

Novel Burgess reagent mediated C-to-N aryl migration reaction in nitrones

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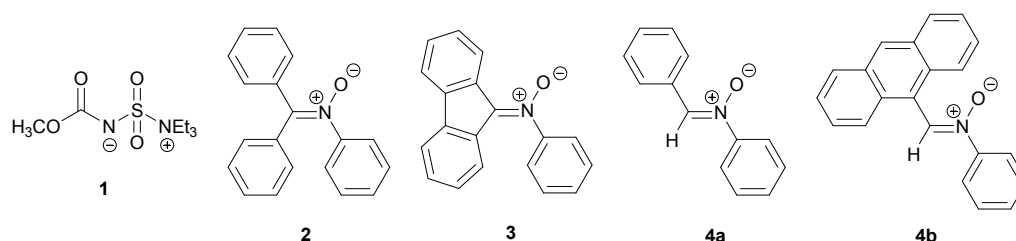
Supplementary Material

Experimental Section

General Techniques

All reactions were carried out in oven dried glassware. All starting materials were purchased from *Sigma-Aldrich* or from *S. D. Fine Chemicals* and were used without further purification unless otherwise mentioned. Progress of reactions were monitored by thin layer chromatography using dried and activated silica gel TLC plates (aluminium sheets coated with silica gel, *E. Merck*). Visualisation of TLC plates was done by exposure to iodine vapors or using a UV lamp. Solvents used for the experiments were distilled and dried by employing standard protocols. Separation and purification of compounds were done by column chromatography using silica gel (*S. D. Fine Chemicals*, 60-120 mesh). Mixtures of ethyl acetate and hexane were used as the eluent. After chromatographic separation, solvent was removed using *Heidolph* rotary evaporator. The products were further purified by recrystallization from appropriate solvent system. Melting points were recorded on *Neolab* melting point apparatus. Elemental analysis was performed on *Elementar Systeme (Vario EL III)*. FAB mass spectra were recorded on *JEOL JMS 600*. IR spectra were recorded on *ABB Bomem (MB Series)* FT-IR spectrometer and *JASCO-FTIR 4100* spectrometer. All ^1H and ^{13}C NMR spectra were recorded at 500 and 125 MHz respectively on *Bruker* FT-NMR spectrometer using CDCl_3 as the solvent. Chemical shifts are given in δ scale with TMS as internal standard. Yields reported are for compounds separated and purified in analytically pure form.

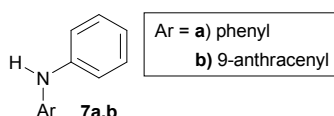
Burgess reagent (**1**) and nitrones **2,3,4a,b** were prepared using the reported procedures. All the reactions were carried out under nitrogen atmosphere in dry, freshly distilled solvents.



General Procedure for Reaction of Nitrones **2,3,4a,b** with Burgess reagent

Three equivalents of Burgess reagent were added under nitrogen to a well stirred solution of nitron in dry dichloromethane at room temperature and the stirring was continued for 3h. Progress of the reaction was monitored by TLC using ethyl acetate:hexane (8:92). In the case of **2** and **3**, the intermediate carbamate product was isolated from the reaction mixture by adding

hexane. Addition of hexane to the reaction mixture gave two layers - a brown colored bottom layer containing the decomposition products of Burgess reagent and the upper layer containing the precipitated carbamate product which was carefully decanted. The filtrate was allowed to settle and washed repeatedly with hexane to get the colorless precipitate of carbamate in pure form. It was further characterized by IR, ¹H NMR, ¹³C NMR, MS (FAB) analysis. Triethylamine-sulfur trioxide complex separated as colorless needles could be isolated under carefully controlled conditions. In the case of **4a,b**, evaporation of hexane layer gave diarylamines **7a,b** as the only isolable product (68-76%).



Hydrolysis of Carabamate **6**

Hydrolysis of carbamate **6** was achieved by acid medium like dilute HCl. Dilute HCl (10%) was added to a solution of **6** in methanol and stirred for 20 min. at room temperature. It was neutralized with sodium bicarbonate solution and diphenylamine was completely separated by extracting with hexane (71%). The aqueous layer was further extracted with ether. Crystals of **8** obtained on evaporating ether was purified by recrystallization from dichloromethane - hexane mixture and characterized on the basis of spectral and analytical data (64%).

Hydrolysis of Carabamate **12**

Hydrolysis of carbamate **12** was achieved by acid medium like oxalic acid adsorbed on silica gel. After hydrolysis, excess acid was neutralized with sodium bicarbonate solution and the products were isolated by solvent extraction.

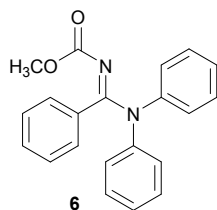
Spectral and Analytical Data of Novel Compounds:

Compound **6**

Yield 2.60 g (78%); mp 172 °C

IR: $\nu_{\max}/\text{cm}^{-1}$ (KBr): 1713, 1616, 1577, 1490, 1372, 1236, 1195, 1118

¹H NMR: δ_{H} (500 MHz; CDCl₃; Me₄Si): 7.41-7.39(2H, m), 7.26-7.20(7H, m), 7.14-7.10(6H, m), 3.4(3H, s)



¹³C NMR: δ_{C} (125 MHz; CDCl₃; Me₄Si): 163.4, 162.5, 144.2, 134.4, 130.1, 129.0, 128.7, 128.2, 127.5, 126.1, 52.7

FAB-MS (m/z): calcd for C₂₁H₁₈N₂O₂: 330.38 (M^+); found 331.17 (M^++1)

Elemental analysis: Found: C, 76.12; H, 5.47; N, 8.50. Calcd for C₂₁H₁₈N₂O₂: C, 76.34; H, 5.19; N, 8.78.

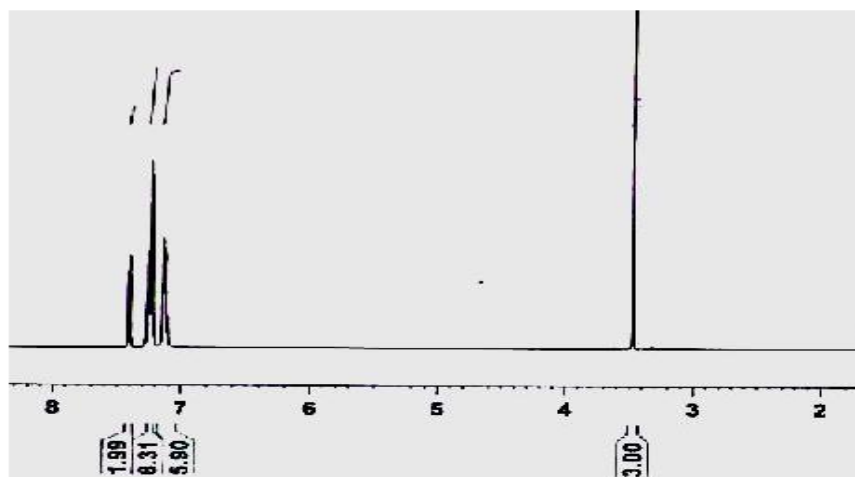


Figure 3. ^1H NMR spectrum of **6**

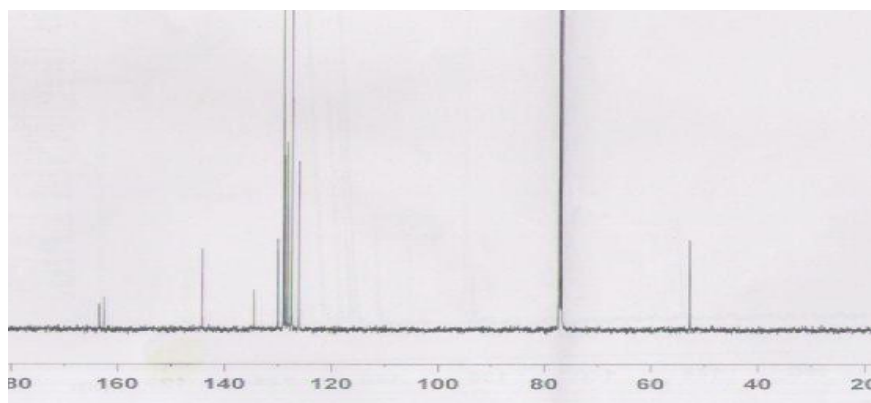


Figure 4. ^{13}C NMR spectrum of **6**

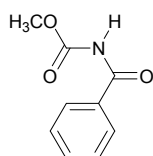
Compound **8**

Yield 1.6 g (64%); mp 116 °C

IR: ν_{max} / cm^{-1} (KBr); 3278, 1778, 1751, 1529, 1209, 1018, 702

^1H NMR: δ_{H} (500 MHz; CDCl_3 ; Me_4Si): 8.09(1H, s), 7.83-7.81(2H, m), 7.61-7.58(1H, m), 7.50-7.47(2H, m), 3.87(3H, s)

FAB-MS (m/z): calcd for $\text{C}_9\text{H}_9\text{NO}_3$: 179.17 (M^+); found 180.12 (M^++1)



8

Elemental analysis: Found: C, 61.12; H, 5.04; N, 7.80. Calcd for $\text{C}_9\text{H}_9\text{NO}_3$: C, 60.83; H, 4.86; N, 7.62.

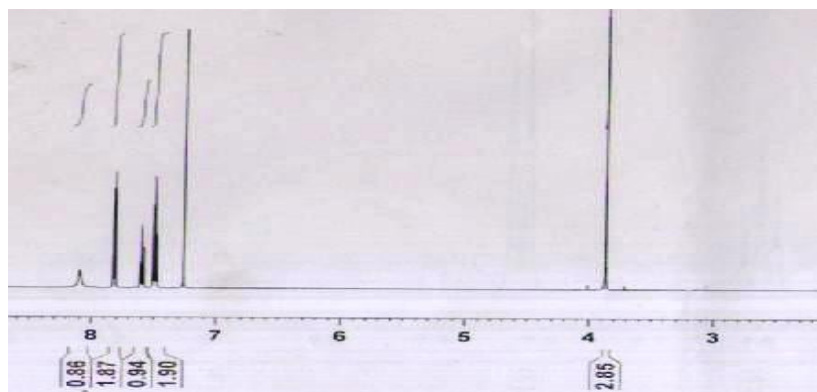


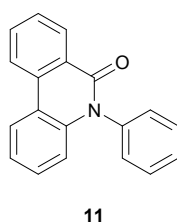
Figure 5 ^1H NMR spectrum of **8**.

Compound 11

Yield 1.97 g (73%); mp 202 °C

IR: ν_{max} / cm^{-1} (KBr): 3066, 1658, 1604, 1486, 1324, 1261, 810, 747

^1H NMR: δ_{H} (500 MHz; CDCl_3 ; Me_4Si) 8.49-8.47 (1H, q), 8.26-8.22 (1H, m), 8.22-8.21 (1H, m), 7.74-7.71 (1H, m), 7.55-7.51 (3H, m), 7.47-7.44 (1H, m), 7.26-7.25 (1H, m), 7.24 (1H, d, $J=7.6$ Hz), 7.23-7.20 (2H, m), 6.62-6.60 (1H, m)



^{13}C NMR: δ_{C} (125 MHz; CDCl_3 ; Me_4Si): 160.6, 138.1, 137.2, 132.9, 131.8, 129.1, 128.0, 127.9, 127.7, 127.1, 124.8, 121.9, 121.6, 120.7, 118.0, 116.0

FAB-MS (m/z): calcd for $\text{C}_{19}\text{H}_{13}\text{NO}$: 271.31 (M^+); found 272.40 (M^++1)

Elemental analysis: Found: C, 83.71; H, 4.81; N, 5.18. Calcd for $\text{C}_{19}\text{H}_{13}\text{NO}$: C, 84.11; H, 5.01; N, 4.98.

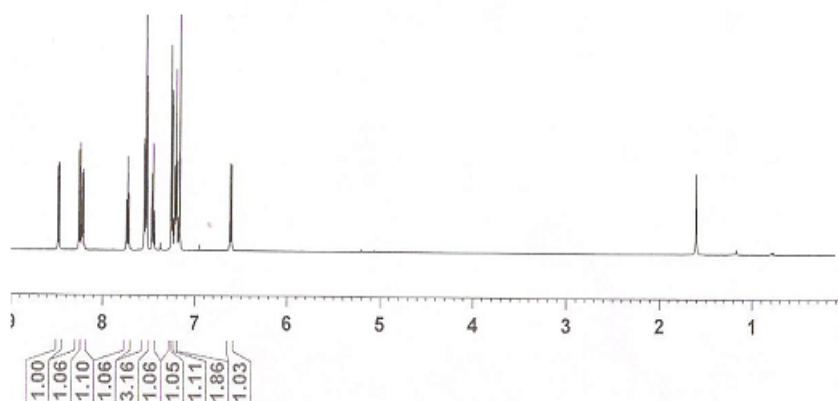


Figure 10 ^1H NMR spectrum of **11**.

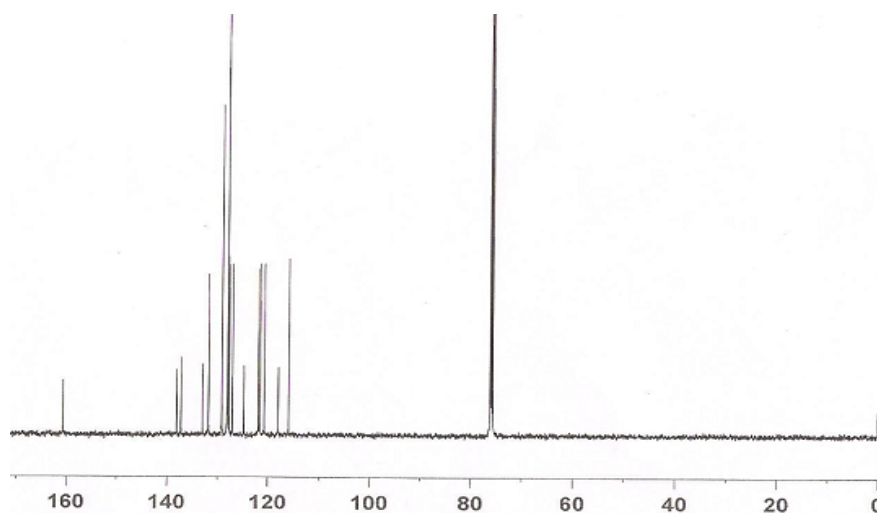


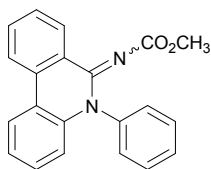
Figure 11 ^{13}C NMR spectrum of **11**.

Compound 12

Yield 2.68 g (82%); mp 149 °C

IR: ν_{max} / cm^{-1} (KBr): 3055, 2949, 1683, 1640, 1601, 1488, 1357, 1191, 1119, 1096

^1H NMR: δ_{H} (500 MHz; CDCl_3 ; Me_4Si): 8.45-8.43(1H, m), 8.30-8.27(1H, m), 8.26-8.25(1H, m), 7.78-7.74(1H, m), 7.62-7.58(2H, m), 7.57-7.53(2H, m), 7.42-7.41(2H, m), 7.27-7.24(2H, m), 6.58-6.56(1H, m), 3.32(3H, s)



12

^{13}C NMR: δ_{C} (125 MHz; CDCl_3 ; Me_4Si): 160.0, 148.5, 139.0, 138.1, 132.8, 132.5, 130.5, 130.2, 129.8, 129.3, 129.2, 129.1, 128.3, 125.3, 123.1, 122.8, 121.8, 119.7, 117.0, 52.2

FAB-MS (m/z): calcd for $\text{C}_{21}\text{H}_{16}\text{N}_2\text{O}_2$: 328.36 (M^+); found 329.26 (M^++1)

Elemental analysis: Found: C, 76.61; H, 4.93; N, 8.55. Calcd for $\text{C}_{21}\text{H}_{16}\text{N}_2\text{O}_2$: C, 76.31; H, 5.11; N, 8.78.

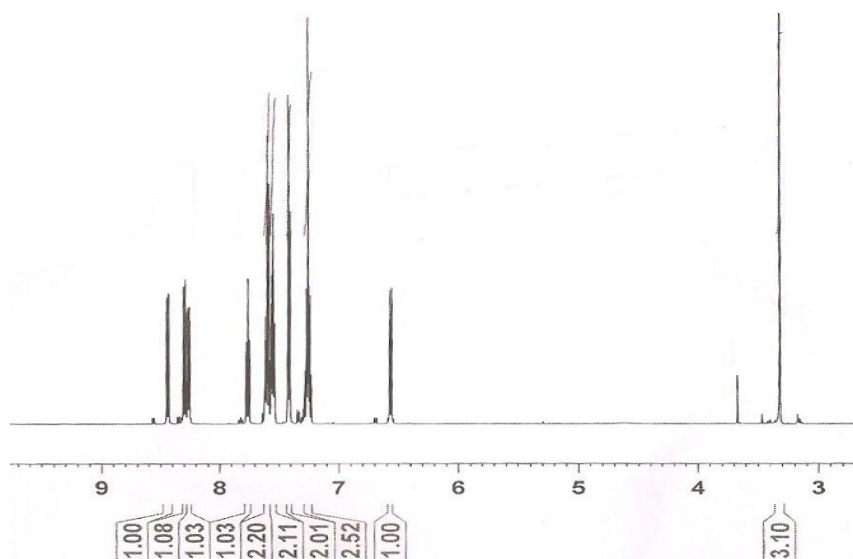


Figure 6 ^1H NMR spectrum of compound **12**.

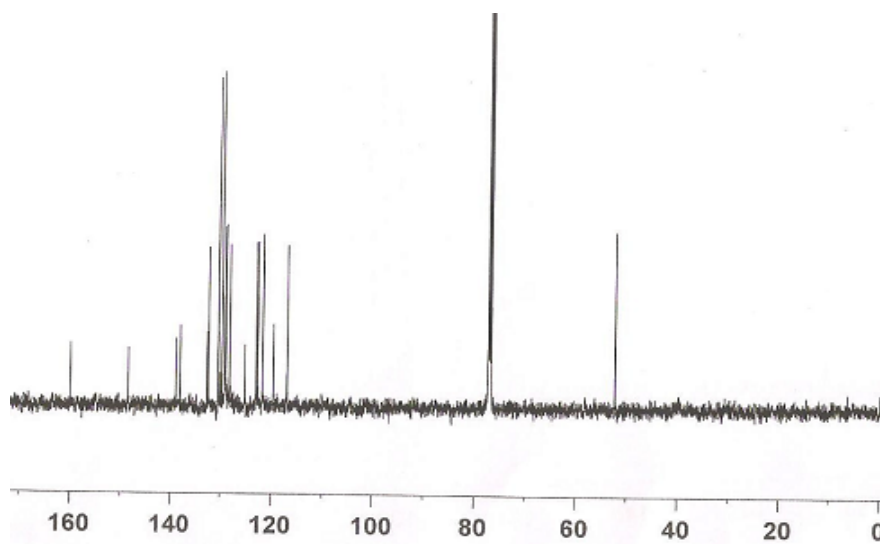


Figure 7 ^{13}C NMR spectrum of compound **12**.

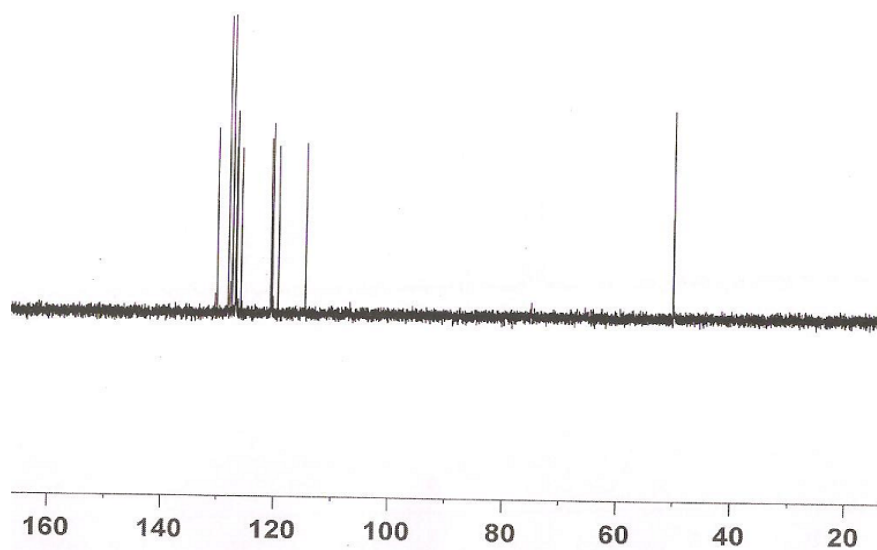


Figure 8 ^{13}C DEPT-135 spectrum of **12**.

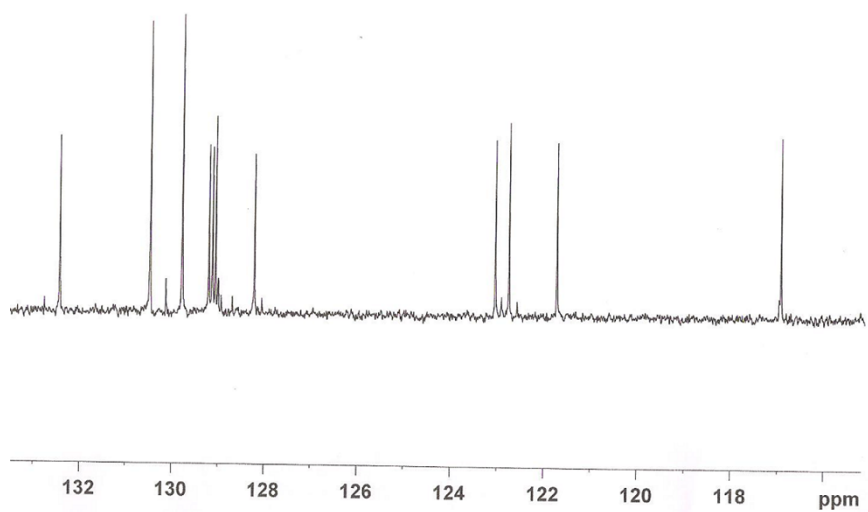


Figure 9 ^{13}C DEPT-90 spectrum of **12**.