

Azoic Compounds Obtained from 1*H*-4-ethoxycarbonyl-3-methyl-5-aminopyrazole and 1,3-disubstituted 1*H*-pyrazol-5-ones

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Abstract: The coupling of 1*H*-4-ethoxycarbonyl-3-methyl-pyrazol-5-yl-diazonium chloride (**2**) with 1*H*-1,3-disubstituted-5-pyrazolones (**3**), was performed in water-alcoholic solution, in the presence of sodium acetate and gave the corresponding 1,3-disubstituted 1*H*-4-(1*H*-4-ethoxycarbonyl-3-methyl-pyrazol-5-yl)azo-5-pyrazolones (**4**). The structure of the new azo dyes was confirmed by IR, VIS and NMR spectroscopy.

Keywords: azoic compounds, 1*H*-4-ethoxycarbonyl-3-methyl-pyrazol-5-yl-diazonium chloride, 1*H*-1,3-disubstituted-4-(1*H*-4-ethoxycarbonyl-3-methyl-pyrazol-5-yl)azo-5-pyrazolones

1. Introduction

Substituted aminopyrazoles present a continuous interest due to their multiple possible applications: ligands in the chemistry of metallo-organic compounds [1,2], chelating agents [2], intermediates in the synthesis of new classes of polycondensed heterocyclic compounds [2-7], biologically active compounds used in agriculture and medicine [2,5-8]. Among these compounds, 3- and 4-monosubstituted 1*H*-5-amino-pyrazoles have been studied for the synthesis of polycondensed heterocyclic compounds [9] through conversion into diazonium salts, followed by coupling with methylene active compounds and cyclization.

On the other hand, the coupling of diazonium salts derived from 3-amino-pyrazoles with pyrazoles and 5-pyrazolones, respectively, has been very little investigated [10,11]. For this reason we took an interest in the study of coupling reactions of 1*H*-4-ethoxycarbonyl-3-methyl-pyrazol-5-yl-diazonium chloride **2** with different mono- and disubstituted pyrazolones **3** and the characterization of the formed products **4** (Figure 1), as a first step in the synthesis of polycondensed heterocyclic systems of the pyrazolo-pyrazolo-triazine and pyrazolo-pyrazolo-triazole types, respectively (Figure 2).

2. Materials and methods

The reagents were from commercial sources (Chimopar, Fluka, Merck) and used as received, and the following starting compounds were obtained according to the literature: 1*H*-5-amino-4-ethoxycarbonyl-3-methyl-pyrazole **1** [12].

The melting points were determined on a Bötius PHMK (Veb Analytik Dresden) apparatus and are not corrected. Thin-layer chromatography was performed on silica gel plates Merck 60 F₂₅₄ using benzene:methanol 7:3 (vol) as eluant.

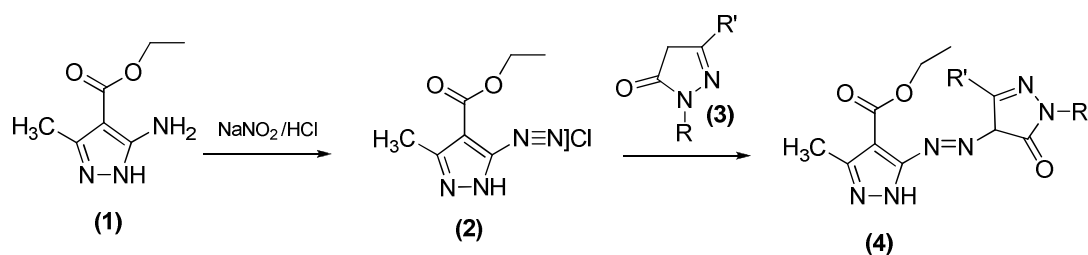
IR spectra were recorded on a Jasco FT/IR-410 spectrophotometer, in KBr pellet. The UV-VIS spectra were recorded in methanolic solution on a Jasco V-530 UV/VIS spectrophotometer. ¹H-NMR spectra were recorded on a Bruker Advance AC200 instrument in DMSO-*d*₆ using TMS as a reference; chemical shifts are given in ppm and the coupling constants in Hz.

Diazotation of 1*H*-5-amino-4-ethoxycarbonyl-3-methyl-pyrazole

Into a flask fitted with a stirrer, dropping funnel, and heating-cooling bath, 10 mL water, 10 mL concentrated HCl and 8.5 g of 1*H*-5-amino-4-ethoxycarbonyl-3-methyl-pyrazole hydrochloride **1** are introduced. After heating to approximately 40°C, the mixture is filtered and cooled to 0-5°C. To the fine formed suspension a solution of 0.35 g NaNO₂ / 1.2 mL water is added dropwise under stirring over approximately 1 hour. The obtained solution is treated with active charcoal and filtered cold. The solution of diazonium salt **2** thus obtained is immediately used in the coupling step.

Coupling of 1*H*-3-methyl-4-ethoxycarbonyl-5-pyrazolil-diazonium hydrochloride with 1,3-disubstituted 5-pyrazolones

To the coupling solution of 0.02 moles **3a-c** in 40 mL ethanol and 0.0062 moles NaOH and 0.02 moles CH₃COONa in 40 mL water, the solution of diazonium salt freshly prepared from 0.02 moles 1*H*-5-amino-4-ethoxycarbonyl-3-methyl-pyrazole hydrochloride is added dropwise under stirring at 0-5°C. The evolution of coupling was checked with an alkaline solution of acid "H" by the halo method. The colored suspension formed is allowed to perfect for half an hour, diluted with water and acidified with hydrochloric acid to pH ~1. After filtration and drying the azo dyes are recrystallized from ethyl alcohol.



3a; 4a: R = H; R' = CH₃
 3b; 4b: R = p-C₆H₄-SO₃H; R' = COOH
 3c; 4c: R = H; R' = COOEt

Figure 1. The coupling of 1H-4-ethoxycarbonyl-3-methyl-pyrazol-5-yl-diazonium chloride (2) with 1H-1,3-disubstituted-5-pyrazolones (3)

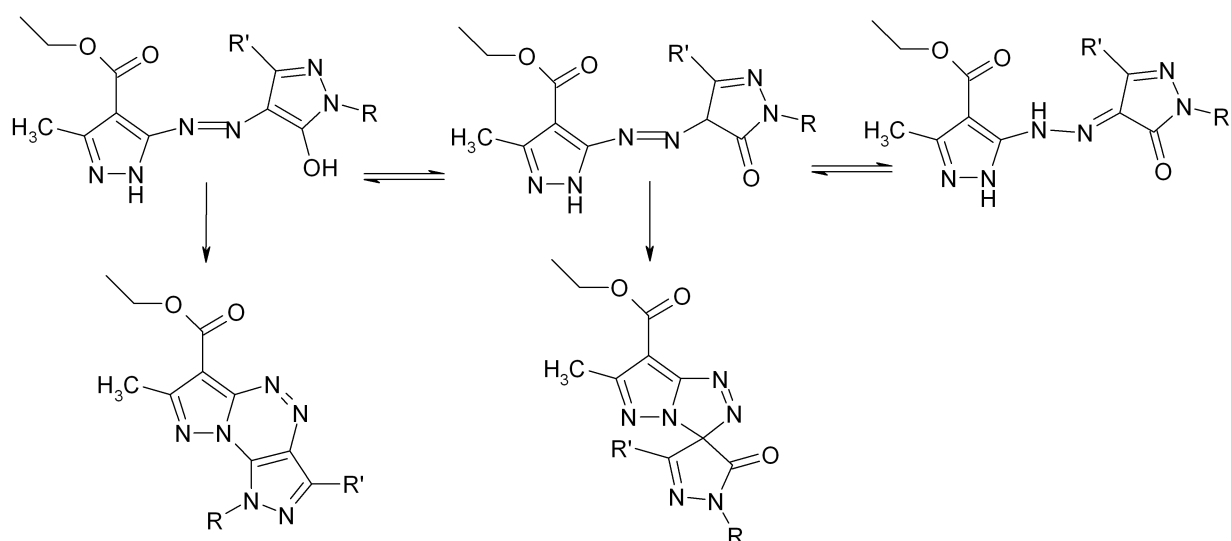


Figure 2. Azo-hydrazo and keto-enolic tautomerism in 1,3-disubstituted 1H-4-(1H-4-ethoxycarbonyl-3-methyl-pyrazol-5-yl)-azo-pyrazol-5-one. Cyclization possibilities.

4a: 1H-4-(1H-4-ethoxycarbonyl-3-methyl-pyrazol-5-yl)-azo-3-methyl-pyrazol-5-one

Yellow powder, m.p.= 294-298°C, yield = 79%

UV-VIZ λ max[nm] ($\epsilon \times 10^4$): 216(1,01); 350(11,3); 401(1,08)

IR (KBr) (ν/cm^{-1}): $\nu_{\text{C=O}}^{\text{as}}(\text{ester})=1205\text{s}$, $\delta_{\text{CH}_3}^{\text{s}}=1370\text{m}$, $\delta_{\text{CH}_3}^{\text{as}}=1438\text{m}$, $\nu_{\text{N=N}}(\text{sin})=1500\text{m}$, $\nu_{\text{C=N}}(\text{pyr})=1588\text{m}$, $\nu_{\text{C=O}}(\text{pyrazolone})=1671\text{s}$, $\nu_{\text{C=O}}(\text{ester})=1714\text{s}$, $\nu_{\text{CH}_3}^{\text{as}}=2935\text{m}$, $\nu_{\text{CH}_3}^{\text{as}}=2986\text{m}$, $\nu_{\text{NH}}(\text{pyr})=3080\text{m}$.

4b: 1H-3-carboxy 4-(1H-4-ethoxycarbonyl-3-methyl-pyrazol-5-yl)azo-1-(4-sulfophenyl) - pyrazol-5-one

Red powder, m.p.=340°C, yield = 93%

UV-VIZ λ max[nm] ($\epsilon \times 10^4$): 210(0,74); 241(0,96); 406(0,78)

IR(KBr)(ν/cm^{-1}): $\nu_{\text{C=O}}(\text{ester})=1197\text{s}$, $\delta_{\text{CH}_3}=1386\text{w}$, $\delta_{\text{CH}_3}=1386\text{w}$, $\delta_{\text{CH}_3}=1444\text{w}$, $\nu_{\text{N=N}}(\text{sin})=1500\text{s}$, $\nu_{\text{C=N}}(\text{pyr})=1548\text{s}$, $\nu_{\text{C=O}}(\text{pyrazolone})=1625\text{s}$,

$\nu_{\text{C=O}}(\text{ester})=1692\text{s}$, $\nu_{\text{CH}_3}^{\text{as}}=2987\text{m}$, 3065m, $\nu_{\text{NH}}(\text{pyr})=3196\text{s}$, $\nu_{\text{OH}}(\text{carboxy})=3440$.

¹H-RMN (DMSO-*d*₆, 200MHz): δ_{H} 7,97 (d, 2H, J=7,6Hz, 2''-H, 6''-H); 7,72 (d, 2H, J = 7,6Hz, 3''-H, 5''-H), 4,28 (q, 2H, J=6,5Hz, -CH₂CH₃); 2,42 (s, 3H, -CH₃); 1,29 (t, 3H, J=6,5Hz, -CH₂CH₃)

4c: 1H-4-(1H-4-ethoxycarbonyl-3-methyl-pyrazol-5-yl)-azo-3-ethoxycarbonyl-pyrazol-5-one

Yellow powder, m.p.= 220-223°C °C, yield = 94,5%

IR (ν/cm^{-1}): $\nu_{\text{C=O}}^{\text{as}}(\text{ester})=1215,9\text{s}$, $\delta_{\text{CH}_3}^{\text{s}}=1388,5\text{m}$, $\delta_{\text{CH}_3}^{\text{as}}=1441\text{m}$, $\delta_{\text{N=N}}(\text{sin})=1500\text{w}$, $\nu_{\text{C=O}}(\text{pyrazolone})=1546\text{s}$, $\nu_{\text{C=O}}(\text{pirazolone})=1684\text{s}$, $\nu_{\text{C=O}}(\text{ester})=1714\text{s}$, $\nu_{\text{CH}_2}^{\text{as}}=2835\text{m}$, $\nu_{\text{CH}_2}^{\text{s}}=2841\text{m}$, $\nu_{\text{CH}_3}^{\text{s}}=2870\text{m}$, $\nu_{\text{CH}_3}^{\text{as}}=2981\text{m}$, $\nu_{\text{NH}}(\text{pyrazolone})=3145\text{m}$, $\nu_{\text{NH}}(\text{pyrazolone})=3340\text{m}$.

UV-VIS: 210 (1,37), 241 (0,62), 422 (1,56).

3. Conclusions

The coupling of 1*H*-4-ethoxycarbonyl-3-methylpyrazol-5-yl-diazonium chloride (**2**) with 3-substituted and 1,3-disubstituted 1*H*-pyrazol-5-ones (**3**) takes place in aqueous solution at a slightly alkaline pH in good yields between 75 – 95 %.

IR spectra display vibrations characteristic to the pyrazole ring ($\nu_{C-O}=1200i$, $\nu_{C-N}=1267i$, $\nu_{C=N}=1640s$, $\nu_{C=O}=1700i$, $\nu_{CH_3}=2927s$, $2987m$, $\nu_{NH}=3453m$), as well as that of the pyrazolonic ($\nu_{C-N}=1300i$, $\nu_{C=N}=1550s$, $\nu_{C=O}=1650i$), with the mention that the exact attribution of the vibrations characteristic to the existing groups on the pyrazolone ring is difficult due to the existence of tautomeric forms, but it was done according to the specifications from the literature [14, 15].

The interpretation of UV-VIS spectra is difficult because of the fact that, along with the azo-hydrazo tautomerism, the tautomerism of pyrazolone rings also occurs. Therefore, in the case of 1-substituted 5-pyrazolones, there are three tautomeric forms.

REFERENCES

1. Lopez, C., Claramunt, R.M., Trofimenko, S., Elguero, J., *Can. J. Chem.*, **1993**, 71, pp. 678.
2. Lang, S.A., Lee, V.J., Five – Membered Ring Systems. In "Comprehensive heterocyclic chemistry", vol. 5, Pergamon Press, Oxford, **1984**.
3. Kurasawa, Y., Kanoh, M., Kamigaki, Y., *J. Het. Chem.*, **1988**, 25, pp. 1015.
4. Elnagdi, M.H., Kamal, U.S., *J. Chem. Soc. Perkin Trans. I*, , 2663.
5. Elnagdi, M.H., Hamza, M.R., *J. Org. Chem.*, **1976**, 41(24), pp. 3781.
6. Partridge, M.W., Stevens, M.F.G., *J. Chem. Soc. (C)*, **1966**, pp. 1127.
7. Elnagdi, M.H., *Tetrahedron*, 1974, 30, pp. 2791.
8. Gavrilenko, B.B., Miller, S.L., *J. Org. Chem.*, **1975**, 40(19), pp. 2720.
9. Ebtisam, A.A.H., Nosrat, M.A., Hamza, E., *Heterocycles*, **1984**, 22(8), pp. 1821.
10. ReimLinger, H., von Overstraeten, A., *Chem. Ber.*, **1961**, 94, pp. 1036.
11. ReimLinger, H., von Overstraeten, A., *Chem. Ber.*, **1966**, 99, pp. 3350.
12. Beyer, H., Wolter, G., Lemke, H., "Über die Pyrazolbildung aus α -Chlor-*acetessigester* und Thiocarbohydrazid", *Chem. Ber.*, **1956**, 89, pp. 2550.
- 13.*** Bios Final Reports nr. 1548, 311; Rotenberg, H., *Chem. Ber.* 25, 3442, **1898**, in "Beilsteins Handbuch der Organischen Chemie", Verlag v. Julius Springer, Berlin, 1920, Band 25, S. 206;
14. Deschamps, J., Arriau, J., Parmentier, P., "Etude par des methodes semi-empiriques de la chimie theorique dans la serie des pyrazolones I", *Tetrahedron*, 1971, 27, pp. 5779.
15. Arriau, J., Deschamps, J., Teysseyre, J., "Etude par des methodes semi-empiriques de la chimie theorique dans la serie des pyrazolinones II", *Tetrahedron*, **1974**, 30(10), pp. 1225.