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Tetrahedron 60 (2004) 6581–6584
Tetrahedron

Synthesis of *N*,*N*-di(arylmethylidene)arylmethanediamines by flash vacuum pyrolysis of arylmethylazides

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Received 19 March 2004; revised 24 May 2004; accepted 1 June 2004

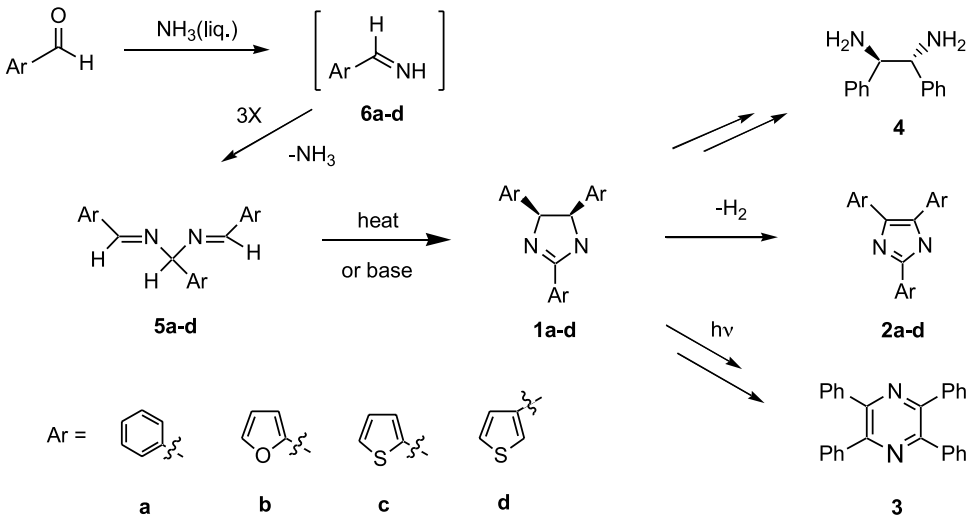
Abstract—Flash vacuum pyrolysis of arylmethylazides **7a-d** gave 2,4-diazapentadienes **5a-d** in high yield (76–92%). The thermal cyclization of **5a-d** gave *cis*-imidazolines **1a-d**, further heating or Swern oxidation of **1a-d** gave dehydrogenated products, imidazoles **2a-d**.

1. Introduction

Amarine **1a** is a very useful precursor for organic synthesis, which was found to give the corresponding imidazole **2a** by dehydrogenation.[1] **1a** can rearrange to 2,3,5,6-tetra-phenylpyrazine (**3**) by irradiation,[2] and converts to ligand **4**,[3] which has been employed for enantioselective synthesis.[4] Amarine **1a** can be prepared by cyclization of the *N*,*N*-di(arylmethylidene)arylmethanediamine **5a** with a strong base or under thermal condition. Compound **5a** was formed previously by condensation of imine **6a**, which was generated in liquid ammonia with benzaldehyde[5] (Scheme 1). Synthesis of **5** and **1** from arylaldehydes has also been accomplished by microwave irradiation or heating with hexamethyldisilazane.[6] Recently, we have synthesized **5a-d** by the flash vacuum pyrolysis of their corresponding arylmethylazides **7a-d**. We report here the results of this work.

2. Results and discussion

Arylmethylazides **7a-d** were prepared from the reported method.[7] FVP of **7a-d** at 450–550 °C and ca. 1×10^{-2} Torr, gave presumably gaseous nitrenes **8a-d** as the primary pyrolysis products. 1,2-Hydrogen shift of **8a-d** would give imines **9a-d**, which then underwent a condensed



Scheme 1.

Keywords: Arylmethylazides; Pyrolysis; *N*,*N*-Di(arylmethylidene)arylmethanediamines.
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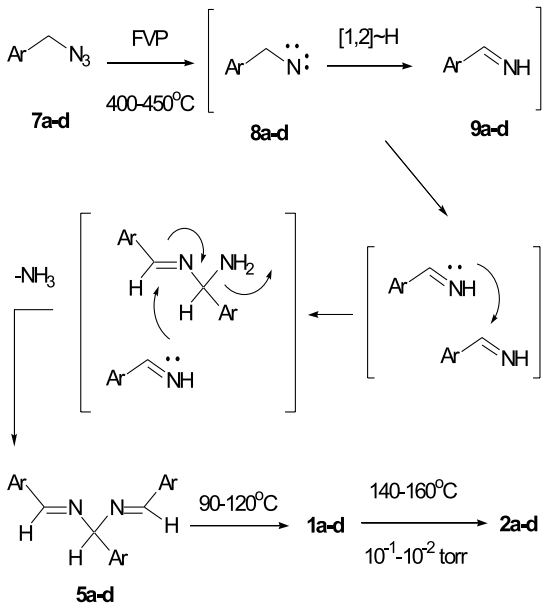
doi:10.1016/j.tet.2004.06.082

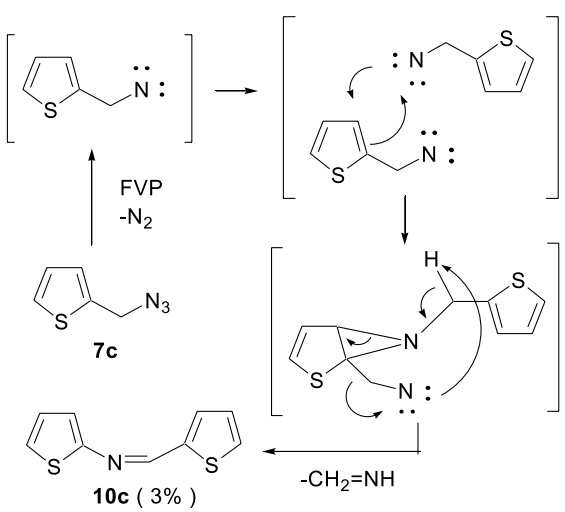


Scheme 2.

trimerization reaction to give **5a**-**d** in high yield (76–92%). Thermal isomerization of compounds **5a**-**d** under 90–120 °C for 4–6 h gave *cis*-imidazolines **1a**-**d**. Further heating of **1a**-**d** at 140–160 °C under low pressure condition (ca. 1×10^{-1} Torr) gave dehydrogenated products, imidazoles **2a**-**d**. The route to the pyrolysis products and thermally isomerized products from **8a**-**d** are summarized in Scheme 2 and the yields of each product are listed in Table 1. Since further heating of **1b** gave only decomposed products and **5d** cyclized directly to give **2d**, we did not isolate **2b** and **1d**.

Table 1. Products and yields from FVP of **7a**-**d**, and from thermolysis of the resulting compounds

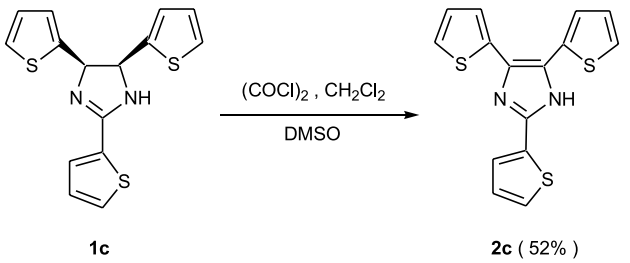
Entry	Starting materials	Products (yields, %)		
		5a-d	**1a-d**	**2a-d**
1	**7a**	92	84	55
2	**7b**	78	79	—
3	**7c**	86	63	31
4	**7d**	76	—	33



Scheme 3.

We also found that FVP of **7c**,**d** gave not only the condensed trimers **5c**,**d** as the major products, but also a small amount of dimers **10c**,**d**. We propose the mechanism for the formation of **10c** as shown in Scheme 3. The formation of **10d** follows the same type of mechanism.

It is noteworthy that the yields of imidazoles **2** from *cis*-imidazolines **1** can be improved by performing Swern oxidation. For instance, the yield of **2c** can be increased to 52% by Swern oxidation of **1c** (Scheme 4) as compared to 31% from simple heating of **1c** (Table 1).[8]



Scheme 4.

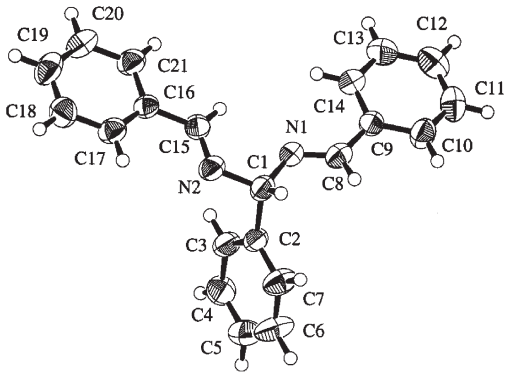


Figure 1. Crystal structure of **5a**.

Pure **5a** can be recrystallized from CH_2Cl_2. The structure of **5a** was analyzed by X-ray crystallography and shown as Figure 1.[9a] Pure **2c** was recrystallized from ethyl acetate and *n*-hexane. The structure of **2c** was analyzed by X-ray crystallography and shown as Figure 2.[9b]

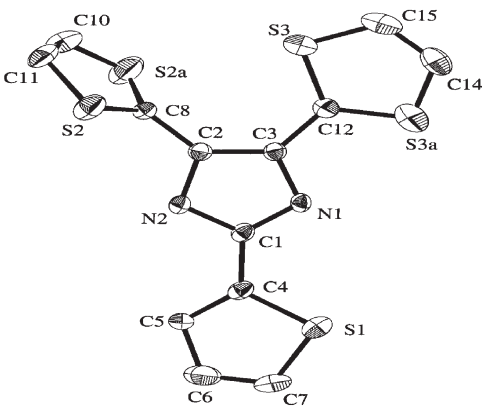


Figure 2. Crystal structure of **2c**. S2/S2a and S3/S3a are the disordered sites for S/CH disorder within the thiophene rings.

3. Conclusion

In conclusion, the flash vacuum pyrolysis of arylmethylazides **7a-d** is a new and efficient method to generate 2,4-diazapentadienes **5a-d**, further heating of **5a-d** can induce ring cyclization to give *cis*-imidazolines **1a-d**. We also found the yield of dehydrogenated products, imidazoles **2a-d** from **1a-d**, can be improved by performing Swern oxidation.

4. Experimental

4.1. General

Infrared spectra were recorded with a FTS-175/185 IR spectrophotometer. ^{1}H and ^{13}C NMR spectra were carried out in $CDCl_3$ or acetone-d_6 in a Varian VXR-300 NMR spectrometer. Chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane (TMS). Mass spectra were recorded with a VG QUATTRO 5022 spectrometer. The X-ray structures were analyzed by a RIGAKU AFC7S diffractoneter.

4.2. General pyrolysis procedure[10]

The furnace was maintained at temperatures in the range 400–450 °C. A sample for pyrolysis was placed into the sample chamber and the system was evacuated to ca. 10^{-2} Torr. During the pyrolysis $CDCl_3$ was deposited into the cold trap through a side arm. After the pyrolysis was completed, nitrogen was introduced into the system, the liquid-nitrogen-cooled trap was warmed to room temperature and all the FVP products were collected. At the exit of the horizontal fused quartz tube, the pure products **5a-d** were obtained without purification. These products were analyzed by ^{1}H, ^{13}C NMR, IR and Mass. The percent yields were determined from ^{1}H NMR.

4.3. Heating of 2,4-diazapentadienes 5a-d and *cis*-imidazolines 1a-d

A sample of FVP products **5a-d** was placed into the sample chamber of the bulb-to-bulb distillation, and the whole system was maintained at a pressure of 10^{-2} Torr. The sample chamber was heated to 120 °C for 5 h to give **1a-d**. Further heating of **1a-d** at 140–160 °C gave dehydrogenated products, imidazoles **2a-d**. These crude products were purified using preparative TLC or column chromatography on silica gel.

4.4. Swern oxidation of imidazoline 1c

A stirred solution of oxalyl chloride (0.79 mL, 1.6 equiv.) in CH_2Cl_2 (20 mL) at −78 °C was treated with DMSO (1.37 mL, 3.2 equiv.) in CH_2Cl_2 (10 mL), dropwise over 5 min. After 10 min, imidazoline **1c** (1.75g, 5.53 mmol) in CH_2Cl_2 (10 mL) was added over 10 min, followed by triethylamine (3.9 mL, 5 equiv.), dropwise over 10 min. The mixture was stirred with gradual warming overnight, and then the reaction was quenched with water. The organic phase was washed with brine, dried over $MgSO_4$, filtered, and concertrated to give the crude product. The crude product was purified by flash chromatography on silica gel using 2:1 *n*-hexane/ethyl acetate to give 0.90 g (52%) imidazole **2c**.

4.5. Spectral data of products

4.5.1. *N*,*N*-Di(phenylmethylidene)phenylmethane diamine (5a). IR ($CDCl_3$, cm^{-1}) 3085, 2844, 1639, 1579. Mp 105–107 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.57 (s, 2H), 7.83–7.86 (m, 4H), 7.18–7.53 (m, 11H), 5.97 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.5, 141.6, 135.9, 130.9, 128.6, 128.5, 128.4, 127.7, 127.1, 92.6. MS (FAB) *m*/*z* (%) 299 [(M+1)$^+$, 5.0]. (Lit. [5a] Mp 101–102 °C).

4.5.2. *N*,*N*-Di[(2-furanyl)methylidene](2-furanyl)methanediamine (5b). IR ($CDCl_3$, cm^{-1}) 1635. Mp 118–119 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.41 (d, J=0.6 Hz, 2H), 7.56 (d, J=1.2 Hz, 2H), 7.39 (d, J=0.6 Hz, 1H), 6.88 (d, J=3.3 Hz, 2H), 6.51 (q, J=1.8 Hz, 2H), 6.39 (d, J=3.3 Hz, 1H), 6.35 (q, J=1.8 Hz, 1H), 6.13 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.7, 151.5, 150.5, 145.3, 142.5, 115.8, 111.8, 110.4, 107.8, 84.1. MS (LR, 70 eV) *m*/*z* (%) 268 (M$^+$, 11.34). (Lit. [5a] Mp 116–117 °C).

4.5.3. *N*,*N*-Di[(2-thienyl)methylidene](2-thienyl)methanediamine (5c). IR (neat, cm^{-1}) 3166, 2252, 1691, 1626. ^{1}H NMR (300 MHz, acetone-d_6): δ 8.75 (s, 2H), 7.65 (d, J=8.5 Hz, 2H), 7.46 (dd, J=6.5, 1.5 Hz, 2H), 7.39 (dd, J=8.5, 1.5 Hz, 1H), 7.14 (dd, J=8.5, 6.0 Hz, 2H), 7.08 (d, J=5.5 Hz, 1H), 6.99–7.01 (m, 1H), 6.23 (s, 1H). ^{13}C NMR (75 MHz, acetone-d_6): δ 155.5, 146.9, 143.4, 133.2, 131.0, 128.6, 127.5, 126.3, 125.2, 87.3. HRMS Calcd for $C_{15}H_{12}N_2S_3$: 316.0163, found: 316.0165.

4.5.4. *N*,*N*-Di[(3-thienyl)methylidene](3-thienyl)methane diamine (5d). IR (neat, cm^{-1}) 2927, 2254, 1692, 1635. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.53 (s, 2H), 7.70 (t, J=1.5 Hz, 2H), 7.65 (d, J=5.0 Hz, 2H), 7.30–7.33 (m, 4H), 7.13–7.14 (m, 1H), 5.93 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.2, 142.9, 140.3, 129.6, 126.5, 126.4, 126.1, 126.0, 122.1, 89.0. HRMS Calcd for $C_{15}H_{12}N_2S_3$: 316.0163, found: 316.0161.

4.5.5. *cis*-2,4,5-Triphenylimidazoline (1a). IR ($CDCl_3$, cm^{-1}) 2834, 2347, 1636. Mp 128–130 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.97 (d, J=8.4 Hz, 2H), 7.53–7.46 (m, 4H), 7.03–6.90 (m, 10H), 5.41 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.5, 138.6, 131.2, 129.5, 128.6, 127.6, 127.4, 127.3, 126.8, 70.6. MS (LR, 70 eV) *m*/*z* (%) 298 (M$^+$, 8.3). (Lit.[5a] Mp 127–128 °C).

4.5.6. *cis*-2,4,5-Tri(2-furanyl)imidazoline (1b). IR ($CDCl_3$, cm^{-1}) 3124, 2936, 2873, 1633. Mp 111–112 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.51 (d, J=0.9 Hz, 1H), 7.19 (t, J=0.6 Hz, 2H), 7.14 (d, J=3.3 Hz, 1H), 6.52 (q, J=1.8 Hz, 1H), 6.17 (q, J=2.1 Hz, 2H), 6.04 (d, J=3.0 Hz, 2H), 5.38 (s, 2H), 5.00 (br, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.2, 151.9, 144.7, 144.2, 141.8, 112.9, 111.9, 110.1, 107.2, 63.3. MS (LR, 70 eV) *m*/*z* (%) 268 (M$^+$, 38.2). (Lit.[5a] Mp 115–116 °C).

4.5.7. *cis*-2,4,5-Tri(2-thienyl)imidazoline (1c). IR (neat, cm^{-1}) 1716, 1699, 1627. Mp 127–128 °C. ^{1}H NMR (300 MHz, acetone-d_6): δ 7.75 (d, J=4.0 Hz, 1H), 7.67 (d,

J=5.0 Hz, 1H), 7.17–7.19 (m, 1H), 7.11–7.12 (m, 2H), 6.76–6.78 (m, 4H), 5.65 (s, 2H), 3.20 (br, 1H). ^{13}C NMR (75 MHz, acetone-d_6): δ 160.3, 144.2, 134.9, 130.5, 129.4, 128.4, 126.9, 126.0, 125.3. HRMS Calcd for $C_{15}H_{12}N_2S_3$: 316.0163, found: 316.0165. (Lit.[6a] Mp 125–126 °C).

4.5.8. 2,4,5-Triphenylimidazole (2a). IR (KBr, cm^{-1}) 3028, 2926, 1786, 1647. Mp 274–275 °C. ^{1}H NMR (300 MHz, acetone-d_6): δ 11.73 (br, 1H), 8.13–8.15 (m, 2H), 7.15–7.68 (m, 13H). ^{13}C NMR (75 MHz, acetone-d_6): δ 148.8, 138.6, 136.2, 131.2, 130.4, 130.1, 129.7, 129.6, 129.5, 129.3, 129.2, 129.1, 128.9, 128.9, 128.2, 127.0. HRMS: Calcd for $C_{21}H_{16}N_2$: 296.1313, found: 296.1317. (Lit.[11] Mp 270–273 °C).

4.5.9. 2,4,5-Tri(2-thienyl)imidazole (2c). IR (neat, cm^{-1}) 3304, 2927, 1736, 1716, 1687. Mp 248–249 °C. ^{1}H NMR (300 MHz, acetone-d_6): δ 7.64–7.65 (m, 1H), 7.59 (br, 2H), 7.51–7.52 (m, 1H), 7.35 (br, 2H), 7.11–7.24 (m, 3H), 6.97 (br, 1H). ^{13}C NMR (75 MHz, acetone-d_6): δ 143.1, 138.5, 135.1, 134.6, 127.9, 129.7, 128.6, 127.4, 125.3. HRMS Calcd for $C_{15}H_{10}N_2S_3$: 314.0006, found: 314.0009.

4.5.10. 2,4,5-Tri(3-thienyl)imidazole (2d). IR (neat, cm^{-1}) 2985, 2252, 1731, 1693. Mp 244–246 °C. ^{1}H NMR (300 MHz, acetone-d_6): δ 7.96 (t, J=1.5 Hz, 1H), 7.73 (d, J=1.5 Hz, 1H), 7.55–7.57 (m, 3H), 7.48 (dd, J=5.0, 3.0 Hz, 2H), 7.30 (dd, J=5.0, 1.0 Hz, 2H). ^{13}C NMR (75 MHz, acetone-d_6): δ 143.4, 135.0, 133.7, 128.4, 127.3, 126.9, 126.5, 122.7, 122.3. HRMS Calcd for $C_{15}H_{10}N_2S_3$: 314.0006, found: 314.0003.

Acknowledgements

We thank the National Science Council of the Republic of China for financial support.

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