ (d, 1H, J = 9 Hz), 1.60 δ (d, 1H, J = 9 Hz); ir (potassium bromide): no NH or C=O.

Anal. Calcd. for $C_{23}H_{26}N_2O_2$: C, 76.21; H, 7.23; N, 7.73. Found: C, 75.96; H, 7.20; N, 7.58.

3,4-Di-(*p*-trifluoromethylbenzyl)-3,4-diazatricyclo[4.2.1.$0^{2,5}$]non-7-ene (**2c**).

This compound was obtained in 89% yield, m.p. 48-49°; ^1H nmr (deuteriochloroform): 7.2-7.7 δ (m, 8H), 5.90 δ (broad s, 2H), 3.96 δ (d, 1H, J = 13 Hz), 3.67 δ (d, 1H, J = 13 Hz); 3.42 δ (s, 2H), 2.85 δ (broad s, 2H), 2.61 δ (d, 1H, J = 9 Hz), 1.63 δ (d, 1H, J = 9 Hz); ^{19}F nmr (deuteriochloroform): 38.20 ϕ (s); ir (potassium bromide): no NH or C=O.

Anal. Calcd. for $C_{23}H_{20}F_6N_2$: C, 63.01; H, 4.60; N, 6.39. Found: C, 62.76; H, 4.51; N, 6.50.

Preparation of 3-Benzoyl-4-hydro-3,4-diazatricyclo[4.2.1.$0^{2,5}$]non-7-ene (**3**).

Diazetidine **1a** (1.1 g. 3.3 mmoles) was added portionwise (10) over 15 minutes to a mixture of 1.1 (29.0 mmoles) of lithium aluminum hydride in 27 ml. of benzene. The solution was stirred for an additional 2 hours, and excess hydride was destroyed with saturated aqueous ammonium chloride. The solution was decanted and dried over magnesium sulfate. Solvent was removed at reduced pressure and the resulting oil was purified by chromatography on florisil with a 9:1 mixture of chloroform:methanol as eluent to give as the only products, unreacted diaroyldiazetidine and, **3** (55%) as a pale yellow oil: nmr (deuteriochloroform): 7.48-8.02 δ (m, 5H), 5.90-6.20 δ (m, 2H), 5.20-5.80 δ (broad s, 1H), 4.66 δ (d, 1H, J = 5 Hz), 3.90 δ (d, 1H, J = 5 Hz), 3.12 δ (broad s, 1H), 2.33 δ (d, 1H, J = 8 Hz), 1.70 δ (d, 1H, J = 8 Hz); ir (salt plate): 3210 cm^{-1} (CN), 1625 cm^{-1} (C=O); ms: parent peak at m/e = 226.

Acknowledgement.

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(10) More rapid addition of diazetidine **1a** had no effect on the yield of **3**.