Manganese(III) acetate mediated oxidation of 1-alkyl-1*H*-indole and 9-methyl-9*H*-carbazole derivatives

Ayhan S. Demir[a,*] and Servet Tural[a,b]

[a]*Department of Chemistry, Middle East Technical University*
06531 Ankara, Turkey
[b] *Department of Chemistry, Dicle University*
21280 Diyarbakir, Turkey
E-mail: asdemir@metu.edu.tr

Abstract

Manganese(III) acetate mediated oxidation of 1-alkyl-1*H*-indole and 9-methyl-9*H*-carbazole was studied. 1-Methyl-1*H*-indole gives the 1-acetoxymethyl derivative with good yield. 1-Methyl-2-phenyl-1*H*-indole furnished the oxidation of the methyl group and C-3 of indole to obtain the corresponding acetoxy derivatives. 1-ethyl-2-phenyl derivative only furnished the C-3 acetoxylation product. 1,2-Dimethyl-1*H*-indole furnished oxidation on both of the methyl groups. The major products are 1-methyl-1*H*-indole-2-carbaldehyde and 1-methyl-2-diacetoxymethyl-1*H*-indole. Manganese(III) acetate oxidation of 9-methyl-9*H*-carbazole furnished (9*H*-carbazol-9-yl)methanol in good yield.

Keywords: Indole, carbazole, oxidation, manganese(III) acetate

Introduction

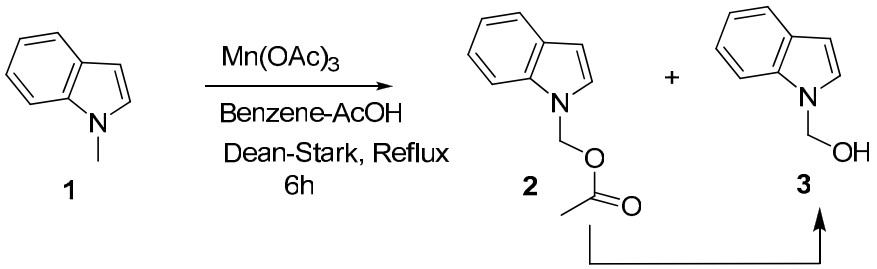
Metal-promoted radical reactions have found widespread use in organic synthesis, in which one of the well-known examples of this application is the manganese(III) acetate mediated reactions.[1] The exciting development in this area is beginning to show its true potential, as evidenced from the application of this methodology in strategy-level bond formation during the synthesis of complex molecules. Manganese(III) acetate dihydrate (abbreviated hereinafter as $Mn(OAc)_3$) mediated free radical reactions have emerged as important synthetic methods for a new bond formation and bond breaking.[2]

$Mn(OAc)_3$ constitutes a mild one-electron oxidant. Direct inner-or outer-sphere one-electron oxidations with $Mn(OAc)_3$ in many cases proceed via the primary formation of an intermediate radical. The fate of this primary radical depends on the nature of the substrate and reaction

conditions. The $Mn(OAc)_3$ mediated selective oxidation of the common functional groups (C=C, C=O, C-O, COOH, etc.) is important in the synthesis of complex natural products[2a,3,4] but the oxidation of amine compounds is not yet well developed. As an example, the oxidation of N-substituted anilines is exemplified by Dewar,[5] and Rindone.[6] At room temperature, in acetic acid or chloroform-acetic acid mixtures, the main product from *N*,*N*-dimethylaniline is *N*-methylacetamide. In a comparative study with Pb(IV) acetate, Co(III) acetate, Tl(III) acetate, and $Mn(OAc)_3$ it was shown that the later oxidant gives cleaner reactions and the highest yields of amides.[6] The oxidation products of 1-methyl-1*H*-indole[7] and 9-methyl-9*H*-carbazole[8] derivatives are interesting intermediates for studying some biological processes, interesting industrial materials, and pharmaceutical compounds.[7] In our ongoing works we have published several papers concerning the $Mn(OAc)_3$-mediated direct oxidation and C-C bond formation reactions.[2a,3a] In this work we are describing $Mn(OAc)_3$ mediated oxidation of 1-methyl-1*H*-indole and 9-methyl-9*H*-carbazole derivatives.

Results and Discussion

According to the improved procedure for the $Mn(OAc)_3$ mediated oxidation reactions[9], commercially available 1-methyl-1*H*-indole is refluxed with $Mn(OAc)_3$ in benzene/AcOH (10:1) under Dean-Stark trap, and the reaction is monitored by TLC. After 6h no more changes to the reaction were observed. After the work up of two definable products, 1-acetoxymethyl-1*H*-indole (**2**) (56%) and (1*H*-indol-1-yl)methanol (**3**)[7a,b] (11% yield) were isolated together with the undefined mixture of the products. The 1-acetoxymethyl-1*H*-indole (**2**) is converted to 1-hydroxymethyl derivative **3** by using the common methods from the literature.[7b] Many attempts were made for increasing the yields but all without any success (Scheme 1).

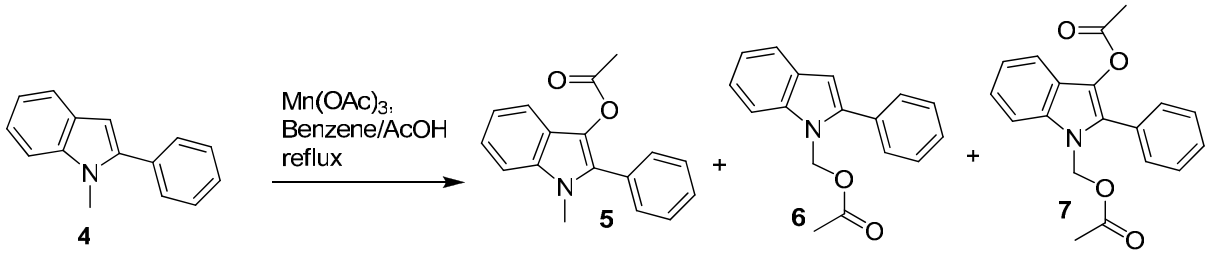


Scheme 1

Under the above-mentioned conditions, indole itself gave no product and was mainly unchanged. Deactivation of the $Mn(OAc)_3$ by free amine (very fast disappearance of the brown color of the reaction) could be the reason for the recovery of the starting material.

The next oxidation reaction was carried out with the substituted derivatives of 1-methyl-1*H*-indole. The reaction of the commercially available 1-methyl-2-phenyl-1*H*-indole (**4**) with

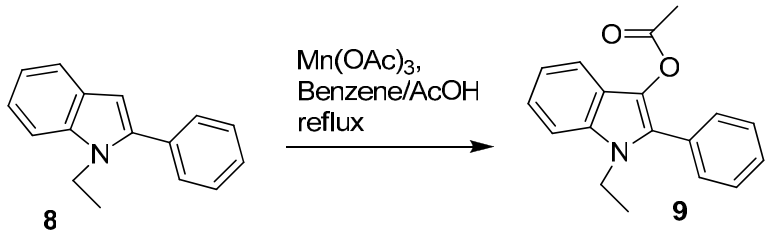
$Mn(OAc)_3$ under the above-mentioned conditions was monitored by TLC. When nearly all of the starting material was consumed, three different products were formed. The products were identified as 1-methyl-2-phenyl-1*H*-indol-3-yl acetate **5** (23%); (2-phenyl-1*H*-indol-1-yl)methyl acetate **6** (18%) and 1-[(acetoxy)methyl]-2-phenyl-1*H*-indol-3-yl acetate **7** (45%) after the separation of the crude mixture by column chromatography (Scheme 2).



Scheme 2

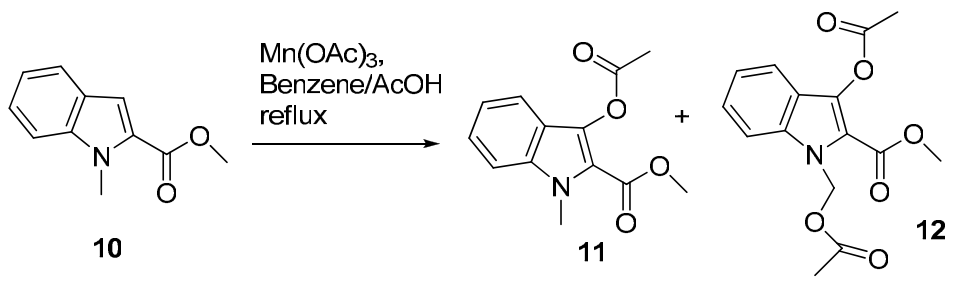
Monitoring the reaction by TLC and NMR showed that the first oxidation took place at C-3 to form **5**, and then at *N*-CH_3 to form **6**. Additional use of Mn(III) acetate along with a prolonged reaction time furnished **7** in 45% yields.

As shown in scheme 3, by using 1-ethyl-2-phenyl-1*H*-indole (**8**) instead of **4**, the C-3 oxidized product 1-ethyl-2-phenyl-1*H*-indol-3yl acetate (**9**) was obtained in a 66% yield. Trace amount of *N*-CH_2 acetoxylation product is also obtained (from crude NMR).



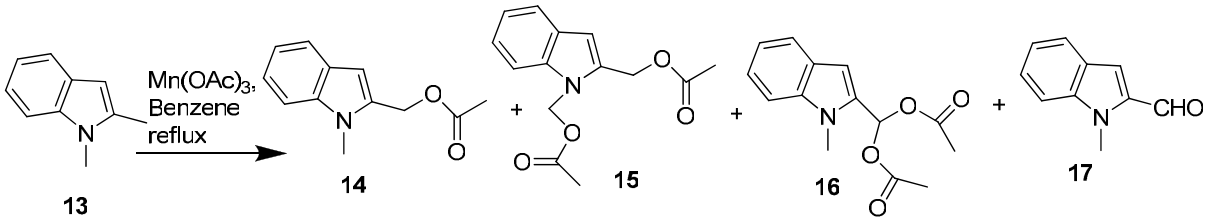
Scheme 3

Similar regioselectivity was found by the oxidation of methyl 1-methyl-1*H*-indole-2-carboxylate (**10**). Accordingly **10** furnished methyl 3-acetoxy-1-methyl-1*H*-indole-2-carboxylate (**11**) and methyl 3-acetoxy-1-(acetoxymethyl)-1*H*-indole-2-carboxylate (**12**) in 44% and 26% yields, respectively (Scheme 4). The products were separated by column chromatography and identified by NMR spectroscopy.



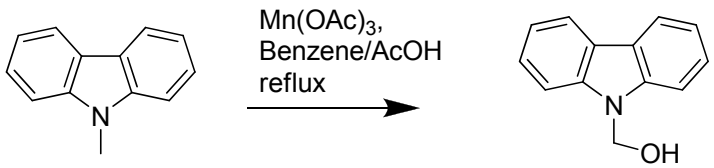
Scheme 4

Next, we conducted the $Mn(OAc)_3$ oxidation study with the commercially available 1,2-dimethyl-1*H*-indole (**13)**. After all of the starting material consumed (7h), four different products were formed. The products were separated by column chromatography and identified as (1-methyl-1*H*-indol-2yl-)methyl acetate (**14**)[7j] (8%), {1-[(acetyloxy)methyl]-1*H*-indol-2-yl}methyl acetate (**15**) (10%), (acetyloxy)(1-methyl-1*H*-indol-2-yl)methyl acetate (**16**) (54%), and 1-methyl-1*H*-indole-2-carbaldehyde (**17**)[7k] (19%)**.** No C-3 oxidation product was observed (Scheme 5). According to the formation sequence of the compounds, first **14** and then **15** finally **17** formed. The formation of **16** from **14** worked faster than other derivatives. This was also proved by the $Mn(OAc)_3$ reaction of the isolated **14**, which gives **16** as major and **17** as minor products.



Scheme 5

The ability of $Mn(OAc)_3$ to oxidize the methyl group was examined by 9-methyl-9*H*-carbazole (**18**). As described by the indole case, **18** was refluxed with $Mn(OAc)_3$ in benzene/AcOH until no more conversion was observed (10h). In addition to several undefined products, (9*H*-carbazol-9-yl)methanol (**19**) was isolated in 67% yield (Scheme 6). **19** is an important compound by the metabolic study of **18** [8], which is synthesized in the literature via the *N*-hydroxymethylation of carbazole with formalin over the basic alumina all under solvent-free conditions with microwave heating.[8d]



18 19

Scheme 6

In conclusion, we studied the manganese (III) acetate oxidation of indole derivatives and found that indole gives no product; 1-methyl-1*H*-indole selectively produces the oxidation of the methyl group in order to form 1-acetoxymethyl-1*H*-indole (**2**) in 56% yield. With 1-methyl-2-phenyl-1*H*-indole (**4**), 1-methyl-2-phenyl-1*H*-indol-3-yl acetate (**5**) (23%); (2-phenyl-1*H*-indol-1-yl)methyl acetate (**6**) (18%) and 1-[(acetoxy)methyl]-2-phenyl-1*H*-indol-3-yl acetate (**7**) (45%). The methyl group has the priority. In the case of the methyl 1-methyl-1*H*-indole-2-carboxylate (**10**) acetoxylation of methyl, the C-3 position was observed. 1,2-dimethyl-1*H*-indole (**13**) furnished the oxidation products in both methyl groups. The major products were (acetyloxy)(1-methyl-1*H*-indol-2-yl)methyl acetate (**16**) (54%) and 1-methyl-1*H*-indole-2-carbaldeyde (**17**) (19%). The $Mn(OAc)_3$ oxidation of 9-methyl-9*H*-carbazole (**18**) furnished (9*H*-carbazol-9-yl)methanol (**19**) in 67% yield.

Experimental Section

General procedure for Mn(III) acetate

A solution of 1 mmol indole or carbazole and 3 mmol $Mn(OAc)_3$ in 11 mL benzene–AcOH (10:1) was stirred under reflux (Dean–Stark apparatus) during which the dark brown color of $Mn(OAc)_3$ disappeared, which was monitored by TLC. After all the starting material was consumed, the reaction mixture was filtered through a pad of silica using ethyl acetate and then washed with brine. The resulting organic phase was dried over $MgSO_4$ and concentrated under vacuum. The crude products were purified by column chromatography using EtOAc–hexane as an eluent.

1-Acetoxymethyl-1*H*-indole (2). (106 mg, 56 %) red oil ; R_f (EtOAc/Hexane 1:10) 0.60.
IR (neat) ν_{max}: 3048, 2926, 1744, 1610, 1463, 1333, 1186, 1014. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.59 (1H, d, *J*= 7.9 Hz, ArH), 7.47 (1H, d, *J*= 8.2 Hz, ArH) , 7.20-7.25 (2H, m, ArH), 7.13 (1H, t, *J*= 7.5 Hz, ArH), 6.50 (1H, d, *J*= 3.2 Hz, ArH), 6.05 (2H, s, O$\underline{CH_2}$), 2.01 (3H, s, Me). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.3, 136.1, 129.1, 128.4, 122.5, 121.1, 120.7, 109.5, 103.7, 68.2, 20.7. Anal. Calcd. for $C_{11}H_{11}NO_2$ (189.21): C, 69.83; H, 5.86; N, 7.40. Found: C, 69.75; H, 5.91; N, 7.33.

1-Methyl-2-phenyl-1*H*-indol-3-yl acetate (5). (62 mg, 23 %) red oil; R_f (EtOAc/Hexane 1:10) 0.55. IR (neat) ν_{max}: 3050, 2936, 1753, 1601, 1455, 1376, 1201. ^{1}H NMR (400 MHz, $CDCl_3$) δ:

7.31-7.41 (6H, m, ArH), 7.24 (1H, d, *J*= 8.4 Hz, ArH) , 7.14 (1H, t, *J*= 7.4 Hz, ArH), 7.05 (1H, t, *J*= 7.4 Hz, ArH) , 3.59 (3H, s, C$\underline{H}_3$N), 2.17 (3H, s, C$\underline{H}_3$COO). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.5, 135.0, 129.9, 129.6, 128.5, 128.2, 126.6, 122.4, 120.7, 120.0, 117.5, 109.7, 103.2, 30.9, 20.5. Anal. Calcd. for $C_{17}H_{15}NO_2$ (265,31): C, 76.96; H, 5.70; N, 5.28. Found: C, 76.82; H, 5.79; N, 5.18.

(2-Phenyl-1*H*-indol-1-yl)methyl acetate (6). (48 mg, 18 %) red oil ;R_f (EtOAc/Hexane 1:10) 0.65. IR (neat) ν $_{max}$: 3053, 2978, 1754, 1606, 1460, 1352, 1207. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34-7.53 (7H, m, ArH), 7.18 (1H, t, *J*= 7.6 Hz, ArH) , 7.12 (1H, t, *J*= 7.4 Hz, ArH), 6.53 (1H, s, ArH), 6.03 (2H, s, OC$\underline{H}_2$), 2.17 (3H, s, Me). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.0, 141.2, 137.7, 131.8, 129.4, 128.6, 128.5, 128.4, 122.7, 121.3, 120.6, 110.1, 104.3, 67.2, 20.9. Anal. Calcd. for $C_{17}H_{15}NO_2$ (265.31): C, 76.96; H, 5.70; N, 5.28. Found: C, 76.79; H, 5.61; N, 5.21.

1-[(Acetoxy)methyl]-2-phenyl-1*H*-indol-3-yl acetate (7). (146 mg, 45 %) red oil; R_f (EtOAc/Hexane 1:10) 0.45. IR (neat) ν $_{max}$: 3054, 2958, 1744, 1602, 1457, 1331, 1222.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.41-7.52 (7H, m, ArH), 7.28 (1H, t, *J*= 7.6 Hz, ArH) , 7.18-7.25 (1H, m, ArH), 6.01 (2H, s, OC$\underline{H}_2$), 2.23 (3H, s, C$\underline{H}_3$COO), 2.03 (3H, s,C$\underline{H}_3$COOCH$_2$N). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.9, 169.1, 134.6, 130.0, 129.7, 128.8, 128.6, 128.5, 128.2, 123.6, 121.8, 121.4, 117.7, 110.4, 66.9, 20.8, 20.4. Anal. Calcd. for $C_{19}H_{17}NO_4$ (323.34): C, 70.58; H, 5.30; N, 4.33. Found: C, 70.39; H, 5.41; N, 4.21.

1-Ethyl-2-phenyl-1*H*-indol-3yl acetate (9). (185mg, 66 %) yellow solid (mp 119-120^{0}C); R_f (EtOAc/Hexane 1:5) 0.50. IR ($CHCl_3$) ν $_{max}$: 3052, 2968, 1740, 1605, 1455, 1335, 1227.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.29-7.41 (7H, m, ArH), 7.15 (1H, t, *J*= 7.6 Hz, ArH) , 7.06 (1H, t, *J*= 7.6 Hz, ArH), 4.03 (2H, q, *J*= 7.2 Hz, C$\underline{H}_2$CH$_3$), 2.14 (3H, s, C$\underline{H}_3$COO), 1.19 (3H, t, *J*= 7.2 Hz, CH$_2$C$\underline{H}_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.7, 133.8, 129.9, 129.8, 129.6, 128.6, 128.4, 126.7, 122.3, 121.0, 119.9, 117.6, 110.0, 38.7, 20.5, 15.3. Anal. Calcd. for $C_{18}H_{17}NO_2$ (279.33): C, 77.40; H, 6.13; N, 5.01. Found: C, 77.38; H, 6.19; N, 4.95.

Methyl 3-acetoxy-1-methyl-1*H*-indole-2-carboxylate (11). (110 mg, 44 %) yellow solid (mp 112-113^{0}C); R_f (EtOAc/Hexane 1:5) 0.25. IR ($CHCl_3$) ν $_{max}$: 3057, 2968, 1740, 1602, 1465. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45 (1H, d, *J*= 8.2 Hz, ArH), 7.28 (2H, d, *J*= 4.2 Hz, ArH) , 7.07 (1H, pent., *J*= 3.8 Hz, ArH), 3.92 (3H,s, O-Me), 3.82 (3H,s, *N*-Me), 2.32 (3H, s, CH_3COO). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.3, 161.4, 136.6, 134.5, 126.0, 120.7, 119.5, 119.0, 117.4, 110.3, 51.7, 31.8, 20.6. Anal. Calcd. for $C_{13}H_{13}NO_4$ (247.25): C, 63.15; H, 5.30; N, 5.67. Found: C, 63.26; H, 5.15; N, 5.78.

Methyl 3-acetoxy-1-(acetoxymethyl)-1*H*-indole-2-carboxylate (12). (80 mg, 26 %) yellow oil; R_f (EtOAc/Hexane 1:10) 0.15. IR (neat) ν $_{max}$: 3051, 2953, 1757,1552, 1473.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45-7.52 (1H, m, ArH), 7.35 (1H, t, *J*= 7.6 Hz, ArH) , 7.13-7.18 (2H, m, ArH), 6.49 (2H, s, OC$\underline{H}_2$N), 3.85 (3H, s, OMe), 2.34 (3H, s, C$\underline{H}_3$COO), 1.97 (3H, s,C$\underline{H}_3$COOCH$_2$N). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.4, 168.7, 160.8, 136.8, 128.2, 127.1122.0, 120.5, 119.2, 116.9, 110.9, 66.8, 51.9, 20.8, 20.6. Anal. Calcd. for $C_{15}H_{15}NO_6$ (305.28): C, 59.01; H, 4.95; N, 4.59. Found: C, 59.17; H, 4.88; N, 4.67.

{1-[(Acetyloxy)methyl]-1*H*-indol-2-yl}methyl acetate (15). (27 mg, 10 %) yellow oil R_f (EtOAc/Hexane 1:5) 0.30. IR (neat) ν $_{max}$: 3056, 2951, 1750, 1552, 1470. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.52 (1H, d, *J*= 7.8 Hz, ArH), 7.44 (1H, d, *J*= 8.2 Hz, ArH) , 7.18-7.23 (1H, m, ArH), 7.11 (1H, t, *J*= 7.6 Hz, ArH), 6.56 (1H, s, ArH), 6.11 (2H, s, OC$\underline{H}_2$N), 5.28 (2H, s, OC$\underline{H}_2$), 2.01 (3H, s, C$\underline{H}_3$COO CH$_2$), 1.97 (3H, s,C$\underline{H}_3$COOCH$_2$N). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.3, 137.6, 133.6, 127.7, 123.4, 122.1, 121.1, 109.9, 106.7, 66.1, 57.7, 20.8, 20.7
Anal. Calcd. for $C_{14}H_{15}NO_4$ (261.27): C, 64.36; H, 5.79; N, 5.36. Found: C, 64.30; H, 5.88; N, 5.39.
(Acetyloxy)(1-methyl-1*H*-indol-2-yl)methyl acetate (16). (142 mg, 54 %) white solid (mp 114-115^{0}C); R_f (EtOAc/Hexane 1:5) 0.37. IR ($CHCl_3$) ν $_{max}$: 3058, 2978, 1757, 1560, 1474, 1370. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.89 (1H, s, C$\underline{H}$(CH$_3$COO)$_2$, 7.54 (1H, d, *J*= 7.9 Hz, ArH), 7.27 (1H, d, *J*= 8.2 Hz, ArH), 7.17-7.21 (1H, m, ArH), 7.04 (1H, t, *J*= 7.4 Hz, ArH), 6.64 (1H, s, ArH), 3.78 (3H,s, *N*-Me), 2.05 (2x3H, s, CH(C$\underline{H}_3$COO)$_2$. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.2, 138.3, 132.7, 126.6, 123.0, 121.5, 120.0, 109.3, 103.3, 84.9, 30.7, 20.7.
Anal. Calcd. for $C_{14}H_{15}NO_4$ (261.27): C, 64.36; H, 5.79; N, 5.36. Found: C, 64.30; H, 5.68; N, 5.43.

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References

1. de Klein, W. J. *In Organic Syntheses by oxidation with metal compounds*, Mijs, W. J.; De Jonge, C. R. H. I. Plenum Press: New York, 1986.
2. (a) Demir, A. S.; Emrullahoglu, M. *Curr. Org. Synth.* **2007**, *4*, 321. (b) Melikyan, G. G. *Synthesis* **1993**, 833. (c) Snider, B. B. *Chem. Rev.* **1996**, *96*, 339. (d) Melikyan, G. G. *Aldrichim. Acta.* **1998**, 50.
3. (a) Demir, A. S.; Jeganathan, A. *Synthesis* **1992**, *235*. (b) Demir, A. S.; Gross, R. S.; Dunlap, N. K.; Hashemi, A. B.; Watt, D. S. *Tetrahedron Lett.* **1986**, *27*, 5567. (c) Dunlap, N. K.; Sabol, M. R.; Watt, D. S. *Tetrahedron Lett.* **1984**, *25,* 5839. (d) Gross, R. S.; Kim, M.; Demir, A. S.; Sabol, M. R.; Dunlap, N. K.; Watt, D. S. *Progress in Terpene Chemistry;* Joulain, D., Ed.; Grasse, 1986; pp 375-382.
4. (a) Demir, A. S.; Saatcioglu, A. *Synth. Commun.***1993**, *23*, 571. (b) Demir, A. S.; Gercek, Z.; Reis, O.; Duygu, A. N.; Arikan, E. *Tetrahedron* **1999**, *55*, 2441. (c) Demir, A. S.; Camkerten,

N.; Akgun, H.; Tanyeli, C.; Mahasneh, A. S.; Watt, D. S. *Synth. Commun.* **1990**, *20*, 2279. (d) Floresca, R.; Kurihara, M.; Watt, D. S.; Demir, A. S. *J. Org. Chem.* **1993**, *58*, 2196.

5. Aratani, T.; Devar, M. J. S. *J. Am. Chem. Soc*. **1966**, *88*, 5479.
6. Rindone, B.; Scolastico, C. *Tetrahedron Lett*. **1974**, *38*, 3379.
7. (a) Deguest, G. B.; Laurent, F.; Corinne, M. F. *Org. Lett*. **2007**, *9*, 1165. (b) Dhanak, D.; Reese, C. B. *J. Chem. Soc., Perkin Trans*. 1; **1986**, 2181. (c) McKillop, A.; Mills, L. S. *Synth. Commun*. **1987**, *17*, 647. (d) Sui, Y.; Liu, L.; Zhao, J –L.; Wang, D.; Chen, Y-J. *Tetrahedron Lett*. **2007**, *48*, 3779. (e) Sapi, J.; Laronze, J.Y. *ARKIVOC* **2004**, *(vii)*, 208. (f) Pore, D. M.; Desai,U. V.; Thopate, T. S.; Wadgaonkar, P. P. *ARKIVOC* **2006**, *(xii)*, 75. (g) Dhanak, D.; Reese, C. B. *J. Chem. Soc. Perkin Trans*. *1* 1986, 2181. (h) Russell, G. A.; Kaupp, G. *J. Am. Chem. Soc*.**1969**, *91*, 3851. (i) Kedderis, G. L.; Rickert, D. E.; Pandey, R.N.; Hollenberg, P.F. *J. Biol. Chem*.**1986**, *261*, 15910. (j) Primault, G.; Legros, J-Y.; Fiaud, J-C. *J. Organomet. Chem.* **2003**, *687*, 353. (k) Merlic, C. A.; You, Y.; McInnes, D. M.; Zechman, A. L.; Miller, M. M.; Deng, Q. *Tetrahedron* **2001**, *57*, 5199.
8. (a) Gorrod, J. W.; Temple, D. J.; Beckett, A. H. *Biochem. J.* **1970**, *117*, 40. (b) Omran, J.; Zander, M. *Chem. Ber*.**1970**, *103*, 3356. (c) Gorrod, J. W.; Temple, D. *J. Xenobiotica* **1976**, *6*, 265. (d) Das, B. P.; Begum, N. A.; Choudhury, D. N.; Banerji, J. *J. Indian Chem. Soc*. **2005**, *82*, 158. (e) Miyata, N.; Kiuchi, H.; Hirobe, M. *Chem. Pharm. Bull*. **1981**, *29*, 1489. (f) Leadini, R.; McNab, H.; Nanni, D.; Parsons, S.; Reed, D.; Tenan, A. G. *J. Chem. Soc., Perkin Trans. 1* **1998**, 1833. (g) Fidesser, E.; Haider, N.; Jbara, R. *ARKIVOC* **2001**, *(v)*, 133. (h) Ivonin, S. P.; Lapandin, A. V. *ARKIVOC* **2005**, (*viii*), 4.
9. (a) Demir, A. S.; Reis, O.; Ozgul-Karaaslan, E. *J. Chem. Soc., Perkin Trans. 1* **2001**, 3042. (b) Demir, A. S.; Reis, O.; Emrullahoglu, M. *J. Org. Chem.* **2003**, *68*, 578. (c) Demir, A.S.; Reis, O.; Emrullahoglu, M. *Tetrahedron* **2002,** *58*, 8055. Demir, A. S.; Reis, O.; Igdir, A. C. *Tetrahedron* **2004**, *60*, 3427.