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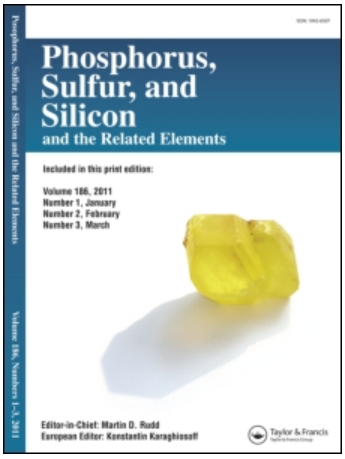

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Synthesis of Some Benzotriazole-Substituted Perimidines

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Synthesis of Some Benzotriazole-Substituted Perimidines

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*2-substituted perimidines **3(a–g)** were prepared from an acid-catalyzed reaction of 1,8-diaminonaphthalene with carboxylic acids using microwave irradiation. Addition of these perimidines to 1-chloromethyl benzotriazole in the presence of the sodium amide under reflux conditions gave benzotriazole-substituted perimidines **5(a–f)**. Yields of these products following recrystallization from water were of the order of 60–65%. IR and ^{1}HNMR spectra and elemental analysis were used for identification of these compounds.*

Keywords Benzotriazole; diaminonaphthalene; perimidine

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INTRODUCTION

Perimidines[1] and compounds containing a benzotriazole moiety[2–4] attached to a heterocyclic system are of wide interest because of their diverse biological activities. Several classical synthetic methods have been reported for the synthesis of perimidine derivatives, which need special reagent or vigorous reaction conditions.[5–7] However, prepartion of perimidies from a cyclocondensation reaction of 1,8-diaminonaphtalene with carboxylic acids under microwave irradiation is the more convenient method. Some interesting features of this method are the rapid reaction rates, simplicity, and cleaner reaction conditions.[8–12] Many hetrocycles containing a benzotriazole moiety have been reported by several articles.[2–4,13–15] However, perimidine derivatives that have a benzotriazole moiety are not well known. The aim of this study is to prepare some perimidines under microwave irradiation. We further studied the reaction of these perimidines with 1-chloromethylbenzotriazole in order to synthesize some new benzotriazole-substituted perimidines.

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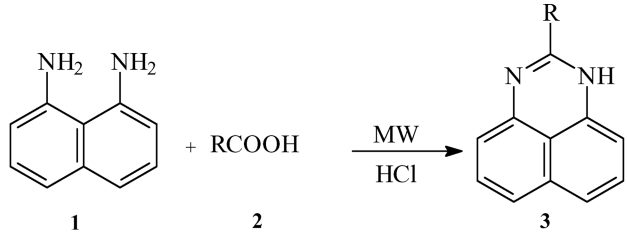
RESULTS AND DISCUSSION

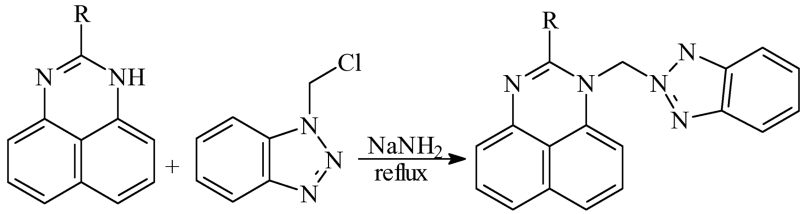
Symmetrical perimidines **3(a–g)** were prepared by treating the acid-catalyzed cyclization of 1,8-diaminonaphthalene **1** with the appropriate carboxylic acid **2** under microwave irradiation (Scheme 1). The nucleophilic addition of perimidines **3(a–f)** to 1-chloromethylbenzotriazole **4** in the presence of a strong base, $NaNH_2$, under reflux afforded benzotriazole-substituted perimidines **5(a–f)**.

^{1}HNMR spectra of **3(e–g)** are simple because the symmetry of their structures and have two distinct signals in the aromatic and aliphatic regions. Comounds **3e** and **3f** show one and two multiplet signals at 2.60 ppm and 1.54–2.22 ppm due to the resonance of the 2 and 4 methylene groups, respectively. Two singlet signals at 6.16 ppm and 10.12 ppm in the ^{1}HNMR spectrum of **3g** are atributed to the resonance of two cis olefinic and two NH protons, respectively. However, in the the ^{1}HNMR spectra of **3e** and **3f**, there is no possibility of the NH signal



1 **2** **3**

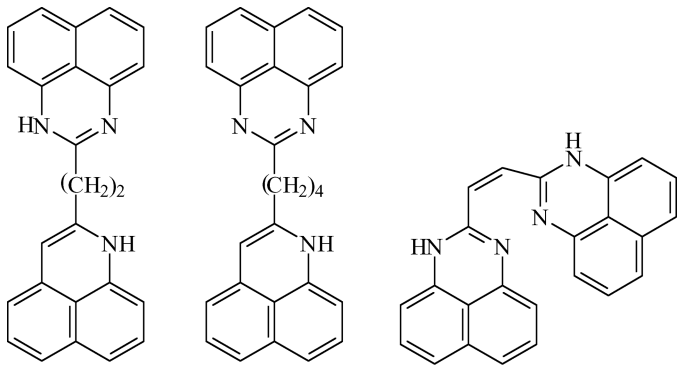
3(a) R = Methyl
3(b) R = Ethyl
3(c) R = Chloromethyl
3(d) R = Trichloromethyl
3(e) R = 2-(1H-perimidine-2-yl)ethyl
3(f) R = 4-(1H-perimidine-2-yl)butyl
3(g) R = (*Z*)-2(1H-perimidine-2-yl)-1-ethenyl



3 **4** **5**

5(a) R = Methyl
5(b) R = Ethyl
5(c) R = Chloromethyl
5(d) R = Trichloromethyl
5(e) R = R = 2-(1H-perimidine-2-yl)ethyl
5(f) R = 4-(1H-perimidine-2-yl)butyl

SCHEME 1



3e **3f** **3g**

SCHEME 2

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resonance presumably because of the fast tautomerism of the NH azoles in the perimidine rings.[5] In the case of **3g** (Scheme 2), the steric effect of two cis bulky perimidines groups hinders the fast tautomerization of two NH azoles and results in their resonance. Also in the ^{1}HNMR spectra of **3c** and **3d**, the NH signal resonance is observed because of an intramolecular hydrogen bonding between the NH proton and the Cl group on the perimidine ring.[16]

In the ^{1}HNMR spectra of **5(a–f)** the protons of the methylene group with the protons of two perimidine and benzotriazole rings resonate at downfield. These protons appeared at 6.05–6.50 ppm for benzotriazole-substituted perimidines with no electron-withdrawing groups. However, the methylene groups of **5c** and **5d** containing perimidine ring with one and three chlorine atoms resonate at 6.70 ppm and 8.35 ppm, respectively.

EXPERIMENTAL

All chemicals including 1,8-diaminonaphthalene and carboxylic acids were of reagent-grade quality and were used without further purification. 1-chloromethybenzotriazole was prepared by the reaction of 1-hydroxymethylbenotriazole and thionyl chloride.[17] ^{1}HNMR spectra were recorded on a Brucker 500 MHz spectrometer. IR spectra were performed on a Galaxy FT-IR 500 spectrophotometer. Reaction progress (for **5a–f**) was routinely monitored by TLC on silica gel plates. Reactions were performed in a Samsung microwave oven with a 230V-50Hz power source, a 900 W output, and a 2450 MHz operating frequency.

General Procedure for Preparation of 2-Arylperimidines

For preparation of **3a–g**, 1,8-diaminonaphthalene (1.0 mmol) was ground with a pestle in a mortar with an equimolar amount of an appropriate carboxylic acid (1.0 and 0.5 mmol for monofunctional and bifunctional acid, respectively). The mixture was placed in a 25-mL-glass beaker and two drops of HCl (4 M) were, added. This beaker was put into a microwave oven and subjected to microwave irradiation at 100% power level for 1–1.5 min. The beaker then was kept at room temperature for 2 h and the crude products were recrystallized from a mixture of ethanol and water (50:50) to give compounds **3a–g**. Perimidines **3a–d** are known compounds.

For the preparation of benzotriazole-substituted perimidines **5(a–f)**, a mixture of sodium amide (1 mmol) and an appropriate perimidine compound (1 mmol) in dry toluene (5 mL) was refluxed for 4 h. Chloromethylbenzotriazole (1 mmol) was added to the hot suspension and refluxed for 9 h. After cooling and collecting on a funnel, the crude product was recrystallized from water.

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2-[2-(1H-perimidine-2-yl)-ethyl]–1H-perimidrne (3e)

Yield 65%, M.P. 227–229°C

IR (KBr): $\nu = 3200, 3060, 2960, 1650, 1525, 1480\ cm^{-1}$

^{1}HNMR (DMSO): δ (ppm) = 2.60 (m, 4H), 7.01 (m, 12H)

Anal. cald. for $C_{24}H_{18}N_4$: C, 79.56; H, 4.97; N, 15.47. Found: C, 79.70; H, 5.10; N, 15.10%.

2-[4-(1H-perimidine-2-yl)-butyl]–1H-perimidrne (3f)

Yield 65%, M.P. 265–267°C

IR (KBr): $\nu = 3440, 3050, 2950, 1660, 1525, 1475\ cm^{-1}$

^{1}HNMR (DMSO): δ (ppm) = 1.54 (m, 4H), 2.22 (m, 4H), 6.99 (m, 12H)

Anal. cald. for $C_{26}H_{22}N_4$: C, 80.00; H, 5.64; N, 14.36. Found: C, 80.40; H, 5.23; N, 14.28%.

2-[(Z)-2-(1H-perimidine-2-yl)-1-ethenyl]–1H-perimidrne (3g)

Yield 75%, M.P. 210–212°C

IR (KBr): $\nu = 3380, 3060, 2950, 1660, 1595, 1425\ cm^{-1}$

^{1}HNMR (DMSO): δ (ppm) = 6.16 (s, 1H), 7.21 (m, 12H), 10.12 (s, 2H)

Anal. cald. for $C_{24}H_{16}N_4$: C, 80.00; H, 4.44; N, 15.56. Found: C, 80.34; H, 4.10; N, 15.51%.

1-(1H-1,2,3-benzotriazole-1-yl-methyl)-2-methyl-1H-perimidine (5a)

Yield 60%, decomposed >290°C

IR (KBr): $\nu = 3180, 2730, 1650, 1595, 1475\ cm^{-1}$

^{1}HNMR (DMSO): δ (ppm) = 2.30 (s, 3H, CH_3), 6.05 (s, 2H, CH_2), 7.75 (m, 10H_{arom})

Anal. cald. for $C_{19}H_{15}N_5$: C, 72.84; H, 4.79; N, 22.36. Found: C, 72.45; H, 4.75; N, 22.75%.

1-(1H-1,2,3-benzotriazole-1-yl-methyl)-2-ethyl-1H-perimidine (5b)

Yield 60%, decomposed >240°C

IR (KBr): $\nu = 3000, 2900, 1680, 1550, 1430\ cm^{-1}$

^{1}HNMR (DMSO): δ (ppm) = 1.70 (t, J = 7.4 Hz, 3H, CH_3), 3.90 (q, 7.4 Hz, 2H, CH_2), 6.10 (s, CH_2-N), 7.70 (m, 10H_{arom})

Anal. cald. for $C_{20}H_{17}N_5$: C, 73.39; H, 5.20; N, 21.41. Found: C, 73.02; H, 5.62; N, 21.29%.

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1-(1H-1,2,3-benzotriazole-1-yl-methyl)-2-chloromethyl-1H-perimidine (5c)

Yield 65%, decomposed >273°C

IR (KBr): $\nu = 3050, 2950, 1600, 1500, 1460\ cm^{-1}$

^{1}HNMR (DMSO): δ (ppm) = 2.30 (s, 2H, CH_2Cl), 6.70 (s, 2H, CH_2N), 7.72 (m, 10H_{arom})

Anal. cald. for $C_{19}H_{14}N_5Cl$: C, 65.61; H, 4.03; N, 20.14; Cl, 10.22. Found: C, 65.98; H, 3.91; N, 20.36; Cl, 9.75%.

1-(1H-1,2,3-benzotriazole-1-yl-methyl)-2-trichloromethyl-1H-perimidine (5d)

Yield 65%, decomposed >232°C

IR (KBr): $\nu = 3070, 2960, 1690, 1615, 1400\ cm^{-1}$

^{1}HNMR (DMSO): δ (ppm) = 8.35 (s, 2H, CH_2N), 7.72 (m, 10H_{arom})

Anal. cald. for $C_{19}H_{12}N_5Cl_3$: C, 54.74; H, 2.88; N, 16.81; Cl, 25.57. Found: C, 54.9; H, 2.96; N, 16.4; Cl, 25.79%.

1-(1H-1,2,3-benzotriazole-1-yl-methyl)-2-[2-(1H-perimidine-2-yl)ethyl]-1H-perimidine (5e)

Yield 60%, decomposed >295°C

IR (KBr): $\nu = 3410, 3060, 2860, 1685, 1620, 1490, 1390\ cm^{-1}$

^{1}HNMR (DMSO): δ (ppm) = 2.27 (m, 4H, CH_2-CH_2), 6.50 (bs, 2H, CH_2N), 7.65 (m, 16H_{arom}), 11.0 (bs, 1H, NH)

Anal. cald. for $C_{31}H_{23}N_7$: C, 75.46; H, 4.67; N, 19.88. Found: C, 75.81; H, 4.50; N, 19.60%.

1-(1H-1,2,3-benzotriazole-1-yl-methyl)-2-[4-(1H-perimidine-2-yl)butyl]-1H-perimidine (5f)

Yield 65%, decomposed >305°C

IR (KBr): $\nu = 3420$, 3150, 2850, 1650, 1550, 1400 cm^{-1}, ^{1}HNMR (DMSO): δ (ppm) = 1.75 (m, 8H, 4 x CH_2), 6.10 (s, 2H, CH_2N), 7.73 (m, 16H_{arom})

Anal. cald. for $C_{33}H_{27}N_7$: C, 76.01; H, 5.18; N, 18.81. Found: C, 75.64; H, 5.30; N, 19.13%.

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