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Phase transfer catalysis and ultrasound in tandem alkylation of azo dyes for bifunctional molecules

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Abstract

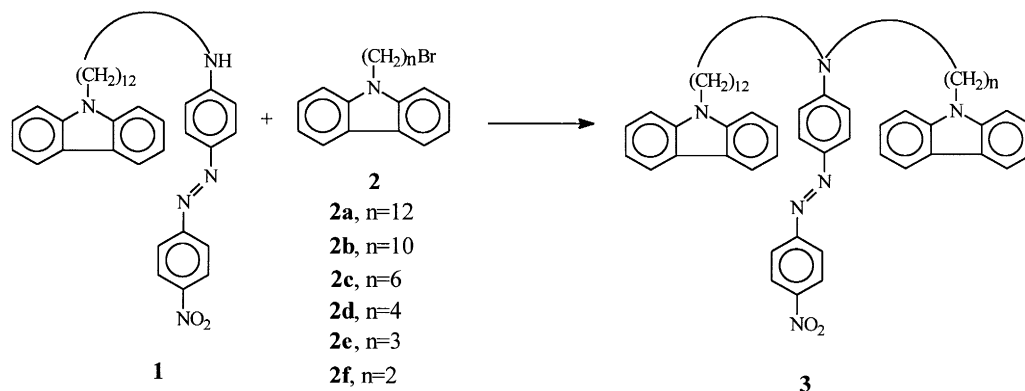
Ultrasound has been found to enhance *N*-substitution against elimination in the reaction of carbazole-containing bromide with disperse orange **3** derivative under PTC conditions. © 2000 Elsevier Science Ltd. All rights reserved.

Effective synthetic methodology for multiple function-containing molecules is essential in the development of fully-functionalized organic photorefractive materials,¹ which require a combination of several active components, including charge transporting (CT) agents and nonlinear optical (NLO) chromophores. Disperse orange **3** is an ideal starting material because of its inherent nonlinear optical property² and availability of an active amine group. During our development of photorefractive materials, we had an opportunity to examine the synthesis of disperse orange **3** based bifunctional molecules. Ideally, derivatization of the amine by CT-containing component can lead to single molecules with CT and NLO components in different ratios and therefore potentially with different photorefractive properties. Here we report tandem alkylation of the amine under both PTC and ultrasound conditions for synthesis of single molecules **3** containing CT and NLO components in 2:1 ratio as well as tunable alkyl chains for other desirable physical properties.

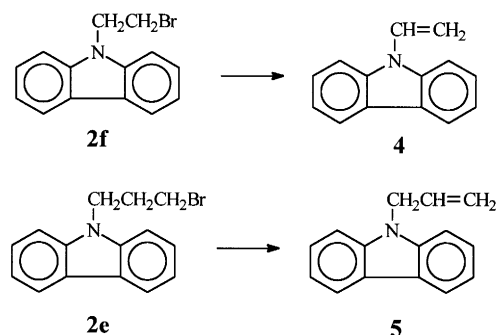
The initial approach to prepare **3** used the PTC³ condition according to Scheme 1. In general, the reaction of **1** with **2** in TBAB/50% aqueous NaOH/CH₂Cl₂ gave **3** in only 20–25% yields. The reaction required more than 100 h to complete as monitored by TLC. In particular, the reaction of **1** with **2f** failed to produce any desired substituted product **3f**. Despite the fact that **1** can be easily *N*-alkylated in 90% yield with simple alkyl bromides,⁴ PTC condition alone was inadequate in the present reaction. The use of carbazole-containing alkyl bromide obviously suffered from low yield and long reaction time. One of the problems that has been identified is a side reaction of the halide **2**, which underwent elimination and led to the formation of the related olefins. For example, the bromide **2f** gave 9-vinylcarbazole **4** while **2e** gave 9-(2-propene)carbazole **5** (Scheme 2).

Competition from elimination prompted us to investigate whether *N*-substitution reaction could be improved in the presence of ultrasound^{5,6} under PTC conditions (Table 1). Ultrasound may promote

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Scheme 1.



Scheme 2.

either elimination or substitution or both.⁷ Although several scenarios are possible, the critical issue is whether the use of ultrasound can selectively accelerate the substitution because a shorter reaction time is expected to help control elimination process. When ultrasound was applied to the reaction of **1** with **2**, the yields improved to 40–52%. For example, **3c** was obtained in 52% in the reaction of **1** with **2c**, compared to 25% yield in the absence of ultrasound. The most dramatic result was observed in the reaction of **1** with **2e**, which gave **3e** in 48% yield compared to less than 20% without ultrasound. As monitored by TLC, the reactions were usually completed in less than 40 h under the present conditions (more than 100 h otherwise). With shorter reaction times, the elimination reaction can effectively be controlled and the yield of *N*-substitution is almost doubled.

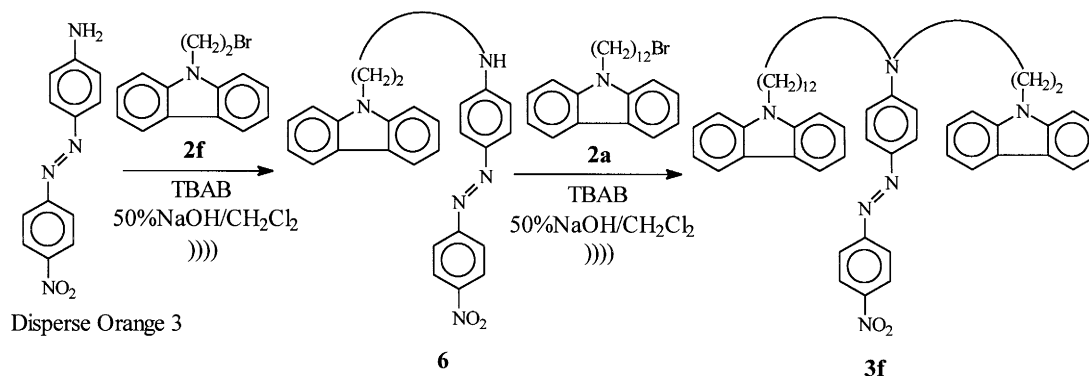
Table 1
Preparation and thermal properties of **3** under PTC condition and ultrasound

3	n	yield (%)	m.p.(°C)	T _g (°C)
3a	12	40	-13.3	-20.7
3b	10	45	0.0	-3.4
3c	6	52	80.8	-1.4
3d	4	47	114.7	14.5
3e	3	48	105.3	29.3
3f	2	<3	126.0	93.8

The ratio of **1** to **2** has been investigated under PTC and ultrasound conditions. The best ratio of **2** to

1 was found to be 4:1. A decrease in **2** would lead to a lower yield. For example, treatment of **2c** ($n=6$) with **1** in 4:1 molar ratio gave **3c** in 52% yield while a 2.5:1 ratio led to **3c** in only 42% yield.

Even with ultrasound assistance, the reaction of **1** with **2f** produced **3f** in less than 3% yield. The use of a primary amine would favor *N*-alkylation over elimination. Thus, a new approach was devised in which 9-(β -bromoethyl)carbazole was reacted with disperse orange **3**, a primary amine (Scheme 3). Indeed, *N*-alkylation was significantly improved, and the new strategy using the combined ultrasound and PTC conditions afforded **6** in 25% yield. The subsequent *N*-alkylation of **6** with **2a** led to the formation of the desired product **3f** in 10% yield.



Scheme 3.

In conclusion, a more efficient synthetic methodology has been developed for the preparation of a series of new bifunctional molecules. The combined ultrasound and PTC conditions have been demonstrated to enhance *N*-substitution against elimination in the reaction of carbazole-containing bromide with disperse orange **3** derivatives. In particular, with ultrasound assistance, the reaction takes place under mild conditions, requires relatively short time, and gives moderate yields of substitution products.

Acknowledgements

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