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Addition Reaction of a *p*-Benzoquinone Diimine Derivative to *p*-Substituted Phenols

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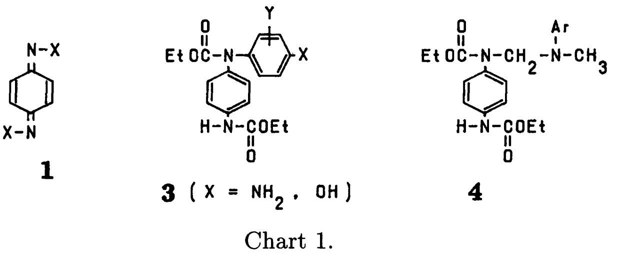
Synopsis. A facile reaction between *N*,*N*′-bis(ethoxycarbonyl)-*p*-benzoquinone diimine and electron-donating *para*-substituted phenols proceeded at room temperature in benzene in the presence of benzoic acid to give adducts which were formed by insertion of the diimine into the O–H bond of the phenols.

While *p*-benzoquinone diimine (**1**: X=H) is an unstable compound, *N*,*N*′-bis(arylsulfonyl)- and *N*,*N*′-diacyl-*p*-benzoquinone diimines (**1**: X=$ArSO_2$ and RCO) are stable enough to be isolated and characterized. Adams and Reifshneider[1)] reported syntheses of a series of the above compounds and their reactions, which were mostly 1,4-addition reactions of acids, alcohols, amines, pyridines, thiols, and other uncleophiles. Photochemical and addition reactions were also studied by other groups.[2—4)] We reported that *N*,*N*′-bis(ethoxycarbonyl)-*p*-benzoquinone diimine (**2**) gave C–N adduct **3** in the reaction with anilines[5b)] and phenols [5c)] which are free of *para*-substituents, while another C–N adduct, **4**, was formed in the reaction with *N*,*N*-dimethylanilines (Chart 1).[5a)]

We describe here that the reaction of **2** with phenols[6)] having electron-donating *para*-substituents,[7)] **5a**—**d**, afforded the O–N adducts, *N*,*N*′-bis(ethoxycarbonyl)-*N*-(*p*-aryloxy)-*p*-phenylenediamine (**6a**—**d**) in good yields as shown in the Scheme 1. It is a new type of adduct in the reaction of *p*-benzoquinone diimine derivatives. The reaction was facile and proceeded in benzene at room temperature in the presence of a small amount of benzoic acid.[8,9)]

The structure of **6** was deduced by elemental analysis, mass spectrometry, and ^{1}H NMR spectroscopy. ^{1}H NMR spectra of **6a**, **6c**, and **6b** showed two sets of AB quartets in the aromatic region, being compatible with the structure of **6**. NMR signals due to the methyl group of **6a** and **6b** and the methylene group of **6c** at the *para*-position of the phenol residue arose at 1.37, 1.07, and 2.05,[10)] respectively, in acetone-d_6, while the corresponding signals of *p*-cresol (**5a**), 3,4-dimethylphenol (**5b**), and *p*-ethylphenol (**5c**) were observed at 2.20, about 2.1,[11)] and 2.52, respectively, in acetone-d_6. The methyl group at the *meta*-position of the phenol residue of **6b** showed the signal at a position (2.14) similar to that of 3,4-dimethylphenol (2.12 or 2.15).[11)] The upfield shifts of the methyl and methylene proton signals of **6a**—**c** suggests that the Ar–N–O–Ar′ bond is folded as shown in Fig. 1, and that the *p*-methyl groups of the phenol residue in **6a**, **b** and the *p*-ethyl group of the phenol residue in **6c** are positioned to be above the *p*-phenylenediamine ring plane.

A study of the reaction mechanism including the acid effects is now proceeding.



1 **3** (X = NH_2, OH) **4**

Chart 1.

Experimental

General Procedure of the Reaction. A reaction solution in benzene was made by mixing 10 ml of a yellow solution of **2**[5a)] (0.2 mol dm^{-3}) with 10 ml of a colorless solution of a *para*-substituted phenol (0.4 mol dm^{-3}) and benzoic acid (0.04 mol dm^{-3}). The solution turned colorless immediately. After standing at room temperature for 1 h, the solution was concentrated under reduced pressure to a syrup, which was submitted to flash column chromatography on silica-gel with petroleum ether–ethyl acetate (2 : 1) as eluent to isolate **6a**—**c**, which were recrystallized from hexane–THF (1 : 1). Because of thermal instability, **6d** was isolated with a column equipped with a jacket, through which cooled water was run. Recrystallization of **6d** was effected by making a THF solution of **6d** with slight warming and storing the solution in a refrigerator after addition of hexane. No other products were isolated except less than 2% of *N*,*N*′-bis(ethoxycarbonyl)-*p*-phenylenediamine. The ^{1}H NMR spectral data of **6a**—**d** are listed in Table 1.

***N*,*N*′-Bis(ethoxycarbonyl)-*N*-(*p*-tolyloxy)-*p*-phenylenediamine (6a).** Mp 167—171 °C. Found: C, 63.70; H, 6.23; N, 7.76%. Calcd for $C_{19}H_{22}N_2O_5$: C, 63.67; H, 6.19; N, 7.82%. MS *m/z* 358 (M^+).

***N*,*N*′- Bis(ethoxycarbonyl)- *N*- (3, 4- xylyloxy)- *p*-phenylenediamine (6b).** Mp 166.5—167.5 °C. Found: C, 64.47; H, 6.51; N, 7.51%. Calcd for $C_{20}H_{24}N_2O_5$: C, 64.50; H, 6.50; N, 7.52%. MS *m/z* 372 (M^+).

***N*,*N*′-Bis(ethoxycarbonyl)-*N*-(*p*-ethylphenoxy)-*p*-phenylenediamine (6c).** Mp 127—128.5 °C. Found: C,

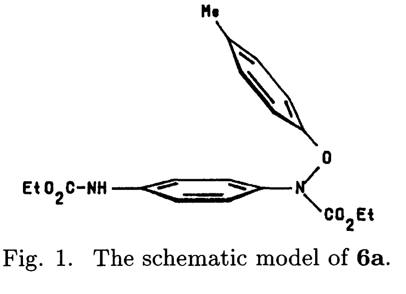
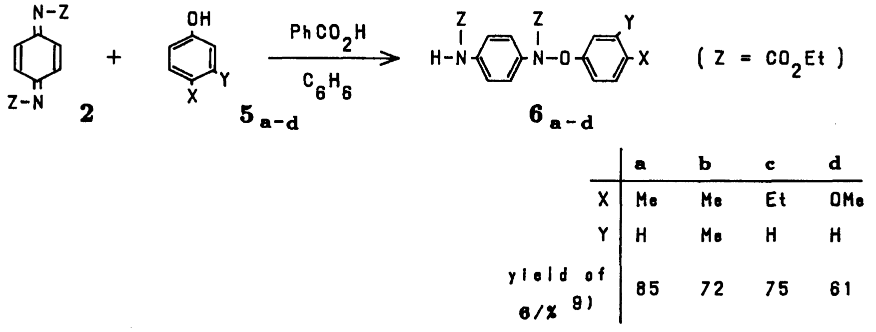


Fig. 1. The schematic model of **6a**.



	a	b	c	d
X	Me	Me	Et	OMe
Y	H	Me	H	H
yield of 6/% 9)	85	72	75	61

Scheme 1.

Table 1. ^{1}H NMR Data of **6a**—**d**: δ/ppm

		EtCOO		ArH		NH$^{e)}$	Ar-R
	Solvent	Me(3H,t$^{c)}$)	CH$_2$(2H,q$^{c)}$)	(4H,ABq$^{d)}$)	Others		
a	a)	1.03	3.96	7.21 & 7.58	6.06 & 7.19	8.75	1.37 (3H,Me,s)
		1.25	4.16	(9.00)	(4H,ABq$^{f)}$)		
b	a)	1.02	3.94	7.31 & 7.63	6.00-7.25	8.74	1.10 (3H,s,Me)
		1.26	4.17	(9.00)	(3H,m)		2.14 (3H,d$^{g)}$,Me)
c	a)	1.04	3.98	7.13 & 7.54	6.10 & 7.07	8.68	0.80 (3H,t$^{i)}$,Me)
		1.25	4.15	(8.78)	(4H,ABq$^{h)}$)		2.05 (2H,q$^{i)}$,CH$_2$)
	b)	1.09	4.04	7.00 & 7.34	6.18 & 6.97	6.69	0.82 (3H,t$^{j)}$,Me)
		1.31	4.22	(8.78)	(4H,ABq$^{f)}$)		2.01 (2H,q$^{j)}$,CH$_2$)
d	a)	1.07	4.02	7.12 & 7.56	6.14 & 7.09	8.79	3.27 (3H,s,OMe)
		1.24	4.15	(9.00)	(4H,ABq$^{f)}$)		

a) acetone-d_6. b) chloroform-d. c) J=7.03 Hz. d) coupling constants (Hz) in parentheses. e) 1H, broad singlet. f) J=10.32 Hz. g) J=1.31 Hz. h) J=10.10 Hz. i) J=7.25 Hz. j) J=7.47 Hz.

64.41; H, 6.47; N, 7.50%. Calcd for $C_{20}H_{24}N_2O_5$: C, 64.50; H, 6.50; N, 7.52%. MS m/z 372 (M$^+$).

***N*,*N*′-Bis(ethoxycarbonyl)-*N*-(*p*-methoxyphenoxy)-*p*-phenylenediamine (6d).** Mp 114.5—116.5 °C. Found: C, 61.03; H, 5.95; N, 7.39%. Calcd for $C_{19}H_{22}N_2O_6$: C, 60.95; H, 5.92; N, 7.48%. MS m/z 374 (M$^+$).

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5) a) Y. Miyagi, K. Maruyama, M. Kurokawa, and A. Yoshii, *Chem. Lett.*, **1988**, 51; b) Y. Miyagi and T. Higashi, *Chem. Express*, **7**, 29 (1992); c) Y. Miyagi, H. Matsushita, and C. Higashi, *Chem. Express*, **7**, 792 (1992).

6) As for the reaction with *p*-cresol, Adams reported that the reduction product of *N*,*N*′-bis(benzenesulfonyl)-*p*-benzoquinone diimine was quantitatively obtained: R. Adams and D. C. Blomstrom, *J. Am. Chem. Soc.*, **75**, 3408 (1953).

7) In the reaction of phenols having an electron-withdrawing *para*-substituent such as chloro, nitro, or ethoxycarbonyl, *N*,*N*′-bis(ethoxycarbonyl)-*p*-phenylenediamine was obtained as the main product with formation of **6** as the second product and a considerable amount of tar.

8) Acetic acid showed a similar effect.

9) The yields of **6** listed in the scheme were those obtained at [PhCO$_2$H]=1×10^{-3} mol dm^{-3} which was a high enough concentration to obtain the maximum yield of **6a** under the reaction conditions ([**2**]$_0$=0.1, [**5a**]$_0$=0.2 mol dm^{-3}). Higher concentrations of benzoic acid did not increase the yield of **6a** any more.

10) The signals of the methylene protons of **6c** in acetone-d_6 at 2.05 were overlapped with weak signals of the residual protons of the solvent, but were clearly observed at 2.01 in chloroform-d (Table 1).

11) The signals due to the two methyl groups of 3,4-dimethylphenol (**5b**) were observed at 2.12 and 2.15 in acetone-d_6.