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AMIDRAZONES 10. STEVENS REARRANGEMENT OF 1-BENZYL AND 1-ALLYL-SUBSTITUTED-3-AMINO-4,5-DIHYDRO-1-PHENYL-1H-PYRAZOLIUM BROMIDES

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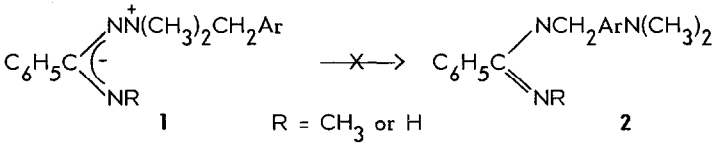
Abstract: 2-Benzyl-3-imino-1-phenylpyrazolidine (**5a**) and 2-allyl-3-imino-1-phenylpyrazolidine (**5b**) are obtained by the base-promoted rearrangement of the title compounds (**4a** and **4b**).

In earlier publications we reported that thermolysis of N^1-benzyl-substituted amidrazone ylides (**1**) gives 1,2-dihydro-*s*-triazines, dimethylamine and aldimines.[1] No detectable Stevens rearrangement products (**2**) were formed in these reactions.



1 R = CH_3 or H **2**

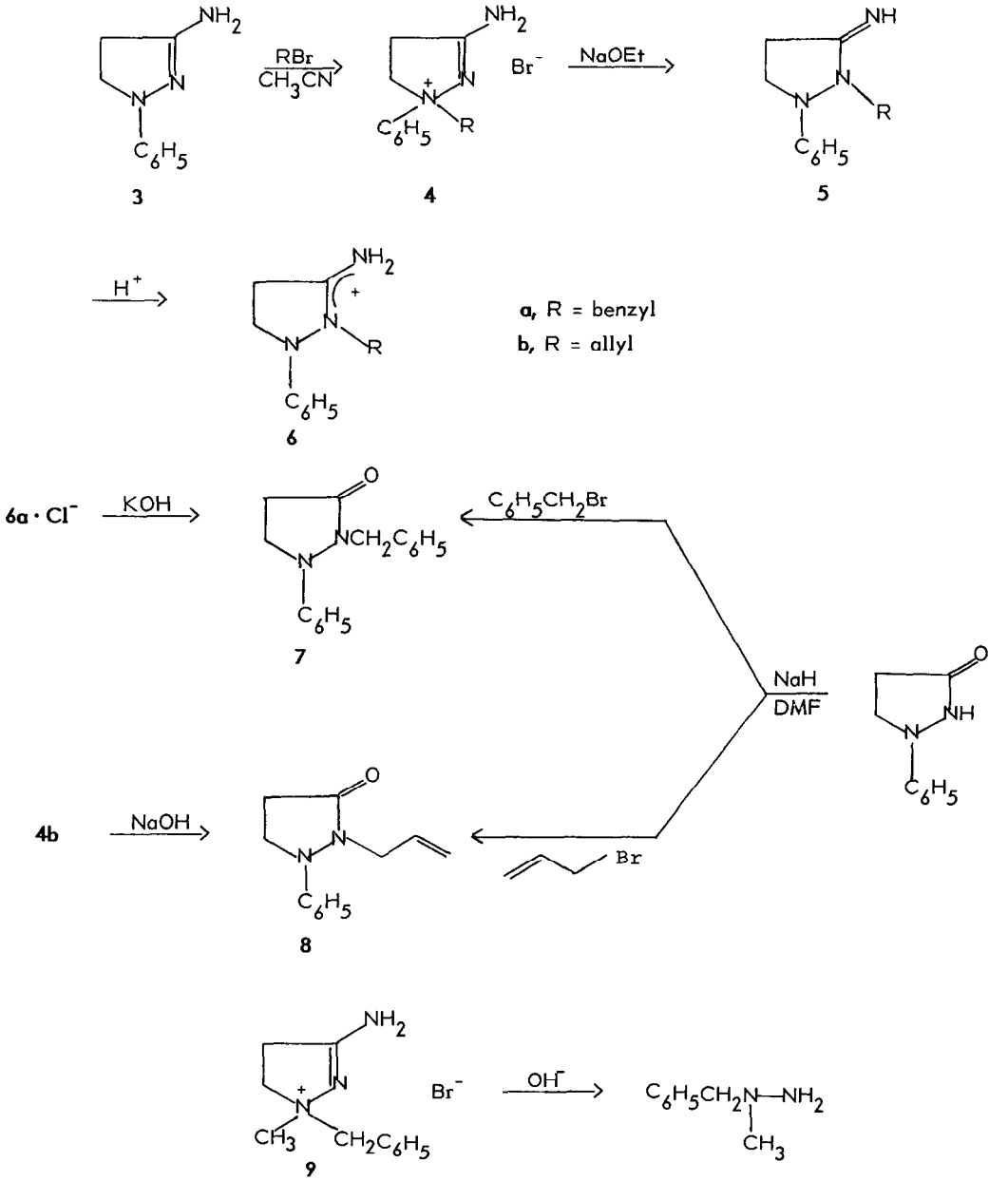
We now report that **4a** (the conjugate acid of a cyclic analog of (**1**) and the corresponding N^1-allyl-substituted compound (**4b**) undergo base-promoted Stevens rearrangements.[2]

3-Amino-1-benzyl-4,5-dihydro-1-phenyl-1H-pyrazolium bromide (**4a**)[3] was prepared in 94% yield from 3-amino-4,5-dihydro-1-phenyl-1H-pyrazole (**3**)[4] and benzyl bromide (CH_3CN, reflux, 2.5 hr), mp 169-171°C. IR (KBr) 1650, 3260, 3330 cm^{-1}. Similarly, the 1-allyl-substituted salt (**4b**) was prepared (reaction time 10 min) in 78% yield, mp 134-136°C. IR (KBr) 1635, 3250 and 3320 cm^{-1}.[5]

Heating **4a** at reflux (4 hr) in NaOEt (1.2 equiv.) -EtOH gave 2-benzyl-3-imino-1-phenylpyrazolidine (**5a**) which was isolated as its hydrochloride salt **6** • Cl^- in 75% yield, mp 236-239°C. IR (KBr) 1638 and strong, broad absorption from 2000-3200 cm^{-1}. The free base (**5a**) was obtained from **6** • Cl^- (NaOMe-MeOH) as a viscous oil that was purified by Kugelrohr distillation, 135°C (0.35 torr). IR (film) 1640 and 3330 cm^{-1}. Hydrolysis of **6**•Cl^- (KOH, 50% aqueous ethanol, reflux) gave 2-benzyl-1-phenyl-3-pyrazolidinone (**7**), mp 64-66°C. IR (film) 1690 cm^{-1}. Compound **7** was also prepared in 90% yield by alkylation of 1-phenyl-3-pyrazolidinone (NaH-DMF-$C_6H_5CH_2Br$). Heating **4a** at reflux in 1 N NaOH affords **5** which is contaminated with 10-20% of **7**.

Heating the allyl salt (**4b**) at reflux in EtOH containing 1.5 equivalents of NaOEt (7 hr) gave 2-allyl-3-imino-1-phenylpyrazolidine (**5b**) in 58% yield, bp 123-128°C (0.25 torr). IR (film) 1630 and 3330 cm^{-1}. Crystalline salts of **5b** could not be prepared but the NMR spectra (see Table) of the conjugate acid (**6b**) were obtained in $(CD_3)_2SO$-CF_3CO_2H. The ^1H NMR spectra of **6a** • Cl^- and **6b** display strongly deshielded NH_2^+ signals (δ 9.5-10.1) which supports[6] their assigned amidinium ion structures. Complete hydrolysis accompanied rearrangement when **4b** was heated in refluxing 1 N NaOH (2 hr). Under these conditions 2-allyl-1-phenyl-3-pyrazolidinone (**8**) was obtained in 57% yield, bp 120°C (0.25 torr). IR (film) 1700 cm^{-1}. Compound **8** was also prepared in 59% yield by alkylation of 1-phenyl-3-pyrazolidinone (NaH-DMF, allyl bromide).

3-Amino-1-benzyl-4,5-dihydro-1-methyl-1H-pyrazolium bromide (**9**) was prepared from 3-amino-4,5-dihydro-1-methyl-1H-pyrazole[7] in 76% yield, mp 278-280°C. Salt **9** did not undergo a Stevens rearrangement. When heated with 1 N NaOH at reflux (1 hr) **9** gave 59% of 1-benzyl-1-methylhydrazine[8] (identified by ^{1}H NMR and IR). The salt was recovered unchanged when treated with refluxing NaOEt-EtOH and NaOMe-MeOH.



TABLE

Selected NMR Data[a]

4a[b] (DMSO-d_6) ^{1}H: 5.01(s, $\underline{CH_2}C_6H_5$), 7.1-7.8(m, C_6H_5 and NH_2, exch.). ^{13}C: 31.01(4-C), 63.91(5-C), 168.09(3-C), 73.10($\underline{CH_2}C_6H_5$).

4b (DMSO-d_6) ^{1}H: 4.62(d, $\underline{CH_2}$CH=), 7.3-8.1(m, C_6H_5 and NH_2, exch.). ^{13}C: 29.97(4-C), 63.28(5-C), 167.02(3-C), 70.05($\underline{CH_2}$-CH=).

5a ($CDCl_3$) ^{1}H: 2.3(t, 2H), 3.38(t, 2H), 5.0(bds, 1H, exch.), 4.40(s, 2H), 6.6-7.4(m, 10H). ^{13}C: 29.90(4-C), 46.56(5-C), 165.32(3-C), 53.46($\underline{CH_2}C_6H_5$).

5b ($CDCl_3$) ^{1}H: 2.45(t, 2H), 3.59(t, 2H), 4.8-6.2(m, 3H), 6.0(s, 1H, exch.)., 6.7-7.4(m, 5H). ^{13}C: 30.16 (4-C), 46.45 (5-C), 163.52(3-C), 53.45($\underline{CH_2}$-CH=).

6a · Cl^- (DMSO-d_6) ^{1}H: 3.21(t, 2H), 3.78(t, 2H), 4.93(s, 2H), 6.7-7.7(m, 10H), 10.60(bds, 2H, exch.). ^{13}C: 28.91(4-C), 46.96(5-C), 163.76(3-C), 53.87($\underline{CH_2}$-C_6H_5).

6b (**5b** in DMSO-d_6-CF_3CO_2H) ^{1}H: 3.10(t, 2H), 3.77(t, 2H), 4.18(d, 2H), 5.0-6.1(m, 3H), 6.8-7.5(m, 5H), 9.52(bds, 1H), 10.10(bds, 1H). ^{13}C: 28.93(4-C), 46.81(5-C), 164.11(3-C), 53.87($\underline{CH_2}$-CH=).

7 ($CDCl_3$) ^{1}H: 2.32(t, 2H), 3.62(t, 2H), 4.43(s, 2H), 6.7-7.5(m, 10H).

8 ($CDCl_3$) ^{1}H: 2.42(t, 2H), 3.80(t, 2H), 3.95(d, 2H), 4.8-6.0(m, 3H), 6.8-7.5(m, 5H).

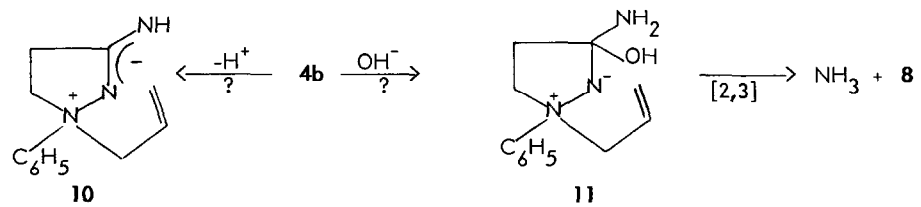
9 (DMSO-d_6) ^{1}H: 3.15(s, 3H), 4.63 and 4.65(singlets, diastereotopic benzylic H's), 7.15(bds, 2H, exch.), 7.45(s, 5H). ^{13}C: 30.29(4-C), 58.47(5-C), 166.46(3-C), 67.32($CH_2C_6H_5$), 57.72(CH_3).

a) In δ units relative to hexamethyldisloxane.

b) Due to the nonequivalence of the protons bonded to 4-C and 5-C, the 60 MHz ^{1}H spectra of the quaternary salts in the region δ 2.8-5.1 are complex.[10]

We have been unable to prepare the ylides derived from the salts **4a** and **4b**. In the conversion of **4b** to **8** the complete hydrolysis of the 3-amino substituent could be accounted for by a concerted [2,3] sigmatropic rearrangement occuring **via** the dipolar species **11** rather than the ylide **10** (formed by deprotonation of **4b**).[9]

We are currently studying the scope and mechanistic aspects of these reactions.



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