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Aryliminodimagnesium Reagents. XI. Two-Electron Oxidation of the Reagent Molecules in the Reaction with Some Oxidizing Agents and with Strongly Push-Pull Substituted α-Benzylideneacetophenones

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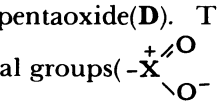
The reactions of an aryliminodimagnesium reagent ($ArN(MgBr)_2$) with four oxidizing agents ((i): I_2, OsO_4, $C_6H_5IO_2$, I_2O_5) and four push-pull substituted α-benzylideneacetophenones(ii) were examined. In the reactions with (i), the maximum yield of *sym*-azobenzene was 50%. In the reactions with (ii), in addition to products formed via condensation and the typical radical processes, unexpected products formed via cleavages of C=C and C_β–H bonds were observed. Summarizing these results, a pathway involving the formation of arylnitrene-like species via disproportionation of arylaminyl radicals ($Ar\dot{N}MgBr$) has been proposed.

Biaryl is frequently formed as a by-product in the reaction of Grignard reagent(ArMgBr) with a substrate via an electron transfer to the substrate and a subsequent radical dimerization. Similarly, symmetrical(*sym*-) azoarene(ArN=NAr) is formed as a by-product in the reaction of aryliminodimagnesium reagent($ArN(MgBr)_2$, aryl-IDMg), especially with nitrobenzenes[1)] and *ortho*-quinones.[2)] The formation of *sym*-azoarene is initiated by electron transfer from the reagent, in spite of its weak electron-donating ability(EDA),[3)] to produce arylaminyl radical($Ar\dot{N}MgBr$).[4)] However, a further removal of electrons is needed for azoarene formation; the pathway has not been studied. The previously reported yield of *sym*-azoarenes, based on the half molar amount of substrate used,[1,2)] must be reexamined for elucidating the reaction pathway.

The present authors first studied *sym*-azoarene formation in a reaction of IDMg with four oxidizing agents: iodine(**A**), osmium tetraoxide(**B**), iodylbenzene(**C**), and iodine pentaoxide(**D**). The latter three agents have functional groups( $-\overset{+}{X}(=O)O^-$: X=Os and I) that are structurally similar to the nitro group(X=N). Agents **A**—**C** proved to be more effective than nitrobenzenes for *sym*-azoarene formation, but the yield never exceeded 50%. On the other hand in the IDMg reaction with some α-benzylideneacetophenones, the formation of an abnormal product via the cleavage of C=C and C_β–H bonds was observed. Summarizing these results, the pathway for the oxidation of IDMg molecules will be discussed.

Results and Discussion

***sym*-Azoarene Formation in IDMg Reactions with Oxidizing Agents.** Oxidants **A**, **C**, and **D** are difficultly soluble in tetrahydrofuran (THF), and reactions with IDMg were carried out by adding a solution of the reagent in THF to the oxidant suspended in the same solvent at room temperature. The resulting mixture was stirred at the same temperature(or at 55 °C) for a certain number of hours. In order to avoid the oxidation of THF, oxidant **B** was dissolved in benzene. Because of the dimeric structure of *sym*-azoarenes, their yields were calculated based on the half molar amount of **A**—**D** used(summarized in Table 1(Runs 1—21)).

In the reaction with **A**(Runs 1—8), the *p*-MeO-substituted reagent is oxidized more easily than *p*-Me- and *p*-Cl-substituted ones(Runs 1, 3, and 6); prolonged heating is also effective for improving the yields (Runs 2 and 7). When two molar equivalents of **A** is used(Runs 4, 5, and 8), the yields given in the table(20 and 25%) correspond to those of 40 and 50%(based on the molar amount of IDMg used). It is thus concluded that the yield does not exceed 50%. The yield was unaffected by the addition of anhydrous $CoCl_2$, which is effective for the formation of biaryl from ArMgBr.[5)]

In the reaction of **B** with *p*-$MeOC_6H_4$–IDMg(Runs 9—12), heating the mixture for half an hour is more effective than the use of two molar equivalents of the reagent. Oxidant **B** is more effective than **A** for *sym*-azoarene formation, but the yield does not exceed 50%(again).

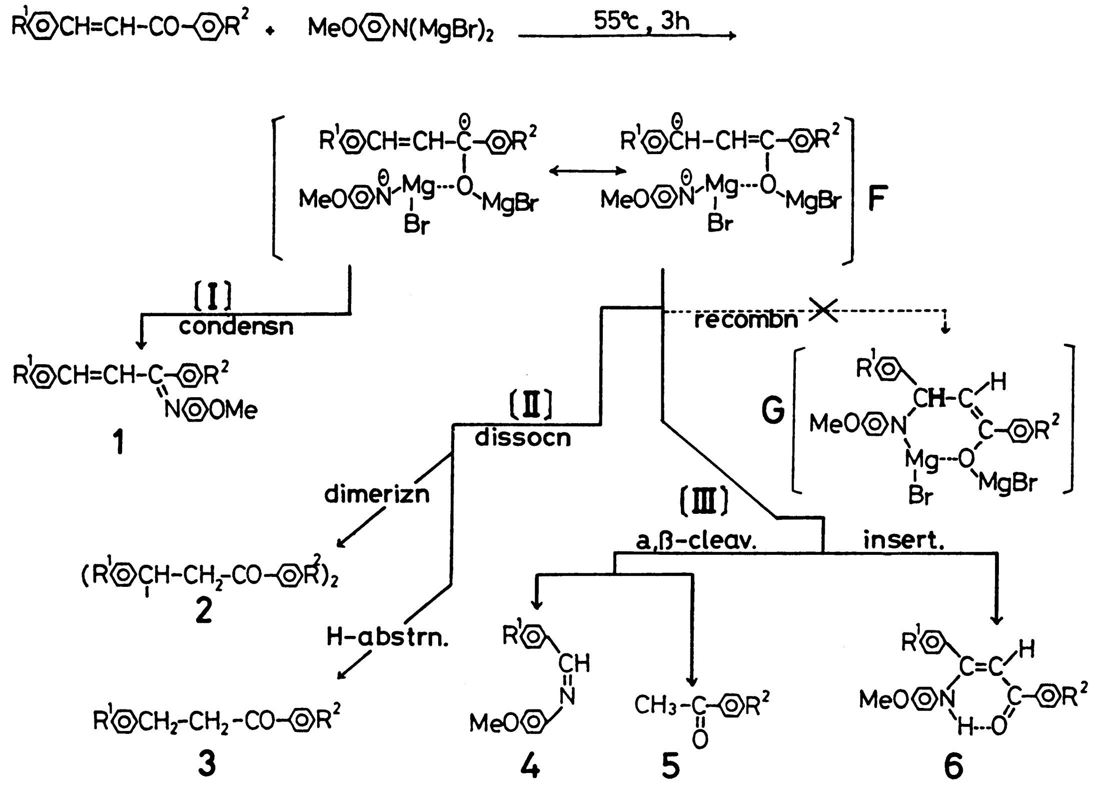
In the reaction with **C**(Runs 13—19), the use of two molar equivalents of IDMg and prolonged heating were needed for improving the yields (Runs 17 and 18), but the use of two molar equivalents of the oxidant is not effective(Run 19). The deoxygenation of **C**, affording iodobenzene in yields of 35—70%, was confirmed by GLC analyses, but the yield of *sym*-azoarene did not exceed 50%(again). An attempt to estimate the electron-accepting ability(EAA) of **C** in THF by measuring the reduction potential with cyclic voltammetry[6)] was unsuccessful due to the insolubility of **C** in the solvent. The low yield in the reaction with **D**(Runs 20 and 21) is due to its insolubility in THF.

Unusual C=C and C_β–H Cleavage of Some α-Benzylideneacetophenones in IDMg Reactions. The

Table 1. Formation of *sym*-Azoarenes from p-RC$_6$H$_4$-IDMg in the Reactions with Oxidants **A**—**D**

Run No.	Oxidant$^{a)}$	Reagent R	Mol. Ratio [Reag]/[Ox]	Reacn time/h		*sym*-Azoarenes yield/%$^{b)}$
				at r.t.	at 55 °C	
1	**A**	Cl	1.0	0	1	24
2	**A**	Cl	1.0	0.5	5	48
3	**A**	Me	1.0	0	1	28
4	**A**	Me	0.5	0.5	1	20
5	**A**	Me	0.5	0.5	5	25
6	**A**	MeO	1.0	0	1	31
7	**A**	MeO	1.0	0	5	42
8	**A**	MeO	0.5	0.5	5	20
9	**B**	MeO	2.0	2.5	0.5	45
10	**B**	MeO	1.0	2.5	0.5	45
11	**B**	MeO	1.0	3.0	0	25
12	**B**	MeO	2.0	2.5	0	29
13	**C**	MeO	1.0	0	1	22
14	**C**	Me	1.0	0	1	28
15	**C**	Me	1.0	1.5	2	23
16	**C**	Me	1.0	0	4	24
17	**C**	Me	2.0	0	3	46
18	**C**	Me	2.0	0	5	45
19	**C**	Me	0.5	0	5	15
20	**D**	Me	1.0	0	2	11
21	**D**	MeO	1.0	0	10	10

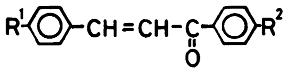
a) **A**: I$_2$, **B**: OsO$_4$, **C**: C$_6$H$_5$IO$_2$, **D**: I$_2$O$_5$. b) Yields based on the half molar amount of oxidant used.



Scheme 1.

IDMg reactions with α-benzylideneacetophenones were independent of those with the oxidants **A**—**C**, and afford no *sym*-azoarene. The results of the reactions with the enones, however, are described in this paper because the formation of some unusual products is explainable(shown below) by a pathway involving two electron oxidation of IDMg molecules. The initial plan was to examine the electronic effect of substituents of the enones on the formation of the 1,4-addition product. This product was obtained in low yield in a preliminary study[2] using an enone having substituents in the weakly pull-push manner, namely, *p*-Cl and *p*-Me substituents on the benzylidene and benzoyl moieties, respectively.

In the present study, enones having substituents in the strongly pull-push(**Ea** and **Ec**) and push-pull(**Eb** and **Ed**) manners were sumbitted to the reaction with 1.2 molar equivalents of *p*-$MeOC_6H_4$-IDMg. The molar ratio of the reagent to enone was the same as that used in the previous study.[2] Six products(**1**—**6**)


$R^1\text{-}C_6H_4\text{-}CH{=}CH\text{-}C(=O)\text{-}C_6H_4\text{-}R^2$

Ea: R^1=Cl, R^2=MeO; **Eb**: R^1=MeO, R^2=Cl;
Ec: R^1=CN, R^2=Me_2N; **Ed**: R^1=Me_2N, R^2=CN.

obtained are shown in Scheme 1 and the yields as well as the amount of recovery are summarized in Table 2. The overall amount of recovery and conversion were sufficiently high with respect to the substrate. In the reaction with **Ea**, *p*-$MeOC_6H_4$-IDMg (oxidation peak potential: 0.941 V[3]) and *p*-MeC_6H_4-IDMg(0.921 V[3]) gave **1**—**6** in almost the same yields.

The relative amounts of recovery(**Ed**>**Eb**>**Ea**>**Ec**) suggest that the σ-complex formation via coordination of an enone carbonyl oxygen to a Mg atom of the reagent governs the reactivity of enone. A similar enhancement of the reactivity by an electron-repelling substituent of the substrate was observed in IDMg reactions with benzophenones.[4] The lowest reactivity of **Ed** may be related to its resonance stabilized structure, indicated by the λ_{max} appearing at much longer wavelnegths (Table 2).

The six products are classified into three types(I—III). Each type of product and its combined yields are given in brackets in the scheme and table. Types-I(**1**) and -II(**2** and **3**) products are those expected from the previous results,[2] the former being formed via condensation and the latter being formed via typical radical pathways: dimerization and hydrogen abstraction. For elucidating the yields of Types-I and -II products, the EAA of enone is an estimate for the rapidness in generating the radical intermediate **F**(Scheme 1). The reduction potentials(redox) of **Ec**(−1.491 V) and **Ed**(−1.527 V) are consistent with the relative reactivities given above and also with the high and low yields of II. The quantumn mechanical calculations were carried out by assuming a planar geometry for estimating the spin density on the carbonyl and β-carbon of anion radicals of **Ec** and **Ed**(Fig. 1). The actual intermediate must be magnesium ketyl(**F**), but not the anion radical; the actual geometry is equivocal. However, the spin density on β-carbon is positive in the case of the

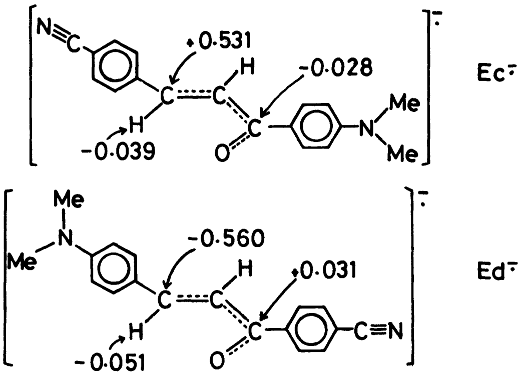


Fig. 1. Spin Density on the Radical Anions of **Ec** and **Ed**.

Table 2. Product Distribution in the Reaction of *p*-MeC_6H_4-IDMg with Pull-Push and Push-Pull α-Benzylideneacetophenones **Ea**, **Eb**, **Ec**, and **Ed**

p-$R^1C_6H_4CH{=}CHCOC_6H_4R^2$-*p*		λ_{max}/nm	Product yield/% [Type]/No.							
R^1	R^2		Recovd.	[I] **1**	[II] **2**	**3**	**4**	[III] **5**[a)]	**6**	Overall
Ea		318		[0]	[38]			[24]		
Cl	MeO		18	0	33	5	9	(10)	15	80
Eb		340		[23]	[14]			[29]		
MeO	Cl		31	23	0	14	3	(2)	26	97
Ec		352		[9]	[48]			[27]		
CN	Me_2N		2	9	48	0	19	(?)	8	86
Ed		424		[12]	[20]			[Trace][b)]		
Me_2N	CN		50	12	5	15	Trace	(0)	Trace	82

a) The yield of **5** should be the same with that of **4**, and is given in parentheses. The reason for the unsuccessful detection of **5c** is obscure. b) The trace amounts of **4d** and **6d** were identified by ^1H NMR on the basis of the singlets at δ 8.9(-CH=N-) and 13.18(>NH···O=C<), respectively.

most reactive **Ec**, while it is negative in the case of the least reactive **Ed**. The positive spin density on the β-carbon of **Ec** ketyl, which is effectively generated, is thus responsible for the high yield of II. The yield of **2** is remarkably higher than that of **3** in cases of more reactive **Ea** and **Ec**, while the yields of **3** is slightly higher than that of **2** in cases of the less reactive **Eb** and **Ed**. The relative yield of the dimeric(**2**) and monomeric(**3**) products indicates the relative rapidness in generating **F** from the former and the latter enones, and is explained similarly.

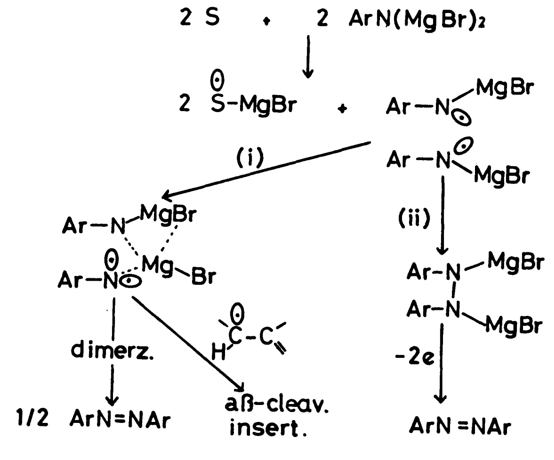
The relative yields of Type-I products(**Eb**>**Ed**>**Ec**>**Ea**) indicate that their formation is favored by the small but positive spin density on the carbonyl carbon of the enone ketyl; the effect, however, is modified by EAA.

Type III products(**4**—**6**) are those formed via an attack of a species generated from IDMg on the β-position of the enone, causing the cleavage of C=C and C_β–H bonds. No evidence for the initially expected attack of the arylaminyl radical on the β-carbon of ketyl leading to 1,4-addition product(**G**, Scheme 1) was obtained. An unusual bond cleavage was observed for the first time in reactions of the enones with Grignard and IDMg reagents;[2] the attacking species will be discussed separately in the following section.

Two-Electron Oxidation of IDMg Molecules. The seemingly poor, but significant, results suggesting the possibility of the formation of an arylnitrene-like species from IDMg molecules were obtained in the following experiments. When reactions of *p*-MeC$_6$H$_4$–IDMg with **C** was carried out in the presence of an equimolar amount of bicyclo[2.2.1] hept-2-ene(norbornene), the main product was the *sym*-azoarene and a trace amount of the corresponding 1-azirine was detected. When IDMg derived from 2-aminobiphenyl in THF was electrolyzed using Bu$_4$NClO$_4$ as a supporting electrolyte, a trace amount of carbazole was detected. No formation of carbazole was observed in reactions of 2-biphenylyl–IDMg with 2,4,6-Me$_3$-, 2-Cl-, and 4-Cl-nitrobenzenes.

In contrast to the good yields of 1-azirine and carbazole obtained in photolyses of the corresponding azides[7] and in the thermal deoxygenation of 2-nitrobiphenyl by phosphorus(III) compounds,[8] the results of the above experiments are quite poor. However, the poor yields are reasonable since the arylnitrene-like species is not free from Mg ions and is not effectively trapped by norbornene and/or by the phenyl group (vide infra). The identification of arylnitrene by the electronic absorption spectra[9] was unsuccessful because the reaction mixture was deeply colored.

The most possible pathway for generating arylnitrene-like species from an arylaminyl radical is its disproportionation shown in Scheme 2(i), which is compatible with the maximum yield of *sym*-azoarenes(vide supra). Another pathway involving the dimerization of arylaminyl radicals (Scheme 2(ii)) is suggested from the formation of a product having an *o*-(*N*,*N*′-diarylhydrazino) group in the IDMg reaction with *o*-MeO–nitrobenzene;[11] the latter scheme, however, is incompatible with the maximum yield of *sym*-azoarenes.



Scheme 2.

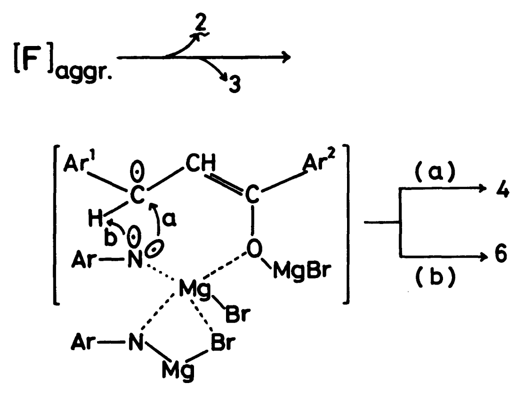
In reactions with enones, the correlation of yields of **4** and **6** with those of **2** and **3**, respectively, supports the proposal of a pathway involving the attack of arylnitrene-like species on the β-position of enone ketyl. The poor yields of **4** and **6** in the reaction with **Ed** is consistent with its weak EAA and the lowest reactivity(vide supra). As the enone varies from **Ec** via **Ea** to **Eb**, the yields of **4** and **2** increase while those of **6** and **3** decrease. The yield of **4** is always less than half of that of **2** while the yield of **6** is always higher than that of **3**.

The enone **Ec** having strong EAA generates **F** rapidly, leading to aggregate formation. Inside an aggregate of **F**, a remarkable part of the ketyl dimerizes to afford **2** in high yields, leaving arylaminyl radical behind. The interaction of two arylaminyl radicals leads to generation of an arylnitrene-like species which attacks the ketyl at its β-carbon having positive spin density to give **4**(Scheme 3a). In the case of the less reactive **Eb**, the aggregate of **F** is not greatly accumulated. A part of the ketyl detached from **F** abstracts hydrogen from the solvent, affording the lower yield of **3**. Due to the interaction of **F** with the arylaminyl radicals left behind, an arylnirene-like species is generated; it attacks the ketyl at its β-hydrogen (which has a low spin density) instead of the β-carbon (which has a negative spin density (Scheme 3b)).

The fact that only 36% molar amount of IDMg is available for affording **1**, **4**, and **6** even in the reaction with **Ec** is also compatible with the pathways of Scheme 3. Whether the other ArN-moiety regenerates IDMg or not remains to be determined. The multiplicity of arylnitrene-like species has not yet been determined because of poor direct evidences. However, a triplet state is possible since a cleavage of the C=C bond of α-benzylideneacetophenone in the manner proposed above resembles formally an effective cleavage of the same enone anion radical via an attack of triplet oxygen.[10]

General Discussion. Most probably, *sym*-azoarenes are formed via the dimerization of an arylnitrene-like species,[9] which is generated according to Scheme 2(i). The substrates having strong EAA generate arylaminyl radicals effectively, and are favorable for *sym*-azoarene formation. Another essential factor assisting its formation is the structure of the substrate. An oxidative dimerization leading to *sym*-azoarenes was observed in IDMg reactions with nitrobenzenes,[1] *ortho*-quinones,[2] and the oxidants **B** and **C**, but was not observed in a reaction with 1,4-naphthoquinones, in spite of its strong EAA.[2] The neighboring oxygen atoms of substrates as well as the iodine atoms of **A** assist the arylaminyl radicals in being generated in proximity to each other, effectively leading to *sym*-azoarenes.

α-Benzylideneacetophenones have weaker EAA's than that of nitrobenzenes and quinones, and are less favorable for the rapid generation of an arylaminyl radical. As shown, however, by the formation of **4** and **6** in the reaction of weakly electron-donating IDMg[3] with weakly electron-accepting enones, the aggregation of **F** (vide supra) participates in generating arylnitrene-like species. In the IDMg reaction with benzophenones,[4] only the condensation and typical radical products are formed, probably because the phenyl groups are more resistant than the -CH=CH- group to the attack of arylnitrene-like species. Also, the poor yield of carbazole in the electrolysis of 2-biphenylyl-IDMg is not unexpected.



Scheme 3.

In accordance with the disproportionation mechanism, the previously reported yields of *sym*-azoarenes calculated based on half molar amount of substrates need not to be revised.

Experimental

Melting points are uncorrected.

Materials and Procedures. The oxidizing agents (**A**, **B**, and **D**) were commercially avilable; **C** was prepared from iodobenzene according to a reported method.[12] The enones **Ea**—**Ed** were prepared according to the usual procedure from the corresponding benzaldehydes and acetophenones. The IDMg reagents in THF were prepared by a reported procedure.[2]

In reactions of IDMg with the oxidants, the reagents(3—5 mmol) in THF(25—40 ml) was added to the suspension of **A**—**D** in THF or benzene(30 ml). The molar ratio of the reagent to the oxidant and the reaction conditions are given in Table 1. In reactions of IDMg with the enones, the substrates(2.6 mmol) dissolved in THF(20 ml) was added at

Table 3. Melting Points and ^{1}H NMR Data of Products

No.	Mp θ_m/°C	^{1}H NMR data/δ
1b	99	7.64—7.84(1H, m), 7.10—7.52(4H, m), 6.42—7.04(7H, m), 3.81(3H, s), 3.79(3H, s).
1c	191	7.39—7.78(6H, m), 6.70—7.12(8H, m), 3.84(3H, s), 3.07(6H, s).
1d	130	7.44—7.90(3H, m), 7.08—7.32(2H, m), 6.86(4H, s), 6.60—6.96(3H, m), 3.82(3H, s), 3.00(6H, s).
2a	oil	6.68 and 7.64(8H, ABq, J=9 Hz), 7.00(8H, s), 3.68(6H, s), 2.82—3.36(6H, m).
2c	196	6.58 and 7.80(8H, ABq, J=10 Hz), 7.20—7.64(8H, m), 3.90—4.10(2H, m), 3.18—3.50 (4H, m), 3.05(12H, s).
2d	oil	7.77 and 8.06(8H, ABq, J=9Hz), 6.48—7.36(8H, m), 3.24—3.96(6H, m), 2.94(6H, m).
3a	oil	7.48—7.72(2H, m), 6.56—7.20(6H, m), 3.78(3H, s), 2.58—3.35(4H, m).
3b	61.5	7.36 and 7.82(4H, ABq, J=9 Hz), 6.72 and 7.06(4H, ABq, J=9 Hz), 3.72(3H, s), 2.92 and 3.06(4H, q, J=8 Hz).
3d	82.5	7.76 and 8.06(4H, ABq, J=8 Hz), 6.70 and 7.16(4H, ABq, J=9 Hz), 2.94—3.38(4H, m), 2.93(6H, s).
6a	114	12.62(1H, s), 7.75—7.88(2H, m), 7.24(4H, s), 6.60—6.94(6H, m), 3.80(3H, s), 3.66 (3H, s).
6b	149	13.04(1H, s), 7.88(2H, d, J=9 Hz), 7.04—7.64(4H, m), 6.56—6.92(6H, m), 5.88(1H, s), 3.90(3H, s), 3.72(3H, s).
6c	176.5	12.69(1H, s), 6.75 and 7.95(4H, ABq, J=8 Hz), 7.50 and 7.64(4H, ABq, J=10 Hz), 6.70(4H, s), 6.02(1H, s), 3.74(3H, s), 3.07(6H, s).
6d	oil	Formation confirmed by 13.18(1H, s) and 6.00(1H, s) signals.

0 °C to a solution of *p*-MeOC$_6$H$_4$–IDMg (3.1 mmol) in THF(25 ml), and the resulting mixture was stirred at 55 °C for 2 h.

All the reaction mixtures were quenched with aqueous NH$_4$Cl and the products were isolated by column chromatography on silica gel(Wako Gel C-200 and C-300).

The reaction of IDMg with **C** in the presence of norbornene was carried out as follows: *p*-MeC$_6$H$_4$–IDMg(4.0 mmol) in THF(45 ml) was added to the suspension of equimolar amounts of **C** and the hydrocarbon in THF(20 ml), and the resulting mixture was stirred under the same conditions as those of Run 15 (Table 1).

The electrolysis of 2-biphenylyl–IDMg was carried out as follows: In a flask equipped with two Pt-wire electrodes, the reagent(6.0 mmol) in THF(40 ml) containing Bu$_4$NClO$_4$ (0.1 M 1 M=21 mol dm^{-3}) was electrolyzed under the conditions of 15.0 V–0.012 A and/or 20.0 V–0.062 A for 8—10 h. Reactions of the same reagent with 2,4,6-Me$_3$-, 2-Cl-, and 4-Cl-nitrobenzenes were carried out using a molar ratio of 2.5 at 55 °C for 2 h; the reaction mixtures were worked up according to the manner described above.

The reduction potentials(redox) of the enones **Ec** and **Ed** were measured in THF according to the reported method.[6]

The calculation of spin density was carried out within the framework of ab initio spin-unrestricted Hartree–Fock-(UHF) theory, using the STO-3G set[13] and standard geometry.[14]

Products. The results of elemental analyses and ^{1}H NMR data of the products **1**, **2**, **3**, and **6** are satisfactory. The melting points and ^{1}H NMR data are summarized in Table 3. Products **4** and **5** were identified by comparing their ^{1}H NMR spectra with those of commercially available and/or easily prepared authentic samples.

A trace amount of 1-azirine derived from norbornene was detected on the basis of the characteristic doublets appearing at δ 1.5—4.5.[7] A trace amount of carbazole was identified by a comparison with the characteristic doublet appearing at δ 8.2.

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