Reactions of N,N -Diarylethylenediimines With Grignard Reagents, Phenylisocyanate and Succinic Anhydride Part-III[+]

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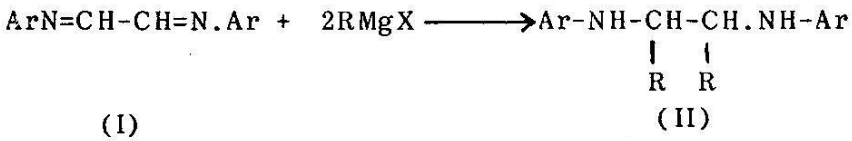
Summary: N,N -Diarylethylenediimines react with Grignard reagents to give the diadducts, with phenyl isocyanate to give the succinanilide derivatives and with succinic anhydride to give the 5,6-bis-(arylimino)-4,7-dioxodecanedioic acid, respectivey.

In the previous work [1], it has been reported that cinnamylideneanilines (-C=C-C=N) consumed one mole of Grignard reagents to give the 1,4-adducts. With a view of studying the effect of substitution of terminal carbon by a basic nitrogen in the above conjugated system on the course of reaction, we have investigated the reaction of N,N -diaryl-ethylenediimines with Grignard reagents.

Thus, treatment of N,N -diarylethylenediimines (Ia and b) with benzyl magnesium chloride, p-anisyl magnesium bromide and cyclohexyl magnesium bromide provides the diadducts (IIa-d).

One possible approach to explain the formation of (II) via the action of Grignard reagents on (I) is the assumption that two moles of the Grignard reagents are consumed in the 1,2-addition to the system -N=C-C=N- with the formation of the intermediate magnesium salt. The latter upon acidification is decomposed to give (II).

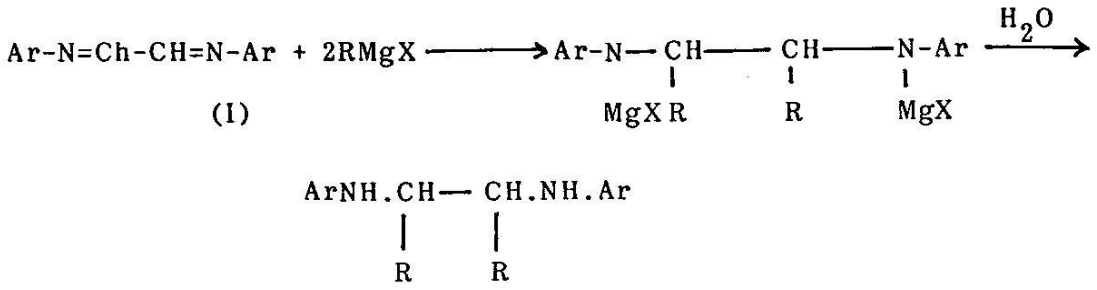


(I) (II)

Ar	Ar	Ar
a; $C_6H_4OCH_3$(p-)	a; $C_6H_6OCH_3$(p-)	$C_6H_5CH_2$
b; C_6H_{11}	b C_6H_{11}	$C_6H_5CH_2$
	c; C_6H_{11}	C_6OCH_3(p-)
	d; C_6H_{11}	C_6H_{11}

[+] Part I Indian J.Chem.; 218, 589 (1982)

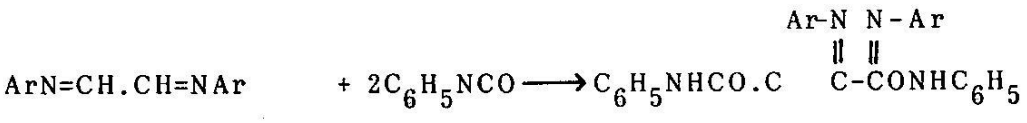
Part II Indian J.Chem.: 1156 (1983).



(I) (II)

The structural elucidation of (IIa-d) was based on elemental analysis, IR spectra which were devoid of C=N absorptions and the mass spectrum of (IIb) displaying the molecular ion peak at m/z 404 (29%).

Thus the reaction, N N -bis(p-anisyl) and N,N -bis (cyclohexyl) tidinone or urea derivatives could be isolated but instead diadducts have been obtained.



(I) (III)

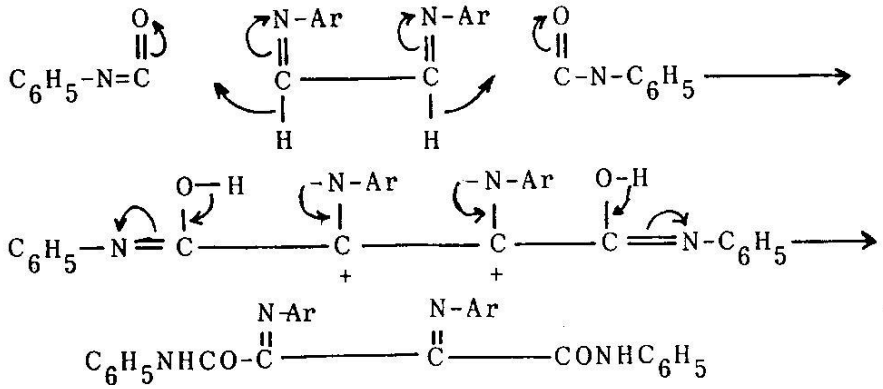
Ar

a; $C_6H_4OCH_3$(p-)

b: C_6H_{11}

It has been reported that anisylidene aniline [2] and benzal-p-anisidine [3] react with phenyl isocyanate to give diazetidinone derivative and p-anisoyl-phenylurea, respectively. In the present investigation the reaction of N,N -diarylethylenediimines with phenyl isocyanate is studied, no diaze-ethylenediimines (Ia and b) with phenyl isocyanate in boiling dry benzene gave 2,3-bis-[(p-methoxy-phenyl)imino succinanilide (IIIa) and 2,3-bis [cyclohexylimino] succinanilide (IIb) respectively.

The reaction possibly takes place according to the following mechanism:



The structure of (III) was derived on the basis of the elemental analysis. IR spectra[++] displayed bands at 3320-3300, 1645-1640 and 1595 corresponding to NH, C=O and C=N, respectively, and the PMR (DMSO-d_6) spectrum of (IIIa) exhibited signals at 8.15 (2H, s, 2xNH), 7.5-6.85 (18H, m, ArH), 3.75 (6H, s, 2x$ArOCH_3$).

It has been reported [3], that succinic anhydride reacts with benzal -p-anisidine or cinnamal-p-anisidine to give directly one and the same compound N-p-anisyl succinic acid via dearylation.

In the present investigation, it has been found that treatment of N,N -diarylethylenediimines (Ia and c) with succinic anhydride in boiling dry benzene provided 5,6-bis-(arylimino) -4-dioxodecanedioic acids (IVa and b), no dearylation products could be isolated.

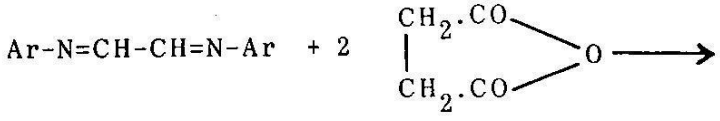
The structure of (IV) was derived on the basis of (i) solubility in aqueous alkali, (ii) correct analytical data, (iii) IR spectra displayed bands at 1695-1690, 1660-1655, 1600-1590 corresponding to C=O (acid), C=O (ketone) and C=N, respectively.

Experimental

Melting points are uncorrected IR spectra in KBr were recorded on a Beckman spectrophotometer. PMR spectrum was run on a Varian A-60 instrument using TMS as internal standard and mass spectrum on a Varian MAT-112 mass spectrometer.

Reaction of (Ia and b) with Grignard reagents: Formation of (IIa-d):

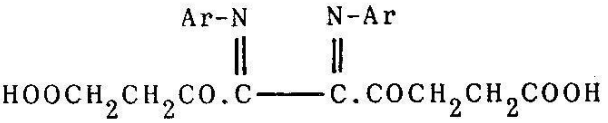
A solution of (I) (0.01 mol) in dry ether (50 ml) was treated with an ethereal solution of a Grignard reagent namely benzyl magnesium chloride, p-anisyl magnesium bromide and cyclohexyl magnesium bromide (0.04 mol) for 30 min. The reaction mixture was heated under reflux for 1 hr, left overnight at room temperature and decomposed with ammonium chloride solution. The aqueous solution was



(I)

a; $C_6H_4OCH_3$(p-)

c: $C_6H_4CH_3$ (o-)



(IV)

Ar

a; $C_6H_4OCH_3$ (p-)

b; $C_6H_4CH_3$ (o-)

++ $^{+}IR\ \lambda_{max}$ in cm^{-1} and PMR chemical shifts in δ, ppm throughout the paper.

Table-1: Physical data of various compounds prepared.

Compd.+	M.p.* °C	Yield %	Compd.+	M.p.* °C	Yield %
(IIa)	91(a)	35	(IIIa)	224(e)	82
(IIb)	167(b)	50	(IIIb)	158(f)	88
(IIc)	163(c)	40	(IVa)	162(a)	60
(IId)	107(d)	43	(IVb)	132(f)	63

+All the compounds gave satisfactory elemental analyses.
*Solvent use for recrystallization were (a) ethanol, (b) benzene/pet.ether 100-120°, (c) pet.ether 60-80°, (d) methanol, (e) toluene, (f) benzene.

extracted with ether and the ethereal layer after evaporation gave a solid substance which was crystallized from a suitable solvent to give (IIa-c).

Reaction of (Ia and b) with phenyl isocyanate: Formation of (IIIa and b):

To a solution of (I) (0.01 mol) in dry benzene (20 ml) was added phenyl isocyanate (0.02 mol). The mixture was heated under reflux for one hour, solvent removed and the crude product crystallized from a suitable solvent to give (III)

Reaction of (Ia and c) with succinic anhydride: Formation of (IVa and b):

A mixture of (I) (0.01 mol) and succinic anhydride (0.02 mol) in dry benzene (20 ml) was heated under reflux for 36 hrs., solvent removed, extraction with aqueous sodium carbonate solution and acidification with HCl gave the crude product which when crystallized from a suitable solvent give (IV).

References

1. A.Sammour, M.I.B. Selim and M. M. Nour Eldeen, *U.A.E. J.Chem.*, **14**(4), 371 (1971).
2. R.Ritcher, *Chem.Ber.*, **102**(3), 938 (1969)
3. A.Sammour, A.F.M. Fahmy and G.Hosni, *Egypt J.Chem.* **16**(6), 481 (1973).