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Studies on the Meerwein Arylation-Based Preparation of 2,3-Diarylbenzene-1,4-diones and Its Theoretical Interpretation

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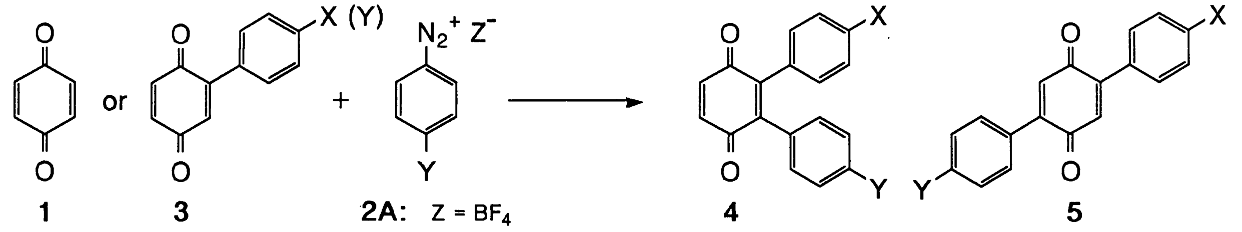
Title compounds possessing a variety of substituents are systematically prepared by means of Meerwein arylation of benzene-1,4-dione. Synthetic aspects and their MNDO calculation-based interpretation are described.

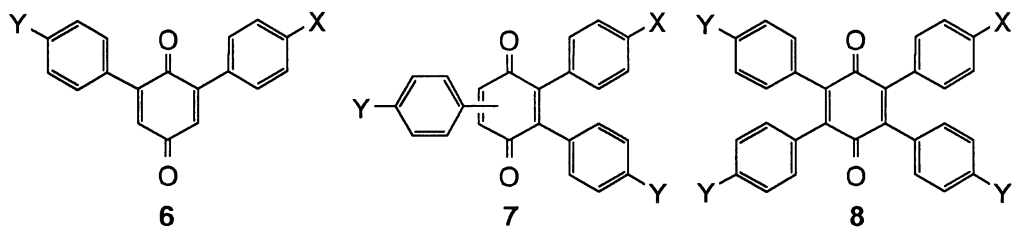
Dyestuffs containing quinone skeletons have attracted greatly our synthetic interest again in recent years, because of their versatility for constructing the useful recording media in the near infrared region.[1,2] In order to obtain the materials possessing appropriate λ_{max} and ε values, arylation reactions have most often been employed. For this purpose, Meerwein arylation, in principle the arylation of olefins using diazonium salts, has often been investigated, since quinones can be considered as the carbonyl-activated olefins.[3]



1 3 2A: Z = BF_4 4 5

2B: Z = Cl

	X, Y
a	NEt_2
b	NMe_2
c	OMe
d	Me
e	H
f	CO_2Me
g	NO_2



6 7 8

Previously we have reported the selective preparation of 2-aryl- and 2,3-diarylnaphthalene-1,4-diones by means of Meerwein arylation, using the reaction of naphthalene-1,4-dione either with aryldiazonium tetrafluoroborates in organic (non-aqueous) solvents or aryldiazonium chlorides in aqueous solution.[4] In addition, we have reported the conformation of aryl-substituted naphthalene-1,4-diones, in which two aryls exhibit the bis-pseudoaxial orientation to the quinone ring in solution, based on nuclear magnetic resonance (NMR) spectroscopic studies.[5] The latter proves that aryl-substituted naphthalene-1,4-diones exist in the "face" conformational orientation,[6] which is indispensable as the "hinge" spacer of macrocyclic and open-chain type host molecules.[7] Based on these findings, the corresponding counterparts, 2,3-diarylbenzene-1,4-diones (**4**), attract our attention as the candidate of the "hinge" spacer.

In general, synthetic strategies of aryl-substituted benzene-1,4-diones (**3**-**8**) in the past can be classified into the following three categories: (i) oxidation of phenolic derivatives of biphenyl or terphenyl;[8] (ii) Meerwein arylation of (arylated) benzene-1,4-dione;[9] (iii) others. The final class covers some newer methods appropriate for a certain compound to generate: benzene-1,4-dione (**1**) + ArHgCl + $LiPdCl_3$ for 2-monoaryl- (**3**) and 2,6-diaryl compounds (**6**);[10] acetylene + $Fe(CO)_5$ in ArH for 2,5-diaryl compounds (**5**);[11] rearrangement of pyrylium or cyclopentadienone for triaryl- (**7**) and tetraaryl compounds (**8**).[12] However, to the best of our knowledge, none has thus far been reported on the preparation of 2,3-diaryl compounds (**4**) in scientific journals. Secondary sources of patents (three in total) state that compounds **4** are utilized in industry as stabilizers of in-forming polymers[13] and as electrolytes for bright copper plating of steel surface.[14] These findings encourage us to investigate the systematic preparation of **4**, based on Meerwein arylation.

In view of the vast experimental results in the past, it has generally been believed that the arylation of **1** or **3** affords 2,5-diaryl compounds (**5**) predominantly, under the standard Meerwein reaction conditions.[8c] On the contrary, application of our "modified" Meerwein procedure, which was established in the preparation of aryl-substituted naphthalene-1,4-diones,[4] proves that 2,3-diaryl compounds (**4**) are predominantly formed, irrespective of substituents Y on diazonium salts (**2**). In this paper, we wish to report the synthetic aspects of 2,3-diarylbenzene-1,4-diones (**4**) and their MNDO calculation-based interpretation.

Experimental procedures of Meerwein arylation in this work are similar to those reported in our preceding papers.[4,5,9d] In general, benzene-1,4-diones (**1**, **3**) are reacted either with aryldiazonium tetrafluoroborates (**2A**) in *N,N*-dimethylformamide (DMF) or with aryldiazonium chlorides (**2B**) in aqueous solution. Precipitates from the reaction mixture after dilution with water are collected, and the obtained crude material is purified by column chromatography. The results are summarized in Table 1.

Our inspection started with the arylation of **1** (RUN 1-3). Thus, small amounts of 2,3-diaryl compounds **4** are found with monoarylated **3** in RUN 1-2; however, this is not true in RUN 3. In order to see some generalized tendencies in the product distribution, we proceeded to the arylation of **3** (RUN 4-18). Thus, whether X = Y or not, 2,3-diaryl compounds (**4**) are found to emerge in all experiments examined, different from widely accepted beliefs. Compounds **4** are the major products, and are often only diaryl compounds in reactions (RUN 4-8, 11-12, 16-17). On the other hand, when compounds **3** possess the electron-withdrawing functionalities (X = CO_2Me, NO_2; RUN 11-12, 16-18), the reaction often does not proceed at room temperature, and therefore, elevated reaction temperature is required (RUN 11, 16-17), and tarry materials are concomitantly formed. In cases where diazonium salts possess the electron-donating functionalities (Y = NEt_2, NMe_2; RUN 4-6, 13), self-coupled azo compounds are often isolated. These facts may also be monitored by the amounts of recovered starting materials (RUN 4, 6, 13).

In general, it has been proposed that Meerwein arylation proceeds by way of tertiary radical adducts, which are formed from the reaction of quinones with *in situ generated* aryl radicals.[16] However, its practical reaction mechanism has not yet been made clear. Out of various possibilities, we focused on the orbital interaction between SOMO of aryl radicals and LUMO of diones (**3**), the coefficients of which were obtained by the MNDO calculation.[17] The results are summarized in Table 2. As to the non-protonated form of **3**, in all substituents examined (X = NEt_2, OMe, H, CO_2Me, and NO_2), C-3 are found to exhibit the larger LUMO coefficients than those of C-5 or C-6, which support the experimental results obtained above.[18] In addition, LUMO coefficients obtained in X = CO_2Me are far smaller in values than any other X, which would reflect the lesser reactivity of **3f** in Meerwein arylation.[19] Further exploitation using 2,3-diarylbenzene-1,4-diones (**4**) are now underway in our laboratory.

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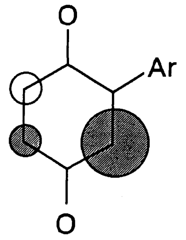
Table 1. Results of Meerwein arylation of benzene-1,4-diones (**1**, **3**)

RUN	sm	Diazonium Salt Compd./eq.		AcONa /eq.	Solvent	Temp /°C	Time /h	X	Y	Product yields/%					
										3	4	5	6	7	8
1	**1**	**2Aa**	1.0	2.0	DMF	rt	3.0	NEt_2	NEt_2	31	5	---	---	---	---
2	**1**	**2Ab**	1.0	2.0	DMF	rt	3.0	NMe_2	NMe_2	24	10	---	---	1	---
3	**1**	**2Ac**	1.0	2.0	DMF	rt	1.5	OMe	OMe	30	---	1	4	---	---
4	**3a**	**2Aa**	1.0	2.0	DMF	rt	6.0	NEt_2	NEt_2	20[e]	15	---	---	---	---
5	**3a**	**2Aa**	1.0	2.0	DMF	45-55	1.5	NEt_2	NEt_2	---	9	---	---	---	---
6	**3b**	**2Ab**	1.0	2.0	DMF	c		NMe_2	NMe_2	44[e]	22	---	---	---	---
7	**3c**	**2Ac**	1.0	2.0	DMF	rt	4.0	OMe	OMe	---	16	---	---	---	---
8	**3c**	**2Ac**	1.0	2.0	DMF	rt	20.0	OMe	OMe	---	18	---	---	---	---
9	**3d**	**2Ad**	1.0	2.0	DMF	rt	5.5	Me	Me	29[e]	22	---	9	9	---
10	**3e**	**2Ae**	1.0	2.0	DMF	rt	5.5	H	H	21[e]	21	7	7	12	2
11	**3f**	**2Af**	1.0	2.0	DMF[a]	40[d]	4.0	CO_2Me	CO_2Me	---	11	---	---	---	---
12	**3g**	**2Ag**	1.0	2.0	DMF	rt	2.0	NO_2	NO_2	21[e]	11	---	---	---	---
13	**3e**	**2Ab**	1.0	2.0	DMF	rt	6.0	H	NMe_2	15[e]	5	2	---	---	---
14	**3e**	**2Ac**	1.0	2.0	DMF	rt	4.0	H	OMe	---	24	7	7	---	---
15	**3e**	**2Bc**	1.0	20.0	b	rt	3.0	H	OMe	---	32	9	12	---	
16	**3f**	**2Ac**	1.0	2.0	DMF	40[d]	4.0	CO_2Me	OMe	---	12	---	---	---	---
17	**3g**	**2Ac**	1.0	2.0	DMF	40	4.0	NO_2	OMe	---	12	---	---	---	---
18	**3g**	**2Ad**	1.0	2.0	DMF	rt	5.5	NO_2	Me	7[e]	14	3	9	2	4

a) In the presence of hydroquinone (cat.). b) H_2O/EtOH/acetone = 6/10/5. c) 1 h at 0-5 °C then 3 h at room temperature. d) Reactions at room temperature resulted in the recoveries of starting materials. e) Recoveries of starting materials.

Table 2. LUMO coefficients of 2-arylbenzene-1,4-diones (**3**) by MNDO method

X	C_3	C_5	C_6
NEt_2	-0.34988	-0.03585	0.05065
OMe	0.38203	0.32707	-0.33327
H	0.39403	0.32994	-0.31748
CO_2Me	0.05479	0.03719	-0.03603
NO_2	-0.35374	-0.33959	0.34834



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15) The following compounds have been reported previously: **3a**, **3b**,[2a] **3c**, **3d**, **3g**,[9a] **3e**,[8a] **4ce**, **4cg**,[14] **5ce**, **7ddd**,[9b] and **7eee**[12a] (alphabet(s) corresponding to certain substituent(s) is(are) suffixed to compound numbers). All new compounds afforded satisfactory results in elemental analyses (C, H, N; or HRMS for **3ce**, **3cg**, and **3dg**) and spectral data. Compound **3f** was prepared in 91% yield from **1**, according to the procedure similar to that reported in Ref. 9a. Compounds **4** can be distinguished from **5** or **6**, based on the anisotropy effect observed in ^{1}H NMR spectra.

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18) In the calculation of protonated **3**, C-6 exhibit the larger LUMO coefficient values than C-3 or C-5.

19) Similar tendencies were found in the related systems in naphthalene-1,4-diones (Ref. 4).

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