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UNUSUAL REACTION OF ENHYDRAZINES WITH OXALYL CHLORIDE

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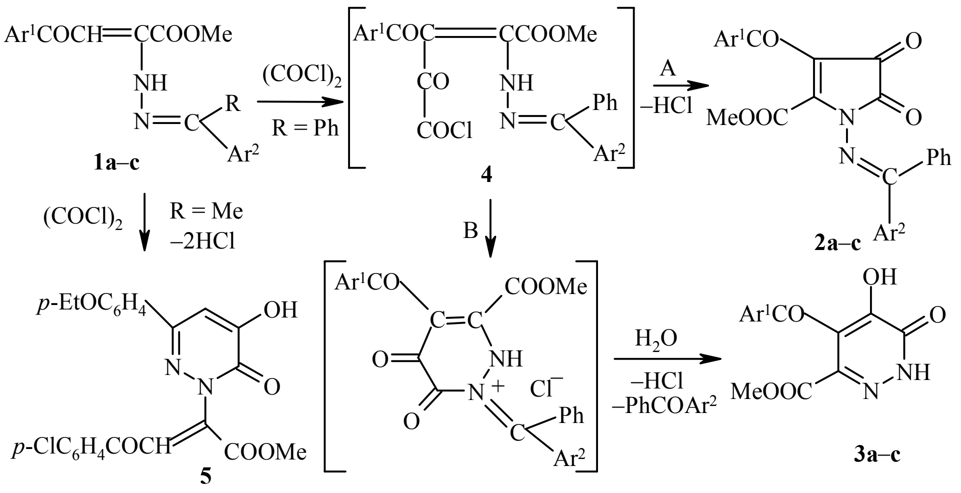
The reaction of primary enamines with oxalyl chloride is the most widely used method for synthesis of substituted 2,3-dihydro-2,3-pyrrolediones [1]. Starting with enhydrazines (substituted N-methyl-N-phenyl- and N,N-diphenyl-N'-vinylhydrazines), this method enables to obtain the corresponding substituted 1-methyl(phenyl)amino- and 1-diphenylamino-2,3-dihydro-2,3-pyrrolediones in practically quantitative yields [2,3]; there have been no reports concerning isolation and identification of other products.

When methyl esters of 4-aryl-2-diarylmethylenehydrazino-4-oxo-2-butenoic acids **1a,b** react with oxalyl chloride, in addition to the expected 4-aroyl-1-diarylmethyleneamino-5-methoxycarbonyl-2,3-dihydro-2,3-pyrrolediones **2a,b**, the minor products 4-aroyl-5-hydroxy-3-methoxycarbonyl-1,6-dihydro-6-pyridazinones **3a,b** are formed. Compound **3b** was identified by comparison with a known sample whose structure was confirmed by X-ray diffraction [4].

When the methyl ester of 4-*p*-chlorophenyl-2-[methyl(*p*-ethoxyphenyl)methylene]hydrazino-4-oxo-2-butenoic acid (**1c**) reacts with oxalyl chloride, instead of the expected 4-*p*-chlorobenzoyl-5-methoxycarbonyl-1-[methyl(*p*-ethoxyphenyl)methylene]amino-2,3-dihydro-2,3-pyrroledione (**2c**) and 4-*p*-chlorobenzoyl-5-hydroxy-3-methoxycarbonyl-1,6-dihydro-6-pyridazinone (**3c**), the compound 3-*p*-ethoxyphenyl-5-hydroxy-1-[methoxycarbonyl(*p*-chlorophenacylidene)methyl]-1,6-dihydro-6-pyridazinone (**5**) is formed.



1-3 a Ar^1 = *p*-MeC_6H_4, Ar^2 = Ph; **b** Ar^1 = Ph, Ar^2 = *p*-$MeOC_6H_4$
c Ar^1 = *p*-ClC_6H_4, Ar^2 = *p*-$EtOC_6H_4$

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Probably the β-C acid chlorides (**4a,b**) formed in the first step of the reaction of enhydrazines **1a,b** with oxalyl chloride are capable to intramolecular cyclization, with acylation of the secondary amino group and closure of the pyrroledione ring (pathway A) or with acylation (possibly reversible) of the nitrogen atom of the azomethine group and closure of the pyridazinone ring (pathway B), followed by hydrolytic cleavage of the diaryl ketone. Taking special precautions to decrease the water content in the reaction mass makes it possible to reduce the yield of pyridazinones **3a,b** to practically zero.

In contrast to the above, when enhydrazine **1c** reacts with oxalyl chloride, acylation of the methyl and amino group of the methyl(aroyl)methylenehydrazine moiety occurs.

5-Methoxycarbonyl-1-diphenylmethyleneamino-4-*p*-toluoyl-2,3-dihydro-2,3-pyrroledione (2a) and 5-Hydroxy-3-methoxycarbonyl-4-*p*-toluoyl-1,6-dihydro-6-pyridazinone (3a). A solution of oxalyl chloride (0.47 ml, 5.5 mmol) in absolute chloroform (2 ml) was added to a solution of ester **1a** (2.00 g, 5.2 mmol) in absolute chloroform (3 ml). This was refluxed for 100 min and cooled. The precipitate of compound **2a** was filtered off. Yield 1.36 g (60%); mp 144-146°C (hexane). IR spectrum (vaseline oil), ν, cm^{-1}: 1740 ($C_{(2)}$=O, COOMe), 1725 ($C_{(3)}$=O), 1630 ($C_{(4)}$–C=O). ^{1}H NMR spectrum (250 MHz, DMSO-d$_6$), δ, ppm: 2.29 (3H, s, CH_3); 3.80 (3H, s, CH_3O); 7.00-7.79 (14H, m, $2C_6H_5+C_6H_4$). **Compound 2a.** Found, %: C 71.68; H 4.41; N 6.20. $C_{27}H_{20}N_2O_5$. Calculated, %: C 71.67; H 4.46; N 6.19.

Compound 3a. 3 ml of solvent was distilled off from the mother liquor and cooled. The precipitate was filtered off. Yield 0.21 g (14%); mp 267-269°C (hexane). IR spectrum (vaseline oil), ν, cm^{-1}: 3260 (OH), 3170 (NH), 1670 ($C_{(6)}$=O). ^{1}H NMR spectrum (250 MHz, DMSO-d$_6$), δ, ppm, *J* (Hz): 2.44 (3H, s, CH_3); 3.70 (3H, s, CH_3O); 7.30 (2H, d, 8.0, 2CH(*m*)); 7.67 (2H, d, 8.0, 2CH(*o*)); 13.60 (1H, s, OH). Found, %: C 58.34; H 4.21; N 9.74. $C_{14}H_{12}N_2O_5$. Calculated, %: C 58.33; H 4.20; N 9.72.

4-Benzoyl-5-methoxycarbonyl-*p*-methoxyphenylmethyleneamino-1-phenyl-2,3-dihydro-2,3-pyrroledione 2b and 4-Benzoyl-5-hydroxy-3-methoxycarbonyl-1,6-dihydro-6-pyridazinone 3b were synthesized similarly.

Compound 2b, yield 57%; mp 145-147°C (hexane). IR spectrum (vaseline oil), ν, cm^{-1}: 1735 ($C_{(2)}$=O, COOMe), 1715 ($C_{(3)}$=O), 1660 ($C_{(4)}$–C=O). ^{1}H NMR spectrum (250 MHz, DMSO-d$_6$, δ, ppm, *J* (Hz)): 3.75 (6H, s, MeO+COOMe); 7.03-8.88 (14H, m, $2C_6H_5+C_6H_4$). Found, %: C 69.21; H 4.29; N 5.99. $C_{27}H_{20}N_2O_6$. Calculated, %: C 69.23; H 4.30; N 9.98.

Compound 3b, yield 18%; mp 264-266°C (acetonitrile). Lit. mp 265-267°C [4]. Found, %: C 56.96; H 3.70; N 10.22. $C_{13}H_{10}N_2O_5$. Calculated, %: C 56.94; H 3.68; N 10.22.

3-*p*-Ethoxyphenyl-5-hydroxy-1-[methoxycarbonyl(*p*-chlorophenacylidene)methyl]-1,6-dihydro-6-pyridazinone (5). A solution of oxalyl chloride (0.23 ml, 2.7 mmol) in absolute benzene (2 ml) was added to a solution of ester **1c** (1.00 g, 2.6 mmol) in absolute benzene (7 ml). This mixture was refluxed for 40 min and cooled, then the precipitate of compound **5** was filtered off. Yield 0.62 g (53%); mp 228-230°C (chloroform). IR spectrum (vaseline oil), ν, cm^{-1}: 3250 (OH), 1730 (COOMe), 1685 ($C_{(6)}$=O), 1640 (COC_6H_4Cl-*p*). ^{1}H NMR spectrum (250 MHz, DMSO-d$_6$, δ, ppm, *J* (Hz)): 1.36 (3H, t, 6.9, CH_3); 3.67 (3H, s, CH_3O); 4.05 (2H, q, 6.9, CH_2O); 5.49 (1H, s, CH); 6.00 (1H, s, CH); 6.91 (2H, d, 7.5, 2CH(*m*) in $C_6H_4OC_2H_5$-*p*); 7.32 (2H, d, 7.5, 2CH(*o*) in $C_6H_4OC_2H_5$-*p*); 7.60 (2H, d, 9.0, 2CH(*m*) in C_6H_4Cl-*p*); 7.94 (2H, d, 9.0, 2CH(*o*) in C_6H_4Cl-*p*). Found, %: C 60.75; H 4.23; N 6.18; Cl 7.80. $C_{23}H_{19}ClN_2O_6$. Calculated, %: C 60.73; H 4.21; N 6.16; Cl 7.79.

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