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OMS Letters

Dear Sir:

Mass Spectral Evidence for Δ^1- Pyrazolines from the 1,3-Dipolar Addition of Diazomethane to 1-Hydroxy-2-Naphthoic Acid and Its Methyl Ester

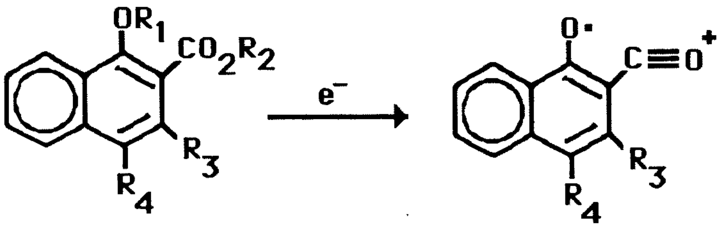
During the course of experiments toward the syntheses of arylmethylnaphthols as coal models, a THF solution of 1-hydroxy-2-naphthoic acid (0.5g; 3 mmol) was reacted with excess ethereal diazomethane (10 mmol), generated from N-methyl-N-nitrosotoluene-p-sulphonamide[1]. After two hours of reaction at room temperature, gas chromatography/mass spectrometry (HP5790A/HP MSD 5970A) analyses indicated nearly complete esterification **1a**. Reflux of this mixture for 16 hours produced 33% of the ether-ester **1b** as determined by gc/ms.

In addition to these expected products, of note in the gc/ms analyses of solution aliquots were the observation of two additional low yield products (<1%), both at longer retention times than either the ester or the ether-ester. Based upon the mass spectral evidence described in Table 1., we have identified these new products as the Δ^1-pyrazolines formed from the 1,3-dipolar addition of diazomethane to 1-hydroxy-2-naphthoic acid and 1-hydroxy-2-methyl naphthoate. The regiochemistry of the products could not be determined by ms, but addition at the 3-4 positions is likely based upon known regio-effects in the dipolar additions of diazomethane[2]. Such addition would lead to illustrated products **2a,b**. Equivalent mass spectra and chromatographs were obtained upon replication of the experimental procedure.

To our knowledge, this represents the first evidence for the dipolar addition of diazomethane to naphthols or phenols. Pyrek and Achmatowicz[3] have reported the electrophilic aromatic substitution of methyl diazonium cation to 2-allyl-1-naphthol, while Dean and Park[2] have observed the 1,3-dipolar additions of several diazo alkanes to a variety of electron deficient coumarins at the 3-4 positions to yield the corresponding Δ^1-pyrazolines. This suggests that the electron withdrawing carbonyl substituent in our model is responsible for the altered chemistry of the naphthol ring from that observed by Pyrek and Achmatowicz.

Table 1. Mass Spectral Data, Assignments and Structural Interpretation

Mass Spectral Data m/e (relative intensity) [assignment]
1a 202 (0.32) [M^+]; 170 (1.00) [- MeOH = **3a**]
1b 216 (0.79) [M^+]; 184 (0.95) [-MeOH]; 114 (1.00)
2a 244 (0.02) [M^+]; 216 (0.27) [-N_2]; 170 (1.00) [-{CH_2N_2/MeOH} = **3a**]
2b 230 (0.24) [M^+]; 202 (0.05) [-N_2]; 170 (1.00) [-{CH_2N_2/HOH} = **3a**]



1. 3.

a. R_1= H, R_2= Me, R_3= H, R_4= H

b. R_1= Me, R_2= Me, R_3= H, R_4= H

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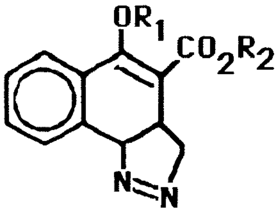

2.

a. R_1= H, R_2= Me

b. R_1= H, R_2= H

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Yours,

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References

1. L. Fieser, M. Fieser, *Reagents for Organic Synthesis*, Wiley, New York, vol. I, p 191 (1967).
2. F. M.Dean, B. K. Park, *J. Chem. Soc. Perkin Trans. I*, 2937 (1980).
3. J. St.Pyrek, O. Achmatowicz, *Tetrahedron Lett.*, 2651 (1970).