Tetrahedron Letters No. 43, pp 4179 - 4182. 0040-4039/78/1022-4179$02.00/0

THE INSERTION OF DIARYL CARBENES INTO AN IMINE N-H BOND

K.N. Mehrotra and G. Prasad

Chemistry Department, Banaras Hindu University, Varanasi-221005, India.

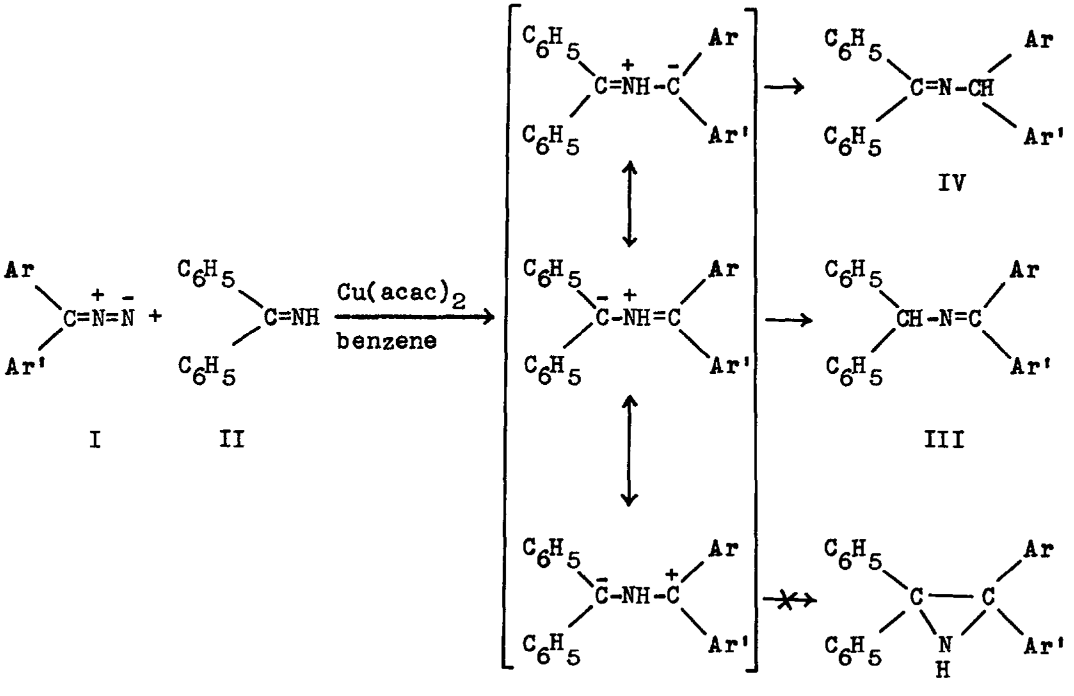
The reaction of diaryldiazomethanes on maleic and fumaric esters to form pyrazolines and cyclopropanes has been reported[1]. In a few cases copper salts have been used as catalysts; an example being the copper sulphate catalysed addition of diphenyl carbene on the carbon-carbon double bond of trimethyl vinyl silane[2]. The present study has shown that the bis (acetylacetonato) copper(II) catalysed decomposition of diaryldiazomethanes (I) gave isomeric substituted imines, formed as the result of insertion of diaryl carbenes into the N-H bond of 1,1-diphenylmethyleneimine (II), instead of the cyclic products as reported in the cases of olefins[1,2].

A solution containing 2.0 g each of diphenyldiazomethane (Ia) and 1,1-diphenylmethyleneimine (II) in 20 ml of dry benzene was slowly added (3 hr) to a refluxing solution of 0.4 g of bis (acetylacetonato) copper (II) in 50 ml of dry benzene. The contents were stirred and heated under reflux for 1 hr and allowed to stand at room temperature for 24 hr. The reaction mixture was passed through neutral alumina (10 g) packed in a column (1.5 cm x 20 cm) and eluted with 100 ml of benzene to remove the copper salt. Evaporation of the solvent under reduced pressure and crystallisation from ethanol gave a white solid[3] (2.3 g, 66%) mp 150-1°. uv max (EtOH): 252 nm. ir ($CHCl_3$, cm^{-1}): 1625s ($\nu_{C=N}$). nmr (δ values): 7.80 (m, 2H, aromatic), 7.35 (m, 18H, aromatic) and 5.60 (s, 1H, benzhydrylic). From the above data and undepressed mixed mp with an authentic sample[4], the product has been assigned a structure, benzophenone N-benzhydrylimine (III).

When 4-methoxyphenylphenyldiazomethane (Ib) was reacted with II in an analogous manner, two products, a white solid IIIb and a thick liquid IVb were obtained. The solid was separated and purified by crystallisation from ethanol and the liquid product was purified by column chromatography. The solid product[3] (65%) mp 129-30° has been identified as 4-methoxybenzophenone N-benzhydrylimine. uv max (EtOH): 274 nm. ir ($CHCl_3$, cm^{-1}): 1620s ($\nu_{C=N}$). nmr (δ values): 7.65 (m, 19H, aromatic), 5.60 (s, 1H, benzhydrylic) and 3.71 (s, 3H, OCH_3). This assigned structure was confirmed by comparison (undepressed mixed mp and ir) with an authentic sample[5]. The liquid product IVb (20%) was characterised as benzophenone N-(4-methoxyphenylphenyl) methylimine. uv max (EtOH): 253 nm. ir (neat, cm^{-1}): 1620s ($\nu_{C=N}$). nmr (δ values): 7.80 (m, 2H, aromatic), 7.32 (m, 17H, aromatic), 5.61 (s, 1H, ArAr'CH) and 3.65 (s, 3H, OCH_3).

Similar reaction between 4,4'-dimethyldiphenyldiazomethane (Ic) and II gave a white solid IIIc (18%) mp 108-9° and a thick liquid IVc (75%). The product IIIc was identified as 4,4'-dimethylbenzophenone N-benzhydrylimine[3]. uv max (MeOH): 258 nm. ir (nujol, cm^{-1}): 1625s ($\nu_{C=N}$). nmr (δ values): 7.35 (m, 18H, aromatic), 5.60 (s, 1H, benzhydrylic) and 2.36 (d, 6H, CH_3 with a separation of 0.05 ppm)[6]. The structure of IIIc was also confirmed by comparison (undepressed mixed mp and ir) with an authentic sample[5]. The product IVc was characterised as benzophenone N-(4,4'-dimethyldiphenyl) methylimine[3]. uv max (EtOH): 253 nm. ir (neat, cm^{-1}): 1620s ($\nu_{C=N}$). nmr (δ values): 7.56 (m, 18H, aromatic), 5.47 (s, 1H, ArAr'CH) and 2.30(s,6H, CH_3). The structure was further confirmed by comparison with an authentic sample[5] (similar ir and nmr). When a solution of either III or IV in benzene was refluxed in presence of bis (acetylacetonato) copper(II) for 48 hr, interconversion was not observed.

The reaction between diaryldiazomethanes (Ia-c) and 1,1-diphenylmethyleneimine (II) can be depicted as:



I II III IV V

a ; Ar = Ar' = C_6H_5

b ; Ar = C_6H_5 ; Ar' = C_6H_4-OCH_3-p

c; Ar = Ar' = C_6H_4-CH_3-p

Absence of tetraarylethane in the reaction mixtures (TLC) supports a direct insertion of diaryl carbenes into the N-H bond of the imine II as an abstraction-recombination route would have given rise to the diaryl methyl radicals[7]. The electrophilic nature of carbenes and absence of radical path has been explained by the formation of a complex of carbene with copper salt[8]. The observed results in the present study can be explained through the possible intervention of ylides giving isomeric imines (IIIb-c and IVb-c) where the product ratio depends on the nature of substituents present in the benzene ring. A similar ylide intermediate has been proposed[9] in the reaction of dichlorocarbene with benzyldimethylamine where an insertion of carbene into the N-benzyl bond occurs. Since aziridine (V) was not isolated, the possible cyclisation of the ylide would have been prevented due to steric factors (presence of four bulky aryl groups on two carbon atoms).[10]

Acknowledgement: We thank Prof. O.P. Malhotra for providing the facilities.

REFERENCES AND FOOTNOTES

1. R. Baltzly, N.B. Mehta, P.B. Russell, R.E. Brooks, E.M. Grivsky and A.M. Steinberg, J. Org. Chem., 26, 3669 (1961).
2. I.A. D'yakonov, G.V. Golodnikov and I.B. Repinskaya, Zh. Organ. Khim., 1, 220 (1965); Chem. Abs., 63, 5671e (1965).
3. All compounds gave satisfactory analyses. The nmr spectra were recorded in $CDCl_3$ on a Varian A-60D 60MHz spectrometer using TMS as internal standard.
4. A. Rahman and M.O. Farooq, Annalen, 585, 200 (1954).
5. The authentic samples were prepared by heating equimolar quantities of the respective ketone and amine in presence of zinc chloride as described in ref.4.
6. D.Y. Curtin, E.J. Grubbs and C.G. McCarty, J. Am. Chem. Soc., 88, 2775 (1966).
7. W. Kirmse, L. Horner and H. Hoffmann, Annalen, 614, 19 (1958).
8. H. Nozaki, H. Takaya, S. Moriuti and R. Noyori, Tetrahedron, 24, 3655(1968).
9. M. Saunders and R.W. Murray, Tetrahedron, 6, 88 (1959); 11, 1 (1960).
10. K.N. Mehrotra and G. Prasad, Indian J. Chem., 16B, 77 (1978).

(Received in UK 29 August 1978; accepted for publication 4 September 1978)