Improved synthesis of 6-(4-methoxyphenyl)-2,4-dichloro-1,3,5-triazine and 2,4-bis(resorcinyl)-substituted UV light absorbing derivatives

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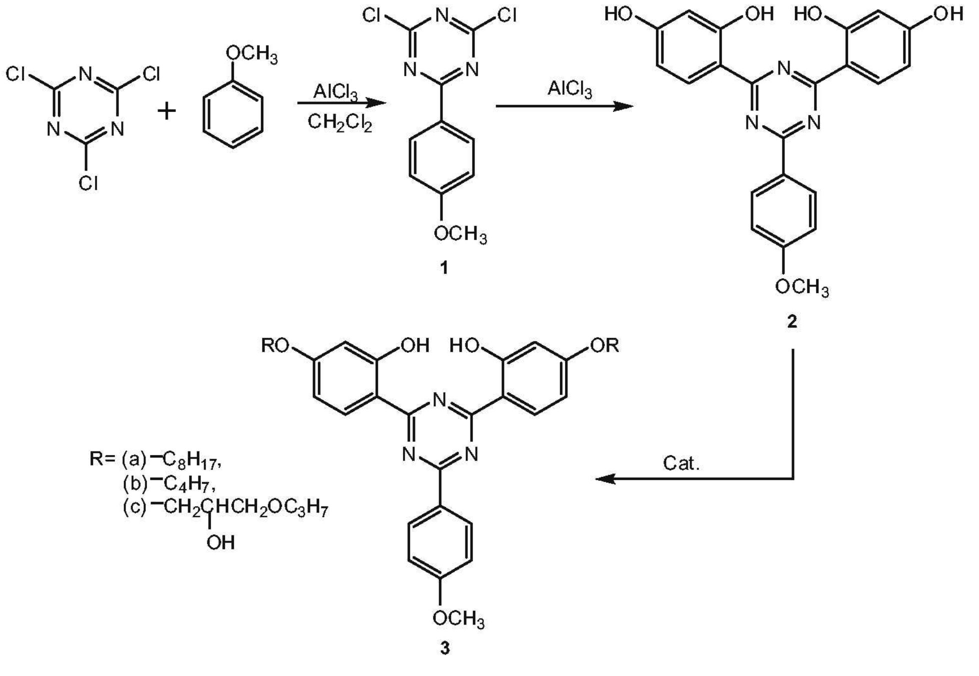
Pure 6-(4-methoxyphenyl)-2,4-dichloro-1,3,5-triazine was synthesised by a method that did not involve the troublesome Grignard reaction of 4-bromo-anisole. A series of bis(resorcinyl) triazine derivatives which can be used as UV light absorbers were subsequently prepared by utilising 6-(4-methoxyphenyl)-2,4-dichloro-1,3,5-triazine as the starting material via alkylation or acid-catalysed addition reactions.

Keywords: 6-(4-methoxyphenyl)-2,4-dichloro-1,3,5-triazine, cocatalyst, bis(resorcinyl) triazine, UV light absorber

A wide variety of materials often degrade as a result of prolonged exposure to UV light and this can be inhibited by the addition of UV light absorbers (UVAs). Benzophenones, benzotriazoles, salicylates, cyanoacrylates and triazines are widely acknowledged to be classical UV light absorbers.[1-4] Amongst these UV light absorbers, trisaryl-1,3,5-triazines are prepared by utilising the important intermediate 6-(4-methoxyphenyl)-2,4-dichloro-1,3,5-triazine as the starting material. These compounds exhibit high inherent light stability and permanence as compared to other classes of UV light absorbers such as benzophenones and benzotriazoles.[5,6] According to both the literature and patents, 6-(4-methoxyphenyl)-2,4-dichloro-1,3,5-triazine can be prepared from cyanuric chloride, a readily available and inexpensive material, by reaction with a Grignard reagent from 4-bromo-anisole.[7,8] This approach to the synthesis of 6-(4-methoxyphenyl)-2,4-dichloro-1,3,5-triazine is restricted by the use of a Grignard reagent from 4-bromo-anisole, which suffers from harsh reaction conditions and high operating cost. In view of wide use of trisaryl-1,3,5-triazine UV light absorbers, it is of interest to develop a simple, reliable and economically attractive process for the synthesis of 6-(4-methoxyphenyl)-2,4-dichloro-1,3,5-triazine. We have developed an improved and efficient one-step process to prepare 6-(4-methoxyphenyl)-2,4-dichloro-1,3,5-triazine by the action of anisole and cyanuric chloride in methylene chloride in the presence of aluminium chloride as the catalyst and resorcinol as a cocatalyst avoiding the use of a Grignard reagent from 4-bromo-anisole (Scheme **1**). We also describe a series of bis(resorcinyl) triazine compounds which have been prepared from the now conveniently accessible 6-(4-methoxyphenyl)-2,4-dichloro-1,3,5-triazine as the starting material via alkylation or acid-catalysed addition reaction.

Results and discussion

We first investigated the reaction conditions for the synthesis of 6-(4-methoxyphenyl)-2,4-dichloro-1,3,5-triazine (**1**) using aluminium chloride as the catalyst and resorcinol as a cocatalyst in methylene chloride. In these experiments, the effect of molar ratios of anisole, cyanuric chloride, catalyst and cocatalyst on the yields at room temperature (25 °C) for 18 h was investigated. It was found the best yields could be obtained under the reaction conditions of n(anisole):n(cyanuric chloride):n($AlCl_3$):n(resorcinol) = 1 : 1 : 1.1 : 0.11. The experimental results were given in Table 1.



Scheme 1 Synthesis of 6-(4-Methoxyphenyl)-2,4-dichloro-1,3,5-triazine and its 2,4-bis(resorcinyl)-derivatives.

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Table 1 Effect of molar ratios of reaction reagents to catalysts on the yields

n(anisole):n(cyanuric chloride):n(AlCl$_3$):n(resorcinol)	1:1:1.1:0	1:1:1.1:0.04	1:1:1.1:0.08	1:1:1.1:0.11	1:1:1.1:0.13
Yield/%	43	46	54	66	57

Table 2 Effect of reaction temperature on the yields

Temperature/°C	15	20	25	30	35
Yield/%	50	54	66	56	49

We also examined the effect of reaction temperature on the yields with the optimum molar ratio of reaction reagents and found that the best yields could be obtained at 25 °C for 18 h. The reaction did not proceed completely at a lower temperature (< 25 °C) and the occurrence of side reactions, such as the catalytic decomposition of anisole, may increase if the reaction temperature is higher than 25 °C.

A series of bis(resorcinyl)triazine ultraviolet light absorbers (**3**) were prepared in a two-step reaction from **1**. The preparation first involved the generation of 2,4-bis(2,4-dihydroxyphenyl)-6-(4-methoxyphenyl)-1,3,5-triazine (**2**) and the second step was easily achieved by Friedel–Crafts alkylation of the resorcinol in the presence of a Lewis acid, in particular aluminium chloride. The following etherification of the free *p*-hydroxyl groups in **2** by alkylation or acid-catalysed addition of glycidyl ethers afforded the target products (**3**).

Experimental

All melting points (°C) were determined on an X-4 microscopic digital melting-point apparatus. ^{1}H NMR spectra were recorded on a Varian INOVA 400 spectrometer at ambient temperature in CDCl$_3$ using TMS as internal standard, and NMR chemical shifts (δ) were quoted in parts per million (ppm). Coupling constants (*J* values) were given in Hz. High-resolution mass spectra were measured using a JEOL JMS-DX300 mass spectrometer. IR spectra were measured on a Nicolet Avatar 360 FT-IR instrument using KBr discs in the 4000–400 cm^{-1} regions. Optical absorbance measurements were recorded on a Jasco UV/Vis spectrophotometer (model UV-550, Japan). Elemental analyses were obtained in an EA 1112 elemental analyser. All the reagents used were AR grade.

6-(4-methoxyphenyl)-2,4-dichloro-1,3,5-triazine (**1**): Cyanuric chloride (3.6 g, 0.02 mol), anisole (2.2 g, 0.02 mol) and resorcinol (0.24 g, 0.0022 mol) were slowly added under atmospheric pressure to a methylene chloride solution (20 ml) containing aluminium chloride (2.9 g, 0.02 mol). After the addition was complete the mixture was stirred for 18 h at room temperature (25°C). The solvent was then removed by simple distillation and water was added to the residue to hydrolyse the aluminium chloride. The solid was filtered off by suction and washed with water until neutral. Recrystallisation of the filter cake from tetrahydrofuran gave the pure product. Yield: 66% (3.4 g). M.p.134–135 °C. ^{1}H NMR (CDCl$_3$) δ: 8.46 (d, 2H, *J* = 8.8 Hz, Ar*H*), 7.00 (d, 2H, *J* = 9.2 Hz, Ar*H*), 3.92 (s, 3H, –OC*H*$_3$). HRMS *m*/*z*: 254.9942 (calcd for $C_{10}H_7N_3OCl_2$, 254.9966). Anal. elem. $C_{10}H_7N_3OCl_2$: Calcd C, 46.90; H, 2.76; N, 16.41; found C, 46.87; H, 2.81; N, 16.49%.

2,4-bis(2,4-dihydroxyphenyl)-6-(4-methoxyphenyl)-1,3,5-triazine (**2**): A mixture of **1** (18.5 g, 0.07 mol) and resorcinol (16.2 g, 0.15 mol) in chlorobenzene was heated at 40°C with stirring. At 40°C, aluminium chloride (22 g 0.16 mol) were slowly introduced. The reaction mixture was stirred at 45–50°C for about 3.5 h until the evolution of HCl finished. The chlorobenzene was removed from the reaction mixture by steam distillation. The residue was filtered off with suction, washed with water until neutral and dried at 80°C *in vacuo*. A yellow powder was obtained. Yield: 92.5% (27.1 g). ^{1}H NMR (CDCl$_3$) δ: 13.15 (s, 2H, –O*H*), 10.49 (s, 2H, –O*H*), 8.26 (d, 2H, *J* = 8.0 Hz, Ar*H*), 7.16 (d, 2H, *J* = 8.0 Hz, Ar*H*), 6.51 (d, 2H, *J* = 4.0 Hz, Ar*H*), 6.49 (s, 2H, Ar*H*), 6.35 (d, 2H, *J* = 4.0 Hz, Ar*H*), 3.88 (s, 3H, –OC*H*$_3$). HRMS *m*/*z*: 403.1190 (Calcd for $C_{22}H_{17}N_3O_5$, 403.1168). IR(v, cm^{-1}): 3323, 3077, 2931, 1619, 1528, 1504, 1261, 846, 804. Anal. $C_{22}H_{17}N_3O_5$: Calcd C, 65.50; H, 4.25; N, 10.42; found C, 65.52; H, 4.19; N, 10.38%.

2,4-bis{[4-(2-ethylhexyloxy)-2-hydroxy]phenyl}-6-(4-methoxyphenyl)-1,3,5-triazine (**3a**): A mixture of **2** (2 g, 0.005 mol) and K_2CO_3 (1.45 g, 0.01 mol) in N,N–dimethylformamide (15 ml) was heated to 100 °C with stirring. 3-Bromomethylheptane (2.4 g 0.012 mol), dissolved in N,N–dimethylformamide (5 ml), was slowly added dropwise over of 1 h. After the addition was complete, stirring at 100 °C was continued for 3 h. The reaction was then filtered and the filtrate was collected. After the N,N–dimethylformamide was removed from reaction mixture under reduced pressure, acetone was added to the filtrate and a viscous, slightly yellow resin was obtained, which crystallised by addition of seed crystals. Yield: 72.3% (4.5 g). M.p. 84–85 °C. ^{1}H NMR (CDCl$_3$) δ: 13.12 (s, 2H, –O*H*), 8.28 (d, 2H, *J* = 8.0 Hz, Ar*H*), 8.25 (d, 2H, *J* = 8.0 Hz, Ar*H*), 7.15 (d, 2H, *J* = 9.6 Hz, Ar*H*), 6.59 (d, 2H, *J* = 8.8 Hz, Ar*H*), 6.48 (s, 2H, Ar*H*), 3.89 (d, 4H, *J* = 5.6 Hz, –OC*H*$_2$), 3.84 (s, 3H, –OC*H*$_3$), 1.27–1.66 (m, 18H, –C*H*$_2$ and –C*H*), 0.84–0.88 (m, 12H, –C*H*$_3$). HRMS *m*/*z*: 627.3618 (Calcd for $C_{38}H_{49}N_3O_5$, 627.3672). IR(v, cm^{-1}): 3368, 3083, 2946, 2934, 1622, 1588, 1536, 1268, 852, 806. Anal. $C_{38}H_{49}N_3O_5$: Calcd C, 72.70; H, 7.87; N, 6.69; found C, 72.66; H, 7.98; N, 6.73%. UV spectrum: λ_{max} = 338 nm, ε_{max} = 47226 l mol^{-1}cm^{-1} (ethanol).

2,4-bis{[4-(2"-methylpropenyloxy)-2-hydroxy]phenyl}-6-(4-methoxyphenyl)-1,3,5-triazine (**3b**): A mixture of **2** (2 g, 0.005 mol) and K_2CO_3 (1.42 g, 0.01 mol) in N,N–dimethylformamide (30 ml) was heated for 1 h to an internal temperature of 100 °C. Methallyl chloride 0.92 g (0.01 mol), dissolved in N,N–dimethylformamide (10 ml), were added dropwise over 20 min to the reddish solution which was obtained. After the addition was complete, stirring was continued at 100 °C for 3 h and then at room temperature for 8 h. Afterwards, the reaction solution was filtered and the filtrate was collected. After N,N–dimethylformamide was removed from reaction mixture under reduced pressure, the filtrate was treated with acetone and concentrated. A yellowish amorphous solid was obtained. Yield: 23% (0.6 g). ^{1}H NMR (CDCl$_3$) δ: 13.42 (s, 2H, –O*H*), 8.23 (d, 2H, *J* = 8.0 Hz, Ar*H*), 8.21 (d, 2H, *J* = 8.0 Hz, Ar*H*), 7.11 (d, 2H, *J* = 8.0 Hz, Ar*H*), 6.54 (d, 2H, *J* = 12.0 Hz, Ar*H*), 6.38 (s, 2H, Ar*H*), 5.02–5.22 (2×s, 2H, C*H*$_2$ =), 4.28 (s, 4H, –OC*H*$_2$), 3.86 (s, 3H, –OC*H*$_3$), 1.86 (s, 6H, –C*H*$_3$). HRMS *m*/*z*: 511.2116 (Calcd for $C_{30}H_{29}N_3O_5$, 511.2107). IR(v, cm^{-1}): 3346, 3082, 2941, 2934, 1620, 1546, 1528, 1264, 848, 804. Anal. $C_{30}H_{29}N_3O_5$: Calcd C, 70.43; H, 5.71; N, 8.21; found C, 70.38; H, 5.78; N, 8.24%. UV spectrum: λ_{max} = 340 nm, ε_{max} = 47636 l mol^{-1}cm^{-1} (ethanol).

2,4-bis{[4-(3-(2-propyloxy)-2-hydroxypropyloxy)-2-hydroxy] phenyl}-6-(4-methoxyphenyl)-1,3,5 -triazine (**3c**): A mixture of **2** (2 g, 0.005 mol), 2,3-epoxypropyl isopropyl ether (1.34 g, 0.012 mol) and of ethyltriphenylphosphonium 0.18 g (0.5 mmol) bromide in xylene (24 ml) N,N–dimethylformamide 6 ml was heated at reflux temperature for 15 h. After the solvent was removed from the reaction mixture, the residue was treated with acetone and a viscous, slightly yellowish resin was obtained, which crystallised by addition of seed crystals. Yield: 60% (1.9 g). M.p. 96–98 °C. ^{1}H NMR (CDCl$_3$) δ: 13.38 (s, 2H, –O*H*), 8.27 (d, 2H, *J* = 8.0 Hz, Ar*H*), 8.25 (d, 2H, *J* = 8.0 Hz, Ar*H*), 7.13 (d, 2H, *J* = 8.0 Hz, Ar*H*), 6.56 (d, 2H, *J* = 12.0 Hz, Ar*H*), 6.46 (s, 2H, Ar*H*), 4.02–4.26 (m, 6H, Ph–O–C*H*$_2$–C*H*–), 3.90 (s, 3H, –OC*H*$_3$), 3.61–3.82 (m, 6H, –C*H*$_2$O and OC*H*–), 1.19 (d, 12H, *J* = 8.0 Hz, –C*H*$_3$). HRMS *m*/*z*: 635.2864 (Calcd for $C_{34}H_{41}N_3O_9$, 635.2842). IR(v, cm^{-1}): 3402, 3086, 2952, 2938, 1624, 1596, 1542, 1271, 854, 804. Anal. $C_{34}H_{41}N_3O_9$: Calcd. C, 64.24; H, 6.50; N, 6.61; found C, 64.18; H, 6.58; N, 6.64%. UV spectrum: λ_{max} = 336 nm, ε_{max} = 50238 l mol^{-1}cm^{-1} (ethanol).

Shuai Zan, an MSc student, is acknowledged for his contribution during the experiments.

Received 6 May 2008; accepted 28 September 2008
Paper 08/5265 doi: 10.3184/030823408X375142

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