

COUPLING OF DIAZOMETHANE WITH α -NAPHTHOLS

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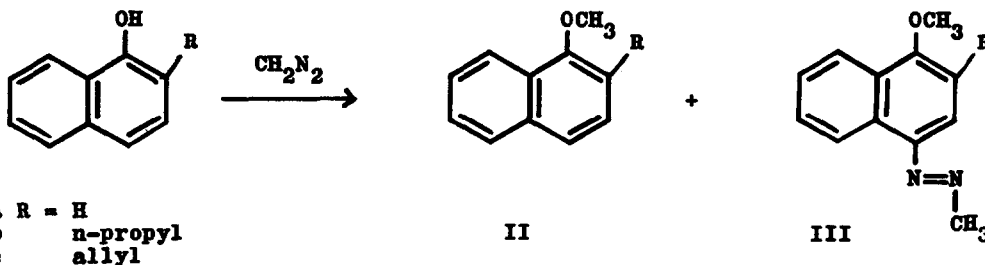
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Recently the reaction of diazomethane with C-H acidic compounds, analogous to that of the aryldiazonium cation, were reported (1,2). As products methyl hydrazones were obtained. A similar reaction was observed for 6-hydroxy-2-pyridone (3). Herein we describe the coupling of α -naphthols with diazomethane, leading to azocompounds, i.e. the electrophilic substitution of an activated aromatic ring, typical for a diazonium cation.

In the course of our synthetic program we tried methylation of 2-allyl-1-naphthol, Ia, with ethereal diazomethane. The reaction was slow and the yield of methyl ether IIc about 30% only. The main isolated product (60%) was a yellow oil containing nitrogen. Analytical (4) and spectral data unequivocally indicated that it is the azocompound IIIc: b.p. $0.6 \sim 100^\circ$; uv: $\lambda_{\text{max}}^{\text{EtOH}}$ 229 ($\lg \epsilon$ 4.67), 331 (3.87) nm; ir: 770 and 890 cm^{-1} - four and single aromatic H respectively; nmr: table.



Nearly the same yield of coupling product was obtained with 2-n-propyl-1-naphthol, Ib: IIIb: b.p. $0.6 \sim 100^\circ$; uv: $\lambda_{\text{max}}^{\text{EtOH}}$ 228 (4.64), 333 (3.84); ir: 765 and 880 cm^{-1} - four and single aromatic H respectively; nmr: table. α -Naphthol in dilute ethereal solution also coupled with diazomethane, to give IIIa, in about 10% yield; m.p. $45-46^\circ$; uv: $\lambda_{\text{max}}^{\text{EtOH}}$ 236 (4.42), 342 (3.99);

ir: 830 and 765cm^{-1} - two and four aromatic H respectively; nmr: table. In concentrated solution, or in the presence of alcohol, there was only fast O-methylation and no coupling. We also did not observe the reaction II \rightarrow III. Carrying out the reaction with excess of deuteriated α -naphthol, we noted nearly total exchange of diazomethane hydrogens.

TABLE: Chemical shifts (δ) of aromatic and methyl protons in nmr spectra of products of O-methylation and coupling (in acetone d_6):

COMPOUND	H-2	H-3	H-5	H-6,7	H-8	O-CH ₃ , N-CH ₃
IIIa	6.91 ABq J=8.5	7.52	8.75m	7.60m	8.25m	4.00s, 4.05s
IIIb	-	7.42s	8.74m	7.55m	8.10m	3.92s, 4.08s
IIIc	-	7.40s	8.74m	7.55m	8.10m	3.93s, 4.09s

Formation of the methyl diazonium cation has seemed to be doubtful and the lack of the coupling reaction was invoked as an argument against its existence (5). Instead proton bridge complexes: diazomethane - acid proton donor were postulated (5,6). In the light of our results and the recent literature data (1,2,3) the existence of the methyl diazonium cation appears to be established. It is possible that diazomethane and α -naphthol are forming an "intimate ion pair", stable in media of low dielectric constant; its dissociation into ions leads to instantaneous decay of the methyl diazonium cation and O-methylation, while dissociation into diazomethane and naphthol causes hydrogen exchange. In this ion pair with suitable orientation of components, electrophilic substitution at the activated position 4 takes place followed by the fast methylation of the formed anion. Proton bridge complexes are not adequate to explain both coupling and proton exchange results.

We are continuing our investigation in this area.

FOOTNOTE AND REFERENCES:

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