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One Pot Hydroformylation/Intramolecular Aldol Condensation Reactions of 1-Allyl-2-carbonylpyrroles: A New Entry into Hydroindolizines Synthesis

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ABSTRACT

7-Formyl-5-methyl-5,6-dihydroindolizine and 7-formyl-6-methyl-5,6-dihydroindolizine were obtained via a domino hydroformylation/cyclization/dehydration reactions sequence starting from the corresponding 1-allyl-2-formylpyrroles. An intramolecular aldol condensation between the carbon atom adjacent to the formyl group in the chain of the produced aldehydes and the carbonyl group directly bonded to the pyrrole ring most likely generates the

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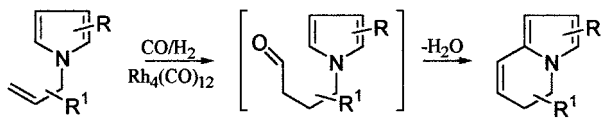
indolizine structure. 7-Formyl-6,8-dimethyl-5,6-dihydroindolizine was similarly synthesized by using 2-acetyl-1-(2-methylprop-2-enyl) pyrrole.

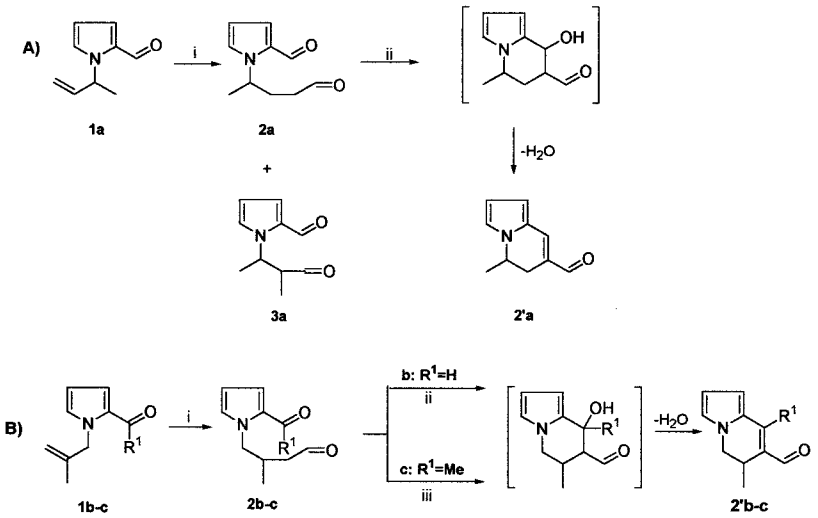
Key Words: Hydroformylation; Catalysis; Aldol condensation; Allylpyrroles; Indolizines.

In the last decade the hydroformylation of olefins has become an attractive synthetic transformation because it can be integrated in tandem or domino reactions sequence, thanks to the versatility of the carbonyl group in the produced aldehydes. Thus, reduction, nucleophilic addition or aldol condensation can occur with enormous synthetic implications.[1] During our studies on the rhodium catalyzed hydroformylation of simple and alkyl substituted 1-allylpyrroles, we found that the formed 4-(pyrrol-1-yl)butanals give rice, under oxo conditions, to 5,6-dihydroindolizines via a tandem intramolecular cyclization/dehydration sequence[2] (Sch. 1).

The 5,6-dihydroindolizines are almost unknown in literature, the synthetic examples being very few and of very different type. Cliff et al. prepared 2-alkyl- or 2-phenyl-substituted 5,6-dihydroindolizines by treatment of the corresponding fully unsaturated structures with various metals.[3] 7-Carboxyethyl-5,6-dihydroindolizine has been synthesized starting from 2-formylpyrrole by using carboethoxycyclopropyltriphenylphosphonium salt as a cycloalkenylation reagent.[4] Katritzky et al. prepared 2-phenyl-5,6-dihydroindolizine via formation of 2-[(benzotriazol-1-yl)methyl]pyrrole as a convenient intermediate.[5] In general hydroindolizines at various degree of unsaturation are an interesting and topical subject occurring in natural products[5,6] and the discovery of general synthetic strategies to these compounds is an important goal for the organic chemist. In order to investigate the potentialities of the hydroformylation based protocol into the synthesis of new 5,6-dihydroindolizines substituted with an electron-withdrawing group on the pyrrole ring, we prepared the 1-allylpyrroles **1a**–**c** bearing a formyl or acetyl group on the C2 pyrrole carbon atom. Under oxo conditions the



Scheme 1.



Scheme 2. (i) $Rh_4(CO)_{12}$, 100 atm CO:H_2 (1:1), 100°C, toluene, 0.5–2 h. (ii) The same conditions as (i), 70 h under N_2 atmosphere, after CO and H_2 removal. (iii) The same conditions as (i), EtONa/EtOH, 5 min, after CO and H_2 removal.

compounds **1a** generates a mixture of the branched (**3a**) and the linear (**2a**) isomers (Sch. 2-**A**) while the vinylidenic substrates **1b** and **1c** exclusively give rise to the pyrrolylbutanals **2b** and **2c** (Sch. 2-**B**). All the formed linear aldehydes **2a–c** selectively gave the corresponding 5,6-dihydroindolizines **2′a–c** characterized by the presence of a formyl group on C7 carbon atom, via a one pot hydroformylation/intramolecular aldol condensation sequence (Sch. 2).

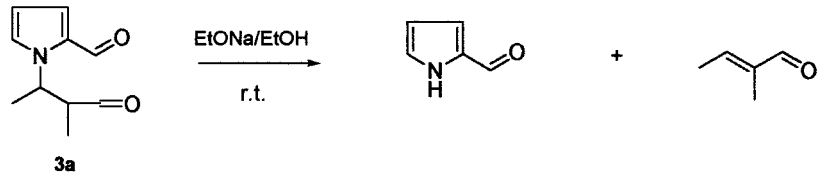
The 2-substituted 1-allylpyrroles **1a–c** were easily prepared from 2-formylpyrrole and 2-acetylpyrrole respectively by treatment with 3-chlorobut-1-ene and 3-chloro-2-methylprop-1-ene respectively under phase transfer conditions. The hydroformylation of the substrates **1a–c** was carried out in the presence of $Rh_4(CO)_{12}$ as catalyst precursor.[7,8]

After 0.5 h at 100°C, the starting olefin **1a** was completely converted into the isomeric dialdehydes 4-(2-formylpyrrol-1-yl)pentanal (**2a**) and 2-methyl-3-(2-formylpyrrol-1-yl)butanal (**3a**) (**2a**/**3a** = 68/32; **2a** + **3a** = 98%) (Sch. 2-**A**). A very low amount of 5-methyl-7-formyl-5,6-dihydroindolizine (**2′a**) (< 2%) was also found. For longer reaction times, an increase of the dihydroindolizine **2′a** was observed together with the reduction of the carbonyl group of both branched and linear dialdehydes **3a** and **2a** to the corresponding hydroxyl groups (GC-MS control). When, at complete pyrrolylolefin conversion, the CO/H_2 gas mixture

was removed and the autoclave was heated at 100°C for additional 70 h, the dialdehyde **2a** disappeared and **2′a** was formed (Sch. 2-**A**), the branched dialdehyde **3a** staying unreacted during all reaction time. Under the same hydroformylation conditions as for **1a**, the vinylidenic olefin 2-formyl-1-(2-methylprop-2-enyl)pyrrole (**1b**) was selectively converted into 7-formyl-6-methyl-5,6-dihydroindolizine (**2′b**) (Sch. 2-**B**) via formation of the sole aldehyde 3-methyl-4-(2-formylpyrrol-1-yl)butanal (**2b**). 2-Acetyl-1-(2-methylprop-2-enyl)pyrrole (**1c**) was submitted to the same hydroformylation conditions adopted for 2-formylderivatives **1a**–**b**; the aldehyde 3-methyl-4-(2-acetylpyrrol-1-yl)butanal (**2c**) was obtained as the exclusive product (Sch. 2-**A**). This compound does not cyclize under the above conditions even for long heating time. However by treating the crude oxo-mixture with EtONa/EtOH for few minutes, the corresponding 7-formyl-6,8-dimethyl-5,6-dihydroindolizine (**2′c**) was selectively obtained (Sch. 2-**A**). Under these last experimental conditions the dihydroindolizines **2′a** and **2′b** were also obtained from **2a** and **2b** respectively. The above findings suggest that the indolizine structures **2′a**–**c** come from the dialdehydes **2a**–**c** likely via an intramolecular aldol addition between the carbon adjacent to the formyl group in the chain and the carbonyl group directly bonded to pyrrole ring. Then a bicyclic hydroxyaldehyde should form (Sch. **2**), which very easily undergoes water elimination to give a double bond conjugated with both pyrrole and formyl group. Whereas in the first two cases a rhodium carbonyl species likely plays an annulation-catalyst role, although at very low rate, in the last one this species is not sufficiently active to overcome the electron-donor effect of the methyl group bonded to the carbonyl in position two of the pyrrole ring. It is to note that, unlike what observed by us for 1-allylpyrroles characterized by an unsubstituted pyrrole ring or an alkyl substituted one,[2] the annulation of **2a**–**c** on C5 pyrrole carbon atom does not occur, the above described aldol condensation being the exclusive process. In fact no traces of 3-formyl or 3-acetyl-5,6-dihydroindolizines, isomers of **2′a**–**c**, were detected. Because of the presence of an electron-withdrawing group on the pyrrole C2 carbon atom, the C5 carbon atom is not nucleophilic enough to bear the electrophilic attack of the carbonyl moiety.

It is to note that under aldol condensation the branched aldehydes **3a** is not stable, giving rise to the corresponding 2-formylpyrrole and the unsaturated aldehydes 2-methylbut-2-enal respectively via a *N*-dealkylation promoted by the basic conditions adopted (Sch. 3).

It is to remark that this process makes the 7-formyl-5-methyl-5,6-dihydroindolizine isolation via chromatographic elution very easy thanks to the very different r_f of the involved compounds.



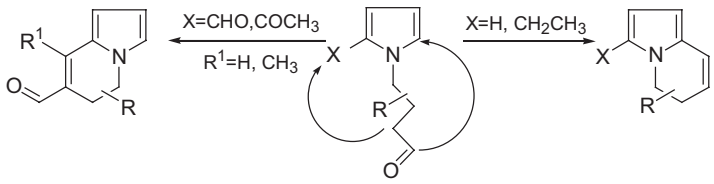
Scheme 3.

The formyl dihydroindolizines **2′a**–**c** are new compounds and were isolated and characterized by ^{1}H and ^{13}C NMR spectroscopy, GC-MS, and elemental analysis. They are stable enough to be handled easily at room temperature without any decomposition and can be stored at 0°C for long periods. All the newly linear aldehydes obtained also were isolated and characterized, these diacyl compounds being much more stable of the analogous ones coming from the previously investigated hydroformylation of 1-allylpyrroles substituted with electrondonor groups.[2]

In conclusion the results reported here constitute the first example of indolizine skeleton building from 1-allyl-2-carbonylpyrroles via a selective tandem hydroformylation/aldol condensation reactions sequence. In light of these findings as well as of our previous data on hydroformylation/cyclodehydration of 1-allylpyrroles,[2] we would like to stress that the 4-(pyrrol-1-yl)butanals, until now unknown in literature, are easily available via oxo from easily available 1-allylpyrroles and constitute versatile and convenient intermediates for indolizine moiety synthesis (Sch. 4).

EXPERIMENTAL

***N*-Allylation of 2-carbonylpyrroles. General procedure. Preparation of 2-formyl-1-(2-methylprop-2-enyl)pyrrole (1b).** To a stirred mixture of 50%



Scheme 4.

aqueous NaOH (20 mL) solution, 2-formylpyrrole (3.0 g, 31.6 mmol) and tetrabutylammonium hydrogen sulfate (1.2 g, 3.5 mmol) in toluene (50 mL), was added 3-chloro-2-methylprop-1-ene (3.3 mL, 3.0 g, 32.9 mmol). The mixture was then heated at 70°C, with vigorous stirring, for 1 h. The cooled mixture was diluted with water and extracted with ether. The combined organic extracts were washed with water, dried (Na_2SO_4), and evaporated in vacuo. The residue was submitted under distillation at reduced pressure (b.p. 30°C, $P = 0.2$ mm Hg) giving 4.2 g (28.2 mmol; 85% yield) of **1b** as a colorless oil. ^{1}H NMR (200 MHz, $CDCl_3$) δ 9.57 (s, 1H), 6.94 (d, $J = 3.3$ Hz, 2H), 6.26 (t, $J = 3.3$ Hz, 1H), 4.90 (s, 2H), 4.84 (s, 1H), 4.49 (s, 1H), 1.75 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 179.5, 142.0, 131.7, 131.4, 124.3, 111.9, 109.7, 53.8, 19.8. MS *m/e* 149 (M^+, 55), 132 (100), 120 (43), 94 (62). Anal. calcd. for $C_9H_{11}NO$: C, 72.48; H, 7.38; N, 9.40. Found: C, 72.39; H, 7.30; N, 9.45.

2-Formyl-1-(1-methylprop-2-enyl)pyrrole (1a). (75% yield), as a colorless oil. B.p. 28°C, $P = 0.2$ mmHg. ^{1}H NMR (200 MHz, $CDCl_3$) δ 9.53 (s, 1H), 7.09 (m, 1H), 6.93 (dd, $J = 1.67$; 3.99 Hz, 1H), 6.25 (dd, $J = 2.67$; 3.93 Hz, 1H), 6.10–5.89 (m, 2H), 5.19–5.00 (dd, $J = 19.8$; 25.7 Hz, 2H), 1.52 (d, $J = 6.8$ Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 179.0, 131.7, 138.3, 127.8, 125.0, 115.8, 110.0, 54.0, 20.5. MS *m/e* 149 (M^+, 30), 148 (30), 132 (63), 120 (20), 106 (26), 94 (100). Anal. calcd. for $C_9H_{11}NO$: C, 72.48; H, 7.38; N, 9.40. Found: C, 72.40; H, 7.31; N, 9.48.

2-Acetyl-1-(2-methylprop-2-enyl)pyrrole (1c). (80% yield), as a yellow oil (SiO_2; hexane/EtOAc = 3:1); ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.97 (dd, $J = 1.7$; 4.0 Hz, 1H), 6.85 (t, $J = 2.1$ Hz, 1H), 6.17 (dd, $J = 3.8$; 4.0 Hz, 1H), 4.90 (s, 2H), 4.79 (m, 1H), 4.37 (m, 1H), 2.45 (s, 3H), 1.72 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 188.0, 142.5, 130.2, 130.1, 119.8, 110.3, 108.0, 54.1, 27.0, 19.8. MS *m/e* 163 (M^+, 30), 148 (100), 120 (63), 106 (25), 94 (44), 80 (35). Anal. calcd. for $C_{10}H_{13}NO$: C, 73.62; H, 7.98; N, 8.60. Found: C, 73.55; H, 7.92; N, 8.65.

Hydroformylation of 1-allylpyrroles 1a–c. General procedure. (i) Preparation of 3-methyl-4-(2-formylpyrrol-1-yl)butanal (2b). A solution of 2-formyl-1-(2-methylprop-2-enyl)pyrrole (**1b**) (0.50 g, 3.35 mmol) and $Rh_4(CO)_{12}$ (6.3 mg, substrate/Rh = 100/1) in toluene (6 mL) was introduced by suction into an evacuated 25 mL stainless steel reaction vessel. Carbon monoxide was introduced, the autoclave was then rocked, heated to 100°C and hydrogen was rapidly introduced to 100 atm ($CO/H_2 = 1/1$) total pressure. After 2 h at 100°C the conversion was complete and the CO/H_2 gas mixture was removed. From the reaction mixture 3-methyl-4-(2-formylpyrrol-1-yl)butanal (**2b**) was obtained

(0.42 g, 2.35 mmol, 70% yield) as a colorless oil by column chromatography (SiO_2; hexane/EtOAc = 1:1); ^{1}H NMR (200 MHz, $CDCl_3$) δ 9.65 (t, $J = 1.6$ Hz, 1H), 9.54 (s, 1H), 6.97–6.91 (m, 2H), 6.25 (m, 1H), 4.25 (d, $J = 7.8$ Hz, 2H), 2.70–2.15 (m, 3H), 0.97 (d, $J = 6.7$ Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 201.1, 179.4, 131.8, 131.6, 125.2, 109.8, 53.9, 47.7, 30.3, 17.9. MS *m/e* 179 (M^+, 4), 161 (52), 150 (100), 132 (25), 118 (41), 117 (39), 108 (40), 94 (17), 80 (46). Anal. calcd. for $C_{10}H_{13}NO_2$: C, 67.04; H, 7.26; N, 7.82. Found: C, 66.95; H, 7.31; N, 7.88.

4-(2-Formylpyrrol-1-yl)pentanal (2a). Isolated as a colorless oil (SiO_2; hexane/EtOAc = 1:1) (60% yield) from 0.5 h time hydroformylation mixture; ^{1}H NMR (200 MHz, $CDCl_3$) δ 9.65 (t, $J = 1.2$ Hz, 1H), 9.52 (d, $J = 1.1$ Hz, 1H), 7.14 (m, 1H), 6.91 (dd, $J = 1.7$; 4.0 Hz, 1H), 6.29 (dd, $J = 2.7$; 4.0 Hz, 1H), 5.4 (m, 1H), 2.54–2.27 (m, 2H), 2.12–2.0 (m, 2H), 1.48 (d, $J = 6.8$ Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 200.7, 179.5, 131.8, 127.0, 125.3, 110.4, 52.1, 40.3, 30.0, 21.5. MS *m/e* 179 (M^+, 2), 150 (52), 122 (26), 94 (100). Anal. calcd. for $C_{10}H_{13}NO_2$: C, 67.04; H, 7.26; N, 7.82. Found: C, 67.10; H, 7.20; N, 7.85.

3-Methyl-4-(2-acetylpyrrol-1-yl)butanal (2c). Isolated as a colorless oil (SiO_2; hexane/EtOAc = 4:1) (75% yield) from 2.0 h time hydroformylation mixture; ^{1}H NMR (200 MHz, $CDCl_3$) δ 9.62 (t, $J = 2.0$ Hz, 1H), 6.98 (dd, $J = 4.1$; 1.7 Hz, 1H), 6.83 (t, $J = 2.1$ Hz, 1H), 6.13 (dd, $J = 4.1$; 2.5 Hz, 1H), 4.22 (d, $J = 7.0$ Hz, 2H), 2.58 (m, 1H), 2.43 (s, 3H), 2.50–2.15 (m, 2H), 0.95 (d, $J = 6.3$ Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 201.8, 188.2, 130.9, 130.2, 121.3, 107.5, 54.8, 47.9, 30.0, 27.1, 17.3. MS *m/e* 193 (M^+, 2), 150 (100), 122 (35), 108 (15), 95 (27), 80 (32). Anal. calcd. for $C_{11}H_{15}NO_2$: C, 68.39; H, 7.77; N, 7.25. Found: C, 68.30; H, 7.71; N, 7.31.

(ii) Preparation of 7-formyl-6-methyl-5,6-dihydroindolizine (2′b). After CO and H_2 removal, the crude reaction mixture coming from (**i**) was heated at 100°C for additional 70 h: the formation of a single product was observed. From the reaction mixture 7-formyl-6-methyl-5,6-dihydroindolizine (**2′b**) was obtained as a yellow oil (SiO_2; hexane/EtOAc = 1:1) (0.40 g, 75% yield); ^{1}H NMR (200 MHz, $CDCl_3$) δ 9.47 (s, 1H), 7.15 (s, 1H), 6.82 (s, 1H), 6.51 (m, 1H), 6.27 (dd, $J = 2.6$, 1.6 Hz, 1H), 3.98 (dd, $J = 12.6$; 5.0 Hz, 1H), 3.86 (dd, $J = 12.6$; 1.3 Hz, 1H), 3.20 (m, 1H), 1.05 (d, $J = 6.84$ Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 190.6, 135.2, 135.1, 127.6, 125.9, 113.3, 110.7, 50.4, 26.5, 17.9. MS *m/e* 161 (M^+, 100), 146 (47), 132 (19), 118 (61), 117 (93), 90 (18). Anal. calcd. for $C_{10}H_{11}NO$: C, 74.53; H, 6.83; N, 8.70. Found: C, 74.15; H, 6.58; N, 8.80.

7-Formyl-5-methyl-5,6-dihydroindolizine (2′a). Prepared as a red oil according to the general procedure starting from **1a**. The product was eluted with SiO_2; hexane/EtOAc = 4:1, (60% yield); ^{1}H NMR (200 MHz, $CDCl_3$) δ 9.54 (s, 1H), 7.22 (s, 1H), 6.91 (bs, 1H), 6.53

(dd, $J = 3.7$; 1.3 Hz, 1H), 6.27 (dd, $J = 3.7$; 2.7 Hz, 1H), 4.18 (m, 1H), 2.86 (dd, $J = 16.7$; 5.7 Hz, 1H), 2.42 (dd, $J = 16.7$; 1.2 Hz, 1H), 1.44 (d, $J = 6.3$ Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 191.2, 135.9, 128.7, 127.9, 123.4, 114.5, 110.8, 45.0, 27.9, 20.0. MS *m/e* 161 (M^+, 95), 146 (55), 132 (48), 118 (80), 117 (100), 104 (15), 91 (25). Anal. calcd. for $C_{10}H_{11}NO$: C, 74.53; H, 6.83; N, 8.70. Found: C, 74.20; H, 6.69; N, 8.85.

7-Formyl-6,8-dimethyl-5,6-dihydroindolizine (2′c). Prepared as a red oil according to the general procedure starting from **1c**. The product was eluted with SiO_2; hexane/EtOAc = 2:1, (75% yield); ^{1}H NMR (200 MHz, $CDCl_3$) δ 10.89 (s, 1H), 6.81 (bs, 1H), 6.62 (dd, $J = 3.8$; 1.3 Hz, 1H), 6.28 (dd, $J = 3.8$; 2.6 Hz, 1H), 3.93 (dd, $J = 12.3$; 4.6 Hz, 1H), 3.81 (d, $J = 12.3$ Hz, 1H), 3.25 (m, 1H), 2.42 (s, 3H), 0.98 (d, $J = 7.0$ Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 188.3, 141.6, 130.1, 129.7, 125.7, 111.5, 110.0, 50.2, 29.6, 26.4, 18.0. MS *m/e* 160 ($M^+ - 15$, 80), 146 (20), 132 (55), 131 (38), 130 (26), 117 (36). Anal. calcd. for $C_{11}H_{13}NO$: C, 75.43; H, 7.43; N, 8.00. Found: C, 75.13; H, 7.20; N, 8.12.

2-Methyl-3-(2-formylpyrrol-1-yl)butanal (3a). Isolated as a colorless oil (SiO_2; hexane/EtOAc = 1:1) from 0.5 h time hydroformylation mixture (the diastereomeric ratio, A/B = 40/60, being in favor of the isomer with higher retention time). ^{1}H NMR (200 MHz, $CDCl_3$) isomer B δ 9.66 (d, $J = 2.2$ Hz, 1H), 9.53 (bs, 1H), 7.18–7.10 (m, 1H), 6.98–6.91 (m, 1H), 6.34–6.25 (m, 1H), 5.74 (q, $J = 7.0$ Hz, 1H), 3.05–2.75 (m, 1H), 1.53 (d, $J = 7.0$ Hz, 3H), 0.95 (d, $J = 7.0$ Hz, 3H); ^{1}H NMR (200 MHz, $CDCl_3$) isomer A δ 9.61 (d, $J = 1.8$ Hz, 1H), 9.53 (bs, 1H), 7.18–7.10 (m, 1H), 6.98–6.91 (m, 1H), 6.34–6.25 (m, 1H), 5.57 (q, $J = 7.4$ Hz, 1H), 3.05–2.75 (m, 1H), 1.47 (d, $J = 7.2$ Hz, 3H), 1.07 (d, $J = 7.1$ Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) isomer A δ 202.0, 179.5, 128.2, 126.1, 110.3, 53.2, 52.5, 16.9, 9.1; ^{13}C NMR (50 MHz, $CDCl_3$) isomer B δ 202.1, 179.6, 128.3, 125.8, 110.4, 52.1, 52.9, 19.0, 10.7. MS *m/e* 151 ($M^+ - 28$, 29), 122 (22), 94 (100).

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REFERENCES

1. Eilbracht, P.; Bärfacker, L.; Buss, C.; Hollmann, C.; Kitsos-Rzychon, B.E.; Kranemann, C.L.; Rische, T.; Roggenbuck, R.; Schmidt, A. Chem. Rev. **1999**, *99*, 3329 and references cited therein.

2. (a) Lazzaroni, R.; Settambolo, R.; Caiazzo, A.; Pontorno, L. J. Organomet. Chem. **2000**, *601*, 320; (b) Settambolo, R.; Caiazzo, A.; Lazzaroni, R. Tetrahedron Lett. **2001**, *42*, 4045.
3. Cliff, G.R.; Jones, G.; Stanyer, J. J. Chem. Soc. C **1971**, 3426.
4. Fuchs, P.L. J. Am. Chem. Soc. **1974**, *96*, 1607.
5. Katritzky, A.R.; Fali, C.N.; Li, J. J. Org. Chem. **1997**, *62*, 4148.
6. (a) Daly, J.W.; Garraffo, H.M.; Spande, T.F. In *Alkaloids: Chemical and Biological Perspectives*; Pelletier, S.W. Ed.; Pergamon: New York, 1999; Vol. 13. Chapter 1, pp. 1–161; (b) Sayah, B.; Pelloux-Léon, N.; Milet, A.; Pardillos-Guindet, J.; Vallée, J. J. Org. Chem. **2001**, *66*, 2522.
7. McCleverty, J.A.; Wilkinson, G. Inorg. Synth. **1966**, *8*, 211.
8. Cattermole, P.E.; Osborne, G.A. Inorg. Synth. **1977**, *17*, 115.

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