Journal of the Serbian Chemical Society
JSCS-info@shd.org.rs • www.shd.org.rs/JSCS
J. Serb. Chem. Soc. *76* (1) 13–20 (2011)
JSCS–4094
UDC 547.48+547.467+547.313+547.239+547.421:542.9
Original scientific paper

A three-component synthesis of functionalized ketenimines by the reaction of alkyl isocyanides and dialkyl acetylenedicarboxylates in the presence of 2-quinolinol

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(Received 18 February, revised 21 June 2010)

Abstract: The 1:1 reactive intermediates generated by the addition of alkyl isocyanides to dialkyl acetylenedicarboxylates were trapped by 2-quinolinol to yield highly functionalized ketenimines and, in some cases, minor amounts of 1-azabuta-1,3-dienes.

Keywords: ketenimines; 1-azadienes; alkyl isocyanides; acetylenic esters; NH-acids; multi-component reaction.

INTRODUCTION

Ketenimines are important reactive intermediates that occur as transient compounds in many thermal and photochemical reactions.[1] There has been intense interest in their reactions, such as cycloaddition,[2] nucleophilic[3,4] and electrophilic addition.[5] They have also found widespread use as reactive starting materials for the formation of four-, five-, and six-membered heterocyclic ring systems.[5–7] Methods for the synthesis of ketenimines have been extensively reviewed.[8] The addition of nucleophilic carbenes, such as isocyanides, to dialkyl acetylenedicarboxylates was investigated in detail.[9] The trapping of the 1:1 intermediate formed between dialkyl acetylenedicarboxylates and isocyanides with OH, NH, and CH acids has been widely studied.[10–14] In continuation of our interest in the application of isocyanides in multi-component reactions, MCR,[15–18] an efficient synthesis of ketenimine **4** from alkyl isocyanides **1** and dialkyl acetylenedicarboxylates **2** in the presence of a strong NH-acid, such as quinolin-2-ol, is reported herein. In some cases, minor amounts (13–25 %) of 1-azadienes **5** were obtained (Scheme 1).

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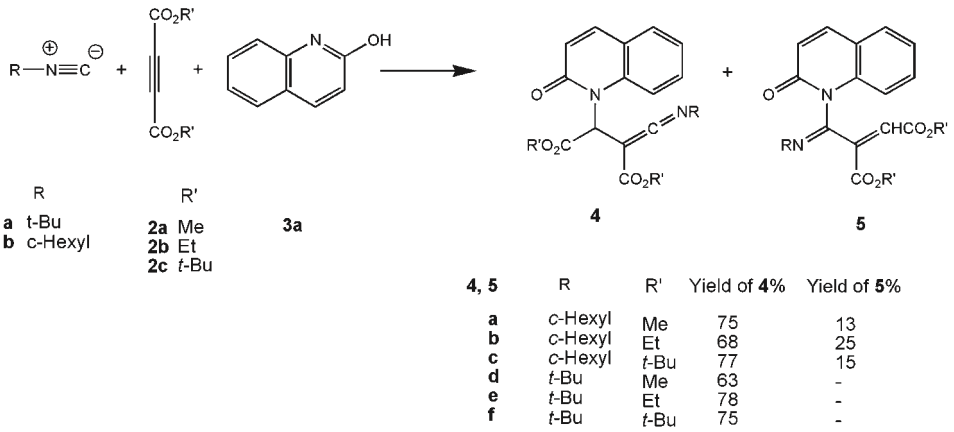
doi: 10.2298/JSC100218011M



4, 5	R	R'	Yield of 4%	Yield of 5%
a	*c*-Hexyl	Me	75	13
b	*c*-Hexyl	Et	68	25
c	*c*-Hexyl	*t*-Bu	77	15
d	*t*-Bu	Me	63	-
e	*t*-Bu	Et	78	-
f	*t*-Bu	*t*-Bu	75	-

Scheme 1. Typical procedure for the synthesis of compounds **4** and **5**.

RESULTS AND DISCUSSION

The reaction of alkyl isocyanides **1** with acetylenic esters **2** in the presence of an NH-acid, such as quinolin-2-ol, afforded the isomeric highly functionalized ketenimines **4** in fairly good yields.

The structures of **4** and **5** were deduced from their elemental analyses, mass spectrometric data, and their ^{1}H- and ^{13}C-NMR, DEPT and IR spectral data, given below.

*Dimethyl 2-(cyclohexylcarbonimidoyl)-3-(2-oxo-1(2*H*)-quinolinyl)succinate (**4a**)*. Yellow oil; yield: 63 %; Anal. Calcd. for $C_{22}H_{24}N_2O_5$: C, 66.65; H, 6.10; N, 7.07 %. Found: C, 66.70; H, 6.07; N, 7.05 %. IR (KBr, cm^{-1}): 2077 (–C=C=N stretching), 1745 (–C=O stretching of –COOR group), 1651 (–C=O stretching of amide group). ^{1}H-NMR (300 MHz, $CDCl_3$, δ / ppm): 1.20–2.07 (10H, *m*, 5 CH_2), 3.72 (6H, *s*, 2 OCH_3), 3.86 (1H, *m*, H–CN), 6.17 (1H, *s*, CH), 6.64 (1H, *d*, aromatic, J = 9.4 Hz, CH), 7.26 (1H, *t*, aromatic, J = 7.5 Hz, CH), 7.58 (1H, *d*, aromatic, J = 7.5 Hz, CH), 7.62 (1H, *t*, aromatic, J = 8.6 Hz, CH), 7.72 (1H, *d*, aromatic, J = 9.4 Hz, CH), 7.86 (1H, *d*, aromatic, J = 8.6 Hz, CH). ^{13}C-NMR (75.4 MHz, $CDCl_3$, δ / ppm): 24.4 (CH_2), 25.0 (CH_2), 25.6 (CH_2) 33.0 (CH_2), 33.4 (CH_2), 52.0 (OCH_3), 53.2 (OCH_3), 55.4 (C–H), 59.7 (**C**=C=N), 60.8 (C–N), 115.3 (CH=), 121.4 (CH=), 122.8 (CH=), 123.0 (CH=), 129.3 (CH=), 131.4 (CH=), 139.7 (C=), 140.6 (C=), 162.5 (C=O), 164.8 (C=O), 168.8 (C=O), 171.5 (C=**C**=N). DEPT (125.7 MHz, $CDCl_3$, δ / ppm): 24.4 (CH_2), 25.7 (CH_2), 25.9 (CH_2) 32.8 (CH_2), 33.4 (CH_2), 52.0 (OCH_3), 53.2 (OCH_3), 55.4 (C–H), 60.8 (C–N), 115.3 (CH=), 121.4 (CH=), 122.9 (CH=), 123.4 (CH=), 129.3 (=CH), 131.4 (=CH), 139 (C=), 140.5 (C=), 160.4 (C=O), 162.7 (C=O), 167.4 (C=O), 170.6 (C=**C**=N). MS (*m*/*z*, (relative abundance, %)): 396 (M^+, 18), 270 (24), 237 (32), 171 (58), 156 (39), 145 (47), 83 (100), 55 (58), 41(56).

*Dimethyl 2-[(*E*)-(cyclohexylimino)(2-oxo-1(2*H*)-quinolinyl)methyl]but-2-enedioate (**5a**)*. Yellow oil; yield: 26 %; Anal. Calcd. for $C_{22}H_{24}N_2O_5$: C, 66.65; H, 6.10; N, 7.07 %. Found: C, 66.69; H, 6.13; N, 7.02 %. IR (KBr, cm^{-1}): 1732 (–C=O stretching of –COOR group), 1668 (–C=O stretching of amide group), 1594 (–C=N stretching of imine group). ^{1}H-NMR (300 MHz, $CDCl_3$, δ / ppm): 1.10–1.90 (10H, *m*, 5 CH_2), 3.10 (1H, *m*, HC–N), 3.67 (3H, *s*, OCH_3), 3.95 (3H, *s*, OCH_3), 5.71 (1H, *s*, CH), 6.70 (1H, *d*, aromatic, *J* = 9.6 Hz, CH), 7.02 (1H, *d*, aromatic, *J* = 8.4 Hz, CH), 7.27 (1H, *t*, aromatic, *J* = 7.8 Hz, CH), 7.50 (1H, *t*, aromatic, *J* = 8.4 Hz, CH), 7.62 (1H, *d*, aromatic, *J* = 7.8 Hz, CH), 7.81 (1H, *d*, aromatic, *J* = 9.6 Hz, CH). ^{13}C-NMR (75.4 MHz, $CDCl_3$, δ / ppm): 23.4 (CH_2), 23.5 (CH_2), 25.5 (CH_2) 32.04 (CH_2), 32.4 (CH_2), 52.3 (OCH_3), 52.7 (OCH_3), 60.9 (C–N), 114.5 (CH=), 119.8 (CH=), 121.4 (CH=), 122.9 (CH=), 123.4 (CH=), 128.9 (C=), 131.4 (CH=), 137.5 (CH=), 141.0 (C=), 144.3 (C=), 144.8 (C=N), 160.1 (C=O), 164.6(C=O), 165.8 (C=O). MS (*m*/*z*, (relative abundance, %)): 396 (M^+, 10), 280 (37), 227 (100), 170 (55), 83 (45), 55 (38).

*Diethyl 2-(cyclohexylcarbonimidoyl)-3-(2-oxo-1(2*H*)-quinolinyl)succinate (**4b**)*. Yellow oil; yield: 71 %; Anal. Calcd. for $C_{24}H_{28}N_2O_5$: C, 67.91; H, 6.65; N, 6.60 %. Found: C, 67.82; H, 6.68; N, 6.69 %. IR (KBr, cm^{-1}): 2093 (–C=C=N stretching), 1741 (–C=O stretching of –COOR group), 1672 (–C=O stretching of amide group). ^{1}H-NMR (300 MHz, $CDCl_3$, δ / ppm): 1.11–1.99 (10H, *m*, 5 CH_2), 1.19 (3H, *t*, *J* = 7.1 Hz, CH_2–C**H**$_3$), 1.23 (3H, *t*, *J* = 7.1 Hz, CH_2–C**H**$_3$), 3.89 (1H, *m*, HC–N), 4.19 (2H, *q*, *J* = 7.1 Hz, OC**H**$_2$–CH_3), 4.29 (2H, *m*, OC**H**$_2$–CH_3), 6.13 (1H, *s*, CH), 6.60 (1H, *d*, aromatic, *J* = 9.4 Hz, CH), 7.24 (1H, *t*, aromatic, *J* = 7.8 Hz, CH), 7.56–7.60 (2H, *m*, aromatic, 2 CH), 7.70 (1H, *d*, aromatic, *J* = 9.4 Hz, CH), 7.88 (1H, *d*, aromatic, *J* = 8.6 Hz, CH). ^{13}C-NMR (75.4 MHz, $CDCl_3$, δ / ppm): 14.0 (CH_3), 14.4 (CH_3), 23.8 (CH_2), 25.3 (2 CH_2), 32.9 (2 CH_2), 55.1 (C–H), 59.7 (**C**=C=N), 60.2 (OCH_2), 60.3 (OCH_2), 61.9 (C–N), 115.0 (=CH), 120.9 (=CH), 121.0 (=CH), 122.3 (=CH), 128.9 (=CH), 130.9 (=CH), 139.4 (C=), 140.2 (C=), 160.2 (C=O), 162.1 (C=O), 167.9 (C=O), 170.8 (C=**C**=N). MS (*m*/*z*, (relative abundance, %)): 424 (M^+, 7), 341 (76), 280 (71), 144 (100), 97 (38), 29 (44).

*Diethyl 2-[(*E*)-(cyclohexylimino)(2-oxo-1(2*H*)-quinolinyl)methyl]but-2-enedioate (**5b**)*. Yellow oil; yield: 19 %; Anal. Calcd. for $C_{24}H_{28}N_2O_5$: C, 67.91; H, 6.65; N, 6.60 %. Found: C, 67.88; H, 6.68; N, 6.63 %. IR (KBr, cm^{-1}): 1741 (–C=O stretching of –COOR group), 1672 (–C=O stretching of amide group), 1590 (–C=N stretching of imine group); ^{1}H-NMR (300 MHz, $CDCl_3$, δ / ppm): 1.06––1.97 (10H, *m*, 5 CH_2), 1.32 (3H, *t*, *J* = 7.1 Hz, CH_2–C**H**$_3$), 1.40 (3H, *t*, *J* = 7.1 Hz, CH_2–C**H**$_3$), 3.09 (1H, *m*, H–CN), 4.15 (2H, *q*, *J* = 7.1 Hz, OC**H**$_2$–CH_3), 4.44 (2H, *m*, OC**H**$_2$–CH_3), 5.71 (1H, *s*, CH), 6.70 (1H, *d*, aromatic, *J* = 9.6 Hz, CH), 7.05 (1H, *d*, aromatic, *J* = 8.5 Hz, CH), 7.29 (1H, *t*, aromatic, *J* = 8.5 Hz, CH), 7.50 (1H, *t*, aromatic, *J* = 7.5 Hz, CH), 7.78 (1H, *d*, aromatic, *J* = 7.8 Hz, CH),

7.80 (1H, *d*, aromatic, *J* = 9.6 Hz, CH). ^{13}C-NMR (75.4 MHz, $CDCl_3$, δ / ppm): 13.6 (CH_3), 13.9 (CH_3), 23.5 (CH_2), 25.1 (CH_2), 25.5 (CH_2), 32.4 (CH_2), 32.6 (CH_2), 60.7 (C–N), 61.3 (OCH_2), 61.7 (OCH_2), 114.7 (=CH), 119.8 (=CH), 121.5 (=CH), 123.2 (=CH), 123.4 (=CH), 128.8 (C=), 131.3 (=CH), 137.5 (C=), 141 (=CH), 144.3 (C=), 144.6 (C=N), 163.8 (C=O), 164.0 (C=O), 165.3 (C=O). MS (*m*/*z*, (relative abundance, %)): 424 (M^+, 7), 280 (31), 253 (56), 227 (100), 171 (48), 83 (41), 29 (35).

Di-tert-*butyl 2-(cyclohexylcarbonimidoyl)-3-(2-oxo-1(2*H*)-quinolinyl)succinate (**4c**)*. Yellow oil; yield: 55 %; Anal. Calcd. for $C_{28}H_{36}N_2O_5$: C, 69.98; H, 7.55; N, 5.83 %. Found; C, 69.51; H, 7.60; N, 5.79 %. IR (KBr, cm^{-1}): 2073 (–C=C=N stretching), 1721 (–C=O stretching of –COOR group), 1673 (–C=O stretching of amide group). ^{1}H-NMR (300 MHz, $CDCl_3$, δ / ppm): 1.06–2.01 (10H, *m*, 5 CH_2), 1.41 (9H, *s*, $C(CH_3)_3$), 1.46 (9H, *s*, $C(CH_3)_3$), 3.85 (1H, *m*, H–CN), 6.04 (1H, *s*, CH), 6.64 (1H, *d*, aromatic, *J* = 9.2 Hz, CH), 7.28 (1H, *t*, aromatic, *J* = 7.5 Hz, CH), 7.55–7.62 (2H, *m*, aromatic, 2 CH), 7.69 (1H, *d*, aromatic, *J* = 9.4 Hz, CH), 7.82 (1H, *d*, aromatic, *J* = 8.4 Hz, CH). ^{13}C-NMR (75.4 MHz, $CDCl_3$, δ / ppm): 24.3 (CH_2), 25.1 (CH_2), 25.8 (CH_2), 28.2 ($C(\mathbf{C}H_3)_3$), 28.9 ($C(\mathbf{C}H_3)_3$), 33.46 (2 CH_2), 57.5 (C–H), 62.5 (**C**=C=N), 68.9 (C–N), 80.5 (C–O), 82.3 (C–O), 115.7 (CH), 121.6 (=CH), 122.5 (=CH), 129.1 (=CH), 130.2 (=CH), 131.1 (=CH), 139.9 (C=), 140.2 (C=), 162.4 (C=O), 165.1 (C=O), 167.9 (C=O), 176.5 (C=**C**=N). MS (*m*/*z*, (relative abundance, %)): 480 (M^+, 11), 336 (47), 202 (74), 158 (100), 122 (36), 83 (49), 57 (100).

Di-tert-*butyl 2-[(*E*)-(cyclohexylimino)(2-oxo-1(2*H*)-quinolinyl)methyl] but-2--enedioate (**5c**)*. Yellow oil; yield: 16 %; Anal. Calcd. for $C_{28}H_{36}N_2O_5$: C, 69.98; H, 7.55; N, 5.83 %. Found; C, 69.94; H, 7.58; N, 5.79 %. IR (KBr, cm^{-1}): 1732 (–C=O stretching of –COOR group), 1660 (–C=O stretching of amide group), 1595 (–C=N stretching of imine group). ^{1}H-NMR (300 MHz, $CDCl_3$, δ / ppm): 1.08–2.00 (10H, *m*, 5 CH_2), 1.42 (9H, *s*, $C(CH_3)_3$), 1.60 (9H, *s*, $C(CH_3)_3$), 3.08 (1H, *m*, H–CN), 5.70 (1H, *s*, CH), 6.72 (1H, *d*, aromatic, *J* = 9.5 Hz, CH), 7.15 (1H, *d*, aromatic, *J* = 8.2 Hz, CH), 7.28 (1H, *t*, aromatic, *J* = 8.2 Hz , CH), 7.50 (1H, *t*, aromatic, *J* = 7.4 Hz, CH), 7.62 (1H, *d*, aromatic, *J* = 7.4 Hz, CH), 7.81 (1H, *d*, aromatic, *J* = 9.5 Hz, CH). ^{13}C-NMR (75.4 MHz, $CDCl_3$, δ / ppm): 23.8 (CH_2), 23.9 (CH_2), 25.9 (CH_2), 28.3 ($C(\mathbf{C}H_3)_3$), 28.5 ($C(\mathbf{C}H_3)_3$), 32.4 (CH_2), 32.6 (CH_2), 60.9 (C–N), 82.1 (C–O), 83.0 (C–O), 115.4 (=CH), 120.2 (=CH), 121.9 (=CH), 123.6 (=CH), 125.0 (=CH), 129.0 (=CH), 131.7 (C=), 138.3 (=CH), 141.2 (C=), 144.0 (C=), 144.9 (C=N), 160.6 (C=O), 163.8 (C=O), 165.4 (C=O). MS (*m*/*z*, (relative abundance, %)):480 (M^+, 11), 336 (37), 253 (48), 227 (100), 144 (45), 83 (47), 57 (35).

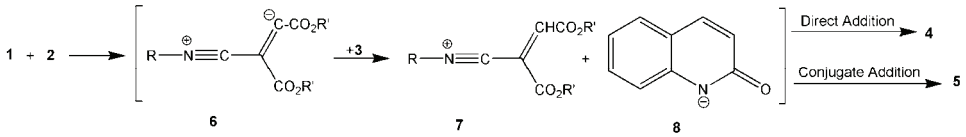
*Dimethyl 2-(*tert-*butylcarbonimidoyl)-3-(2-oxo-1(2*H*)-quinolinyl)succinate (**4d**)*. Yellow oil; yield: 87 %; Anal. Calcd. for $C_{20}H_{22}N_2O_5$: C, 64.85; H, 5.99; N, 7.56 %. Found: C, 64.89; H, 5.94; N, 7.60 %. IR (KBr, cm^{-1}): 2079 (–C=C=N

stretching), 1750 (–C=O stretching of –COOR group), 1670 (–C=O stretching of amide group). ^{1}H-NMR (300 MHz, $CDCl_3$, δ / ppm): 1.43 (9H, *s*, $C(CH_3)_3$), 3.70 (3H, *s*, $–OCH_3$), 3.72 (3H, *s*, $–OCH_3$), 6.12 (1H, *s*, CH), 6.63 (1H, *d*, aromatic, *J* = 9.4 Hz, CH), 7.24 (1H, *t*, aromatic, *J* = 7.5 Hz, CH), 7.51–7.62 (2H, *m*, aromatic, 2 CH), 7.70 (1H, *d*, aromatic, *J* = 8.9 Hz, CH), 7.80 (1H, *d*, aromatic, *J* = 8.6 Hz, CH). ^{13}C NMR (75.4 MHz, $CDCl_3$, δ / ppm): 30.0 ($C(\mathbf{C}H_3)_3$), 51.7 (OCH_3), 52.8 (OCH_3), 54.8 (C–H), 60.9 (**C**=C=N), 68.1 (C–N), 114.8 (=CH), 121.1 (=CH), 122.5 (=CH), 128.9 (=CH), 131.0 (=CH), 132.4 (=CH), 139.2 (C=), 140.3 (C=), 162.0 (C=O), 167.7 (C=O), 168.3 (C=O), 171.0 (**C**=C=N). MS (*m*/*z*, (relative abundance, %)):370 (M^+, 4), 313 (31), 226 (29), 143 (85), 57 (100), 41 (34).

*Diethyl 2-(*tert*-butylcarbonimidoyl)-3-(2-oxo-1(2*H*)-quinolinyl)succinate (**4e**)*. Yellow powder; yield: 73 %; m.p. 93–97 °C; Anal. Calcd. for $C_{22}H_{26}N_2O_5$: C, 68.71; H, 7.56; N, 6.14; found: C, 68.73; H, 7.50; N, 6.12. IR (KBr, cm^{-1}): 2073 (–C=C=N stretching), 1747 (–C=O stretching of –COOR group), 1646 (–C=O stretching of amide group). ^{1}H-NMR (300 MHz, $CDCl_3$, δ / ppm): 1.18 (3H, *t*, *J* = 7.1 Hz, $CH_2–C\mathbf{H}_3$), 1.24 (3H, *t*, *J* = 7.1 Hz, $CH_2–C\mathbf{H}_3$), 1.43 (9H, *s*, $C(CH_3)_3$), 4.20 (2H, *q*, *J* = 7.1 Hz, $OC\mathbf{H}_2–CH_3$), 4.29 (2H, *m*, $OC\mathbf{H}_2–CH_3$), 6.09 (1H, *s*, CH), 6.63 (1H, *d*, aromatic, *J* = 9.4 Hz, CH), 7.24 (1H, *t*, aromatic, *J* = 7.8 Hz, CH), 7.51–7.56 (2H, *m*. aromatic, 2 CH), 7.70 (1H, *d*, aromatic, *J* = 9.4 Hz, CH), 7.83 (1H, *d*, aromatic, *J* = 8.6 Hz, CH). ^{13}C-NMR (75.4 MHz, $CDCl_3$, δ / / ppm): 14.1 (CH_3), 14.3 (CH_3), 30.1 ($C(\mathbf{C}H_3)_3$), 51.9 (C–H), 54.8 (**C**=C=N), 60.3 (C–N), 61.9 (OCH_2), 62.2 (OCH_2), 114.9 (=CH), 121.0 (=CH), 122.4 (=CH), 128.9 (=CH), 130.7 (=CH), 133.7 (=CH), 136.6 (C=), 139.4 (C=), 162.0 (C=O), 164.8 (C=O), 167.8 (C=O), 170.7 (C=**C**=N). MS (*m*/*z*, (relative abundance, %)): 398 (M^+, 21), 342 (57), 269 (50), 254 (61), 223 (42), 195 (31), 145 (100), 57 (76), 41(42).

Di-tert-*butyl 2-(*tert*-butylcarbonimidoyl)-3-(2-oxo-1(2*H*)-quinolinyl)succinate (**4f**)*. Yellow powder; yield: 79 %; m.p. 94–98 °C; Anal. Calcd. for $C_{26}H_{34}N_2O_5$: C, 68.70; H, 7.54; N, 6.16 %. Found: C, 68.73; H, 7.50; N, 6.12 %. IR (KBr, cm^{-1}): 2073 (–C=C=N stretching), 1743 (–C=O stretching of –COOR group), 1666 (–C=O stretching of amide group). ^{1}H-NMR (300 MHz, $CDCl_3$, δ / / ppm): 1.40 (18H, *s*, 2 $C(CH_3)_3$), 1.46 (9H, *s*, $C(CH_3)_3$), 5.99 (1H, *s*, CH), 6.63 (1H, *d*, aromatic, *J* = 9.4 Hz, CH), 7.22 (1H, *t*, aromatic, *J* = 7.4 Hz, CH), 7.55––7.60 (2H, *m*, aromatic, 2 CH), 7.67 (1H, *d*, aromatic, *J* = 9.4 Hz, CH), 7.75 (1H, *d*, aromatic, *J* = 8.6 Hz, CH). ^{13}C-NMR (75.4 MHz, $CDCl_3$, δ / ppm): 27.8 ($C(\mathbf{C}H_3)_3$), 28.4 ($C(\mathbf{C}H_3)_3$), 30.0 ($C(\mathbf{C}H_3)_3$), 51.6 (C–H), 55.3 (**C**=C=N), 61.7 (C–N), 80.0 (C–O), 81.9 (C–O), 115.0 (CH=), 120.8 (CH=), 121.2 (CH=), 122.1 (CH=), 128.7 (CH=), 130.8 (CH=), 139.6 (C=), 139.5 (C=), 161.7 (C=O), 161.9 (C=O), 166.7 (C=O), 169.5 (C=**C**=N). MS (*m*/*z*, (relative abundance, %)): 454 (M^+, 2), 310 (24), 254 (23), 198 (35), 145 (82), 57 (100), 41 (30).

The ^{1}H-NMR spectrum of **4a** exhibited three sharp lines for methoxy (δ 3.72 and 3.86 ppm) and methine (δ 6.17 ppm) protons. The cyclohexyl and quinolinol moiety appeared at δ 1.20–2.07 ppm and 6.63–7.80 ppm. The ^{13}C-NMR spectrum of **4a** exhibited distinct resonances in agreement with the proposed structure. The DEPT spectrum of **4a** exhibited fifteen sharp lines in agreement with dimethyl 2-(cyclohexylcarbonimidoyl)-3-(2-oxo-1(2*H*)-quinolinyl)succinate. Partial assignments of these resonances are given above. The ^{1}H-NMR spectra of **4b**–**f** are similar to that of **4a**, except for the signals of the cyclohexyl and ester moiety. The ^{1}H-NMR spectrum of **5a** displayed sharp signals for the methoxy (δ 3.67 and 3.95 ppm), and vinyl (δ 5.71 ppm) protons. The ^{13}C-NMR spectrum of **5a** exhibited distinct resonances in agreement with dimethyl 2-[(*E*)-(cyclohexylimino)(2-oxo-1(2*H*)-quinolinyl)methyl]but-2-enedioate. A partial assignment of these resonances is given above. The structural assignments of **5a**–**c** made on the basis of their NMR spectra were supported by their IR spectra. Of special interest is the strong ketenimine absorption band at about 2079 cm^{-1}. Based on the well-established chemistry of isocyanides,[19–22] it is reasonable to assume that **4** and **5** result from an initial addition of the alkyl isocyanide to the acetylenic ester and subsequent protonation of the 1:1 adduct by the NH-acid. Then, the positively charged ion **7** can be attacked at two positions by the nitrogen atom of the anion of the NH-acid. Conjugate addition produces the ketenimines **4** and direct addition leads to the 1-azadienes **5** (Scheme 2).



Scheme 1. A possible mechanism for the preparation of **4** and **5**.

EXPERIMENTAL

Melting points were measured on an Electrothermal 9100 apparatus. Elemental analyses for C, H, and N were performed using a Heraeus CHNO-Rapid analyzer. The IR spectra were measured on a Shimadzu IR-460 spectrometer. The ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker DRX-300 Avance instrument with $CDCl_3$ as the solvent at 300 and 75 MHz, respectively. The mass spectra were recorded on a Finnigan-Matt 8430 mass spectrometer operating at an ionization potential of 70 eV. The alkyl isocyanides, dialkyl acetylenedicaboxylates and 2-quinolinol were obtained from Fluka and were used without further purification.

*Typical procedure for the synthesis of ketenimines and 1-azadienes (**4** and **5**)*

To a stirred solution of dialkyl acetylenedicarboxylate (2 mmol) and alkyl isocyanide (2 mmol) in 10 mL of CH_2Cl_2, 2-quinolinol (2 mmol) was added dropwise at 0 °C over 10 min. The reaction mixture was then allowed to warm to room temperature and stand for 24 h. The solvent was removed under reduced pressure and the residual solid was recrystallized from diethyl ether. The oily products were purified by preparative TLC on silica gel (Merck silica

gel DC-Fertigplatten 60/Kieselguhr F254) 20 cm×20 cm plates using *n*-hexane-AcOEt (2:1) as the eluent.

CONCLUSIONS

In conclusion, a method for the preparation of highly functionalized ketenimines and 1-azadienes has once more been demonstrated. The present method carries the advantage that not only is the reaction performed under neutral conditions, but also the starting materials and reagents can be mixed without any activation or modification.

ИЗВОД

ТРОКОМПОНЕНТНА СИНТЕЗА ФУНКЦИОНАЛИЗОВАНИХ КЕТЕНИМИНА ДОБИЈЕНИХ РЕАКЦИЈОМ АЛКИЛ-ИЗОЦИЈАНИДА И ДИАЛКИЛ-АЦЕТИЛЕНДИКАРБОКСИЛАТА У ПРИСУСТВУ 2-ХИНОЛИНОЛА

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Смеша интермедијера, добијених у односу 1:1 адицијом алкил-изоцијанида на диалкил-ацетилендикарбоксилате, трапована је 2-хинолином, и као производ су добијени функционализовани кетенимини у високом приносу, а у неким примерима добијене су мале количине 1-азабута-1,3-диена.

(Примљено 18. фебруара, ревидирано 21. јуна 2010)

REFERENCES

1. T. T. Tidwell, *Acc. Chem. Res.* **23** (1990) 273
2. M. H. Mosslemin, I. Yavari, M. Anary-Abbasinejad, M. R. Nateghi, *J. Fluorine Chem.* **125** (2004) 1497
3. K. Sung, T. T. Tidwell, *J. Am. Chem. Soc.* **120** (1998) 3043
4. C. Fromont, S. Masson, *Tetrahedron* **55** (1999) 5405
5. R. Aumann, *Angew. Chem. Int. Ed. Eng.* **27** (1988) 1456
6. R. Aumann, B. Jasper, M. Lage, B. Krebs, *Organometallics* **13** (1994) 3502
7. R. Gertzmann, M. H. Moller, U. Rodewald, R. Frohlich, M. Grehl, E.-U. Wurthwein, *Tetrahedron* **51** (1995) 3767
8. J. P. Michael, C. B. D. Koning, in *Comprehensive organic functional group transformations*, A. R. Katritzky, O. Meth-Cohn, C. W. Rees, Eds., Elsevier, Cambridge, 1995, p. 555
9. H. Junjappa, M. K. Saxena, D. Ramaiah, B. B. Loharay, N. P. Rath, M. V. George, *J. Org. Chem.* **63** (1998) 9801
10. I. Yavari, M. Anary-Abbasinejad, A. Alizadeh, Z. Hossaini, *Tetrahedron* **59** (2003) 1289
11. I. Yavari, H. Zare, B. Mohtat, *Mol. Diversity* **10** (2006) 24
12. I. Yavari, F. Nasiri, H. Djahaniani, *Mol. Diversity* **8** (2004**)** 431
13. M. Anary-Abbasinejad, H. Anaraky-Ardakani, F. Rastegari, A. Hassanabadi, *J. Chem. Res.* **10** (2007) 602
14. M. Adib, M. H. Sayahi, B. Behnam, E. Sheibani, *Monatsh. Chem.* **137** (2006) 191

15. I. Yavari, H. Djahaniani, F. Nassiri, *Monatsh. Chem.* **134** (2004) 543
16. I. Yavari, H. Djahaniani, F. Nassiri, *Collect. Czech. Chem. Commun.* **69** (2004) 1499
17. I. Yavari, L. Moradi, F. Nasiri, H. Djahaniani, *Mendeleev Commun.* **15** (2006) 156
18. I. Yavari, M. Davar-Panah, M. Heydari, K. Najafian, A. Zonouzi, *Monatsh. Chem.* **127** (1996) 963
19. I. Ugi, *Angew. Chem. Int. Ed. Eng*. **21** (1982) 810
20. A. Domling, *Chem. Rev*. **106** (2006) 17
21. H. M. Walborsky, M. P. Periasamy, in *The Chemistry of Functional Groups*, C. Suppl, S. Patai, Z. Rappoport, Eds., Wiley, New York, 1983, p. 835
22. V. Nair, A. U. Viond, J. S. Nair, A. R. Sreekanth, N. P. Rath, *Tetrahedron Lett.* **41** (2000) 6675.