410 **RESEARCH PAPER** JUNE, 410–411 JOURNAL OF CHEMICAL RESEARCH 2004

Formation of benzil diimines by microwave-assisted reaction of benzil with aromatic amines on alumina surface without solvent

G.S. Singh[a]* and D.S. Mahajan[b]

[a]*Chemistry Department University of Botswana, Private Bag: 0022, Gaborone, Botswana*

[b]*Basic Sciences Department, Botswana College of Agriculture, Private Bag: 0027, Gaborone, Botswana*

The microwave-assisted solvent-free reaction of benzil with aromatic amines (in 1 : 2 molar ratio) on an alumina surface for 4 min affords benzil diimines (1,2,3,4-tetraaryl-1,4-diaza-1,3-butadienes).

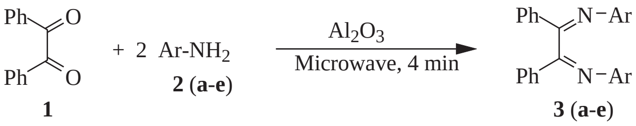
Keywords: benzil, aromatic amines, alumina surface

Imines constitute an important class of organic compounds. Diimines have been used as building blocks for diverse class of biologically important heterocycles such as imidazolines, pyrimidines and bis-azetidinones.[1-4] However, both mono- and diimines of 1,2-diketones such as benzil are known to form with difficulty requiring high temperatures and longer times. Padwa has reported an equimolar reaction of benzil with amines at 175ºC in 2–3 h leading to the formation of benzil monoimines.[5] The formation of benzil diimines has been reported by Armesto and coworkers by reaction of benzil with large excesses of amines (1 : 75–100) using zinc chloride or titanium chloride as catalysts in 2–4 days.[6] Recent literature shows the interest of synthetic organic chemists in developing simple and green protocols for the synthesis of imines and diimines.[7] To develop a quick and environment-friendly method for the synthesis of mono- and diimines of different types of 1,2-diketones for an ongoing project on β-lactams, we considered it pertinent to explore the utility of microwave irradiation, that has been employed in diverse types of reactions in last decade.[8] The present paper reports the formation of benzil diimines (1,2,3,4-tetraaryl-1,4-diaza-1,3-butadienes) by 1 : 2 molar reaction of benzil with aromatic amines on an alumina surface under solvent-free conditions using microwave irradiation. Alumina has been used previously as a solid support in such reactions.[9]

A mixture of benzil **1** and aniline **2a** in 1 : 2 molar ratio on an alumina surface without any solvent afforded a yellow crystalline compound in reasonable yield as the main product (Scheme 1) on irradiation with microwaves. This product has been characterised as 1,2,3,4-tetraphenyl-1,4-diaza-1,3-butadiene **3a** on the basis of satisfactory analytical and spectral (IR, MS and ^{1}H and ^{13}C NMR) data (see experimental). The TLC, however, showed the presence of benzil **1** and benzil monoanil in trace amounts (identified by comparison with authentic samples).[6] Efforts to increase the yield of the product by (i) increasing the reaction time up to 6 min, (ii) taking **2a** in excess and (iii) using the K-10 Clay, which was used by Verma and coworkers[8b] as a catalyst in benzaldehyde imine formation, proved fruitless.

In order to study the generality of this reaction, we carried out reactions of benzil with 4-methyl-, 4-methoxy-, 4-chloroaniline **2b–d**, and with 1-naphthylamine **2e** (this compound is a suspected carcinogen), which also afforded the diimines **3b–e** as the main products. An attempt to synthesise benzil monoimines by an equimolar reaction of benzil with primary amines under similar reaction conditions, however, afforded a complex mixture of products. The TLC showed six spots from which three compounds, monoimines, diimines and benzil could be identified.

In conclusion, this paper reports a rapid, simple and green protocol for the preparation of benzil diimines, which may give an impetus to research on chemistry of such diimines.



Ar = **a**. Ph, **b**. 4-MeC$_6$H$_4$, **c**. 4-MeOC$_6$H$_4$, **d**. 4-ClC$_6$H$_4$ and **e**.1-naphthyl

Scheme 1

Experimental

Melting points were recorded on a Stuart Scientific melting point apparatus and are uncorrected. The IR spectra were recorded on a Perkin-Elmer-781 IR spectrophotometer using KBr disc of the sample. The NMR and mass spectra were recorded on a Bruker^{TM} 300 MHz spectrometer in a CDCl$_3$ solution and on a Mat SSQ 7000 spectrometer, respectively using dichloromethane as a solvent.

CAUTION: **2e** (1-naphthylamine) is a suspected carcinogen.

General reaction procedure: The experimental procedure involved mixing of benzil (**1**, 1 mmole, 0.210 g) and amines (2.2 mmoles) in minimum amount of CH$_2$Cl$_2$ (5-8 ml). This mixture was adsorbed on neutral alumina (1 g per 1 mmol) and air-dried. The mixture was then placed in an alumina bath (used as heat sink) inside a 900-W domestic microwave oven and irradiated at full power for 4 min. The reaction mixture was extracted with CH$_2$Cl$_2$ (3 × 10 ml) and the solvent removed on a rotary evaporator. The residue was triturated with ethanol and left overnight in the refrigerator to get the solid product, which was filtered, dried and recrystallised from ethanol. The characterisation data of the products are given below:

3a: Yield 62 %; m.p. 140°C (lit. m.p. 147°C),[10] IR (KBr, cm^{-1}): 1616 (C=N); ^{1}H NMR (CDCl$_3$, δ ppm): 7.92–6.56 (m, H, arom); ^{13}C NMR (CDCl$_3$, δ ppm): 164.29, 149.70, 138.04, 131.52, 129.17, 128.80 (two C), 125.30, 120.86; MS *m/z* (r. i.): 361 (M$^+$, 100), 269 (8). Found: C, 86.27; H, 5.76; N, 7.89 %. Calcd for C$_{26}$H$_{20}$N$_2$: C, 86.66; H, 5.55; N, 7.77 %.

3b: Yield 69 %; m.p. 154°C, IR (KBr, cm^{-1}): 1620 (C=N); ^{1}H NMR (CDCl$_3$, δ ppm): 7.89 (dt, 4H, arom),7.39 (m, 6H, arom),6.98 (d, 4H, arom),6.53 (dt, 4H, arom), 2.26 (s, 6H, Me).; ^{13}C NMR(CDCl$_3$, δ ppm): 164.17, 147.14, 137.93, 134.96, 131.30, 129.38, 129.06, 128.61, 120.70, 21.32; MS *m/z* (r. i.): 389 (M$^+$, 100), 183 (5). Found: C, 86.40; H, 6.38; N, 7.38 %. Calcd for C$_{28}$H$_{24}$N$_2$: C, 86.59; H, 6.18; N, 7.21 %.

3c: Yield 72 %; m.p. 159°C, IR (KBr, cm^{-1}): 1621 (C=N); ^{1}H NMR (CDCl$_3$, δ ppm): 7.88 (dt, 4H, arom),7.36 (m, 6H, arom),6.68 (dt, 8H, arom),3.74 (s, 6H, MeO).; ^{13}C NMR (CDCl$_3$, δ ppm): 163.67, 157.72, 142.84, 137.80, 131.21, 129.09, 128.45, 122.52, 114.12, 55.73; MS *m/z* (r. i.): 421 (M$^+$, 100), 407 (5), 389 (10), 282 (7) . Found: C, 80.28; H, 5.95; N, 6.38 %. Calcd for C$_{28}$H$_{24}$N$_2$O$_2$: C, 80.00; H, 5.71; N, 6.66 %.

3d: Yield 58 %; m.p. 165°C, IR (KBr, cm^{-1}): 1612 (C=N); ^{1}H NMR (CDCl$_3$, δ ppm): 7.88 (dt, 4H, arom), 7.46 (m, 6H, arom),7.08 (dt, 4H, arom), 6.46 (dt, 4H, arom).; ^{13}C NMR (CDCl$_3$, δ ppm): 164.73, 148.11, 137.60, 131.97, 130.84, 129.32, 128.96, 128.72, 128.86; MS *m/z* (r. i.): 429 (M$^+$, 100), 394 (4), 303 (25). Found: C, 73.01; H, 3.95; N, 6.37 %. Calcd for C$_{26}$H$_{18}$N$_2$Cl$_2$: C, 72.80; H, 4.20; N, 6.54 %.

3e: Yield 72 %; m.p. 225°C, IR (KBr, cm^{-1}): 1615 (C=N); ^{1}H NMR (CDCl$_3$, δ ppm): 8.11 (dt, 4H, arom), 7.50 (m, 7H, arom), 7.25 (m, 3H, arom), 7.01, (m, 6H, arom), 6.83 (m, 2H, arom), 6.69 (dd, 2H, arom); ^{13}C NMR (CDCl$_3$, δ ppm): 164.15, 146.21, 138.61,133.65, 131.52, 129.23, 128.92, 127.88, 127.17, 125.75, 125.67, 124.97, 124.88, 123.07, 111.70; MS *m/z* (r. i.): 461 (M$^+$, 100), 318 (20). Found: C, 88.96; H, 5.45; N, 6.32 %. Calcd for C$_{34}$H$_{24}$N$_2$: C, 88.69; H, 5.21; N, 6.08 %.

---

* Correspondence. E-mail: singhgs@mopipi.ub.bw

We are grateful to the Heads, Chemistry Department, University of Botswana and Basic Sciences Department, Botswana College of Agriculture, for providing the facilities, and to Professor J. Scholz of the University of Koblenz Landau, Koblenz, Germany, for providing the literature on compound **3a**.

Received 24 November 2003; accepted 18 May 2004
Paper 03/2245

References

1 H. Hoberg and G. Barluenga, *Synthesis*, 1970, 363.
2 G. Tuchtenhagen and K. Ruhlmann, *Ann.*, 1968, **711**, 174.
3 P. Karupaiyan, V.G. Puranik, A.R.A.S.; Deshmukh and B.H. Bhawal, *Tetrahedron*, 2000, **56**, 8555.
4 S.H. Park, S.Y. Lee and A.K. Bose, *Bull. Chem. Soc. Korea,* 2001, **22**, 493.
5 A. Padwa, *J. Am. Chem. Soc.*, 1965, **87**, 4365.
6 D. Armesto, P. Bosch, M.G. Gallego, J.F. Martin, M.J. Ortiz, R. Perez-Ossorio and A. Ramos, *Org. Prep. Proc. Intl.*, 1987, **19**, 181.
7 A. Simion, C. Simion, T. Kanda, S. Nagashima, Y. Mitoma, T. Yamada, K. Mimura and M. Tashiro, *J. Chem. Soc. Perkin Trans. 1*, 2001, 2071.
8 (a) A. Loupy, A. Petit, J. Hamelin, F. Texier-Boullet, P. Jacquault and D. Mathe, *Synthesis*, 1998, 1213; (b) R.S. Varma, R. Dahiya and S. Kumar, *Tetrahedron Lett.*, 1997, **38**, 2039; (c) R.S. Varma and R. Dahiya, *Synlett,*, 1997, 1245.
9 F. Texier-Boullet, *Synthesis*, 1985, 679.
10 J. Scholz, B. Richter, R. Goddard and C. Kruger, *Chem. Ber.*, 1993, **126**, 57.