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Eco-Friendly Chemical Routes for Transformation of Terpenoids in Green Solvents to Effective Additive Materials by using Ruthenium Complexes

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New terpenoids were prepared by ruthenium catalyzed cross-metathesis of terpenes (**1a-c**) with methyl acrylate (**2**) under environmental friendly conditions in glycerol. The new terpenoids compounds were fully characterized by FT-IR, ^{1}H, ^{13}C spectra and by HRMS analysis. Furthermore, the synthesis of some diazecin-3-ones is described *via* reaction of compound **4** with hydrazine hydrate or phenyl hydrazine in glycerol at reflux. The new compounds **5** were characterized by FT-IR, HRMS analysis and NMR spectral data.

Keywords: Terpenoids, Ruthenium, Cross-metathesis, Diazecin-3-ones.

INTRODUCTION

Monoterpenes are highly hydrophobic substances present in essential oils. They represent the most diverse class of natural products found in plants, with tens of thousands of reported structures. They are the substances derived from isoprene (2-methyl-1,3-butadiene) and originated by the attachment of two or more isoprene molecules. They cover a wide spectrum of biological effects actions of great importance in many different areas from food chemistry and chemical ecology to pharmacology and pharmaceutics[1-7].

The transformation of terpenes using efficient and selective methods is also of great interest for the preparation of new molecules of potential utility in the perfume or medicinal industry[8]. A straight forward route for the modification of terpenes is constituted by direct transformation of terpenes by cross-metathesis reactions. Direct transformations of several terpenes by cross-metathesis with methyl acrylate were presented in this paper. We performed these reactions in $CHCl_3$, xylene and glycerol solvents that were recently shown to be a green alternative to the undesirable dichloromethane or toluene in ruthenium catalyzed olefin metathesis transformations[9-11] or under solvent free conditions.

EXPERIMENTAL

All the reactions were conducted under an inert atmosphere of argon using standard Schlenck tube techniques. Solvents were dried by distillation prior to their use. $CHCl_3$, was dried over CaH_2, xylene over Na. All terpenoids were purchased from Acros Organics and were used as they were received. linalol (93 %), geraniol (95 %), citral (95 %, *cis* + 5 % *trans* mixture). Methyl acrylate was purchased from Acros Organics and stored under argon over 3 Å molecular sieves prior to their use. The key reactions were double checked. Elemental analyses were performed on Perkin-Elmer 2400 elemental analyzer and the values found were within ± 0.3 % of the theoretical values. ^{1}H NMR and ^{13}C NMR spectra were carried on a Varian Gemini 200 (300 MHz) spectrometer using TMS as internal standard (δ = 0 ppm) and were recorded in $CDCl_3$ or DMSO-d_6 solutions spectra were recorded on a Perkin-Elmer 398 spectrophotometer.

General procedure for the cross-metathesis reactions with methyl acrylate: A dry and degassed Schlenck tube was loaded under argon with 100 mg of terpenoid (about 0.65 mmol), 8.0-8.3 mg of Hoveyda catalyst A (about 13.10-3 mmol, 2 mol %), 115-118 µL of methyl acrylate (about 1.3 mmol, 2 equiv.) and 2 mL of solvent. The reaction was stirred under the mentioned conditions. After solvent evaporation, the products were purified by column chromatography on silica gel using of EtOAc/petroleum ether mixtures.

Compound 2: Yield = 73 % (0.16 g), IR (KBr, ν_{max}, cm^{-1}): 3295 (OH), 1656 (C=C), 1685 (C = O), ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 1.36 (s, 3H, CCH_3), 1.68-1.76 (m, 2H, H5), 2.13-2.30 (m, 2H, H6), 3.74 (s, 3H, CO_2CH_3), 3.71 (s, 3H, CO_2CH_3), 5.81 (d, 1H, *J* = 15, 4 Hz, H8), 6.05 (d, 1H, *J* = 15, 4 Hz, H7), 6.94 (m, 2H, H1,8). ^{13}C NMR (50 MHz, $CDCl_3$, ppm): δ = 27.1 (CH_3), 28.5 (C6), 40.2 (C5), 51.9 (CO_2CH_3),

52.1 (CO_2CH_3), 73 (C4), 119.3 (C8), 121.5 (C7), 149.2 (C2), 154 (C3), 167.4 (C1), 167.5 (C9). HRMS (ESI): $[M+Na]^+$ calculated for ($C_{12}H_{18}O_5Na$) = 265.1153. Measured: 265.1152. Anal. calcd. for $C_{12}H_{18}O_5$: C, 59.43; H, 7.42. Found: C, 59.23; H, 7.50.

Compound 3: Yield = 75 % (0.153 g), IR (KBr, ν_{max}, cm^{-1}): 3310 (OH), 1659 (C=C), 1689 (C=O), ^1H NMR (300 MHz, $CDCl_3$, ppm): δ = 0.91 (s, 3H, CH_3), 1.35-1.64 (m, 4H, $H_{4,5}$), 3.68 (t, 1H, OH, J_{OH}, H8 = 3.6 Hz), 3.72 (s, 3H, CO_2CH_3), 5.83 (d, 1H, *J* = 15.6Hz, H_2), 6.94-7.02 (m, 1H, H_3), 5.4 (m, 1H, H_7), 6.8 (m, 2H, H_8).^{13}C NMR (50 MHz, $CDCl_3$, ppm): δ = 19.6 (CH_3), 30.1 (C_4), 35.6 (C_5), 138.5 (C_6),40.0 (C_7), 51.8 ($CO_2\underline{C}H_3$), 61.2 (C8), 121.2 (C_7), 122.1 (C_2), 150.1 (C_3), 167.6 (C_1). HRMS (ESI): $[M+Na]^+$ calculated for ($C_{10}H_{16}O_3Na$) = 207.1154. Measured: 207.1153. Anal. calcd. for $C_{10}H_{16}O_3$: C, 58.76; H, 7.83. Found: C, 58.60; H, 7.50.

Compound 4: Yield = 76 % (0.140g), IR (KBr, ν_{max}, cm^{-1}): 1659 (C = C), 1684 (C=O),^1H NMR (300 MHz, $CDCl_3$, ppm): 1.97- 2.16 (2s, 3H, CH_3, *cis* + *trans*), 2.33-2.50 and 2.68-2.72(m, 4H, CH_2 *cis* + *trans*), 3.71 (s, 3H, OCH_3), 5.80-5.89 (m, 2H, $H_{2,3}$), 6.86 (m, 1H, H7), 9.91, 9.98 (2d, 8Hz, 1H, CHO *cis* + *trans*). ^{13}C NMR (50 MHz, $CDCl_3$, ppm): 18.0, 25.1 (CH_3, *cis* + *trans*),* 29.8, 31.4 (CH_2, *cis* + *trans*), 38.9 (CH_2), 51.9 (OCH_3), 122.4, 122.7 (CH, *cis* + *trans*), 128.0, 129.3 (CH, *cis* + *trans*), 147.0, 147.3 (CH, *cis* + *trans*), 162.0, 162.2 (CO_2Me, *cis* + *trans*), 166.9, 167.0 (C, *cis* + *trans*), 190.6, 191.4 (CHO, *cis* + *trans*). HRMS (ESI): $[M+Na]^+$ calculated for ($C_{10}H_{14}O_3Na$) = 205.1153. Measured: 205.1152. Anal. calcd for $C_{10}H_{14}O_3$: C, 65.85; H, 7.68. Found: C, 65.80; H, 7.60.

Synthesis of diazecin-3-ones (5): A mixture of compound **4** and hydrazine hydrate or phenylhydrazine in 20 mL of glycerol was stirred at reflux under nitrogen atmosphere for a further 24 h. The precipitate **5** was filtered, washed with glycerol The product is soluble in DMSO.

Compound 5a (R=H): Yield = 75 % (0.3 g), IR (KBr, ν_{max}, cm^{-1}): 3300 (NH), 1662(C = N), 1685 (C = O),^1H NMR (300 MHz, DMSO-d_6, ppm) δ = 7.50 (s, 1H, HC = N), 5.8 (s, 1H, H_1), 5.6 (s, 1H, H_2), 2.13 (t, 2H, $\underline{H}_7$, $JH_{6,7}$ = 3.4 Hz), 2.13 (t, 2H, $\underline{H}_6$, $JH_{6,7}$ = 3.4 Hz), 2.1 (s, 1H, HC=C), 4.5 (s, 1H, C=CH), 1.7 (s, 1H, $C\underline{H}_3$), 7.1 (s, 1H, NH), ^{13}C NMR (50 MHz, DMSO-d_6, ppm) δ = 24.5 ($\underline{CH}_2CH_2$), 33.2 ($CH_2\underline{CH}_2$), 167.5 ($\underline{C}O$), 154.6 (C=N), 143.5 ($\underline{CH}$=CHCO), 122.6 (CH = $\underline{CH}$CO), 147.4 ($\underline{CH}$=CHC=N), 154.1 (CH=$\underline{CH}$C=N), 23.4 ($\underline{CH}_3$). $[M+Na]^+$ calculated for ($C_9H_{12}ONa$) = 159.1153. Measured: 159.1152. Anal. calcd. for $C_9H_{12}N_2O$: C, 65.77; H, 7.30; N, 17.05. Found: C, 65.60; H, 7.20; N, 16.1

Compound 5b (R = Ph): Yield = 73 % (0.25 g), IR (KBr, ν_{max}, cm^{-1}): 1665 (C=N), 1689 (C=O),^1H NMR (300 MHz, DMSO-d_6, ppm) δ = 7.50 (s, 1H, HC = N), 5.9 (s, 1H, H_1), 5.8 (s, 1H, H_2), 2,10 (t, 2H, $\underline{H}_7$, $JH_{6,7}$ = 3.4Hz), 2.10 (t, 2H, $\underline{H}_6$, $JH_{6,7}$ = 3.4Hz), 4.8 (s, 1H, HC = C), 1.8 (s, 1H, $C\underline{H}_3$), 7.1-7.65 (m, 5H, Harom), ^{13}C NMR (50 MHz, DMSO-d_6, ppm) δ = 24.7 ($\underline{CH}_2CH_2$), 33.3 ($CH_2\underline{CH}_2$), 168.1 ($\underline{C}O$), 154.7 (C=N), 143.1 ($\underline{CH}$=CHCO), 123.6 (CH=$\underline{CH}$CO), 147.5 ($\underline{CH}$=CHC=N), 154.1 (CH=$\underline{CH}$C=N), 23.2 ($\underline{CH}_3$). $[M+Na]^+$ calculated for ($C_{15}H_{16}ONa$) = 235.1153. Measured: 235.1152 Anal. calcd. for $C_{15}H_{16}N_2O$: C, 74.90; H, 6.65; N, 11.65 Found: C, 74.80; H, 6.50; N, 11.45.

RESULTS AND DISCUSSION

The transformation of several terpenes **1a-c** was achieved by using three commercially available ruthenium based catalysts (Fig. 1).

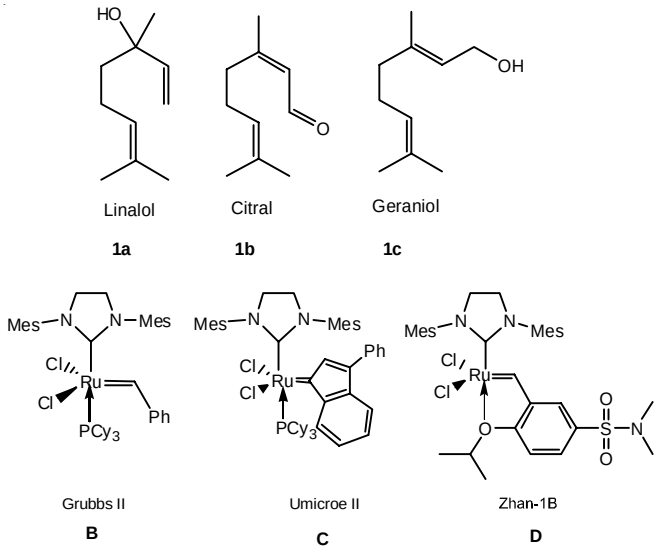
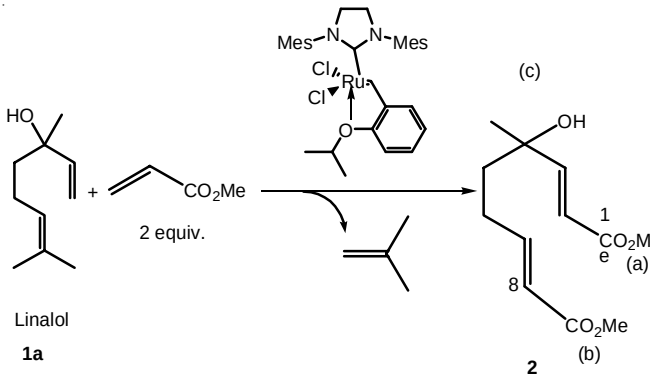


Fig. 1. Terpenoids and ruthenium based catalysts tested in cross metathesis

Condensation of linalool with methyl acrylate under mild condensation in chloroforme, xylene and glycerol afforded the corresponding terpenoids (**2**). **Scheme-I** describes the synthesis of compound **2** starting from linalol with methyl acrylate (MA). We used second generation Hoveyda catalyst A for screening the reaction conditions since it was previously proved to be the best catalyst in several transformations of compounds coming from biomass[12-15].



Scheme-I: Cross metathesis of linalol with methylacrylate

The compound **2** was characterized by using NMR and mass spectroscopic techniques and the proposed structure was supported the spectroscopic data. The ^1H NMR spectra of compound **2** showed a singlet at δ 1.36 ppm for the CH_3 protons. A characteristic multiplet signal at δ 1,72 ppm was assigned to H-5 proton. In addition, the protons $H_{2,3,7,8}$ are observed between δ 5.77 and δ 6.99 ppm and the expected multiplet for H_6 is observed at δ 2.22 ppm.

The formation of the compound **2** was further confirmed by recording ^{13}C NMR spectroscopy. The signal at δ 28.5 ppm corresponds to the C_6, C_5 carbon was observed at 40.2 ppm.

TABLE-1
CROSS METATHESIS OF LINALOL WITH METHYL ACRYLATE[a]

Entry	Solvent	Equiv. AM	Cata. (mol % A)	T (°C)	Time (h)	Conversion (%)[a]	Yield CPG (%)[a]	Yield isolated (%)
1	$CHCl_3$	2	2	80	15	100	58	40
2	Xylene	2	2	80	15	100	60	42
3	Glycerol	4	2	80	15	100	61	44
4	Glycerol	10	2	80	15	100	65	43
5	Glycerol	2	0.5	60	15	74	50	35
6[b]	Glycerol	2	0.5	70	3h	100	65	40
7[c]	Glycerol	2	0.5	70	3h	100	70	35

[a]Linalol (100 mg, 0.65 mmol), methyl acrylate (117 mL, 1.3 mmol, 2 eq.), A (8.2 mg, 13.10-3 mmol, 2 mol %), solvent (2 mL). Conversions and GC yields determined using dodecane as an internal standard. [b]4 eq. of methyl acrylate. [c]10 eq. of methyl acrylate.

Other signals attributed respectively to the chemical shifts 51.9 ppm, 52.1 ppm and 73 ppm, corresponding to the carbons C_b, C_a and C_4.

As shown in Table-1, similar results were achieved by reaction at low temperature in the three solvents tested showing that the greener solvent was perfectly suitable for this type of transformation. The GC and isolated yields were somehow low with regard to the conversion. The reaction outcome was not improved by the use of a larger excess of methyl acrylate and was even found to be detrimental when 10 eq. were employed (Table-1, entrie 4). A real improvement was represented by these results with regard to reported syntheses where the same compound was obtained in only 40 % yield using Grubbs 2nd generation catalyst in dichloromethane[16].

After successful synthesis of terpenoid **2** by using the best conditions with second generation Hoveyda catalyst A we extended this protocol to three other commercially available catalysts of different architectures (Fig. 2).

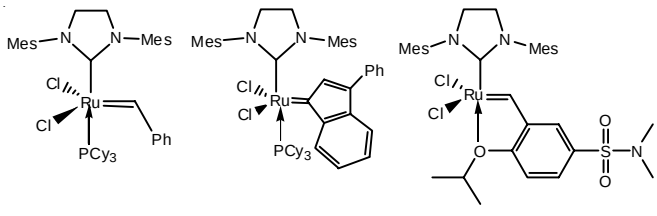


Fig. 2. Tested commercially olefin metathesis catalysts

Interestingly, only the Zannan catalyst D featuring a structure close to A provided similar results whereas catalysts B and C showed poor efficiency (Table-2).

TABLE-2
CROSS METATHESIS OF LINALOL WITH METHYLACRYLATE[a]

Conversion[b]	Catalyst	Time (h)	GC yield[b] (%)
90	B	3	30
98	C	3	20
92	D	3	85

[a]Linalol (100 mg, 0.65 mmol), catalyst (0.5 mol %), methyl acrylate (117 mL, 1.3 mmol, 2 eq.), glycerol (2 mL), 80 °C, 3 h. [b]Conversion and yields determined by gas chromatography using dodecane as internal standard.

It is worth-considering that the cross-metathesis reaction was stereoselective producing only the *E* isomer. Decreasing the catalyst loading further to 1 mol % resulted in an extended polymerization side reactions requiring long and fastidious workup[17]. With contrast to the results obtained with methyl acrylate, under solvent free conditions catalysts B, C and D showed similar results as compared to A; *i.e.* full conversions and GC yields ranging between 90 and 98 %. The suggested mechanism for formation of compound **2** is given in **Scheme-II**.

The second double bond of linalool will engage in a second catalytic cycle identical to the first by reacting with methyl acrylate to form the final product 2 of cross metathesis between linalool and methyl acrylate.

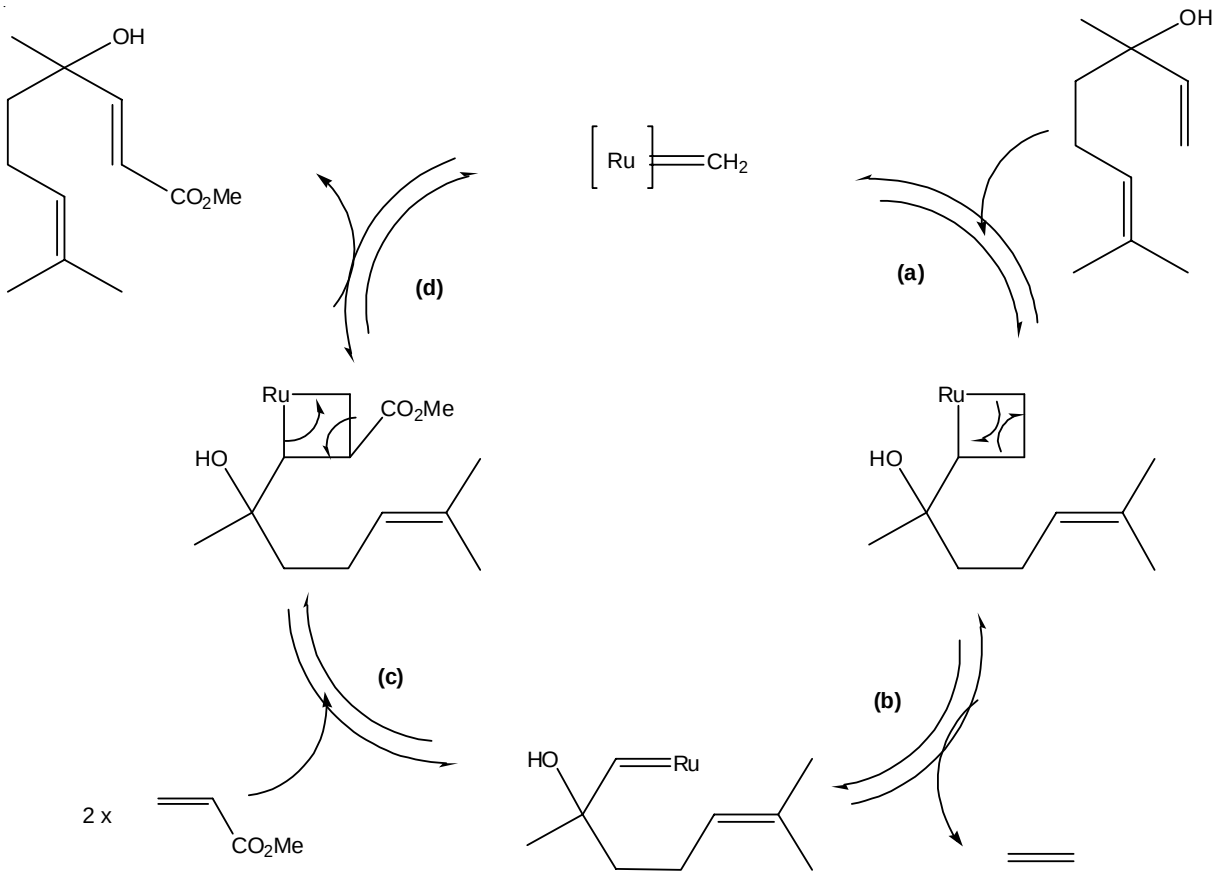
Terpenoid (**3**) was synthesized *via* treatment of geraniol with methyl acrylate in glycerol, as depicted in **Scheme-III**. The reaction was performed under reflux either for 24h to yield compound **3** in good yield. Compound **3** was isolated by column chromatography and well characterized by spectral data.

Geraniol first reacted at low temperatures using 2 mol % of Hoveyda catalyst A and a two-fold excess of methyl acrylate. It is noteworthy that the reaction proceeded better in glycerol than in chloroform or xylene (Table-3, entries 1-3). This tendancy was confirmed at 60 °C where glycerol again produced the best results.

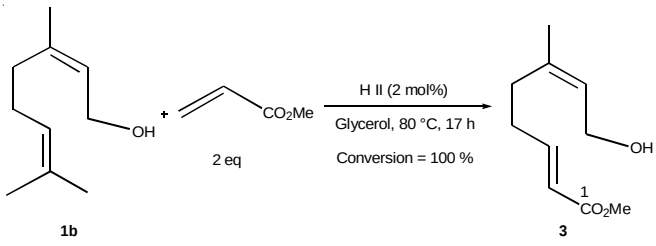
It was proved here that the use of glycerol was not favourable for side reactions (Table-3, entry 4, 5). This is the first time that such a solvent effect is observed with glycerol in an olefin metathesis transformation. This improvement led to a 10 % decrease of the transformation *E* factor[18,19]. Hence, using olefin cross-metathesis, the (*E*)-3 stereoisomer was stereoselectively prepared in 68 % yield thus showing an improvement with regard to the previously reported procedure where compound **3** was obtained in less than 60 % yield from a non-commercially available lactone[20].

As we have observed in cross-metathesis of linalol, catalysts B, C and D were not as efficient as A. It was to be noted that the catalyst B was completely inactive for this transformation whereas catalysts C and D provided low to modest conversions of 32 and 70 %, respectively.

Then the commercially available citral was tested in cross-metathesis reactions with methyl acrylate (**Scheme-IV**). Condensation of citral with methylacrylate in different solvents: chloroform, xylene and glycerol. The reaction was undergoing smoothly to give terpenoid **4** in a good yield. Its



Scheme-II: Proposed mechanism for the synthesis of compound **2**



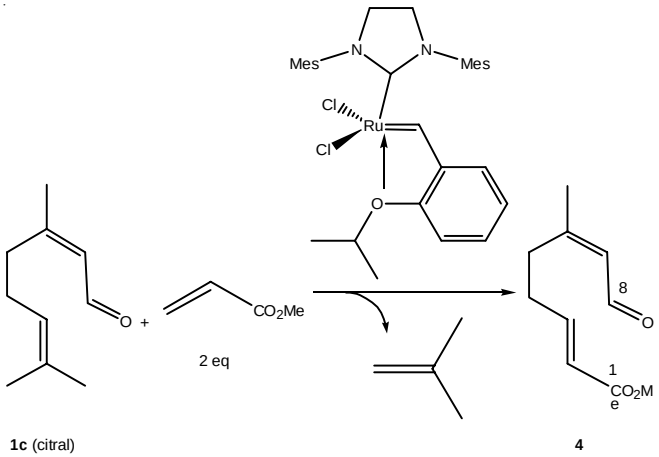
Scheme-III: cross metathesis of geraniol with methyl acrylate

TABLE-3
CROSS METATHESIS OF GERANIOL WITH METHYL ACRYLATE[a]

Entry	Catalyst A (mol %)	Solvent	Temp. (°C)	Conversion (%)	Yield (%)	Time (h)
1	2 eq	$CHCl_3$	35	100	n.d	15
2	2 eq	Xylene	40	100	22	15
3	2 eq	Glycerol	40	100	32	15
4	2 eq	Glycerol	60	100	10	15
5	2eq	Glycerol	60	100	15	15
6	2 eq	Xylene	80	100	10	15
7	2 eq	Xylene	80	100	43	24

[a]Citronellol (100 mg, 0.64 mmol), methyl acrylate (115 mL, 1.3 mmol, 2 eq.), A (8.1 mg, 13.10-3 mmol, 2 mol %), solvent (2 mL). [b]Conversion (%)/Gas Chromatography yield (%)/isolated yield (%). Conversions and GC yields were determined using dodecane as an internal standard. n.d = not determined.

structure was identified by their IR, ^1H, ^{13}C NMR and mass spectra as well as by either their elemental analysis or high resolution exact mass measurement.



Scheme-IV: Cross metathesis of citral with methyl acrylate

The IR spectrum of compound **4** indicated a characteristic adsorption bands at 1685 to 1604 cm^{-1}. These bands were attributed respectively to the C=O and C=C stretching vibrations. Its ^1H NMR spectrum gave signals at δ 3.80, 5.70 and 9.70 ppm, characteristic respectively for CH_3, H_3 and CHO group.

The first tests with citral rapidly showed that the full conversion could be obtained and that the reaction proceeded with similar efficiency in xylene and glycerol (Table-4, entries 1-3). Therefore, the reaction was not selective and the required product **5** was the only product isolated but in a modest 44 % yields (Table-4).

TABLE-4
CROSS METATHESIS OF CITRAL WITH METHYL ACRYLATE[a]

Entry	Solvent	Equiv. AM	Cata. (mol %)	Temp. (°C)	Time (h)	Conversion (%)[a]	Yield CPG (%)[a]	Isolated yield (%)
1	Xylene	2	2	80	15	100	58	40
2	Glycerol	2	2	80	15	100	60	42
3	Xylene	4	2	80	15	100	61	44
4	Glycerol	10	2	80	15	100	65	43
5	Glycerol	2	2	60	15	74	50	35

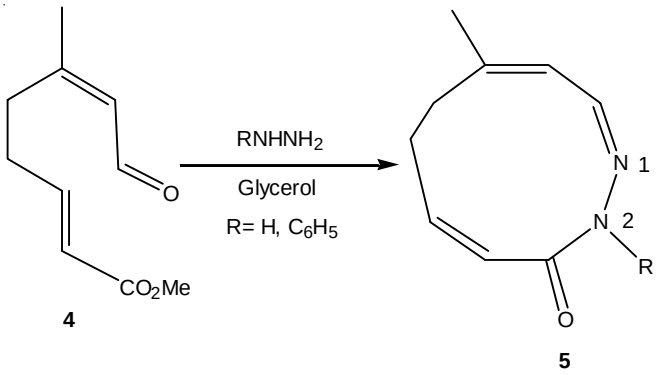
[a]Conversion and yield were determined GC using dodecane as internal standard.

Attempts to isolate and identify the side products produced during the reaction failed but it must be mentioned that no conversion of citral with 2 mol % of A at 80 % C in xylene was observed[21-26].

Reactivity of compound 4 towered hydrazines: Formation of heterocycles: The reactivity of compound **4** towards hydrazine hydrate or phenyl hydrazine was studied and the reaction proceeded *via* an addition reaction on to the aldehyde group followed by intramolecular cyclization to produce the diazecin-3-ones (**5**) ring as in compound **5**

By reacting compound **4** with either hydrazine hydrate or phenyl hydrazine, respectively in the presence of glycerol at reflux diazecin-3-ones (**5**) was obtained in 65 % yield (**Scheme-V**).

The structures of compounds **5** were proved by spectral data and were consistent with the proposed structures.



Scheme-V: General synthesis of diazecin-3-ones (**5**)

The ^{1}H NMR representative spectrum of compound **5a** revealed the absence of the methoxy group protons and showed signal at 5.90 ppm for NH. The olefinic protons H_4 and H_5 resonate respectively at 7.66 and 5.82 ppm as doublets with J = 15.8 Hz, indicating an E stereochemistry.

The ^{13}C NMR spectrum of compound **5a** show chemical shift signals at 167.5 ppm for C=O, 154.7 ppm for C=N, 143.5 (CH=CHCO) and 147.4 (CH=CHC=N).

Conclusion

In summary, we have prepared a series of new terpenoids by ruthenium catalyzed stereoselective cross-metathesis reactions. This catalytic transformation allowed the one step synthesis of terpenoids in higher yields than previously reported multistep procedures. Thus, not only were the product yields improved but also the waste production and energy consumption were decreased. Furthermore, these transformations were performed under environmental friendly conditions in glycerol. This type of transformation could certainly be extended to other terpenes or terpenoids and other cross metathesis partners. However, it will be necessary to identify and when possible to control the side reactions in order to improve further the performances of this process. We have also demonstrated the efficiency of olefin cross-metathesis for the synthesis of terpenoids, the control of the chemoselectivity of the cross-metathesis reaction is important and ring closing metathesis (RCM) reactions may also occur. Furthmore, the synthesis of some diazecin-3-ones is described *via* reaction of compound **4** with hydrazine hydrate or phenyl hydrazine in glycerol.

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