J. Chem. Soc. Pak. Vol. 3, No. 1, 1981

A New Approach to the Synthesis of N-Arylated Aromatic Amines – A Novel Carbazole Synthesis**

ATTA-UR-RAHMAN* AND SADIQA FIRDOUS

H.E.J. Postgraduate Institute of Chemistry, University of Karachi, Karachi-32, Pakistan.

(Received 26th November, 1980)

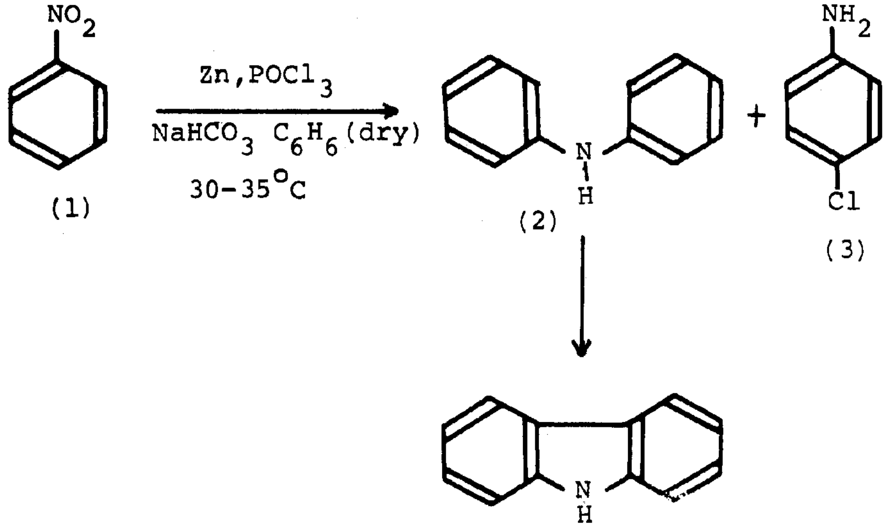
In continuation of our efforts to develop new synthetic methods,[1-9] a new method for preparing N-arylated aromatic nitro compounds with Zn-$POCl_3$-$NaHCO_3$ is now described. The reaction product obtained is then photochemically cyclized to the carbazole alkaloidal system.[10]

Nitrobenzene (1) was reduced with Zn-$POCl_3$-$NaHCO_3$ in dry benzene at 30-35°C for several hours. Most of the starting material was found to be converted. As a result two products were obtained in moderate yields. The two products were isolated by preparative T.L.C.

The mass spectrum of the faster running reaction product (2) afforded the molecular ion at m/e = 169 with other major peaks at m/e = 87, 85, 83, 77 and 58. The fragmentation pattern was found to be identical to that of diphenylamine. The I.R. spectrum showed the presence of amino group at 3440 cm^{-1}. The U.V. spectrum showed maxima at 208 and 285 nm and the N.M.R. spectrum in $CDCl_3$ showed a broad hump for N-H at δ 5.7 with aromatic protons ranging from δ 7- δ 7.5. The substance was identified as diphenylamine (2) by chromatographic and spectroscopic comparisons. It was further confirmed by co-chromatography with an authentic sample of diphenylamine.

The slower-moving reaction product (3) was obtained as a white crystalline solid in about 60% yield. The mass spectrum of the substance afforded M^+ at m/e = 127/129 and the other major peaks appeared at m/e = 92, 87, 85 and 83. A major M-35 fragment at m/e 92 in the mass spectrum was indicative of the presence of Cl in the molecule. The U.V. spectrum showed maxima at 208, 224 and 300 nm. The I.R. spectrum showed the presence of amino group at 3400 cm^{-1} and afforded strong absorption at 820 cm^{-1}, typical for p-disubstituted aromatic compounds. The N.M.R. spectrum in $CDCl_3$ showed a broad hump for N-H at δ 3.7 while the aromatic protons resonated at δ 6.55 (2H, doublet, J=9Hz, ortho to amino group), (2H, doublet, J=9Hz, ortho to chlorine). On the basis of the above data, the product was identified as p-chloroaniline.

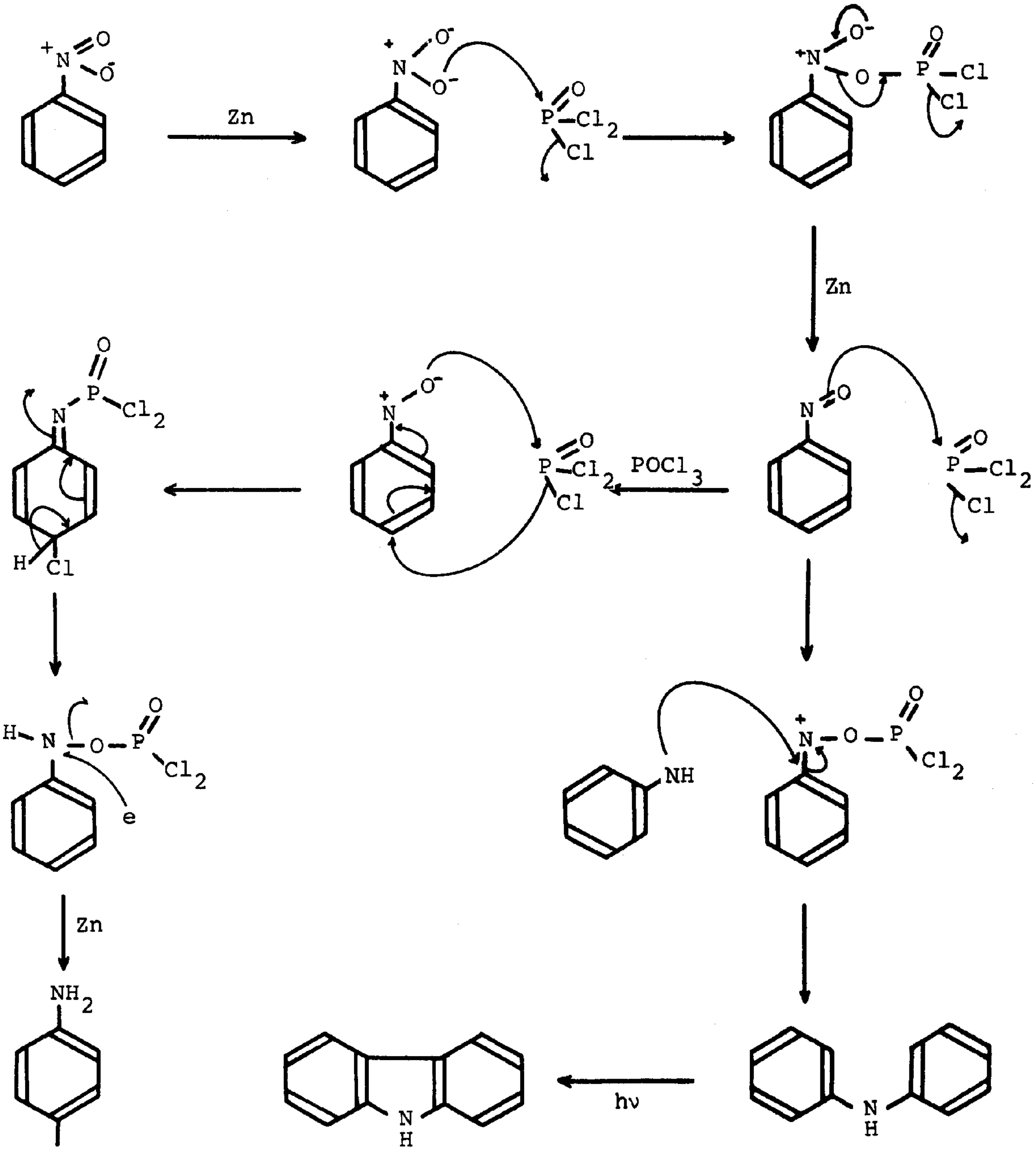
Similar reductions were performed with other aro-



---

*Author to whom requests for reprints should be addressed.

**An abstract of the paper has been published at the 4th Asian Symposium on Medicinal Plants and Spices, Bangkok, Thailand, 15-19 September, 1980.



(3)

Scheme 1

(2)

Table

Compound	Product I	Yield	Product II	Yield
Nitrobenzene	$(Ph)_2NH$	40%	$C_6H_4NH_2Cl$	60%
o-nitrotoluene	$(Ph)_2CH_3NH$	20%	$C_6H_3CH_3NH_2Cl$	50%
m-nitrotoluene	$(Ph)_2CH_3NH$	20%	$C_6H_3CH_3NH_2Cl$	80%
p-nitrotoluene	$(Ph)_2CH_3NH$	20%	$C_6H_3CH_3NH_2Cl$	80%
2:4-dinitrotoluene	–	–	$C_6H_2CH_3(NH_2)_2Cl$	2%
m-dinitrobenzene	No reaction.			

matic nitro compounds under corresponding reaction conditions. It was observed that the reduction proceeded smoothly and the reduction products obtained corresponded to those obtained previously with nitrobenzene.

In the case of 2;4-dinitrotoluene and meta-dinitrobenzene no reaction was observed at room temperature and almost no reaction even at higher temperature.

In the case of 2:4-dinitrotoluene only a very small amount (2%) conversion was observed on refluxing the reaction mixture for many hours whereupon most of the starting material were found to be unreacted. The reduction product obtained was identified as 2:4-diamino-5-chlorotoluene on the basis of spectral data.

From the above results it may be concluded that the presence of electron withdrawing group in the aromatic ring reduces the rate of reduction while the presence of Me group in nitrolotuene enhances the formation of the chlorosubstituted product. A plausible mechanism for the reaction is presented in Scheme I. This method offers a new approach to the synthesis of carbazole system[10] by the known photochemical cyclisation procedure.

References

1. Atta-ur-Rahman, A. Basha, N. Waheed and S. Ahmad, *Tetrahedron Letters*, 1976, 3, 219.
2. A. Basha and Atta-ur-Rahman, *Experientia*, 1977, 33, 101.
3. Atta-ur-Rahman, A. Basha and V.U. Ahmad, *Experientia*, 1976, 32, 1491.
4. Atta-ur-Rahman and A. Basha, *J. Chem. Soc. Chemical Communications*, 1976, 594.
5. Atta-ur-Rahman and N. Waheed, *Z Naturforsch.*, 1976, 31b, 287.
6. Atta-ur-Rahman, *J. Chem. Soc.*, 1972, 736.
7. Atta-ur-Rahman and N. Waheed, *Tetrahedron Letters*, 1977, 47, 4101.
8. Atta-ur-Rahman and N. Waheed, *Tetrahedron Letters*, 1979, 19, 1715.
9. Atta-ur-Rahman, M. Ghazala, N. Sultana and M. Bashir, *Tetrahedron Letters*, 1980, 21, 1773.
10. H. Linschitz and K.H. Gerllman, *J. Am. Chem. Soc.*, 1964, 86(2), 303.