Reactions of a 1,4-Benzquinone Diimine Derivative with Diphenylamines and Related Compounds

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The reaction of N₁,N₄-bis(ethoxycarbonyl)-1,4-benzoquinone diimine (1), a derivative of 1,4-benzoquinone, with diphenylamines, anilines, and phenols gives two types of products: oxidative coupling products (or the oxidized product of an oxidative coupling product) with a reduced product, and adducts. Both types of products are formed through a radical cage pair that is produced by electron and proton transfer within an electron donor-acceptor complex. Electronically or sterically stabilized radicals escape from the radical cage to undergo a radical homo-coupling reaction. Radicals that are not stabilized undergo radical coupling inside the radical cage to yield adducts.

Keywords: benzoquinone diimine, electron donor-acceptor complex, radical cage pair, radical coupling

1. Introduction

The reactions of 1,4-benzoquinone diimine and related compounds attracted our interest because 1,4-benzoquinone undergoes versatile reactions. While 1,4-benzoquinone diimine is not sufficiently stable to be isolated due to oxidation and the addition of nucleophiles, the substitution of the hydrogen atoms of the NH-groups with electron-withdrawing groups such as acyl, aryl, or benzenesulfonyl groups yields isolable compounds with various reactivities, including 1-addition with nucleophiles, 1,2-cycloaddition with dienes and diazomethanes, 1,3-cycloaddition with enamines, B⁢F₃-promoted 1,3-cycloaddition with alkenes, and the addition of phosphorous compounds.

As reported previously, N₁,N₄-bis(ethoxycarbonyl)-1,4-benzoquinone diimine (1) underwent addition reactions with substituted anilines and phenols at room temperature to give adducts in good yields, and the reaction of 1 with a sterically hindered phenol gave a diphenoquinone. The reactions of N₁,N₄-dibenzoyl and N₁,N₄-bis-4-toluenesulfonyl-1,4-benzoquinone diimine with anilines and phenols gave similar adducts, which were not sufficiently soluble in hot solvents to be recrystallized. Because the isolation and purification of the adducts of 1 with anilines and phenols are easily performed, we thoroughly investigated the reactions of 1.

This article describes the reaction of 1 with 4,4'-disubstituted diphenylamines (2) to give oxidative coupling products, tetraaryldihydrazines (3), in good yields. The reaction likely proceeds through the homo-coupling of N-radicals that are formed by electron and proton transfer in an electron donor-acceptor complex. This finding prompted us to reexamine the addition reactions of 1 with aniline and phenol, especially the reaction with the latter. The reactions with phenol were analyzed to determine the effects of the solvent, acids, and bulky substituents. The addition reaction likely proceeds through radical coupling inside a radical cage pair that is also formed by electron and proton transfer in an electron donor-acceptor complex.

2. Results and Discussion

2.1 Reaction of N₁,N₄-bis(ethoxycarbonyl)-1,4-benzoquinone diimine (1) with diarylamines (2)

Upon mixing a yellow solution of 1 (0.20 M) with an equal volume of a colorless solution of a diarylamine (2) (0.44 M), the color of the solution turned reddish purple. After the solution was left standing at room temperature, the color faded, and a tetraaryldihydrazine (3) and N₁,N₄-bis(ethoxycarbonyl)-1,4-phenylenediamine (4) were obtained. A preliminary experiment to monitor the reaction in benzene with TLC analysis demonstrated that twice as much 2a as 1 (on a molar basis) was required for the complete consumption of 1. The yields of 3a-d
and 4 in the reaction of 1 with 2a-d in benzene are shown in Table 1. The yields of 3a-c were higher, but 3d was obtained in a lower. The yield of 4 was higher irrespective of the substituents of 2. To analyze the solvent effect, the reaction of 1 with 2a was also carried out in acetonitrile (MeCN) and tetrahydrofuran (THF). As shown in Table 2, the formation of 3a was not seriously affected by the solvent.

Monitoring the reaction with TLC analysis showed that the reactions of 1 with 2a, 2b, and 2d in benzene were completed in 2 h under the reaction conditions described at the footnote in Table 1, whereas the complete consumption of 1 in the reaction with 2c required 25 d. The reaction of 1 with 2a in the other solvents was also completed within 2 h. The reaction of 1 with 2a in benzene under an argon atmosphere proceeded to give 3a as observed under aerobic conditions.

**Table 1. Yields of 3a-d in the reaction of 1 with 2a-d in benzene**

<table>
<thead>
<tr>
<th>Solvent</th>
<th>3a (%)</th>
<th>3b (%)</th>
<th>3c (%)</th>
<th>3d (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeCN</td>
<td>78</td>
<td>70</td>
<td>77</td>
<td>30</td>
</tr>
<tr>
<td>THF</td>
<td>78</td>
<td>79</td>
<td>84</td>
<td>83</td>
</tr>
</tbody>
</table>

[1]₀ = 0.10, [2a]₀ = 0.22 M

**Table 2. Yields of 3a in the reaction of 1 with 2a**

<table>
<thead>
<tr>
<th>Solvent</th>
<th>3a (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeCN</td>
<td>78</td>
</tr>
<tr>
<td>THF</td>
<td>78</td>
</tr>
</tbody>
</table>

[1]₀ = 0.10, [2a]₀ = 0.22 M

An electronic absorption spectrum of a solution of 1 and a diarylamine (2) showed a weak CT absorption band at approximately 500 nm. The spectra observed for a solution of 1 and 2a in MeCN are shown in Figure 1A. When the concentration of either 1 or 2a was less than 10⁻² M, no CT absorption bands were detectable. A solution containing 1 (0.02 M) and 2a (0.01-0.05 M) showed a CT absorption band at 500-600 nm that increased in intensity with an increasing concentration of 2a although the solution was still yellow with a slight darkening (the yellow color was due to 1, which exhibits a broad tail on the strong absorption band at 281 nm that stretches over 470 nm). The CT absorption band was observed more distinctly in benzene (Figure 1B). A solution prepared for the synthesis of 3a was reddish purple, as described above.

**Figure 1A.** Electronic absorption spectra of the solutions of 1 and 2a in MeCN: (a) [1] = 0, [2a] = 2 x 10⁻²; (b) [1] = 2 x 10⁻³, [2a] = 0; (c) [1] = [2a] = 2 x 10⁻²; (d) [1] = [2a] = 2 x 10⁻¹; (e) [1] = [2a] = 2 x 10⁻¹; (f-k) [1] = 2 x 10⁻³, [2a] = 0 (f), 1 x 10⁻³ (g), 2 x 10⁻² (h), 3 x 10⁻² (i), 4 x 10⁻² (j), and 5 x 10⁻² M (k).

**Figure 1B.** Electronic absorption spectra of the solutions of 1 and 2a in benzene: [1] = 2 x 10⁻² (a-f); [2a] = 0(a), 1 x 10⁻¹ (b), 2 x 10⁻² (c), 3 x 10⁻² (d), 4 x 10⁻² (e), and 5 x 10⁻² M (f).

As shown in Scheme 1, the most plausible route for the formation of 3a is the radical coupling of diarylaminyl radical 6, which is produced by electron and proton transfer inside an electron donor-acceptor complex between 1 and 2. The slow reaction rate of 1 with 2c can be explained by the electron-withdrawing ability of the substituent, which retards the electron transfer in the complex. Another radical species 7 derived from radical cage pair 5 is expected to abstract the H atom from 2 to give 4 and 6, and/or disproportionate to give 1 and 4. The formation of 3d in a lower yield can be explained by the consumption of radical intermediate 6d by oligomerization, which was postulated to explain the thermal decomposition of 3d.
It is possible that 6 is produced by the decomposition of 8, which may be formed by radical coupling inside radical cage pair 5 as in the reaction of 1 with aniline (see the Section 2.2). When monitoring the reaction in C₆D₆ with ¹H NMR spectroscopy, a singlet due to the methyl group of 3a at δ 2.01 appeared immediately after mixing a solution of 1 with a solution of 2a in C₆D₆, and no other signals suggesting other chemical species, such as 8a, were observed. These observations indicate that 6 is sufficiently stabilized by the conjugation of two aryl groups to escape from radical cage pair 5.

Table 3. Yields of 9 in the reaction of 1 with aniline

<table>
<thead>
<tr>
<th>Solvent</th>
<th>C₆H₆</th>
<th>MeCN</th>
<th>THF</th>
</tr>
</thead>
<tbody>
<tr>
<td>9 (%)</td>
<td>85</td>
<td>82</td>
<td>73</td>
</tr>
</tbody>
</table>

The solution used for the synthesis of 9 was orange-yellow. The CT absorption spectrum of a solution of 1 and aniline in benzene is shown in Figure 2. This spectrum had an increased slope for the strong absorption band of 1.

The reaction is thought to proceed through Scheme 2; that is, electron and proton transfer occur in an electron donor-acceptor complex between 1 and aniline to give radical cage pair 10. The components of 10 couple inside the radical cage to give iminocyclohexadienyl compound 11, which isomerizes to yield 9. The formation of oxidative coupling product 13 does not proceed because the stabilization of aminyl radical 12 by one phenyl group is not sufficient for 12 to escape from the radical cage.

2.2 Reaction of N₁,N₄-bis(ethoxycarbonyl)-1,4-benzoquinone diimine (1) with diarylamines (2)

Tetraarylhydrazines (3) have been previously prepared by the oxidation of 2 with KMnO₄¹¹-¹⁴ or PbO₂¹¹,¹⁵ and by the oxidation of diphenylamidates with iodine,¹⁶ for which the yields were generally lower and repeated purification was required. The reaction of 1 with 2 provides an alternative route for the synthesis of 3 because the reaction proceeds easily at room temperature with facile isolation.

![Scheme 1. Reaction of N₁,N₄-bis(ethoxycarbonyl)-1,4-benzoquinone diimine (1) with diarylamines (2)](image)

Table 3. Yields of 9 in the reaction of 1 with aniline

<table>
<thead>
<tr>
<th>Solvent</th>
<th>C₆H₆</th>
<th>MeCN</th>
<th>THF</th>
</tr>
</thead>
<tbody>
<tr>
<td>9 (%)</td>
<td>85</td>
<td>82</td>
<td>73</td>
</tr>
</tbody>
</table>

Figures 2. Electronic absorption spectra of the solutions of 1 and aniline in benzene: [1] = 2 x 10⁻² (a-f); [aniline] = 0 (a), 1 x 10⁻² (b), 2 x 10⁻² (c), 3 x 10⁻² (d), 4 x 10⁻² (e), and 5 x 10⁻² M (f).

![Scheme 2. Reaction of 1 with aniline](image)
2.3 Reaction of $N^1, N^4$-bis(ethoxycarbonyl)-1,4-benzoquinone diimine (1) with phenols (14)

2.3.1 Reaction of $N^1, N^4$-bis(ethoxycarbonyl)-1,4-benzoquinone diimine (1) with phenol (14a)

As for the reaction with aniline, the reaction of 1 with phenol (14a) in benzene gave an addition product, $N^1, N^4$-bis(ethoxycarbonyl)-N$^1$-(4-hydroxyphenyl)-1,4-phenylenediamine (15a), at room temperature in the presence of benzoic acid, as reported previously. To examine the effects of benzoic acid and solvents, the reaction of 1 with 14a was carried out in benzene, MeCN, and THF in the presence of various concentrations of benzoic acid. As shown in Table 4, the yields of 15a increased in each solvent with increasing benzoic acid concentrations and were higher in benzene than in the other solvents. At a lower concentration of benzoic acid, the yield of 15a was lower in all solvents, and a considerable amount of 4 was formed together with tarry products, from which no characterizable compounds were isolated. Monitoring the reaction with TLC analysis revealed that 1 was consumed in a few hours in any of the above solvents without benzoic acid and was more rapidly consumed in the presence of benzoic acid.

In contrast to the color of the solution of 1 and aniline, the color of a solution of 1 remained unchanged after the addition of a solution of 14a, and no broadening of the absorption band of 1 was detected. The reaction of 1 with 14a is thought to proceed through the reaction pathway depicted in Scheme 3 based on the reactions of 1 with 2,6-di-t-butylphenol (14d) (see the Section 2.3.4). Due to the weaker electron-donating ability of 14a, the molecular interaction in the electron donor-acceptor complex between 1 and 14a is so weak that the addition reaction does not proceed effectively, resulting in a lower yield of 15a. The ability of benzoic acid to increase the yield of 15a can be explained by the acid catalysis of the electron and proton transfer in the electron donor-acceptor complex because the acid catalysis of electron and proton transfer in these complexes is well documented. The higher yield of 15a in benzene than in the other solvents can be explained by supposing the favorable formation of an electron donor-acceptor complex in benzene because the equilibrium concentration of the CT complex is generally higher in non-polar solvents than in polar solvents.

An alternative pathway is a reaction through the electrophilic attack of phenol by the protonated form of 1, that is, the conventional mechanism of electrophilic aromatic substitution. However, this type of mechanism is not possible for our reaction because 1 did not react with anisole, which is more reactive than phenol.

![Table 4](image)

Table 4. Y yields of 15a and 4 in the reaction of 1 with phenol

<table>
<thead>
<tr>
<th>Solvent</th>
<th>MeCN</th>
<th>THF</th>
</tr>
</thead>
<tbody>
<tr>
<td>BA*(M)</td>
<td>2.0x10^-4</td>
<td>2.0x10^-3</td>
</tr>
<tr>
<td>15a (%)</td>
<td>21</td>
<td>45</td>
</tr>
<tr>
<td>4 (%)</td>
<td>21</td>
<td>18</td>
</tr>
</tbody>
</table>

![Scheme 3](image)

Scheme 3. Reaction of 1 with phenols (14a-c)

2.3.2 Reaction of $N^1, N^4$-bis(ethoxycarbonyl)-1,4-benzoquinone diimine (1) with 3,5-di-t-butylphenol (14b)

Upon mixing a yellow solution of 1 with a colorless solution of 3,5-di-t-butylphenol (14b) in benzene in the absence of benzoic acid, the solution instantaneously turned colorless to give an adduct in 75% yield. The yield of the adduct increased to 87% in the presence of benzoic acid (2 x 10^-4 M). The $^1$H and $^{13}$C NMR spectra of the adduct identified the product as $N^1, N^4$-bis(ethoxycarbonyl)-N$^1$-(2,6-di-t-butyl-4-oxo-2,5-cyclohexadienyl)-1,4-phenylenediamine (17b). This identification of 17b as the product of this reaction supports the hypothesis that the reaction of 1 with 14a proceeds through Scheme 3 via 17a, which isomerizes immediately to 15a by proton transfer. The C-1 position...
of the 4-oxo-2,5-cyclohexadienyl moiety of 17b is blocked by two neighboring t-butyl groups, allowing the isolation of 17b.

2.3.3 Reaction of \(N^1, N^4\)-bis(ethoxycarbonyl) - 1,4-benzoquinone diimine (1) with 3-t-butylphenol (14c)

When 1 was reacted with 3-t-butylphenol (14c) in benzene in the presence of benzoic acid (2 x 10^{-3} M), \(N^1, N^4\)-bis(ethoxycarbonyl) - 1,4-phenylenediimide (15c) was obtained in 91% yield. The reaction is expected to proceed through Scheme 3 via 17c. The attack by a base on the H atom at C-1 of the 4-oxo-2,5-cyclohexadienyl moiety of 17c may be partially hindered by the t-butyl group at C-2, thus decreasing the rate of the conversion of 17c into 15c. Therefore, the transient concentration of 17c is expected to be sufficiently high to be observed by \(^1H\) NMR spectroscopy.

![Figure 3. \(^1H\) NMR spectral changes of a solution of 1 and 14c (each 5 x 10^{-2} M) in C_{6}D_{6} at room temperature: (A) at 14 min after mixing in the absence of benzoic acid; (B) - (E) at 16, 38, 65, and 254 min, respectively, after mixing in the presence of benzoic acid (2 x 10^{-3} M). Peak assignments; a, t-Bu of 14c; b, t-Bu of 17c; c, t-Bu of 15c.](image)

Thus, the reaction of 1 with 14c (each 5 x 10^{-2} M) in C_{6}D_{6} was monitored by \(^1H\) NMR spectroscopy. Soon after making a solution of 1 and 14c without benzoic acid, there appeared a strong singlet (signal a) at \(\delta 1.22\) due to the t-butyl group of 14c and another faint singlet (signal b) at \(\delta 1.06\) (Figure 3, A). Immediately after making another solution containing benzoic acid (2 x 10^{-3} M) \(^2\), there appeared another singlet, signal b, with a strong intensity and another weak singlet (signal c) at \(\delta 1.26\) in addition to signal a (Figure 3, B). As time passed (Figure 3, C-E), the intensity of signal a decreased gradually, and that of signal c increased, whereas the intensity of signal b increased at the early stage and then decreased. Finally, signal c was present, and signals a and b disappeared. The chemical shift of signal c coincided with that of the t-butyl group of 15c in C_{6}D_{6}. With the assignment of the signal b to the t-butyl group of 17c, the above changes in the \(^1H\) NMR spectrum over time are indicative of the formation of 15c through 17c.

2.3.4 Reaction of \(N^1, N^4\)-bis(ethoxycarbonyl) - 1,4-benzoquinone diimine (1) with 2,6-di-t-butylphenol (14d)

As reported previously, \(^9\) the reaction of 1 with 2,6-di-t-butylphenol (14d) proceeded through the routes shown in Scheme 4 in the absence of benzoic acid to give 3,3',5,5'-tetra-t-butyl-4,4'-diphenoquinone (21) and 4. Phenox radical 18, the radical center of which is blocked by bulky substituents, escapes from radical cage pair 16d to undergo a homo-coupling reaction to give 19, which is oxidized to 21 through 20. The formation of 21 proceeded rapidly in polar solvents such as MeCN, and THF and slowly in non-polar solvents such as chloroform and benzene. The slower rate in the latter solvents is due to the slower conversion of 19 into 20 in those solvents.

![Scheme 4. Reaction of 1 with 2,6-di-t-butylphenol (14d)](image)

3. Conclusion

Two types of reactions were observed in the reaction of 1 with diarylamines (2), aniline and phenols (14). In the reaction of 1 with diarylamines 2a-d and 2,6-di-t-butylphenol (14d), oxidative homo-coupling proceeded to give 3a-d and 19, respectively, with a concomitant formation of 4. The isomerization of 19 with successive oxidation gave 21 as the isolated...
product. In the reaction of 1 with aniline and phenols 14a-c, addition reactions proceeded to give adducts 11 and 17a-c respectively. While 11, 17a and 17c isomerized to give 9, 15a and 15c respectively, 17b was stable to be isolated. Either type of reactions, that is, oxidative-coupling and addition, can be systematically interpreted as proceeding through a radical cage pair that is formed by electron and proton transfer in an electron donor-acceptor complex. A radical that is not stabilized as above undergoes coupling inside the radical cage to give an adduct. Thus, the reaction mode shifts from radical coupling inside a radical cage pair to give a reaction outside a radical cage based on the stability of the intermediate radical.

From a synthesis viewpoint, 1 is useful as a mild oxidizing reagent for diarylamines to give tetraarylhydrazines because the reaction proceeds easily at room temperature with a simple isolation procedure.

4. Experimental

4.1 General

N₁, N₄-bis(ethoxycarbonyl)-1,4-benzoquinone diimine (1) was synthesized according to the procedure described by Adams and Anderson,²² with use of 1,2-dichloroethane as a solvent instead of diethyl ether. The solvents used for the reaction of 1 were purified as follows. Benzene (guaranteed grade) was distilled and dried at ca. 80 °C in vacuo. After the reactions of 1,4-benzoquinone diimine (1) with 1.0 mmol each of diarylamines, the concentrated filtrate of the reaction solution was recrystallized from THF-hexane. The purification of 3b by chromatography on a silica-gel column was unsuccessful because 3b was partly decomposed. In the reaction with diphenylamine (2d), the black concentrated residue of the filtrate was repeatedly extracted with hot hexane, but a considerable amount of tar was left unextracted. The combined extract was concentrated, yielding a brown semi-solid that was subjected to chromatography on a short column to give 3d, which was recrystallized from hexane.

4.2 Reaction of N₁, N₄-bis(ethoxycarbonyl)-1,4-benzoquinone diimine (1) with diarylamines (2)

A solution of 1.0 mmol of 1 in 5 mL of a solvent was combined with a solution of 2.2 mmol of a diarylamine (2) in 5 mL of the same solvent. While the solution was left standing at room temperature, the intense color of the solution faded, and a colorless solid, N₁, N₄-bis(ethoxycarbonyl)-1,4-phenylenediamine (4), was crystallized out. After being filtered off, the solid was recrystallized from THF-hexane.

After the reactions of 1 with di-4-tolyamine (2a) and bis-(4-bromophenyl)amine (2c), the concentrated residues of the filtrates of the reaction solutions were purified by chromatography on a short column to give 3a and 3c respectively, which were recrystallized from hexane-ethyl acetate. In the reaction with bis-(4-t-butylphenyl)amine (2b), the solid residue obtained by concentrating the filtrate of the reaction solution was recrystallized from benzene-methanol to give 3b. The purification of 3b by chromatography on a silica-gel column was unsuccessful because 3b was partly decomposed. In the reaction with diphenylamine (2d), the black concentrated residue of the filtrate was repeatedly extracted with hot hexane, but a considerable amount of tar was left unextracted. The combined extract was concentrated, yielding a brown semi-solid that was subjected to chromatography on a short column to give 3d, which was recrystallized from hexane.

4.2.1 Tetra-4-tolyldihydrazine (3a)

Mp 136-138 °C (lit. 136 12, 143-144 °C ¹³); ¹H NMR (400 MHz, CDCl₃): δ 2.21 (s, 3H), 7.04 (d, J = 8.8 Hz, 2H), 7.17 (d, J = 8.8 Hz, 2H); ¹³C NMR (400 MHz, CDCl₃): δ 20.6, 117.8 (2C), 129.6 (2C), 130.9, 141.3.

4.2.2 Tetra-4-t-butyldihydrazine (3b)

Mp 167-168 °C (lit. 179-180 °C ¹⁴); ¹H NMR (400 MHz, CDCl₃): δ 1.26 (s, 9H), 7.18 (d, J = 8.8 Hz, 2H), 7.21 (d, J = 8.8 Hz, 2H); ¹³C NMR (400 MHz, CDCl₃): δ 31.4 (3C), 34.1, 117.5 (2C), 125.7 (2C), 141.7, 144.1.

4.2.3 Tetra-4-bromophenylhydrazine (3c)

Mp 131-134 °C (lit. 144-145 °C ¹⁵); ¹H NMR (400 MHz, CDCl₃): δ 7.08 (d, J = 8.8 Hz, 2H), 7.31 (d, J = 8.8 Hz, 1H); ¹³C NMR (400 MHz, CDCl₃): δ 115.1, 119.6 (2C), 132.4 (2C), 141.6.

4.2.4 Tetraphenylhydrazine (3d)

Mp 143-144 °C (lit. 141-142 °C ¹², 144 ¹¹, 147 °C ¹⁶); ¹H NMR (400 MHz, CDCl₃): δ 6.89 (t, J = 7.2 Hz, 1H), 7.19 (dd, J = 7.2 and 7.6 Hz, 2H), 7.30 (d, J = 7.6 Hz, 2H); ¹³C NMR (400 MHz, CDCl₃): δ 118.0 (2C), 122.0, 129.0 (2C), 143.4.
4.2.5 $N^1, N^4$-Bis(ethoxy carbonyl)-1,4-phenylenediamine (4)

M p 201-203°C (lit. 194-195°C); $^1$H NMR (400 MHz, THF-d$_8$): $\delta$ 1.24 (t, $J$ = 7.2 Hz, 3H), 4.46 (q, $J$ = 7.2 Hz, 2H), 7.33 (s, 2H), 8.47 (s, 1H); $^{13}$C NMR (400 MHz, THF-d$_8$): $\delta$ 15.1, 60.9, 119.3 (2C), 135.5, 154.4.

4.3 Reaction of $N^3, N^5$-bis(ethoxy carbonyl)-1,4-benzoquinone diimine (1) with aniline

A solution of 1 mmol of 1 in 5 mL of a solvent was combined with a solution of 2 mmol of aniline in 5 mL of the same solvent. After the reaction, the reaction solution was concentrated to a syrup, from which the colorless solids $N^3, N^5$-bis(ethoxy carbonyl)-$N^1, N^4$- (4-aminophenyl)-1,4-phenylenediamine (9) was isolated by column chromatography and recrystallized from acetone-hexane.

4.3.1 $N^3, N^5$-Bis(ethoxy carbonyl)-$N^1$- (4-aminophenyl)-1,4-phenylenediamine (9)

M p 137-139°C; $^1$H NMR (400 MHz, acetone-d$_6$): $\delta$ 1.15 (t, $J$ = 7.2 Hz, 3H), 1.23 (t, $J$ = 7.2 Hz, 3H), 4.11 (q, $J$ = 7.2 Hz, 2H), 4.15 (q, $J$ = 7.2 Hz, 2H), 4.64 (s, 2H), 6.64 (d, $J$ = 8.8 Hz, 2H), 6.96 (d, $J$ = 8.8 Hz, 2H), 7.21 (d, $J$ = 8.8 Hz, 2H), 7.49 (d, $J$ = 8.8 Hz, 2H), 8.58 (s, 1H); $^{13}$C NMR (400 MHz, acetone-d$_6$): $\delta$ 14.8, 14.9, 61.1, 61.8, 115.1(2C), 119.1(2C), 127.6(2C), 129.1(2C), 133.4, 137.6, 139.4, 147.7, 154.5, 155.6.

4.4 Reaction of $N^3, N^5$-bis(ethoxy carbonyl)-1,4-benzoquinone diimine (1) with phenols (14)

A solution of 1 mmol of 1 in 5 mL of a solvent was combined with a solution of 2 mmol of phenol (14a) in 5 mL of the same solvent containing benzoic acid, the concentrations of which are listed in Table 4. The reaction solution was left standing overnight at room temperature. The colorless solid $N^3, N^5$-bis(ethoxy carbonyl)-$N^1$-(4-hydroxyphenyl)-1,4-phenylenediamine (15a) crystallized out. In the reaction in THF, a smaller amount of 15a crystallized out than in the other solvents. After the crystals were filtered off, the filtrate was combined with a solution of 2 mmol of aniline in 5 mL of a solvent was isolated by column chromatography to give 4 and more 15a. Both 4 and the combined crystals of 15a were recrystallized from THF-hexane.

The reaction of 1 with 3,5-di-t-butylphenol (14b) in benzene was carried similarly in the absence and presence of benzoic acid (2 x $10^{-2}$ M). In both reactions, 1 was immediately consumed, and the solids $N^3, N^5$-bis(ethoxy carbonyl)-$N^1$-(2,6-di-t-butyl-4-oxocyclohexadienyl)-1,4-phenylenediamine (17b) and $N^3, N^5$-bis(ethoxy carbonyl)-$N^1$-(2-t-butyl-4-hydroxyphenyl)-1,4-phenylenediamine (15c) crystallized out after standing overnight. More product was recovered from the supernatant by column chromatography. The combined crystals of 17b and those of 15c were recrystallized from THF-hexane.

4.4.1 $N^3, N^5$-Bis(ethoxy carbonyl)-$N^1$-(4-hydroxyphenyl)-1,4-phenylenediamine (15a)

M p 163-165°C; $^1$H NMR (400 MHz, acetone-d$_6$): $\delta$ 1.15 (t, $J$ = 7.2 Hz, 3H), 1.23 (t, $J$ = 7.2 Hz, 3H), 4.12 (q, $J$ = 7.2 Hz, 2H), 4.15 (q, $J$ = 7.2 Hz, 2H), 6.82 (d, $J$ = 8.8 Hz, 2H), 7.12 (d, $J$ = 8.8 Hz, 2H), 7.21 (d, $J$ = 8.8 Hz, 2H), 7.51 (d, $J$ = 8.8 Hz, 2H), 8.38 (s, 1H), 8.61 (s, 1H); $^{13}$C NMR (400 MHz, acetone-d$_6$): $\delta$ 14.8, 14.9, 61.1, 62.0, 116.2(2C), 119.2(2C), 128.0(2C), 129.4(2C), 135.9, 137.9, 139.0, 154.5, 155.5, 156.4.

4.4.2 $N^3, N^5$-Bis(ethoxy carbonyl)-$N^1$-(2,6-di-t-butyl-4-oxocyclohexadienyl)-1,4-phenylenediamine (17b)

M p 178-180°C; $^1$H NMR (400 MHz, C$_6$D$_6$): $\delta$ 0.83 (t, $J$ = 7.0 Hz, 3H), 1.02 (t, $J$ = 7.0 Hz, 3H), 1.16 (s, 18H), 3.94 (q, $J$ = 7.0 Hz, 2H), 4.03 (q, $J$ = 7.0 Hz, 2H), 6.07 (s, 2H), 6.41 (s, 1H), 6.91 (s, 1H), 6.86 (d, $J$ = 8.7 Hz, 2H), 7.47 (s, $J$ = 8.7 Hz, 2H); $^{13}$C NMR (400 MHz, DM SO-d$_6$): $\delta$ 14.4, 14.5, 28.5(6C), 35.8(2C), 50.1, 60.1, 61.6, 117.1(2C), 126.5(2C), 128.3, 132.0(2C), 138.4, 153.3(2C), 155.4, 163.9, 186.8; MS (EI): m/z 456 (M$^+$); Anal. Found: C, 68.27; H, 8.02; N, 6.16. Calcd. for C$_{28}$H$_{38}$N$_2$O$_5$: C, 68.39; H, 7.95; N, 6.14.

4.4.3 $N^3, N^5$-Bis(ethoxy carbonyl)-$N^1$-(2-t-butyl-4-hydroxyphenyl)-1,4-phenylenediamine (15c)

M p 183-185°C; $^1$H NMR (400 MHz, acetone-d$_6$): $\delta$ 1.15 (t, $J$ = 7.2 Hz, 3H), 1.20 (s, 9H), 1.23 (t, $J$ = 7.2 Hz, 3H), 4.12 (q, $J$ = 7.2 Hz, 4H), 6.78 (dd, $J$ = 8.4 and 2.8 Hz, 1H), 6.95 (d, $J$ = 8.4 Hz, 1H), 7.03 (d, $J$ = 2.8 Hz, 1H), 7.25 (d, $J$ = 9.2 Hz, 2H), 7.46 (d, $J$ = 9.2 Hz, 2H), 8.39 (s, 1H), 8.52 (s, 1H); $^{13}$C NMR (400 MHz, acetone-d$_6$): $\delta$ 14.3, 14.4 32.1(3C), 35.8, 60.5, 61.5, 114.1, 115.8, 118.2, 123.2 (2C), 131.2, 134.1 (2C), 135.4, 139.2, 148.3, 153.9, 155.3, 157.1; MS (FA): m/z 400 (M$^+$); Anal. Found: C, 65.91; H, 7.07; N, 6.89. Calcd. for C$_{22}$H$_{26}$N$_2$O$_5$: C, 65.98; H, 7.05; N, 7.00.
References and notes


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17. A cetic acid gave similar results. We used benzoic acid because the handling was easier.

18. A slight reddish color was observed when adding a colorless solution of 3-methoxyphenol to a yellow colorless solution of 3 -methoxyphenol to a yellow solution of 1 . This color change was accompanied by a discernible increase in the slope of the strong absorption band of 1 .

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21. At benzoic acid concentrations higher than $2 \times 10^{-3}$ M, the reaction proceeded too fast to be followed by NMR.


1, 4-ベンゾキノンジイミン誘導体とジフェニルアミン関連化合物との反応

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1, 4-ベンゾキノンジイミン誘導体と、ジフェニルアミン、アニリン、フェノールを反応させると、両者の付加体、または、後者の化合物間で酸化的に二量化した化合物を与える。両者とも、ドナーアクセプター錯体を形成し、電子移動と水素イオン移動によって生じたラジカルケージ対を経て反応が進行する。どちらの生成物を与えるかは後者から生じたラジカルの安定性によって統一的に解釈でき、電子的・立体的に安定化されたラジカルはケージ外に出て二量化し、安定化されていないラジカルはケージ内で反応して付加生成物を与える。

キーワード： ベンゾキノンジイミン、ドナーアクセプター錯体、ラジカルケージ対、ラジカルカップリング

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