Microwave-Assisted Synthesis of Novel Functionalized Ketenimines and Azadienes via a Solvent-Free Reaction of Isatoic Anhydride, Alkyl-Isocyanides and Dialkyl Acetylenedicarboxylates

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ABSTRACT: *Ketenimines and azadienes are transient intermediates in organic chemistry especially in elimination-addition processes and in the formation of heterocyclic systems. These compounds play a considerable role as intermediates in the synthesis of heterocyclic ring systems. In this present research synthesis of novel ketenimines and azadienes via multicomponent reactions (MCRs) based on alkyl-Isocyanides is reported. Following our ongoing interest in isocyanide-based MCRs, we reported stereoselective reactions between 4H-3,1-benzoxazine-2,4(1H)-dione (isatoic anhydride) with dialkylacetylenedicarboxylates in the presence of alkyl isocyanides under solvent-free microwave conditions which leads to novel functionalized ketenimines and azadienes in a green route. The results show that the microwave-assisted leaching process has advantages over the conventional ones, concerning energy-consumption, processing time, and environmental protection.*

KEYWORDS: *Microwave-Assisted; Alkyl-Isocyanides; KetenimineAzadiene, Isatoic anhydride.*

INTRODUCTION

Microwave-Assisted Organic Synthesis (MAOS) is one of the new methods in modern synthetic organic chemistry. Microwave instruments are becoming part of the equipment in numerous laboratories providing researchers with a new tool to enhance the arsenal of reactions [1–6]. Microwave irradiation usually decreases reaction times and increases reaction efficiency. The approachability of single-mode microwave reactors, which provides accurate control of the reaction conditions, has extended the use of microwave-assisted manners in the equivalent synthesis. For Multi-Component Reactions (MCRs) based on isocyanides can be mentioned to Ugi and Passerini reactions [7–9]. In recent years, the synthesis of functionalized heteroallenes has been widely investigated [10-16]. Ketenimines play a considerable role as intermediates in the synthesis of heterocyclic ring systems [17–20]. The spectroscopic properties of ketenimines have been investigated [21]. In the application of isocyanides in MCRs, recently, we have contributed to MAOS's popularity describing solvent-free access to of novel highly functionalized ketenimines **4** and azadienes **5** through a multi-component reaction

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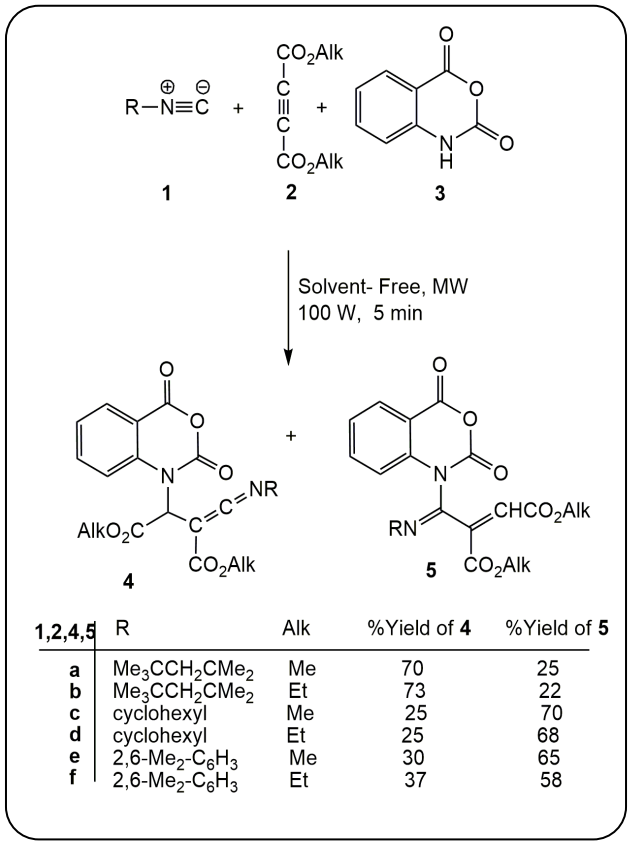


1,2,4,5	R	Alk	%Yield of **4**	%Yield of **5**
a	$Me_3CCH_2CMe_2$	Me	70	25
b	$Me_3CCH_2CMe_2$	Et	73	22
c	cyclohexyl	Me	25	70
d	cyclohexyl	Et	25	68
e	2,6-Me_2-C_6H_3	Me	30	65
f	2,6-Me_2-C_6H_3	Et	37	58

Scheme 1: Synthesis of compounds 4 and 5.

between 4H-3,1-benzoxazine-2,4(1H)-dione (isatoic anhydride) and dialkylacetylenedicarboxylates in the presence of alkyl isocyanides under microwave irradiation in only 5 min at 100°C. Thus, the reaction of isocyanides **1** with acetylenedicarboxylates **2** in the presence of 4H-3,1-benzoxazine-2,4(1H)-dione (isatoic anhydride) **3** as a proton source/nucleophile leads to stable dialkyl2-((alkylimino-methylene)-3-(2,4-dioxo-2H-benzo[d][1,3]oxazin -1(4H)-yl)succinates **4a**–**4f** and dialkyl 2-((alkylimino)(2,4-dioxo-2H-benzo[d][1,3]oxazin -1(4H)-yl)alkyl)maleates **5a-5f** in appropriate yields (scheme 1).

EXPERIMENTAL SECTION

General

The experimental procedure involves a simple mixing and grinding of 4H-3,1-benzoxazine-2,4(1H)-dione (isatoic anhydride) and dialkylacetylenedicarboxylates in the presence of alkyl isocyanides and irradiating the reaction mixture in a microwave oven for about 5 min in the absence of any solvent. The microwave oven was a domestic National model NN-6653 (maximum 900 W) with five select power levels (one of which was used for this experiment; high 100% wattage). This extremely rapid, manipulatively simple, and inexpensive protocol avoids the use of excess and toxic solvent Chemicals were purchased from Fluka and were used without further purification; IR spectra: Shimadzu IR-460 spectrometer; ^{1}H- and ^{13}C-NMR spectra: Bruker DRX-300AVANC instrument; in $CDCl_3$ at 300 and 75 MHz, respectively, δ in ppm, J in Hz; EI-MS (70 eV): Finnigan MAT-8430 mass spectrometer, in m/z. Elemental analyses (C, H, and N) were performed with a Heraeus CHN-O-Rapid analyzer. The results agreed favourably with the calculated values.

General procedure for the preparation of compounds 4

To a mixture of isatoic anhydride (**3**, 2 mmol, 0.33g) and acetylenic ester (**2**, 2 mmol) was added alkyl isocyanide (**1**, 2 mmol) under solvent free conditions. Then the mixture was irradiated in a crimped 0.5e2 mL microwave vial for 5 min. After completion of the reaction [5 min; TLC (hexane/AcOEt 3:1 the residue was purified by column chromatography [silica gel (230–240 mesh; Merck), hexane/AcOEt 3:1)].

dimethyl 2-((2,4,4-trimethylpentan-2-ylimino)methylene)-3-(2,4-dioxo-2H-benzo[d][1,3]oxazin-1(4H)-yl)succinate (4a)

Yellow oil, yield: 0.31 g (70%). ^{1}H-NMR, *δ*: 1.06 (9 H, s, 3 Me), 1.56(3 H, s, Me), 1.60 (3 H, s, Me), 1.68 (2 H, s, CH_2), 3.71 (3 H, s, MeO), 3.78 (3 H, s, MeO), 6.00 (1 H, s, CH), 7.29-8.19 (4H, m, 4CH). ^{13}C-NMR, *δ*: 31.3 (C*Me*$_3$), 31.4 (C*Me*$_2$), 32.0 (*C*Me$_3$), 51.9 (*C*H$_2$), 53.7 (*Me*O), 54.6 (*Me*O), 57.0 (*C*Me$_2$), 58.2(*C*H), 65.7 (*C*=C=N), 111.8 (*C*), 115.2 (*C*H), 124.6 (*C*H), 131.2 (*C*H), 137.9 (*C*H), 141.7 (*C*), 147.8, 156.5, 158.6, 167.6 and 171.7 (C=*C*=N and 4 *C*=O). IR (ν_{max}/cm^{-1}): 2072 (C=C=N), 1783 and 1737 (C=O). EI-MS: *m/z* (%) = 444 (M+, 15), 331 (77), 317 (57), 139 (14), 113 (33), 71(29), 59 (34), 57 (100). Anal. Calcd for $C_{23}H_{28}N_2O_7$ (444.48): C, 62.15%; H, 6.35%; N, 6.30%; found: C, 62.10%; H, 6.31%; N, 6.25%.

dimethyl 2-((2,4,4-trimethylpentan-2-ylimino)(2,4-dioxo-2H-benzo[d][1,3]oxazin-1(4H)-yl)methyl)maleate (5a)

Yellow oil, yield: 0.11 g (25%). ^{1}H-NMR, *δ*: 1.09(9 H, s, 3 Me), 1.57(3 H, s, Me), 1.59 (3 H, s, Me), 1.71 (2 H, s, CH_2), 3.72 (3 H, s, MeO), 3.78 (3 H, s, MeO), 7.10

(1 H, s, CH), 7.46-8.31 (4H, m, 4CH). ^{13}C-NMR, δ: 31.3 (C*Me*$_3$), 31.4 (C*Me*$_2$), 32.3 (*C*Me$_3$), 51.7 (*C*H$_2$), 53.9 (*Me*O), 55.0 (*Me*O), 57.8 (*C*Me$_2$), 123.1 (*C*), 127.2 (*C*H), 127.6(*C*H), 127.8 (*C*H), 132.5 (*C*H), 134.8 (*C*H), 140.9(*C*), 147.1 (*C*), 147.3, 150.8, 162.2, 164.0 and 164.4 (*C*=N and 4 *C*=O). IR (ν_{max}/cm^{-1}): 1758 and 1737 (C=O), 1690 (C=N). EI-MS: *m/z* (%) = 444 (M+, 16), 331 (56), 317 (64), 301 (12), 113 (34), 71 (27), 59 (31), 57 (100). Anal. Calcd for $C_{23}H_{28}N_2O_7$ (444.48): C, 62.15%; H, 6.35%; N, 6.30%; found: C, 62.10%; H, 6.31%; N, 6.25%.

diethyl 2-((2,4,4-trimethylpentan-2-ylimino)methylene)-3-(2,4-dioxo-2H benzo[d][1,3]oxazin-1(4H)-yl)succinate (4b)

Yellow oil, yield: 0.34 g (73%). ^{1}H-NMR, δ: 1.07 (9 H, s, 3 Me), 1.25 (3 H, t, ^3J 7.2 Hz, Me), 1.27 (3 H, t, ^3J 7.2 Hz, Me), 1.56 (3 H, s, Me), 1.60 (3 H, s, Me), 1.67 (2 H, s, CH$_2$), 4.19 (2 H, q, ^3J 7.2 Hz, CH$_2$O), 4.26 (2 H, q, ^3J 7.2 Hz, CH$_2$O), 5.98 (1 H, s, CH), 7.28-8.18 (4H, m, 4CH). ^{13}C-NMR, δ: 14.4 (*Me*), 14.8 (*Me*), 31.3 (C*Me*$_2$), 31.5 (C*Me*$_3$), 32.0 (*C*Me$_3$), 54.6 (*C*H$_2$), 57.2 (*C*Me$_2$), 58.6 (*C*H), 60.8(*C*H$_2$O), 63.0 (*C*H$_2$O), 65.7 (*C*=C=N), 111.7 (*C*), 115.3 (*C*H), 124.5 (*C*H), 131.1 (*C*H), 137.8 (*C*H), 141.8(*C*), 147.7, 157.4, 158.7, 167.1 and 171.3 (C=*C*=N and 4 *C*=O). IR (ν_{max}/cm^{-1}): 2081 (C=C=N), 1747 and 1700 (C=O). EI-MS: *m/z* (%) = 472 (M+, 12), 359 (57), 345 (61), 139 (15), 113 (36), 73 (30), 71(29), 57 (100). Anal. Calcd for $C_{25}H_{32}N_2O_7$ (472.53): C, 63.54%; H, 6.83%; N, 5.93%; found: C, 63.48%; H, 6.77%; N, 5.86%.

diethyl 2-((2,4,4-trimethylpentan-2-ylimino)(2,4-dioxo-2H-benzo[d][1,3]oxazin-1(4H)-yl)methyl)maleate (5b)

Yellow oil, yield: 0.10 g (22%). ^{1}H-NMR, δ: 1.09 (9 H, s, 3 Me), 1.28 (3 H, t, ^3J 7.2 Hz, Me), 1.29 (3 H, t, ^3J 7.2 Hz, Me), 1.58 (3 H, s, Me), 1.65 (3 H, s, Me), 1.70 (2 H, s, CH$_2$), 3.96 (2 H, q, ^3J 7.2 Hz, CH$_2$O), 4.01 (2 H, q, ^3J 7.2 Hz, CH$_2$O), 7.20 (1 H, s, CH), 7.45-8.30(4H, m, 4CH). ^{13}C-NMR, δ: 14.5 (Me), 14.9 (Me), 31.2 (C*Me*$_2$), 31.5 (C*Me*$_3$), 32.1(*C*Me$_3$), 54.7 (CH$_2$), 57.3 (*C*Me$_2$), 60.9(CH$_2$O), 63.2 (CH$_2$O), 123.13 (C), 127.4 (CH), 127.7(CH), 127.9 (CH), 132.3 (CH), 134.6 (CH), 140.8(C), 147.2 (C), 147.4, 150.9, 162.3, 164.3 and 164.5 (*C*=N and 4 C=O). IR (ν_{max}/cm^{-1}): 1750 and 1735 (C=O), 1685 (C=N). EI-MS: *m/z* (%) = 472 (M+, 15), 359 (53), 345 (52), 301 (14), 113 (33), 73 (31), 71 (25), 57 (100). Anal. Calcd for $C_{25}H_{32}N_2O_7$ (472.53): C, 63.54%; H, 6.83%; N, 5.93%; found: C, 63.48%; H, 6.77%; N, 5.86%.

dimethyl 2-((cyclohexylimino)methylene)-3-(2,4-dioxo-2H-benzo[d][1,3]oxazin-1(4H)-yl)succinate (4c)

Yellow oil, yield: 0.10 g (25%). ^{1}H-NMR, δ: 1.25-2.00 (10 H, m, 5 CH$_2$), 3.55 (3 H, s, MeO), 3.82 (3 H, s, MeO), 4.20 (1 H, m, CHN), 5.10 (1 H, s, CH), 6.57-8.28 (4H, m, 4CH). ^{13}C-NMR, δ: 25.3 (*C*H$_2$), 25.7 (*C*H$_2$), 33.1 (*C*H$_2$), 33.6 (*C*H$_2$), 34.1 (*C*H$_2$), 51.3 (*Me*O), 51.7 (*Me*O), 57.2 (*C*HN), 59.4 (*C*H), 63.7 (*C*=C=N), 111.9 (*C*), 116.1 (*C*H), 125.3 (*C*H), 130.8 (*C*H), 137.4 (*C*H), 144.0 (*C*), 144.7, 147.5, 158.2, 163.3 and 165.8 (C=*C*=N and 4 *C*=O). IR (ν_{max}/cm^{-1}): 2072 (C=C=N), 1741 and 1737 (*C*=O). EI-MS: *m/z* (%) = 414 (M+, 12), 331 (100), 296 (10), 109 (14), 97 (13), 83 (25), 59 (34). Anal. Calcd for $C_{21}H_{22}N_2O_7$ (414.41): C, 60.86%; H, 5.35%; N, 6.76%; found: C, 60.81%; H, 5.29%; N, 6.71%.

dimethyl 2-((cyclohexylimino)(2,4-dioxo-2H-benzo[d][1,3]oxazin-1(4H)-yl)methyl)maleate (5c)

Yellow oil, yield: 0.29 g (70%). ^{1}H-NMR, δ: 1.19-2.77 (10 H, m, 5 CH$_2$), 3.68 (1 H, m, CHN), 3.69 (3 H, s, MeO), 3.87 (3 H, s, MeO), 7.20 (1 H, s, CH), 7.46-8.31 (4H, m, 4CH).^{13}C-NMR, δ: 25.5 (*C*H$_2$), 26.8 (*C*H$_2$), 28.7 (*C*H$_2$), 28.8 (*C*H$_2$), 29.6 (*C*H$_2$), 52.9 (*Me*O), 53.7 (*Me*O), 54.1 (*C*HN), 122.9 (*C*), 127.0 (*C*H), 127.4 (*C*H), 127.8 (*C*H), 132.7 (*C*H), 134.6 (*C*H), 140.5(*C*), 147.5 (*C*), 147.3, 150.8, 162.2, 164.0 and 164.4 (*C*=N and 4 *C*=O). IR (ν_{max}/cm^{-1}): 1750 and 1730 (C=O), 1681 (C=N). EI-MS: *m/z* (%) = 414 (M+, 12), 331 (100), 317 (61), 271 (14), 83 (37), 59 (35). Anal. Calcd for $C_{21}H_{22}N_2O_7$ (414.41): C, 60.86%; H, 5.35%; N, 6.76%; found: C, 60.81%; H, 5.29%; N, 6.71%.

diethyl 2-((cyclohexylimino)methylene)-3-(2,4-dioxo-2H-benzo[d][1,3]oxazin-1(4H)-yl)succinate (4d)

Yellow oil, yield: 0.10 g (23%). ^{1}H-NMR, δ: 1.26 (3 H, t, ^3J 7.2 Hz, Me), 1.29 (3 H, t, ^3J 7.2 Hz, Me), 1.23-2.19 (10 H, m, 5 CH$_2$), 4.02 (2 H, q, ^3J 7.2 Hz, CH$_2$O), 4.17 (1 H, m, CHN), 4.28 (2 H, q, ^3J 7.2 Hz, CH$_2$O), 5.12 (1 H, s, CH), 6.61-8.31 (4H, m, 4CH). ^{13}C-NMR, δ: 14.3 (*Me*), 14.6 (*Me*), 25.5 (*C*H$_2$), 25.8 (*C*H$_2$), 27.0 (*C*H$_2$), 33.1 (*C*H$_2$), 34.1 (*C*H$_2$), 57.1 (*C*HN), 59.4 (*C*H), 60.6

(CH_2O), 60.9 (CH_2O), 62.0 (*C*=C=N), 111.1 (*C*), 116.2 (*C*H), 124.5 (*C*H), 129.5 (*C*H), 137.4 (*C*H), 144.1 (*C*), 147.5, 158.3, 162.3, 163.6 and 165.4 (C=*C*=N and 4 *C*=O). IR (ν_{max}/cm^{-1}): 2080 (C=C=N), 1745 and 1735 (C=O).EI-MS: *m/z* (%) = 442 (M+, 12), 359 (100), 296 (10), 109 (15), 97 (14), 83 (27), 73 (35). Anal. Calcd for $C_{23}H_{26}N_2O_7$ (442.46): C, 62.43%; H, 5.92%; N, 6.33%; found: C, 62.38%; H, 5.88%; N, 6.28%.

diethyl 2-((cyclohexylimino)(2,4-dioxo-2H-benzo[d][1,3]oxazin-1(4H)-yl)methyl)maleate (5d)

Yellow oil, yield: 0.31 g (69%). ^{1}H-NMR, δ: 1.02 (3 H, t, ^3J 7.2 Hz, Me), 1.04 (3 H, t, ^3J 7.2 Hz, Me), 1.19-2.77 (10 H, m, 5 CH_2), 3.98 (1 H, m, CHN), 4.06 (2 H, q, ^3J 7.2 Hz, CH_2O), 4.32 (2 H, q, ^3J 7.2 Hz, CH_2O), 6.49 (1 H, s, CH), 7.31-8.31 (4H, m, 4CH). ^{13}C-NMR, δ: 14.4 (*Me*), 14.7 (*Me*), 25.6 (CH_2), 25.9 (CH_2), 27.0 (CH_2), 33.7 (CH_2), 34.5 (CH_2), 54.1 (*C*HN), 63.1(CH_2O), 63.2 (CH_2O), 121.9 (*C*), 127.0 (*C*H), 127.4 (*C*H), 127.8 (*C*H), 132.7 (*C*H), 134.3 (*C*H), 140.5 (*C*), 147.3 (*C*), 147.5, 150.8, 162.7, 164.0 and 164.9 (*C*=N and 4 *C*=O). IR (ν_{max}/cm^{-1}): 1743 and 1730 (C=O), 1675 (C=N). EI-MS: *m/z* (%) = 442 (M+, 14), 359 (100), 345 (60), 271 (11), 83 (37), 73 (31). Anal. Calcd for $C_{23}H_{26}N_2O_7$ (442.46): C, 62.43%; H, 5.92%; N, 6.33%; found: C, 62.38%; H, 5.88%; N, 6.28%.

dimethyl 2-((2,6-dimethylphenylimino)methylene)-3-(2,4-dioxo-2H-benzo[d][1,3]oxazin-1(4H)-yl)succinate (4e)

Yellow oil, yield: 0.13 g (30%). ^{1}H-NMR, δ: 2.10 (6 H, s, 2CH_3), 3.45 (3 H, s, MeO), 3.72 (3 H, s, MeO), 6.16 (1 H, s, CH), 7.00-8.37 (4H, m, 4CH). ^{13}C-NMR, δ: 18.5 (2*Me*), 52.7 (*Me*O), 53.1 (*Me*O), 57.6 (*C*H), 60.8 (*C*=C=N), 111.8 (*C*), 115.2 (*C*H), 124.6 (*C*H), 129.1 (2*C*H), 129.4 (*C*H), 132.2 (*C*H), 135.3 (2*C*), 137.0 (*C*), 137.9 (*C*H), 141.7 (*C*), 147.7, 157.4, 158.7, 167.1 and 171.3 (C=*C*=N and 4 *C*=O). IR (ν_{max}/cm^{-1}): 2072 (C=C=N), 1740 and 1735 (C=O). EI-MS: *m/z* (%) = 436(M+, 16), 331 (100), 318 (10), 131 (13), 119 (21), 105 (24), 59 (34). Anal. Calcd for $C_{23}H_{20}N_2O_7$ (436.41): C, 63.30%; H, 4.62%; N, 6.42%; found: C, 62.96%; H, 4.60%; N, 6.38%.

dimethyl 2-((2,6-dimethylphenylimino)(2,4-dioxo-2H-benzo[d][1,3]oxazin-1(4H)-yl)methyl)maleate (5e)

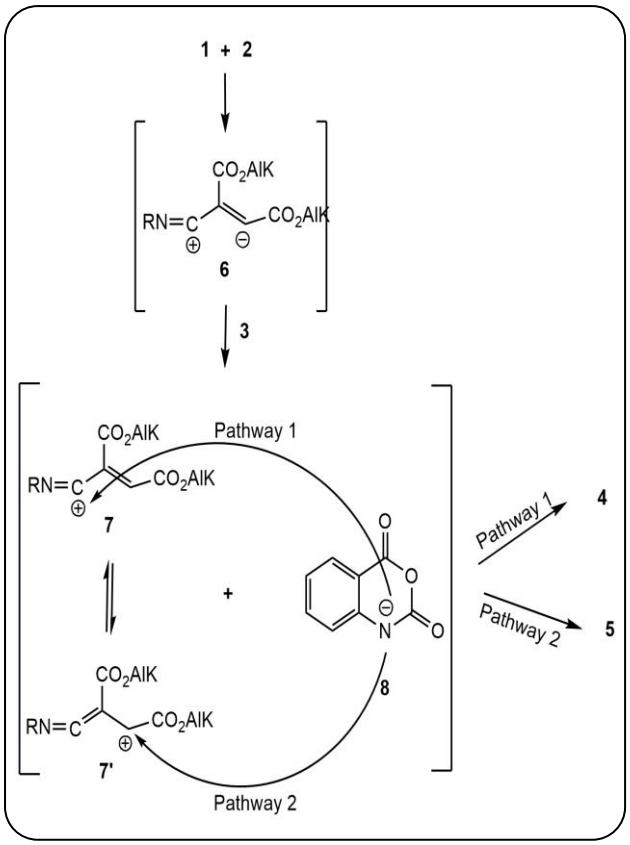
Yellow oil, yield: 0.28 g (65%). ^{1}H-NMR, δ: 2.11 (6 H, s, 2CH_3), 3.51 (3 H, s, MeO), 3.72 (3 H, s, MeO), 6.70 (1 H, s, CH), 7.12-8.41 (4H, m, 4CH). ^{13}C-NMR, δ: 18.5 (2*Me*), 52.7 (*Me*O), 52.9 (*Me*O), 121.9 (*C*), 127.7 (*C*H), 128.1 (*C*H), 128.2 (*C*H), 129.0 (2*C*H), 130.9 (*C*H), 132.4 (*C*H), 134.3 (2*C*), 135.1 (*C*H), 131.4 (*C*), 137.8 (*C*H), 139.6 (*C*), 147.9, 148.8, 161.2, 163.7and 164.6 (*C*=N and 4 *C*=O). IR (ν_{max}/cm^{-1}): 1747 and 1735 (C=O), 1650 (C=N). EI-MS: *m/z* (%) = 436 (M+, 17), 331 (100), 317 (52), 293 (11), 105 (33), 59 (28). Anal. Calcd for $C_{23}H_{20}N_2O_7$ (436.41): C, 63.30%; H, 4.62%; N, 6.42%; found: C, 62.96%; H, 4.60%; N, 6.38%.

diethyl 2-((2,6-dimethylphenylimino)methylene)-3-(2,4-dioxo-2H-benzo[d][1,3]oxazin-1(4H)-yl)succinate (4f)

Yellow oil, yield: 0.17 g (37%). ^{1}H-NMR, δ: 1.25 (3 H, t, ^3J 7.2 Hz, Me), 1.37 (3 H, t, ^3J 7.2 Hz, Me), 2.12 (6 H, s, 3Me), 4.16 (2 H, q, ^3J 7.2 Hz, CH_2O), 4.35 (2 H, q, ^3J 7.2 Hz, CH_2O), 6.15 (1 H, s, CH), 6.83-7.86(4H, m, 4CH). ^{13}C-NMR, δ: 14.2 (*Me*), 14.7 (*Me*), 18.6 (2*Me*), 60.7(CH_2O), 61.2(CH_2O), 61.9(*C*H), 62.5 (*C*=C=N), 111.0 (*C*), 114.9 (*C*H), 125.0 (*C*H), 129.0 (2*C*H), 129.3 (*C*H), 132.3 (*C*H), 135.2 (2*C*), 137.0 (*C*), 137.9 (*C*H), 139.5 (*C*), 147.7, 157.4, 158.7, 166.0 and 171.3 (C=*C*=N and 4 *C*=O). IR (ν_{max}/cm^{-1}): 2073 (C=C=N), 1747 and 1735 (C=O). EI-MS: *m/z* (%) = 464 (M+, 14), 359 (100), 318 (10), 131 (11), 119 (21), 105 (30), 73 (32). Anal. Calcd for $C_{25}H_{24}N_2O_7$ (464.47): C, 64.65%; H, 5.21%; N, 6.03%; found: C, 64.59%; H, 5.17%; N, 5.99%.

diethyl 2-((2,6-dimethylphenylimino)(2,4-dioxo-2H-benzo[d][1,3]oxazin-1(4H)-yl)methyl)maleate (5f)

Yellow oil, yield: 0.27 g (58%). ^{1}H-NMR, δ: 1.09 (3 H, t, ^3J 7.2 Hz, Me), 1.11 (3 H, t, ^3J 7.2 Hz, Me), 2.12 (6 H, s, 3Me), 3.93 (2 H, q, ^3J 7.2 Hz, CH_2O), 4.12 (2 H, q, ^3J 7.2 Hz, CH_2O), 6.15 (1 H, s, CH), 7.12-8.40 (4H, m, 4CH). ^{13}C-NMR, δ: 14.3 (2*Me*), 18.5 (2*Me*), 60.9 (*C*H2O), 61.3 (*C*H2O), 121.6 (*C*), 127.7 (*C*H), 128.1 (*C*H), 128.2 (*C*H), 128.6 (2*C*H), 130.4 (*C*H), 132.0 (*C*H), 134.4 (2*C*), 135.1 (*C*H), 131.4 (*C*), 138.1 (*C*H), 139.6 (*C*), 147.9, 149.4, 161.2, 163.4 and 164.2 (*C*=N and 4 *C*=O). IR (ν_{max}/cm^{-1}): 1750 and 1740 (C=O), 1665 (C=N). EI-MS: *m/z* (%) = 464 (M+, 14), 359 (100), 345 (50), 293 (9), 105 (37), 73 (30). Anal. Calcd for $C_{25}H_{24}N_2O_7$ (464.47): C, 64.65%; H, 5.21%; N, 6.03%; found: C, 64.59%; H, 5.17%; N, 5.99%.



Scheme 2: Proposed mechanism for the formation of compounds 4 and 5.

RESULTS AND DISCUSSION

In this research, we report the results of our studies involving the reactions of alkylisocyanides **1** with dialkylacethylenedicarboxylates **2** in the presence of 4H-3,1-benzoxazine-2,4(1H)-dione (isatoic anhydride) **3** proceeded under solvent-free microwave conditions for 5 min. The IR, ^{1}H NMR and ^{13}C NMR spectra of the products clearly indicated the formation of stable ketenimines **4** and azadienes **5** (Scheme 1).

The structures of compounds **4a-4f** and **5a-5f** were characterized by spectroscopic (IR, ^{1}H NMR, ^{13}C NMR, mass) and elemental analysis) methods. The ^{1}H NMR spectrum of **4a** showed one signal in δ= 1.06 ppm for three methyl protons, two signals in δ = 1.56 and 1.60 ppm for two methyl protons, one signal in δ= 1.73 ppm for methylene protons, two signals in δ = 3.71 and 3.78 ppm for two methoxy protons, one signal in δ = 6.00 ppm f or methine proton and signals in the range of δ = 7.27–8.19 ppm for the aromatic protons. The ^{13}C-NMR of **4a** showed 20 distinct signals which confirmed the proposed structure. ^{1}H and ^{13}C-NMR spectra of **4b**–**4f** were similar to compound **4a** except in the side-chains. The carbon atom of the ketenimine functional group (*C*=C=N) in compounds **4** observed at about δ = 62.0-65.7 ppm. IR spectra of compounds **4** exhibited sharp absorption signals at about 2072-2082 cm^{-1} for the C=C=N group. Also the ^{1}H NMR spectrum of **5a** showed one signal in δ = 1.09 ppm for three methyl protons, two signals in δ = 1.56 and 1.58 ppm for methyl protons, one signal in δ = 1.71 ppm for methylene protons, two signals in δ= 3.72 and 3.78 ppm for two methoxy protons, one signal in δ = 7.10 ppm for methine proton and signals in the range of δ = 7.46-8.31 ppm for the aromatic protons. The ^{13}C-NMR of **5a** showed 20 distinct signals which confirmed the proposed structure. ^{1}H and ^{13}C-NMR spectra of **5b**–**5f** were similar to compound **5a** except in the side-chains. Also all elemental analysis corresponded to formed compounds.

A plausible mechanism for formation of **4** and **5** is shown in Scheme 2. The reaction of alkylisocyanides **1** with dialkylacethylenedicarboxylates **2** leads to the 1:1 zwitterionic intermediate **6**. The protonation of **6** by the acidic NH of 4H-3,1-benzoxazine-2,4(1H)-dione (isatoic anhydride) **3** leads to intermediate **7** and the subsequent attack of the resulting nucleophile **8** on the intermediates 7 or 7' depending on location of the nucleophilic attack leads to the formation of ketenimine **4** and azadiene **5.** The results of spectroscopy clearly proved the proposed mechanism. (Scheme 2).

CONCLUSION

In summary, a microwave-assisted, rapid green synthetic method for novel stable functionalized ketenimines and azadienes has been developed. The speed of the reaction and a variety of commercially available reagents provide a broad access for these classes of compounds. This novel procedure has the advantages of appropriate yields, green conditions, and simple work-up conditions.

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