SHORT PAPER

Selective preparation of fluorescent 1,8-naphthalimides using acidic alumina under microwave irradiation[†]

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7*H*-benzimidazo[2,1-*a*]benz[*de*]isoquinolin-7-one compounds were prepared in a selective manner by reaction between *o*-phenylenediamines and appropriate 1,8-naphthalenedicarboxylic anhydrides using acidic alumina under microwave irradiation.

Keywords: fluorescent 1,8-naphthalimides, acidic alumina

Interest in the use of microwave irradiation in organic synthesis has been growing in recent years and a number of reviews have advocated the use of microwave irradiation in organic reactions.[1,2] Its main advantages derive from almost instantaneous 'in core' heating of material in a homogenous and selective manner. On the other hand, there are numerous potential advantages for the use of solid supports in organic synthesis.[3,4] The most important are: improvement in the reactivity of reagents and in reaction selectivity, reduced pollution and easier handling and work up. The coupling of these two techniques (microwave and solid support) has attracted much attention.[5]

Fluorescent 1,8-naphthalimide compounds have found wide applications in a number of areas, outside their traditional usage as dyes and pigments,[5] including biological fields[6,7] and polymer science.[8,9]

Substituted 7*H*-benzimidazo[2,1-*a*]benz[*de*]isoquinolin-7-ones (compound P) are usually prepared by two methods.

compound P
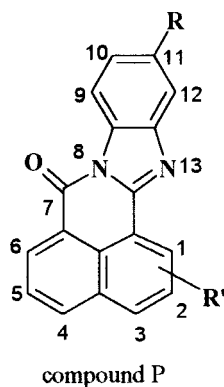
The first, employs the reaction between naphthalene-1,8-dicarboxylic anhydride derivatives and appropriately substituted *o*-phenylenediamines.[10,11] In the second method, the reaction between naphthalene-1,8-dicarboxylic anhydrides and appropriately substituted *o*-nitroanilines produces an intermediate-*N*-substituted-naphthalimide, which, in a second step, can be converted into the final product by chemical reduction and condensation.

It has been recognised (in cases where R′=H) that the second method utilising *o*-nitroanilines is superior to the first method when the corresponding *o*-phenylenediamine reaction can and does give two isomers. For example, Okazaki demonstrated a 63 / 37 ratio of 11- to 10-methoxy and 55/45 ratio of 11- to 10-methyl isomers when 3,4-diaminoanisole and 3,4-diaminotoluene were reacted respectively with naphthalene-1,8-dicarboxylic anhydride,[12] whereas pure isomers could be obtained when the appropriately substituted *o*-nitroanilines were first reacted with the anhydride, followed with chemical reduction and condensation. However, this method yields only one isomer, is an elaborate synthesis and in the some cases is unsuitable.

On the other hand, when R = H and R′= substituent group and the second method is inefficient the use of the first method usually yields two isomers in approximately similar amounts. For example, Grayshan and Peters reported a 55.3/44.7 ratio of 1- to 6-nitro and 63.8/36.2 ratio of 2- to 5-nitro isomers when 1,2-phenylenediamine was reacted with 2-nitronaphthalene-1,8-dicarboxylic anhydride and 3-nitronaphthalene-1,8-dicarboxylic anhydride respectively.[10] The formation of the product takes place through an intermediate aminonaphthalimide stage and cyclisation of this compound can be carried out using each of the two carbonyl groups (Scheme 1).

On agreement with the selectivity of alumina catalysed organic reactions reported previously, we found that with the use of acidic alumina and microwave irradiation for the preparation of fluorescent 1,8-naphthalimides gave a reaction with high selectivity and yield (Scheme 2).

7H-Benzimidazo-[2,1-*a*]benz[*de*]isoquinolin-7-one compounds were simply formed by microwave irradiation of a mixture of naphthalene-1,8-dicarboxylic anhydride and the aromatic diamine (1/1) for 7–9 min., followed by isolation and purification to give the product in more than 90% yield and with selectivity for one isomer. With this procedure we prepared the parent compound and a series of 7*H*-benzimidazo-[2,1-*a*]benz[*de*]isoquinolin-7-ones that have a substituent in the diamine or anhydride ring (Table 1).

In conclusion, fluorescent 1,8-naphthalimide compounds can be prepared in a mild and selective reaction using acidic alumina as catalyst and with solid support and microwave irradiation.

Experimental

All experiments were carried out in a Westinghouse 1400W (900W output) continuous wave domestic microwave oven on high power. The structures of the obtained 1,8-naphthalimides were established by IR spectroscopic data, melting points and comparison on TLC plates with samples obntained by literature procedures. Melting points were determined on a Buchi melting point apparatus and are uncorrected.
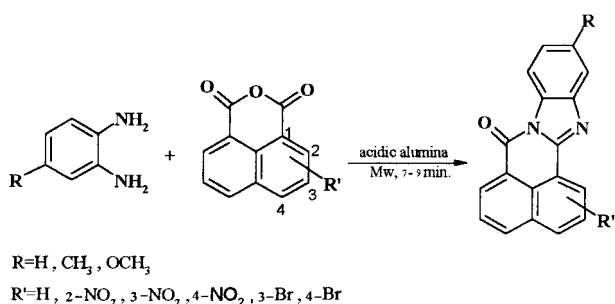
General procedure for the synthesis of fluorescent 1,8-naphthalimides: Naphthalene-1,8-dicarboxylic anhydride (1 mmol), aromatic

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Scheme 1

R=H , CH₃ , OCH₃

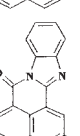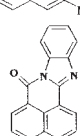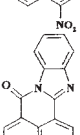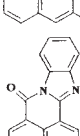R'=H , 2-NO₂ , 3-NO₂ , 4-NO₂ , 3-Br , 4-Br
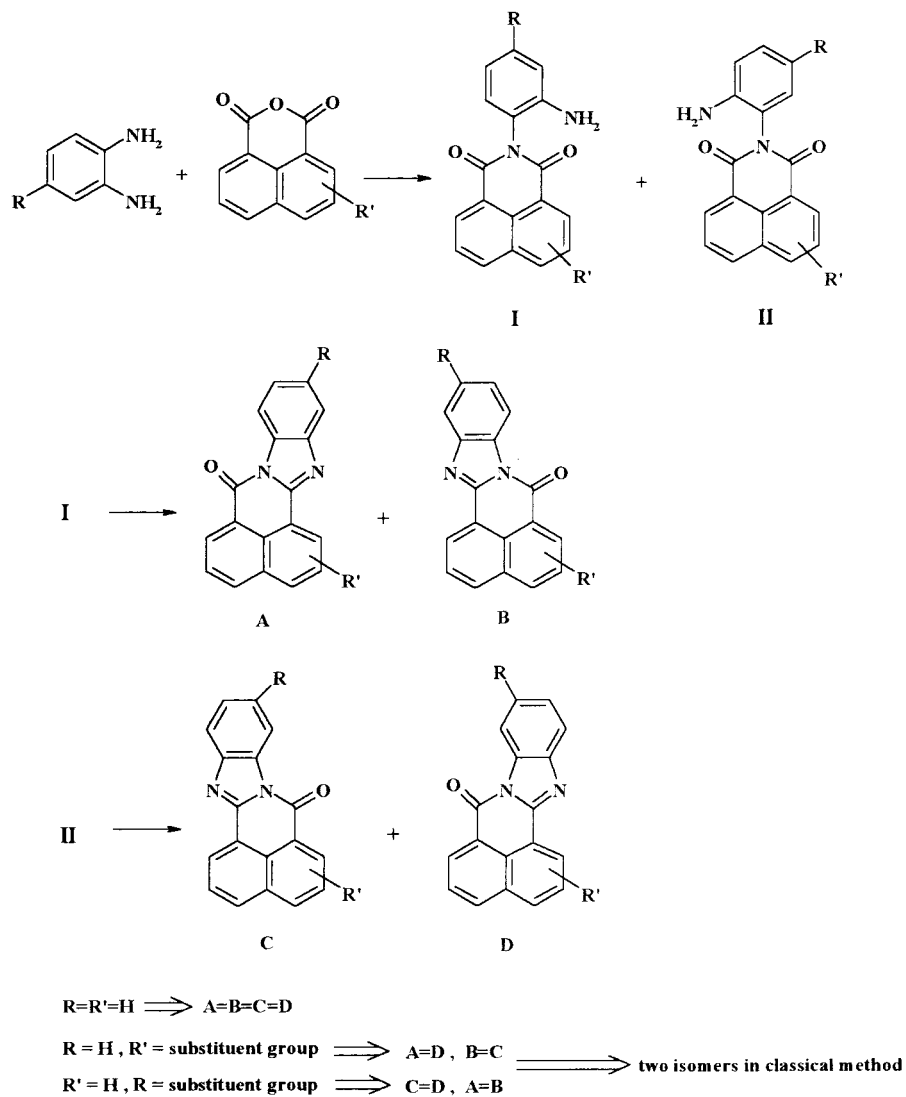
Scheme 2
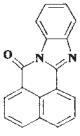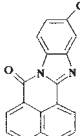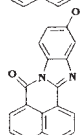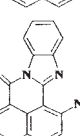
diamine (1 mmol) and acidic alumina (3g-Merck, 1078) were mixed with grinding. The mixture was irradiated in a 50 ml beaker in a microwave oven for the times indicated in Table 1. At the end of the irradiation, the reaction mixture was cooled to room temperature and extracted with dichloromethane. The extracts were evaporated to dryness and purified by thick layer plate chromatography on silica gel using hexane/ethylacetate (4/1) as eluent.

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Table 1

Entry	R^a	R′ ^{b}	Irradiation time/min	Product	Selectivity	Yield/%	m.p. /°C	(Lit.m.p) /°C	IR/ cm^{-1}, CO
1	H	H	9		——	95	205–206	(205–206.5)[13]	1700
2	CH$_3$	H	9		92	97	214	(212–213)[13]	1700
3	OCH$_3$	H	8		95	92	198–198.5	(197)[12]	1698
4	H	2-NO$_2$	7		93	96	300–301	(298–299)[11]	1707
5	H	3-NO$_2$	7		91	96	312–313	(312–313)[11]	1702
6	H	4-NO$_2$	7		91	96	294–294.5	(294)[11]	1705
7	H	3-Br	9		92	95	296–297	(296)[12]	1700
8	H	4-Br	9		97	98	224–224.5	(221–223)[12]	1700

^{a}In the case of diamine compound.
^{b}In the case of anhydride compound.