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Manganese(III) Acetate Mediated Free Radical Cyclization of 1,3-Dicarbonyl Compounds with Sterically Hindered Olefins

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The manganese(III) acetate mediated radical cyclization of dimedone **1a**, 2,4-pentanedione **1b**, ethyl acetoacetate **1c**, 1,3-cyclohexanedione **1d** and 5-phenyl-1,3-cyclohexanedione **1e** with 1,1-diphenyl-1-butene **2a** afforded 4,5-dihydrofurans **(3c, 3e)** and tetrahydrobenzofurans **(3a, 3g, 3h)** in good yields (55% - 77%). Additionally, the reactions of trifluoromethyl-group containing 1,3-dicarbonyls, 4,4,4-trifluoro-1-phenylbutane-1,3-dione **1f** and 4,4,4-trifluoro-1-thien-2ylbutane-1,3-dione **1g** with **2a** 3-trifluoroacetyl-4,5-dihydrofurans gave in 74% and 78% yields, respectively. Treatment of **1a**, **1b** and **1c** with 1,2-diphenyl-1-pentene **2a** resulted in the formation of tetrahydrobenzofuran **3b** and 4,5-dihydrofurans **3d** and **3f** in lower yields.

Key Words: Manganese(III) acetate, free radical cyclization, 1,3-dicarbonyl, 4,5-dihydrofuran, tetrahydrobenzofuran, trifluoroacetyl, oxidative addition.

Introduction

In the past 2 decades, attention has been paid to the synthetic opportunities offered by high-valent transition metal salts (Mn^{3+}, Ce^{4+}, Co^{3+}, Ag^{+} etc.) oxidation of 1,3-dicarbonyl compounds in the presence of unsaturated systems[1−3]. Among these metal salts, manganese(III) acetate is a prominent. Enolizable 1,3-dicarbonyl compounds (β-diketone, β-ketoester, β-ketoamide) can be oxidized by manganese(III) acetate to generate α-carbon radicals which can attack alkenes to form new C-C bonds. Thus, it provides a versatile protocol for the formation of highly functionalized products, such as furans[4−6], dihydrofurans[7−10], γ-lactones[11], biologically active compounds and natural products[11−15]. Nitromethylation[16] and malonylation[17] of aromatic compounds, the α-acetoxylation[18−22] of enones and aryl couplings[23−25] are among the other known reactions of $Mn(OAc)_3$.

We have reported the formation of dihydrofuran and furan derivatives as a result of $Mn(OAc)_3$ mediated oxidative cyclizations of 1,3-dicarbonyl compounds with alkenes and alkynes[6]. Additionally, we have

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reported the synthesis of carbomoyl-4,5-dihydrofurans and tetralones due to the reaction of 1,3-dicarbonyls with α, β-unsaturated amides[26]. Previously, we have described the synthesis of 3-trifluoroacetyl-4,5-dihydrofurans and 3-(dihydrofuran-2(3*H*)-ylidene)-1,1,1-trifluoroacetones by the treatment of trifluoromethyl-1,3-dicarbonyl compounds with conjugated alkenes[27].

The mechanism of the $Mn(OAc)_3$ mediated radical cyclization of 1,3-dicarbonyls with alkenes has been studied by Snider and Kurosawa thoroughly[9,11,28]. In this study we performed the $Mn(OAc)_3$ mediated radical cyclization reactions of 1,3-dicarbonyl compounds **1a-g** with sterically hindered olefins.

Experimental

Melting points were determined on a Gallencamp capillary melting point apparatus. IR spectra (KBr disc) were obtained with a Matson 1000 FT-IR in the 400-4000 cm^{-1} range with 4 cm^{-1} resolution. ^{1}H-NMR (400 MHz), ^{19}F-NMR (376 MHz) and ^{13}C-NMR (100 MHz) spectra were recorded on Bruker DPX 400 and Varian Mercury-400 high performance digital FT-NMR spectrophotometers. The electron impact mass spectra (MS, APCI, 100-150 eV) were measured on Micromass UK LC/MS and Shimadzu GC-17A/GC-MS-QP5000 spectrophotometers. Elemental analyses were performed on Leco 932 CHNS-O instrument.

Thin layer chromatography (TLC) was performed on Merck aluminum-packed silica gel plates. Purification of products was performed by column chromatography on silica gel (Merck silica gel 60, 230-400 mesh) or preparative TLC on silica gel from Merck ($PF_{254-366nm}$). All 1,3-dicarbonyl compounds and reagents were purchased from Merck.

1,1-Diphenyl-1-butene (2a)

Colorless oil, bp: 296-298 °C; ^{1}H-NMR, δ (ppm): 1.04 (t, 3H, J = 7.5 Hz, -CH_3), 2.04 (m, 2H, -CH_2), 6.0 (t, 1H, J = 7.5 Hz, H-2), 7.01-7.31 (m, 10H, arom.).

Synthesis of 1,2-diphenyl-1-pentene (2b)

Benzyltriphenylphosphonium bromide (40 g, 92 mmol, obtained from benzyl bromide and triphenylphosphine in toluene) was added to a stirred suspension of NaH (3.68 g, 92 mmol, 60% in mineral oil) in THF and the mixture was stirred at 15 °C for 30 min. 1-Phenylbutanone (12.6 mL, 85 mmol) was added and the mixture was heated under reflux for 3 h. The solvent was removed under reduced pressure and the residue was extracted with Et_2O. This solvent was evaporated and the crude product was distilled under reduced pressure to give 11.5 g (61%) of 1,2-diphenyl-1-pentene **(2b)**. As a colorless oil, bp: 249-250 °C; ^{1}H-NMR, δ (ppm): 0.96 (t, 3H, J = 7.6 Hz, -CH_3), 1.49 (m, 2H, -CH_2), 2.74 (td, 2H, J = 6.4, 2.0 Hz, -CH_2), 6.96 (t, 1H, J = 2.0 Hz, H-1), 7.12-7.43 (m, 8H, arom.), 7.6 (dd, 2H, J = 8.4, 1.2 Hz, arom.).

General procedure

A solution of manganese(III) acetate dihydrate (6 mmol, 1.64 g) in glacial acetic acid (30 mL) was heated under nitrogen atmosphere at 80 °C until it dissolved. After $Mn(OAc)_3$ dissolved completely, the solution was cooled to 60 °C. A solution of **1a-g** (4 mmol) and olefin (2 mmol) in 5 mL acetic acid was added to the mixture and the temperature was raised to 80 °C. The reaction was completed when the dark brown

color of the solution disappeared. Acetic acid was evaporated under reduced pressure. Water was added to the residue and extracted with EtOAc (3 x 20 mL). The combined organic phases were neutralized with satd. $NaHCO_3$ solution, and dried over anhydrous Na_2SO_4 and evaporated. Crude products were purified by column chromatography on silica gel or preparative TLC (20 x 20cm plates, 2 mm thickness) using n-hexane/EtOAc (4:1) as eluent.

3-Ethyl-6,6-dimethyl-2,2-diphenyl-3,5,6,7-tetrahydro-1-benzofuran-4(2*H*)-one (3a): colorless solid, mp: 111-113 °C; IR, υ_{max}: 3053, 2961, 2930 (C-H), 1637 (C=O), 1620 (C=C), 1178 (C-O-C); ^{1}H-NMR, δ (ppm): 0.55 (t, 3H, J = 7.5 Hz, -CH_3), 0.93 (s, 3H, -CH_3), 1.08 (s, 3H, -CH_3), 1.29 (m, 2H, -CH_2), 2.11 (d, 1H, J = 16.2 Hz, Ha-5), 2.16 (d, 1H, J = 16.1 Hz, Hb-5), 2.22 (dd, 1H, J = 17.8, 1.6 Hz, Ha-7), 2.39 (d, 1H, J = 17.6 Hz, Hb-7), 3.77 (t, 1H, J = 6.3 Hz, H-3), 7.21-7.28 (m, 8H, arom.), 7.43 (m, 2H, arom.); ^{13}C-NMR, δ (ppm): 11.4 (CH_3), 24.8 (CH_3), 28.2 (CH_3), 29.1 (CH_2), 34.0 (CH_2), 38.1 (CH_2), 47.9, 51.3, 98.7 (C-2), 117.1 (C-3a), 126.5, 126.8, 127.3, 127.8, 128.0, 128.2, 140.7, 144.6, 169.8, 174.2 (C-7a), 194.5 (C=O); MS (APCI, 150 eV), m/z (%): 347 (MH^+, 58.2), 287 (M^+ -2CH_3 -C_2H_5, 1.5), 269 (M^+-C_6H_5, 9.4), 243 (MH^+-C_6H_5CO, 18.6), 219 (M^+-$C_8H_{15}O$, 5.4), 208 ($C_{16}H_{16}^+$, 1.1), 167 ($C_{13}H_{11}^+$, 100.0), 105 ($C_6H_5CO^+$, 16.7), 91 ($C_6H_5CH_2^+$, 15.9); Anal. calcd. for $C_{24}H_{26}O_2$: C 83.2; H 7.5; found: C 83.3; H 7.35.

2-Propyl-6,6-dimethyl-2,3-diphenyl-3,5,6,7-tetrahydro-1-benzofuran-4(2*H*)-one (3b): colorless solid, mp: 169-172 °C; IR, υ_{max}: 3026, 2955, 2872 (C-H), 1641 (C=O), 1632 (C=C), 1032 (C-O-C); ^{1}H-NMR, δ (ppm): 0.64 (t, 3H, J = 7.3 Hz, -CH_3), 0.82 (m, 1H, -CH), 1.16 (s, 3H, -CH_3), 1.22 (m, 1H, -CH), 1.28 (s, 3H, -CH_3), 1.43 (m, 2H, -CH_2), 2.23 (d, 1H, J = 16.3 Hz, Ha-5), 2.26 (d, 1H, J = 16.25 Hz, Hb-5), 2.58 (dd, 1H, J = 17.7, 1.9 Hz, Ha-7), 2.65 (d, 1H, J = 17.65 Hz, Hb-7), 4.40 (s, 1H, H-3), 7.29-7.43 (m, 10H, arom.); ^{13}C-NMR, δ (ppm): 14.2 (CH_3), 17.5 (CH_3), 29.1 (CH_3), 29.3 (CH_2), 34.3 (CH_2), 38.3 (CH_2), 40.4, 47.2, 51.5, 58.0, 98.5 (C-2), 118.5 (C-3a), 125.1, 128.0, 128.1, 129.2, 129.3, 139.0, 146.6, 176.6 (C-7a), 196.8 (C=O); MS (APCI, 150 eV), m/z (%): 361 (MH^+, 100.0), 283 (MH^+ -C_6H_5, 5.0), 243 (MH^+ -C_6H_5 -C_3H_8, 27.1), 91 ($C_6H_5CH_2^+$, 5.4); Anal. calcd. for $C_{25}H_{28}O_2$: C 83.3; H 7.8; found: C 83.2; H 7.5.

1-(4-ethyl-2-methyl-5,5-diphenyl-4,5-dihydrofuran-3-yl)ethanone (3c): pale yellow oil; IR, υ_{max}: 3038, 2965, 2930 (C-H), 1625 (C=O), 1600 (C=C), 1215 (C-O-C); ^{1}H-NMR, δ (ppm): 0.45 (t, 3H, J = 7.4 Hz, -CH_3), 1.30 (m, 2H, -CH_2), 2.19 (s, 3H, -CH_3), 2.23 (s, 3H, -CH_3), 3.77 (t, 1H, J = 5.5 Hz, H-4), 7.13-7.37 (m, 8H, arom.), 7.44 (d, 2H, J = 7.7 Hz, arom.); MS (APCI, 150 eV), m/z (%): 307 (MH^+, 20.8), 289 (MH^+ -H_2O, 13.9), 247 (M^+ -CH_3 -CH_3CO, 43.2), 219 (M^+ -CH_3 -C_2H_5 -CH_3CO, 12.4), 167 ($C_{13}H_{11}^+$, 75.2), 105 ($C_6H_5CO^+$, 79.3), 91 ($C_6H_5CH_2^+$, 91.4); Anal. calcd. for $C_{21}H_{22}O_2$: C 82.4; H 7.2; found: C 82.6; H 6.8.

1-(2-methyl-4,5-diphenyl-4-propyl-4,5-dihydrofuran-3-yl)ethanone (3d): pale yellow oil; IR, υ_{max}: 3059, 2957, 2926 (C-H), 1670 (C=O), 1600 (C=C), 1124 (C-O-C); ^{1}H-NMR, δ (ppm): 0.53 (t, 3H, J = 7.3 Hz, -CH_3), 0.67 (m, 1H, -CH), 1.09 (m, 1H, -CH), 1.26 (m, 2H, -CH_2), 1.66 (s, 3H, -CH_3), 2.45 (s, 3H, -CH_3), 4.29 (s, 1H, H-4), 7.22-7.34 (m, 10H, arom.); MS (APCI, 150 eV), m/z (%): 321 (MH^+, 29.2), 261 (M^+ -CH_3 -CH_3CO, 28.6), 243 (M^+ -C_6H_5, 12.6), 219 (M^+ -CH_3CO -C_3H_8 -CH_3, 34.4), 167 (M^+ -2C_6H_5, 14.8), 91 ($C_6H_5CH_2^+$, 100.0); Anal. calcd. for $C_{22}H_{24}O_2$: C 82.5; H 7.5; found: C 82.3; H 7.8.

Ethyl 4-ethyl-2-methyl-5,5-diphenyl-4,5-dihydrofuran-3-carboxylate (3e): yellow oil; IR, υ_{max}: 3059, 2970, 2936 (C-H), 1695 (C=O), 1648 (C=C), 1215 (C-O-C); ^{1}H-NMR, δ (ppm): 0.62 (t, 3H, J

= 7.5 Hz, -CH_3), 1.32 (t, 3H, J = 7.1 Hz, -CH_3), 1.43 (m, 2H, -CH_2), 2.33 (s, 3H, -CH_3), 3.83 (t, 1H, J = 5.1 Hz, H-4), 4.20 (q, 2H, J = 7.1 Hz, -OCH_2), 7.29-7.40 (m, 8H, arom.), 7.60 (dt, 2H, J = 7.1, 1.5, arom.); ^{13}C-NMR, δ (ppm): 10.7, 14.4, 14.7, 24.6, 50.0, 59.5, 95.0 (C-5), 108.7 (C-3), 126.2, 126.7, 127.0, 127.6, 127.7, 128.1, 141.1, 145.5 (C-2), 165.9 (C=O); MS (APCI, 100 eV), m/z (%): 337 (MH^+, 12.8), 291 (M^+ -C_2H_5O, 100.0), 275 (M^+ -C_2H_5O -CH_3, 21.1), 263 (M^+ -$C_3H_5O_2$, 5.4), 167 ($C_{13}H_{11}^+$, 4.7), 105 ($C_6H_5CO^+$, 5.4), 91 ($C_6H_5CH_2^+$, 5.1); Anal. calcd. for $C_{22}H_{24}O_3$: C 78.6; H 7.1; found: C 78.9; H 6.8.

Ethyl 2-methyl-4,5-diphenyl-4-propyl-4,5-dihydrofuran-3-carboxylate (3f): colorless oil; IR, υ_{max}: 3045, 2959, 2922 (C-H), 1700 (C=O), 1650 (C=C), 1124 (C-O-C); ^{1}H-NMR, δ (ppm): 0.62 (t, 3H, J = 7.3 Hz, -CH_3), 0.96 (t, 3H, J = 7.1 Hz, -CH_3), 1.05 (t, 1H, J = 7.1 Hz, -CH), 1.28 (m, 1H, -CH), 1.37 (m, 2H, -CH_2), 2.51 (s, 3H, -CH_3), 3.95 (q, 2H, J = 7.2 Hz, -OCH_2), 4.36 (s, 1H, H-4), 7.35-7.41 (m, 10H, arom.); MS (APCI, 100 eV), m/z (%): 351 (MH^+, 100.0), 305 (M^+ -C_2H_5O, 58.7), 273 (M^+ -C_6H_5, 15.8), 263 (M^+ -$C_3H_5O_2$ -CH_3, 17.4), 91 ($C_6H_5CH_2^+$, 1.9); Anal. calcd. for $C_{23}H_{26}O_3$: C 78.9; H 7.4; found: C 80.1; H 7.7.

3-Ethyl-2,2-diphenyl-3,5,6,7-tetrahydro-1-benzofuran-4(2*H*)-one (3g): colorless solid, mp: 113-115 °C; IR, υ_{max}: 3055, 2959, 2928 (C-H), 1656 (C=O), 1631 (C=C), 1219 (C-O-C); ^{1}H-NMR, δ (ppm): 0.53 (t, 3H, J = 7.4 Hz, -CH_3), 1.29 (m, 2H, -CH_2), 1.98 (m, 2H, -CH_2), 2.22 (m, 2H, -CH_2), 2.33 (m, 1H, -CH), 2.56 (m, 1H, -CH), 3.78 (t, 1H, J = 4.8 Hz, H-3), 7.20-7.28 (m, 8H, arom.), 7.42 (dd, 2H, J = 7.0, 1.62 Hz, arom.); ^{13}C-NMR, δ (ppm): 11.2, 21.5, 24.2, 24.7, 36.9, 48.0, 98.5 (C-2), 118.3 (C-3a), 126.5, 126.8, 127.3, 127.8, 128.0, 128.2, 140.7, 144.6, 175.1 (C-7a), 195.2 (C=O); MS (APCI, 150 eV), m/z (%): 319 (MH^+, 35.7), 241 (M^+ -C_6H_5, 14.8), 167 ($C_{13}H_{11}^+$, 100.0), 105 ($C_6H_5CO^+$, 28.6), 91 ($C_6H_5CH_2^+$, 30.2); Anal. calcd. for $C_{22}H_{22}O_2$: C 83.0; H 6.9; found: C 83.0; H 6.8.

3-Methyl-2,2,6-triphenyl-3,5,6,7-tetrahydro-1-benzofuran-4(2*H*)-one (3h): yellow oil; IR, υ_{max}: 3034, 2959, 2920 (C-H), 1635 (C=O), 1605 (C=C), 1053 (C-O-C); ^{1}H-NMR, δ (ppm): 0.65 (t, 3H, J = 7.4 Hz, -CH_3), 1.39 (m, 2H, -CH_2), 2.63 (m, 2H, -CH_2), 2.91 (m, 2H, -CH_2), 3.51 (m, 1H, -CH), 3.92 (t, 1H, J = 5.2 Hz, H-3), 7.24-7.39 (m, 13H, arom.), 7.55 (t, 2H, J = 6.9 Hz, arom.); MS (APCI, 150 eV), m/z (%): 395 (MH^+, 100.0), 317 (M^+ -C_6H_5, 12.3), 167 ($C_{13}H_{11}^+$, 74.3), 105 ($C_6H_5CO^+$, 16.3), 91 ($C_6H_5CH_2^+$, 15.3); Anal. calcd. for $C_{23}H_{26}O_3$: C 85.3; H 6.6; found: C 85.0; H 6.9.

[4-ethyl-5,5-diphenyl-2-(trifluoromethyl)-4,5-dihydrofuran-3-yl](phenyl) methanone (3i): colorless solid, mp: 174–176 °C; IR, υ_{max}: 3059, 2965, 2930 (C-H), 1646 (C=O), 1606 (C=C), 1211 (C-O-C), 1134 (C-F); ^{1}H-NMR, δ (ppm): 0.67 (t, 3H, J = 7.43 Hz, -CH_3), 1.55 (m, 1H, -CH), 1.67 (m, 1H, -CH), 4.23 (t, 1H, J = 5.41 Hz, H-4), 7.27-7.34 (m, 5H, arom.), 7.36-7.49 (m, 5H, arom.), 7.56 (t, 1H, J = 7.3 Hz, arom.), 7.65 (d, 2H, J = 7.5 Hz, arom.), 7.78 (d, 2H, J = 7.3 Hz, arom.); ^{13}C-NMR, δ (ppm): 10.7, 25.4, 49.7, 97.5 (C-5), 113.4 (C-3), 120.6 (q, J_{C-F} = 286.4 Hz, -CF_3), 126.6, 126.9, 127.9, 128.3, 128.5, 128.7, 128.8, 129.9, 130.5, 132.5, 140.2, 144.0, 171.4 (C-2) 176.3 (q, J_{C-F} = 34.5 Hz, C=O); ^{19}F-NMR, δ (ppm): -78.5 (s, -CF_3); MS (APCI, 100 eV), m/z (%): 423 (MH^+, 0.1), 422 (M^+, 0.3), 404 (M^+ -H_2O, 0.3), 393 (M^+ -C_2H_5, 1.9), 353 (M^+ -CF_3, 0.2), 317 (M^+ -C_6H_5CO, 4.1), 296 (M^+ -C_2H_5 -CF_3CO, 3.6), 165 ($C_{13}H_{10}^+$, 15.0), 105 ($C_6H_5CO^+$, 100.0), 91 ($C_6H_5CH_2^+$, 4.7), 77 ($C_6H_5^+$, 62.7), 43 ($C_3H_7^+$, 7.2); Anal. calcd. for $C_{26}H_{19}F_3O_2$: C 73.9; H 5.0; found: C 73.5; H 5.3.

[4-ethyl-5,5-diphenyl-2-(trifluoromethyl)-4,5-dihydrofuran-3-yl](thien-2-yl)methanone (3j): yellow oil; ^{1}H-NMR, δ (ppm): 0.46 (t, 3H, J = 7.4, -CH_3), 1.52 (m, 2H, -CH_2), 4.12 (t, 1H, J = 5.2 Hz, H-4), 7.14 (t, 1H, J = 4.1 Hz, arom.), 7.19 (t, 2H, J = 3.8 Hz, arom.), 7.20 (t, 4H, J = 7.0 Hz, arom.), 7.36 (d, 2H, J = 7.2 Hz, arom.), 7.55 (d, 2H, J = 7.5 Hz, arom.), 7.64 (dd, 1H, J = 5.0, 0.9 Hz, arom.), 8.53 (dd, 1H, J = 3.9, 0.9 Hz, arom.); ^{13}C-NMR, δ (ppm): 12.1, 25.7, 50.5, 95.5 (C-5), 105.4 (C-3), 119.6 (q, J_{C-F} = 292.4 Hz, -CF_3), 125.6, 126.1, 126.7, 127.4, 127.8, 128.1, 128.5, 128.7, 129.4, 129.9, 131.1, 136.0, 138.6, 150.2, 174.2 (C-2) 175.7 (q, J_{C-F} = 35.1 Hz, C=O); ^{19}F-NMR, δ (ppm): -76.8 (s, CF_3); MS (APCI, 100 eV), m/z (%): 429 (MH^+, 6.6), 428 (M^+, 1.56), 399 (M^+-C_2H_5, 10.7), 317 (M^+-C_5H_3OS, 5.4), 302.0 (M^+ - CF_3CO -C_2H_5, 12.0), 165.0 ($C_{13}H_{10}^+$, 11.2), 111.0 ($C_5H_3OS^+$, 100.0), 105.0 ($C_6H_5CO^+$, 46.3), 91 ($C_6H_5CH_2^+$, 6.8), 77 ($C_6H_5^+$, 24.7), 69 (CF_3^+, 4.9); Anal. calcd. for $C_{24}H_{19}F_3O_2S$: C 67.3; H 4.4; found: C 67.6; H 4.2.

Results and Discussion

We studied the $Mn(OAc)_3$ mediated radical cyclizations of dimedone **1a**, 2,4-pentanedione **1b**, ethyl acetoacetate **1c**, 1,3-cyclohexanedione **1d,** 5-phenyl-1,3-cyclohexanedione **1e**, 4,4,4-trifluoro-1-phenylbutane-1,3-dione **1f** and 4,4,4-trifluoro-1-thien-2ylbutane-1,3-dione **1g** with 1,1-diphenyl-1-butene [29] **2a** and 1,2-diphenyl-1-pentene **2b**. As a result of these reactions we obtained polysubstituted 4,5-dihydrofuran, tetrahydrobenzofuran and 3-trifluoroacetyl-4,5-dihydrofuran derivatives.

The manganese(III) acetate dihydrate used as radical oxidant was obtained from the bipolar packed-bed reactor by the electrochemical method described in the literature[30]. **2a** was prepared by removing water from the carbinol formed during the Grignard reaction of phenylmagnesium bromide and 1-phenylbutanone. **2b** was synthesized through the Wittig method with benzyltriphenylphosphonium bromide and 1-phenylbutanone. **2a** and **2b** olefins were purified by distillation under reduced pressure and were characterized by ^{1}H-NMR.

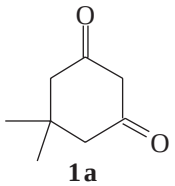
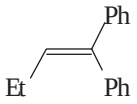
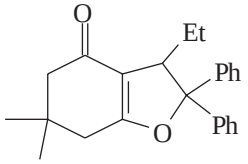
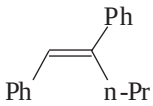
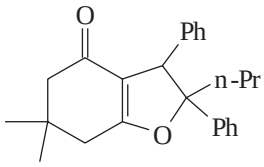
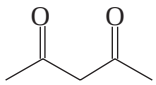
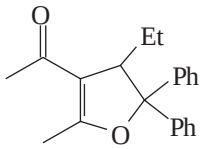
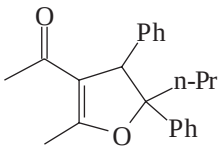
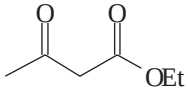
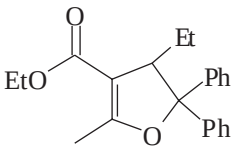
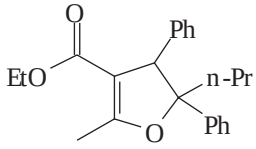
Radical cyclization reactions were performed in 2:1:3 molar ratio (1,3-dicarbonyl:olefin:$Mn(OAc)_3$, respectively) under N_2 atmosphere, at 80 °C, in HOAc. Products were purified by column chromatography or preparative TLC. The results of the reactions of **1a-c** with **2a** and **2b** are given in Table 1.

We performed the radical cyclizations of **1a-c** with 1,1-diphenyl substituted and 1,2-diphenyl substituted olefins comparatively. The treatment of **1a** with 1,1-diphenyl substituted olefin **2a** formed **3a** in a good yield (77%). However, we obtained tetrahydrobenzofuran **3b** in a lower yield (42%) as a result of the treatment of **1a** with 1,2-diphenyl substituted olefin **2b**. The treatments of **1b** and **1c** with **2a** gave **3c** (72%), **3e** (63%) polysubstituted 4,5-dihydrofurans, respectively, and we obtained **3d** and **3f** from the reactions of **1b** and **1c** with **2b** in moderate yields. From these results we conclude that 1,1-diphenyl substituted olefin is more reactive than 1,2-diphenyl substituted olefin; this is the result of the high stability of the intermediate product formed with the addition of α-carbon radical, which was obtained by the treatment of $Mn(OAc)_3$ and 1,3-dicarbonyl. Both of the intermediate products are tertiary radical carbons in the addition reactions to olefins. However, since the tertiary radical forming on 1,1-diphenyl-1-butene **2a** is conjugated with phenyl groups, its stability is higher than that of the tertiary radical forming on **2b**, and more stable intermediate product cyclization forms dihydrofuran in a higher yield.

The results of $Mn(OAc)_3$ mediated radical cyclization of **2a** with **1d-g** are given in Table 2. We obtained tetrahydrobenzofurans **3g** (61%) and **3h** (55%) by the treatment of **1d** and **1e** with **2a**. The best

result was obtained from **1a** in the radical cyclizations of **1a-e** with **2a,** and the reaction activities of the other 1,3-dicarbonyls decreased in the following order: **1b**, **1c**, **1d**, and **1e**.

Table 1. The radical cyclizations of **1a-c** with **2a** and **2b**.

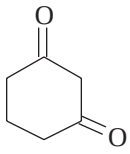
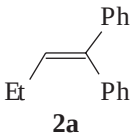
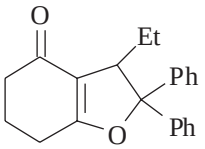
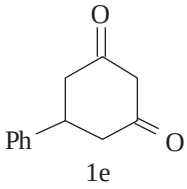
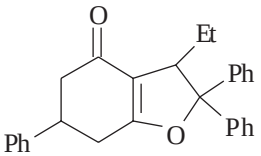
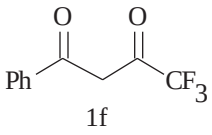
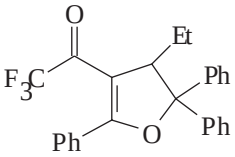
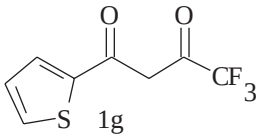
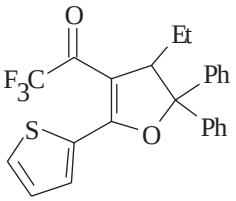
Entry	1,3-dicarbonyl	olefin	dihydrofuran and tetrahydrobenzofuran	product and yield (%)[a]
1	 **1a**	 **2a**		**3a** (77)
2	**1a**	 **2b**		**3b** (42)
3	 **1b**	**2a**		**3c** (72)
4	**1b**	**2b**		**3d** (28)
5	 1c	**2a**		**3e** (63)
6	**1c**	**2b**		**3f** (24)

a: Yield of isolated product based on the olefin

3-Trifluoroacetyl-4,5-dihydrofurans **(3i** and **3j)** were formed by the treatment of **1f** and **1g** with **2a** in good yields. We assume that these results are derived from the enol forms of **1f** and **1g,** which speed up the formation of the Mn(III)-enolate complex of 1,3-dicarbonyls and $Mn(OAc)_3$, in higher ratios (100% and 97%, respectively). In the literature it is reported that **1g** is present in only 1 enol form, whereas **1f** has 2 possible enol forms[31]. Since the cyclization of the adduct intermediate product occurs on the enol form

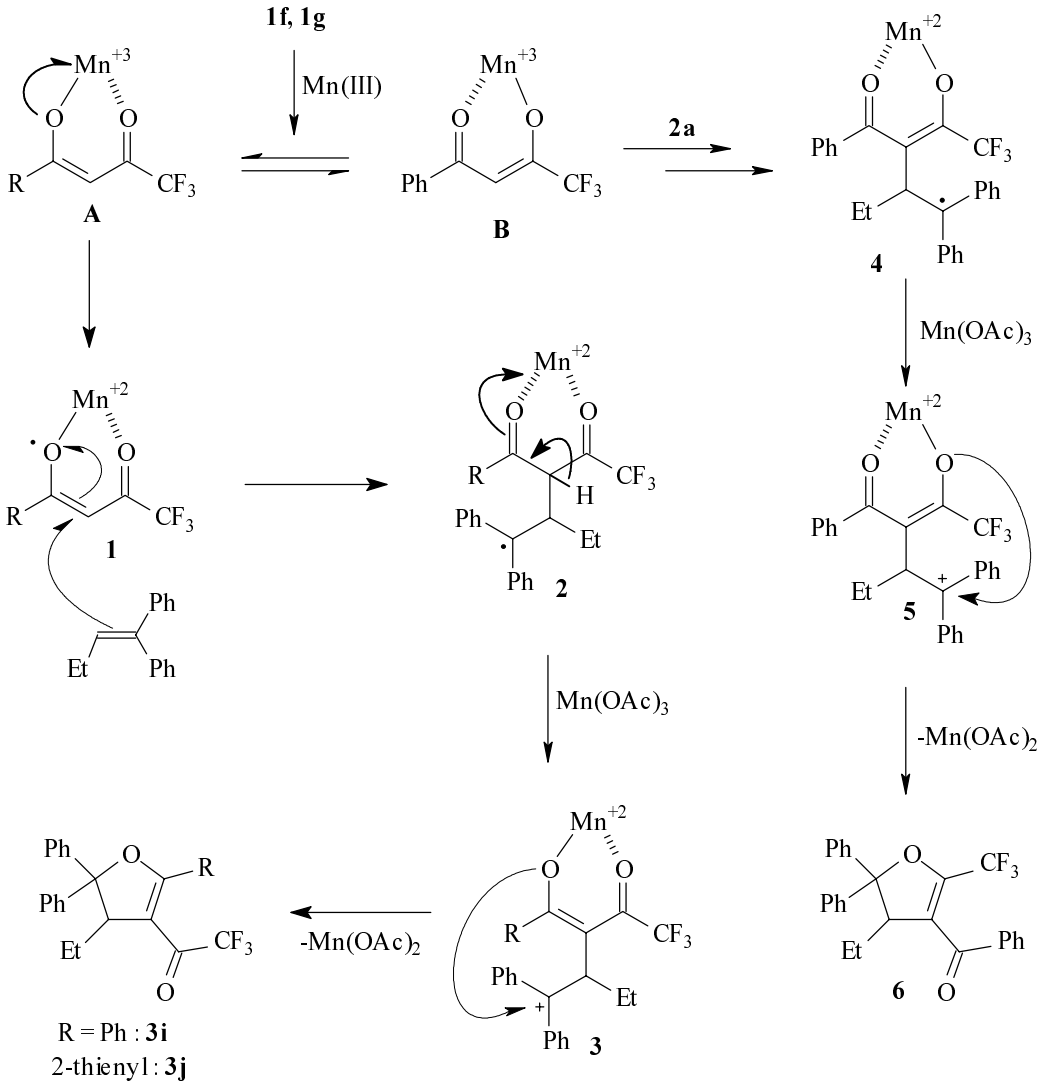
of 1,3-dicarbonyl, 2 possible enol forms of **1f** bring about the formation of 2 different dihydrofurans. The reaction mechanisms of **1f** and **1g** with **2a** are given in the Scheme.

Table 2. Synthesis of tetrahydrobenzofurans and 3-trifluoroacetyl-4,5-dihydrofurans.

Entry	1,3-dicarbonyl	olefin	dihydrofuran and tetrahydrobenzofuran	product and yield (%)[a]
1	 1d	 **2a**		**3g** (61)
2	 1e	**2a**		**3h** (55)
3	 1f	**2a**		**3i** (74)
4	 1g	**2a**		**3j** (78)

a: Yield of isolated product based on the olefin

$Mn(OAc)_3$ forms Mn(III)-enolate complexes (structures **A** and **B**) with the enol forms of **1f** and **1g**. Here while Mn^{+3} is reduced to Mn^{+2}, the oxo-radical forms on the 1,3-dicarbonyl compound. A radical intermediated product **(2)** is obtained in the addition of an electron from alkene to 1,3-dicarbonyl. Mn(II)-enolate complex is formed by removing α-H from this structure and the radical is oxidized to carbocation **3** with the equivalent $Mn(OAc)_3$. The intramolecular cyclization of **2** with oxanion forms 3-trifluoroacetyl-4,5-dihydrofurans (**3i** and **3j**). The intramolecular cyclization of the carbocation intermediate product **5,** which forms when the α-carbon radical **B** obtained from the other enol form of **1f** follows the same steps, gives 2-trifluoromethyl-4,5-dihydrofuran **6.** However, since the chemical shift value in the isolated compound's ^{13}C-NMR spectrum of the neighboring carbon on which -CF_3 is bound is 176.3 ppm (q, J_{C-F} = 34.5 Hz), the -CF_3 group is neighboring the carbonyl. Therefore, in the reaction of **1f** with **2a** 2-trifluoromethyl-4,5-dihydrofuran **6** does not form, which indicates that the tautomeric form of **B** does not appear.



Scheme

Acknowledgments

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