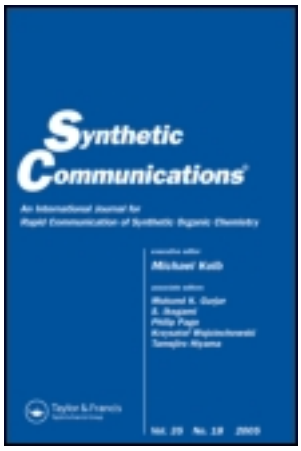

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Microwave Assisted Synthesis of 2,4,6-Triarylamino-1,3,5-triazines as Potential UV Absorbent

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ABSTRACT

2,4,6-Triarylamino-1,3,5-triazines was synthesized in a few minutes by reaction of cyanuric chloride with aromatic amines under microwave irradiation. This method is featured with rapid reaction, convenient operation, high yield, and clean. UV-absorption was tested for each compound.

Key Words: Microwave; 2,4,6-Triarylamino-1,3,5-triazine; UV-absorbent.

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1. INTRODUCTION

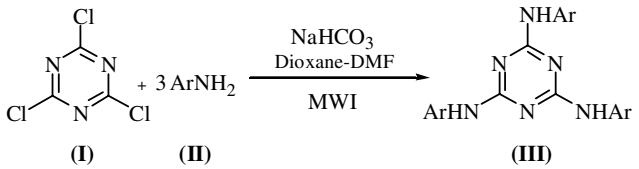
Since Gedyes et al.'s[1] application of microwave irradiation in organic synthesis, microwave irradiation (MWI) has been introduced into each aspect of organic chemistry.[2,3] In recent years there has been increasing interest on 1,3,5-triazine chemistry, because of its molecular symmetry[4–8] and electronic properties.[9,10] Microwave assisted synthesis of 2,4,6-triaryloxy-1,3,5-triazines has been reported.[11] 2,4,6-Triarylamino-1,3,5-triazines have practical application in reactive dye,[12] printing ink components,[13,14] UV-filters in light screening compositions,[15] and chiral solvating agent.[16] This kind of compounds was all synthesized from cyanuric chloride and corresponding aliphatic or aromatic amines in a few days, although sodium or sodium hydride were used to promote the reaction and at as high as 300°C in some articles. So, it is important to find a simple and fast synthetic method.

2. RESULTS AND DISCUSSION

The microwave assisted synthesis of 2,4,6-triarylamino-1,3,5-triazines(**III**) was through the reaction of cyanuric chloride(**I**) with aromatic amines(**II**) (Sch. 1) in a mixed solvent (1,4-dioxane:DMF). Sodium hydrogen carbonate was used as base.

Results are shown on Table 1. Through microwave irradiation, the reaction time was shortened to a few minutes from a few days reported. HPLC analysis of the reaction mixture showed little side product. Products have good absorption between 250 nm to 400 nm, they are potential UV-absorbent.

The microwave assisted synthesis of 2,4,6,-triarylamino-1,3,5-triazines has the feature of rapid reaction, convenient operation, high yield, and clean.



(I) (II) (III)

Scheme 1. Reaction of cyanuric chloride with aromatic amines.

Table 1. Synthesis of 2,4,6-triarylamino-1,3,5-triazines.[b]

Entry III	Ar	Reaction time (min)	Yield (%)	M.p. (°C)	UV-λ_{max} (nm)
III-1	Phenyl	2	96	239 (232)[18]	270, 280
III-2	2-Me-phenyl	2	95	233–234	265
III-3	3-Me-phenyl	2	95	232–233	265
III-4	4-Me-phenyl	2	98	238–239	270, 285
III-5	2,6-Di-Me-phenyl	2.5	86	259–261	240
III-6	2-F-phenyl	2	90	173–174	263
III-7	3-F-phenyl	2	94	244–245	268
III-8	4-F-phenyl	2	97	184–186	268, 290
III-9	2,4-F_2-phenyl	2	95	202–204	260
III-10	2,5-F_2-phenyl	3	82	182–183	263, 290
III-11	2-Cl-phenyl	2	95	172–173	270
III-12	3-Cl-phenyl	3	85	145–148	270
III-13	4-Cl-phenyl	2	98	262–264	270, 290
III-14	4-Br-phenyl	2	94	274–276	282
III-15	2,4,6-Br_3-phenyl	2	95	136–138	248, 315
III-16	4-NO_2-phenyl	3	80	154–160	360

[b]III-2–16 are new compounds.[19]

3. EXPERIMENTAL

3.1. General Consideration

The microwave oven is S∧MSUNG-S7A73, 650 W, 2450 Hz. Middle fire was used. Through a hole on the top of oven, the reaction flask was linked to a outside refluxing column.[17]

3.2. General Procedure

To a 50 mL round bottom flask was added 1.8 g (0.01 mol) cyanuric chloride, 15 mL 1,4-dioxane, 4.5 mL DMF, 2.5 g sodium hydrogen carbonate, and 0.03 mol aromatic amine. The flask was then put into microwave oven and connected with refluxing column. After microwave irradiation, solvent was distilled out under reduced pressure and a solid was obtained. This solid was washed thoroughly with water, dried, and then recrystallized from suitable solvent. All compounds have passed the elemental analysis, FAB-MS, IR, and UV-absorption.

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19. **III-1.** FAB-MS *m*/*z*: 355.28 $(M+H)^+$ (100%), 377.15 $(M+Na)^+$ (15%); **III-2.** FAB-MS *m*/*z*: 397.85 $(M+H)^+$ (100%), 419.38 $(M+Na)^+$, (50%); Anal. calcd. for $C_{24}H_{24}N_6$: C 72.70, H 6.10, N 21.20. Found: C 72.55, H 6.15, N 21.20; **III-3.** FAB-MS *m*/*z*: 397.35 $(M+H)^+$ (100%), 419.19 $(M+Na)^+$ (10%). Anal. calcd. for $C_{24}H_{24}N_6$: C 72.70, H 6.10, N 21.20. Found: C 72.46, H 5.95, N 21.19; **III-4.** FAB-MS *m*/*z*: 397.37 $(M+H)^+$ (100%), 419.17 $(M+Na)^+$ (20%). Anal. calcd. for $C_{24}H_{24}N_6$: C 72.35, H 6.10, N 21.20. Found: C 72.60, H 6.08, N 21.16; **III-5.** FAB-MS *m*/*z*: 439.90 $(M+H)^+$ (100%), 461.63 $(M+Na)^+$ (10%). Anal. calcd. for $C_{27}H_{30}N_6$: C 73.94, H 6.89, N 19.16. Found: C 73.87, H 6.85, N 19.15; **III-6.** FAB-MS *m*/*z*: 409.23 $(M+H)^+$ (100%), 431.14 $(M+Na)^+$ (75%). Anal. calcd. for $C_{21}H_{15}F_3N_6$: C 61.76, H 3.70, N 20.58. Found: C 61.73, H 3.72, N 20.55; **III-7.** FAB-MS *m*/*z*: 409.19 $(M+H)^+$ (100%), 431.13 $(M+Na)^+$ (15%). Anal. calcd. for $C_{21}H_{15}F_3N_6$: C 61.76, H 3.70, N 20.58. Found: C 61.74, H 3.71, N 20.59; **III-8.** FAB-MS *m*/*z*: 409.18 $(M+H)^+$ (100%), 431.12 $(M+Na)^+$ (45%). Anal. calcd. for $C_{21}H_{15}F_3N_6$: C 61.76, H 3.70, N 20.58. Found: C 61.76, H 3.69, N 20.62; **III-9.** FAB-MS *m*/*z*: 463.12

$(M+H)^+$ (100%), 485.05 $(M+Na)^+$ (25%). Anal. calcd. for $C_{21}H_{12}F_6N_6$: C 54.55, H 2.62, N 18.18. Found: C 54.52, H 2.61, N 18.22; **III-10.** FAB-MS *m/z*: 463.11 $(M+H)^+$ (100%), 485.05 $(M+Na)^+$ (30%). Anal. calcd. for $C_{21}H_{12}F_6N_6$: C 54.55, H 2.62, N 18.18. Found: C 54.51, H 2.63, N 18.21; **III-11.** FAB-MS *m/z*: 457.22 $(M+H)^+$ (100%), 459.12 $(M+H)^+$ (95%). Anal. calcd. for $C_{21}H_{15}Cl_3N_6$: C 55.10, H 3.30, N 18.36. Found: C 55.13, H 2.29, N 18.33; **III-12.** FAB-MS *m/z*: 457.22 $(M+H)^+$ (90%), 459.12 $(M+H)^+$ (100%). Anal. calcd. for $C_{21}H_{15}Cl_3N_6$: C 55.10, H 3.30, N 18.36. Found: C 55.11, H 2.31, N 18.37; **III-13.** FAB-MS *m/z*: 457.23 $(M+H)^+$ (80%), 459.07 $(M+H)^+$ (100%). Anal. calcd. for $C_{21}H_{15}Cl_3N_6$: C 55.10, H 3.30, N 18.36. Found: C 55.09, H 2.32, N 18.34; **III-14.** FAB-MS *m/z*: 437.2 $(M\text{-}BrC_6H_3)^+$ (25%), 274.35 $(M\text{-}2BrC_6H_5)^+$ (80%). Anal. calcd. for $C_{21}H_{15}Br_3N_6$: C 42.67, H 2.56, N 14.22. Found: C 42.70, H 2.55, N 14.25; **III-15.** FAB-MS *m/z*: 767.32 $(M+Na\text{-}Br_3C_6H_2)^+$ (5%), 454.11 $(M+Na\text{-}2Br_3C_6H_3)^+$ (5%). Anal. calcd. for $C_{21}H_9Br_9N_6$: C 23.69, H 0.85, N 7.90. Found: C 23.64, H 0.84, N 7.92; **III-16.** FAB-MS *m/z*: 383.03 $(M+2Na\text{-}NO_2C_6H_4NH\text{-}O)^+$ (30%), 357.01 $(M+Na\text{-}H_2O\text{-}NO_2C_6H_4NH\text{-})^+$ (30%). Anal. calcd. for $C_{21}H_{15}N_9O_6$: C 51.54, H 3.09, N 25.76. Found: C 51.56, H 3.10, 25.78.

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