Aryliminodimagnesium Reagents. XIX.[1] Effects of Miscellaneous Metal Halides on Oxidative Self-Coupling of the Reagent, and on Its Condensation with Nitrobenzene. A New Preparative Route to *o,o′*-Dihydroxyazobenzene

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Fourteen metal halides (MX_n) were each added to the solutions of aryliminodimagnesium (p-$RC_6H_4N(MgBr)_2$, IDMg) in tetrahydrofuran, and the effect of MX_n on relative yields of products was examined in the following three IDMg reactions: (A) oxidative coupling leading to symmetrical azobenzene, (B) condensation with nitrobenzene, and (C) condensation with *o*-hydroxy-substituted (*o*-HO) nitrobenzene. Reaction A was promoted by addition of $CuCl_2$, and the yield of azoxybenzenes in reaction B was improved by addition of $NiCl_2$ or $CdCl_2$. Reaction C was similarly modified by addition of $CdCl_2$ so as to improve the yield of *o*-HO-azoxybenzenes. Their acetyl derivatives underwent a facile photoinduced migration of azoxy oxygen and were successively hydrolyzed to afford bidentate chelating agents, *o,o′*-$(HO)_2$-azobenzenes.

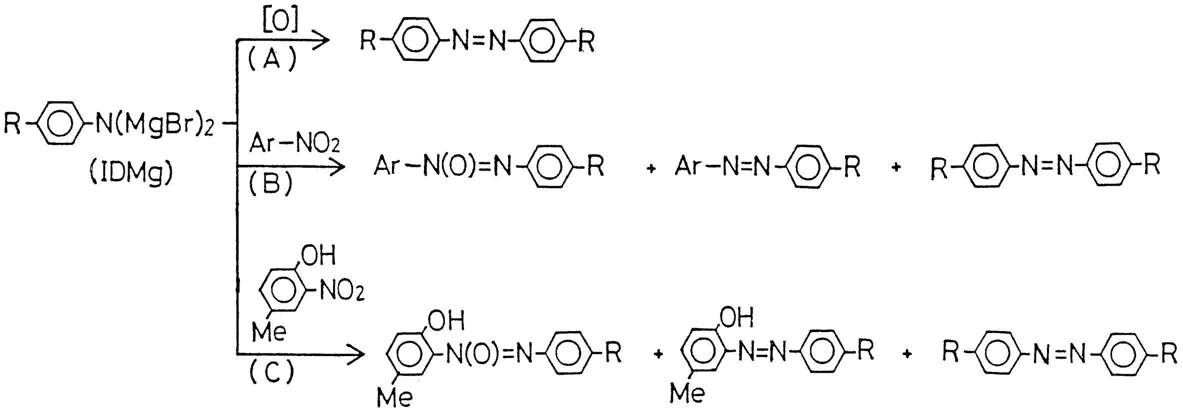
Modification of the reaction mode and reactivity of Grignard reagents by addition of miscellaneous metal halides was studied early by Kharasch[2] and later by Kochi[3] and their co-workers. The studies have contributed to the development of the vast and fascinating field of organometallic chemistry.

The nitrogenating ability of N–Mg reagent, aryliminodimagnesium ($RC_6H_4N(MgBr)_2$, IDMg) derived from anilines, via condensation with aromatic carbonyl and nitro compounds has been established.[4] The utility of the IDMg procedure is thus desired to be developed, and the effect of addition of each of fourteen metal halides on typical IDMg reactions was examined. The reactions selected are oxidative coupling to give symmetrical (*sym*-) azobenzenes[5] and condensation with nitrobenzenes to give unsymmetrical (*unsym*-) azoxy- and azobenzenes[4b,c] (Scheme 1: A and B). Reaction A was sufficiently promoted solely by $CuCl_2$ of the metal halides examined, whereas reaction B was modified by $NiCl_2$ or $CdCl_2$ to improve the yield of *unsym*-azoxybenzenes. The latter result was applied to condensation with *o*-hydroxy-substituted (*o*-HO) nitrobenzene (reaction C),[6a] and the obtained *o*-HO-azoxybenzene in improved yield was converted into a bidentate chelating agent, *o,o′*-$(HO)_2$-azobenzene. The results will be summarized and reported in this paper.

Results and Discussion

The metal halides examined are listed below according to their atomic numbers given in brackets: $TiCl_3$[22], $CrCl_3$[24], $MnCl_2$[25], $FeCl_3$[26], $CoCl_2$[27], $NiCl_2$[28], Cu(I)Cl[29], Cu(II)X_2[29], (X=Cl, Br), $ZrCl_4$ [40], $MoCl_5$[42], AgCl[47], $CdCl_2$[48], Sn(II)Cl_2[50], Sn(IV)Cl_4[50], $HgCl_2$[80], and $BiCl_3$[83].

Relative yields of products will be discussed in terms of reported governing factors. The principal factor of reactions of IDMg and ArMgBr is the relative efficiency of single electron transfer (SET) regardless of the normal condensation and addition modes; the combination of electron-donating and -accepting abilities (EDA and EAA) was evaluated by the difference (ΔE) between oxidation and reduction potentials of reactants.[7] Owing to the weaker EDA of



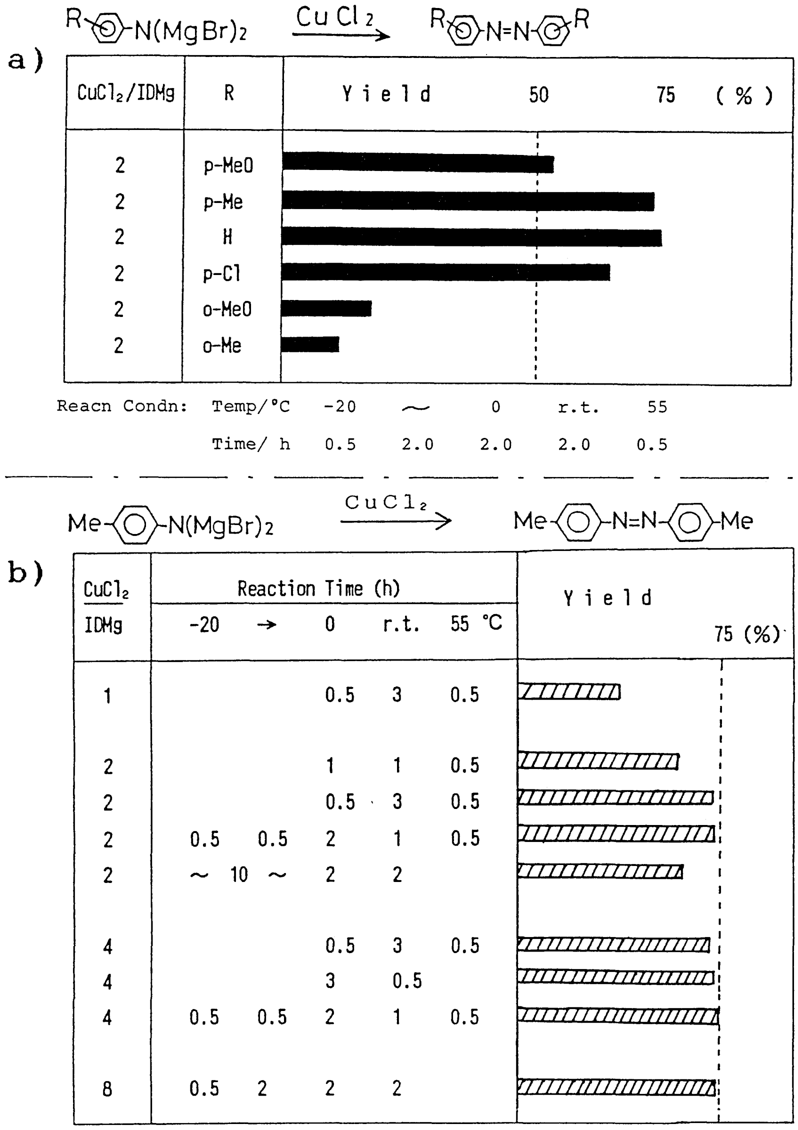
Scheme 1.

IDMg than that of ArMgBr,[6] a second factor originating from aggregation of IDMg molecules was disclosed.[6]

(A) Effect of Added CuCl$_2$ on Oxidative Coupling of IDMg. Concerning the formation of *sym*-azobenzenes from anilines, air oxidation in the presence of Cu(I)Cl and pyridine[9] and oxidative coupling of IDMg[5] by use of I$_2$, $C_6H_5IO_2$, and OsO_4 in tetrahydrofuran (THF) were reported. The use of Cu(II)Cl$_2$ for reaction A leads to higher yield than that in a previous study,[5] and is available for *sym*-azobenzene preparation. The coupling took place only by use of CuX$_2$ (X=Cl, Br) or FeCl$_3$, the latter giving poor yield. The use of CuBr$_2$ led to lower conversion probably due to its larger redox potential than that of CuCl$_2$.

Figure 1a illustrates the effect of substituents (R) of IDMg on its conversion by use of two molar equivalents of CuCl$_2$ under fixed conditions: R=*p*-Me and H are more favorable than R=*p*-MeO and *p*-Cl, whereas R=*o*-Me and *o*-MeO give poor yields due to steric hindrance. Figure 1b illustrating effects of reaction conditions shows that *p*-Me reagent is sufficiently converted by use of CuCl$_2$ in two molar equivalents. The maximum yield, 75%, however, was not further improved by adding CuCl$_2$ at −20 or 0 °C. Neither addition at lower temperatures (−40 and −78 °C) nor use of greater amounts of CuCl$_2$ was effective. Mechanistic reasons why the retained 25% is not overcome and the *p*-MeO and *p*-Cl groups are less favorable, remain to be examined.

(B) Moderating Effect of NiCl$_2$ and CdCl$_2$ on the Condensation with Nitrobenzene. The condensation



CuCl$_2$/IDMg	R
2	p-MeO
2	p-Me
2	H
2	p-Cl
2	o-MeO
2	o-Me

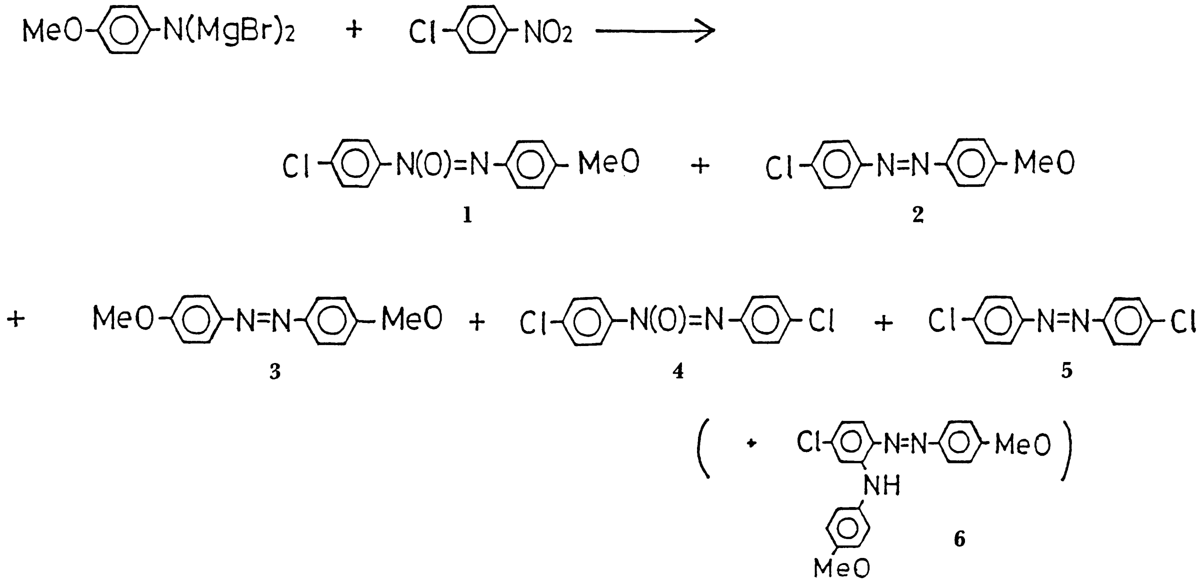
Reacn Condn: Temp/°C -20 ~ 0 r.t. 55

Time/ h 0.5 2.0 2.0 2.0 0.5

CuCl$_2$/IDMg	Reaction Time (h) -20	→	0	r.t.	55 °C
1			0.5	3	0.5
2			1	1	0.5
2			0.5	3	0.5
2	0.5	0.5	2	1	0.5
2	~ 10 ~		2	2	
4			0.5	3	0.5
4			3	0.5	
4	0.5	0.5	2	1	0.5
8	0.5	2	2	2	

Fig. 1. Effect of CuCl$_2$ addition on the oxidative coupling of IDMg reagents (reaction A). a): Substituent effect on the yield of azobenzene under fixed conditions of reaction. b): Effect of reaction conditions on the oxidative coupling of *p*-MeC$_6$H$_4$-IDMg.

with nitrobenzene (Scheme 1B) is composed of two normal successive processes, I (condesation) and II (deoxygenation), both being favored by aggregation of IDMg.[6a,b] Of reactions of IDMg, reaction B is most important not only because this provides a new method for independent preparation of ONN and NNO isomers of *unsym*-azoxybenzenes by exchange of substituents of the nitro- and aminobenzenes[4c] but also because this and the Grignard addition to Ar_2CO are "SET-controlled" reactions having comparable ΔE values.[7] Thus, preparation of azoxybenzene (**1**) from combination of R=MeO and Ar=*p*-ClC_6H_4 (Scheme 2) encounters difficulties under ordinary conditions: High SET efficiency (small ΔE) is responsible not only for rapid I and II but also for oxidative and reductive couplings of IDMg and $ArNO_2$, respectively, to give **2**,



Scheme 2.

Table 1. Yields of Products **1**—**5** Affected by MX_n Addition in the Condensation Reaction B (See Scheme 2)

MX_n M^n	Atom No.	Yield[a)]/%						
		1	2	3	4	5	Recov.	Overall
—	—	41	15	18	24	0	0	98
(Type **a**)								
Cr(III)	[24]	35	32	30	0	0	0	97
Mn(II)	[25]	43	21	25	10	Trace	0	99
Ni(II)	[28]	58	20	17	5	0	0	100
Cu(I)	[29]	24	10	28	38	0	0	100
Zr(IV)	[40]	15	44[b)]	23	0	0	0	82
Ag(I)	[47]	51	12	30	7	Trace	0	100
Cd(II)	[48]	65	13	16	0	0	0	94
Sn(IV)	[50]	51	30	17	2	0	0	100
Ni[c)]	—	56	20	18	6	0	0	100
Cd[d)]	—	63	17	20	0	0	0	100
(Type **b**)								
Ti(III)	[22]	0	27	10	0	0	0	37
Fe(III)	[26]	0	19	39	0	0	0	58
Sn(II)	[50]	20	6	0	12	10	0	42
(Type **c**)								
Co(II)	[27]	45	5	12	0	0	34	97
Mo(V)	[42]	0	0	46	0	0	49	95
Hg(II)	[80]	27	21	21	0	0	31	100
Bi(III)	[83]	20	2	6	0	0	52	90

a) Yields obtained at the ratio $[IDMg]:[ArNO_2]:[MX_n]=4:1:4$ unless otherwise noted. b) Yield of **2** includes that of **6** (see text). c) $[IDMg]:[ArNO_2]:[MX_n]=4:1:1$. d) $[IDMg]:[ArNO_2]:[MX_n]=4:1:0.5$.

3, and **4**. The dimeric abnormal products, **3** and **4**, are formed via SET taking place from aggregated IDMg due to "pre-interaction[7b] between reactants having small ΔE." With use of this combination, "moderating effect" caused by NiCl$_2$ or CdCl$_2$ to improve the yield of **1** was disclosed.

By comparison with the yields of **1**—**5** without use of MX$_n$ (Table 1), characteristic variation in the yields caused by an equimolar amount of MX$_n$ was surveyed, and manners of variation were classified into three types **a**—**c**. Type **a**: no recovery and improved combined yield of **1** plus **2** with two exceptional cases; **b**: no recovery and poor overall yield; **c**: appreciable recovery and fairly good overall yields.

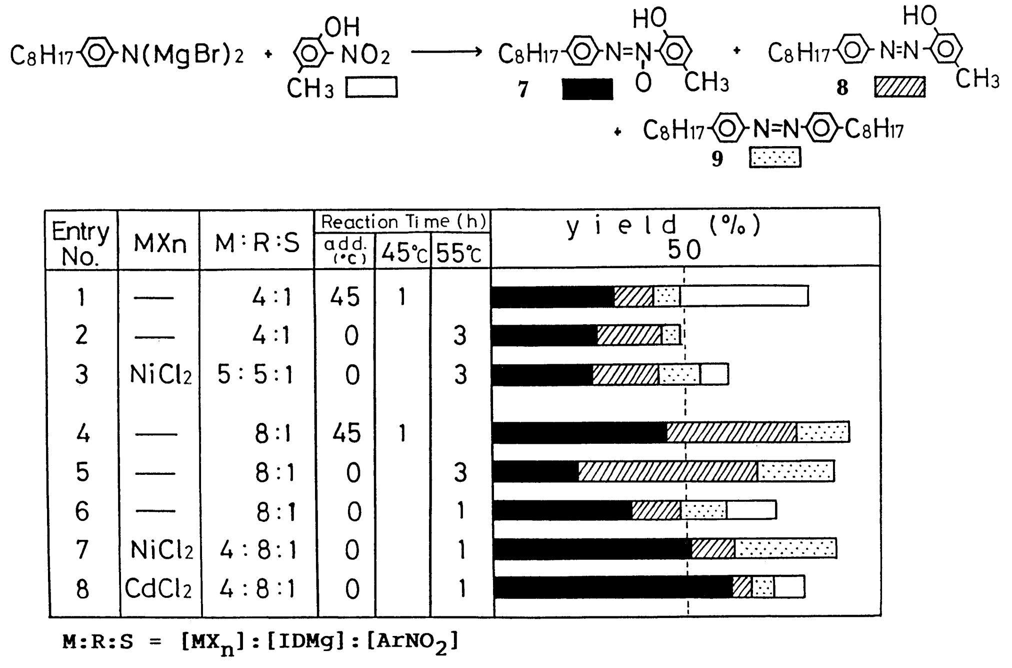
In type **a**, i.e., improved efficiency of the reaction indicated by no recovery, effects of MX$_n$ on the relative yields of **1** and **2** are classified into four kinds: (i) Improved effciency of I at the expense of **4** by addition of Ni, Ag, Cd, or Sn(IV) chloride; (ii) improved efficiency of II by addition of CrCl$_3$; (iii) the combined yield of **1** and **2** is not improved due to reductive coupling to give **4** by addition of Mn(II) or Cu(I) chloride; (iv) the highest yield of azo products, including **2** and an *o*-anilino-substituted one **6**, indicating a very rapid SET,[10] by addition of ZrCl$_4$.

According to the EDA-EAA concept, type **b**, poor efficiency of I and II and no recovery, implies that ArNO$_2$ is decomposed via a much accelerated SET. Type **c**, depression of the reaction itself indicated by recovery of ArNO$_2$, implies that the SET is retarded. The peculiar effect caused by MoCl$_5$ is noted; only **3** was formed due to oxidative coupling of IDMg in the presence of ArNO$_2$ but not formed in the absence.

Even from the preliminary results obtained under unoptimized conditions, the effect of MX$_n$ on IDMg reactions is distinct from that on Grignard reactions. Whereas Grignard reagent is oxidatively coupled by Co(II) and Ag(I) salts,[2b,3b] IDMg is unaffected (see Reaction A). The formation of mild C–Cd reagent by addition of Cd(II) salt to Grignard solution[11] seems different from a "catalytic" effect suggested from the comparable yields obtained by use of NiCl$_2$ and CdCl$_2$ in 1/1 and 1/4 or 1/8 molar amounts (see Table 1); no evidence for N–Cd bond formation is obtained.

The effect of NiCl$_2$ and CdCl$_2$, i.e., improved yield of **1** at the expense of **4** (Table 1), is noted. The EDA-EAA concept claims that[7,8] this originates from moderate SET, modified EDA being suggested. Moreover, a modified state of IDMg aggregation[6] is also suggested from the almost completely reduced yield of **4** contrary to the difficultly reduced yield of **3**. The modifications must arise from interaction of IDMg with d-orbitals of metal ions, remaining to be studied in detail. Nevertheless, the "catalytic moderating effect" is applied to preparation of *unsym-o*-HO-azoxybenzenes described below.

(C)-Synthetic Use of CdCl$_2$: Preparation of *o*-HO-Azoxybenzene and Conversion into *o,o′*-(HO)$_2$-Azobenzene. *sym-o,o′*-(HO)$_2$-Azobenzenes, utilizable as chelating agents, have so far been prepared by coupling of appropriate aryldiazonium salt by use of hydroxylamine–CuSO$_4$.[12] *unsym-p′*-Methyl- and *p′*-octyl-*o*-HO-azobenzenes, also utilized for selective solvent extraction of Ag(I) and Cu(II) ions,[13] are prepared by coupling of the cooresponding arenediazonium salt with phenols. An alternative prepara-



Entry No.	MXn	M:R:S	Reaction Time (h) add. (°C)	45°C	55°C
1	—	4:1	45	1	
2	—	4:1	0		3
3	NiCl$_2$	5:5:1	0		3
4	—	8:1	45	1	
5	—	8:1	0		3
6	—	8:1	0		1
7	NiCl$_2$	4:8:1	0		1
8	CdCl$_2$	4:8:1	0		1

M:R:S = [MX$_n$]:[IDMg]:[ArNO$_2$]

Fig. 2. Effect of addition of NiCl$_2$ and CdCl$_2$ on the condensation of *p*-octyl-C$_6$H$_4$–IDMg with 2-HO-5-Me-nitrobenzene (reaction C).

tion of *unsym-o*-HO-azo compounds by use of IDMg (Scheme 1C) was reported,[6a] and modified by addition of $CdCl_2$ to provide a synthetic route to *unsym-o,o'*-$(HO)_2$-azo compounds.

Reaction C using 2-HO-5-Me-nitrobenzene and 4.0 or 8.0 molar equivalents of *p*-octyl-C_6H_4-IDMg was carried out in the absence and presence of $NiCl_2$ or $CdCl_2$. Figure 2 illustrates the effect of reaction conditions on the yields of *o*-HO-azoxybenzene (**7**), *o*-HO-azobenzene (**8**), *sym*-azobenzene (**9**), and the amount of recovery. In accord with previous results obtained by use of *p*-Me-C_6H_4–IDMg,[6a] the use of four molar equivalents of *p*-octyl-C_6H_4-IDMg (both in the absence and in the presence of $NiCl_2$) led to a combined yield of **7** plus **8** lower than 50%, i.e., insufficient efficiency of condensation. Though the combined yield was improved so as to exceed 70% by the use of eight molar equivalents of IDMg, the yield of **7** was still lower than 45% in the absence of $NiCl_2$ or $CdCl_2$.[6a] However, in the presence of the latter, the yield of **7** was improved to more than 60%.

Direct photoconversion of the *o*-HO-azoxy compound **7** (R=Me) into *o,o'*-$(HO)_2$-azo product by Wallach-type azoxy-ortho migration of oxygen[14] is quite sluggish due to intramolecular hydrogen bonding, and instead, deoxygenation predominates after a longer time of irradiation (see Table 2). However, evoking the behavior of some *o*-MeO- and *o*-halo-azoxybenzenes,[14] the *o*-acetyl-azoxy compound derived from **7** was easily photoconverted into *o*-acetyl-*o'*-HO-azo product, which was successively hydrolyzed to give the desired *o,o'*-$(HO)_2$-azo compound (Scheme 3). The *p'*-octyl derivative of **7** (R=octyl) behaves similarly.

For the use of bidentate *o,o'*-$(HO)_2$-azobenzenes for solvent extraction, the facile and complete recovery of *p'*-octyl derivative from the binary solvent system due to reduced solubility in water is of greater advantage than for *p'*-methyl derivative.

Experimental

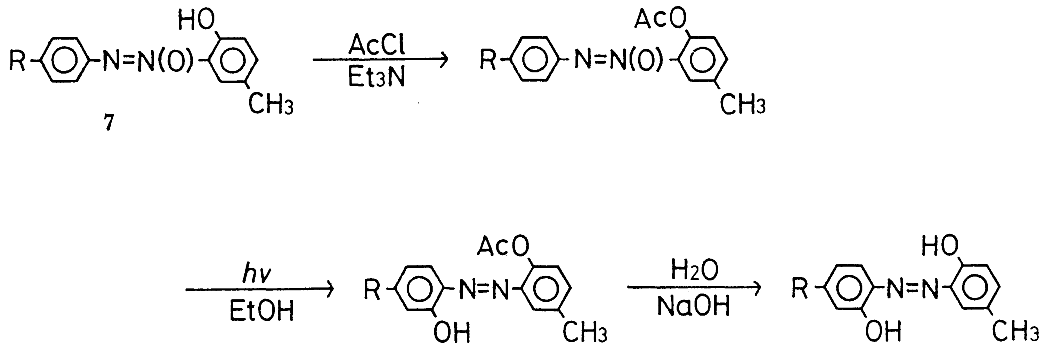
Materials and Procedures. Guaranteed grade anhydrous metal halides were commercially available and used without further purification. The IDMg reagents were prepared on a 6—8 mmol scale in 50 ml THF by treatment of the corresponding anilines with two molar equivalents of EtMgBr.[4b,8] For reaction A, a calculated amount of $CuCl_2$ was added to the IDMg solution in THF at −20 or 0 °C, and the mixture was stirred under the time and temperature conditions indicated in Figs. 1a and 1b. The mixture was quenched with aqueous ammonium chloride, and the azobenzene was chromatographically separated on silica gel (Wako Gel FC-40).

For reaction B (see Scheme 2), a calculated amount of MX_n was added at 0 °C to the THF solution of IDMg with subsequent addition of the nitrobenzene. The resulting mixture was stirred at room temperature for 3 h and at 55 °C for 0.5 h. Product mixtures were similarly separated. The yields of products **1**—**6** are given in Table 1. Reaction C was similarly carried out, and molar ratios of reagent versus substrate, reaction temperatures and times, and yields of products **7**—**9** are shown in Fig. 2. The distinctive behavior of *o*-HO- and o-acetoxy-azoxy compounds under photoirradiation using the given concentration in ethanol[14] (see Scheme 3) is shown by the product yields given in Table 2.

All the products are known, and the structures were determined by ^1H NMR spectra: The signals appearing at δ=8.1—8.3 and δ=7.7—7.9 were assigned to the ortho protons of azoxy and azo products, respectively.[4c] The

Table 2. Behavior of *o*-RO-Substituted (R=H, CH_3CO) Azoxybenzenes under Photoirradiation in Ethanol (0.002 mol dm^{-3}) (See Scheme 3)

Azoxy R	Irradn. time/h	Yield/%		Recov.	Overall
		o-RO-*o'*-HO	*o*-RO		
H(**7**)	0.5	6	15(**8**)	77	98
H(**7**)	3.0	17	47(**8**)	15	79
CH_3CO	0.5	51	0	23	74



Scheme 3.

signal of the HO protons of 7 appearing at δ=11.92 indicates intramolecular hydrogen bonding.

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