

TANDEM GENERATION OF FURO [3, 4-b] PYRAZINE AND FURO [3, 4-b] QUINOXALINE INTERMEDIATES USING FISCHER CARBENE COMPLEXES AND TRAPPING FOR SYNTHESIS OF NITROGEN HETEROCYCLES

Abstract

An unique method for tandem generation of furo[3,4-b]pyrazine and furo[3,4-b]quinoxaline intermediates using Fischer carbene complexes and then trapping with suitable dienophiles to generate nitrogen heterocycles has been described. The intermediate is trapped with a dienophile to generate quinoxaline or phenazine ring system respectively.

Keywords: Fischer Carbene Complexes, Dotz Benzanullation, Heterocycles, Cycloaddition, Benzannulation.

Author

Priyabrata Roy
Department of Chemistry
Victoria Institution (College)
Kolkata, India

I. INTRODUCTION

Quinoxaline derivatives have attracted the attention of the medicinal industry due to their useful properties as antifungals, antiviral, anti-inflammatory drugs and kinase inhibitors.¹ They have also been assessed as antitumor, anthelmintic agents, antifungal and pesticides.² Additionally, quinoxaline core is a component of many antibiotics (such as echinomycin, levomycin, and actinomycin) that are recognized to prevent the growth of Gram-positive microbes and have activity against many types of cancer.³ Also they have found applications in colorants, electroluminescent ingredients, organic semiconductors, cavitands, chemical switches, and DNA disintegration agents.^{4,5} They exhibit a wide range of biological properties. So, they are considered suitable models in combinatorial drug research. Available drugs containing quinoxaline ring system include lamprene for leprosy, XK-469 as antitumor and BMS-238497 for kinase inhibitors (Figure 2.1).

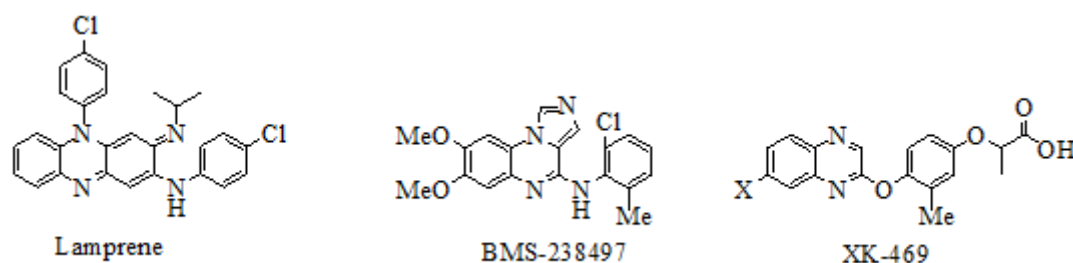


Figure 2.1: Biologically active quinoxalines.

Natural products containing phenazine rings are particularly remote as secondary metabolites from terrestrial or marine habitats of *Pseudomonas*, *Streptomyces*, and some other genera. The biological properties of these natural products are antibacterial, antifungal and antiviral. The role of phenazine pigments as anti-inflammatory and virulence agents has recently been briefly reviewed.⁶ Human infectious diseases are also inhibited by their derivatives. For example, pyocyanin induces neutrophil apoptosis, and a defect in pyocyanin synthesis in a strain of *P. aeruginosa* affects the immune system of pneumonia in mice.⁷ Since the lungs of almost all patients with cystic fibrosis have been colonized by *Pseudomonas aeruginosa* and have low life expectancy,⁸ phenazine derivatization and production may be a way to influence the drug activity.

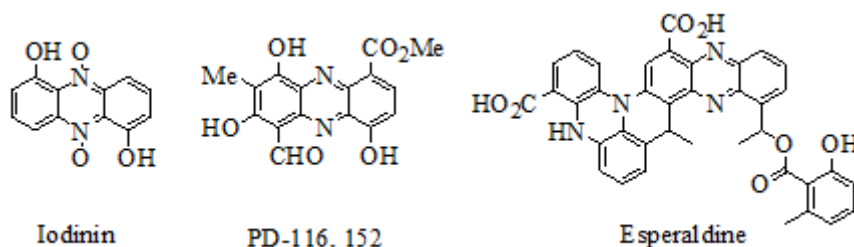
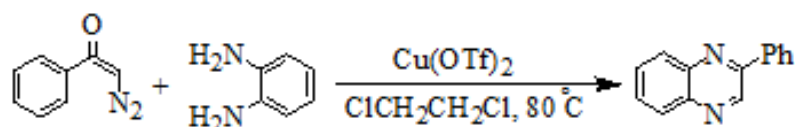


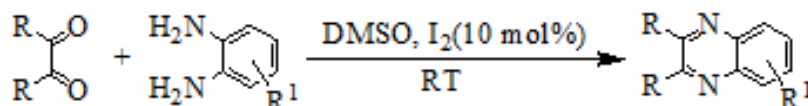
Figure 2.2: Biologically active phenazines.

These heterocyclic systems are often combined by cyclizing the heterocycle onto an existing benzene ring.⁹ Yadav and co-workers reported quinoxaline synthesis from α -diazoketone and aryl 1,2-diamine using 10 mol% copper(II) trifluoromethanesulfonate in good yield and high selectivity.^{9a} Rh₂(OAc)₄ has also been shown to be a good catalyst for this conversion (Scheme 2.1).



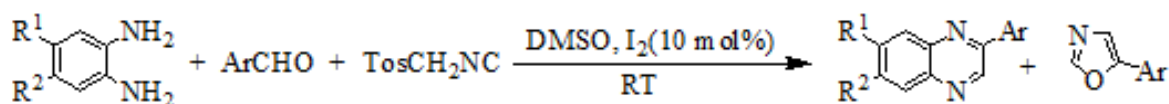
Scheme 1

1,2-Dicarbonyl compounds react with different o-phenylenediamines in DMSO at room temperature using the catalytic value of molecular iodine to provide different functionalized quinoxalines in good yield (Scheme 2.2).^{9e}



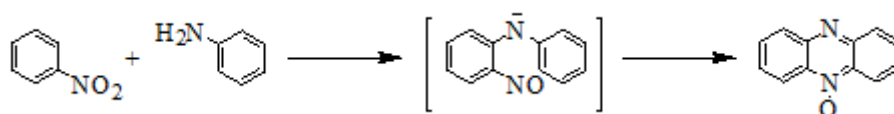
Scheme 2

Tsoleridis and co-workers reported the production of quinoxaline in excellent yield on the basis of a novel reaction involving o-phenylenediamine, aldehyde, and p-toluenesulfonylmethylisocyanide (TosMIC) (Scheme 2.3).^{9g}



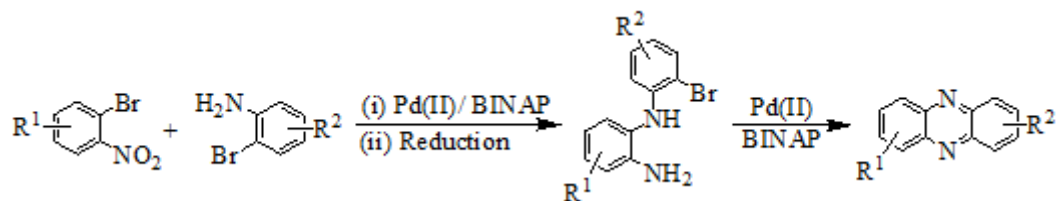
Scheme 3

Wohl and co-workers published a method for the preparation of phenazines in 1901.¹⁰ They established that aniline and nitrobenzene produce phenazine or phenazine-N-oxide when heated to 200 °C in the presence of a strong base (Scheme 4). The disadvantage of this method is that it is less efficient and produces large amount of byproducts in the drastic reaction condition (Scheme 2.4).



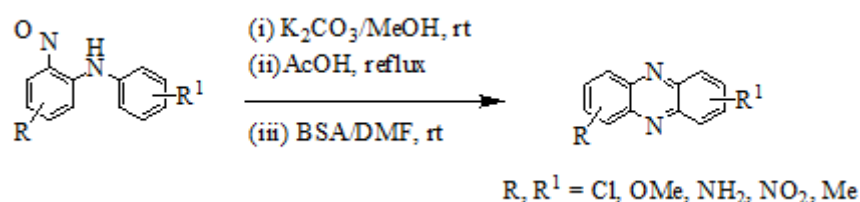
Scheme 4

Emoto and co-workers reported the synthesis of phenazines via palladium(II)-catalyzed aryl amination using BINAP as ligand (Scheme 2.5).^{11a}



Scheme 5

Reaction of nitroaromatic hydrocarbons with anilide anions generates N-aryl-2-nitrosoaniline which on cyclization produces phenazine ring systems. Potassium carbonate in methanol, N,O-bis(trimethylsilyl)acetamide (BSA) in aprotic solvent and acetic acid promote the reaction. The process is exemplified by the preparation of 1-methoxyphenazines, the starting material of pyocyanin, starting from the suitable nitroarene-aniline pair (Scheme 2.6).^{11b}



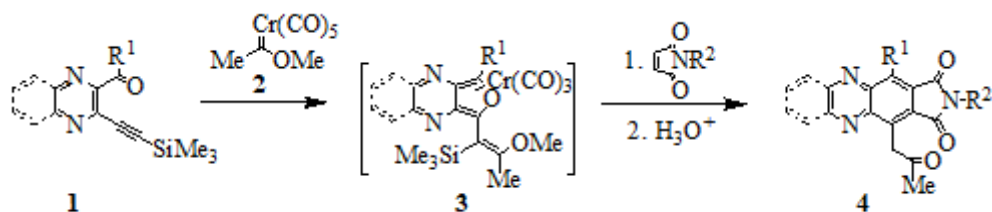
Scheme 6

II. PRESENT WORK

Multicomponent reaction (MCR) can simply be defined as a process in which at least three reactants added simultaneously in a reaction vessel to form a new product containing all the reactants or its part. They are very useful method for diversity-oriented synthesis in combinatorial chemistry with higher atom economy. In addition, Fischer carbene complexes (FCCs) of group VI metal which act as valuable reagent in synthetic organic chemistry can be used as important building blocks in MCRs. Several reviews have appeared in this area describing the versatile use of FCCs in MCRs.¹²

In this Chapter, we have demonstrated a multicomponent coupling approach for the synthesis of quinoxaline and phenazine derivatives by using chromium Fischer carbene complexes. Our strategy toward quinoxaline and phenazine syntheses are based on the pioneering work of Herndon and co-workers.¹³ Quinoxaline or phenazine ring systems are synthesized in one pot through in situ generation and trapping of azaisobenzofuran intermediates.¹⁴ This synthesis involves coupling of First, Fischer carbene complex 2 combine with 2-alkynyl-3-pyrazinecarbonyl derivative 1A to produce hitherto unknown intermediates furan [3,4-b]pyrazine 3A. Then, This diene trapped with a suitable dienophile to generate quinoxaline derivatives. The same procedure applied for synthesis of phenazine

derivatives. In this case, starting material was 2-alkynyl-3-quinoxalinecarbonyl derivative **1C**. The reaction goes through generation of the furo[3,4-b]quinoxaline intermediate **3C** (Option 2.7).¹⁵



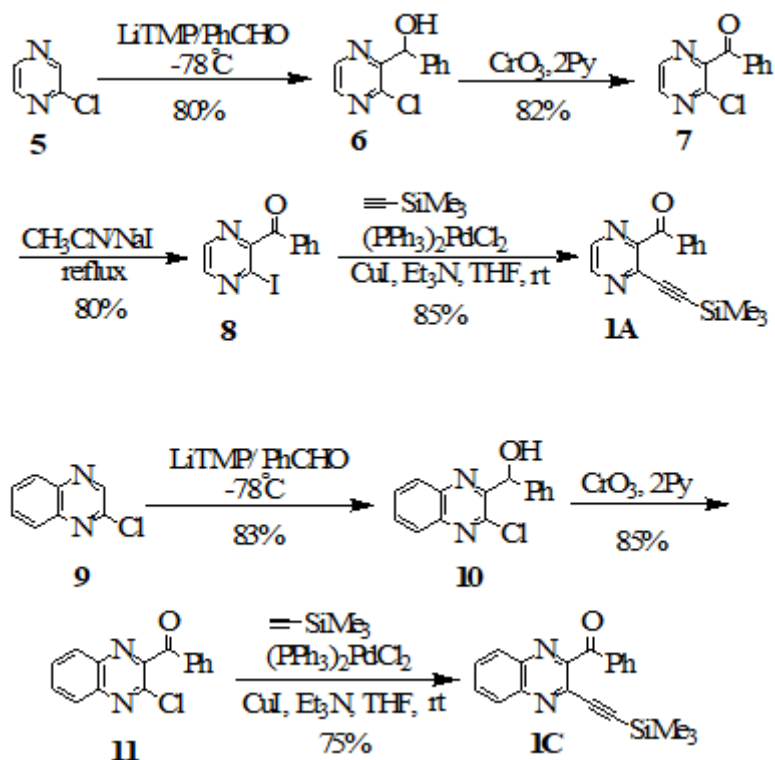
Scheme 7

III. RESULTS AND DISCUSSION

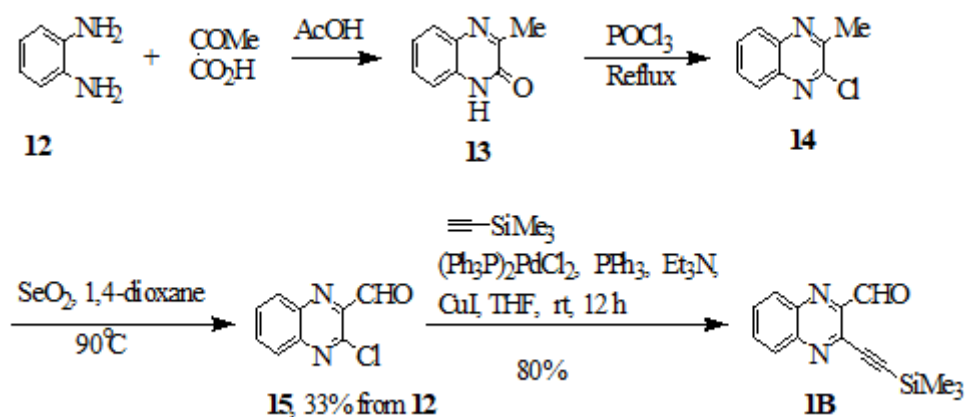
1. Synthesis of Alkynyl-Carbonyl Derivatives 1: Alkynyl-carbonyl derivatives **1A/1C** required for the synthesis of quinoxalines and phenazines were prepared according to the sequence of reactions in Scheme 2.8. Chloroketones **7/11** were prepared by the regioselective ortho-lithiation of 2-chloropyrazine (**5**)/ 2-chloroquinoxaline (**9**) with LiTMP at $-78\text{ }^{\circ}\text{C}$ followed by quenching with benzaldehyde and subsequent oxidation according to the procedure Turck and co-workers.¹⁶ Iodoketone **8** was prepared in 80% yield from (3-chloro-2-pyrazinyl)phenylmethanone¹⁷ by halogen exchange with NaI in acetonitrile. Iodoketone **8** or chloroketone **11** were reacted with (trimethylsilyl)acetylene under palladium catalysis in the presence of a catalytic amount CuI to give requisite o-alkynylcarbonyl derivatives **1A** or **1C** respectively.

The synthesis of 2-alkynyl 3-formylquinoxaline derivative **1B** commenced with coupling of commercially available *o*-phenylenediamine **12** and pyruvic acid. The coupled product **13**, thereafter was reacted with POCl_3 in reflux condition to give the chloro derivative **14**. Subsequent oxidation with selenium dioxide where 1,4-dioxane was used as solvent, delivered the 2-chloro-3-quinoxaline carboxaldehyde **15**.¹⁸ Sonogashira coupling of **15** with (trimethylsilyl)acetylene at room temperature under palladium catalysis in the presence of a catalytic amount CuI afforded the requisite alkynyl carbonyl derivatives **1B**.

TANDEM GENERATION OF FURO [3, 4-b] PYRAZINE AND FURO [3, 4-b] QUINOXALINE INTERMEDIATES USING FISCHER CARBENE COMPLEXES AND TRAPPING FOR SYNTHESIS OF NITROGEN HETEROCYCLES

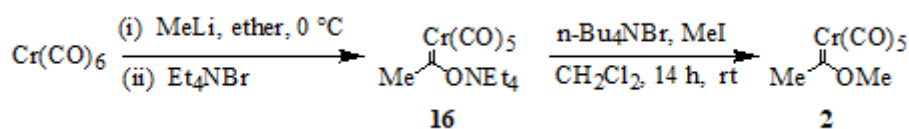


Scheme 8



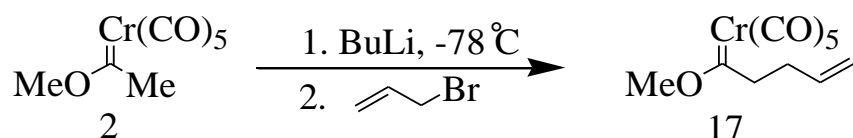
Scheme 9

2. **Preparation of Carbene Complexes:** Pentacarbonyl(methoxymethylcarbene)chromium (2)¹⁹ was prepared from the methyl lithium and chromium hexacarbonyl at 0 °C under argon atmosphere, followed by the conversion to the ammonium salt 16²⁰ with the addition of tetraethylammonium bromide and then treatment with methyl iodide in presence tetrabutylammonium bromide (Scheme 2.10).²¹



Scheme 10

The γ,δ -unsaturated Fischer carbene complex **17** was prepared from the methoxymethylcarbene complex **2** in 66% yield via deprotonation using *n*-BuLi (0.95 eq) at -78°C followed by addition of an excess allylic bromide at once at 0°C as reported by Herndon and co-workers (Scheme 2.11).^{22,23}

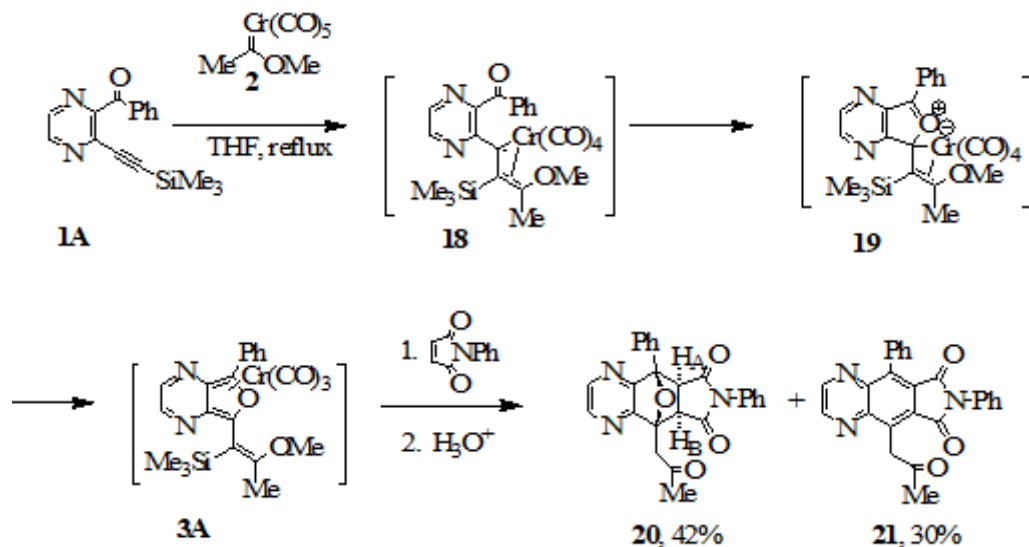


Scheme 11

3. Three-component Coupling Reaction of Carbene Complex, Alkynyl Carbonyl Derivatives and Dienophiles

- **Synthesis of Quinoxaline Derivatives:** First, pyrazinyl ketone 1A, carbene complex 2, and *N*-phenylmaleimide (1:1:1 ratio) were coupled in a reaction vessel in solvent THF at refluxing temperature (Scheme 2.12). This reaction leads to the synthesis of A mixture of oxonorbornene derivative 20 and quinoxaline derivative 21 were synthesized through this reaction. The reaction goes through generation and trapping of furo[3,4-*b*]pyrazine intermediate 3A.

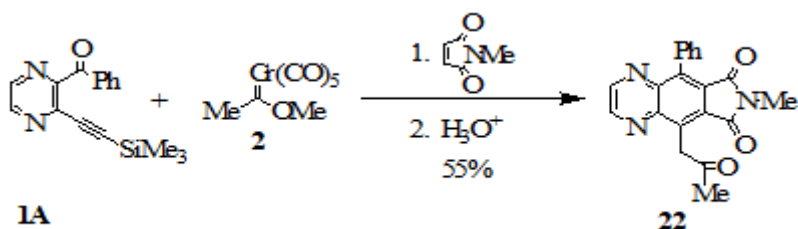
Fischer Carbene Complex 2 couple with alkyne derivative 1A to generate a alkyne carbene complex 18. Then it is captured by oxygen to generate the carbonyl-ylide derivative 19. Loss of metal from carbonyl-ylide derivative 19 yields isobenzofuran intermediate 3A which is basically a diene. So, it is easily trapped with a dienophile *N*-phenylmaleimide via a (4+2) cycloaddition to generate the oxygen brazed adduct 20 in 42% yield and desired quinoxaline derivative 21 in 30% yield. All these compounds were confirmed by analyzing their spectral data. Presence of absorption band at 1713 cm^{-1} due to carbonyl group in the IR spectra; in the ^1H NMR spectrum, the two



Scheme 12

pyrazinyl protons can be easily assigned since the protons are largely deshielded and they appears at δ 8.37 (d, 1H, $J=2.8$ Hz) and 8.33 (d, 1H, $J=2.8$ Hz). Other characteristic signals are at 3.68 and 3.59 (d, $J = 18.0$ Hz, AB system) for CH_2COMe , 3.95 and 3.56 (d, 1H, $J = 6.8$ Hz) for two CHCON and 2.40 (s, 3H) for CH_2COCH_3 ; peaks at δ 202.9 (COCH_3), 172.9 & 171.2 (two CONPh), 89.4 & 85.3 (bridged COC), 52.4 and 50.3 (two CHCON) along with other 14 lines in the ^{13}C NMR spectrum and the molecular ion peak at m/z 426 ($[\text{MH}]^+$, $\text{C}_{25}\text{H}_{19}\text{N}_3\text{O}_4$) in the mass spectrum revealed the formation of compound **20**. The stereochemistry of the oxa-bridged adduct **20** is exo which can be anticipated from the chemical shifts of H_A and H_B (< 4 ppm).²⁵ The structure of **21** was also assigned from the spectral data. Presence of absorption band at 1714 cm^{-1} due to carbonyl group in the IR spectra; in the ^1H NMR spectrum, the two pyrazinyl protons can be easily assigned since the protons are largely deshielded and they appears at δ 8.99 (d, 1H, $J=1.5$ Hz) and 8.97 (d, 1H, $J=1.5$ Hz). 5.08 (s, 2H, CH_2COCH_3) and 2.50 (s, 3H, CH_2COCH_3) and disappearance of signals at 3.68 and 3.59 (d, 1H, CH_2COMe), 3.95 and 3.56 (d, 1H, CHCON) corresponding to the oxa-bridged adduct **20** and the molecular ion peak at m/z 408 ($[\text{MH}]^+$, $\text{C}_{25}\text{H}_{20}\text{N}_3\text{O}_4$) in the mass spectrum thus indicating that this is a fully aromatized compound. In the ^{13}C NMR appearance of 21 lines and the disappearance of signals at δ 52.4 & 50.3 (two CHCON) and 89.4 & 85.3 (bridged COC) accounts for the structure of compound **21**.

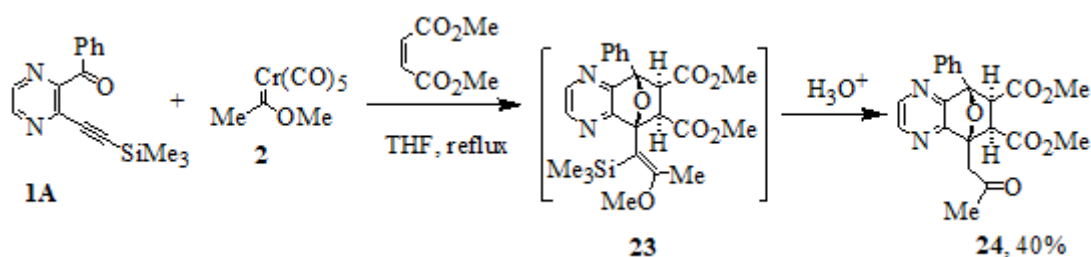
Similar type of coupling was also tested using *N*-methylmaleimide as dienophile. In this reaction the in situ generated α -methylsubstituted furo[3,4-*c*]pyrazine intermediate underwent a [4+2] cycloaddition reaction with the dienophile afforded quinoxaline derivative **222** as the sole product (Scheme 2.13). In this reaction, initially formed Diels–Alder oxa-bridged adduct **26** were not stable under reaction conditions and readily converted to the quinoxaline derivatives **22**.



Scheme 13

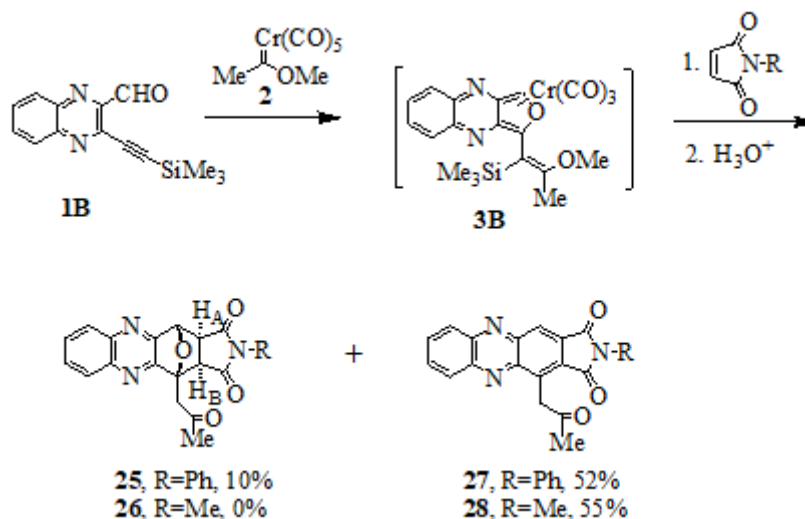
Dimethyl maleate was used as the dienophile in this reaction investigation (Section 2.14). As discussed previously pyrazinyl ketone **1A**, Fischer carbene complex **2**, and dimethyl maleate were coupled in the same manner to produce compound **24** in 40% yield via intermediate enol ether **23** formation. Even under weak acidic treatment, no aromatization products were isolated.

The structure of quinoxaline derivative **24** was evident from spectral data. The presence of molecular ion peak at m/z 379 ($[\text{MH}]^+$, $\text{C}_{21}\text{H}_{20}\text{N}_2\text{O}_6$) in the mass spectrum. In the ^1H NMR spectrum, the two pyrazinyl protons can be easily assigned since the protons are largely deshielded and they appear at δ 8.33 (bs, 2H). Other characteristic signals are at 3.71 and 3.33 (d, $J = 17.4$ Hz, AB system) for CH_2COMe , 3.95 and 3.46 (d, 1H, $J = 4.8$ Hz) for two CHCON , 3.78 and 3.51 (s, 3H) for two CO_2CH_3 , 2.27 (s, 3H) for CH_2COCH_3 ; peaks at δ 203.0 (COCH_3), 171.2 and 169.9 (two CO_2Me), 88.2 and 85.3 (bridged COC), 30.9 (CH_2COCH_3) along with other 13 lines in the ^{13}C NMR spectrum and the molecular ion peak at m/z 379 ($[\text{MH}]^+$, $\text{C}_{21}\text{H}_{20}\text{N}_2\text{O}_6$) in the mass spectrum revealed the formation of compound **24**.



Scheme 14

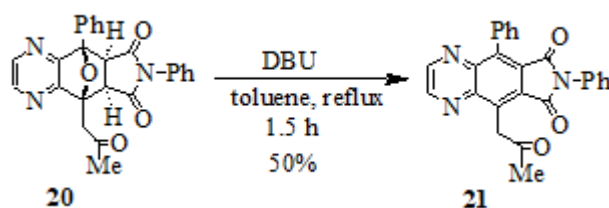
- Synthesis of Phenazine Derivatives:** Reaction between *o*-alkynylquinoxaline carbonyl derivative **1B** and carbene complex **2** generates furo[3,4-*b*]quinoxaline intermediate **3B**. In situ trapping of this intermediate with *N*-phenylmaleimide were also performed and the product was corresponding heteropolycyclic phenazine derivative **27** (Scheme 2.15). A stable oxa-bridged adduct **25** generated from [4+2] cycloaddition was also isolated. This product can be easily converted to more stable phenazine derivative on treatment with chloroform at room temperature.



Scheme 15

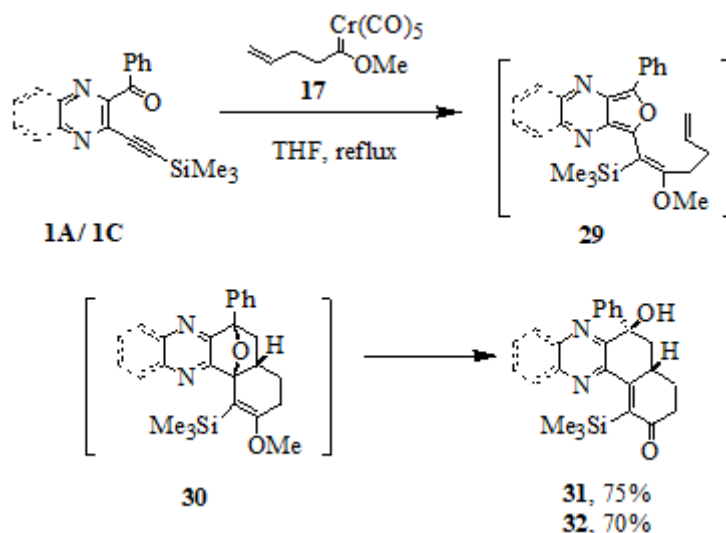
The presence of signals at δ 5.87 (s, 1H, CHOC), 3.62 and 3.55 (AB pattern) and doublets at 3.76 and 3.46 (CHCON) in the ^1H NMR confirmed the formation of the oxa-bridged adduct **25**. The stereochemistry of the oxa-bridged adduct **25** was assigned as exo based on the zero Hz coupling of H_A and H_B the chemical shifts of H_b and H_c (< 4 ppm).²⁵ The gross structure of phenazine derivative **27** is settled on the basis of the spectral data. In the IR spectrum, the presence of absorption bands at 1713 cm^{-1} confirms the presence of keto group. The ^1H NMR spectrum of **27** shows characteristic signals at δ 8.77 (s, 1H, aromatic proton), 5.15 (s, 2H, CH_2OCH_3), 2.53 (s, CH_2COCH_3) with the disappearance of signals at 5.87 (s, 1H, CHOC), 3.62 and 3.55 (AB patterns) and doublets at 3.76 and 3.46 (CHCON) in **25**. Similar type of coupling was also tested using N-methylmaleimide as dienophile. In this reaction the in situ generated α -methylsubstituted furo[3,4-c]quinoxaline intermediate **3B** underwent a [4+2] cycloaddition reaction with the dienophile afforded quinoxaline derivatives **28** as the sole product. In this reaction, initially formed Diels–Alder adducts **26** were not stable under reaction conditions and readily converted to the quinoxaline derivatives **28**. The structure of the phenazine derivative **28** was established with the help of spectral data as previously described.

- Synthesis of Heterocyclic Analogues of 1-arylnaphthalene Lignans:** Heterocyclic analogues of 1-arylnaphthalene lignans are synthetic analogues of lignan in which the naphthalene ring has been replaced by a heteroaromatic ring, and or pendant aromatic ring by heteroaromatic ring. These compounds have attracted the attention of both synthetic and medicinal chemists because many of them exhibit interesting biological activities. In our studies, the initially formed oxa-bridged cycloadduct **20** from the three-component coupling of alkynyl carbonyl derivative **1A**, carbene complex **2** and the dienophile, could be readily cleaved leading to the substituted quinoxaline **21** using DBU in refluxing toluene (Scheme 2.16).²⁶ The quinoxaline derivatives **21** and **22** may be viewed as heterocyclic analogue of 1-arylnaphthalene lignans.



Scheme 16

4. Synthesis of Azahydrophenanthrone Derivatives using γ,δ -unsaturated Fischer Carbene Complexes: Treatment of ortho-alkynylpyrazine/quinoxaline carbonyl derivatives 1A/1C with γ,δ -unsaturated Fischer carbene complex 17 yields aza analogues of hydrophenanthrene natural products (such as morphine alkaloids and abietanes) and tetracyclic triterpenes. This multistep reaction involves the formation of azaisobenzofurans (29) followed by exoselective intramolecular Diels–Alder reaction and ring opening of adduct 30 to yield azahydrophenanthrones 31/32 in satisfactory yields (Diagram 2.17). As described previously intramolecular Diels–Alder reaction of isobenzofuran is goes through six membered transition state and generally exo selective.²⁷ Aza-isobenzofuran intermediates also follow the same pathway. The first Diels–Alder adduct (30) created from 29 appears to be unstable compared to ring opening process. The crude product consists an impurity, enol ether **30** (benzo analogue), which is easily hydrolyzed to **32** during silica gel based column chromatographic purification. This was confirmed by the presence of peak at 3.71ppm due to OCH₃ in the proton NMR spectrum of the impure crude product.



Scheme 16

The structural assignment for **31/32** is based on the interpretation of IR, ¹H-, ¹³C-NMR spectra as well as elemental analysis. For compound **31**, IR spectrum displayed absorption at 3417 and 1649 cm⁻¹ representing a hydroxyl group and an α, β -unsaturated ketone functionality in the system; in the ¹H NMR spectrum, the two pyrazinyl protons can

be easily assigned since the protons are largely deshielded and they appears at δ 8.61 (d, 1H, $J=2.2$ Hz) and 8.58 (d, 1H, $J=2.2$ Hz). The aliphatic region is rather crowded and the signals at δ 4.15 (s, 1H, exchangeable with D_2O , OH), 2.43 (dd, 1H, $J=12.8, 3.7$ Hz), 1.93 (m, 1H), 1.82 (m, 1H), 0.20(s, 9H) which are indicative of the formation of compound **31**. Additionally, in the ^{13}C NMR presence of carbon signals at δ 203.7 (CO), 75.4 (C(OH)PH), 2.9 (3C, SiCH₃) and the presence of molecular ion peak at m/z 365 ($[MH]^+$, C₂₁H₂₄N₂O₂Si) in MS and anal. calcd for C₂₁H₂₄N₂O₂Si: C, 69.19; H, 6.64; N, 7.69. Found: C, 69.01; H, 6.86; N, 7.76.

IV. CONCLUSION

The chapter covers the tandem formation of intermediate furo[3,4-b]pyrazine/furo[3,4-b]quinoxal by combining ortho-alkynylheteroarylcarbonyl derivatives with Fisher carbene complexes. The intermediate can be captured by a Diels–Alder reaction with a dienophile, allowing the one-pot synthesis of nitrogen-containing heterocyclic analogs of quinoxaline and phenazine, respectively.

REFERENCES

- [1] (a) Sakata, G.; Makino, K.; Kuraswa, Y. *Heterocycles* **1988**, 27, 2481; (b) He, W.; Meyers, M. R.; Hanney, B.; Sapada, A.; Blider, G.; Galzeinski, H.; Amin, D.; Needle, S.; Page, K.; Jayyosi, Z.; Perrone, H. *Bioorg. Med. Chem. Lett.* **2003**, 13, 3097; (c) Kim, Y. B.; Kim, Y. H.; Park, J. Y.; Kim, S. K. *Bioorg. Med. Chem. Lett.* **2004**, 14, 541.
- [2] Sakata, G.; Makino, K.; Kuraswa, Y. *Heterocycles* **1988**, 27, 2481, and references cited therein.
- [3] (a) Dell, A.; William, D. H.; Morris, H. R.; Smith, G. A.; Feeney, J.; Roberts, G. C. K. *J. Am. Chem. Soc.* **1975**, 97, 2497; (b) Bailly, C.; Echeperre, S.; Gago, F.; Waring, M. *Anti-Cancer Drug Des.* **1999**, 15, 291; (c) Sato, S.; Shiratori, O.; Katagiri, K. *J. Antibiot.* **1967**, 20, 270.
- [4] (a) Katoh, A.; Yoshida, T.; Ohkanda, J. *Heterocycles* **2000**, 52, 911; (b) Thomas, K. R. J.; Velusamy, M.; Lin, J. T.; Chuen, C. H.; Tao, Y. T. *Chem. Mater.* **2005**, 17, 1860; (c) Dailey, S.; Feast, W. J.; Peace, R. J.; Sage, I. C.; Till, S.; Wood, E. L. *J. Mater. Chem.* **2001**, 11, 2238.
- [5] (a) Sessler, J. L.; Maeda, H.; Mizuno, T.; Lynch, V. M.; Furuta, H. *J. Am. Chem. Soc.* **2002**, 124, 13474; (b) Crossley, M. J.; Johnston, L. A.; *Chem. Commun.* **2002**, 1122; (c) Yamaguchi, T.; Matsumoto, S.; Watanabe, K. *Tetrahedron Lett.* **1998**, 39, 8311.
- [6] Kerr, J. R. *Infect. Dis. Rev.* **2000**, 2, 184.
- [7] (a) Allen, L.; Dockrell, D. H.; Pattery, T.; Lee, D. G.; Cornelis, P.; Hellewell, P. G.; Whyte, M. K. *J. Immunol.* **2005**, 174, 3643; (b) Lau, G. W.; Hassett, D. J.; Ran, H.; Kong, F. *Trends Mol. Med.* **2004**, 10, 599.
- [8] Heijerman, H. J. *Cyst. Fibros.* **2005**, 4 Suppl 2, 3.
- [9] (a) Yadav, J. S.; Reddy, B. V. S.; Rao, Y. G.; Narsaiah, A. V. *Chem. Lett.* **2008**, 37, 348. (b) Brown, D. J. *Quinoxalines: Supplement II. In The Chemistry of Heterocyclic Compounds: A Series of Monographs; Taylor, E. C.; Wipf, P., Eds.; John Wiley & Sons: New Jersey, 2004; Vol. 61.* (c) Huang, T. K.; Shi, L.; Wang, R.; Guo, X. Z.; Lu, X. X. *Chin. Chem. Lett.* **2009**, 20, 161. (d) Zhao, Z.; Wisnoski, D. D.; Wolkenberg, S. E.; Leister, W. H.; Wang, Y.; Lindsley, C. W. *Tetrahedron Lett.* **2004**, 45, 4873. (e) Bhosale, R. S.; Sarda, S. R.; Ardhapure, S. S.; Jadhav, W. N.; Bhusare, S. R.; Pawar, R. P. *Tetrahedron Lett.* **2005**, 46, 7183. (f) Bouilly, L.; Darabantu, M.; Turck, A.; Ple, N. J. *Heterocycl. Chem.* **2005**, 42, 1423. (g) Neochoritis, C.; Stephanidou-Stephanatou, J.; Tsoleridis, C. A. *Synlett* **2009**, 2, 302. (h) Beifuss, U.; Tietze, M. *Methanophenazine and Other Natural Biologically Active Phenazines. In Topics in Current Chemistry; Mulzer, J., Ed.; Springer: Berlin, Germany, 2005; Vol. 244, pp 77.* (i) Davarani, S. S. H.; Fakhari, A. R.; Shaabani, A.; Ahmar, H.; Maleki, A.; Fumani, N. S. *Tetrahedron Lett.* **2008**, 49, 5622. (j) Pachter, J.; Kloetzel, M. C. *J. Am. Chem. Soc.* **1951**, 73, 4958–4961.
- [10] Wohl; *Aue Chem. Ber.* **1901**, 34, 2442.

- [11] (a) Emoto, T.; Kubosaki, N.; Yamagiwa, Y.; Kamikawa, T. *Tetrahedron Lett.* **2000**, 41, 355. (b) Kwast, A.; Stachowska, K.; Trawczyński, A.; Wróbel, Z. *Tetrahedron Lett.* **2011**, 152, 6484.
- [12] (a) Barluenga, J.; Fernández-Rodríguez, M. A.; Aguilar, E. J. *Organomet. Chem.*, **2005**, 690, 539. (b) Fernández-Rodríguez, M. A.; García- García, P.; Aguilar, E. *Chem. Comm.* **2010**, 46, 7670. (c) Herndon, J. W. *Coord. Chem. Rev.* **2010**, 254, 103. (d) Dötz, K. H.; Stendel, J. *Chem. Rev.* **2009**, 109, 3227. (e) Santamaría, J. *Curr. Org. Chem.* **2009**, 13, 31. (f) Waters M. L.; Wulff, W. D. *Org. React.* **2008**, 70, 121. (g) Sierra, M. A.; Fernández I.; Cossío F. P. *Chem. Commun.* **2008**, 4671. (h) Sierra, M. A. Gómez-Gallego, M.; Martínez-Álvarez, R. *Chem.–Eur. J.* **2007**, 13, 736.
- [13] (a) Jiang, D.; Herndon, J. W.; Lam, Y.-F. *Org. Lett.* **2000**, 2, 1267. (b) Ghorai, B. K.; Herndon, J. W. *Org. Lett.* **2001**, 3, 3535. (c) Luo, Y.; Herndon, J. W.; Lee, F. C. *J. Am. Chem. Soc.* **2003**, 125, 12720. (d) Ghorai, B. K.; Herndon, J. W. *Organometallics*, **2003**, 22, 3951. (e) Camacho-Davila, A.; J. W. Herndon, J. *Org. Chem.* **2006**, 71, 6682. (f) Chen, Y.; Ye, S.; Jiao, L.; Liang, Y.; Sinha-Mahapatra, D. K.; Herndon, J. W.; Yu, Z.-X. *J. Am. Chem. Soc.* **2007**, 129, 10773. (g) Ghorai, B. K.; Jiang, D.; Herndon, J. W. *Org. Lett.* **2003**, 5, 4261.
- [14] (a) Basak, S.; Ghosh, S. K.; Sarkar, T. K. *J. Indian Inst. Sci.* **2001**, 81, 431. (b) Jana, G. P.; Ghorai, B. K. *Tetrahedron* **2007**, 63, 12015. (c) Jana, G. P.; Ghorai, B. K. *Lett. Org. Chem.* **2009**, 6, 372. (d) Mukherjee, S.; Jana, G. P.; Ghorai, B. K. *J. Organomet. Chem.* **2009**, 694, 4100.
- [15] Haddadin, M. J.; Yavrouian, A.; Issidorides, C. H. *Tetrahedron Lett.* **1970**, 11, 1409.
- [16] Turck, A.; Ple, N.; Tallon, V.; Queguiner, G. J. *Heterocycl. Chem.* **1993**, 30, 1491.
- [17] Turck, A.; Mojovic, L.; Queguiner, G. *Synthesis* **1988**, 881.
- [18] Yoshida, K.; Otomasu, H.; *Chem. Pharm. Bull.* **1984**, 32, 3361 and references cited therein.
- [19] Fischer, E. O.; Maasbol, A. *Angew. Chem., Int. Ed.* **1964**, 3, 580.
- [20] Fischer, E. O.; Aumann, R. *Chem. Ber.* **1968**, 101, 954.
- [21] Hoye, T. R.; Chen, K.; Vyvyan, J. R. *Organometallics* **1993**, 12, 2806.
- [22] Camacho-Davila, A.; Herndon, J. W.; *J. Org. Chem.* **2006**, 71, 6682.
- [23] Wulff, W. D.; Anderson, B. A.; Issacs, L. D. *Tetrahedron Lett.* **1989**, 30, 4061.
- [24] Sarkar, T. K.; Panda, N.; Basak, S. *J. Org. Chem.* **2003**, 68, 6919–6927.
- [25] (a) Tobia, D.; Rickborn, B. *J. Org. Chem.* **1987**, 52, 2611. (b) Payne, A. D.; Wege, D. *Org. Biomol. Chem.* **2003**, 1, 2383.
- [26] (a) Sarkar, T. K.; Basak, S.; Panda, N. *Tetrahedron Lett.* **2002**, 43, 1341. (b) Sarkar, T. K.; Panda, N.; Basak, S. *J. Org. Chem.* **2003**, 68, 6919.
- [27] (a) Tobia, D.; Rickborn, B. *J. Org. Chem.* **1987**, 52, 2611. (b) Payne, A. D.; Wege, D. *Org. Biomol. Chem.* **2003**, 1, 2383. (c) Meegalla, S. K.; Rodrigo, R. *Synthesis* **1989**, 942. (d) Yamaguchi, Y.; Yamada, H.; Hayakawa, K.; Kanematsu, K. *J. Org. Chem.* **1987**, 52, 2040.

