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Dedicated to the memory of Professor Margareta Avram
on the remembrance of her 100th anniversary

RING SIZE EFFECT IN McMURRY CYCLIZATION OF 1,ω-DI((AZULEN-1-YL)-CARBONYL)ALKANES

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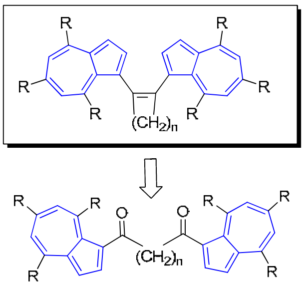
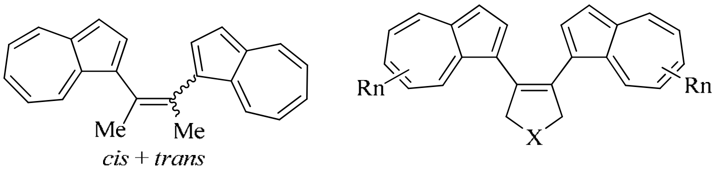
New researches on the reductive McMurry cyclization of α,ω-(diazulen-1-yl)-α,ω-diketones allowed the synthesis of 6- or 4-membered cycloalkenes with azulen-1-yl in 1 and 2 positions. The used routes for the generation of the starting diketones as well as their McMurry reaction are compared with those already reported for the corresponding 5-membered compounds.



INTRODUCTION

Our research was directed for a long time on the synthesis, structure and properties of azulenes substituted in position 1 with homo and heteroatom double bonds and a detailed review on this subject was recently published.[1] Special attention was paid to the study of the synthesis and properties of 1,2 di(azulen-1-yl)ethenes. Such derivatives were obtained in various ways[2,3] even by McMurry coupling of 1-azulenecarbonyl derivatives.[3] The limited number of obtained alkenes and the moderate preparative yields as well as the scientific and practical importance[4] of such compounds motivated us to thoroughly explore this area. Thus, our recent researches on the McMurry reaction of azulenes with α-carbonyl group in 1-position allowed the synthesis of various linear and cyclic 1,2-di(azulen-1-yl)ethenes as shown in Scheme 1.[5–7]



X = CH_2; Rn = H, 4,6,8-Me_3; 3,6-Me_2-5-*i*Pr
X = O or S; Rn = H

Scheme 1 – 1,2-Di(azulen-1-yl)ethenes.

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Depending on azulen-1-yl moieties and reaction conditions, the reaction products were ethene along with its precursor 1,2-diol and, surprisingly, the product of pinacol-pinacolone rearrangement. In previous papers[2,3] the protocol for obtaining 1,5-diketones with azulene-1-yl moieties in 1 and 5 positions followed by their McMurry internal coupling was developed and several considerations on the reactions mechanism have been advanced. In the context with these researches, the present paper expanded the study of McMurry reaction to the corresponding 1,6 and 1,4-diketones. Our interest was focused on the synthesis of diketones and on their behavior in the McMurry reaction taking into account both the number of methylene groups between the two carbonyl groups and different azulene-1-yl moieties at the end of molecule.

RESULTS AND DISCUSSION

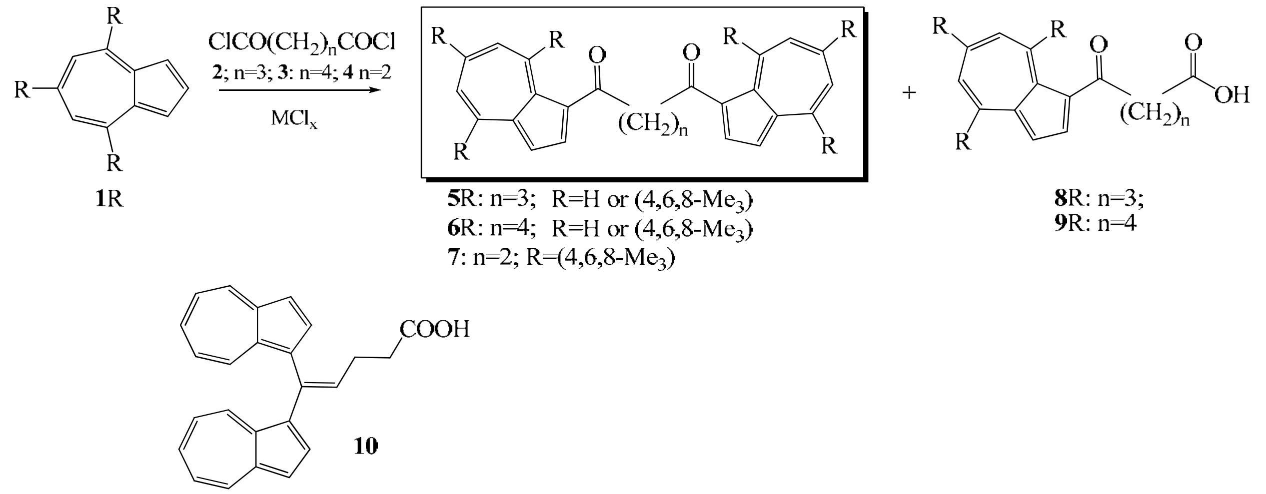
Synthesis of starting diketones

As we already reported the 1,5-di(azulene-1-yl)pentane-1,5-dione, **5**H, was obtained in 64% yield by microwave assisted Vilsmaier-Haack reaction.[3] To our surprise, when the same reaction conditions were applied to alkylated azulenes the expected diketones were not formed, even in trace amounts; however, these diketones were provided in good yields by Friedel-Crafts acylation. Thus, starting from glutaroyl dichloride, the diketone **5**(4,6,8-Me$_3$) resulted in 59 % yield in the presence of SnCl$_4$ in CCl$_4$ (Scheme 2 and Table 1) along with 16 % of keto acid **8**(4,6,8-Me$_3$).[3] Unexpectedly, the main product at the Friedel-Crafts acylation of parent azulene was the unsaturated acid **10** (55 %) and only low amounts of diketone **5**(H) and keto acid **8**(H) were found in the reaction mixture (Table 1, Entry 1). The generation of acid **10** was explained by the formation of δ,δ-di(azulene-1-yl)-δ-lactone as intermediate in the reaction. The azulene substitution, as in 4,6,8-trimethylazulene, hinders the *gem*-position of azulenyl moieties, thereby prevents also the lactonization and leads to the bis acylation.

Now, the same protocol for Friedel–Crafts acylation is used for the reaction of adipoyl and succinoyl dichloride, **3** and **4** with azulenes **1**R. While SnCl$_4$ catalyzes the reaction of dichloride **3**, it is inert for the acylation with dichloride, **4**, which reacts only in the presence of stronger catalyst, AlCl$_3$, and at higher temperature in dichloromethane (Entry 5 in Table 1).

Interesting, the reaction of both azulene and 4,6,8-trimethylazulene with adipoyl dichloride, **3**, produces diketone and keto acid in similar amounts. It should be noted that when parent azulene was reacted the unsaturated acid 6,6-di(azulen-1-yl)pent-5-enoic acid was not formed. It is possible that in this case the γ-lactoide ring closure, leading to the formation of key intermediate γ,γ-diazulenyl-γ-lactone, occurs more difficult as the closure to δ-lactone, the precursor of acid **10**.

As mentioned above, the succinoyl dichloride, **4**, reacts only in severe reaction conditions which enable the electrophilic acylation with both COCl groups however this procedure reduces the amount of diketone **7** due to the high sensitivity of azulenyl moiety towards AlCl$_3$.



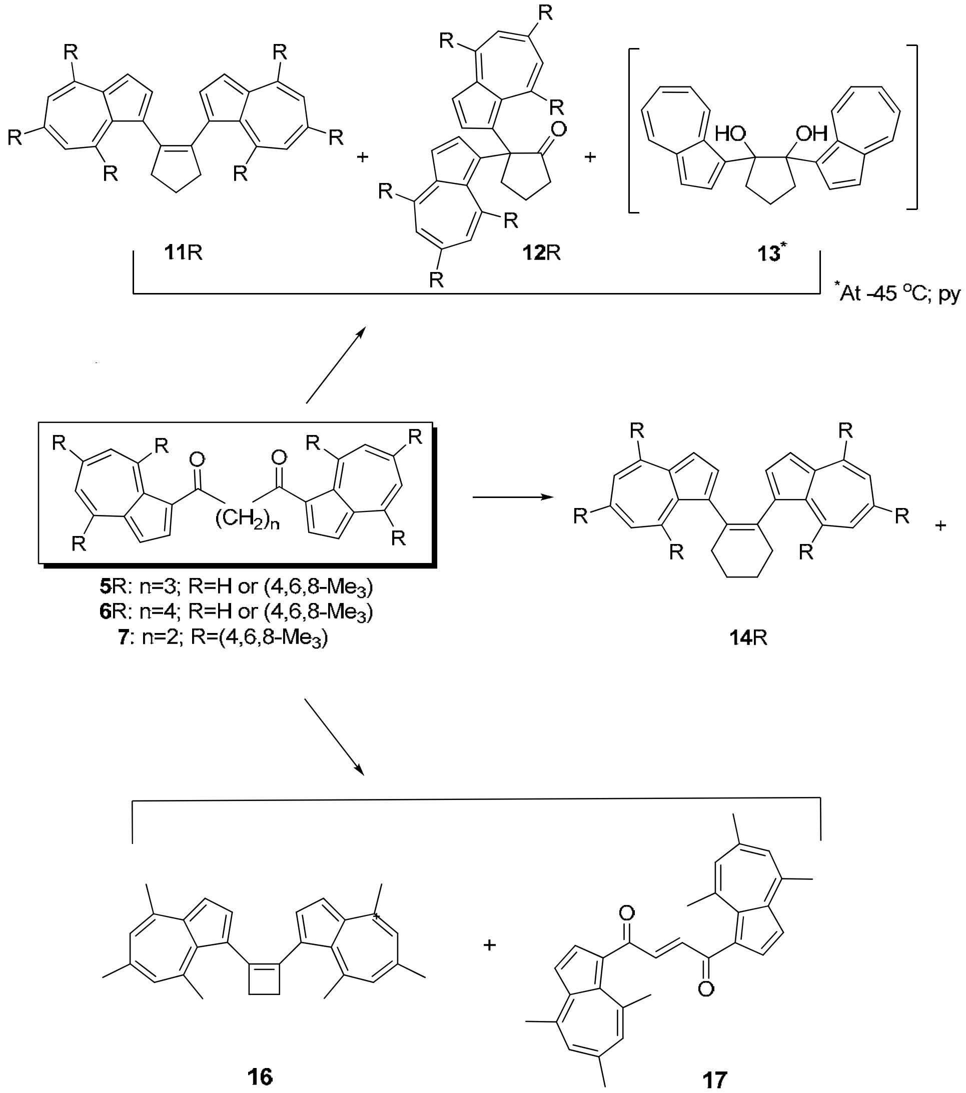
Scheme 2 – Acylation of azulenes.

Table 1

Friedel-Crafts reaction of azulenes **1**R with acid dichlorides **2** - **4**

Entry	Acid chloride	Azulene	Reaction conditions	Product / Yield (%)	
				Diketone	Ketoacid
1[a]	**2** (n=3)	**1**(H)	SnCl$_4$, in CCl$_4$, 0 °C, 1,5 h	**5**(H) / 13	**8**(H) / 8[b]
2[a]		**1**(4,6,8-Me$_3$)		**5**(4,6,8-Me$_3$) / 59	**8**(4,6,8-Me$_3$) / 16
3	**3** (n=4)	**1**(H)		**6**(H) / 44	**9**(H) / 16
4		**1**(4,6,8-Me$_3$)		**6**(4,6,8-Me$_3$) / 55	**9**(4,6,8-Me$_3$) / 14
5	**4** (n=2)	**1**(4,6,8-Me$_3$)	AlCl$_3$ in DCM at 25 °C, 3 h	**7** (31)	-

[a]Reference.[3] [b]The reaction mixture also contained 55 % 5,5-di(azulen-1-yl)pent-4-enoic acid, **10**.



Scheme 3 – McMurry coupling of diketones.

Table 2

McMurry coupling of diketones **6**R, **7**R

Entry	Diketone	Reaction conditions[a]	Products (yield in %)	
			Cycloalkene	Pinacolone
5[b]	**6**(H)	$TiCl_4$/Zn, 25 °C, 3 h	**14**(H) (31)	**15**(H) (44)
6[b]		$TiCl_4$–Zn–py, 25 °C, 3 h	**14**(H) (10)	**15**(H) (54)
7[b]	**6**(4,6,8-Me_3)	$TiCl_4$–Zn, refl., 10 min	**14**(4,6,8-Me_3) (75)	–
7[b]		$TiCl_4$–Zn–py, refl., 10 min	**14**(4,6,8-Me_3) (75)	–
1	**5**(H)	$TiCl_4$/Zn, 0 °C, 1h	**11**(H) (77)	**12**(H) (22)
2	**5**(4,6,8-Me_3)		**11**(4,6,8-Me_3) (85)	-
3	**5**(H)	$TiCl_4$/Zn–py, 0 °C, 1 h	**11**(H) (88)	**12**(H) (10)
4	**5**(4,6,8-Me_3)		**11**(4,6,8-Me_3) **(**87)	–

[a]Solvent THF. [b]Reference.[3]

McMurry internal coupling of diketones

The previous studies on the reductive McMurry cyclization of diketones **5**R established that in the reaction which occurred in the presence of Ti/Zn in tetrahydrofuran the ratio between the formed products, cycloalkenes **11**R and pinacolones **12**R, depended on the reaction time and temperature (Scheme 3 and Table 2). Likewise, the addition of pyridine in the reaction medium enhanced the ratio alkene/pinacolone.[3] The presence of a low amount of diol **13** was observed only starting from azulene **1**(H) at very low temperature and in the presence of pyridine (Scheme 3).

Applying the same protocol to McMurry reaction of diketones **6**R the results shown in Scheme 3 and Table 2 are obtained. At first glance, the comparison between the couplings of diketones **5** and **6** shows the lower reactivity of the second compounds that necessitates increased temperature and reaction time which decrease significantly the overall yields of products. Whereas using the diketone **5**(H) the cycloalkene **11**(H) represents the main product, starting from diketone **6**(H) the amount of pinacolone **15**(H) exceeds that of the cycloalkene **14**(H). This difference can be explained by the higher temperature required for the reaction of diketone **6**(H) which facilitates the pinacol/pinacolone rearrangement. Interestingly, for **6**(H) the ratio cycloalkene/pinacolone decreases in the presence of pyridine as compared with the reaction in its absence.

The well-known difficulty to generate the four-membered ring seems to prevent the reaction which involve the 1,4-di(azulen-1-yl)butan-1,4-dione in the McMurry cyclization and the above described reaction conditions produces only tar. Yet, the microwave-assisted coupling of diketone **7** with substituted azulene-1-yl moieties in the presence of pyridine affords defined compounds but in low yields (Scheme 4). Despite the reduced amount of separated products they have fully characterized as cyclobutenone **16** and 1,4-di(4,6,8-trimethylazulen-1-yl)but-2-ene-1,4-dione, **17**.

EXPERIMENTAL

Materials and techniques

All reagents were purchased from commercial suppliers and used without further purification. Tetrahydrofuran (THF) was distilled under inert atmosphere from $LiAlH_4$ and stored over 4 Å molecular sieve. Dichloromethane (DCM) was refluxed and distilled over fresh CaH_2. Microwave reactions were performed in sealed glass vessels using a Biotage Initiator 2.0 reactor. Melting points were determined with a Koehler Automatic Melting Point Range Apparatus (K90190). Elemental analyses were carried out on a Perkin Elmer CHN 240B analyzer. FT-IR spectra were acquired on a Bruker Vertex 70 Spectrometer, with horizontal device for attenuated reflectance and diamond crystal, on a spectral window ranging from 4000 to 400 cm^{-1}. ^1H NMR (400 MHz) and ^{13}C NMR (100.56 MHz) spectra were recorded on a Bruker Avance DRX4 spectrometer in $CDCl_3$ with TMS as an internal standard at room temperature. COSY and HETCOR correlation experiments were used for the structure assignment. Mass spectra were recorded with a Varian 1200L Quadrupole MS/MS spectrometer by direct injection in ESI, positive mode.

Synthesis of starting materials

*Acylation of azulenes **1**R with adipoyl dichloride catalyzed by $SnCl_4$.* To the ice-cooled solution of azulenes (4.4 mmol) and adipoyl dichloride, **3**, (338 mg, 2 mmol) in dry carbon tetrachloride (15 mL) under inert atmosphere, $SnCl_4$ (0.56 mL, 4.8 mmol) was added dropwise. The resulting mixture was stirred for 1.5 h at 0°C and then quenched by addition of water. This mixture was extracted with DCM and the resulted organic solution was successively washed with water, 5% aqueous Na_2CO_3 solution, and again with water, dried over Na_2SO_4 and the solvent was removed in vacuum. The residue was purified by alumina column chromatography with gradient elution (from DCM to DCM:AcOEt, 5:1) to afford diketone **6**R. The basic solution was washed with ether, acidified with 1N HCl until pH = 2, and then extracted with ether. The extracts were washed with water, dried over Na_2SO_4 and the solvent was removed in vacuum. The residue was purified on silica gel column using methanol as eluent giving the keto acid **9**R. The resulted yields are reported in Table 1.

Acylation of 4,6,8-trimethylazulene 1(4,6,8-Me$_3$) with succinoyl dichloride catalyzed by AlCl$_3$. To the stirred suspension of $AlCl_3$ (333 mg, 2.5 mmol) in DCM (20 mL) the solution of 4,6,8-trimethylazulenes (307 mg, 2.4 mmol) and adipoyl dichloride, **4**, (169 mg, 1 mmol) in DCM (30 mL) was added dropwise at 0 °C. The reaction mixture was stirred at the room temperature for 3 h and, after cooling at 0 ^{o}C, the mixture was quenched at this temperature with water. After careful extraction with DCM, the solvent was removed in vacuum and the residue was chromatographed on alumina with DCM for recovery of unreacted 4,6,8-trimethylazulenes and then, with a mixture of DCM and AcOMe, eluted the diketone **7** (yield 31 %).

McMurry reductive cyclization

McMurry reaction of diketones 6R. To an ice-cooled suspension of active zinc dust (295 mg, 4.5 mmol) in dry THF (10 mL) under inert atmosphere, freshly distilled $TiCl_4$ (0.25 mL, 2.25 mmol) was added dropwise. The mixture was allowed to warm to room temperature, and then heated at reflux for 2 h to yield dark brown slurry of low-valent titanium reagent. When pyridine (0.37 mL, 4.5 mmol) was used, it was added to the low-valent titanium slurry at 0 ^{o}C and the resulting mixture was stirred at this temperature for 15 min. To this, a solution of the diketone **6**R (0.45 mmol) in THF (10 mL) was added in one portion and the reaction mixture was stirred for one hour at 0 ^{o}C. The reaction was then quenched with 10% aqueous K_2CO_3 (10 mL) and carefully extracted with DCM. The organic extracts were washed with water, dried over Na_2SO_4 and the solvent was removed in vacuum. Column chromatography on alumina, using a mixture of n-pentane and DCM with gradient elution, afforded at the beginning the alkene **14**R followed by pinacolone **15**R in the yield reported in Table 2.

McMurry reaction of diketones 7. To the slurry of low-valent titanium reagent (2.25 mmol) in THF, obtained as above, pyridine (0.36 mL) was added and the mixture was stirred for 15 min. Then, the solid diketone **7** (190 mg, 0.45 mmol) was at once added and the mixture was heated in the MW reactor at 100 ^{o}C (80 watt) for 1 h. After addition of a solution of K_2CO_3 in water (10 %) the obtained suspension was carefully extracted with DCM. The organic extracts were washed with water and dried on Na_2SO_4. After the solvent removal, the residue was chromatographed on alumina when a large amount from the mixture remained in start. The mixture with n-pentane and DCM eluted the cycloalkene **16** (7 %) as green solution followed by a green-violet solution of unsaturated diketone **17** (4 %). A small amount of unreacted diketone **7** was recovered from the column with a mixture of DCM and AcOEt. Between these products eluted very small amounts of uncharacterized compounds.

1,6-di(Azulen-1-yl)hexan-1,6-dione, **6(H).** Red solid, m.p. 134–135 ^{o}C. ^{1}H–NMR (400 MHz, CDCl$_3$): δ = 9.89 (d, J = 10.0 Hz, 2 H, 8'-H), 8,47 (d, J = 9.6 Hz, 2 H, 4'-H), 8.32 (d, J = 4.0 Hz, 2 H, 2'-H), 7.81 (t, J = 9.8 Hz, 2 H, 6'-H), 7.59 (t, J = 9.8 Hz, 2 H, 7'-H), 7.46 (t, J = 9.8 Hz, 2 H, 5'-H), 7.27 (d, J = 4.4 Hz, 2 H, 3'-H), 3.18–3.15 (m, 4 H, 2-, 5-H), 1,98 (q, J = 6.9 Hz, 2 H, 3-, 4-H) ppm. ^{13}C–NMR (100.56 MHz, CDCl$_3$): δ = 198.0, 145.0, 140.2, 140.0, 139.6, 139.5, 138.5, 129.2, 127.2, 124.9, 117.8, 41.1, 25.2 ppm. IR (solid): ν_{max}: 1630 (C=O) cm^{-1}. MS(ESI): m/z = 367 [M+H]$^+$. Anal. Calcd for $C_{26}H_{22}O_2$: C, 85.22, H 6.05. Found: C 85.18, H 6.07.

1,6-di(4,6,8-Trimethylazulen-1-il)hexan-1,6-dione, **6(4,6,8-Me$_3$).** Red solid, m.p. 186–187 ^{o}C. ^{1}H–NMR (400 MHz, CDCl$_3$): δ = 7.91 (d, J = 4.4 Hz, 2 H, 2'-H), 7.27 (s, 2 H, 7'-H), 7.23 (s, 2 H, 5'-H), 7.16 (d, J = 4.4 Hz, 2 H, 3'-H), 3.15–3.12 (m, 4 H, 2-, 5-H), 2.88 (s, 6 H, 8'-CH$_3$), 2.83 (s, 6 H, 4'-CH$_3$), 2.64 (s, 6 H, 6'-CH$_3$), 2.00-1.92 (m, 4 H, 3-, 4-H) ppm. ^{13}C–NMR (100.56 MHz, CDCl$_3$): δ = 200.6 (C=O), 149.6, 147.5, 146.8, 140.7, 136.4, 134.6, 132.3, 130.8, 130.3, 114.5, 42.9, 29.4, 28.4, 25.8, 25.6 ppm. IR (solid): ν_{max}: 1645 (C=O) cm^{-1}; MS(ESI): m/z = 451 [M+H]$^+$. Anal. Calcd for $C_{32}H_{34}O_2$: C 85.29, H 7.61. Found: C 85.33, H 7.59.

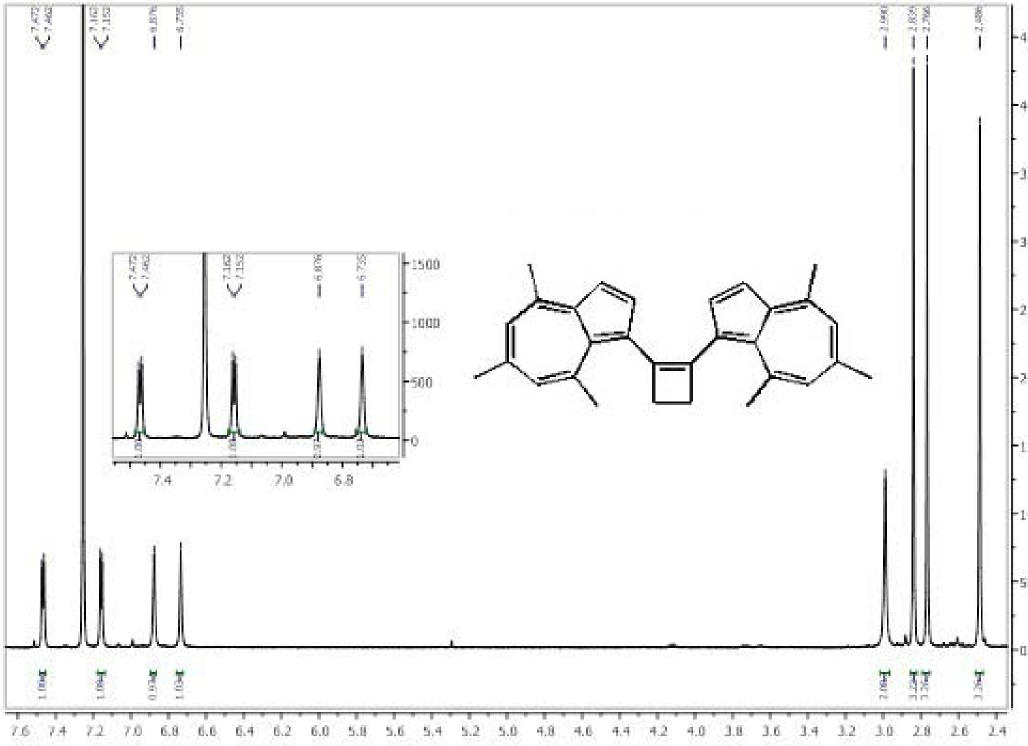
6-(Azulen-1-yl)-6-oxohexanoic acid, **9(H).** Red solid, m.p. 112–114 ^{o}C. ^{1}H–NMR (400 MHz, CDCl$_3$): δ = 9.83 (d, J = 10.0 Hz, 1 H, 8'-H), 8.41 (d, J = 10.0 Hz, 1 H, 4'-H), 8.23 (d, J = 4.0 Hz, 1 H, 2'-H), 7.75 (t, J = 9.8 Hz, 1 H, 6'-H), 7.54 (t, J = 10.0 Hz, 1 H, 7'-H), 7.41 (t, J = 9.6 Hz, 1 H, 5'-H), 7.21 (d, J = 4.0 Hz, 1 H, 3'-H), 3.07 (t, J = 6.9 Hz, 2 H, 5-H), 2.37 (t, J = 7.1 Hz, 2 H, 2-H), 1.84–1.27 (m, 4 H, 3-, 4-H) ppm. ^{13}C–NMR (100.56 MHz, CDCl$_3$): δ = 211.0, 197.8, 178.7, 145.3, 140.5, 140.0, 139.7, 138.7, 129.5, 127.5, 124.8, 117.9, 40.7, 34.1, 24.8, 24.6 ppm. IR (solid): ν_{max}: 2400–3200, 1696 (CO$_2$H), 1630 (C=O) cm^{-1}. MS(ESI): m/z = 257 [M+H]$^+$. Anal. Calcd for $C_{16}H_{16}O_3$: C 74.98, H 6.29. Found: C 74.94, H 6.27.

6-Oxo-6-(4,6,8-trimethylazulen-1-yl)hexanoic acid, **9(4,6,8-Me$_3$).** Red solid, m.p. 108–109 ^{o}C. ^{1}H–NMR (400 MHz, CDCl$_3$): δ = 7.95 (bs, 1 H, 2'-H), 7.33 (s, 1 H, 7'-H), 7.30 (s, 1 H, 5'-H), 7.21 (d, J = 2.4 Hz, 1 H, 3'-H), 3.14 (t, J = 6.8 Hz, 2 H, 5-H), 2.93 (s, 3 H, 8'-CH$_3$), 2.88 (s, 3 H, 4'-CH$_3$), 2.69 (s, 3 H, 6'-CH$_3$), 2.48 (t, J = 7.2 Hz, 2 H, 2-H), 1.92-2.00 (m, 2 H, 4-H) 1.88-1.80 (m, 2 H, 3-H) ppm. ^{13}C–NMR (100.56 MHz, CDCl$_3$): δ = 200.0, 178.6, 149.7, 147.6, 146.9, 140.9, 136.4, 134.7, 132.4, 130.6, 130.4, 114.6, 42.3, 33.8, 29.4, 28.4, 25.8, 24.9, 24.6 ppm. IR (solid): ν_{max}: 2400–3100, 1710 (CO$_2$H), 1651 (C=O) cm^{-1}. MS(ESI): m/z = 299 [M+H]$^+$. Anal. Calcd for $C_{19}H_{22}O_3$: C 76.48, H 7.43. Found: C 76.53, H 7.41.

1,4-di(4,6,8-Trimethylazulen-1-yl)butan-1,4-dione, **7.** Red solid, m.p. 195–199 °C. ^{1}H–NMR (400 MHz, CDCl$_3$): δ = 8.08 (d, J = 4.8 Hz, 2 H, 2'-H), 7.27 (s, 2 H, 7'-H), 7.22 (s, 2 H, 5'-H), 7.19 (d, J = 4.4 Hz, 2 H, 3'-H), 3.61 (s, 4 H, 2-, 3-H), 2.88 (s, 6 H, 8'-CH$_3$), 2.86 (s, 6 H, 4'-CH$_3$), 2.64 (s, 6 H, 6'-CH$_3$) pm. ^{13}C–NMR (100.56 MHz, CDCl$_3$): δ = 199.3, 149.7, 147.3, 146.7, 140.6, 136.6, 134.5, 132.2, 130.8, 130.1, 114.6, 37.7, 29.3, 28.4, 25.8 ppm. IR (solid): ν_{max}: 1652 (C=O) cm^{-1}. MS (ESI): m/z = 423 [M + H]$^+$. Anal. Calcd for $C_{30}H_{30}O_2$: C 85.27, H 7.16. Found: C 85.33, H 7.17.

1,2-di(Azulen-1-yl)cyclohex-1-ene, **14(H).** Green solid, m.p. 162–164 °C. ^{1}H–NMR (400 MHz, CDCl$_3$): δ = 8.14 (d, J = 9.6 Hz, 2 H, 8'-H), 7.94 (d, J = 9.6 Hz, 2 H, 4'-H), 7.53 (d, J = 3.6 Hz, 2 H, 2'-H), 7.29 (t, J = 9.8 Hz, 2 H, 6'-H), 7.01 (d, J = 3.6 Hz, 2 H, 3'-H), 6.84 (t, J = 9.8 Hz, 2 H, 5'-H), 6.77 (t, J = 9.8 Hz, 2 H, 7'-H), 2.69 (bs, 4 H, 3-, 6-H), 2.02 (bs, 4 H, 4-, 5-H) ppm. ^{13}C–NMR (100.56 MHz, CDCl$_3$): δ = 140.6, 137.6, 136.9, 135.8, 135.2, 134.4, 134.0, 132.4, 122.0, 121.4, 116.7, 33.6, 23.7 ppm. MS (ESI): m/z = 335 [M + H]$^+$. Anal. Calcd for $C_{26}H_{22}$: C 93.37, H 6.63. Found: C 93.40, H 6.61.

1,2-di(4,6,8-Trimethylazulen-1-yl)cyclohex-1-ene, **14(4,6,8-Me$_3$).** Violet solid, m.p. 173–174 °C. ^{1}H–NMR (400 MHz, CDCl$_3$): δ = 7.16 (bs, 2 H, 2'-H), 6.95 (s, 2 H, 7'-H), 6.93 (bs, 2 H, 3'-H), 6.81 (s, 2 H, 5'-H), 3.20 (s, 6 H, 8'-CH$_3$), 2.65 (s, 6 H, 4'-CH$_3$), 2.56–2.37 (m, 7 H, 3-, 5-H, 6'-CH$_3$), 1.99–1.86 (m, 4 H, 4-, 5-H) ppm. ^{13}C–NMR (100.56 MHz, CDCl$_3$): δ = 146.2, 144.8, 144.1, 136.0, 134.9, 134.4, 134.2, 133.1, 127.4, 125.8, 115.3, 35.7, 28.3, 25.2, 25.1, 23.5 ppm. MS (ESI): m/z = 419 [M + H]$^+$. Anal. Calcd for $C_{32}H_{34}$: C 91.81, H 8.19. Found: C 91.78, H 8.20.



2,2-di(Azulen-1-yl)cyclohexanone, **15,** Blue solid, m.p. 155–156 °C. ^{1}H–NMR (400 MHz, $CDCl_3$): δ = 8.29 (d, J = 9.6 Hz, 2 H, 8'-H), 8.02 (d, J = 9.6 Hz, 2 H, 4'-H), 7.56 (d, J = 4.0 Hz, 2 H, 2'-H), 7.49 (t, J = 9.8 Hz, 2 H, 6'-H), 7.30 (d, J = 4.0 Hz, 2 H, 3'-H), 7.10 (t, J = 9.6 Hz, 2 H, 5'-H), 6.95 (t, J = 9.8 Hz, 2 H, 7'-H), 2.96 (t, J = 5.8 Hz, 2 H, 6-H), 2.39 (t, J = 6.6 Hz, 2 H, 3-H), 2.14–2.07 (m, 4 H, 4-, 5-H) ppm. ^{13}C–NMR (100.56 MHz, $CDCl_3$): δ = 210.4, 142.2, 138.0, 137.6, 136.9, 136.5, 135.0, 130.7, 123.1, 122.4, 116.7, 58.6, 41.7, 40.6, 27.9, 23.1 ppm. IR (solid): ν_{max}: 1694 (C=O) cm^{-1}; MS(ESI): m/z = 351 $[M+H]^+$. Anal. Calcd for $C_{26}H_{22}O$: C 89.11, H 6.33. Found: C 89.16, H 6.34.

1,2-di(4,6,8-Trimethylazulen-1-yl)cyclobut-1-ene, **16.** Green solid, m.p. 139–140 °C. ^{1}H–NMR (400 MHz, $CDCl_3$): δ = 7.47 (d, J = 4.0 Hz, 2 H, 2'-H), 7.16 (d, J = 4,0 Hz, 2 H, 3'-H), 6.88 (s, 2 H, 7'-H), 6.74 (s, 2 H, 5'-H), 2,99 (s, 4 H, 3-, 4-H), 2.84 (s, 6 H, 8'-CH_3), 2.77 (s, 6 H, 4'-CH_3), 2.49 (s, 6 H, 6'-CH_3) ppm. ^{13}C–NMR (100.56 MHz, $CDCl_3$): δ = 147.6, 145.6, 144,7, 139.3, 137.3, 135.4, 132.5, 128.4, 128.1, 126.7, 115.5, 32.6, 28.2, 26.9, 25.4 ppm. MS (ESI): m/z = 391 $[M + H]^+$. Anal. Calcd for $C_{30}H_{30}$: C 92.26, H 7.74. Found: C 92.30, H 7.73.

1,4-di(4,6,8-Trimethylazulen-1-yl)but-2-ene-1,4-dione, **17.** Green-brown solid, m.p. 91–92 °C. ^{1}H–NMR (400 MHz, $CDCl_3$): δ = 7.76 (d, J = 4.0 Hz, 2 H, 2'-H), 7.34 (d, J = 4.0 Hz, 2 H, 3'-H), 7.05 (s, 2 H, 7'-H), 7.00 (s, 2 H, 5'-H), 6.46 (s, 2 H, 2-, 3-H), 2.88 (s, 6 H, 8'-CH_3), 2.70 (s, 6 H, 4'-CH_3), 2.58 (s, 6 H, 6'-CH_3) pm. ^{13}C–NMR (100.56 MHz, $CDCl_3$): δ = 152.6, 148.2, 146.7, 146.1, 140.0, 136.8, 133.1, 129.7, 127.8, 120.8, 115.0, 110.3, 28.6, 27.0, 25.7 ppm. IR (solid): ν_{max}: 1572 (C=O) cm^{-1}. MS (ESI): m/z = 421 $[M + H]^+$. Anal. Calcd for $C_{30}H_{28}O_2$: C 85.68, H 6.71. Found: C 85.72, H 6.74.

CONCLUSIONS

The researches on the reductive McMurry cyclization of 1,6-(diazulen-1-yl)-1,6-diketones and 1,4-(diazulen-1-yl)-1,4-diketones as well as the synthesis of these starting diketones were compared with those already reported for the corresponding 1,5 compounds. The used routes allowed the synthesis of 6- or 4-membered cycloalkenes with azulene-1-yl) moieties in 1 and 2 positions which were characterized. The reaction of ketones possessing unsubstituted azulene-1-yl moieties afforded also the products of pinacol-pinacolone rearrangement.

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