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Aryliminodimagnesium Reagents. V. The Reaction with Bifunctional Nitroarenes

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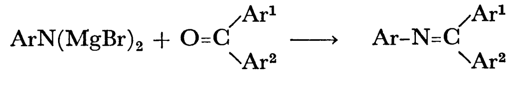
The reactions of *p*-methylphenyliminodimagnesium reagent (p-MeC$_6$H$_4$N(MgBr)$_2$) with *p*- and *m*-dinitrobenzenes, bis(*p*-nitrophenyl)methane, bis(*p*-nitrophenyl) sulfide and ether, *p*- and *m*-nitrobenzaldehydes as well as 4-nitro-4′-methylbenzophenone were investigated. *p*-Dinitrobenzene, which is the strongest electron-acceptor among the substrates used, gave *ca.* 30% combined yield of bis(azoxy) and azoxy azo products. The oxidative coupling product, 4,4′-dimethylazobenzene, was isolated in 20—30% yields. About 60% combined yield of the bis(azoxy) and azoxy azo products was obtained in the same reaction with *m*-dinitrobenzene, which is less electron-accepting than the *p*-isomer. In the reaction of bis(*p*-nitrophenyl)methane, bis(*p*-nitrophenyl) sulfide and ether with five molar amounts of the reagent, *ca.* 70% combined yields of bis(azoxy), azoxy azo, and bis(azo) products were obtained. On the treatment of the nitrobenzaldehydes and the nitrobenzophenone, in contrast, the reaction took place exclusively on the nitro group. The results are discussed in terms of the electron-accepting ability of substrates.

The aryliminodimagnesium reagents ($ArN(MgBr)_2$, aryl-IDMg) condense with diaryl ketones to give the anils (Scheme 1),[1,2] and also with nitroarenes to give azoxy- and azoarenes (Scheme 2).[3,4] On the basis of the previous results,[1–4] the IDMg reaction with an aromatic dinitro compound is expected to provide a new route for the one step preparation of the corresponding bis(azoxy) and bis(azo) compounds. The expectation was verified in the reaction of *p*-methylphenyl-IDMg with *p*- and *m*-dinitrobenzenes (**1** and **2**), bis(*p*-nitrophenyl)methane (**3**), bis(*p*-nitrophenyl) sulfide (**4**) and ether (**5**).



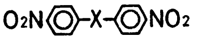
$$\mathrm{ArN(MgBr)_2 + O{=}C}\begin{array}{l}/\mathrm{Ar^1}\\ \backslash\mathrm{Ar^2}\end{array} \longrightarrow \mathrm{Ar{-}N{=}C}\begin{array}{l}/\mathrm{Ar^1}\\ \backslash\mathrm{Ar^2}\end{array}$$

Scheme 1.

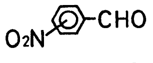
$$\mathrm{ArN(MgBr)_2 + O_2NAr^1 \longrightarrow ArN{=}N(O)Ar^1 + ArN{=}NAr^1}$$

Scheme 2.

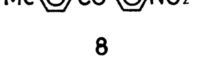
1: p-NO_2
2: m-NO_2



3: X= CH_2
4: X= S
5: X= O



6: p-NO_2
7: m-NO_2



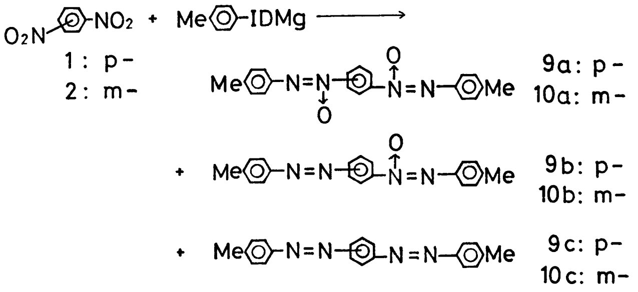
8

Similarly, the treatment of *p*- and *m*-nitrobenzaldehydes (**6** and **7**) as well as 4-nitro-4′-methylbenzophenone (**8**) with the same reagent is also expected to afford the corresponding azoxy azomethines and azo azomethines. Even by use of an excessive amount of the reagent, however, the reaction took place exclusively on the nitro group and not on the carbonyl group.

In this paper, the results of the IDMg reaction with the bifunctional nitro compounds, **1**—**8**, will be reported and explained in terms of their relative electron-accepting ability.

Results and Discussion

IDMg Reaction with p- *and* m-*Dinitrobenzenes.* In the reaction of *p*-dinitrobenzene, **1**, with five or six molar equivalents of *p*-methylphenyl-IDMg, the expected bis(azoxy) (**9a**), azoxy azo (**9b**), and bis(azo) (**9c**) products were obtained (Scheme 3 and Table 1).



Scheme 3.

The yields of the deoxygenative condensation products; **9a**, **9b**, and **9c**, are affected by the reaction conditions, especially by the temperature at which the addition is done (Expts 1—5). The yields were poor when the addition was carried out at 0 °C, and were improved by the addition at −78 °C. The formation of 4,4′-dimethylazobenzene is due to the oxidative coupling of the reagent molecules,[3] and that of an unidentifiable black material is due to the polymerization of the substrate initiated by one-electron reduction.[3] Their formation is reasonable, since the substrate **1** is highly electron-accepting.[5] The possible nitro azoxy product was not detected even by the treatment with the smaller excess of the reagent (Expt 2).

The reaction with *m*-dinitrobenzene, **2**, was carried out by adding its solution at −78 °C (Expts 6 and 7). The less electron-accepting **2**[5] gave the better combined yield of the bis(azoxy) (**10a**) and azoxy azo (**10b**) products, which were deoxygenated to afford **10b** and **10c**, respectively, by the treatment with

TABLE 1. DISTRIBUTION OF PRODUCTS IN THE REACTION OF p-MeC$_6$H$_4$-IDMg WITH p- AND m-DINITROBENZENES

Expt No.	Substrate	[IDMg]/[Substrate]	Addition		Yields/%				
			Manner[a]	Temp/°C	**9a**	**9b**	**9c**	(p-MeC$_6$H$_4$N=)$_2$	Recovered **1**
1	**1**	5	N	0	6	5	0	32	9
2	**1**	3	N[b]	0	−0	−0	−0	20	50
3	**1**	5	N	−78	20	13	0	17	10
4	**1**	6	R	0	0	6	18	23	16
5	**1**	6	R	−78	26	11	0	25	3
					10a	**10b**	**10c**		Recovered **2**
6	**2**	5	N	−78	43	15	0	18	—
7	**2**	10	N	−78	0	17	29	26	—

a) N and R designate "normal" and "reverse" additions respectively. b) The diluted THF solutions of the reagent and the substrate were used.

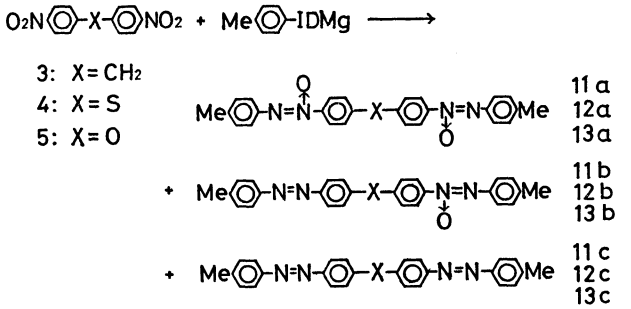
TABLE 2. DISTRIBUTION OF PRODUCTS IN THE REACTION OF p-MeC$_6$H$_4$-IDMg WITH BIS-(p-NITROPHENYL) COMPOUNDS

Substrate	Yields/%[a]			
	Bis(azoxy)	Azoxy azo	Bis(azo)	(p-MeC$_6$H$_4$N=)$_2$
3(X=CH$_2$)	26	31	9	25
4(X=S)	29	30	8	22
5(X=O)	27	32	10	29

a) Five molar equivalents of the reagent were used.

a larger excess of the reagent. The better yields of the condensation products in the reaction of **2** than those in the reaction of **1** suggests the importance of the combination of the electron-accepting and -donating abilities of the reactants.[6]

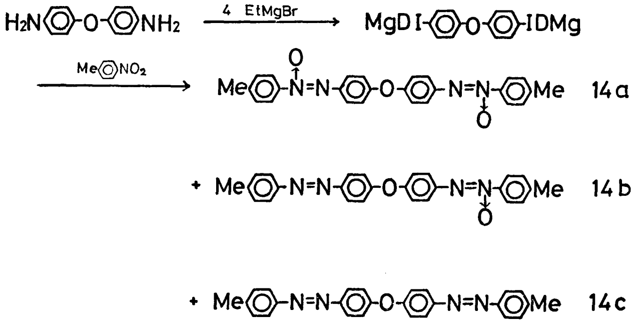
*IDMg Reaction with Bis(*p*-nitrophenyl)methane, Bis(*p*-nitrophenyl) Sulfide and Ether.* The bis(p-nitrophenyl) compounds, **3**, **4**, and **5**, the two nitro groups of which are located on the different phenyl groups, gave high combined yields of the corresponding bis(azoxy), azoxy azo, and bis(azo) products, **11a**—**c**, **12a**—**c**, and **13a**—**c** (Scheme 4 and Table 2).



Scheme 4.

The high combined yield of the products is ascribed to the moderate electron-accepting ability of **3**, **4**, and **5**. The electron-accepting effects of the individual nitro groups seem to be additive, but not synergic as in the case of **1**, since the formation of the unidentifiable black material is negligible and that of 4,4′-dimethylazobenzene *per* one nitro group is comparable to that obtained in the case of monofunctional nitroarenes.[3] The effect of the central atoms, C, S, and O, of the substrates on the distribution of the three types of the products is negligible.

The good result of the reaction of Scheme 4 forced the authors to examine the preparation and the reaction of bis(iminodimagnesium) reagents. An attempt to prepare the reagent from p-phenylenediamine by treating it with four molar equivalents of EtMgBr was unsuccessful: a voluminous white precipitate appeared and hardly any evolution of ethane[1] was observed. In contrast, bis(p-aminophenyl) ether gave the bis(iminodimagnesium) reagent. Its reaction with p-nitrotoluene(1.6 mol equiv., Scheme 5) gave the corresponding bis(azoxy) product (**14a**, 12%) and azoxy azo product (**14b**, 13%), which were isomeric with **13a** and **13b** respectively. A 22% of the substrate was recovered in this case.



Scheme 5.

IDMg Reaction with Nitrobenzaldehydes and a Nitrobenzophenone. It should be noted that the IDMg reaction with the substrates having nitro and carbonyl groups took place exclusively on the nitro group. The reaction of p-nitrobenzaldehyde, **6**, with five molar

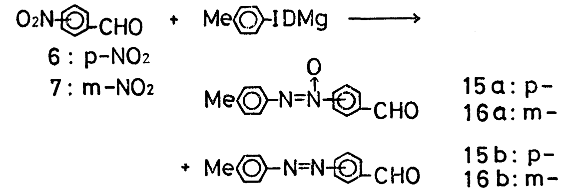
TABLE 3. DISTRIBUTION OF PRODUCTS IN THE REACTION OF *p*-MeC_6H_4-IDMg WITH *p*- AND *m*-NITROBENZALDEHYDES

Substrate	$\frac{[\text{IDMg}]}{[\text{Substrate}]}$	Reaction time/h	Yields/%		
			Azoxy aldehyde	Azo aldehyde	(*p*-$MeC_6H_4N=)_2$
			15a	**15b**	
6	5	3	30	25	13
			16a	**16b**	
7	8	6	0	82	18

TABLE 4. ANALYTICAL DATA AND PHYSICAL CONSTANTS OF PRODUCTS

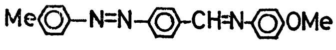
Product No.	Mp θ_m/°C	Formula	Found(Calcd)(%)			NMR data, δ in $CDCl_3$
			C	H	N	
9a	145—147.5	$C_{20}H_{18}N_4O_2$	69.61 (69.36)	4.98 (5.20)	16.09 (16.18)	8.52(4H, s), 8.26 and 7.38(8H, ABq), 2.46 (6H, s).
9b	185—189.5	$C_{20}H_{18}N_4O$	72.62 (72.73)	5.62 (5.45)	17.10 (16.97)	8.54 and 8.08(4H, ABq), 8.27 and 7.96(4H, ABq), 7.50—7.30(4H, ABq), 2.48(3H, s), 2.45 (3H, s).
9c	209.5—213	$C_{20}H_{18}N_4$	76.55 (76.43)	5.80 (5.73)	17.65 (17.83)	8.10(4H, s), 7.92 and 7.36(8H, ABq), 2.46 (6H, s).
10a	164—165.5	$C_{20}H_{18}N_4O_2$	69.56 (69.36)	5.08 (5.45)	16.21 (16.18)	9.18(1H, m), 8.50—8.46(2H, m), 8.14 and 7.24(8H, ABq), 7.56(1H, m), 2.40(6H, s).
10b	124.5—128	$C_{20}H_{18}N_4O$	72.78 (72.73)	5.56 (5.45)	17.19 (16.97)	8.76(1H, m), 8.38—7.44(7H, m), 7.36—7.16 (4H, m), 2.38(6H, s).
10c	131—133.5	$C_{20}H_{18}N_4$	76.37 (76.43)	5.69 (5.73)	17.94 (17.83)	8.08—7.60(8H, m), 7.30(4H, d), 2.38(6H, s).
11a	169—173	$C_{27}H_{24}N_4O_2$	74.25 (74.31)	5.38 (5.50)	12.93 (12.84)	8.30(8.10) and 7.18(8H, ABq), 8.10(8.30) and 7.18(8H, ABq), 4.08(2H, s), 2.40(6H, s).
11b	190—198	$C_{27}H_{24}N_4O$	76.98 (77.14)	5.77 (5.71)	13.43 (13.33)	8.32—8.06(4H, m), 7.94—7.79(4H, m), 7.42—7.20(8H, m), 4.10(2H, s), 2.40(6H, s).
11c	231—233	$C_{27}H_{24}N_4$	80.25 (80.20)	5.89 (5.94)	13.86 (13.86)	7.96—7.82(8H, m), 7.46—7.26(8H, m), 4.16 (2H, s), 2.44(6H, s).
12a	171—174	$C_{26}H_{22}N_4O_2S$	68.81 (68.72)	4.92 (4.85)	12.29 (12.33)	8.30(8.16) and 7.48(8H, m), 8.16(8.30) and 7.30 (8H, m), 2.42(6H, s).
12b	182.5—185	$C_{26}H_{22}N_4OS$	71.29 (71.23)	4.13 (5.02)	12.92 (12.78)	8.32—8.04(4H, m), 7.92—7.74(4H, m), 7.60—7.40(8H, m), 2.41(3H, s), 2.38(3H, s).
12c	218—220.5	$C_{26}H_{22}N_4S$	74.02 (73.93)	5.38 (5.21)	13.21 (13.27)	7.92(7.86) and 7.52(8H, ABq), 7.86(7.92) and 7.32(8H, ABq), 2.42(6H, s).
13a	150—154	$C_{26}H_{22}N_4O_3$	71.29 (71.23)	4.97 (5.02)	12.91 (12.78)	8.28(8.06) and 7.24(8H, ABq), 8.06(8.28) and 7.08(8H, ABq), 2.38(6H, s).
13b	159—163.5	$C_{26}H_{22}N_4O_2$	74.02 (73.93)	5.25 (5.21)	13.31 (13.27)	8.38—7.72(8H, m), 7.34—7.02(8H, m), 2.42 (3H, s), 2.40(3H, s).
13c	215—218	$C_{26}H_{22}N_4O$	76.91 (76.84)	5.39 (5.41)	13.82 (13.79)	7.90(7.78) and 7.26(8H, ABq), 7.78(7.90) and 7.14(8H, ABq), 2.42(6H, m).
14a	166—172	$C_{26}H_{22}N_4O_3$	71.32 (71.23)	5.09 (5.02)	12.91 (12.78)	8.32(8.20) and 7.28(8H, ABq), 8.20(8.32) and 7.16(8H, ABq), 2.40(6H, m).
14b	172—176.5	$C_{26}H_{22}N_4O_2$	74.04 (73.93)	5.10 (5.21)	13.32 (13.27)	8.42—8.20(4H, m), 8.02—7.80(4H, m), 7.40—7.10(8H, m), 2.44(6H, s).
15a[a)]	—	—	—	—	—	10.16(1H, s), 8.50 and 8.02(4H, ABq), 8.20 and 7.30(4H, ABq), 2.42(3H, s).
15b[a)]	—	—	—	—	—	10.04(1H, s), 8.96(4H, s), 7.83 and 7.28(4H, ABq), 2.42 (3H, s).
16b[a)]	—	—	—	—	—	9.80(1H, s), 8.24—6.90(8H, m), 2.36(3H, s).
17	175—179	$C_{21}H_{19}NO$	76.73 (76.60)	5.81 (5.77)	12.68 (12.76)	8.56(1H, s), 8.04(4H, s), 7.84 and 7.32(4H, ABq), 7.24 and 6.96(4H, ABq), 3.84(3H, s), 2.44(3H, s).
18	153—155	$C_{21}H_{18}N_2O_2$	76.30 (76.36)	5.39 (5.45)	8.55 (8.48)	8.56 and 7.99(4H, ABq), 8.29 and 7.39(4H, ABq), 7.84 and 7.39(4H, ABq), 2.54(3H, s), 2.50(3H, s).
19	136—139	$C_{21}H_{19}NO$	83.75 (83.72)	6.44 (6.31)	4.72 (4.65)	7.90 and 7.06(4H, ABq), 7.84 and 7.34(4H, ABq), 7.16(4H, s), 5.94(1H, broad s), 2.42 (3H, s), 2.34(3H, s).

a) The azoxy and azo aldehydes, **15a**, **15b**, and **16b**, were identified by NMR; they were not purified. They were used for converting into the imino compounds.



Scheme 6.

equivalents of *p*-methylphenyl-IDMg gave the corresponding azoxy and azo aldehydes, **15a** and **15b** (Scheme 6 and Table 3). Even by use of eight molar equivalents of the reagent, *m*-nitrobenzaldehyde, **7**, afforded solely an excellent yield of the azo aldehyde, **16b**. Neither azoxy azomethine nor azo azomethine were detected. In an attempt to convert the isolated **15b** into the corresponding azo azomethine by treating with the more electron-donating *p*-methoxyphenyl-IDMg, the substrate was recovered unchanged. The expected azo azomethine, **17**, was prepared quantitatively by the treatment of **15b** in refluxing dry benzene with *p*-methoxyaniline in the presence of *p*-toluenesulfonic acid.[7] For the purpose of converting an aromatic aldehyde into the aldimine, the IDMg method is not advisable:[2] *p*-chlorobenzaldehyde was converted into the aldimine in only a 32% yield by the treatment with 1.2 molar equivalents of *p*-methylphenyl-IDMg.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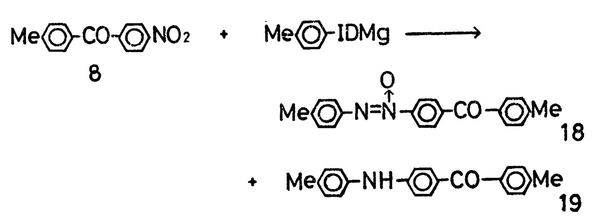
The inertness of the carbonyl functional group is consistent with the fact that the one-electron reduction of nitro-substituted benzophenones gives the ESR spectra assigned to the benzoyl-substituted nitrobenzene anion radicals.[9] The higher oxidizing ability of nitroarenes compared with that of diaryl ketones[10] also supports the present result.

4-Nitro-4'-methylbenzophenone, **8**, also gave products which originated from the reactions exclusively on the nitro group by the treatment with five molar equivalents of *p*-methylphenyl-IDMg (Scheme 7). The normal condensation product, **18**, and the replacement product, **19**, were obtained in 38% and 28% yields, respectively; the oxidative coupling product, 4,4'-dimethylazobenzene, was also isolated in 21% yield. The formation of **19** is reasonable, since the nitro group is responsible for the replacement in the reaction of 4-nitroquinoline *N*-oxide and related compounds with alkali alkoxides and alkanethiolates.[11] The present result, however, may be the first example for the replacement of nitro group in organomagnesium reactions.



Scheme 7.

All the results obtained in the reactions of Schemes 1—7 are preliminary ones, but they show the important role of the electron-accepting ability of the substrates.

Experimental

The melting points are uncorrected.

The bifunctional nitro compounds **1**—**7** were obtained commercially. The nitrobenzophenone, **8**, was prepared by p-nitrobenzoylation of toluene by the Friedel-Crafts method.

The procedures for the reactions and for the isolation of products were reported previously.[1—4]

The melting points, the results of elemental analyses, and the NMR data of the products **9**—**19** are summarized in Table 4. Among the NMR data, several aromatic proton signals consisting of two or three AB quartets are not assigned and the δ values are given in parentheses.

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