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).
(29) "Sadtler Standard Spectra", Sadtler Research Laboratories, Philadelphia, Pa.
(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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(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).

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

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.

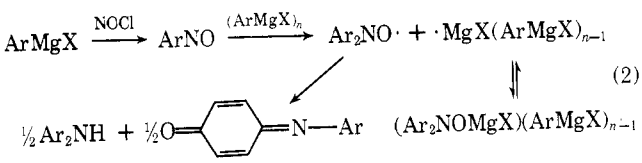
Table I

Aryl halide	Diarylamine yield, %[a,b]	Other products	Yield, %[a]
o-Bromotoluene	23.8[c]		
m-Bromotoluene	11.6[c]	m-Nitrosotoluene	1.4
p-Bromotoluene	28.4		
p-Bromoanisole	16.7	Anisole	18.0
		p-Nitrosoanisole	10.4
		p-Nitrosophenol	5.0
Bromomesitylene	0.0	Nitrosomesitylene	22.8
		Trimesitylhydrazine	11.7
α- and β-Bromonaphthalene	0.0	Naphthalene	21.0

[a] Yields are based on aryl Grignard Reagent. [b] A 2:1 Grignard-NOCl stoichiometry is assumed; see ref 1a. [c] Calculations are based on isolated HBr salt.

Discussion

The mechanism of the phenylmagnesium bromide–nitrosyl chloride reaction has already been discussed.[1a] From the results described above this mechanism would seemingly hold for the substituted phenyl Grignards as well. Thus the nitroso and nitric oxide intermediates[1a] are involved in the present reactions (eq 2).



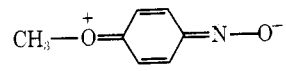
(2)

Although the hydroxylamine was never isolated by us and only once by Gilman,[1a,6] its presence was certainly proven by Wieland[7] and Maruyama.[8] Its conversion to diarylamine does not require excess NOCl or Grignard reagent and apparently occurs via its dissociated radical form.[1a]

Diarylamine Formation. While the three bromotoluenes and p-bromoanisole gave significant yields of diarylamine, the corresponding mesityl compound gave none of the product. One would assume that this result reflects the steric requirements of the second step in eq 2.[9] In support of this argument it is noted that in the mesityl case the yield of nitroso product was correspondingly high. The fact that no diarylamine was formed from the naphthyl Grignard reagents was probably due to the peculiar physical nature of these reagents in diethyl ether as mentioned earlier. Modification of the reaction conditions, e.g., solvent, etc., would perhaps allow formation of diarylamine.

Nitrosoarene Formation. The two cases in which no nitroso products were isolated (excluding α- and β-naphthalene) are the two instances of highest amine production (Table I). It would appear, therefore, that the second step in eq 2 is relatively fast compared to the first for compounds like the o- and p-tolyl Grignards. Although a more detailed kinetic argument could be advanced here to explain the results with the tolyl Grignards—especially the ortho and para isomers vs. the meta isomer—it would be risky to do so based on yield data alone, especially when 75% of the starting material was not accounted for.

The apparent stability of nitrosomesitylene and p-nitrosoanisole certainly deserves some mention. As noted above, the first probably owes its unreactivity toward more Grignard reagent to an ortho steric effect. The second, however, must be purely electronic in nature, and could perhaps be related to a resonance structure such as 1. Contribution of 1 would make p-nitrosoanisole less likely to undergo addition across the N–O bond for ground state reasons. The effect of such a resonance contribution to the transition state of the second step in eq 2 is, of course, speculative since the exact nature of that step has not yet been determined. However, no obvious destabilization is apparent.



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Reaction By-products. In addition to the amine and nitroso products the reaction of p-anisylmagnesium bromide with NOCl gave substantial amounts of anisole and p-nitrosophenol. Although it was first suspected that anisole was the result of unreacted Grignard reagent, a Gilman test shortly before hydrolysis showed the absence of any organomagnesium compound. Also, previous work with phenylmagnesium bromide and nitrosobenzene[1a] showed that the production of benzene began only after the yield of diarylamine had already peaked, and was therefore not connected with the conversion to the amine. Clearly, then, the formation of anisole must be a competing reaction which the Grignard reagent can undergo after the concentration of NOCl has been sufficiently lowered. The exact mechanism of its formation, i.e., the source of the acidic hydrogen, has not yet been discovered.

The by-product p-nitrosophenol is probably the result of the well-known alkyl cleavage reaction of aryl alkyl ethers by Grignard reagents.[10] p-Nitrosoanisole should be especially susceptible to this type of cleavage owing to participation of resonance structure 1.

Finally, the formation of trimesitylhydrazine from mesitylmagnesium bromide and NOCl rates some attention. Based on Bamberger's hypothesis that nitrosobenzene slowly disproportionates to nitrobenzene and phenylhydroxylamine,[11] and Busch and Hobein's observation that the reaction of phenylhydroxylamine and phenylmagnesium bromide gives triphenylhydrazine as the major isolated product,[12] it is supposed that a similar path occurs for nitrosomesitylene. The fact that such hydrazine-type products were not isolated in the other reactions may be explained by their facile oxidation to a radical species and subsequent dimerization.[13]

Conclusion

The reaction of aryl Grignard reagents with nitrosyl chloride is definitely a convenient laboratory method for the preparation of symmetrical diarylamines. Although yields are not high by this method, the secondary amines are uncontaminated by isomeric impurities and easy to isolate. Future investigations will include the formation of unsymmetrical diarylamines via the preformed nitroso compound and various phenyl-substituted Grignard reagents.

Experimental Section

Melting points were taken on a Mel-Temp melting point apparatus and are uncorrected. All gas chromatography work was done on 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 NOCl with Aryl Grignard Reagents. General Procedure. In a typical reaction 100 mmol of aryl bromide was treated under a nitrogen atmosphere with 100 mmol of 1,2-dibromoethane and 600 mmol of magnesium in a total of 500 ml of dry diethyl ether. After addition of the bromide, the mixture was heated under reflux for 2 hr. A measured aliquot was then removed and hydrolyzed, and the dried ether solution was analyzed by VPC in the presence of tetralin (VPC internal standard). By comparing

the amount of benzene in the solution with that in a flash-distilled aliquot of Grignard solution, it was determined that 95–97% conversions of aryl bromide to arylmagnesium bromide usually occurred.

The unfiltered Grignard solution was next cooled to −78° under a nitrogen atmosphere. To this, 45 mmol of NOCl in 150 ml of dry ether was added in a dropwise fashion over several hours. The solution was stirred for an additional 2 hr and then hydrolyzed with a minimum of pH 10 buffer solution ($NaOH–Na_2CO_3$). The orange ethereal phase was separated, the solid was washed three times with 25-ml portions of ether, and the combined solutions were steam distilled. Concentration of an ether extract of the 5-l. distillate usually afforded the crystalline amine. In cases where the amine had a low melting point, HBr was bubbled through the ether extract and the precipitated salt collected. Regeneration of the amine with hot NaOH solution and subsequent recrystallization from ligroin gave solid amine.

***p*-Tolylmagnesium bromide** (83.8 mmol) was allowed to react with 45 mmol of NOCl at −78° as described above. An ether extract of the steam distillate yielded 2.34 g (11.9 mmol, 28.4%) of di-*p*-tolylamine: mp 77–78° (lit.[14] mp 79°); ir (melt) 3400, 3030, 2920, 1800, 1610, 1520, 1100, and 800 cm^{-1}; NMR δ ($CDCl_3$) 2.28 (s, 6), 5.4 (s, broad, 1), 6.89 (d, J = 9.0 Hz, 4), and 7.09 (d, J = 9.0 Hz, 4).

***o*-Tolylmagnesium bromide** (93.5 mmol) and 45 mmol of NOCl yielded only an oil upon evaporation of the ether extract. HBr treatment gave 3.10 g (111 mmol, 23.8%) of di-*o*-tolylamine hydrobromide: mp 197–202°; ir (KBr) 2860–2440, 1480, 760, and 740 cm^{-1}. Di-*o*-tolylamine, mp 48.5–9.5° (lit.[14] mp 52–53°), was regenerated from the amine salt with hot NaOH and subsequent crystallization from ligroin. Spectra were as follows: ir (melt) 3430, 3020, 1480, 1290, 1140, 740, and 710 cm^{-1}; NMR δ ($CDCl_3$) 2.09 (s, 6), 5.0 (s, broad, 1), 6.9 (s, 8).

***m*-Tolylmagnesium bromide** (89.2 mmol) and 45 mmol of NOCl yielded 1.3 g of a green oil as the first portion of the steam distillate. Upon standing at 0° the oil precipitated 150 mg (1.2 mmol, 1.4%) of *m*-nitrosotoluene: mp 48–50°, white crystals to green melt (lit.[15] mp 53.5°); ir (melt) 3040, 2900, 1400, 1380, 780, and 680 cm^{-1}.

Continuation of the steam distillation gave 3.1 g of an orange-red oil which upon HBr treatment yielded 1.45 g (5.10 mmol, 11.6%) of di-*m*-tolylamine hydrobromide: mp 192–196°; ir (KBr) 2860–2420, 1560, and 725 cm^{-1}. Conversion to the free amine with NaOH gave di-*m*-tolylamine: oil (lit.[15] mp <−12°); ir (neat) 3370, 3015, 2900, 1590, 1570, 1470, 1300, 760, and 680 cm^{-1}.

The steam distillation pot residue was extracted with ether, yielding 4.2 g of brownish-black oil. No attempt was made to identify this material.

***p*-Anisylmagnesium bromide** (79.2 mmol) and 45 mmol of NOCl were allowed to react in the usual manner, but stirred for an additional 3 days. The first 125-ml portion of steam distillate yielded 2.66 g of a green oil which was shown to be 58% anisole and 42% *p*-nitrosoanisole by weight (GC, 10 ft × 0.125 in. 10% FFAP, tetralin standard). Thus the oil contained 1.54 g (14.2 mmol, 18.0%) of anisole (GC coinjection with known anisole, ir and NMR comparison with known anisole) and 1.12 g (8.21 mmol, 10.4%) of *p*-nitrosoanisole: ir (neat) 1410, 1265, 1110, and 835 cm^{-1}; NMR δ ($CDCl_3$) 3.70 (s, 3), 6.80 (d, J = 9.1 Hz, 2), and 7.75 (d, J = 9.1 Hz, 2).

The second 750 ml of the steam distillate yielded 490 mg (3.98 mmol, 5.0%) of *p*-nitrosophenol: mp 130° dec from Et_2O–hexane (lit.[16] mp 132–134° dec); ir identical with Sadtler[17] Spectrum No. 23689; NMR δ ($DCDl_3$) 6.60 (d, J = 10.0 Hz, 2) and 7.64 (d, J = 10.0 Hz, 2); MS M^+ m/e 123. Anal. Calcd for $C_6H_5NO_2$: C, 58.53; H, 4.10; N, 11.38. Found: C, 58.24; H, 3.71; N, 11.20.

The final 15-l. portion of the steam distillate and the pot residue yielded a total of 1.51 g (6.59 mmol, 16.7%) of di-*p*-anisylamine: mp 93–96° from hexane (lit.[18] mp 96.8°); ir identical with Coblentz[19] Spectrum No. 2521; NMR δ ($CDCl_3$) 2.8 (s, broad, 1), 3.75 (s, 6), and 6.9 (m, 8); MS M^+ m/e 229, base 214.

Mesitylmagnesium bromide (90.4 mmol) and 45 mmol of NOCl yielded a yellow crystalline precipitate upon hydrolysis of the reaction mixture. Extraction of these crystals with excess Et_2O gave 3.07 g (20.6 mmol, 22.8%) of nitrosomesitylene: mp 117–117.5° white crystals to green melt, from EtOH (lit.[20] mp 122–123°); ir agreement with literature;[21] NMR δ (CS_2) 2.38 (s, 3), 2.43 (s, 3), 2.67 (s, 3), 6.99 (m, 2); MS M^+ m/e 140, 134, 119, and 104.

The ethereal mother liquors from the above isolation yielded 4.7 g of tarry material, from which 1.38 g of ether insoluble brown powder (mp 235° dec from CCl_4–hexane) was obtained. The material was tentatively identified as trimesitylhydrazine: MS M^+ m/e 386, 385, 267, 252, and 134; NMR δ ($CDCl_3$) 2.02 (s, broad, 6), 2.30 (s, broad, 3), 6.90 (m, 2); ir (KBr) 3400, 2920, 1595, 1480, 1315, and 860 cm^{-1}; ESR unsymmetrical multiplet at $\sim G$ = 2.003.

α- or β-naphthylmagnesium bromide (ca. 100 mmol) and 45 mmol of NOCl did not yield any isolable product besides 2.69 g of naphthalene (21.0 mmol, 21.0%): mp 65–72° (lit.[14] mp 80.5°); ir identical with Sadtler[17] Spectrum No. 865. Excessive high molecular weight tars were formed by the reaction, probably owing to the extreme heterogeneous nature of the naphthyl Grignard reagents at even room temperature.

Registry No.—NOCl, 2696-92-6; *p*-tolyl bromide, 106-38-7; di-*p*-tolylamine, 620-93-9; *o*-tolyl bromide, 95-46-5; di-*o*-tolylamine HBr, 56553-64-1; di-*o*-tolylamine, 617-00-5; *m*-tolyl bromide, 591-17-3; *m*-nitrosotoluene, 620-26-8; di-*m*-tolylamine HBr, 56553-65-2; di-*m*-tolylamine, 626-13-1; *p*-anisyl bromide, 104-92-7; *p*-nitroanisole, 100-17-4; *p*-nitrosophenol, 104-91-6; di-*p*-anisylamine, 101-70-2; mesityl bromide, 576-83-0; nitrosomesitylene, 1196-12-9; trimesitylhydrazine, 56553-66-3; α-naphthyl bromide, 90-11-9; β-naphthyl bromide, 580-13-2.

References and Notes

(1) (a) See W. L. Waters and P. G. Marsh, *J. Org. Chem*, preceding paper in this issue. This work was supported in part by the National Science Foundation, NSF Grant GP-18317, Water Resources Research Center Grant 983, and the University of Montana Foundation, Grants 841-0/0 and 840-9/K. (b) In partial fulfillment of the requirements of the Ph.D. degree, University of Montana. Department of Chemistry, University of Calgary, Calgary, Alberta, Canada.

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(9) Alternatively one could argue that the diarylamine precursor, dimesitylamine oxide, could not easily undergo disproportionation as shown in eq 2, owing to the nature of its substitution.

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