PSCHORR REACTION ON 1-(2-AMINOPHENYL)-1,2,3,4-TETRAHYDRO-2-METHYLISOQUINOLINE

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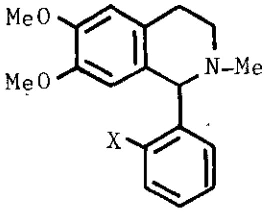
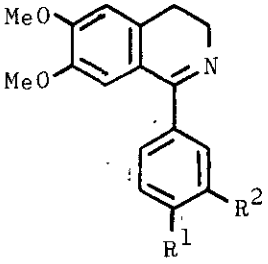
Diazotisation and Pschorr reaction of 6-amino-N-methyl-6,7-dimethoxy-1-(3,4-methylenedioxyphenyl)isoquinoline, gave besides the deaminated product, the corresponding 3,4-dihydroisoquinoline with N-demethylation and concomittant oxidation at the 1,2-position. 6-Amino-N-methyl-6,7-dimethoxy-1-(3,4-dimethoxyphenyl)isoquinoline, under identical conditions gave, besides the deaminated product, a deep orange compound, which has been assigned the structure 3,4-dihydro-6,7,11,12-tetramethoxy-5-nitroazafluoranthene.

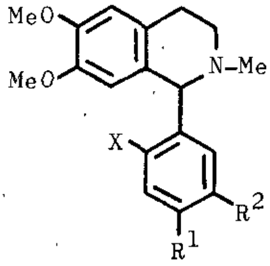
An earlier study[3] on the diazotisation and Pschorr reaction on 1-(2-aminophenyl)-1,2,3,4-tetrahydro-6,7-dimethoxy-2-methylisoquinoline 1a gave 1b and 1c besides 3,4-dihydro-6,7-dimethoxy-1-phenylisoquinoline 2a. In continuation of this work, we now report our studies on the diazotisation and Pschorr reaction on 3a and 3b. 3a gave 2b and 3c; while 3b gave besides 2c, a deep orange crystalline compound melting at 180 - 182°C, whose nmr spectrum showed eighteen protons and the presence of four methoxyls (singlets at δ 4.0, 4.05, 4.06 and 4.10), two aromatic protons



1 a. $X=NH_2$
b. $X=H$
c. $X=OH$

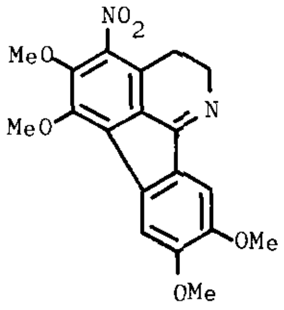


2 a. $R^1=R^2=H$
b. $R^1=R^2=OCH_2O$
c. $R^1=R^2=OMe$



3 a. $R^1=R^2=OCH_2O$
$X=NH_2$
b. $R^1=R^2=OMe$
$X=NH_2$
c. $R^1=R^2=OCH_2O$
$X=H$

(singlet at δ 7.46) and two aliphatic methylene groups (two triplets at δ 2.86 and 4.30). On the basis of its analysis (Found C, 61.66; H, 5.06; $C_{19}H_{18}O_6N_2$ requires C, 61.61; H, 4.90) and mass spectrum [m/e 370 (M^+)], its molecular formula was deduced to be $C_{19}H_{18}O_6N_2$; uv λ_{max}^{EtOH} 240, 272 nm (log ε 4.28, 4.54). The ir $\nu_{max}^{CHCl_3}$ showed bands at 1532 and 1305 cm^{-1} (nitro group). The most probable structure of this compound is 4 though alternate structures 5 and 6 could not be entirely ruled out on the basis of spectral data. However Campbell and Reid[4] reported that in the 3,4-dihydroazafluoranthene 7, position 5 and 12 are readily susceptible for nitration and it is likely that in the compound under investigation



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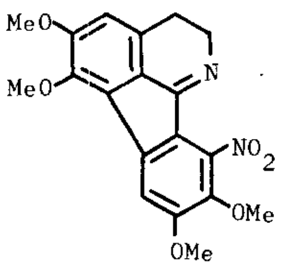

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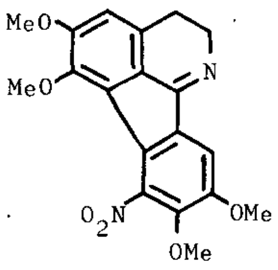

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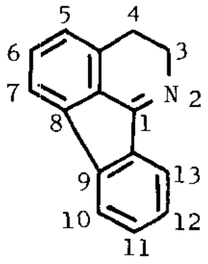

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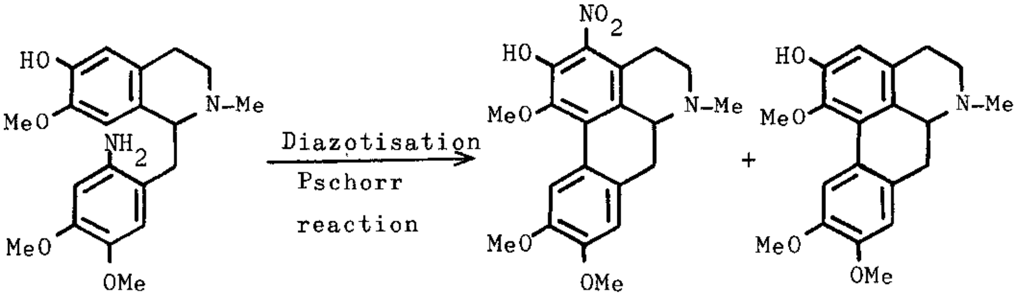
postion 12 being substituted, position 5 is nitrated under diazotisation and Pschorr reaction conditions. Perhaps the only other reported case of nitration of an aromatic ring during diazotisation conditions is by Kametani.[5] In the course of the synthesis of predicentrine by diazotisation and Pschorr reaction of 8 predicentrine (10) and nitropredicentrine (9) were also obtained. In all the three 1-(2-aminophenyl)-1,2,3,4-tetrahydro-2-methylisoquinolines (1a, 3a, and 3b) that were diazotised and subjected to Pschorr reaction, one of the unusual products of the reaction was the formation of the corresponding 3,4-dihydro-1-phenylisoquinoline resulting from concomittant deamination, N-demethylation and 1,2-double bond formation of the parent compound. As far as we are aware this is a novel reaction and no such product formation seems to have been reported so far. It is interesting in this connection to note that Cava and his coworkers[6] isolated two azafluoranthene alkaloids 11a and 11b and established their structure on the basis of spectral data and confirmed it by synthesis.



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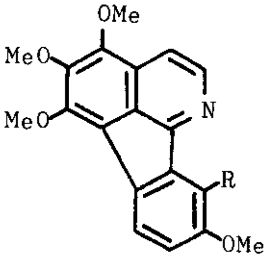
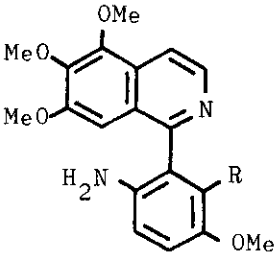


11 a. R=OMe
b. R=H



12 a. R=OMe
b. R=H

The synthesis was carried out by diazotisation and Pschorr reaction of 12a and 11b. The azafluoranthenes were formed in satisfactory yields only when OCH_3 group was present in position 5 of the isoquinoline 12. In all other cases, during diazotisation only deaminated products were obtained.

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