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# 1-(1-Adamantyl)diaziridine

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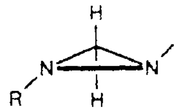
The reaction of 1-aminoadamantane with $CH_2O$ and $H_2NOSO_3H$ in the presence of $K_2CO_3$ under phase-transfer conditions leads to hitherto unknown 1-(1-adamantyl)diaziridine and (1-adamantyl)aminoacetonitrile, characterized by spectral data.

**Key words:** 1-(1-adamantyl)diaziridine, (1-adamantyl)aminoacetonitrile, $^1$H and $^{13}$C NMR spectra.

Recently, we demonstrated the possibility of synthesis of 1,2-di-*tert*-alkyldiaziridines **1**[1] and **2**,[2] which opens the way to study the sterically hindered inversion of nitrogen atoms.



R = R' = $\mathrm{Bu}^t$ (**1**), Ad (**2**)
R = H, R' = $\mathrm{Bu}^t$ (**3**)

**1—3**

One line of investigation is to introduce a second bulky substituent into diaziridines of type **3** (for example, the addition of β-substituted acrylates), separate the diastereomers, and determine the inversion barriers of nitrogen atoms by studying the kinetics of epimerization. Another line is to introduce a bulky achiral substituent (for example, β,β-dimethylacrylates) and separate the enantiomers using their carboxyl derivatives. In the past,[1,3,4] diaziridine **3** has been obtained in yields no higher than 15% and characterized by spectral data.[1] In the present work, crystalline diaziridine **4** was synthesized for the first time, which is more convenient for the above-mentioned studies (Scheme 1). The structure of this diaziridine was unambiguously confirmed by the spectral data.

Similar values of spin-spin coupling constants $^3J_{\mathrm{H_a,H_c}}$ and $^3J_{\mathrm{H_b,H_c}}$ typical of analog **3**[1] and the high-field position of the $^{13}$C signal of the diaziridine ring, which is characteristic of sterically hindered diaziridines **1**—**3**,[1,2] are observed in the NMR spectra of diaziridine **4**. In the mass spectrum (electron impact, 70 eV) of

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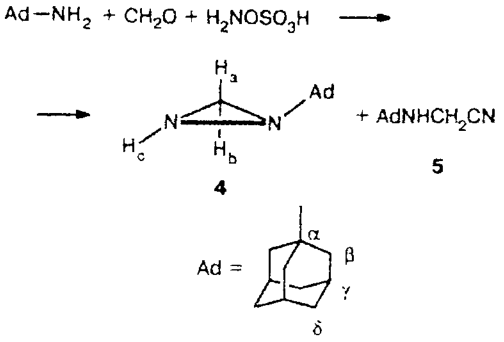
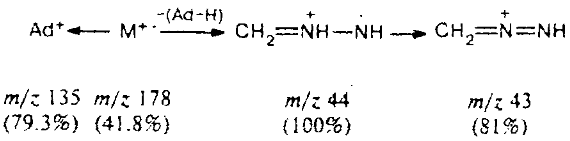
Scheme 1



diaziridine **4** there is an intense molecular ion peak whose fragmentation under electron impact corresponds to the structure (*cf.* Ref. 1).



$$\begin{array}{ccccc} Ad^{+} & \longleftarrow\ M^{+\cdot} & \xrightarrow{-(Ad-H)} & CH_2{=}\overset{+}{N}H{-}\dot{N}H & \longrightarrow\ CH_2{=}\overset{+}{N}{=}NH \\ m/z\ 135 & m/z\ 178 & & m/z\ 44 & m/z\ 43 \\ (79.3\%) & (41.8\%) & & (100\%) & (81\%) \end{array}$$

(1-Adamantyl)aminoacetonitrile (**5**), a product of the aminomethylation of HCN formed in interaction of $H_2NOSO_3H$ with $CH_2O$ (*cf.* Ref. 5), was isolated along with diaziridine **4**. This product was identified by comparing its spectral data with those for the known analogs.[1,4,5]

## Experimental

IR spectra were recorded on a UR-20 spectrometer (KBr). $^1H$ and $^{13}C$ NMR spectra were recorded on a Bruker WM-400 spectrometer ($^1H$, 400.13 MHz; $^{13}C$, 100.62 MHz) with TMS as the internal standard. TLC was performed on Silufol UV-254 plates, spots were detected by $I_2$ vapor and, independently, by spraying with a solution of diphenylamine in acetone followed by heating the plates. Mass spectra were measured on a Varian MAT CH-6 spectrometer (70 eV).

**1-(1-Adamantyl)diaziridine (4) and (1-adamantyl)aminoacetonitrile (5).** Paraform (0.3 g, 10 mmol), $K_2CO_3$ (2 g, 14.5 mmol), and 3 mL of $H_2O$ were successively added with stirring to a solution of 1-aminoadamantane (1.51 g, 10 mmol) in a mixture of 10 mL of $CHCl_3$ and 10 mL of ether. Then $H_2NOSO_3H$ (1.49 g, 12.5 mmol) and 10 mg of triethylbenzylammonium chloride were added with vigorous stirring, and the reaction mixture was stirred at 30—35 °C for 12 h. The organic layer was separated, dried with $K_2CO_3$, and concentrated. Products **4** and **5** were isolated by column chromatography of the residue on silica gel (100—160 μm, the eluent was $CHCl_3$—MeOH, 20 : 1).

**Diaziridine** (**4**), yield 72 mg (4%), m.p. 43—45 °C, $R_f$ 0.38 ($CHCl_3$—MeOH, 10 : 1). Found (%): N, 15.43. $C_{11}H_{18}N_2$. Calculated (%): N, 15.73. $^1H$ NMR ($C_6D_6$), δ: 1.54 (br.s, 6 H, β-$CH_2$); 1.66 (br.s, 1 H, NH); 1.67 (br.s, 6 H, δ-$CH_2$, the spectrum of the AB type, $\Delta\nu$ = 28.0 Hz; $^2J = -12.2$ Hz); 1.95 (br.s, 3 H, γ-CH); 2.25 (dd, 1 H, $H_b$, $^2J$ = 5.5 Hz; $^3J_{HCNH}$ = 7.3 Hz); 2.37 (dd, 1 H, $H_a$, $^2J$ = 5.5 Hz; $^3J_{HCNH}$ = 6.7 Hz). $^{13}C$ NMR ($CDCl_3$), δ: 29.14 (br.d, γ-C, $^1J$ = 133.7 Hz); 36.60 (br.t, δ-C, $^1J$ = 126.4 Hz); 39.03 (br.t, β-C, $^1J$ = 127.9 Hz); 40.55 (td, $NCH_2N$, $^1J$ = 174.8 Hz; $^2J_{CNH}$ = 2.9 Hz); 54.79 (br.s, α-C).

**Compound 5**, yield 251 mg (13%), m.p. 49—50 °C, $R_f$ 0.48 ($CHCl_3$—MeOH, 10 : 1). IR, ν/cm$^{-1}$: 2250 (CN); 2880, 2920 (CH); 3360 (NH). $^1H$ NMR ($CDCl_3$), δ: 1.65 (br.m, 13 H, β,δ-$CH_2$, HN); 2.08 (br.s, 3 H, γ-$CH_2$); 3.54 (s, 2 H, $CH_2N$). $^{13}C$ NMR ($CDCl_3$), δ: 28.95 (t, $CH_2N$, $^1J$ = 142.4 Hz); 29.09 (br.d, γ-CH, $^1J$ = 133.7 Hz); 36.05 (br.t, δ-$CH_2$, $^1J$ = 126.4 Hz); 42.00 (br.t, β-$CH_2$, $^1J$ = 126.4 Hz); 51.01 (br.s, α-C); 119.88 (t, CN, $^2J$ = 7.3 Hz).

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