N-Bromosuccinimide (NBS): A Novel and Efficient Catalyst for the Synthesis of 14-Aryl-14*H*-dibenzo[*a,j*]xanthenes under Solvent-Free Conditions

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A novel procedure for the synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthenes through one-pot condensation of naphthalen-2-ol with arenecarbaldehydes in the presence of *N*-bromosuccinimide (NBS) as catalyst under solvent-free conditions is described.

Introduction. – The synthesis of xanthene derivatives is currently of much interest, and various methods have been reported for their synthesis (see, *e.g.*, [1–3]). However, these methods suffer from one or more disadvantages such as a long reaction time, low yield, use of toxic solvents, requirement of excess of reagents/catalysts, laborious workup procedures, and harsh reaction conditions. Thus, the development of an environmentally benign methodology for the synthesis of benzoxanthene derivatives is of great interest.

Results and Discussion. – In continuation of our confirming research on various transformations by halogenating agents [4–10], here we report the use of *N*-bromosuccinimide (NBS) as a more robust and efficient catalyst in a one-pot synthesis of the 14-aryl-14*H*-dibenzo[*a,j*]xanthene derivatives **3a**–**3o** by reaction of naphthalen-2-ol (**2**) with different benzaldehydes **1** in excellent yields (87–97%) under solvent-free conditions (*Scheme 1* and *Table*). As shown in the *Table*, the reactions occurred within 55–75 min. The results indicate that the most effective conversion occurred when a substrate/NBS mol ratio of 1:0.19 was used. Longer reaction times were required when lower amounts of NBS were employed. It is important to note that no 14-aryl-14*H*-dibenzo[*a,j*]xanthenes derivatives were obtained when the reactions were performed in the absence of NBS.

Scheme 1

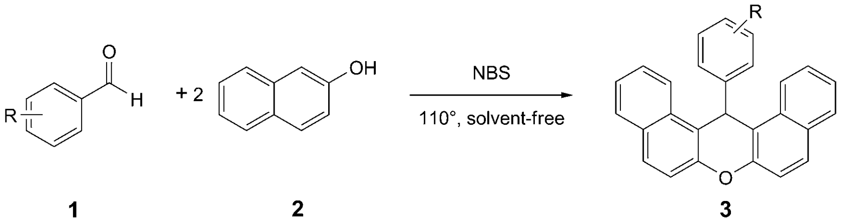


Table. *NBS-Catalyzed Synthesis of 14-Aryl-14*H*-dibenzo[*a,j*]xanthenes from Benzaldehydes* **1**[a])

Entry	R	Product[b])	Time [min]	Yield [%][c])	M.p. [°][d])
1	H	**3a**	55	95	181 (183)
2	4-Cl	**3b**	65	94	288 (287)
3	2-Cl	**3c**	68	90	214 (215)
4	4-Br	**3d**	59	93	298 (296)
5	3-Br	**3e**	62	91	191 (190)
6	4-NO_2	**3f**	68	89	309 (312)
7	2-NO_2	**3g**	75	87	292 (293)
8	3-NO_2	**3h**	65	90	214 (213)
9	4-Me	**3i**	51	96	227 (228)
10	3-Me	**3j**	55	95	206 (205)
11	4-MeO	**3k**	52	97	199 (197)
12	2-MeO	**3l**	56	95	95 (93)
13	2,4-Cl_2	**3m**	74	90	225 (227)
14	4-OH	**3n**	53	95	141 (140)
15	4-F	**3o**	66	92	237 (238)

[a]) See also *Scheme 1*. [b]) All products are known, and they were characterized by IR- and NMR-spectral analysis, and compared with authentic samples. [c]) Yields of isolated products. [d]) Melting points of compounds are consistent with reported values [1–3] (in parentheses).

The reaction likely proceeds *via* initial formation of intermediate **4**. The oxonium species **5** is then formed on reaction with naphthalen-2-ol, which then undergoes dehydration to afford the desired product **3** (*Scheme 2*).

The advantages or the characteristic aspects of the method described in this work in comparison with other previously reported procedures are *i*) the yields of products were higher than those reported previously; *ii*) the catalyst NBS is inexpensive and not moisture-sensitive, and *iii*) no special measures are required for the reaction.

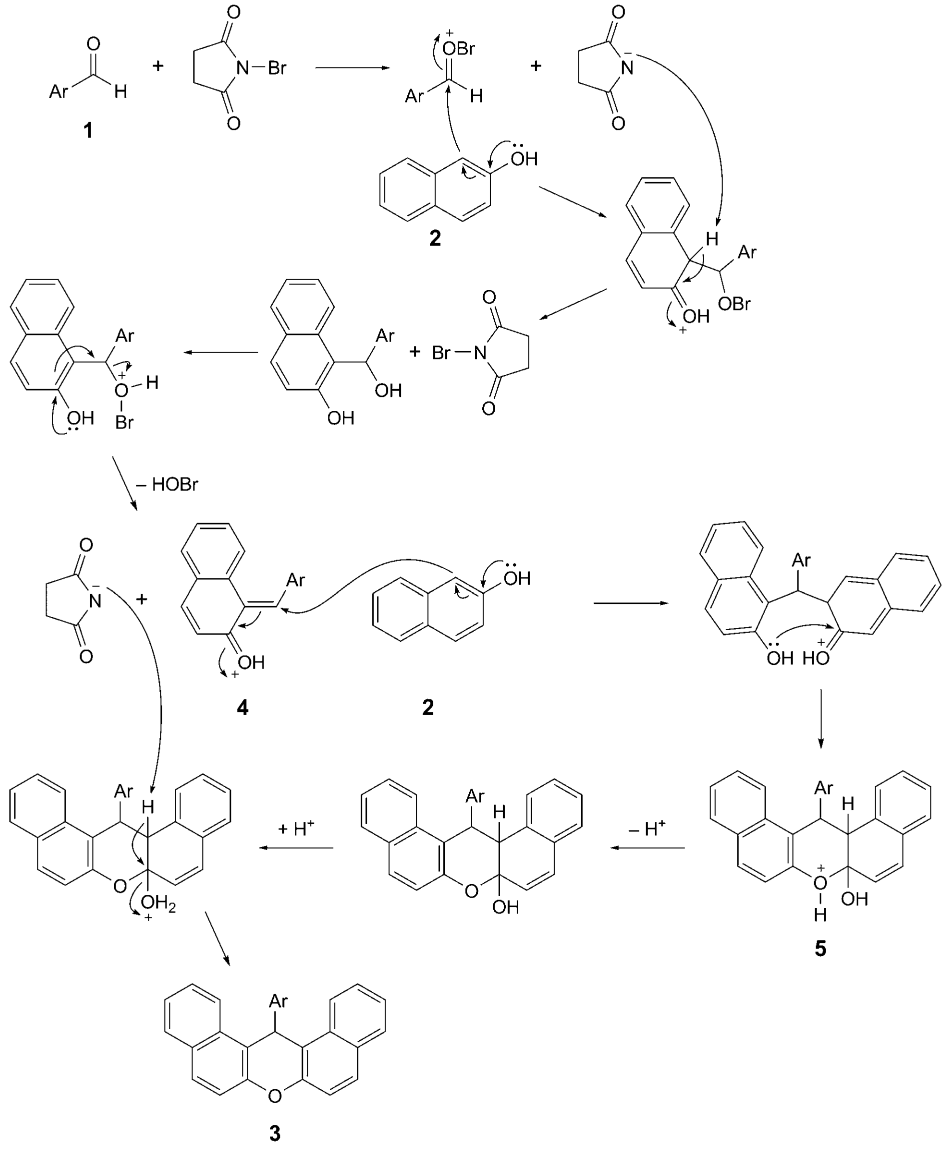
In summary, the present methodology shows that NBS is an efficient catalyst in the one-pot synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthene derivatives. The main advantages of the presented protocol are mild, clean, and environmentally benign reaction conditions, as well as the high yields. Furthermore, this method is also expected to find application in organic synthesis due to the low cost of the reagent. It is believed that this method will be a useful addition to modern synthetic methodologies.

Experimental Part

General. The chemicals were obtained from either *Merck* or *Fluka*. M.p.: *Büchi 530* melting-point apparatus; uncorrected. IR Spectra: *Shimadzu-435-U-04* spectrophotometer (KBr pellets). NMR Spectra: in $CDCl_3$, 90-MHz *JEOL FT* NMR spectrometer.

*Typical Procedure for the Synthesis of 14-Aryl-14*H*-dibenzo[*a,j*]xanthenes.* To a mixture of benzaldehyde (1 mmol) and naphthalen-2-ol (2 mmol), *N*-bromosuccinimide (NBS; 0.19 mmol, 0.43 mg) was added, and the mixture was inserted in an oil-bath and heated at 110° for the appropriate time (*cf.* the *Table*). Completion of the reaction was indicated by TLC. After the reaction was completed, EtOH was added, and the mixture was heated until the solid crude product was dissolved. Then, the heterogeneous catalyst was isolated from the mixture by simple filtration. In continuation of workup, the filtered EtOH soln. was concentrated. Aq. EtOH (15%) was added to the crude product, and the precipitate was separated and then recrystallized (2×) from aq. EtOH (15%). The desired pure

Scheme 2



product(s) was characterized by comparison of the physical data with those of known dibenzoxanthenes [1][11].

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