Reaction of Nitrosyl Chloride with Phenylmagnesium Bromide[1a]

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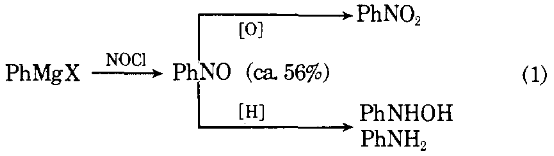
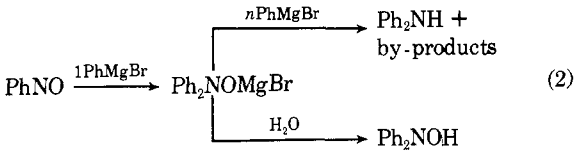
The reaction between nitrosyl chloride and phenylmagnesium bromide in dilute diethyl ether solution was studied at −78°. The predominant volatile product was diphenylamine, and not nitrosobenzene as reported in the earlier literature. Under varying reaction conditions the yield of the secondary amine ranged between 0 and 31%. A mechanistic study included an investigation of the reaction between nitrosobenzene and phenylmagnesium bromide. Contrary to the literature, a 1:1 stoichiometry was evident and several heretofore proposed reaction paths were disproved. The overall reaction occurs via a 2:1 NOCl–Grignard stoichiometry and involves nitrosobenzene and probably diphenylnitric oxide as reaction intermediates.

The thought of developing a simple, relatively mild method for introducing nitrogen functionality into the aromatic nucleus prompted us to explore the reactions of certain nitrogen-containing electrophiles with organometallic compounds. Of primary interest was the possible reaction between Grignard reagents and nitrosyl chloride, since in 1908 Oddo[2] had reported a 56% yield of nitrosobenzene from the reaction of phenylmagnesium bromide and NOCl. If nitroso products were indeed formed, synthesis of any nitrogen derivative would be possible (eq 1).



$$\mathrm{PhMgX} \xrightarrow{\mathrm{NOCl}} \mathrm{PhNO}\ (\text{ca. }56\%) \begin{cases} \xrightarrow{[\mathrm{O}]} \mathrm{PhNO_2} \\ \xrightarrow{[\mathrm{H}]} \mathrm{PhNHOH},\ \mathrm{PhNH_2} \end{cases} \qquad (1)$$

However, in apparent contradiction of Oddo's work, Wieland and Roseeu[3a] showed that phenylmagnesium bromide underwent a rapid addition reaction with nitrosobenzene, yielding the magnesium salt of diphenylhydroxylamine. This compound was then quickly converted to diphenylamine, the final product (eq 2).



$$\mathrm{PhNO} \xrightarrow{1\mathrm{PhMgBr}} \mathrm{Ph_2NOMgBr} \begin{cases} \xrightarrow{n\mathrm{PhMgBr}} \mathrm{Ph_2NH} + \text{by-products} \\ \xrightarrow{\mathrm{H_2O}} \mathrm{Ph_2NOH} \end{cases} \qquad (2)$$

where $n = 1-2$

Both Wieland and Roseeu,[3b] and later Gilman and McCracken,[4] presented somewhat differing, but apparently sound mechanisms for the formation of the diarylamine product.

Consideration of the above reports caused us to reinvestigate the reaction between nitrosyl chloride and phenylmagnesium bromide.

Results

Reaction of Nitrosyl Chloride and Phenylmagnesium Bromide. Volatile Products. Phenylmagnesium bromide and NOCl, reacting under a variety of experimental conditions at −78°, produced diphenylamine in yields of 0 to 31%, based on Grignard reagent. Five other products were isolated in lesser yields. They were identified as nitrosobenzene, phenol, biphenyl, phenylmethylcarbinol, and 4-nitrodiphenylamine. The results of these reactions are listed in Table I.

From Table I it is evident that the major volatile product in most cases was diphenylamine. Moreover, nitrosobenzene was detected as a reaction product only once and then in a quite minor amount. Repeated attempts to prepare nitrosobenzene under Oddo's conditions (reaction 8, Table I) yielded only diphenylamine.

Nonvolatile Products. Since ca. 75% of the starting materials could not be accounted for in the reactions of Table I, a search for the nonvolatile products was conducted. Assuming that the nonvolatiles were formed by a further reaction of NOCl with diphenylamine, inverse addition reactions similar to reaction 10, Table I, were carried out under conditions of a large excess of NOCl. From these reactions a large amount of various nitroso- and nitro-substituted diphenylamine products was obtained. Separation of the complex mixture was not attempted, but one product, 2,2′-dinitro-4,4′-dichlorodiphenylamine, was isolated (7.5%) in nearly pure form owing to its relative insolubility in all common solvents.

The above reactions also involved DCl or D_2O hydrolysis steps in an attempt to ascertain the origin of the diphenylamine proton. In all cases the isolated diarylamine was the H_{11} species.

Reaction of Nitrosobenzene and Phenylmagnesium Bromide. Since nitrosobenzene was the expected intermediate of the reactions listed in Table I, its course of action with phenyl Grignard reagent was studied. The reaction was run in two different ways. In the first an ether solution of nitrosobenzene was added to ethereal phenylmagnesium bromide at −78°. Analysis of the product mixture showed a 49.2% yield of diphenylamine plus seven other compounds (see Table II, reaction 1).

The second mode of reaction involved the addition of ethereal phenylmagnesium bromide in incremental amounts to a solution of nitrosobenzene at −78°. The results for this series of Grignard additions are listed as reactions 2–7, Table II.

Table II shows that the major volatile products of the nitrosobenzene–phenyl Grignard reaction are diphenylamine and benzene. Although these results indicate that the nitrosobenzene from the nitrosyl chloride–phenylmagnesium bromide reaction most certainly reacts with more Grignard reagent, other possible fates of the nitroso intermediate are possible and were therefore investigated.

Reaction of Nitrosobenzene with Nitrosyl Chloride. Although earlier work in our laboratory had determined that 0.1 *M* nitrosobenzene in ether was unaffected by large amounts of NOCl at both −78 and 0°, the reactants were tested under more extreme conditions. At 27° nitrosobenzene and NOCl yielded small amounts of nitrobenzene, benzene, phenol, and biphenyl. No quantitative analyses of these volatile products were attempted owing to their low yield.

It was simultaneously noted that virtually no decomposition of nitrosobenzene had taken place, since the well-documented products of that reaction were not found.[6]

Table I
Volatile Products from the Reaction of Nitrosyl Chloride and Phenylmagnesium Bromide

Reaction	Mode of addition[a]	Solvent	Hydrolysis conditions	Mole ratio Grig/NOCl	PhNO[c]	Ph$_2$NH	PhOH[c]	% yields[b] Ph$_2$	PhMe-CHOH[c]	(4-NO$_2$)-PhNHPh[c]
1	NOCl (soln). to PhMgBr	Et$_2$O	NH$_4$Cl	1.9	0.0	16.8[c]	1.7	1.3	3.7	1.8
2	NOCl (soln) to PhMgBr	Et$_2$O	NaOH–NaHCO$_3$	1.5	2.0	31.0[c]	0.1			
3	NOCl (soln) to PhMgBr	Et$_2$O	NaOH–NaHCO$_3$	5.3	0.0	0.0[d]				
4	NOCl (soln) to PhMgBr	Et$_2$O	NaOH–NaHCO$_3$	2.8	0.0	9.3[d]				
5	NOCl (soln) to PhMgBr	Et$_2$O	NaOH–NaHCO$_3$	1.9	0.0	24.3[d]				
6	NOCl (soln) to PhMgBr	Et$_2$O	NaOH–NaHCO$_3$	0.8	0.0	18.8[d]				
7	NOCl (soln) to PhMgBr	THF	NH$_4$Cl	1.4	0.0	6.6[c]	5.6	0.6	0.0	
8	NOCl (g) to PhMgBr	Et$_2$O	NH$_4$Cl		0.0	13.5[d]				
9	NOCl (soln) and PhMgBr to Et$_2$O	Et$_2$O	NaOH–NaHCO$_3$	2.1	0.0	9.5[d]				
10	PhMgBr to NOCl (soln)	Et$_2$O	NH$_4$Cl	1.5	0.0	3.7[c]	0.4	1.5		6.6

[a] Reaction temperature −76°C. [b] Yield values for PhNO are based on NOCl; other products on PhMgBr. A blank indicates no analysis. [c] Yields by VPC analysis, after correction for starting material impurities. [d] Isolated yields of HBr salt.

Table II
Results of the Nitrosobenzene–Phenylmagnesium Bromide Reaction

Reaction	Mole ratio Grig/PhNO	PhNO reacted[a]	PhMgBr reacted[a]	Ph$_2$NH formed[a]	PhH formed[a, b]	% yield Ph$_2$NH[c]
1[d]	1.38	25.4	45.0	12.5	17.1	49.2
2[e]	0.33	3.2	5.0	1.0	1.0[f]	59.4
3[e]	0.68	8.0	10.0	4.6	1.6[f]	55.1
4[e]	1.03	12.2	15.0	6.8	7.0	59.0
5[e]	1.38	12.3	20.0	7.8	9.4	63.4
6[e]	1.74	13.3[f]	25.0	7.7	17.2	57.9
7[e]	2.10	13.9[f]	30.0	7.9	26.7	56.8

[a] Values in millimoles, ±2%, by VPC analysis. [b] Corrected for PhH in Grignard solution. [c] Percent yields based on reacted PhNO, ±2%, [d] PhNO added to PhMgBr; other isolated products were PhNO$_2$ (5.9%), PhOH (4.5%), azoxybenzene (9.2%), PhMeCHOH (2.2%), and PhPh (1.3%). [e] PhMgBr added to PhNO. The Gilman test[5] for active Grignard was negative after each addition of PhMgBr. [f] These values ±15% owing to integration imprecision at low signal to noise ratio.

Reaction of Nitrosyl Chloride with Diethyl Ether and Diphenylamine. At room temperature diethyl ether proved to be essentially inert toward NOCl. However, after a 15-min reaction time, diphenylamine and NOCl produced a 30% yield of 4-nitro-*N*-nitrosodiphenylamine.

Discussion

Reaction of Nitrosyl Chloride with Phenylmagnesium Bromide. Reaction Products. The low (or zero) yields of nitrosobenzene place Oddo's conclusions[2] in doubt. It would seem unlikely, based on our collective experiments, including repeated duplications of Oddo's conditions (reaction 8, Table I), that nitrosobenzene[7] was ever isolated as the major product from the reaction[8] of NOCl and phenylmagnesium bromide.

Of course, diphenylamine was the major volatile product in all reactions. However, a change of solvent from diethyl ether to THF produced a substantial lowering of the diphenylamine yield. An explanation for this could be that since NOCl is 20 times more soluble in THF than in ether,[9] the rate of further nitrosation steps, as mentioned above, would be increased.

A factor which increased amine yield was the change to a basic hydrolyzing medium. The presence of a base would minimize the above-mentioned nitrosation and/or chlorination of diphenylamine which might occur during the hydrolysis step.

The mole ratio of reagents also obviously affected the yield of diphenylamine. Reactions 3–6 (Table I) were patterned after the style of Gilman,[4] who used optimized yields in his mechanistic arguments. From our results it is clear that as the Grignard/NOCl mole ratio is varied from ca. 2:1, the yield of diphenylamine is reduced. This reduction is especially severe when the ratio is large. This fact would seem to indicate that before hydrolysis the amine precursor can react in a different manner with excess Grignard reagent. Of course, the yield of diphenylamine is also lowered when the Grignard/NOCl ratio is very small for reasons already mentioned.

An attempt to reduce side reactions by maintaining a 2:1 Grignard/NOCl ratio throughout the reaction (reaction 9, Table I) apparently failed. Although the solutions were added together in a constant 2:1 ratio, the yield of amine dropped to 9.5%. One possible explanation is that the first step of the reaction, i.e., between Grignard and NOCl, is much faster than the later step(s). Thus the simultaneous addition of phenylmagnesium bromide and NOCl approximates the condition of excess Grignard, e.g., reactions 3 and 4, Table I.

The small yields of phenol and biphenyl are probably the result of the normal amount of oxygenation and coupling which accompany most Grignard reactions. Certainly these yields contradict the proposed mechanisms of Wieland[3] and Gilman[4] for the latter steps of the overall mechanism (see the nitrosobenzene–Grignard discussion).

The yield of phenylmethylcarbinol (3.7%) obtained in reaction 1 (Table I) is normal for ethereal phenyl Grignard reactions. There are two proposed mechanisms for its formation,[10,11] and neither predicts any phenylmethylcarbinol when the solvent is changed to THF, as was the case in reaction 7 (Table I).

The formation of 4-nitrodiphenylamine in reaction 1 and reaction 10 (Table I) most certainly arises from para nitrosation of diphenylamine by NOCl, since this reaction was examined,[12] found to be very fast, and declared to be the final step of the Fischer–Hepp rearrangement.[13] Under conditions of excess NOCl (reaction 10, Table I), this process is accordingly more dominant. Further oxidation is most likely caused by the hydrolysis mixture of any excess nitrosyl chloride (eq 3).[14]

$$3NOCl + 2H_2O \longrightarrow HNO_3 + 2NO + 3HCl \qquad (3)$$

The 30% yield of 4-nitro-*N*-nitrosodiphenylamine from diphenylamine and NOCl strengthens the above mechanistic interpretation.

Thus the probable fate of much of the diphenylamine in the reactions of Table I was repeated nitrosation and oxidation, forming a myriad of expected nitrosated and/or nitrated products.[13,15]

Competing Reactions. The results of the thermal decomposition of nitrosobenzene suggest that this process does not occur to any significant extent during the reaction of NOCl and phenyl Grignard reagent. Neither azoxybenzene nor nitrobenzene, the major decomposition products, were detected in the latter reaction. Likewise the nitrosobenzene-NOCl reaction seems unimportant.

Reaction of Nitrosobenzene with Phenylmagnesium Bromide. Since nitrosobenzene was the expected primary intermediate of the NOCl–Grignard reaction, and since the literature[3,4] is at odds as to the exact mechanism of the nitrosobenzene–Grignard reaction, a decision was made to investigate this step of the overall reaction.

Wieland,[3a] Gilman,[4] and later Maruyama[16] showed that the reaction of nitrosobenzene with phenyl Grigrand reagent produces, initially, the magnesium sale of diphenylhydroxylamine (eq 2). Although the salt is reportedly[3,4] reactive toward more Grignard reagent, it apparently can be isolated in pure form and upon hydrolysis yields large amounts[16] of diphenylhydroxylamine. The fact that the hydroxylamine was never isolated or detected during our studies and isolated only once by Gilman[4] reflects its extreme sensitivity to the work-up procedure.[17]

Wieland[3b] explained the formation of diphenylamine as resulting from a reaction between the magnesium salt of diphenylhydroxylamine and excess Grignard reagent (eq 4).

$$PhNO + PhMgBr \longrightarrow Ph_2NOMgBr \xrightarrow{PhMgBr}$$
$$Ph_2NMgBr + PhOMgBr \xrightarrow{H_2O} Ph_2NH + PhOH \qquad (4)$$

Support for this explanation came from the fact that relatively large amounts of phenol were isolated from the product mixture and also that an apparent 2:1 Grignard–nitrosobenzene ratio was needed for optimum diphenylamine yield.

Gilman[4] discounted the above explanation when during his studies of the reaction he noticed formation of a significant amount of biphenyl but *no* phenol. This fact, coupled to his observation that a mole ratio of 3 Grignard to 1 nitrosobenzene was necessary to give a positive test[5] for active Grignard reagent, led him to a different mechanism (eq 5).

$$PhNO + PhMgBr \longrightarrow Ph_2NOMgBr \xrightarrow{2PhMgBr}$$
$$Ph_2NMgBr + Ph_2 + O(MgBr)_2 \xrightarrow{H_2O} Ph_2NH \qquad (5)$$

Our results appear to disprove both Wieland's and Gilman's mechanisms. Like Gilman we found very little phenol in the product mixture.[18] The low yield of this product could suggest that either a small amount of O_2 was present in the reaction atmosphere, or that Wieland's mechanism (eq 4) does play a minor role. Likewise, the finding of only minuscule amounts of biphenyl (Tables I and II) from both the NOCl–Grignard and nitrosobenzene–Grignard reactions seriously jeopardizes the validity of Gilman's hypothesis (eq 5).[19] The small amount of the hydrocarbon which was found may indicate the relative unimportance of the free radical Grignard species[20] in this particular case.

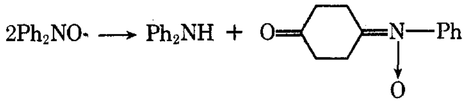
Besides not finding phenol or biphenyl in significant amounts, our results (Table II) clearly rule out a 3:1 or 2:1 Grignard–nitrosobenzene stoichiometry. In fact, Table II shows that the Grignard reagent reacts in a 1:1 fashion with nitrosobenzene until the concentration of the latter has been significantly reduced. At this point the Grignard reagent continues to react (negative Gilman tests[5]) but resulting mainly in the production of benzene. Moreover, the fact that the yield of benzene is negligible until over half of the nitrosobenzene has reacted, and over three-quarters of the diphenylamine has been formed, indicates that its formation[21] is not involved in the production of the diarylamine.

Another point of this particular reaction deserves mentioning. The amount of diphenylamine produced (Table II) was consistently near 50% of the amount of nitrosobenzene reacted. This result is not only evident from our work, but Gilman[4] also achieved isolated (distillation) yields of only 30–40%. Moreover, in perhaps the most definitive reaction studied by Gilman, the author realized only a 40% isolated yield of diphenylamine starting with diphenylhydroxylamine.[22] Now, since the first step of this reaction should certainly be quantitative,[23] it remains that the conversion of the magnesium salt of diphenylhydroxylamine to diphenylamine may be limited to a ca. 50% yield on mechanistic grounds.

Diphenylnitric Oxide. An obvious solution to the above puzzle would involve some type of disproportion step in the overall process. Fortunately, such a step is available if one assumes the importance of diphenylnitric oxide as a viable reaction intermediate. In this connection Maruyama[16] proved that the initial products from the reaction of nitrosobenzene and phenylmagnesium bromide consist of an equilibrium mixture of diphenylnitric oxide and bound magnesium salt (eq 6).

$$\begin{array}{l} PhNO + (PhMgBr)_n \\ \quad\big\downarrow \\ Ph_2NO\cdot + \cdot MgBr(PhMgBr)_{n-1} \rightleftharpoons (Ph_2NOMgBr)(PhMgBr)_{n-1} \end{array} \qquad (6)$$

Under conditions of excess Grignard reagent the equilibrium lay far to the right, whereas a mole ratio of 1.0 produced a 77% yield of the radical species at equilibrium.[24] This same radical, diphenylnitric oxide, first prepared in 1914 by Wieland[25a] and later studied by the same group,[25b] had been shown to decompose quickly in the presence of dilute mineral acid and "sometimes in pure ether" into diphenylamine and "quinoneanil oxide" (eq 7).



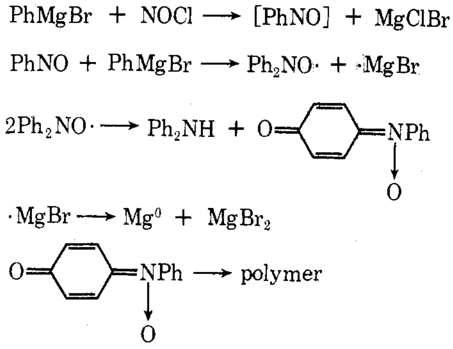
(7)

By combining the various aspects of the above discussion, a likely mechanism for the nitrosobenzene–phenylmagnesium bromide reaction can be formulated. The process most certainly involves a 1:1 addition of Grignard reagent to the nitroso π bond, including equilibration between radical and ionic species. This is followed by a rapid disproportion of the diphenylnitric oxide to diphenylamine and oxidized quinoidal-type molecule, thereby giving a 50% theoretical yield for the secondary amine under conditions where eq 6 lies far to the left.[26] Although the oxidized species was never isolated, the isolation techniques would probably cause rapid polymerization of this type of molecule, thereby producing some of the nonvolatile materials commonly formed in these reactions.

Additional evidence for the above mechanism is the failure of the reaction to incorporate any deuterium into the diphenylamine product.[27] Certainly this fact would require formation of the secondary amine *before* hydrolysis, whereas Wieland[3b] and Gilman[4] had assumed that protonation occurred *during* hydrolysis (eq 4 and 5).

Nitrosyl Chloride and Phenylmagnesium Bromide. Reaction Mechanism. The present study did not investigate the first step of the reaction of nitrosyl chloride with phenylmagnesium bromide. If the nitroso cation were involved, one would expect a simple and highly exothermic bonding with the very nucleophilic carbon of the Grignard reagent. On the other hand, the reaction of covalent nitrosyl chloride might be compared to the analogous reaction of acid halides with Grignard reagents.[28]

The remaining steps of the overall reaction, i.e., the reaction between nitrosobenzene and phenyl Grignard reagent, probably involve the sequence already outlined above. The entire mechanism is summarized below.



(8)

The third and fourth steps of the above mechanism, although not proven, seem justified based on the nature of the reacting species.

Experimental Section

Melting points were taken on a Mel-Temp melting point apparatus and are uncorrected. All gas chromatography work was done with a Varian 1700 gas chromatograph. Infrared, nuclear magnetic resonance, electron spin resonance, and mass spectral data were recorded on the Beckman IR-33, Varian HA-60, Varian E-3, and Varian Mat-111 instruments, respectively. Elemental analyses were performed by Meade Microanalytical Laboratory, Amherst, Mass., and Galbraith Laboratories, Inc., Knoxville, Tenn.

Reaction of Nitrosyl Chloride with Phenylmagnesium Bromide. Volatile Products. In a typical reaction (reaction 1, Table I) magnesium (3.64 g, 150 mmol) and naphthalene (2.45 g, 19.1 mmol) were added to 250 ml of dry ether in a 1-l., three-neck flask. Under N_2 the reaction was initiated with a small amount of 1,2-dibromoethane, following which 8.32 g (53.0 mmol) of bromobenzene in 250 ml of dry ether was added dropwise. After the addition was complete, the reaction mixture was heated under reflux for 2 hr and the Grignard solution then filtered under N_2 through glass wool. Two aliquots were removed and hydrolyzed with a saturated NH_4Cl solution. VPC analysis (10 ft × 0.125 in. 10% SE-30 column) of the ether extracts of the hydrolysis mixtures showed a 97% conversion to phenylmagnesium bromide. Naphthalene was used as the internal standard and the amount of benzene produced during hydrolysis was corrected for the trace amount present in a flash distillate of the Grignard solution.

One hundred milliliters of a 0.237 *M* (determined by standard iodiometric titrations) solution of NOCl (Matheson Gas Products), bp −5.8°, in dry ether was cooled to −78° in a jacketed pressure-equalizing dropping funnel and added dropwise to the stirred Grignard solution (0.137 *M*, 44.6 mmol), also at −78°. After addition, the suspension was stirred for 3 hr at −78° and then hydrolyzed with 150 ml of a saturated NH_4Cl solution. The dark red ethereal layer was separated and added to two ether extracts of the aqueous phase, now at pH 7–8. The ether solution was further washed with saturated NH_4Cl and dried over $MgSO_4$. VPC analysis (10% SE-30 column) showed the presence of 633 mg (3.74 mmol, 16.8%) of diphenylamine: VPC coinjection with known compound on 10% SE-30 and 10 ft × 0.25 in. 10% Carbowax 20M columns; ir (melt) of VPC effluent identical with spectrum of known Ph_2NH.

VPC analysis of the above solution showed a total of 14 volatile products. The major products were identified by the VPC coinjection technique and comparison of the ir spectra of the VPC collected compounds with known spectra. These products included, in order of elution, benzene (yield undetermined), phenol (0.77 mmol, 1.7%), phenylmethylcarbinol (0.28 mmol, 1.3%), diphenylamine (see above), and 4-nitrodiphenylamine (0.40 mmol, 1.8%): ir identical with Sadtler Spectrum[29] no. 34522. The other eight products were not present in sufficient quantity to permit VPC collection and structure assignment.

Several variations of the above procedure were carried out. In the first (reaction 2, Table I), an NOCl solution (29.0 mmol) was quickly added to the unfiltered Grignard mixture (43.1 mmol) and the hydrolyzing medium was changed to a pH 10 NaOH–$NaHCO_3$ solution. After filtration, tetralin was added as an internal VPC standard and the solution worked up as before. The light green ether extracts of the acidified aqueous layer suggested the presence of nitrosobenzene. VPC analysis (10% SE-30 column) of the combined ether solutions showed a 6.68-mmol (31.0%) yield of diphenylamine as well as 0.04 mmol (0.09%) of phenol and 0.85 mmol (2.0%) of nitrosobenzene. Products were again identified by the VPC coinjection technique and comparison of their respective ir spectra with spectra of the known compounds. None of the other volatile components were identified.

A second variation of the original procedure involved the use of THF as the reaction solvent (reaction 7, Table I). Thus, 46.0 mmol of Grignard and 33.1 mmol of NOCl yielded diphenylamine (1.53 mmol, 6.6%), phenol (2.57 mmol, 5.6%), and biphenyl (0.28 mmol, 0.6%). No phenylmethylcarbinol was detected.

A third experimental variation (reaction 10, Table I) involved the inverse addition of reagents. Thus 37.0 mmol of Grignard was added dropwise to 29.0 mmol of NOCl in ether. Analysis of the hydrolyzed product mixture showed 0.68 mmol (3.7%) of diphenylamine, 0.13 mmol (0.35%) of phenol, 0.28 mmol (1.5%) of biphenyl, and 1.23 mmol (6.6%) of 4-nitrodiphenylamine.

A fourth experimental variation (reaction 9, Table I) involved the simultaneous addition of reagents. The filtered Grignard reagent (85.2 mmol) and NOCl solution (41.2 mmol) were added simultaneously at −78° to 200 ml of dry ether. The two rates of addition were adjusted such that a constant 2:1 Grignard–NOCl ratio was maintained throughout the reaction. After addition, the orange slurry was stirred for an additional 1 hr and worked up in the usual fashion, except that steam distillation was used to remove the reaction volatiles after hydrolysis, and the diphenylamine was precipitated from an ether extract of the steam distillate by conversion to its HBr salt with dry HBr gas. Diphenylamine hydrobromide (4.04 mmol, 9.5%) was isolated and identified by ir and reconversion to diphenylamine with hot NaOH. The product mixture was not further analyzed.

The last experimental variation of this series (reaction 8, Table I) was an attempt to duplicate exactly Oddo's[2] reaction conditions. Thus, gaseous NOCl was bubbled through 50.9 mmol of Grignard reagent at 0° until no further color changes appeared to take place. Hydrolysis and steam distillation gave only an orange-brown distillate (PhNO gives a brilliant green distillate), and VPC analysis of an ether extract showed no nitrosobenzene, whereas treatment with dry HBr yielded 3.44 mmol (13.5%) of diphenylamine hydrobromide.

Nonvolatile Products. Several reactions were run after which only the nonvolatile products were analyzed. Thus, using inverse addition, i.e., adding Grignard to NOCl, 24 mmol of filtered phenylmagnesium bromide in 200 ml of Et_2O at −78° was slowly added to 72 mmol of NOCl in 300 ml of Et_2O at −78°. Following addition and hydrolysis (H_2O, pH 7), the ether layer was dried and evaporated in vacuo, causing a pungent reddish-brown gas to appear. The remaining dark red oil (4.25 g) showed a complex mixture of nitroso- and nitro-substituted diphenylamines in its ir and NMR spectra. After multiple recrystallizations from acetone, the oil yielded 0.30 g (7.5%) of 2,2′-dinitro-4,4′-dichlorodiphenylamine:

mp 248.8–249.9° from acetone; ir (KBr) 3290, 3100, 1507, 1338, 1253, and 816 cm^{-1};[30] MS *m/e* 327 (2 Cl), 281, 280, 264, and 235; NMR (Me_2SO-d_6) δ 7.7 (AB q, J = 9.0 and 2.3 Hz, 2); 8.3 (d, J = 2.3 Hz, 1); uv, see below.[31]

λ_{max}, nm (ϵ) in acetonitrile	Plus KOH	Plus CO_2
235 (20000)	245 (25300)	238 (20000)
261 (22000)	274 (15500)	261 (22400)
299 (14000)	342 (12100)	298 (14700)
440 (11700)	576 (8950)	440 (12600)

Anal. Calcd for $C_{12}H_7N_3O_4Cl_2$: C, 43.93; H, 2.15; Cl, 21.61; N, 12.81. Found: C, 42.54; H, 3.06; Cl, 19.80; N, 12.74.

Hydrolysis by D_2O or DCl. The above reaction was repeated twice more with the hope of incorporating deuterium into the product via D_2O or DCl hydrolysis. Thus, 78.5 and 44.3 mmol of Grignard reacted with 240 and 250 mmol of NOCl, respectively, by D_2O and PCl_3–D_2O[32] hydrolyses, to yield 2.07 and 2.81 g, respectively, of an unknown white crystalline compound: mp 180.2–181.1° from acetone; ir (KBr) 3360, 3060, 1580, 1510, 1320, 870, and 800 cm^{-1}; NMR ($CDCl_3$) δ 7.25–7.75 (m, ~15), 6.30 (broad s, ~1); MS m/e 486 (4 Br); uv λ_{max} (ϵ) 243 (10500) and 293 (19500) in EtOH and no shift with KOH, etc.

Anal. Calcd for $C_{24}H_{14}N_2OBr_7$: C, 31.82; H, 1.56; Br, 61.75; N, 3.09; O, 1.77. Found: C, 31.96; H, 1.54; Br, 58.70; N, 3.10; O, 1.83.

The filtrates from the isolations of the unknown compound yielded a black oil when the solvent was removed. An ir spectrum of the oil showed practically pure diphenylamine, H_{11} in each case. Not only did the spectrum not show any N–D stretch, but the very distinctive N–D bending and C–N stretching bands of *N*-deuteriodiphenylamine[33] were completely absent.

Diphenylamine, H_{10}, was prepared by stirring the amine overnight in a dioxane–D_2O solution.[34] The solvent was removed and the ir spectrum of a melt of the crystals (NaCl plate) was recorded. The spectrum agreed completely with a literature[33] spectrum for the N-deuterated compound. The crystals were allowed to stand in air room temperature for 2 days and the ir spectrum rerun. The new spectrum was essentially unchanged.

Yield Optimization of Diphenylamine. In a series of reactions between phenylmagnesium bromide and NOCl (reactions 3–6, Table I) the mole ratio of Grignard reagent to NOCl was systematically changed and the yields of diphenylamine HBr salt noted. Thus, using basic hydrolysis conditions and the "normal" mode of addition (NOCl to PhMgBr), mole ratios (Grignard–NOCl) of 5.3, 2.8, 1.9, and 0.8 produced yields of diphenylamine corresponding to 0.0, 9.3, 24.3, and 18.8%, respectively. No other products were isolated or identified.

Reaction of Nitrosobenzene with Phenylmagnesium Bromide. Nitrosobenzene (32.5 mmol) in ether was added dropwise at −78° to a stirred ether solution of phenylmagnesium bromide (44.9 mmol) containing naphthalene as an internal VPC standard. After addition (under N_2) the brown slurry was stirred for 2 hr and hydrolyzed with a saturated NH_4Cl solution. Analysis of the organic phase by VPC (10 ft × 0.25 in. SE-30) showed benzene (17.1 mmol), diphenylamine (12.5 mmol), nitrosobenzene (7.1 mmol), phenol (2.0 mmol), nitrobenzene (1.9 mmol), azoxybenzene (1.5 mmol), phenylmethylcarbinol (1.0 mmol), and biphenyl (0.3 mmol). All products were identified by coinjection with known compounds and ir analysis. Prior to that reaction a portion of hydrolyzed Grignard solution failed to show any phenol, phenylmethylcarbinol, or biphenyl by VPC analysis.

A second reaction between nitrosobenzene and phenylmagnesium bromide was carried out in which the Grignard reagent was added in 5-mmol portions to a stirred Et_2O solution of nitrosobenzene (15 mmol) at −78°. After each addition the mixture was stirred for 2 hr and a 10-ml aliquot withdrawn. Five milliliters of the aliquot was flash distilled and the distillate analyzed (VPC) for benzene. The remaining 5 ml was hydrolyzed with a saturated NH_4Cl solution and analyzed (VPC) only for diphenylamine, benzene, and nitrosobenzene. Throughout the course of additions and aliquot withdrawals the Gilman test[5] for the presence of active Grignard reagent was negative. Also, a flash distillation of a sample of the Grignard solution gave a distillate containing ca. 0.2 mmol of benzene per 10 ml of aliquot. The calculated benzene yields were accordingly adjusted. The product yields of the above reactions are listed in Tables II and III.

Thermal Decomposition of Nitrosobenzene. A solid mixture containing 2.848 g (26.6 mmol) of nitrosobenzene and 1.263 g (9.9 mmol) of napthalene was sealed under vacuum in a glass tube at −78°. The tube was heated at 73° for 45 min and the contents dissolved in benzene. VPC analysis of the solution on 10 ft × 0.25 in. SE-30 and QF-1 columns showed six products, accounting for 99.3% of the decomposed nitrosobenzene. By coinjection with known compounds on the two columns and ir analysis of the collected compounds from a 10 ft × 0.375 in. 20% SE-30 column, the products were identified as azoxybenzene (78.6%), nitrobenzene (14.1%), azobenzene (2.7%), aniline (0.5%), and two unknown compounds (3.4%, based on assumed molecular weights from VPC retention values).

Reaction of Nitrosyl Chloride with Nitrosobenzene. To a pressure bottle containing 100 ml of a saturated ether solution of NOCl (24 mmol) was added 1.772 g (16.6 mmol) of nitrosobenzene and 1.136 g (8.9 mmol) of naphthalene. The bottle was capped and shaken for 1.5 hr, by which time a large amount of white crystals had precipitated. The crystals were highly reactive in air, forming quickly a dark red liquid and producing small explosions upon gentle heating. The reaction mixture was cooled to 0° and saturated again with NOCl gas. The brown slurry was shaken for an additional 1 hr and added to ice water, and the highly acidic aqueous phase was adjusted to pH 8 with NaOH. VPC analysis of the dried ether layer showed small amounts of nitrobenzene, benzene, phenol, and biphenyl. A quantitative analysis of the product mixture was not performed owing to the large amount of tarry material formed. Previous work had shown that 0.06–0.12 *M* solutions of nitrosobenzene were unaffected by NOCl at both −78 and 0°.

Reaction of Nitrosyl Chloride with Diphenylamine. Diphenylamine (1.69 g, 10.0 mmol) was dissolved in 100 ml of dry ether at room temperature and the solution was saturated with NOCl gas (ca. 24 mmol). After 15 min the reaction mixture was poured into 50 ml of a pH 10 buffered hydrolyzing solution. After evaporation of solvent, the dried ethereal layer yielded 2.08 g of an oily yellow solid which upon recrystallization from ether–pentane gave 0.73 g (3.0 mmol, 30%) of 4-nitro-*N*-nitrosodiphenylamine: mp 111° dec from ether–pentane (lit.[15] mp 132–133°); ir (KBr) identical with known spectrum;[35] NMR ($CDCl_3$) δ 8.27 (m, 2), 7.53 (m, 4), 7.03 (m, 3).

Anal. Calcd for $C_{12}H_9N_3O_3$: C, 59.26; H, 3.73; N, 17.28; O, 19.74. Found: C, 59.14; H, 3.64; N, 17.03; 0, 20.19.

The product, 4-nitro-*N*-nitrosodiphenylamine, exhibited the same color change with KOH as did 2,2′-dinitro-4,4′-dichlorodiphenylamine. The change back from purple was affected by CO_2 or O_3 but not O_2.

Reaction of Nitrosyl Chloride with Ether. After saturating 100 ml of dry Et_2O with NOCl at room temperature the solution was allowed to stand for 1 hr and the volatiles removed. Only a small amount (ca. 1%) of high molecular weight material remained.

Registry No.—Nitrosyl chloride, 2696-92-6; phenyl bromide, 108-86-1; diphenylamine, 122-39-4; 2,2′-dinitro-4,4′-dichlorodiphenylamine, 56553-63-0; nitrosobenzene, 586-96-9; 4-nitro-*N*-nitrosodiphenylamine, 3665-70-1; Et_2O, 60-29-7.

References and Notes

(1) (a) This research was supported by the National Science Foundation, Grant GP-18317, Water Resources Research Center Grant 983, and the University of Montana Foundation, Grants 941-0/0 and 840-9/K. A preliminary report of this work has been published: P. G. Marsh and W. L. Waters, *Proc. Mont. Acad. Sci.*, **31**, 141 (1971), and parts have been presented at the 26th Annual NWRACS Meeting, Bozeman, Mont., June 1971, and the 27th Annual NWRACS Meeting, Corvallis, Oreg., June 1972. (b) In partial fulfillment of the requirements for the Ph.D. degree, University of Montana. Department of Chemistry, University of Calgary, Calgary, Alberta, Canada.

(2) B. Oddo, *Gazz. Chim. Ital.*, **39**, 659 (1909).

(3) (a) H. Wieland and A. Roseeu, *Ber.*, **45**, 494 (1912); (b) *ibid.*, **48**, 1117 (1915).

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(5) H. Gilman and F. Schulze *J. Am. Chem. Soc.*, **47**, 2002 (1925).

(6) See Experimental Section. Our results parallel nicely the work done by Bamberger on the thermal and photochemical decomposition of nitrosobenzene: E. Bamberger, *Ber.*, **35**, 1606 (1902).

(7) In this connection Oddo did not mention the green distillate of steam distilled nitrosobenzene. The reported melting point and carbon–hydrogen data combined are unique for nitrosobenzene, however; the first matches biphenyl and *N*-nitrodiphenylamine and the second fits 2- or 4-nitrodiphenylamine and is approximate for *N*-nitrosodiphenylamine.

(8) The actual identity of NOCl in Oddo's paper is unclear, and a real possibility exists that the gaseous reagent used was something other than NOCl. Also, neither Oddo nor we ourselves assigned any limiting percent values for transition metal impurities in the magnesium used for Grignard preparation. Hence the product discrepancies might be the result of small differences in metal purity.

(9) W. L. Waters and P. G. Marsh, unpublished results. The fact that Gri-

gnard reagents are monomeric in THF may also be important.
(10) See, for example, H. Hock, H. Kropf, and F. Ernst, *Angew. Chem.*, 541 (1951); K. C. Bass, M. J. Cape, and D. Collings, *Chem. Ind.* (*London*), 326 (1969), and references cited therein.
(11) H. Gilman and A. Wood, *J. Am. Chem. Soc.*, **48**, 806 (1926).
(12) B. T. Baliga, *J. Org. Chem.*, **35**, 2031 (1970), and references cited therein.
(13) O. Fischer and E. Hepp, *Ber.*, **19**, 2291 (1886).
(14) Air Products and Chemicals, Inc., "Nitrosyl Chloride, an Annotated Bibliography", 1970.
(15) H. Ryan and P. Ryan, *Proc. R. Ir. Acad.*, **34**, 212 (1919). Chlorination most probably occurred during hydrolysis, when, upon removal of NO, HNO_3 and HCl (eq 3) give rise to Cl_2, H_2O, and more NOCl.[13]
(16) K. Maruyama, *Bull. Chem. Soc. Jpn.*, **37**, 1013 (1964).
(17) H. Gilman and L. Heck, *Recl. Trav. Chim. Pays-Bas*, **50**, 522 (1931). Gilman found that just the presence of magnesium and magnesium halide would catalyze the decomposition of the hydroxylamine to diphenylamine and other unidentified products.
(18) Actually Gilman (ref 4) did not allow for the formation of *any* phenol during the reaction, and proposed that the small amount found was in the stock solution of Grignard reagent. The use of VPC techniques in the present study has verified a small yield of this product.
(19) It should be pointed out that while our reaction temperature was fairly similar to Wieland's (−78 vs. −15°), Gilman worked at room temperature. The formation of biphenyl and thus a different mechanism for diphenylamine formation may be real at higher temperatures. Gilman (ref 4) denied that such a temperature effect exists.
(20) See, for example, K. Maruyama, *Bull. Chem. Soc. Jpn.*, **37**, 897 (1964).
(21) The formation of a parent hydrocarbon from Grignard reagent plus nitrosobenzene has been noted before: H. Gilman and R. E. Fothergill, *J. Am. Chem. Soc.*, **49**, 2815 (1927). The authors reported 1.09 "active hydrogens" present in nitrosobenzene as a result of the amount of ethane liberated from the mixing of nitrosobenzene and ethylmagnesium bromide.
(22) Gilman assumed that 2 mol of Grignard reagent was necessary to convert the magnesium salt to diphenylamine, since only after the third molar equivalent of phenylmagnesium bromide was added to the hydroxylamine did a positive test for active Grignard result.
(23) Gilman indicated an instant reaction during the addition of the first equivalent of Grignard reagent.
(24) Maruyama also showed that the initial product of the reaction was diphenylnitric oxide and *not* the magnesium salt.
(25) (a) H. Wieland and M. Offenbacher, *Ber*, **47**, 2111 (1914); (b) H. Wieland and K. Roth, *ibid.*, **53**, 210 (1920).
(26) Equation 6 predicts decreasing diphenylamine yields as the Grignard–NOCl ratio is raised over 2:1 (Table I). However, the alternate product, diphenylhydroxylamine, was not isolated or even detected by VPC, perhaps owing to its instability (ref 3 and 4). All attempts at preparing the pure intermediate failed.
(27) Hydrogen exchange during work-up cannot be completely ruled out. Although diphenylamine, D_1, did not exchange when kept neat at room temperature for 2 days (see Experimental Section), the obviously acidic nature of these work-up conditions could possibly cause an exchange process.
(28) J. March, "Advanced Organic Chemistry: Reactions, Mechanisms, and Structure", McGraw-Hill, New York, N.Y., 1968 p 688. The reaction might also be the result of direct substitution of the phenyl moiety for chlorine as recently suggested in the study of the NOCl–arylthallium system. See E. C. Taylor and R. H. Danforth, *J. Org. Chem.*, **38**, 2088 (1973).
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(30) Of all the possible nitroso- and nitro-substituted diphenylamines (see ref 34), only 2,2′-dinitrodiphenylamine exhibits an ir spectrum similar to that of the dichloro derivative.
(31) In absolute EtOH, λ_{max} 428 nm. This agrees closely with the value for 2,2′-dinitrodiphenylamine. See W. A. Schroeder, E. W. Malmberg, L. L. Fond, K. N. Trueblood, J. D. Landerl, and E. Hoerger, *Ind. Eng. Chem.*, **41**, 2818 (1949).
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(33) D. Hadzi and M. Skrbljak, *J. Chem. Soc.*, 843 (1957).
(34) H. Levitsky, G. Norvitz, and D. E. Chasan, *Appl. Spectrosc.*, **22**, 493 (1968).
(35) Spectrum No. 7, Document 10027, ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D.C.

Synthesis of Symmetrical Diarylamines[1a]

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A relatively simple preparation of di-*o*-, *m*-, and *p*-tolylamines and di-*p*-anisylamine is described. The procedure involves the reaction of the corresponding aryl Grignard reagent with nitrosyl chloride. Although yields are not high by this method (≤28%), the secondary amines are uncontaminated by isomeric impurities and easy to isolate. The attempted synthesis of dimesitylamine failed, producing mainly nitrosomesitylene.

Several routes to symmetrically substituted diarylamines exist in the literature. Various procedures include acid, alumina, or acid–alumina catalyzed condensations of aniline derivatives at 300–500°,[2] condensation of 1,1-diarylhydrazines with dichlorocarbene,[3] and iodine-catalyzed condensation of aniline derivatives at normal reflux temperatures.[4] Of all the synthetic methods, the latter appears to be the simplest and one of the best suited for small-scale laboratory preparation.

As an alternate to the above procedures, we decided to extend[5] our investigation of the phenyl Grignard–nitrosyl chloride reaction,[1a] since the major product of the reaction proved to be diphenylamine (eq 1).

$$\mathrm{PhMgBr} + \mathrm{NOCl} \xrightarrow[\mathrm{Et_2O}]{-78^\circ} \mathrm{Ph_2NH} \qquad 31\% \qquad (1)$$

Thus, the ethereal Grignard reagents from *o*-, *m*-, and *p*-bromotoluene, *p*-bromoanisole, bromomesitylene, and 1- and 2-bromonaphthalene were allowed to react with nitrosyl chloride at −78°. After hydrolysis and steam distillation the respective amine product was isolated either as the HBr salt or as the free amine. Product identification was made by spectral analysis as well as by melting point correlation with literature values.

Results

Table I outlines the volatile products isolated from NOCl addition to various aryl Grignard reagents.

As noted in the above table, *o*- and *p*-bromotoluene yielded only the respective diarylamine product. In the case of the para isomer steam distillation gave a solid amine product and isolation was simple. Steam distillation of the *o*-bromotoluene product, however, gave an oil which necessitated conversion to the HBr salt. This done, later reconversion to the free amine with NaOH gave the amine in high purity.

Diarylamine products were also formed from *m*-bromotoluene and *p*-bromoanisole, but their production was accompanied by significant yields of the corresponding nitroso derivatives. In addition, the *p*-anisyl Grignard reagent gave the parent ether, anisole, as well as a 5% yield of methyl-cleaved *p*-nitrosophenol.

The mesityl and naphthyl Grignard reagents failed to give any diarylamine product. The first produced a relatively large amount of nitrosomesitylene and a secondary product which we have tentatively identified as trimesitylhydrazine. The second, both the α and the β isomers, gave mostly intractable tars in addition to ca. 20% yields (or recoveries) of the parent hydrocarbon, naphthalene.