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NITROSO COMPOUNDS

III *. THE REACTION OF BROMOMAGNESIUM DIPHENYLCUPRATE AND PHENYLCOPPER REAGENTS WITH NITROSOBENZENE

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Summary

Bromomagnesium diphenylcuprate reagent reacts with nitrosobenzene to give diphenylhydroxylamine, biphenyl, diphenylamine, azoxybenzene and phenol. It reacts with alkyl nitrites to give the above products as well as the corresponding alkanols. Phenylcopper reagent behaves similarly but somewhat sluggishly. A mechanism involving an initial electron-transfer process is proposed.

Introduction

Recently we have reported [1] that *N*-nitrosoamines react with phenylcopper and bromomagnesium diphenylcuprate reagents to give products resulting from the cleavage of the N—N bonds. This contrasted with their reactions both with phenylmagnesium bromide [2—4] and phenyllithium [5] in which the N—N bonds of the nitrosoamines remained unaffected. Here we report the reactions of bromomagnesium diphenylcuprate and phenylcopper reagents with nitrosobenzene and some alkyl nitrites (*o*-nitroso compounds).

Results and discussion

Reaction of bromomagnesium diphenylcuprate with nitrosobenzene

Phenylmagnesium bromide is reported [6] to react with nitrosobenzene via a diphenylnitric oxide intermediate [7] to give diphenylamine and an unidentified "quinoneal oxide". Phenyllithium on the other hand adds to nitrosobenzene in a reverse manner to give phenol and diphenylamine [8]. We find that the

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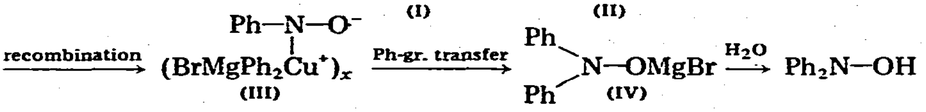
* For part II see ref. 1.

reaction of nitrosobenzene with bromomagnesium diphenylcuprate is more complex than its reaction with either phenylmagnesium bromide or phenyllithium and appears to follow a different course.

In the absence of any information on the structure of bromomagnesium diphenylcuprate, we represent it as $(BrMgPh_2Cu)_x$, although on the basis of the structural information available on some cuprates it may be dimeric and may have a cluster of four metal atoms bonded to organic ligands. Furthermore it may form complexes with solvent molecules and metal salts as ligands [9].

The various products obtained from the reaction of bromomagnesium diphenylcuprate with nitrosobenzene are given in Table 1. The formation of azoxy benzene (always formed in the electrolytic reduction of nitrosobenzene [10]), diphenylhydroxylamine, and biphenyl may be explained by proposing an initial electron-transfer step to give the species I and II. A similar electron-transfer reaction has been observed before for the conjugate addition of lithium diorganocuprates to α,β-unsaturated carbonyl compounds [11—13]. Recombination of the transient species I and II to give III, followed by a phenyl-group transfer and subsequent hydrolysis of IV could account for the formation of diphenylhydroxylamine (eq. 1). Further oxidation [14—16] of II by nitrosobenzene

$$PhN{=}O + (BrMgPh_2Cu)_x \rightarrow \underset{(I)}{Ph{-}\dot{N}{-}O^-} + \underset{(II)}{(BrMgPh_2Cu)_x^{+\cdot}}$$

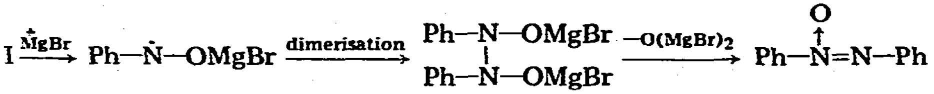


(1)

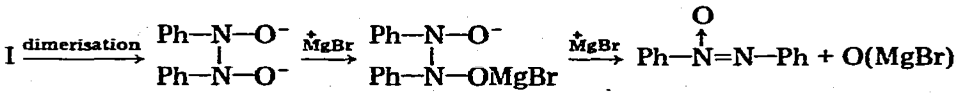
would lead to biphenyl (eq. 2). Nitrosobenzene is reduced at a less negative

$$\mathrm{II} \xrightarrow[\text{PhNO as acceptor}]{-e} x\,BrMg^+ + y\,Ph_2 + (PhCu)_n \qquad (2)$$

potential [10] than nitrobenzene, so like nitrobenzene it might be expected [14,17] to cause oxidative coupling of the organocuprate, but more readily. The relatively high yield of biphenyl in this reaction compared to that in a similar reaction with butyl nitrite reflects the greater oxidizing ability of nitrosobenzene as compared to that of the nitrite. The combination of $BrMg^+$ with I and the dimerisation of the adduct, followed by elimination of $(BrMg)_2O$ would account for the formation of azoxybenzene (eq. 3a). However eq. 3b can also account



$$\mathrm{I} \xrightarrow{\overset{+}{M}gBr} Ph{-}\dot{N}{-}OMgBr \xrightarrow{\text{dimerisation}} \begin{array}{c} Ph{-}N{-}OMgBr \\ | \\ Ph{-}N{-}OMgBr \end{array} \xrightarrow{-O(MgBr)_2} Ph{-}\overset{\overset{O}{\uparrow}}{N}{=}N{-}Ph \qquad (3a)$$



$$\mathrm{I} \xrightarrow{\text{dimerisation}} \begin{array}{c} Ph{-}N{-}O^- \\ | \\ Ph{-}N{-}O^- \end{array} \xrightarrow{\overset{+}{M}gBr} \begin{array}{c} Ph{-}N{-}O^- \\ | \\ Ph{-}N{-}OMgBr \end{array} \xrightarrow{\overset{+}{M}gBr} Ph{-}\overset{\overset{O}{\uparrow}}{N}{=}N{-}Ph + O(MgBr)_2 \qquad (3b)$$

for the formation of azoxybenzene. Although we did not have any evidence for the existence of the species III, we did observe the formation of a trace amount of phenylhydroxylamine. The latter could have come from the hydrolysis of III before the phenyl-group transfer could occur [18] (eq. 4). By anal-

$$\mathrm{III} \xrightarrow{H_2O} Ph{-}NH{-}OH \qquad (4)$$

TABLE 1

THE REACTION OF PHENYLCOPPER AND BROMOMAGNESIUM DIPHENYLCUPRATE WITH NITROSOBENZENE AND SOME ORGANIC NITRITES

Copper reagent (mol)	Nitroso comp.[a] (mol)	Solvent (ml)	Temp. (°C)	Time (h)	Products[b], % yield[c]						
					ROH	Ph_2	Ph_2NH	Ph_2NOH	PhOH	PhN(O)NPh	$4\text{-}O_2NC_6H_4NHPh$
$BrMgPh_2Cu$ 0.075[d]	PhNO 0.075	THF 150	−15	2		47	13	11	18	40	Absent[i]
$BrMgPh_2Cu$ 0.1[e]	n-BuONO 0.1	THF 150	−15	2	68	32[f]	20	12	16	10	8
PhCu[g] 0.05	n-BuONO 0.05	THF 75	−15	3	57	16	11	6	8	10	4
PhCu 0.1	n-BuONO 0.1	THF 150	0	3	37	13	12	Some	Some	Some	
PhCu[h] 0.05	n-BuONO 0.05	THF 75	−15	3	51	35[h]	11	6	9	11	4
PhCu 0.1	$n\text{-}C_5H_{11}ONO$ 0.1	THF 150	−15	3	60	12	9	Some	Some	Some	
PhCu 0.1	$C_6H_{11}ONO$ 0.1	THF 150	0	3	62	Some	Some	Some	Some	Some	

[a] Unless otherwise stated, a solution of a nitroso compound was added to the copper reagent. [b] In every reaction some unreacted nitroso compound and a little tar were present. [c] The yield of an alkanol is based on the starting amount of the corresponding nitrite, the yield of biphenyl on the copper reagent and the yields of all other products on nitroso compounds. [d] Prepared from 0.15 mol of phenylmagnesium bromide and 0.075 mol of copper(I) chloride. [e] Prepared from 0.20 mol of phenylmagnesium bromide and 0.1 mol of copper(I) chloride. [f] The high yield of biphenyl reflects the relative ease with which a cuprate undergoes oxidative coupling. [g] No structures are implied by the notation used for the phenylcopper reagent. [h] Phenylcopper reagent was added to the nitrite. The high yield of biphenyl in this case was probably due to thermal decomposition of some PhCu as its temperature could not be effectively controlled during the addition. [i] Plus a trace of PhNOH.

ogy with the reactions of nitrosoamines with the phenylcopper reagents [1], it is probable that diphenylamine and phenol are formed by the secondary reactions of IV. One possibility is shown in eq. 5.

$$\text{IV} + (\text{BrMgPh}_2\text{Cu})_x\,[\text{or }(\text{PhCu})_n] \rightarrow \text{Ph}_2\text{NM} + \text{PhOM} \xrightarrow{\text{H}_2\text{O}} \text{Ph}_2\text{NH} + \text{PhOH} \qquad (5)$$

(M = MgBr or Cu)

Phenylcopper appears to react with nitrosobenzene in a similar manner to give the same types of products but the reaction is sluggish [19].

Reaction of bromomagnesium diphenylcuprate and phenylcopper reagents with alkyl nitrites

Gilman and Robinson [20] reported that phenylmagnesium bromide reacts with n-butyl nitrite to give diphenylamine, biphenyl and n-butanol. With n-butyl nitrite, phenylcopper and bromomagnesium diphenylcuprate give these products as well as some diphenylhydroxylamine, azoxybenzene, phenol and 4-nitrodiphenylamine. Other nitrites behave similarly (Table 1).

The major products i.e., the alkanols, are presumed to be formed by the cleavage of the O—N bonds of the nitrites. This may occur in any of the following ways (eq. 6—9. exemplified by bromomagnesium diphenylcopper).

$$\begin{tikzcd}
 & \underset{(\text{V})}{\text{R—O—N(Ph)—OM}} \arrow[r, "(\text{BrMgPh}_2\text{Cu})_x", "(9)"'] \arrow[d, "(7)"] & \underset{(\text{VI})}{\text{R—OM}} + \underset{(\text{VII})}{\text{Ph}_2\text{N—OM}} \\
\text{R—O—N=O} \arrow[ur, "(\text{BrMgPh}_2\text{Cu})_x\ (6)"] \arrow[dr, "(8)"'] & & \\
 & \underset{(\text{VI})}{\text{R—OM}} + \text{Ph—N=O} &
\end{tikzcd}$$

Hydrolysis of VI would give the alkanols. The adduct V could have originated by the nucleophilic attack of the copper cluster on the nitroso nitrogen or by the electron-transfer process described above. The formation of azoxybenzene may indicate the involvement of nitrosobenzene as an intermediate (eq. 6, 7 or 8), although the latter could not be detected in the reaction mixture. If nitrosobenzene was formed, it would be expected to react quickly with more copper reagent (eq. 1—5) giving the observed products and thus escape detection. Since the formation of azoxybenzene has been observed in the reaction of alkyl nitrites with either phenylcopper or bromomagnesium diphenylcuprate reagent, it is likely that a part of this reaction proceeds either by eq. 6, 7 or directly by eq. 8. The eq. 6, 9 cannot reasonably explain the formation of azoxybenzene although it can explain the formation of all other products. For example, oxidative coupling of the copper reagents in the presence of the nitrites would produce biphenyl and hydrolysis of VI and VII would give the alkanol and diphenylhydroxylamine respectively. Further reaction of VII with the copper reagents could lead to the formation of diphenylamine and phenol [1].

The formation of 4-nitrodiphenylamine, which is also formed [19] in a trace amount when dimethylnitrosamine or diphenylnitrosamine reacts with either phenylcopper reagent or the "ate" complex is difficult to explain at the moment. However, under similar conditions nitrosobenzene does not produce 4-nitrodiphenylamine.

Experimental

General. The reactions were carried out under a positive pressure of dry, oxygen-free nitrogen. Tetrahydrofuran (THF) was dried over sodium and distilled from sodium-benzophenone ketyl prior to use. Copper(I) chloride was obtained commercially and was further purified [21] before use. The IR spectra were recorded on a PYE SP 1000, the NMR spectrum on a JEOL 100 MHz (TMS as internal standard), mass spectrum on an MS 30 and UV on a SP800 machine. All temperatures quoted are uncorrected.

Preparation of starting materials and authentic samples. Nitrosobenzene [22], m.p. 66—67°C; n-butyl nitrite [23], b.p. 75°C; n-amyl nitride [24], b.p. 104°C; cyclohexyl nitrite [25], b.p. 136—137°C; diphenylhydroxylamine [8,26] were prepared by published procedures.

Preparation of organometallic reagents. Phenylmagnesium bromide [27] and phenylcopper [28] reagents were prepared by previously reported methods.

Bromomagnesium diphenylcuprate reagent was prepared [1,29] by adding copper(I) chloride (x moles) to phenylmagnesium bromide (prepared from $2x$ g-atom of magnesium and $2x$ moles of bromobenzene in 100 ml of THF at 20°C) in a stepwise manner and stirring the mixture at —15°C for 2 h. During this period Gilman Test I [30] became negative. The organocuprate thus prepared was used immediately in subsequent reactions.

Reaction of bromomagnesium diphenylcuprate reagent with n-butyl nitrite. To bromomagnesium diphenylcuprate, prepared at —15°C from phenylmagnesium bromide (0.2 mol) and copper(I) chloride (0.1 mol) in THF (100 ml) was added n-butyl nitrite (0.1 mol) in THF (50 ml) with constant stirring. The addition of the nitrite took 45 min during which time the colour of the mixture changed from pale through greenish-yellow to bright orange-red. After the mixture was stirred at —15°C for 2 h, it was allowed to warm gradually to room temperature and then treated with a saturated solution of aq. ammonia/ammonium chloride. The organic material was extracted with ether (3 × 50 ml), the ether extract washed several times with aq. NH_3/NH_4Cl solution and dried over anhydrous sodium sulphate. Removal of the ethereal solvents gave a brown liquid which was a mixture of several compounds (TLC). Distillation under normal pressure gave n-butanol (5.0 g, 68%), b.p. 116—117°C (lit. [31] b.p. 116.7—116.8°C), identical (TLC, IR) with an authentic sample. The residual brown viscous liquid was chromatographed (silica gel column; a number of eluents of increasing polarity was used) and the following products were obtained: (a) biphenyl, (4.9 g, 32%), m.p. 69—70°C (lit. [32] m.p. 70.5°C), identical (TLC, IR; undepressed mixture m.p.) with an authentic sample; (b) diphenylamine (3.4 g, 20%), m.p. 53—54°C (lit. [33] m.p. 54°C), identical (TLC, IR; undepressed mixed m.p.); (c) azoxybenzene (1.0 g, 10%), m.p. 35—36°C (lit. [34] m.p. 36°C) identical (TLC, IR, mixed m.p.) with an authentic sample; (d) 4-nitrodiphenylamine (0.9 g, 8%), m.p. 134—135°C (lit. [35] m.p. 135.1—135.7°C). The UV and IR spectra agreed with the reported frequencies; NMR ($CDCl_3$) (δ, ppm): centered at 8.1 (2 H, d), 6.9 (2 H, d), 7.25 (5 H, m) and 6.39 (1 H, broad s); mass spectrum: m/e 214 (M^+, base peak), 184 $(M - NO)^+$, 168 $(M - NO_2)^+$, 167 $(M - NO_2H)^+$, 77 $(Ph)^+$, 30 $(NO)^+$; (e) phenol (1.5 g, 16%), b.p. 180—181°C (lit. [36] b.p. 182°C), identical (TLC, GLC, IR) with an authentic sample; (f) diphenylhydroxylamine (2.3 g, 12%), identical (TLC, IR) with an authentic sample prepared by a published procedure [8,26]. Additionally some unreacted nitrite and tar were present in the product-mixture.

The details of other reactions are given in Table 1.

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