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Electron Transfer Initiated Replacement of Bromo and Methoxyl Groups with Aryliminodi-, Arylamino-, and Arylthiomagnesium Reagents

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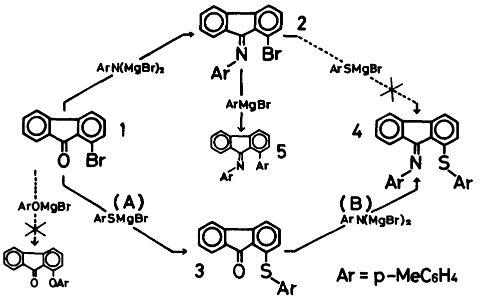
Synopsis. The replacement of bromo and methoxyl groups of fluorenone, *N*-(9-fluorenylidene)aniline, and α-benzylideneacetophenone with ArSMgBr(***S***), ArNHMgBr(***NH***), and ArN(MgBr)$_2$(***N***) were examined. The distribution of products obtained in the reactions with the reagents including ArMgBr(***C***) and ArOMgBr(***O***) were explained in terms of relative electron-donating abilities of reagents: ***C***>***S***>***NH***>***N***>***O***.

Grignard(ArMgBr, ***C***) and aryliminodimagnesium(ArN(MgBr)$_2$, aryl-IDMg, ***N***) reagents react with polar double bonds in the manners of addition and condensation, respectively.[1–4] However, the electron transfer from reagent to substrate is common to the reactions of ***C*** and ***N***, and the distribution of products is explained qualitatively in terms of the combination of relative electron-donating and -accepting abilities(EDA and EAA) of reactants.[5] The lower EDA of reagent ***N*** than that of ***C*** suggested on the basis of product distribution[5] was established by polarographic measurement of oxidation peak potentials.[6]

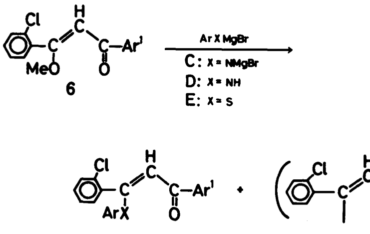
The study was thus extended to the electron transfer initiated replacement of 1-bromo substituent on fluorenone and *N*-(9-fluorenylidene)aniline[7,8] as well as that of methoxyl group on the benzylic position of α-benzylideneacetophenone[2] in the reaction with not only ***C*** and ***N*** but also with arylamino-, arylthio-, and aryloxymagnesium reagents (***NH***, ***S***, and ***O***). The product distribution will be explained in terms of relative EDA of the five magnesium reagents.

Results and Discussion

A set of reactions examined in order to convert 1-bromofluorenone (**1**) into *N*-(1-arylthio-9-fluorenylidene)aniline (**4**) and related reactions using ***C***,[7] ***N***,[7] ***S***, and ***O*** are shown in Scheme 1. Another set of reactions examined are the replacement reactions of methoxyl group of α-(α-methoxybenzylidene)acetophenone(**6a—6d**)[9] by the treatment with ***N***, ***NH***, and ***S*** shown in Scheme 2. The yields of normal and abnormal products are summarized in Table 1 (Runs A—E).



Scheme 1.



Scheme 2.

In Runs A, B, and E, the involvement of electron transfer is indicated explicitly by the formation of abnormal products due to typical radical processes: hydrogen abstraction from solvent (Run A), oxidative dimerization of reagent (Runs B$_1$ and B$_2$), reductive dimerization of substrate (Runs E$_1$—E$_5$), and radical recombination (Run A). On the treatment of **6** with ***N*** and ***NH*** having *para*- and *meta*-substituents (Runs C$_1$, C$_2$, D$_1$, and D$_3$), normal product **7** is formed in excellent yields. Abnormal product **9b**, however, is formed when the reagents have 2,6-dimethyl groups, which favor the demethoxylation followed by dimerization over the replacement (Runs C$_3$ and D$_4$) because the electron transfer is suppressed slightly and the process for the formation of **7** greatly. The latently involved electron transfer in the reactions of benzophenone with ***C*** and ***N*** is revealed similarly by use of *o*-Me-substituted reagents.[1,3] The reactivity of magnesium reagents must thus be estimated on the basis of their EDA instead of nucleophilicity.

The variation of yields of normal and abnormal products in the reactions of the same type of substrates with the different reagents is interpreted as follows. Imine **2** reacts with ***C***[7] but not with ***S*** (Scheme 1) because EDA of ***S*** is lower than that of ***C***. In the reaction with **6** (Scheme 2), ***S*** gives almost exclusively the abnormal product **9c** (Run E$_1$) while ***NH*** gives excellent yields of normal products **7a** and **7d** (Runs D$_1$ and D$_3$): The results are ascribed to the distinctly high EDA of ***S*** responsible for vigorous electron transfer compared with the medium EDA of ***NH*** for the mild and latent electron transfer. The low yield of **7a** obtained by use of a small excess of ***NH*** in Run D$_2$, in comparison with the good result of Run D$_1$, suggests the possibility that one mol of ***NH*** is consumed for electron transfer and another mol for product formation. Attempted variation of conditions of the reaction with ***S*** was not satisfactorily effective for improvement of the yield of **8** (Runs E$_2$—E$_5$). The substrates **1** and **6b** were recovered unchanged from the mixtures with ***O***: The red-brown coloration of the mixtures with ***O*** as well as that of ***S*** with **2** indicates that σ-complexes are formed (*vide infra*) but

TABLE 1. PRODUCTS IN THE REACTIONS OF MAGNESIUM REAGENTS ***S***, ***NH***, AND ***N*** WITH SUBSTRATES **1**, **3**, AND **6a—6d**

Run	Substrate[a]		Reagent[a,b]		Products[c]			
					(normal)		(abnormal)	
	No.	$Ar^1=R^1Ph$	Type	Ar=RPh	No.	Yield/%	No.	Yield/%
A	**1**	—	***S***	*p*-Me	**3**	92	2-ArS-THF[d]	38
B_1	**3**	—	***N***	*p*-Me	**4**	31	$(ArN=)_2$[e]	3
B_2	**3**	—	***N***	*p*-Me	**4**	84	$(ArN=)_2$[e]	8
C_1	**6a**	H	***N***	*p*-Me	$\mathbf{7a}^{\mathrm{Me}}$	85	—	—
C_2	**6d**	DMB[f]	***N***	*p*-Me	$\mathbf{7d}^{\mathrm{Me}}$	88	—	—
C_3	**6b**	*p*-Me	***N***	TM[g]	**7b**	39	**9b**	58
D_1	**6a**	H	***NH***	*m*-MeO	$\mathbf{7a}^{\mathrm{MeO}}$	92	—	—
D_2	**6a**	H	***NH***	*m*-MeO	$\mathbf{7a}^{\mathrm{MeO}}$	30	—	—
D_3	**6d**	DMB[f]	***NH***	*m*-MeO	$\mathbf{7d}^{\mathrm{MeO}}$	96	—	—
D_4	**6b**	*p*-Me	***NH***	TM[g]	**7b**	33	**9b**	66
E_1	**6c**	*p*-MeO	***S***	*p*-Me	**8c**	trace	**9c**	90
E_2	**6c**	*p*-MeO	***S***	*p*-Me	**8c**	25	**9c**	65
E_3	**6c**	*p*-MeO	***S***	*p*-Me	**8c**	9	**9c**	85
E_4	**6b**	*p*-Me	***S***	*p*-Me	**8b**	14	**9b**	75
E_5	**6b**	*p*-Me	***S***	*p*-Me	**8b**	31	**9b**	60

a) The substituents R^1 of **6a—6d** and R of reagents are given. b) The abbreviations of reagents are given in the text. Molar equivalent amount of reagents and addition manner are given in Experimental. c) Yields based on the substrates used. d) *p*-Methylphenyl 2-oxolanyl sulfide. e) 4,4′-Dimethylazobenzene. f) 2,6-Dimethyl-4-*t*-butyl. g) 2,4,6-Trimethyl.

the electron transfer is impossible because of much lower EDA's compared with the respective EAA's. Taking the polarographically determined order (***C***>***NH***>***N***)[6] into account, all the results of the reactions of Schemes 1 and 2 are interpretable in terms of the relative EDA: ArMgBr>ArSMgBr>ArNHMgBr>$ArN(MgBr)_2$>ArOMgBr.

Since magnesium has strong affinity for oxygen, the reactions are initiated with the coordination of carbonyl oxygen to Mg atom of reagent. The rate-determining nature of *σ-complex formation* in the condensation of ***N*** with diaryl ketones was proposed on the basis of the fact that electron-repelling substituents of substrate favor the product formation.[3,5] In contrast, the rate-determining nature of *electron transfer* in the reaction of ***C*** with benzophenones established by thermochemical measurement[10] was confirmed by the acceleration of ketyl formation by electron-attracting substituent of substrate.[1,11] Accordingly, the rate-determining process of the reactions with ***C***, ***S***, ***NH***, and ***N*** is localized on one of the two essentially common initial processes; subsequent ones for the product formation are not rate-determining. The dependence of product distribution on the EDA's of different types of reagent is reasonable.

The simple concept will be helpful in utilizing variuos types of magnesium reagents, and is expected to be quantified.

Experimental

The substrates **1** and **2** were prepared previously.[7] The solutions of reagents ***S***, ***NH***, ***N***, and ***O*** were prepared by the addition of calculated amount of benzenethiol, aniline, and phenol to the EtMgBr solution in tetrahydrofuran (THF).[7]

In the typical Runs, substrate(3.23 mmol) dissolved in THF(15 ml) was mixed with the THF solution(30 ml) of given amount of reagent. Molar equivalent amounts of reagents used in individual runs are: 1.5(D_2), 2.0(B_1), 2.2(E_2, E_4, and E_5), 3.0(A, C_3, D_1, D_3, D_4, E_1, and E_4), 4.0(C_1 and C_3), and 5.0(B_2). In Runs A—D and E_1, the substrates were added in normal manner at once at 0 °C(A, B_1, and B_2), at once at room temperature(C_1—C_3 and D_1—D_4), and over the period of 5 min at −78 °C(E_1). In Runs E_2—E_5, the reagent ***S*** was added in reverse manner at −78 °C over the period of 20 min(E_2, E_4, and E_5) and 60 min(E_3).

The mixtures were neated at 55 °C for 3 h (A—D) and 1 h (E). No reaction took place on the treatment of **2** with ***S*** and **1**(or **6b**) with ***O*** even by use of 8.0 mol of reagents.

The products mixtures were chromatographed on silica gel (Wako Gel, C-200 and C-300). All the ^{1}H-NMR spectra and elemental analyses of products were satisfactory.

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