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Coupling of Ethyl Malonate, Cyanoacetate, and Acetoacetate and Malonodinitrile with 2-Cyanoaryldiazonium Bisulfates

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The reactions of aryldiazonium salts with compounds containing an activated CH_2 group give coupling products I

$$\operatorname{ArN}_{2}^{+}X^{-} + -\operatorname{CH}_{2} \xrightarrow{|}_{-HX} \operatorname{ArNHN} = \operatorname{C}^{-}$$
(I)

The aryldiazonium salts used in these reactions are normally chlorides (X = Cl). It should be noted that the preparation of aryldiazonium salts from aromatic amines containing strong electron-withdrawing groups in the *ortho*-position to the amino group is faced with substantial difficulties, because the syntheses of the initial amines are multistep procedures, as well as because of the low basicity of these amines.

Previously, we developed an original, simple, and effective method for the synthesis of 2-cyanoaryldiazonium bisulfates (**II**), which involves the treatment of 2-hydrazones of isatin and its derivatives (**III**) with nitrosylsulfuric acid [1]



 $R = H, Br, NO_2.$

In this study, we performed coupling of bisulfates **II** with compounds **IV**, which gave rise to previously unknown (2-cyanoaryl)hydrazones (**V**–**XVI**)

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$$\begin{split} & \text{R}, \text{R}^{1}, \text{R}^{2} = \text{H}, \text{COOC}_{2}\text{H}_{5}, \text{COOC}_{2}\text{H}_{5} (\textbf{V}); \text{H}, \text{CN}, \\ & \text{COOC}_{2}\text{H}_{5} (\textbf{VI}); \text{H}, \text{CN}, \text{CN} (\textbf{VII}); \text{H}, \text{COCH}_{3}, \\ & \text{COOC}_{2}\text{H}_{5} (\textbf{VIII}); \text{Br}, \text{COOC}_{2}\text{H}_{5}, \text{COOC}_{2}\text{H}_{5} (\textbf{IX}); \\ & \text{Br}, \text{CN}, \text{COOC}_{2}\text{H}_{5} (\textbf{X}); \text{Br}, \text{CN}, \text{CN} (\textbf{XI}); \text{Br}, \text{COCH}_{3}, \\ & \text{COOC}_{2}\text{H}_{5} (\textbf{XII}); \text{NO}_{2}, \text{COOC}_{2}\text{H}_{5} (\textbf{COOC}_{2}\text{H}_{5} (\textbf{XIII}); \\ & \text{NO}_{2}, \text{CN}, \text{COOC}_{2}\text{H}_{5} (\textbf{XIV}); \text{NO}_{2}, \text{CN}, \text{CN} (\textbf{XV}); \\ & \text{NO}_{2}, \text{COCH}_{3}, \text{COOC}_{3}\text{H}_{5} (\textbf{XVI}). \end{split}$$

This reaction was carried out at 20 to 25° C in aqueous ethanol in the presence of sodium acetate. Compounds **V**–**XVI** were characterized by elemental analysis data, melting points, and IR, UV, and ¹H NMR spectra.

The ¹H NMR spectra of compounds **V** and **VII** each exhibit two signals corresponding to the NH-group protons. Hence, these products exist as two (evidently, rotational) isomers, the **Va** (or **VIIa**) to **Vb** (or **VIIb**) ratio being 4: 6.



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The ¹H NMR spectrum of compound **VI** exhibits only one signal for the NH proton. This compound exists as a single isomer, having, apparently, E configuration



(**VI**)

The ¹H NMR spectrum of compound **VIII** exhibits two signals for the COCH₃ protons and two signals for the NH protons. This indicates the existence of two geometrical isomers **VIIIa** (*Z*) and **VIIIb** (*E*) (stabilized by an intramolecular hydrogen bond), present in the ratio Z : E = 3 : 7.





(**VIIIb**, *E*)

EXPERIMENTAL

IR spectra were recorded on a Specord M-80 spectrophotometer (KBr pellets); UV spectra were measured on a Uvidek 610 spectrophotometer in methanol. ¹H NMR spectra were recorded on a Bruker AM-300 instrument in DMSO-d₆–CCl₄ solvent mixtures.

2-Cyanophenylhydrazone V. Concentrated sulfuric acid (2.5 ml) was placed in a porcelain beaker and cooled to 0–5°C in a water bath, and sodium nitrite (1.4 g, 0.02 mol) was added with stirring over a period of 30 min. Hydrazone III (R = H) (1 g, 0.0062 mol) was added to the resulting mixture with stirring over a period of 15 min. During this period, glacial acetic acid (8 ml) was added at intervals. Then the mixture was stirred for 30 min at 5–10°C and poured into a mixture of water (50 ml) and ice (50 g). A solution of ethyl malonate (1.0 g, 0.0062 g) in ethanol (10 ml) was added to the resulting mixture while it was stirred and cooled with ice, and a solution of sodium acetate (10 g) in water (50 ml) was added with stirring. The reaction mixture was stirred for 1 h at room temperature, heated in a water bath at 50°C for 15 min, and cooled to 20°C. The precipitate was filtered off, washed three times in a filter with water, and recrystallized from a water-DMF mixture. Yield 0.5 g (23%), mp 168–169°C. IR (KBr, v, cm⁻¹): 2224 (C=N), 1614 (C=N), 3298 (N–H), 1745 (C=O), 1092 (C–O–C). ¹H NMR (DMSO-d₆-CCl₄, δ , ppm): 1.38 (t, 6H, CH₂CH₃), 4.26–4.41 (m, 4H, CH₂CH₃), 6.91–7.68 (m, 4H, CH_{arom}), 10.83, 12.63 (both m, 1H, NH).

For C₁₄H₁₅N₃O₄ anal. calcd. (%): C, 58.12; H, 5.23; N, 14.53.

Found (%): C, 58.74; H, 5.03; N, 14.19.

2-Cyanophenylhydrazone VI. Yield 56%, mp 153–154°C (from H₂O–DMF). IR (KBr, v, cm⁻¹): 2228 (C=N), 1636 (C=N), 3296 (N–H), 1692 (C=O), 1096 (C–O–C). ¹H NMR (DMSO-d₆-CCl₄, δ , ppm): 1.42 (3, CH₂CH₃), 4.40–4.48 (m, 2H, CH₂CH₃), 13.30 (s, NH).

For $C_{12}H_{10}N_4O_2$ anal. calcd. (%): C, 59.50; H, 4.16; N, 23.13.

Found (%): C, 58.91; H, 4.18; N, 22.68.

2-Cyanophenylhydrazone VII. Yield 76%, mp 162–163°C (from aqueous ethanol). IR (KBr, v, cm⁻¹): 2232 (C=N), 1621 (C=N), 3270 (N–H). UV (λ_{max} , nm, log ϵ): 202.3 (2.09), 216.8 (1.94), 257.6 (1.83), 319.2 (1.59), 350.4 (1.65), 398.4 (1.57). ¹H NMR (DMSO-d₆-CCl₄, δ , ppm): 6.89–8.00 (m, 4 H, CH_{arom}), 10.84, 11.14 (both s, 1H, NH).

For C₁₀H₅N₅ anal. calcd. (%): C, 61.53; H, 2.58; N, 35.88.

Found (%): C, 62.01; H, 2.37; N, 36.31.

2-Cyanophenylhydrazone VIII. Yield 68%, mp 104–106°C (from H₂O–DMF). IR (KBr, v, cm⁻¹): 2224 (C=N), 1638 (C=N), 3240 (N–H), 1706 (C=O), for COOC₂H₅, 1738 (C=O), 1084 (C–O–C). ¹H NMR (DMSO-d₆-CCl₄, δ , ppm): 1.36 (t, 3H, CH₂CH₃), 4.28–4.42 (m, 2H, <u>CH</u>₂CH₃), 7.21–7.83 (m, 4H, CH_{arom}), 2.48, 2.57 (both s, 1H, NH).

For C₁₃H₁₃N₃O₃ anal. calcd. (%): C, 60.22; H, 5.05; N, 16.21.

Found (%): C, 60.18; H, 5.41; N, 15.79.

4-Bromo-2-cyanophenylhydrazone IX. Yield 39%, mp 176–177°C (from H₂O–DMF). IR (KBr, v, cm⁻¹): 2188 (C=N), 1614 (C=N), 3248 (N–H), 1736 (C=O), 1118 (C–O–C).

For $C_{14}H_{14}BrN_3O_4$ anal. calcd. (%): C, 45.70; H, 3.84; N, 11.42.

Found (%): C, 46.12; H, 3.71; N, 11.57.

4-Bromo-2-cyanophenylhydrazone X. Yield 65%, mp 159–160°C (from H₂O–DMF). IR (KBr, v, cm⁻¹): 2234 (C≡N), 1612 (C=N), 3204 (N–H), 1734 (C=O), 1118 (C–O–C).

For $C_{12}H_9BrN_4O_2$ anal. calcd. (%): C, 44.88; H, 2.82; N, 17.45.

Found (%): C, 44.48; H, 2.64; N, 17.78.

4-Bromo-2-cyanophenylhydrazone XI. Yield 83.8%, mp 175–176°C (from aqueous ethanol). IR (KBr, v, cm⁻¹): 2240 (C=N), 1615 (C=N), 3240 (N–H). UV (λ_{max} , nm, logɛ): 205.6 (1.91), 216.0 (1.83), 268.0 (1.56), 348.0 (1.45), 403.2 (1.56).

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For $C_{10}H_4BrN_5$ anal. calcd. (%): C, 43.82; H, 1.47; N, 25.68.

Found (%): C, 43.29; H, 1.43; N, 26.17.

4-Bromo-2-cyanophenylhydrazone XII. Yield 70%, mp 117–118°C (from H₂O–DMF). IR (KBr, v, cm⁻¹): 2228 (C≡N), 1645 (C=N), 3218 (N–H), 1730 (C=O), for COOC₂H₅, 1117 (C–O–C).

For $C_{13}H_{12}BrN_3O_3$ anal. calcd. (%): C, 46.17; H, 3.58; N, 12.43.

Found (%): C, 45.71; H, 3.43; N, 12.21.

4-Nitro-2-cyanophenylhydrazone XIII. Yield 35%, mp 195–197°C (from H₂O–DMF). IR (KBr, v, cm⁻¹): 2218 (C≡N), 1620 (C=N), 3328 (N–H), 1730 (C=O), 1121 (C–O–C), 1545, 1334 (NO₂).

For $C_{14}H_{14}N_4O_6$ anal. calcd. (%): C, 50.30; H, 4.22; N, 16.76.

Found (%): C, 49.73; H, 5.54; N, 16.28.

4-Nitro-2-cyanophenylhydrazone XIV. Yield 53%, mp 165–167°C (from H₂O–DMF). IR (KBr, v, cm⁻¹): 2218 (C≡N), 1621 (C=N), 3228 (N–H), 1722 (C=O), 1117 (C–O–C), 1531, 1334 (NO₂).

For $C_{12}H_9N_5O_4$ anal. calcd. (%): C, 50.18; H, 3.16; N, 24.38.

Found (%): C, 50.49; H, 2.87; N, 23.97.

4-Nitro-2-cyanophenylhydrazone XV. Yield 66.9%, mp 201–202°C (from aqueous ethanol). IR (KBr, v, cm⁻¹): 2182 (C=N), 1628 (C=N), 3240 (N–H), 1564, 1368 (NO₂). UV (λ_{max} , nm, logɛ): 203.2 (2.03), 221.6 (1.94), 263.2 (1.61), 320.8 (1.79).

For $C_{10}H_4N_6O_2$ anal. calcd. (%): C, 50.00; H, 1.68; N, 34.99.

Found (%): C, 50.13; H, 1.87; N, 35.27.

4-Nitro-2-cyanophenylhydrazone XVI. Yield 42%, mp 125–126°C (from H₂O–DMF). IR (KBr, v, cm⁻¹): 2220 (C \equiv N), 1648 (C=N), 1706 (C=O), for COOC₂H₅ 1733 (C=O), 1117 (C–O–C), 1566, 1324 (NO₂).

For $C_{13}H_{12}N_4O_5$ anal. calcd. (%): C, 50.31; H, 3.97; N, 18.41.

Found (%): C, 51.71; H, 3.58; N, 18.03.

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