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

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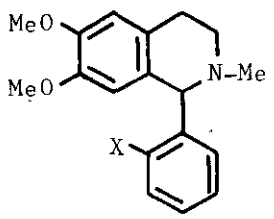
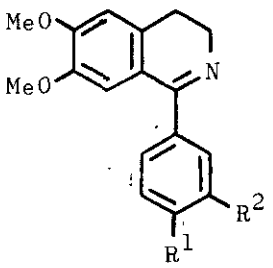
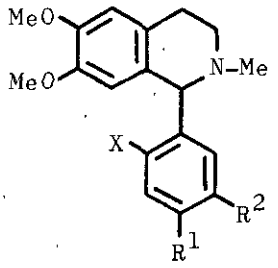
Diazotisation and Pschorr reaction of 6-amino-N-methyl-6,7-dimethoxy-1-(3,4-methylenedioxyphenyl)isoquinoline, gave besides the deaminated product, the corresponding 3,4-dihydroisoquinoline with N-demethylation and concomittant oxidation at the 1,2-position. 6-Amino-N-methyl-6,7-dimethoxy-1-(3,4-dimethoxyphenyl)isoquinoline, 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. $R^1=R^2=OCH_2O$

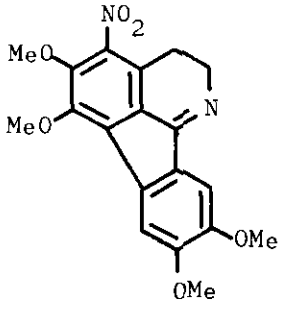
c. $R^1=R^2=OMe$

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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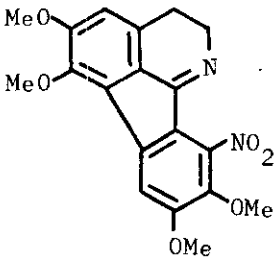

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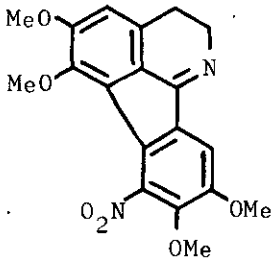

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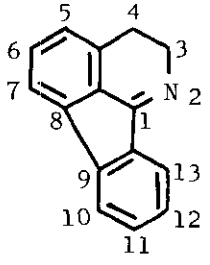

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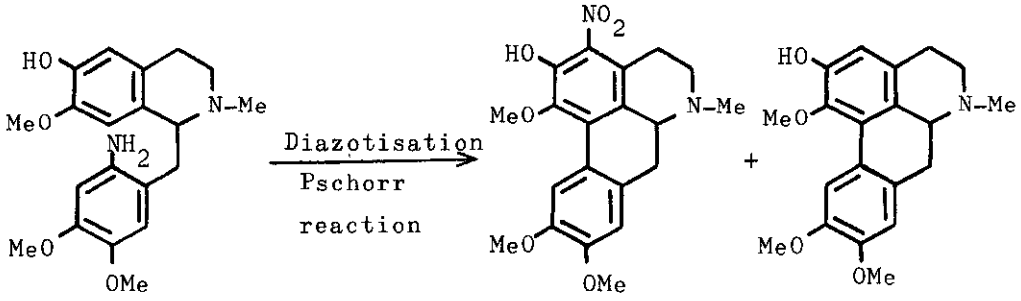
postion 12 being substituted, position 5 is nitrated under diazotisation and Pschorr reaction conditions. Perhaps the only other reported case of nitration of an aromatic ring during diazotisation conditions is by Kametani.[5] In the course of the synthesis of predicentrine by diazotisation and Pschorr 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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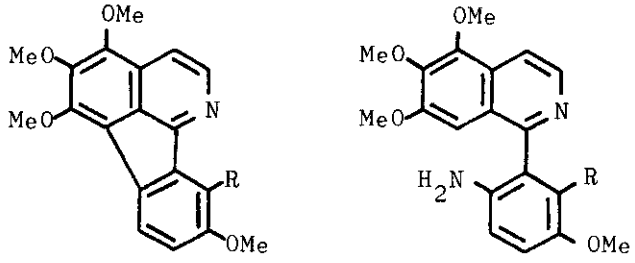

11 a. R=OMe
b. R=H

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.

ACKNOWLEDGEMENT We thank Professor Maurice Shamma ror the N. M. Rand mass spectral data of 4 and Professor T. R. Govindachari and Dr. S. Selvavinayakam for analytical data. We also thank Professor Cava, for his interest in this work. R. C. is grateful to the C. S. I. R. (India) for a Pool Officership, and M. S. P. to the University Grants Commission (India) for a Junior Research Fellowship.

REFERENCES

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Received, 10th March, 1975