Improved Preparation of 6,13-Dichlorotriaryldioxazines using (Diacetoxyiodo)benzene†

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6,13-Dichlorotriaryldioxazines (DClTADO) **1** have been synthesized from 2,5-bis(arylamino)-3,6-dichloro-1,4-benzoquinones (BADClBQ) **2** by oxidation with (diacetoxyiodo)benzene (DIB) under mild conditions in good yields.

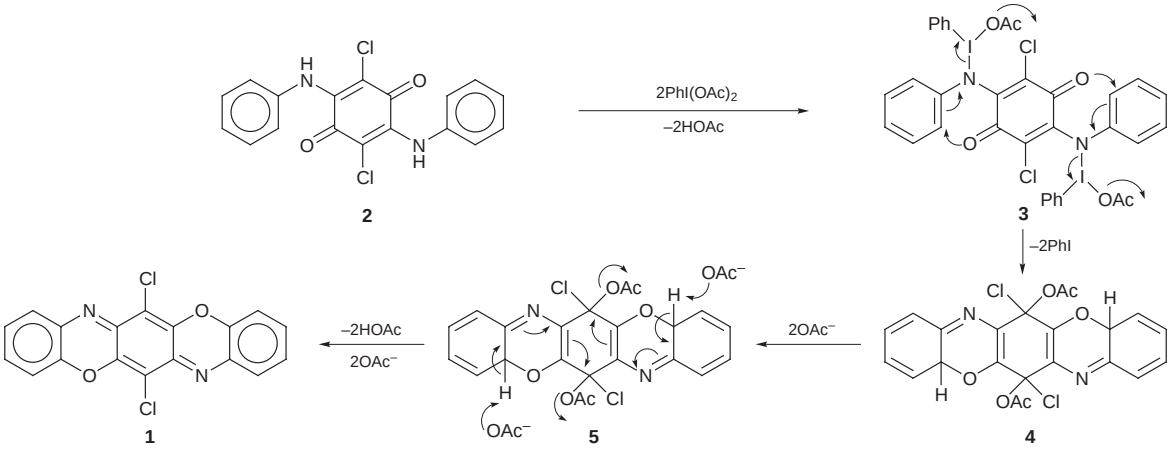
6,13-Dichlorotriaryldioxazines (DClTADO) **1** are important and efficient purple dyes or pigments which have found widespread use in fibers, printing, polymers[1] and as laser dyes,[2] fluorescent dyes,[3] polymer photostablizers[4] and so on. Normally, they can be prepared by two methods:[5] condensations of *o*-aminophenols with chloranil yield 1,2,4-trichloro-3*H*-aryloxazin-3-one intermediates which on condensations with another equivalent of *o*-aminophenols give DClTADO **1**, or by direct condensations of 2 equivalents *o*-aminophenols with chloranil in an alcoholic medium in the presence of NaOAc under reflux; condensations of 2 equivalents of arylamines with chloranil in an alcoholic medium in the presence of anhydrous NaOAc and cyclizing the resulting 2,5-bis(arylamino)-3,6-dichloro-1,4-benzoquinones by refluxing with benzoyl chloride or toluene-*p*-sulfonyl chloride in nitrobenzene or *o*-dichlorobenzene. Also, electrochemical anodic oxidation of BADC1BQ **2** gives good yields.[6] Some patents have also reported that cyclization from **2** to **1** can be accomplished by adding oxidants, such as persulfates,[7] hydrogen peroxide,[8] halogens[9] or oleum.[10]

Recently, hypervalent iodine compounds have attracted much interest in organic synthesis.[11] Among the various species of hypervalent iodine compounds, (diacetoxyiodo)benzene (DIB) is one of the most significant and useful reagents due to its excellent oxidizing property, especially for various organonitrogen compounds.[12] Since oxidative cyclization from BADClBQ **2** is the key step for the synthesis of DClTADO **1**, we propose that DIB could be utilized as the oxidant.

We took 2 equivalents BID and 1 equivalent 2,5-bis(anilino)-3,6-dichloro-1,4-benzoquinone, obtained by the reaction of aniline with chloranil,[5] as an example. The reaction could be carried out at room temperature in MeOH–DMF (2:1) and completed in 2 h with the purple solution giving triphenodioxazines in 51% yield. Interestingly, the yield could be increased to 87% by adding 2 equivalents $NaOAc{\cdot}3H_2O$. It seemed the reaction had an acetate-catalysed mechanism which could account for some reactions involving DIB.[13] We propose the mechanism in Scheme 1.

At first, 2 equivalents DIB exchanged acetates with 2,5-bis(anilino)-3,6-dichloro-1,4-benzoquinone at the nitrogens by elimination of 2 equivalents acetic acid to form the hypervalent iodine intermediate **3**. By reductive elimination of 2 equivalents iodobenzene, the cyclization was accomplished by intramolecular carbonyl oxygen attack to form the intermediate **4** which then underwent an acetate-catalysed intramolecular elimination of 2 equivalents acetic acid to give the product triphenodioxazine **1**.

Based on the above results, we extended the oxidative cyclization to other 2,5-bis(arylamino)-3,6-dichloro-1,4-benzoquinones (Scheme 2) and the results was shown in Table 1. Electronic effects had a great influence on the reaction. When R were electron-donating groups (entries 4–7) the reaction took place at room temperature in 0.5–3 h with good yields. With strong electron-withdrawing groups (entry 10) the reaction was unsuccessful, even if carried out at high temperature for extended time.



Scheme 1

In summary, we have found an improved method for the synthesis of 6,13-dichlorotriaryldioxazines **1** by oxidative cyclization of 2,5-bis(arylamino)-3,6-dichloro-1,4-benzoquinones **2** with (diacetoxyiodo)benzene which has the

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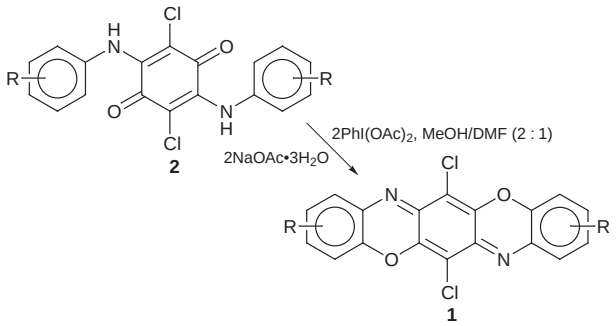

Scheme 2

Table 1 Oxidative cyclization of BADClBQ **2** to DClTADO **1** by DIB[a]

Entry	R	*t*/h	*T*/°C	Isolated yield(%)
1[b]	H	2	25	51
2	H	2	25	87
3[b]	*p*-CH_3	1	25	57
4	*p*-CH_3	1	25	92
5	*o*-CH_3	1	25	81
6	*p*-CH_3O	0.5	25	88
7	*p*-NHAc	3	25	76
8	*o*-Cl	3	35	74
9	*p*-Cl	3	35	81
10	*p*-O_2N	5	60	—

[a] The reaction was carried out with 2 mmol DIB, 1 mmol BADClBQ and 2 mmol NaOAc·$3H_2O$ in 15 ml MeOH–DMF (2:1). [b] The reaction was carried out under the same conditions as *a* except for the absence of NaOAc·$3H_2O$.

advantages of reaction at room temperature for a short time with good yields instead of refluxing for a long time with considerable amounts of by-products.

Experimental

General Procedure for the Preparation of 6,13-*Dichlorotriaryldioxazines* **1**.—At room temperature, 2.0 mmol DIB were added in one portion to a mixture of 1.0 mmol BADClBQ **2** and 2.0 mmol NaOAc·$3H_2O$ in 15 ml MeOH–DMF (2:1). The resulting mixture was stirred at the appropriate temperature. After reaction for the required time, the mixture was filtered and the filtrate poured into 30 ml water to give the colored solid which was dissolved in 3 ml DMF. The solution was subjected to TLC (silica gel) with *n*-hexane–ethylacetate (3:7) as eluent to afford the product which was purified by recrystallization from acetone.

Reactions 1 *and* 2 (*see Table* 1). Mp > 360 °C (lit.[14] > 360 °C), reddish violet. ^{1}H NMR (60 MHz, DMSO-d_6): δ 6.83–6.97 (m, 6 H), 7.50 (m, 2 H). IR (KBr): 3040, 1620, 1600, 1570, 1480, 1440, 1260, 1210, 1130, 1110, 1070, 1010, 750 cm^{-1}. UV (DMF): λ_{max}/nm = 520. Calc. for C_9H_4ClNO: C, 60.84; H, 2.25; N, 7.88. Found: C, 60.79; H, 2.12; N, 7.79%.

Reactions 3 *and* 4. Mp > 360 °C (lit.[5] > 360 °C), red. ^{1}H NMR (60 MHz, DMSO-d_6): δ 2.40 (s, 3 H), 6.96–7.10 (m, 4 H) 7.46 (m, 2 H). IR (KBr): 3030, 2980, 1625, 1605, 1570, 1480, 1440, 1245, 1150, 1120, 1110, 1070, 1020, 850, 830, 730, 700 cm^{-1}. UV (DMF): λ_{max}/nm = 532. Calc. for $C_{10}H_6ClNO$: C, 62.66; H, 3.13; N, 7.31. Found: C, 62.63; H, 3.04; N, 7.24%.

Reaction 5. Mp 296 °C (decomp.) (lit.[15] 300 °C), brown. ^{1}H NMR (60 MHz, DMSO-d_6): δ 2.47 (s, 3 H), 7.00–7.17 (m, 6 H). IR (KBr): 3040, 2960, 1620, 1600, 1585, 1470, 1250, 1140, 1120, 1105, 1050, 1020, 1000, 770, 700 cm^{-1}. UV (DMF): λ_{max}/nm = 508. Calc. for $C_{10}H_6ClNO$: C, 62.66; H, 3.13; N, 7.31. Found: C, 62.64; H, 3.07; N, 7.26%.

Reaction 6. Mp 313 °C (decomp.) (lit.[6] 316 °C), purple. ^{1}H NMR (60 MHz, DMSO-d_6): δ 3.83 (s, 3 H), 7.07–7.23 (m, 4 H) 7.58 (m, 2 H) IR (KBr): 3040, 2980, 2960, 1630, 1600, 1560, 1480, 1440, 1250, 1220, 1150, 1120, 1100, 1050, 1020, 850, 830, 725, 700, 690 cm^{-1}. UV (DMF): λ_{max}/nm = 540. Calc. for $C_{10}H_6ClNO_2$: C, 57.83; H, 2.89; N, 6.74. Found: C, 57.80; H, 2.82; N, 6.69%.

Reaction 7. Mp > 360 °C (lit.[6] > 360 °C), green. ^{1}H NMR (60 MHz, DMSO-d_6): δ 2.17 (s, 3 H), 7.13–7.33 (m, 4 H), 7.60 (2 H), 8.20 (s, 1 H). IR (KBr): 3280, 3030, 1650, 1620, 1600, 1570, 1480, 1440, 1250, 1210, 1170, 1120, 1105, 1070, 1030, 840, 825, 750, 720, 700 cm^{-1}. UV (DMF): λ_{max}/nm = 560. Calc. for $C_{11}H_7ClN_2O_2$: C, 56.29; H, 3.00; N, 11.94. Found: C, 56.26; H, 2.91; N, 11.87%.

Reaction 8. Mp 298 °C (decomp.) (lit.[15] 300 °C), reddish brown. ^{1}H NMR (60 MHz, DMSO-d_6: δ 7.07–7.17 (m, 6 H). IR (KBr): 3060, 1620, 1595, 1575, 1470, 1440, 1260, 1210, 1160, 1140, 1105, 1050, 1020, 750, 690 cm^{-1}. UV (DMF): λ_{max}/nm = 487. Calc. for $C_{11}H_7ClN_2O_2$: C, 50.94; H, 1.41; N, 6.60. Found: C, 50.92; H, 1.34; N, 6.53%.

Reaction 9. Mp > 360 °C (lit.[16] > 360 °C), reddish blue. ^{1}H NMR (60 MHz, DMSO-d_6): δ 7.03–7.14 (m, 4 H), 7.53 (m, 2 H). IR (KBr): 3030, 1625, 1600, 1555, 1480, 1440, 1265, 1230, 1205, 1160, 1120, 1100, 1060, 1030, 850, 830, 725, 700, 690 cm^{-1}. UV (DMF): λ_{max}/nm = 517. Calc. for $C_{11}H_7ClN_2O_2$: C, 50.94; H, 1.41; N, 6.60. Found: C, 50.91; H, 1.31; N, 6.57%.

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