



Synthesis of aryl and hetero aryl azo compounds

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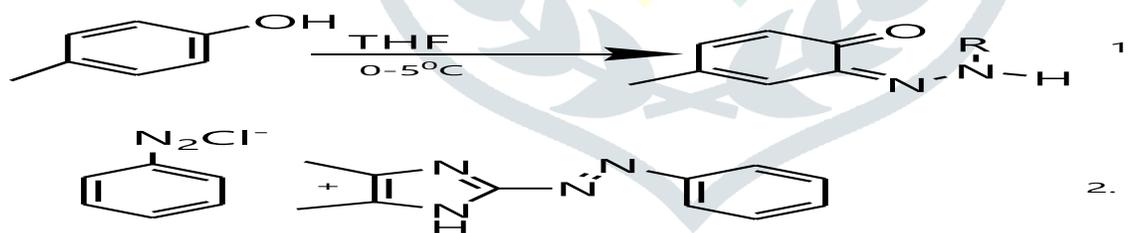
Abstract: Synthesis of aromatic and heteroaromatic compounds, metal co-ordination compounds, metal chelates have been emphasized by using Phase Transfer Catalysis. A series of novel azo compounds containing pyrazole and quinoline is prepared which is used for synthesis of 3D-Metal co-ordination compounds with metals like Ni, Zn, Pd, Cu with desired site.

Keywords : Phase transfer catalyst, Azoligands, Metal Chelates.

Introduction: In the Co-ordination metal chemistry, organometallic chemistry plays an important role of phase transfer catalyst of two and tri phase catalytic reaction. Such type of transformation includes heterocyclic azo compounds of nearly 90% yield. Not only aromatic but also heterocyclic diazonium salts, mercapto compounds, azo compounds readily forms metal chelates complexes.

Experimental Section: 1,5-dimethyl-2-phenyl-1,2-dihydro-3H-pyrazol-3-one-2-yl is synthesized by coupling diazonium salt and N-phenyl-2-naphthylamine in DMF by using Na₂CO₃ dark red crystals were obtained which were purified by column chromatography and compound is confirmed by M.P. obtained is 227 °C with 90% yield and further it is confirmed by LCMS, and NMR data.

¹H NMR in (DMSO), δ (ppm): 2.74 (s, 3H,), 3.36 (s, 3H,), 7.09-7.80 (m, 15H, C), 12.09 (s, 1H,).



2) 4-[(E)-(2-Hydroxy-1-naphthyl)diazenyl]-1,5-dimethyl-2-phenyl-1,2-dihydro-3H-pyrazol-3-one (1,5-dimethyl-2-phenyl-1,2-dihydro-3H-pyrazol-3-one-2-yl,) was synthesized by using 2-hydroxynaphthalene as a substrate. Bright red crystals were obtained after recrystallization from toluene M.P. 247 °C. with Yield 95 %.

NMR 1H (DMSO), δ (ppm): 2.69 (s, 3H,), 3.34 (s, 3H,), 7.12-7.74 (m, 11H,), 14.16 (s, 1H,).

3) (4Z)-3-Methyl-1-phenyl-1H-pyrazole-4,5-dione-4-(quinolin-8-ylhydrazone)

It is synthesized by analogous method according to scheme (6). Orange crystals (from toluene). Yield 95 %.

NMR 1H (DMSO), δ (ppm): 2.3 (s, 3H,); 7.2-9.0 (m, 5H,); 14.5 (s, 1H,).

4) (4Z)-3-Methyl-1-phenyl-5-thioxo-1,5-dihydro-4H-pyrazol-4-one quinolin-8-ylhydrazone It is synthesized according to scheme (8). Red crystals (from toluene). Yield 85 %. Anal. NMR 1H (CDCl₃), δ (ppm): 2.45 (s, 3H,); 7.2-9.0 (m, 5H,); 17.5 (s, 1H,).

The synthesis of the $M(L)_2$ metallocomplexes on the base of aromatic and heterocyclic compounds, as exemplified by scheme (9) was performed through interaction of ligands 1, 6, 8, 9. and metal acetates ($M = Co, Ni, Cu, Zn$) in 2:1 molar ratio in ethanol under refluxing during 30 min. Palladium complexes 10 were obtained using acetonitrile as a solvent.

5) 1,5-dimethyl-2-phenyl-1,2-dihydro-3H-pyrazol-3-one-2-yl, R1 = 5,6-benzo). Dark violet crystals, mp 320 °C.

NMR 1H (DMSO), δ (ppm): 2.89 (s, 6H, 2); 3.64 (s, 6H,); 6.59-7.74 (m, 30H, CH_{arom}).

6) 1,5-dimethyl-2-phenyl-1,2-dihydro-3H-pyrazol-3-one-2-yl,

Red-brown crystals, m.p. 320 °C.

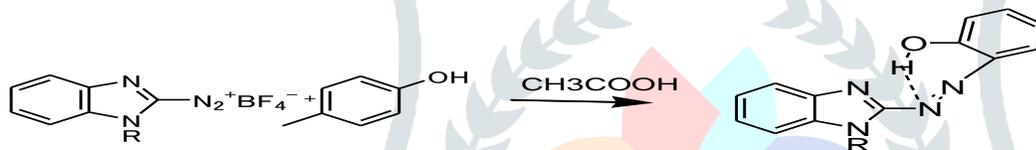
NMR 1H (DMSO), δ (ppm): 2.75 (s, 6H, 2); 3.63 (s, 6H, 2); 6.60-7.82 (m, 20H, CH_{arom}).

Metal coordination compounds were synthesized by heating ethanol solutions of ligands and $AlCl_3 \cdot 6H_2O$ during 20 min.

Result & Discussion: The reactions 1,2 represents coupling for the synthesis of azo ligands of metal co-ordination compounds by using TFPB(3,5-bis(trifluoromethyl)phenyl chlorate) to give azoheterocycle.

Metallochemistry is helpful to fitting ligands to stereo and electrochemical requirements, tautomeric form of ligands and regioselectivity.

Not only aromatic, but also heterocyclic diazonium salts were used in the synthesis of azo ligands of metal coordination compounds. Thus, a series of azo compounds 4 was obtained based on the diazonium salts prepared from 2-amino-1-alkylbenzimidazoles.



The azo compounds containing a mercapto group in the ring are rather unstable and are readily oxidized in the air. Therefore o-thiocyanateazobenzenes were used as their precursors in the synthesis of the metal chelates.

Conclusions:

The properties of metal chelate complexes caused by structural modifications of the azo-containing ligands. Less influence of strong electron-withdrawing and electron-releasing substituents in the aryl rings of the aromatic and heterocyclic azo compounds, which is essential for defining basicity and ligating abilities of the nitrogen centers in azo groups.

References:

- Garnovskii, A. D.; Kharisov, B. I. Eds.; Synthetic Coordination and Organometallic Chemistry; Marcel Dekker: New York, 2003.
- Makosza, M.; Mawrzyniewicz, M. Tetrahedron Lett. 1969, 4659.
- Starks, C.M. J. Am. Chem. Soc. 1971, 93, 195.
- Starks, C.M.; Owens, R.M. J. Am. Chem. Soc. 1973, 95, 3613.
- Garnovskii, A.D; Garnovskii, D.A.; Vasilchenko, I.S.; Burlov, A.S.; Sadimenko, A.P.; Sadekov, I.D. Russ. Chem. Rev. 1997, 66, 389.
- Garnovskii, A.D.; Sadimenko, A.P. Adv. Het. Chem. 1998, 72, 1.
- Minkin, V.I.; Garnovskii, A.D.; Elguero, J.; Katritzky, A.R.; Denisko, O.V. Adv. Het. Chem. 2000, 76, 157.
- Zhdanov, Yu.A.; Alexeev, Yu.E. Zhurn. Vsesoyusn. Khim. Ob-va im. D.I.Mendeleeva 1986, 31, 188.
- Michelin, R.A.; Pombeiro, A.J.L.; Guedas da Silva, M.F.C. Coord. Chem. Rev. 2001, 218, 75.
- Gokel, G.W.; Widera, R.P.; Weber, W.P. Organic Synthesis. 1975, 55, 96.

11. Kukushkin, V.Yu.; Pombeiro, A.J.L. Chem. Rev. 2002, 102, 1771.
12. Alexeev, Yu.E.; Garnovskii, A.D.; Zhdanov, Yu.A. Russ. Chem. Rev. 1998, 67, 649.
13. Alexeev, Yu.E.; Garnovskii, A.D.; Vasilchenko, I.S.; Zhdanov, Yu.A. Russ. J. Inorg. Chem. (Suppl. I s. 3). 2001, 46, 235.
14. Alexeev, Yu.E.; Zhdanov, Yu.A. Russ. Chem. Rev. 2002, 71, 969. 27. Gerbeleu, N.V.; Arion, V.B.; Burgess, J. Template Synthesis of Macrocyclic Compounds. Weinheim: Wiley-VCH, 1999.
15. Makosza, M.; Kacprowirz, A. Roczn. Chem. 1974, 48, 2129.
16. Garnovskii, A. D.; Nivorozhkin, A.L.; Minkin, V. I. Coord. Chem. Rev. 1993, 126, 1.
17. Garnovskii, A.D.; Vasilchenko, I.S. Russ. Chem. Rev. 2002, 71, 943.
18. Bortolini, O.; Di Furia, F.; Modena, G.; Seraglia, R. J. Org. Chem. 1985, 50, 2688.
19. Burmeister, J.L. Coord. Chem. Rev. 1990, 105, 65.

