

Synthesis of Some Aryl Azo-Compounds Under Mild Conditions

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Some aryl azo compounds **2(a-h)** were synthesized by reaction of corresponding aromatic amine and phenol derivatives under mild conditions. The yields of the products after recrystallization from acetic acid were in the order of 65-95 %. IR and ¹H NMR spectroscopy and elemental analysis were used for the identification of these compounds.

Key Words: Azo compound, Phenol, Azophenyl.

INTRODUCTION

Azo compounds refer to the chemical compounds bearing the functional group R-N=N-R' in which R and R' can be either aryl or alkyl group. Aliphatic azo compounds (R and/or R'=aliphatic) are less common. One example is diethylazene (Et-N=N-Et), which is not very stable. However, aromatic azo compounds (R=R'=aromatic) are usually stable due to the delocalization of the *p*-electron system and have vivid colors such as red, orange and yellow¹. Therefore, they are used as dyes², which are called azo dyes. Another application of azo compounds is in analytical chemistry³⁻⁷, where some of these compounds are used as indicators in pH, redox or complexometric titration. Azo compounds are also used in the pharmaceutical industry⁸⁻¹². At elevated temperature or by irradiation, two carbon-nitrogen bonds are cleaved simultaneously with the loss of nitrogen gas generate carbon-centered radicals which is widely used as an initiator in polymerization.

Aromatic azo compounds can be synthesized using an azo coupling reaction, which is an electrophilic substitution reaction on aromatic rings with diazonium salts. Diazonium salts usually decompose at temperature warmer than about 5 °C. So the reaction must take place in the solution under freezing condition. In view of these reports, effort has been made to synthesize some aromatic azo compounds by reaction of corresponding phenols and amines under mild conditions.

EXPERIMENTAL

All chemicals were of reagent grade quality and used without further purification. IR spectra were performed on a Galaxy FT-IR 5000 spectrophotometer. ¹H NMR

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spectra were recorded on a Bruker 300 MHz spectrometer. Chemical shifts (ppm) were referenced to the internal standards tetramethyl silane (TMS). Microanalyses were performed by the elemental analyzer (elemental, Vario EL III) at the Arak University. Microanalyses results were agreed favourably with the calculated values. Reactions were monitored by thin layer chromatography using silica gel F₂₅₄ aluminum sheets (Merck). Melting points are uncorrected. All materials were used as obtained without further purification.

General procedure for preparation of 2(a-h): A solution of corresponding aniline or *p*-amino benzoic acid (0.054 mol) in hydrochloric acid (16 mL, 37 %) was prepared. The obtained salt was dissolved in water (15-20 mL). The solution was cooled in an ice-bath for 15 min and then added dropwise (due to 15-20 min) to a cooled basic solution of phenol derivatives (0.054 mol in 10 mL NaOH 0.03 M) and vigorously stirred for 15-20 min. The temperature was allowed to rise above room temperature. The mixture was filtered and the obtained solid washed with diethyl ether and air dried. The crude product was recrystallized from acetic acid.

4-Ethyl-2(*p*-carboxyl azophenyl) phenol (2a): Brown crystals, m.p. 171-173 °C, yield 92 %. IR (KBr, ν_{\max} , cm^{-1}): 3225 (OH), 3078 (CH_{arom}), 2962 (CH_{aliph}), 3300-2500 (COOH), 1683 (C=O), 1593 (C=C). ¹H NMR (DMSO-*d*₆): δ : 1.02 (t, 3H, CH₃), 2.66 (q, 2H, CH₂), 7.07-7.99 (m, 7H, CH_{arom}), 8.01 (d, 1H, OH), 10.61 (bs, 1H, COOH). Anal. calcd. (%) for C₁₅H₁₄N₂O₃: C, 66.65; H, 5.23; N, 10.37. Found. (%): C, 65.93; H, 5.32; N, 10.22.

4-Methyl-2(azophenyl)phenol (2b): Yellow crystals, m.p. 126-128 °C, yield 95 %. IR (KBr, ν_{\max} , cm^{-1}): 3225.58 (OH), 3078 (CH_{arom}), 2956 (CH_{aliph}), 1593 (C=C). ¹H NMR (DMSO-*d*₆): δ : 2.35 (s, 3H, CH₃), 6.8 (m, 1H, CH_{arom}), 7.19-7.26 (m, 2H, CH_{arom}), 7.46 (m, 2H, CH_{arom}), 7.93 (m, 2H, CH_{arom}), 9.83 (bs, 1H, OH). Anal. calcd. (%) for C₁₃H₁₂N₂O: C, 73.55; H, 5.71; N, 13.20. Found. (%): C, 73.69; H, 5.50; N, 13.31.

4-Flouro-2-(azophenyl)phenol (2c): Black brown crystals, m.p. 101-103 °C, yield 85 %. IR (KBr, ν_{\max} , cm^{-1}): 3205.89 (OH), 3159.58 (CH_{arom}), 1610.25 (C=C). ¹H NMR (DMSO-*d*₆): δ : 7.07-7.99 (m, 8H, CH_{arom}), 8.01 (d, 1H, OH), 10.61 (bs, 1H, COOH). Anal. calcd. (%) for C₁₂H₉N₂OF: C, 66.65; H, 4.20; N, 12.96 %. Found. (%): C, 66.34; H, 4.30; N, 13.22.

2,3-Dichloro-4-(azophenyl)phenol (2d): Orange crystals, m.p. 230-233 °C, yield 65 %. IR (KBr, ν_{\max} , cm^{-1}): 3213 (OH), 3061 (CH_{arom}), 1591 (C=C). ¹H NMR (DMSO-*d*₆): δ : 6.33-6.51 (m, 2H, CH_{arom}), 7.43-7.68 (m, 5H, CH_{arom}), 7.00-7.85 (d, 2H, OH). Anal. calcd. (%) for C₁₂H₈N₂OCl₂: C, 53.95; H, 3.02; N, 10.49. Found. (%): C, 54.21; H, 2.84; N, 10.41.

2,6-Dichloro-4-(azophenyl)phenol (2e): Yellow crystals, m.p. 142-144 °C, yield 70 %. IR (KBr, ν_{\max} , cm^{-1}): 3508 (OH), 3084 (CH_{arom}), 1570 (C=C). ¹H NMR (DMSO-*d*₆): δ : 6.33-6.51 (m, 2H, CH_{arom}), 7.43-7.68 (m, 5H, CH_{arom}), 7.85 (d, 2H, -OH). Anal. calcd. (%) for C₁₂H₈N₂OCl₂: C, 53.95; H, 3.02; N, 10.49. Found. (%): C, 53.86; H, 3.26; N, 10.35.

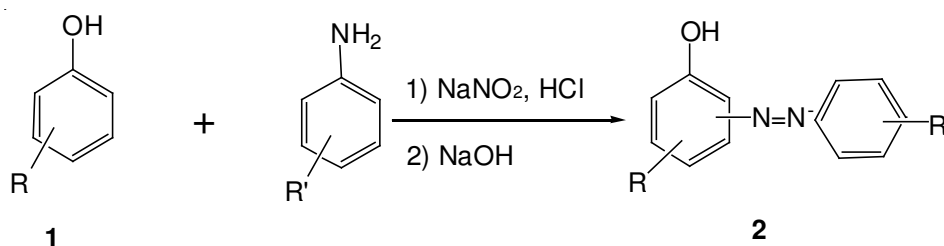
2-Hydroxy-3-(azophenyl)benzaldehyde (2f): Pink crystals, m.p. 151-153 °C, yield 95 %. IR (KBr, ν_{\max} , cm^{-1}): 3207 (OH), 3040 (CH_{arom}), 1591 (C=C). $^1\text{H NMR}$ ($\text{DMSO-}d_6$): 6.89-6.96 (m, 3H, CH_{arom}), 7.48-7.53 (m, 2H, CH_{arom}), 7.77-7.85 (m, 2H, CH_{arom}), 11.31 (bs, 2H, OH, COH). Anal. calcd. (%) for $\text{C}_{13}\text{H}_{10}\text{N}_2\text{O}_2$: C, 69.01; H, 4.46; N, 12.38. Found. (%): C, 69.28; H, 4.67; N, 12.35.

4-Chloro-2-(azophenyl) phenol (2g): Brown crystals, m.p. 161-163 °C, yield 72 %. IR (KBr, ν_{\max} , cm^{-1}): 3311 (OH), 3057 (CH_{arom}), 1591. (C=C). $^1\text{H NMR}$ ($\text{DMSO-}d_6$): 7.10 (d, 1H, CH_{arom}), 7.43-7.64 (m, 5H, CH_{arom}), 7.99 (s, 2H, CH_{arom}), 10.85 (bs, 1H, OH). Anal. calcd. (%) for $\text{C}_{12}\text{H}_9\text{N}_2\text{OCl}$: C, 61.94; H, 3.91; N, 12.04. Found. (%): C, 61.69; H, 4.08; N, 12.21.

4-(Phenyldiazenyl)benzene-1,2-diol (2h): Red crystals, m.p. 152-155 °C, yield 95 %. IR (KBr, ν_{\max} , cm^{-1}): 3213.61 (OH), 3061 (CH_{arom}), 1591 (C=C). $^1\text{H NMR}$ ($\text{DMSO-}d_6$): 6.08-6.11 (m, 2H, CH_{arom}), 6.32-6.73 (m, 6H, CH_{arom}), 8.79 (s, 2H, OH). Anal. calcd. (%) for $\text{C}_{12}\text{H}_{10}\text{N}_2\text{O}_2$: C, 67.27; H, 4.71; N, 13.08. Found. (%): C, 67.42; H, 4.57; N, 13.19.

RESULTS AND DISCUSSION

Reaction of phenol derivative **1** with appropriate aniline compound gave **2(a-h)** as shown in **Scheme-I**. The reaction was carried out under mild condition and gave products in suitable yield, which is the advantage of this method. However, the effect of substituents in the phenol component of the reaction is substantial. For example when compound **1d** or **1e** with one more electron withdrawing group is used as a component, the yield of reaction is low compared to others.



- 2a)** R = 4-ethyl, R' = 4-carboxyl
- 2b)** R = 4-methyl, R' = H
- 2c)** R = 4-fluoro, R' = H
- 2d)** R = 2,3-dichloro, R' = H
- 2e)** R = 2,6-dichloro, R' = H
- 2f)** R = 2-carbaldehyde, R' = H
- 2g)** R = 4-chloro, R' = H
- 2h)** R = 2-hydroxy, R' = H

Scheme-I

The ^1H NMR spectra and elemental analysis data of all synthesized compounds are consistent with the expected structures. For example the ^1H NMR spectrum of **2a** shows a broad singlet at 10.61, which attributed to the resonance of the carboxylic group. Seven aromatic protons related to two aromatic rings are appeared as a multiplet at 7.07-7.99 ppm. The aliphatic protons, CH_2 and CH_3 groups resonate as quartet and triplet at 2.66 and 1.02 ppm, respectively. The resonance of the OH group, attached to the phenyl ring, is appeared at 8.01 ppm

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