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High Efficient of the Intermolecular Radical Reactions Through three-Component Carbo-Oximation Process using New Ready Available Sulfonyloxime

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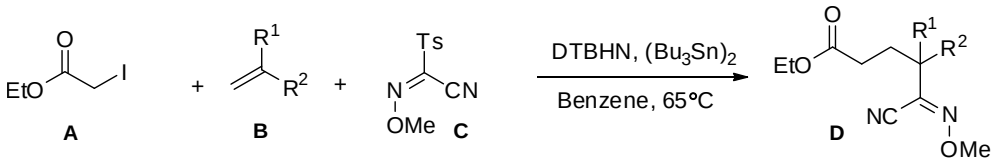
Addition of functionalized carbon fragments across the olefinic π-system through a free-radical carbo-oximation process offers a straightforward access to valuable intermediatesfor organic synthesis. For this purpose, we designed a new protectedsulfonyl oxime, which enable rapid radical addition with high yields under mild conditions.

Key words: Carbo-oximation processes, free three multicomponent reactions, sulfonyl oxime acceptor.

INTRODUCTION

Free radical multicomponent reactions (MCR) aremore flexible and fulfillfor an efficient carbo-functionalizationof olefins[1].Radical MCRs have thus attracted a considerableattention.More recently, the addition of carbonfragments across the π-bond of non-activated olefins throughfree-radical pathways has received intense scrutiny, resulting inthe description of useful transformations, such as for instancecarbo-alkenylation[2,3], carbo-alkynylation[4] andcarbo-allylationofolefins.These processes also illustrate the importance of theinfluence of polar effects in free-radical MCRs[5]. Various electrophilic species maybe envisioned, but sulfones including vinyl[6]-,alkynyl-,allyl[7]- and azido-sulfones[8]hold a prominent place, due to the fast and efficient β-fragmentation of the sulfonyl moiety.Sulfones also allow to install other R^3 substituents on the olefinic backbonesuch as (SPh, CN,N_3,Cl, etc..)[9].Kimand co-workers[10]have thus shown that sulfonyloximes are also excellent radical acceptors[11], enabling the incorporationof an oxime onto a carbon framework as electrophilic radical traps.The strategy of the present work relies on the generalizationof carbo-oximation of olefins as a formal carbo-formylationprocess.Carbo-formylation of an olefin under radicalconditions has been described by Ryu et al. using carbon monoxideas the radical trap[12].The use of Kim's sulfonyl oxime constitutesa more practical surrogate to toxic CO[13],which generally requiresrelatively high pressure, and therefore specific autoclave equipment[14].



Scheme 1: Three-component Carbo-oximation of Olefins

EXPERIMENTAL

General: Equipment, Chemicals and Work Technique

All reactions were carried out under argon atmosphere with dry solvents under anhydrous conditions. Yields refer to chromatographically and spectroscopically (^{1}H NMR) homogeneous materials. Commercial reagents were used without purification. Benzene was distilled over sodium and benzophenone.DCE were distilled from CaH_2.^{1}H NMR and ^{13}C NMR were recorded on Bruker DPX-200 FT (^{1}H: 200 MHz, ^{13}C: 50.3 MHz), Bruker Advance- 300FT (^{1}H: 300 MHz, ^{13}C: 75.5 MHz),. All NMR spectra present in this work were measured in $CDCl_3$ solution. All chemical shifts are given in ppm.The chemical shifts (ä) and coupling constants (J) are expressed in ppm and Hz respectively. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad.High resolution mass spectra were recorded on a Micromass ZABSpec TOF, on a Q-Tof Applied Biosystems and on Waters Q-Tof 2 apparatus. IR spectra were recorded on a Perkin-Elmer 1710 spectrophotometer or on a Perkin-Elmer aragon 1000 FT-IR spectrophotometer.Thin Layer Chromatography (TLC): Merck Kieselgel 60 F254 on aluminium foil from Macherey-Nagel. Detection was carried out under UV light at 254 nm and 365 nm. Column chromatography was performed with Merck Silica Gel 60 (70-230 mesh), (230-400 mesh ASTM) and Baker silica gel (0.063-0.200 mm) were used for flash chromatography.

General procedure for the three-component carbo-oximation with sulfonyloxime (C) (Table 1). Three-component adducts (11-20)

In a dry two-neck round-bottom flask equipped with a condenserand a magnetic stirrer were successively added oximeC(2 equiv, See Table 1), iodoesterA(1 equiv) and the desired alkenepartner B(4 equiv) in benzene (0.4 M). Argon was bubbleddirectly into the flask for 30 min. $(Bu_3Sn)_2$ (1.5 equiv) was injected and the flask was heated to 60°C. DTBHN was added after5 min, then every 90 min if required (TLC). After total consumptionof the starting iodide, the resulting mixture was concentrated *in vacuo* and purified by silica gel chromatography (Petroleum ether/EtOAc) to afford the desired product.

Tert-butyl-2-(cyano(methoxyimino)methyl)-3-(2-ethoxy-2-oxoethyl)piperidine-1-carboxylate (11)

Compound 11 was obtained according to the general procedure described above from ethyl iodoacetateA (53 mg, 0.25 mmol, 1 equiv), sulfonyl oxime C (119 mg, 0.5 mmol, 2 equiv), tert-butyl 3,4-dihydropyridine-1(2H)-carboxylate1(197 mg, 1 mmol, 4 equiv), $(Bu_3Sn)_2$ (0.19 mL,0.38 mmol), and DTBHN (4 mg, 0.04 mmol, 10 mol %) added by 5 mol % portion every 1.5 h, in degassed benzene (1.5 mL). Concentration *in vacuo*, followed by purification by flash chromatography (silica gel, 90/10 PE / EtOAc) afforded 11(69 mg, 78%) as a colorless oil.R_f= 0.4 (PE/EtOAc90/10). IR (ATR)ν_{max} (cm^{-1}) =2957, 2855, 2711, 1732, 1690, 1513, 1278, 939.^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) =4.91 (d, 1H, *J* = 6 Hz, CH), 4.18 (q, 2H *J* = 3 and 6 Hz, CH_2), 4.02 (s, 3H, CH_3), 3.94-3.89 (m, 1H, CH), 3.39-3.34 (m, 1H, CH), 2.43-2.34 (m, 2H, CH_2), 2.18-2.11 (m, 2H, CH_2), 1.91-1.77 (m, 2H,CH_2), 1.45 (s, 9H, 3CH_3), 1.38 (appearant t, 3H, *J* = 6 and 3 Hz, CH_3), 1.25-1.19 (m, 1H, CH).^{13}C NMR ($CDCl_3$, 75.5 MHz): δ (ppm) = 174.9 (C=O ester), 156.9 (C=O ester), 138.4 (C), 105.5 (CN), 81.0 (C),61.2 (C), 60.6 (C), 60.4 (C), 43.3 (C), 37.3 (C), 36.3 (C), 28.4 (C), 26.8 (C), 23.3 (C), 14.7 (C).HRMS (ESI): $[M+H]^+$ $C_{17}H_{28}N_3O_5$calcd. 354.1993, found 354.19330.

ethyl 2-(2-(cyano(methoxyimino)methyl) tetrahydro-2H-pyran-3-yl)acetate (12)

Compound 12 was obtained according to the general procedure described above from ethyl iodoacetate A (53 mg, 0.25 mmol, 1 equiv), sulfonyl

oxime C (119 mg, 0.5 mmol, 2 equiv), 3,4-dihydro-2H-pyran 2 (84 mg, 1 mmol, 4 equiv), $(Bu_3Sn)_2$ (0.19 mL,0.38 mmol), and DTBHN (4 mg, 0.04 mmol, 10 mol %) added by 5 mol % portion every 1.5 h, in degassed benzene (1.5 mL). Concentration *in vacuo*, followed by purification by flash chromatography (silica gel, 88/12 PE / EtOAc) afforded 12(64 mg, 81%) as a colorless oil.R_f= 0.4 (PE/EtOAc88/12). IR (ATR) ν_{max} (cm^{-1}) =2970, 1730, 1652, 1447, 1308, 1149, 1085, 688..^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) =5.17 (d, 1H, *J* = 6 Hz, CH), 4.17 (appearantq, 2H *J* = 3 and 6 Hz, CH_2), 3.99 (s, 3H, CH_3), 3.80-3.76 (m, 1H, CH), 3.71-3.67 (m, 1H, CH), 2.91-2.82 (m, 1H, CH), 2.30-2.26 (m, 1H, CH), 2.23-2.16 (m, 1H,CH), 2.06-2.01(m, 1H, CH), 1.38 (appearant t, 3H, *J* = 6 and 3 Hz, CH_3), 1.20-1.13 (m, 1H, CH).^{13}C NMR ($CDCl_3$, 75.5 MHz): δ (ppm) = 174.9 (C=O ester), 132.1 (C), 110.8 (CN), 75.5 (C), 67.5 (C),61.2 (C), 60.6 (C), 60.4 (C), 36.8 (C), 34.8 (C), 25.9 (C), 24.7 (C), 14.7 (C).HRMS (ESI): $[M+H]^+$ $C_{12}H_{19}N_2O_4$calcd. 255.1345, found 252.1344.

ethyl 4-(cyano(methoxyimino)methyl)decanoate (13)

Compound 13 was obtained according to the general procedure described above from ethyl iodoacetateA (53 mg, 0.25 mmol, 1 equiv), sulfonyl oxime C (119 mg, 0.5 mmol, 2 equiv), oct-1-ene3 (112 mg, 1 mmol, 4 equiv), $(Bu_3Sn)_2$ (0.19 mL,0.38 mmol), and DTBHN (4 mg, 0.04 mmol, 10 mol %) added by 5 mol % portion every 1.5 h, in degassed benzene (1.5 mL). Concentration in vacuo, followed by purification by flash chromatography (silica gel, 95/5 PE / EtOAc) afforded 13(64 mg, 91%) as a colorless oil.R_f= 0.4 (PE/EtOAc95/5). IR (ATR)ν_{max} (cm^{-1}) =2976, 2957, 2855, 2711, 1732, 1690, 1513, 1278, 939.^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) =4.17 (q, 2H, *J* = 3 Hz, CH_2), 4.06-4.03 (m, 1H CH), 4.00 (s, 3H, CH_3), 2.30 (appearant t, 2H,*J* = 3 and 6 Hz, CH_2), 2.00-1.96 (m, 1H, CH), 1.92-1.88 (m, 1H, CH), 1.57-1.55 (m, 2H, CH_2), 1.48-1.31 (m, 1H,CH and 5CH_2), 0.99 (appearant t, 3H, *J* = 6 and 3 Hz, CH_3).^{13}C NMR ($CDCl_3$, 75.5 MHz): δ (ppm) = 174.3 (C=O ester), 135.3 (C), 114.9 (CN), 61.2 (C), 60.4 (C),34.2 (C), 32.9 (C), 32.6 (C), 31.6 (C), 29.9 (C), 29.3 (C), 27.8 (C), 22.9 (C), 14.7 (C), 14.0 (C).HRMS (ESI): $[M+H]^+$ $C_{15}H_{27}N_2O_7$calcd. 283.2021, found 283.2021.

ethyl 3-(1-(cyano(methoxyimino)methyl) cyclohexyl) propanoate (14)

Compound 14 was obtained according to the general procedure described above from ethyl iodoacetateA (53 mg, 0.25 mmol, 1 equiv), sulfonyl oxime C (119 mg, 0.5 mmol, 2 equiv), methylenecyclohexane4 (96 mg, 1 mmol, 4 equiv), $(Bu_3Sn)_2$ (0.19 mL,0.38 mmol), and DTBHN (4 mg, 0.04 mmol, 10 mol %) added by 5 mol % portion every 1.5 h, in degassed benzene (1.5 mL). Concentration in vacuo, followed by purification by flash chromatography (silica gel, 94/6 PE / EtOAc) afforded 14(59 mg, 89%) as a colorless oil.R_f= 0.36 (PE/EtOAc94/6). IR (ATR)δ_{max} (cm^{-1}) = 1680, 1305, 1145, 1020, 987.^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) =4.17 (q, 2H, *J* = 3 Hz, CH_2), 4.00 (s, 3H CH_3), 2.29 (appearant t, 2H,*J* = 3 and 6 Hz, CH_2), 1.91 (appearant t, 2H,*J* = 3 and 6 Hz, CH_2), 1.87-1.82 (m, 2H, CH_2), 1.73-1.53 (m, 8H, 4CH_2), 1.37 (m, 2H, CH_2), 1.73-1.53appearant t, 3H, *J* = 6 and 3 Hz, CH_3).^{13}C NMR ($CDCl_3$, 75.5 MHz): δ (ppm) = 174.4 (C=O ester), 127.7 (C), 116.2 (CN), 61.2 (C), 60.4 (C),49.5 (C), 33.0 (C), 30.6 (C), 28.1 (C), 25.6 (C), 22.2 (C), 14.7 (C).HRMS (ESI): $[M+H]^+$ $C_{14}H_{23}N_2O_3$calcd. 267.1708, found 267.1709.

ethyl 3-(1-(cyano(methoxyimino)methyl) cyclopentyl) propanoate (15)

Compound 15 was obtained according to the general procedure described above from ethyl iodoacetateA (53 mg, 0.25 mmol, 1 equiv), sulfonyl oxime C (119 mg, 0.5 mmol, 2 equiv), methylenecyclopentane 5 (68 mg, 1 mmol, 4 equiv), $(Bu_3Sn)_2$ (0.19 mL,0.38 mmol), and DTBHN (4 mg, 0.04 mmol, 10 mol %) added by 5 mol % portion every 1.5 h, in degassed benzene (1.5 mL). Concentration in vacuo, followed by purification by flash chromatography (silica gel, 94/6 PE / EtOAc) afforded 15(55 mg, 87%) as a colorless oil.R_f= 0.36 (PE/EtOAc94/6). IR (ATR) ν_{max} (cm^{-1}) = 1690, 1304, 1140, 1015, 980.^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) =4.17 (appearantq, 2H, *J* = 3 and 6 Hz, CH_2), 3.99 (s, 3H CH_3), 2.36 (appearant t, 2H,*J* = 3 and 6 Hz, CH_2), 2.34 (appearant t, 2H,*J* = 3 and 6 Hz, CH_2), 1.91-1.80 (m, 2H, CH_2), 1.72-1.54 (m, 6H, 3CH_2), 1.38 (t, 3H, *J* = 3 Hz, CH_3).^{13}C NMR ($CDCl_3$, 75.5 MHz): δ (ppm) = 174.4 (C=O ester), 127.6 (C), 116.5 (CN), 61.2 (C), 60.4 (C),59.9 (C), 36.1 (C), 30.6 (C), 30.2 (C), 23.6 (C), 14.7 (C).HRMS (ESI): $[M+H]^+$ $C_{13}H_{21}N_2O_3$calcd. 253.1552, found 253.1553.

ethyl 4-(cyano(methoxyimino)methyl)-4-ethylhexanoate (16)

Compound 16 was obtained according to the general procedure described above from ethyl iodoacetateA (53 mg, 0.25 mmol, 1 equiv), sulfonyl oxime C (119 mg, 0.5 mmol, 2 equiv), 3-methylenepentane 6 (84 mg, 1 mmol, 4 equiv), $(Bu_3Sn)_2$ (0.19 mL,0.38 mmol), and DTBHN (4 mg, 0.04 mmol, 10 mol %) added by 5 mol % portion every 1.5 h, in degassed benzene (1.5 mL). Concentration in vacuo, followed by purification by flash chromatography (silica gel, 94/6 PE / EtOAc) afforded 16(59 mg, 92%) as a colorless oil.R_f= 0.35 (PE/EtOAc94/6). IR (ATR)ν_{max} (cm^{-1}) = 1679, 1300, 1148, 1018, 980.^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) =4.43 (appearant t, 2H, *J* = 3 and 6 Hz, CH_2), 4.22 (q, 2H, *J* = 3 Hz, CH_2), 4.02 (s, 3H,CH_3), 2.06 (appearant t, 2H,*J* = 3 and 6 Hz, CH_2), 1.84 (appearant q,2H, 2H, *J* = 3 and 6 Hz, CH_2), 1.58 (appearant q, 2H, *J* = 3 and 6 Hz, CH_2), 1.39 (t, 3H, *J* = 3 Hz, CH_3), 1.01 (t, 6H, *J* = 3 Hz, CH_3).^{13}C NMR ($CDCl_3$, 75.5 MHz): δ (ppm) = 174.4 (C=O ester), 126.4 (C), 116.3 (CN), 61.2 (C), 60.4 (C),51.0 (C), 30.6 (C), 27.5 (C), 27.4 (C), 14.7 (C), 8.2 (C).HRMS (ESI): $[M+H]^+$ $C_{13}H_{23}N_2O_3$calcd. 255.1708, found 255.17080.

ethyl 5-cyano-5-(methoxyimino)-4-((trimethyl silyl)methyl)pentanoate (17)

Compound 17 was obtained according to the general procedure described above from ethyl iodoacetateA (53 mg, 0.25 mmol, 1 equiv), sulfonyl oxime C (119 mg, 0.5 mmol, 2 equiv), allyltrimethylsilane 7 (11.4 mg, 1 mmol, 4 equiv), $(Bu_3Sn)_2$ (0.19 mL,0.38 mmol), and DTBHN (4 mg, 0.04 mmol, 10 mol %) added by 5 mol % portion every 1.5 h, in degassed benzene (1.5 mL). Concentration in vacuo, followed by purification by flash chromatography (silica gel, 96/4 PE / EtOAc) afforded 17(68 mg, 95%) as a colorless oil.R_f= 0.35 (PE/EtOAc96/4). IR (ATR)ν_{max} (cm^{-1}) = 1700, 1670, 1150, 1201, 1015, 940.^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) =4.14 (q, 2H, *J*= 3Hz, CH_2), 4.02 (s, 3H,CH_3), 3.53-3.48 (m, 1H,CH), 2.49 (appearant t, 2H,*J* = 3 and 6 Hz, CH_2), 1.92-1.84 (m, 2H, 2H,CH_2), 1.37 (appearantt, 3H, *J* = 3 and 6 Hz, CH_3), 1.03-0.99 (m, 1H,CH), 0.74 (m, 1H, CH), 0.27 (s, 9H, $3CH_3$).^{13}C NMR ($CDCl_3$, 75.5 MHz): δ (ppm) = 174.3 (C=O ester), 130.1 (C), 114.9 (CN), 61.2 (C), 60.4 (C),37.2 (C), 32.6 (C), 30.2 (C), 14.7 (C), 14.1 (C).HRMS (ESI): $[M+H]^+$ $C_{13}H_{25}N_2O_3$Sicalcd. 285.1634, found 285.1634.

ethyl 5-cyano-4-ethoxy-5-(methoxyimino) pentanoate (18)

Compound 18 was obtained according to the general procedure described above from ethyl iodoacetateA (53 mg, 0.25 mmol, 1 equiv), sulfonyl oxime C (119 mg, 0.5 mmol, 2 equiv), ethoxyethene 8 (72 mg, 1 mmol, 4 equiv), $(Bu_3Sn)_2$ (0.19 mL,0.38 mmol), and DTBHN (4 mg, 0.04 mmol, 10 mol %) added by 5 mol % portion every 1.5 h, in degassed benzene (1.5 mL). Concentration in vacuo, followed by purification by flash chromatography (silica gel, 90/10 PE / EtOAc) afforded 18(51 mg, 85%) as a colorless oil.R_f= 0.35 (PE/EtOAc90/10). IR (ATR) δ_{max} (cm^{-1}) = 1700, 1680, 1630, 1307, 1144, 1070.^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) =4.85 (appearant t, 1H, *J* = 3 and 6 Hz, CH), 4.17 (q, 2H, *J* = 3 Hz, CH_2), 2.38 (appearant t, 2H, *J* = 3 and 6 Hz, CH_2), 2.19-2.09 (m, 2H, CH_2), 1.38 (t, 3H,*J* = 3 Hz, CH_3), 1.20 (appearant t,3H, *J* = 3 and 6 Hz, CH_3).^{13}C NMR ($CDCl_3$, 75.5 MHz): δ (ppm) = 174.3 (C=O ester), 135.4 (C), 109.5 (CN), 74.0 (C), 64.6 (C),61.2 (C), 60.4 (C), 31.0 (C), 30.6 (C), 15.5 (C), 14.7 (C).HRMS (ESI): $[M+H]^+$ $C_{11}H_{19}N_2O_4$calcd. 243.1345, found 243.1345.

3-(cyano(methoxyimino)methyl)-6-ethoxy-3-methyl-6-oxohexyl benzoate (19)

Compound 19 was obtained according to the general procedure described above from ethyl iodoacetateA (53 mg, 0.25 mmol, 1 equiv), sulfonyl oxime C (119 mg, 0.5 mmol, 2 equiv), 3-methylbut-3-en-1-yl benzoate 9 (72 mg, 1 mmol, 4 equiv), $(Bu_3Sn)_2$ (0.19 mL,0.38 mmol), and DTBHN (4 mg, 0.04 mmol, 10 mol %) added by 5 mol % portion every 1.5 h, in degassed benzene (1.5 mL). Concentration in vacuo, followed by purification by flash chromatography (silica gel, 92/8 PE / EtOAc) afforded 19(71 mg, 79%) as a colorless oil.R_f= 0.37(PE/EtOAc92/8). IR (ATR) ν_{max} (cm^{-1}) = 2955, 1750, 1733, 1446, 1430, 1300, 1280, 1080, 750.^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) =7.94(d, 2H, CH_{ar}), 7.48-7.37 (m, 3H, CH_{ar}), 4.24 (appearant t, 2H, *J* = 3 and 6 Hz, CH_2), 4.16(q, 2H, *J* = 3 Hz, CH_2), 3.99 (s, 3H,CH_3), 2.31 (t, 2H, *J* = 6 Hz, CH_2), 2.13-2.04 (m, 4H, $2CH_2$), 1.32 (s, 3H, CH_3).^{13}C NMR ($CDCl_3$, 75.5 MHz): δ (ppm) = 174.4 (C=O ester), 167.0 (C=O ester), 133.0 (C), 130.2 (C_{ar}), 129.6(C_{ar}), 128.8 (C_{ar}),

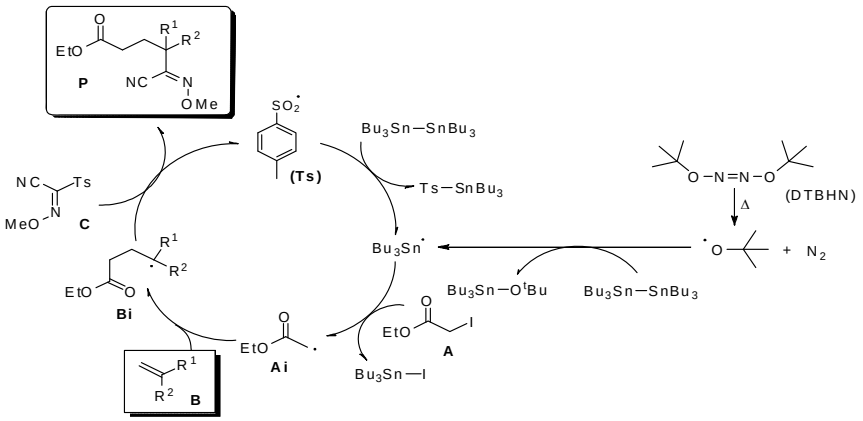
113.2(CN), 64.4 (C), 61.2 (C),60.4 (C), 38.7 (C), 36.8 (C), 30.5 (C), 29.7 (C), 25.0 (C), 14.7 (C).HRMS (ESI): $[M+H]^+$ $C_{19}H_{25}N_2O_5$calcd. 361.1763, found 361.17630.

ethyl 4-(cyano(methoxyimino)methyl)-6-hydroxy-4-methylhexanoate (20)

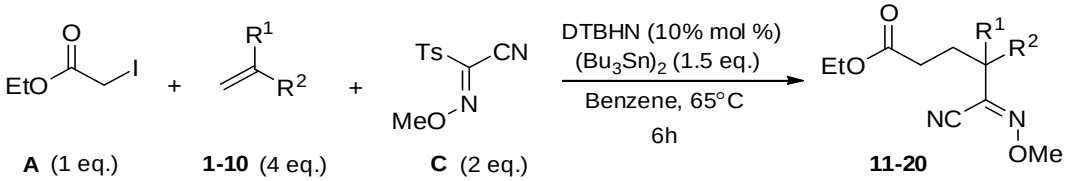
Compound 20 was obtained according to the general procedure described above from ethyl iodoacetateA (53 mg, 0.25 mmol, 1 equiv), sulfonyl oxime C (119 mg, 0.5 mmol, 2 equiv), 3-methylbut-3-en-1-ol 10 (86 mg, 1 mmol, 4 equiv), $(Bu_3Sn)_2$ (0.19 mL,0.38 mmol), and DTBHN (4 mg, 0.04 mmol, 10 mol %) added by 5 mol % portion every 1.5 h, in degassed benzene (1.5 mL). Concentration in vacuo, followed by purification by flash chromatography (silica gel, 94/6 PE / EtOAc) afforded 20(47 mg, 76%) as a colorless oil.R_f= 0.34 (PE/EtOAc90/10). IR (ATR) ν_{max} (cm^{-1}) = 2920, 1730, 1650, 1315, 1201, 1105, 939.^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) =4.16(appearant q,2H, *J* = 3 and 6 Hz, CH_2), 4.01(s, 3H, CH_3), 3.49 (appearant t, 2H, *J* = 3 and 6 Hz, CH_2), 2.31 (appearantt, 2H, J = 3and 6 Hz, CH_2), 2.01 (t, 2H, J = 6 Hz, CH_2), 1.85 (appearant t, 2H, J = 3 and 6 Hz, CH_2), 1.37 (t, 3H, *J* = 3 Hz, CH_3), 1.31 (s, 3H, CH_3), 0.56 (s, 1H, OH).^{13}C NMR ($CDCl_3$, 75.5 MHz): δ (ppm) = 174.4 (C=O ester), 128.8 (C), 113.2 (CN), 61.2 (C), 60.4 (C),59.9 (C), 38.7(C), 38.0 (C), 30.5 (C), 29.7 (C), 25.0 (C), 14.7 (C).HRMS (ESI): $[M+H]^+$ $C_{12}H_{21}N_2O_4$calcd. 257.1501, found 257.1501.

RESULTS AND DISUSSION

The 3-component carbo-oximation process was first carried outusing new sulfonyl oxime, ready available from the corresponding á-sulfonyl nitrile[15]. Such reactions proceed through the preliminary decomposition of DTBHN initiator to produce nitrogen gas and ^{t}BuO radical. Addition of the latter onto tin compound produced tin radical. Tin radical can then abstract the iodide group from ethyliodoacetate(A)and form the electrophilic radical (Ai). Addition of an electron-poor radical to the less hindered end of an olefin (B), forminga new nucleophilic radical(Bi), which can then be trapped by anelectrophilic partner such as cyanosulfonyloxime(C), affording the expected products (P) and expel the tosylate group through β-fragmentation processto propagate the radical chain Scheme 2.



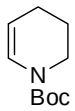
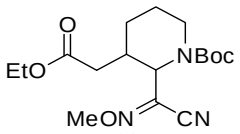
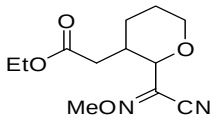
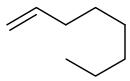
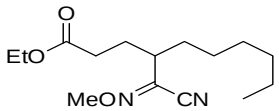
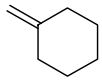
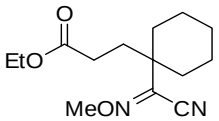
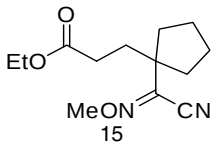
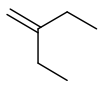
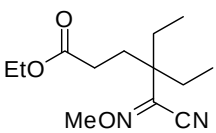
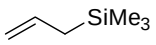
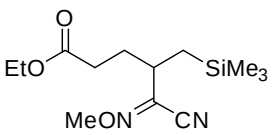
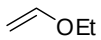
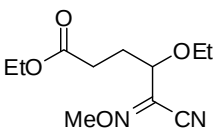
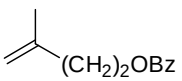
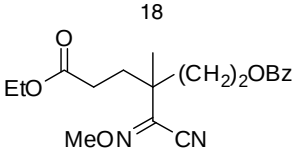
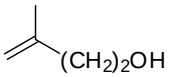
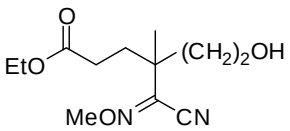
Scheme 2: The mechanism of three-component free-radical carbo-alkenylation processes



A (1 eq.) **1-10** (4 eq.) **C** (2 eq.) **11-20**

Scheme 3: Synthesis of carbo-oximation products

Table 1: Three-component Carbo-oximation of various Olefins using sulfonyloxime nitrile

Entry	Olefin Substrate	Olefin Structure	Product	Yield %
1	1		 11	78
2	2		 12	81
3	3		 13	91
4	4		 14	89
5	5		 15	87
6	6		 16	92
7	7		 17	95
8	8		 18	85
9	9		 19	79
10	10			76

The 3-component carbo-oximation process was first carried outusing cyanosulfonyloxime B(2 eq.), an excess of the olefins1-10(4eq.), ethyliodoester as precursor A (1 eq.), and $(Bu_3Sn)_2$(1.5 equiv) in benzene (degassed) as a solvent. The reaction wasinitiated using di-tert-butylhyponitrite (DTBHN) (10 mol %). Theresults are summarized in Scheme 3(Table 1)below. Generally good andreproducible yields of the 3-component adducts 11-20were obtained(76-95%).The final oximes were easily isolated throughchromatography over silica gel. A broad variety of substituents onthe olefin is compatible with the reaction conditions. The reaction conditions were found to be compatible with Boc-protected amines and dihydro-pyranas an electron-rich olefins (entry 1 and 2). The iodoester substrate A was also shown to react efficiently with normal olefin and methylene cyclohexene as well asmethylene cyclopentene(entry 3-6). The reactionwas extended with using electron-rich olefins such asallylsilanes and vinylether, which produced the expected products17 and18in very good yields (entry 7 and 8). Generation of products 19and 20with quaternary center carbon was also obtained with a good yield (entry 9 and 10).

CONCLUSION

In summary, a sequential carbo-oximation protocol involvinga three-component radical process wasdeveloped under mild conditions in a single potstarting from readily available ehtyliodoacetate, different olefins and new sulfonyl oxime acceptor. This three-component reaction proceed through the addition of a radical species derived from a iodoester and a vinylsulfone across the olefinic groups backbone and formation of two new carbon-carbon bonds, which enables facile hydrolysis of the oxime under mild conditions after post-functionalization of the carbo-oximation products and provides a rapid access to lactones, afterMukaiyamaaldol or Sakurai allylation reactions ormore complexpiperidinones using Pictete-Spengler processes.

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