The Replacement of Electronegative Substituents by an Electron-transfer Mechanism. The Factors Governing the Reaction of Carbonyl and Imino Compounds with Organomagnesium Reagents

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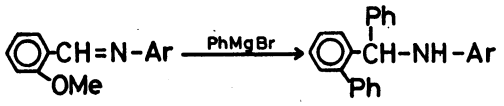
For the purpose of studying the electron-transfer initiated replacement of *ortho*-methoxy and *ortho*-halogeno substituents of diaryl ketone anils by the aryl group of ArMgBr, eight anils were prepared. The expected *o*-methoxy replacement by the phenyl group of PhMgBr, however, was extremely slow, and no *o*-chloro replacement took place. In contrast, anils of 1-substituted (MeO, Br, Cl) fluorenones gave the replacement products: The distribution of by-products formed *via* radical pathway in the cases of halogeno-anils was clearly different from that in the case of the methoxy-anil. In the reaction with $ArN(MgBr)_2$, 1-halogenofluorenones afforded the normal condensation products, while 1-methoxyfluorenone gave the "condensation-replacement" product. On the basis of the characteristic product-distributions obtained in the two organomagnesium reactions, the mechanism of methoxy replacement was distinguished from that of halogen replacement. Factors governing the two reactions were proposed and discussed: The structures of the substrates favorable to spin-delocalization, the electron-accepting ability of the substrates, the electron-donating ability of the reagents, the leaving ability of substituents, and their leaving manner.

During the past decade, the electron-transfer mechanism in the Grignard addition to carbonyl compounds has been studied extensively, and it was finally established very recently.[1] However, the electron-transfer-initiated replacement of electronegative substituents, such as the methoxy,[2,3] cyano,[2] and halogeno[4] groups of carbonyl and imino compounds, has been reported independently, and a systematic investigation is needed. In this paper, the authors wish to report the results of their study of the replacement of methoxy, bromo, and chloro substituents on the 1-position of 9-fluorenylidene compounds in the reaction with organomagnesium reagents: the reaction of aryliminodimagnesium ($ArN(MgBr)_2$, aryl-IDMg)[5] reagent with fluorenones and that of the Grignard (ArMgBr) reagent with fluorenone anils. The product-distributions found in the reactions with methoxy-substituted substrates are clearly different from those in the reactions with halogeno-substituted ones. On the basis of these results, factors governing the replacement reaction will be discussed.

On the basis of the previous observation[3] that the imino compound, **1**, reacts with PhMgBr (Eq. 1) much more moderately than with carbonyl compounds and that ESR evidence for electron-transfer is obtained in the Grignard reaction with diaryl ketone anils (Eq. 2), a replacement reaction initiated by electron-transfer can be expected to proceed moderately in the Grignard reaction (Eq. 3) with anils of *o*-methoxy- and *o*-chlorobenzophenones, **2**.

In the following, the results of the study to find the best route for preparing anils, **2**, will first be described.



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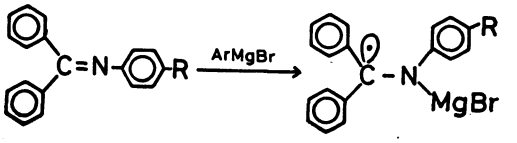

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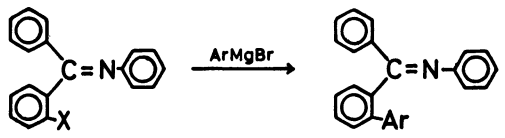


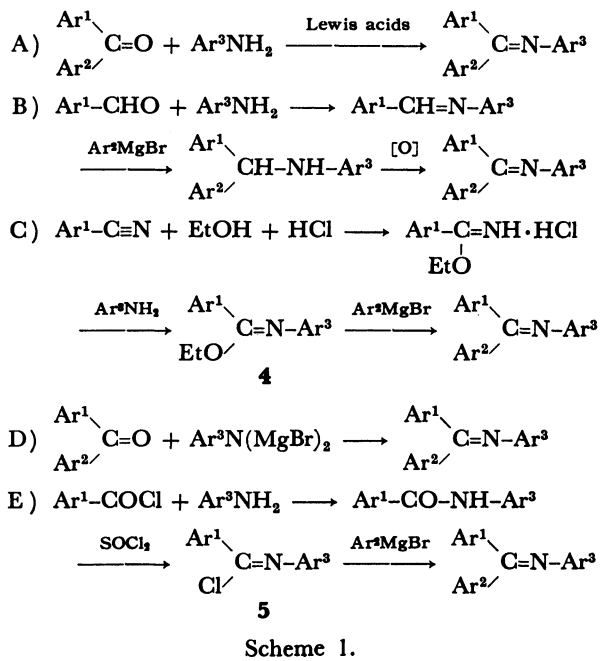
2 X = OMe, Cl (3)

The reaction of Eq. 3, however, is too sluggish, and so the study was extended to the reaction of anils with a planar fluorenylidene system (Schemes 4 and 5).

Results and Discussion

Preparation of Anils of o-*Methoxy- and* o-*Chlorobenzophenone.* In order to prepare anils of *ortho*-substituted benzophenones effectively, five possible methods (A—E, Scheme 1) were examined.

Method A is the conventional one, but it cannot be



Scheme 1.

used for *o*- and *p*-methoxy-substituted ketones and anilines.[5] Method B proved to be ineffective because the *o*-methoxy group on Ar^1 was replaced by the Ar^2 group of the Grignard reagent (*cf.* Eq. 1).[3]

Method C, which consists of an ethoxy-relacement reaction can be expected to be applicable for synthesizing the anils, since the well-known "*N*-(ethoxymethylene)aniline (**3**) procedure[6] for aldehyde synthesis" involves a quite similar reaction (Eq. 4). After

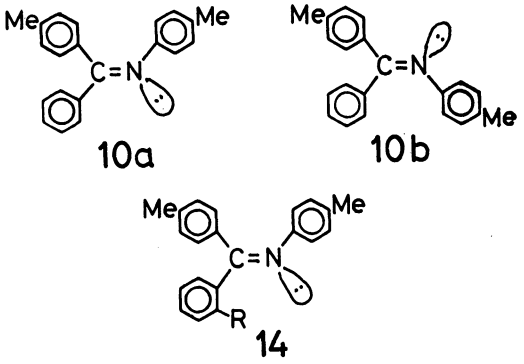
$$\underset{\mathbf{3}}{EtO\text{-}CH{=}N\text{-}Ph} \xrightarrow{ArMgBr} Ar\text{-}CH{=}N\text{-}Ph \xrightarrow{HCl} ArCHO + PhNH_2 \quad (4)$$

treatment with excess PhMgBr at 55 °C for 5 h, however, *N*-(α-ethoxybenzylidene)-*p*-methylaniline **4** ($Ar^1=C_6H_5$, $Ar^2=p\text{-}MeC_6H_4$) was recovered unchanged: this result will be discussed in the final section.

Method D, using the aryl-IDMg reagent, reported recently, is effective for preparing anils with strongly electron-releasing substituents.[5] However, the reaction of *o*-methoxybenzophenone with phenyl-IDMg gave only a 25% yield of the expected anil, even when excess molar amounts of the reagent were used.[7] The addition of excess metallic magnesium, which acts as a more efficient electron-donor than PhMgBr,[7] caused the methoxy group to be replaced by the Ar^3NH-group, the yield of the replacement product being less than 20%.

Method E proved to be the best one: It was reported earlier,[8] but was not extensively studied. When *N*-(α-chlorobenzylidene)aniline, **5**, obtained almost quantitatively by treating the corresponding benzanilides with $SOCl_2$,[8] was added at 0 °C into a THF solution of equimolar *o*-$MeOC_6H_4MgBr$, a strong exothermic reaction took place. After heating at 55 °C for 2 h and quenching with aqueous NH_4Cl, followed by usual work-up, good yields of the **6**—**13** anils were obtained (Table 1). The *o*-chloro-derivative, **9**, was prepared by the treatment of *N*-(α,*o*-dichlorobenzylidene)aniline, which had been obtained from the corresponding benzanilide, with *p*-MeC_6H_4MgBr. The *p*-chloro-derivative, **12**, was prepared similarly utilizing *o*-MeC_6H_4MgBr.

Twisted Molecular Structure and Sluggish o-*Methoxy Replacement of a Benzophenone Anil in a Grignard Reaction.* Among the anils listed in the table, the *ortho*-unsubstituted anil, **10**, shows unusual physical data. Its wide range of melting temperatures and its split pattern of CH_3-proton signals of NMR (3 : 1.5 : 1.5) indicate that the product is an equimolar mixture of *syn* and *anti* isomers, **10a** and **10b**. Taking the fact and the steric hindrance effect of *ortho*-substituents into account, the data of the other anils are assignable to the sterically preferred configuration, **14** (R=Me, MeO, and Cl).



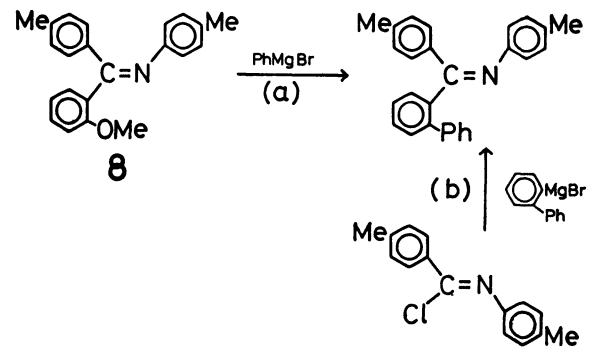
A characteristic purple coloration indicative of radical formation is observed on the treatment of the **8**, **9**, and **10** anils with PhMgBr (*cf.* Eq. 2[3]). The relative concentration of the radicals, as estimated by ESR measurement, is *o*-Cl>H>*o*-MeO.

The expected methoxy replacement of the **8** anil (Scheme 2, Path a) takes place, but the reaction is too sluggish: treatment with five molar equivalents of PhMgBr at 55 °C for 5 h afforded only a 13% yield of the replacement product, which was identified by comparison with an authentic sample prepared by an independent procedure (Path b). The addition of excess metallic magnesium[7] does not improve the yield of the

Table 1. Anils of *ortho*-substituted benzophenones prepared by Method E

No.	Anils[a] $Ar^1(Ar^2)C{=}N\text{-}Ar^3$		Mp θ_m/°C	Yield %	NMR data (δ)
6	C_6H_5, *o*-$MeOC_6H_4$	C_6H_5	78—79	87	6.60—7.92(14H,m) 3.60(3H,s)
7	C_6H_5, *o*-$MeOC_6H_4$	*p*-MeC_6H_4	136—138	73	6.52—7.84(13H,m) 3.62(3H,s) 2.21(3H,s)
8	*p*-MeC_6H_4, *o*-$MeOC_6H_4$	*p*-MeC_6H_4	132—134	79	6.50—7.72(12H,m) 3.56(3H,s) 2.36(3H,s) 2.18(3H,s)
9	*o*-ClC_6H_4, *p*-MeC_6H_4	*p*-MeC_6H_4	136—137	65	6.64—7.68(12H,m) 2.36(3H,s) 2.17(3H,s)
10	*p*-MeC_6H_4, C_6H_5	*p*-MeC_6H_4	57—68	93	6.46—7.86(13H,m) 2.24(3H,s) 2.39(1.5H,s) 2.32(1.5H,s)
11	C_6H_5, *o*-MeC_6H_4	*p*-MeC_6H_4	56—58	95	6.62—7.84(13H,m) 2.18(3H,s) 2.02(3H,s)
12	*p*-ClC_6H_4, *o*-MeC_6H_4	*p*-MeC_6H_4	111—113	61	6.60—7.80(12H,m) 2.20(3H,s) 2.02(3H,s)
13	*p*-MeC_6H_4, *p*-$MeOC_6H_4$	*p*-MeC_6H_4	126—127	81	6.60—7.80(12H,m) 3.80(3H,s) 2.18(3H,s) 2.03(3H,s)

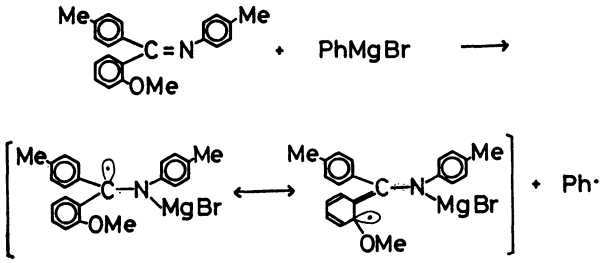
a) Group Ar^2 was introduced as Ar^2MgBr.



Scheme 2.

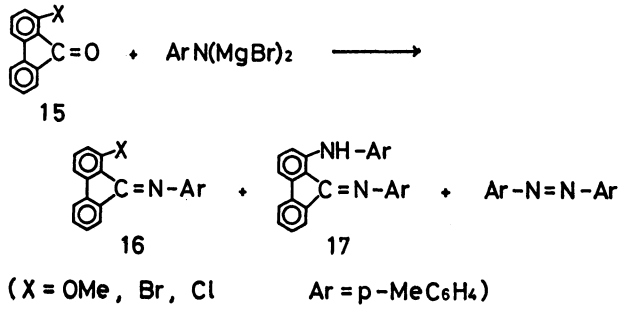
replacement product. The *o*-chloro-substituted anil, **9**, was recovered unchanged after being treated under the same reaction conditions.

On the basis of the previous observation that the free spin of the ketyl radicals of hindered benzophenones is delocalized mainly on their unhindered phenyl group,[2] the low replacement reactivity of **8** and **9** is ascribable to restricted spin-delocalization onto their *ortho*-substituted phenyl groups due to their twisting out of the plane of the >C=N– group (*cf.* Scheme 3). This suggestion is verified by the results obtained in the reaction with anils of 1-substituted fluorenones. The ESR spectrum of the radical derived from the non-substituted fluorenone anil show that the free spin is delocalized solely on its fluorenylidene moiety.[3]



Scheme 3.

Facile Replacement Reaction of 1-Substituted Fluorenones and their Anils with Aryliminodimagnesium and Grignard Reagents. Facile methoxy replacement takes place simultaneously in the condensation of 1-methoxyfluorenone, $\mathbf{15}_{MeO}$, with the *p*-methylphenyl-IDMg reagent, the reaction being carried out in preparing the



Scheme 4.

Table 2. Products in the reaction (Scheme 4) of 1-substituted fluorenones **15** with *p*-$MeC_6H_4N(MgBr)_2$

Substituent X	Molar ratio	Manner[a] of addition	Yields/%[b] 16	17	Azo	Recovery
MeO	3.0	N	20	38	0	40
MeO	1.5	R	50	11	0	39
Br	3.0	N	44	0	1	52
Cl	3.0	N	56	0	1	40

a) N and R designate "normal" and "reverse" additions respectively. b) Yields obtained after heating the reaction mixture at 55 °C for 2 h.

anil[5] (Scheme 4 and Table 2; *cf.* Scheme 1D): The normal condensation product, $\mathbf{16}_{MeO}$, and condensation-replacement product, **17**, were obtained. In contrast, 1-halogenofluorenones, $\mathbf{15}_{Br}$ and $\mathbf{15}_{Cl}$, afforded only "normal" condensation products, $\mathbf{16}_{Br}$ and $\mathbf{16}_{Cl}$, accompanied by small amounts of the azo compound, the formation of the latter being ascribable to the oxidative coupling of the reagent molecules initiated by electron-transfer due to the higher electron-accepting ability of the halogeno-fluorenones.

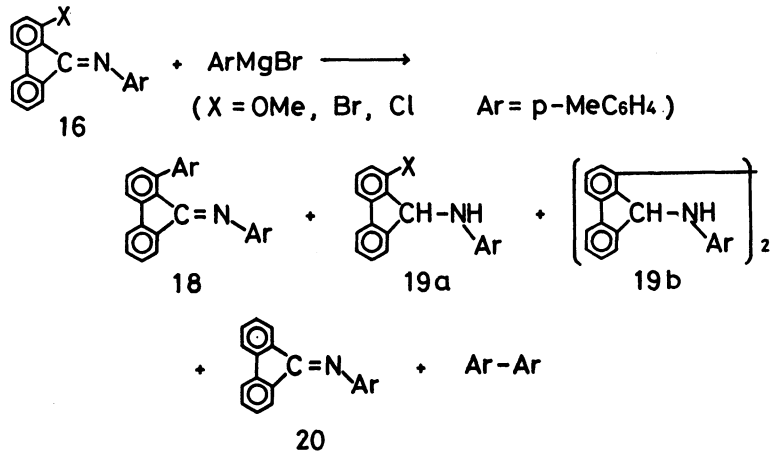
Isolated "normal" anils, $\mathbf{16}_{MeO}$, $\mathbf{16}_{Br}$, and $\mathbf{16}_{Cl}$, were submitted to the study of the reaction with *p*-MeC_6H_4MgBr (Scheme 5 and Table 3). The main reaction was the expected replacement affording **18**, the formation of by-products, **19** and **20**, being clearly explainable by the radical pathways given in Scheme 6.

The monomeric reduction product, **19a**, found only in the case of $\mathbf{16}_{MeO}$, originates from the hydrogen-abstraction of the THF molecule (Step 2) by the radical, I, resulting from the initial electron-transfer (Step 1). The dimeric reduction product, **19b**, found in the cases of $\mathbf{16}_{Br}$ and $\mathbf{16}_{Cl}$, originates from the radical, II, produced after the release of the halide anions (Step 3); the structure of the radical II is given tentatively and a detailed mechanism for the formation of **19b** is still equivocal. The dehalogenated anil, **20**, found in the reaction of $\mathbf{16}_{Br}$ and $\mathbf{16}_{Cl}$, originates from the hydrogen-abstraction of the solvent molecule (Step 4) by the radical II. Biaryl, observed in the cases of the halogeno-anils, is formed by the dimerization (Step 7) of the aryl radical generated *via* Step 1: no biaryl was detected in a control experiment carried out without the addition of a substrate. Unexpectedly, in the case of $\mathbf{16}_{MeO}$, a 1-methoxyfluorenone, $\mathbf{15}_{MeO}$, was isolated; its formation is ascribable to the attack of the water molecule upon the I radical because $\mathbf{16}_{MeO}$ itself is not

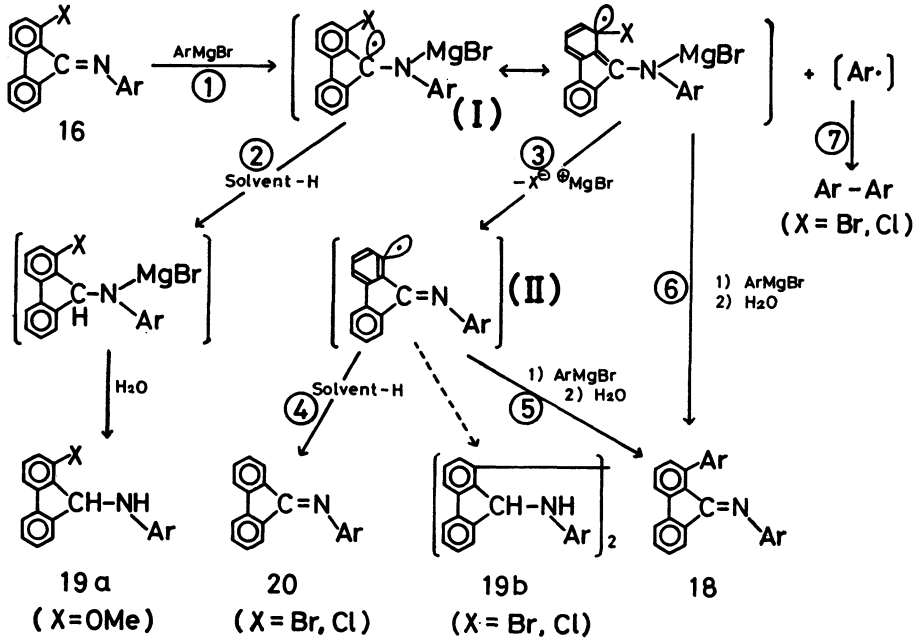
Table 3. Products in the reaction (Scheme 5) of anils of 1-substituted fluorenones **16** with *p*-MeC_6H_4MgBr

Substituent X	Molar ratio	Yields/%[b] 18	19a	19b	20	15	Ar–Ar	Recovery
MeO	3.0	67	13	0	0	14	0	5
Br	3.0	54	0	20	23	0	14	0
Cl	3.0	30	0	25	23	0	14	22

a) Yields obtained after heating the reaction mixture at 55 °C for 2 h.



Scheme 5.



Scheme 6.

hydrolyzed during treatment with aqueous NH_4Cl.

Factors Governing the Replacement Initiated by Electron-transfer. The two clearly different patterns of distribution of the main by-products observed in the Grignard reaction of Scheme 5 should be noted: $\mathbf{16}_{Br}$ and $\mathbf{16}_{Cl}$ give two dehalogenated by-products, **19b** and **20**, while $\mathbf{16}_{MeO}$ affords the methoxy-retaining **19a**. This result is indicative that, according to Scheme 6, the replacement reaction of $\mathbf{16}_{MeO}$ proceeds *via* the methoxy-retaining radical I (Step 6), while the reactions of $\mathbf{16}_{Br}$ and $\mathbf{16}_{Cl}$ proceed *via* the dehalogenated radical II (Step 5). These features are symbolically represented: an S_N1-like mechanism operates for halogen replacement, whereas an S_N2-like one operates for methoxy replacement.

The mechanistic difference is interpretable on the basis of five governing factors: i) The structure of the substrates favorable to spin-delocalization, ii) the electron-accepting (*i.e.*, oxidizing) ability of the substrates, iii) the electron-donating (*i.e.*, reducing) ability of the reagents, iv) the leaving ability of the substituents, and v) their leaving manner. The term "low (or high) reduction potential" can be substituted for "high (or low) electron-accepting ability," and the term "low (or high) oxidation potential" can be substituted for "high (or low) electron-donating ability." The lower electrophilicity of imino compounds in comparison with carbonyl compounds was reported previously;[3] however, the term "electron-accepting ability" should be substituted for "electrophilicity," since the latter term is used for explaining the reactivity in ordinary ionic reactions.

The effect of the first factor, the structure of substrates, is demonstrated by the results given above: the planar fluorenylidene structure is evidently more favorable to replacement than the twisted diarylmethylene structure. The second factor, the electron-accepting ability of the substrates (Cl>Br>MeO),

affects the initial electron-transfer from the reagent.[9] The higher electron-accepting $\mathbf{16}_{Cl}$ and $\mathbf{16}_{Br}$ cause a higher radical concentration which, in comparison with that in the case of the lower electron-accepting $\mathbf{16}_{MeO}$, is responsible for the formation of two dehalogenated products, **19b** and **20**. The formation of biaryl in the Grignard reaction of $\mathbf{16}_{Br}$ and $\mathbf{16}_{Cl}$, like that of azoarene in the IDMg reaction of $\mathbf{15}_{Br}$ and $\mathbf{15}_{Cl}$, is also ascribable to the high electron-accepting ability of the halogeno substrates.

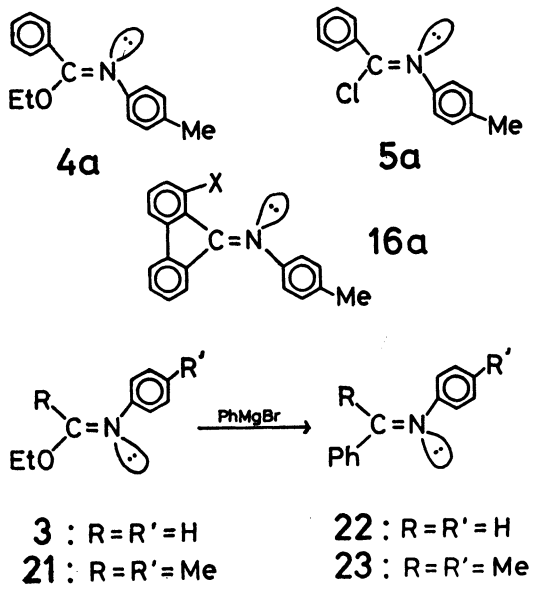
The third factor, the electron-donating ability of the reagents, also affects the intial electron-transfer process. Since the thermographic study of the Grignard reaction[1b] correlates the extent of heat evolution with that of initial electron-transfer, the very slight heat evolution detected in the reaction of $ArN(MgBr)_2$ with benzophenones[5] is indicative that the reagent is moderately electron-donating in comparison with ArMgBr. The absence of the condensation-replacement product, **17**, in the IDMg reaction with highly electron-accepting $\mathbf{15}_{Cl}$ and $\mathbf{15}_{Br}$ is ascribable to the moderate electron-donating ability of the reagent. Even *p*-methoxyphenyl-IDMg, which is more electron-donating than the *p*-methylphenyl reagent, does not afford **17** in the reaction with $\mathbf{15}_{Br}$: an improved yield of the normal anil $\mathbf{16}_{Br}$ (Ar=*p*-$MeOC_6H_4$, 78%), *ca.* a 1% yield of the debrominated anil **20** (Ar=*p*-$MeOC_6H_4$), and a trace amount of the corresponding azoarene were obtained. The effect of the electron-donating ability will be discussed again below in connection with the replacement manner of the methoxy substituent.

The fourth factor, the leaving ability of the substituents (Br>Cl>MeO), is responsible for the considerable recovery of $\mathbf{16}_{Cl}$ in comparison with the absence of any recovery of $\mathbf{16}_{Br}$, even in the reaction with highly electron-donating ArMgBr. This result is compatible with the leaving ability of groups found in ordinary S_N reactions.[10]

The fifth factor, the leaving manner of the substituents, is important for understanding the characteristic behavior of the methoxy substituent in the reactions of Schemes 4 and 5. It should be noted that the group is easily replaced by the use of the "normal addition" procedure, but the replacement is noticeably suppressed by use of the "reverse addition" procedure (Table 2). At the initial stage of the former procedure, an extremely high molar ratio of the moderately electron-donating IDMg reagent to the substrate is realized, the condition being favorable to an S_N2-like replacement of the substituent. In the reaction with the highly electron-donating Grignard reagent, even the least electron-accepting $\mathbf{16}_{MeO}$ affords a sufficiently high concentration of the radical I responsible for the formation of **19a**, which retains the methoxy substituent. The formation of **18** in this case is thus ascribable to its S_N2-like replacement manner.

The behavior of halogeno substituents in the two reactions should be discussed again in terms of their S_N1-like leaving manner. Even by the "normal addition" of the highly electron-accepting halogeno fluorenones, the moderately electron-donating IDMg reagent gives no sufficiently high radical concentration responsible for an S_N1-like halogen release, leading to the formation of **17**. In the reaction with the highly electron-donating Grignard reagent, halogeno-anils give radical concentrations sufficiently high for an S_N1-like halogen release, leading to the formation of **19b** and **20**.

Also explainable in terms of the proposed factors is the apparent contradiction found in the Grignard reactions carried out for preparing benzophenone anils (Scheme 1); Method E owes its success to the high reactivity of chloro-imine **5** whereas Method C fails because of the inertness of ethoxy-imine **4**, despite of their quite similar preferred configurations, **4a**, and **5a**. However, ethoxy-imines, **3** and **21** (Eq. 5), are converted into an aldimine, **22**,[6] and an anil, **23**, respectively, though the latter formation is slower than the former. The sterically preferred configurations and observed reactivities of the three ethoxy-imines suggest that S_N2-like alkoxy replacement requires a "syn-located" lone pair of nitrogen. Regardless of the seemingly unfavorable configuration, **5a**, its high electron-accepting ability and the S_N1-like leaving manner of chlorine supports the success of Method E.



(5)

Taking the additional factor, the configuration of the imines, into account, it is clear that the preferred configuration, **16a**, of the fluorenone anils is responsible not only for the S_N1-like halogen replacement, but also for the S_N2-like methoxy replacement with the Grignard reagent. Properly selected combinations of substrates with reagents, *i.e.*, the combination of highly oxidizing fluorenones with moderately reducing $ArN(MgBr)_2$ as well as that of moderately oxidizing anils with highly reducing ArMgBr, provides useful results for clarifying the factors which depend on each other and which govern the replacement reaction.

Experimental

The melting and boiling points are uncorrected.

Materials. *N*-(α-Ethoxybenzylidene)-*p*-methylaniline, **4**, was obtained by treating a slurry of α-ethoxybenzylideneamine hydrochloride[11] in dry benzene with equimolar *p*-

methylaniline at 60 °C for 5 h:[12] bp 125—128 °C/0.5 mmHg; NMR (CCl_4): δ=6.44—7.38 (9H, m), 4.36 (2H, q), 2.24 (3H, s), 1.40 (3H, t). The similar treatment of α-ethoxybenzylideneamine hydrochloride[11] with *p*-methyl aniline afforded *N*-(α-ethoxyethylidene)-*p*-methylaniline, **21**: bp 63 °C/0.5 mmHg; NMR (CCl_4): δ=6.94 (2H, d), 6.50 (2H, d), 4.14 (2H, q), 2.12 (3H, s), 1.72 (3H, s), 1.26 (3H, t). An authentic sample of *N*-(α-methylbenzylidene)-*p*-methylaniline, **22**, was prepared according to the reported method using $ZnCl_2$(*p*-$MeC_6H_4NH_2)_2$:[13] bp 138—143 °C/0.5 mmHg; NMR (CCl_4): δ=6.60—8.12 (9H, m), 2.45 (3H, s), 2.18 (3H, s).

N-(α-Chlorobenzylidene)-aniline and -*p*-methylaniline, as well as their nuclear-substituted derivatives, **5**, were obtained in good yields by the treatment of the corresponding benzanilides with excess $SOCl_2$.[8] An authentic sample of the *o*-phenylated anil (Scheme 2) was prepared according to Method E using the Grignard reagent derived from 2-bromobiphenyl: mp 106—107 °C; NMR ($CDCl_3$); δ=5.94—7.80 (17H, m), 2.36 (3H, s), 2.16 (3H, s).

1-Methoxyfluorenone, $\mathbf{15}_{Meo}$, was obtained by the methylation of 1-hydroxyfluorenone with Me_2SO_4 and NaOH,[14] the 1-hydroxy derivative being prepared by the diazotation of 1-aminofluorenone, followed by heating at 75—80 °C.[14] 1-Halogenofluorenones, $\mathbf{15}_{Br}$[15] and $\mathbf{15}_{Cl}$.[16] were prepared by the Sandmeyer reaction of 1-aminofluorenone. 1-Aminofluorenone was prepared starting from fluoranthene: oxidation with CrO_3 to 9-oxo-1-fluorenecarboxylic acid[17] and conversion to the amide,[15] followed by a Hofmann reaction using NaOCl.[16] For the purification of 1-substituted fluorenones, **15**, sublimation under reduced pressure was applied more conveniently than column chromatography.[14]

Procedures. All the Grignard reactions of Scheme 5 were carried out using 4.0 mmol of substrates in THF (50 ml) under N_2. The IDMg reactions were done according to the previously reported method[5] using 2.2—2.5 mmol of substrates and THF (40 ml). The Grignard reaction in the presence of metallic Mg was carried out using a reagent solution prepared from bromobenzene and a calculated excess of Mg. The yield of *o*-phenylated product of Scheme 2 was estimated by means of high-pressure liquid chromatography, using the calibration line of an authentic sample: MeOH–H_2O (65 : 35) was used as the eluent.

The ESR measurement was carried out according to the previously reported manner.[18]

Products. For the isolation and purification of the product formed in reactions of Schemes 4 and 5, column chromatography was used.

The melting point and NMR spectrum of **20** were compared with those of an authentic sample.[19] The by-product, **19a** (X=MeO), was identified by converting it into **16** (X=MeO) by dehydrogenation with freshly prepared MnO_2 in refluxing dry benzene.[20] Anils of 1-bromo- and 1-chlorofluorenone, **16**, gave the same by-product, **19b**: its dimeric structure was confirmed by molecular-weight measurement.

The melting points, NMR data, and results of elemental analyses of *N*-fluorenylideneaniline obtained in the reactions of Schemes 4 and 5 are given below: $\mathbf{16}_{Meo}$: mp 143—145 °C; NMR (CCl_4): δ=6.50—7.66 (11H, m), 4.00 (3H, s), 2.40 (3H, s). Found: C, 84.31, H, 5.65, N, 4.69%. Calcd for $C_{21}H_{17}NO$: C, 84.28, H, 5.69, N, 4.68%. $\mathbf{16}_{Br}$: mp 113—115 °C; NMR (CCl_4): δ=6.64—7.88 (11H, m), 2.42 (3H, s). Found: C, 69.01, H, 4.10, N, 3.99%. Calcd for $C_{20}H_{14}BrN$: C, 68.97, H, 4.02, N, 4.02%. $\mathbf{16}_{Cl}$: mp 139—141 °C; NMR (CCl_4): δ=6.58—7.62 (11H, m), 2.42 (3H, s). Found: C, 78.99, H, 4.57, N, 4.65%. Calcd for $C_{20}H_{14}ClN$: C, 79.08, H, 4.61, N, 4.61%. **17**: mp 118—120 °C; NMR (CCl_4): δ=9.92 (1H, s), 6.64—7.64 (15H, m), 2.44 (3H, s), 2.32 (3H, s). Found: C, 86.59, H, 5.82, N, 7.59%. Calcd for $C_{27}H_{22}N_2$: C, 86.63, H, 5.88, N, 7.49%. **18**: mp 171—173 °C; NMR (CCl_4): δ=6.54—7.68 (15H, m), 2.36 (6H, broad s). Found: C, 90.71, H, 5.81, N, 3.48%. Calcd for $C_{27}H_{31}N$: C, 90.25, H, 5.85, N, 3.90%. $\mathbf{16}_{Br}$ (Ar=*p*-$MeOC_6H_4$): mp 144—146 °C; NMR ($CDCl_3$): δ=6.72 (11H, m), 3.88 (3H, s). Found: C, 65.84, H, 3.79, N, 3.87%. Calcd for $C_{20}H_{14}BrNO$: C, 65.93, H, 3.84, N, 3.84%.

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