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Dedicated to the memory of
Professor Mircea D. Banciu (1941–2005)

REACTION OF AZULENES WITH DERIVATIVES OF AROMATIC DICARBOXYLIC ACIDS

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The reaction of azulenes with phthalic and naphthalene-1,8-dicarboxylic acid derivatives was investigated. Working with acids dichloride in the presence of Lewis acids ($SnCl_4$ and $AlCl_3$) the obtained products were *gem*-di-(azulen-1-yl)-lactones, di-(1-azulenoyl) ketones and (1-azulenoyl)-carboxylic acids. The reaction of phthalic anhydride in the same conditions occurred with low yields affording only corresponding lactone whereas the naphthalic anhydride was recovered unreacted. The Vilsmeier reaction of azulenes with both diamides failed. The reaction route starting from the dichloride was discussed.

INTRODUCTION

Recently, we have published the results on the study regarding the synthesis of azulenic β-diketones and their use in the generation of five-membered aromatic heterocycles.[1] In this paper we turn our attention on the synthesis of other dicarbonylic compounds with azulene bonded to the C=O groups, starting from derivatives of aromatic dicarboxylic acids in the conditions of Friedel-Crafts reaction. Besides the possibility to use these compounds as building blocks in several interesting reactions (*e.g.*, heterocyclic syntheses or McMurray cyclization), the obtained experimental results contribute to the clarification of controversial reaction mechanism.

RESULTS AND DISCUSSION

Reaction of acid derivatives and azulenes

The condensation between the derivatives of phthalic acid and naphthalene-1,8-dicarboxylic acid (naphthalic acid), namely anhydride and chloride, and azulenes was carried out in the presence of $SnCl_4$ or $AlCl_3$ as catalysts. After several preliminary experiments we have established that boiling tetrachloromethane can be used as reaction medium for the first catalyst and that in the presence of the last catalyst the reaction occurred better in dichloromethane (DCM) at 0^0C.

The results obtained starting from the two phthalic acid derivatives, anhydride, **1**, and dichloride, **2**, are shown in Scheme 1 and Table 1. From the reported data one can see the very low conversion of anhydride **1** and the strong dependence of the nature of obtained products and their ratio on the used catalyst starting from azulene **3** and dichloride **2**. The reduced conversion of anhydride in the reaction can be explained by its low reactivity and mainly by its very low solubility in the reaction medium. As products of the anhydride reaction small amounts of acylated benzoic acid **6a** or phthalide **4a** were obtained. Therefore, this reaction does not present interest from synthetically point of view.

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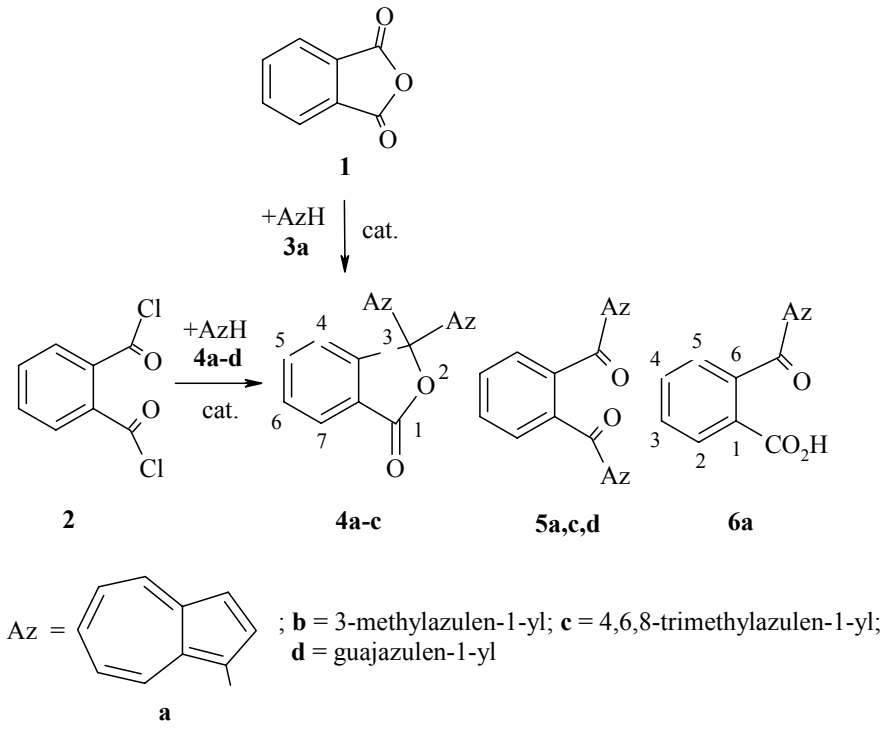


Scheme 1

Starting from dichloride **2**, in the presence of $SnCl_4$ a high tendency to form phthalide **4** was observed whereas with $AlCl_3$, the diketone **5** resulted; sometimes an amount of phthalide was also formed. For both catalysts, the generation of phthalides is restricted when bulky azulenes, as 4,6,8-trimethylazulene, was reacted due to the high steric hindrance induced by the neighborhood of the two azulene moieties as in **4c**. Contrary, the better yields in diketones obtained starting from substituted azulenes **3c** and **3d** are explained by the absence of steric hindrance in the ring opened products and the high distance between the azulene moieties. The decrease in the reaction yield for azulenes **3d** and mainly **3b** could be explained by their high intrinsic reactivity which can react on other routes giving tar. However, despite the moderate reaction yields obtained, this route seems to be the only one for the generation of phthalides **4** and mainly of diketones **5**.

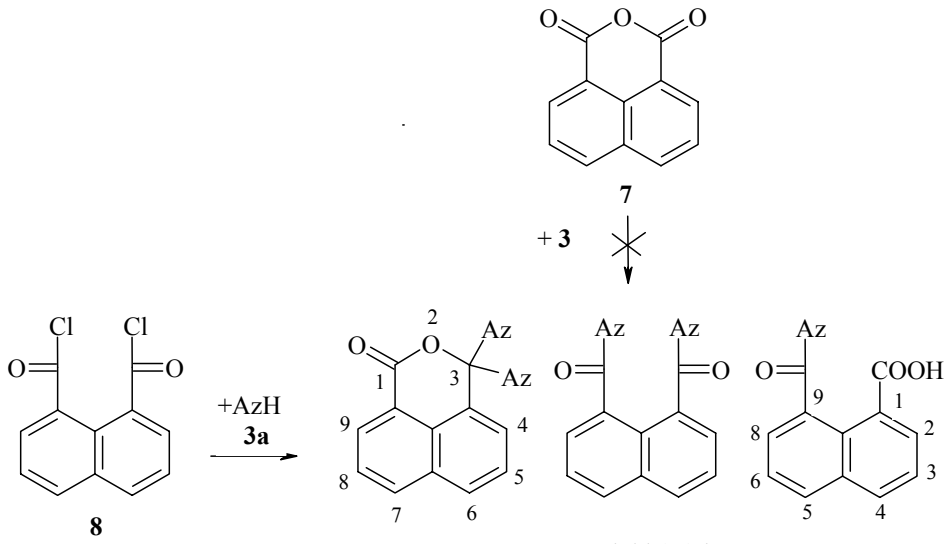
Table 1

Reaction of azulenes with phthalic acid derivatives[a]

Starting compounds		Catalyst/ solvent	Time (min)	Unreacted azulene (%)	Yield (%)	
					4a-d	**5a,c,d**
2	**3a**	$SnCl_4$/	240	36	40	0
	3b	CCl_4	180	17	6	0
	3c		240	50	20	0
	3d		180	42	traces[b]	0
	3a	$AlCl_3$/	10	45	30	13
	3b	CH_2Cl_2	1	30	4	0
	3c		10	50	0	33
	3d		1	50	0	16
1[c]	**3a**	$SnCl_4/CCl_4$	360	43	5	0
		$AlCl_3/CH_2Cl_2$	60	0	0[d]	0

[a]The reactions with $SnCl_4$ were performed at 90^0C and with $AlCl_3$ at 0^0C. [b]The presence of **4d** was attested only by the mass spectrum and some characteristic signals in ^{1}H-NMR. [c] Almost all quantity of anhydride was recovered unreacted. [d]As reaction product under 2 %, acid **6a** was obtained.

Due to the resemblance in the reactivity and solubility of phthalic anhydride, **1**, and naphthalic anhydride, **7**, it is not surprising that the last anhydride was also inert towards azulenes in the presence of both catalysts (Scheme 2). Starting from dichloride **8** and using $AlCl_3$ as catalyst, higher amounts of lactone **9** and aroylated acid **11** were formed; diketone **10** resulted however only in traces. The amount of obtained diketone **10** increased when $SnCl_4$ catalyzed the reaction but the resulted mixture still contained mainly the compounds **9** and the **11**. Our attempts to generate the diketone **10** by Vilsmeier reaction starting from the diamide of naphthalic acid failed. Therefore, despite the low yield, Friedel-Crafts reaction remained the only route for synthesis of the interesting diketone **10**.



	Yield (%) in		
$SnCl_4$ in CCl_4,	**9**	**10**	**11**
3 h at reflux; Recovered naphthalene-1,8 -dicarboxylic acid, 25 %	10	11	32
$AlCl_3$ in CH_2Cl_2, 10 min at 0 ^{0}C; Recovered naphthalene-1,8 -dicarboxylic acid, 12 %	34	traces	51

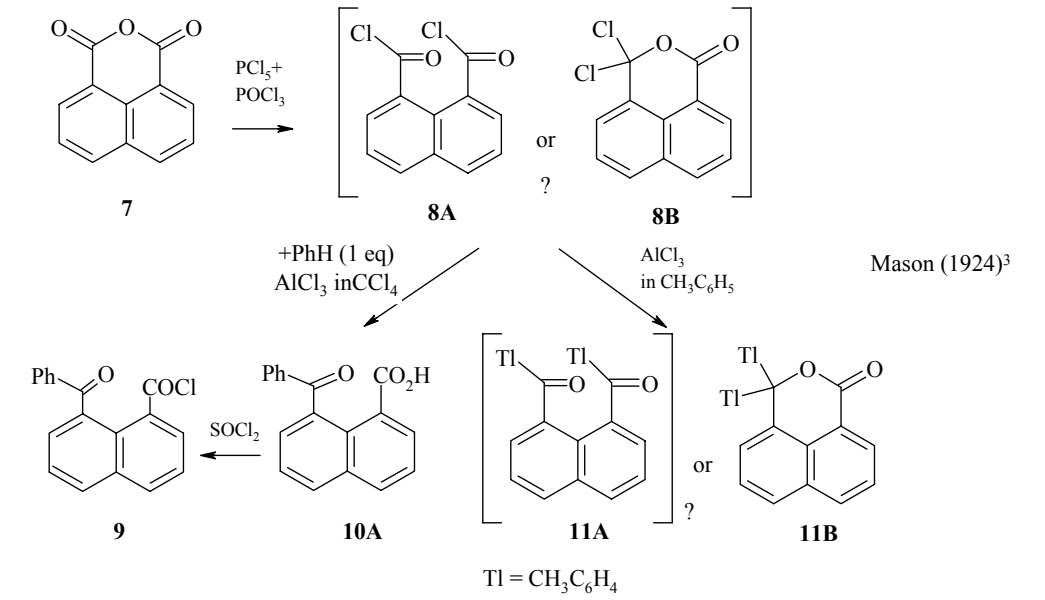
Scheme 2

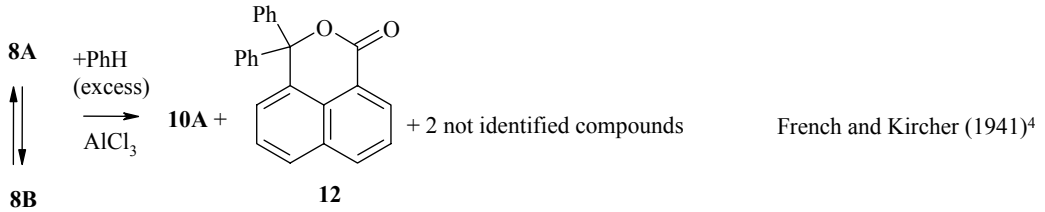
Mechanistic insight in the Friedel-Crafts reaction of phthalic- and naphthalene-1,8-dicarboxylic acids derivatives.

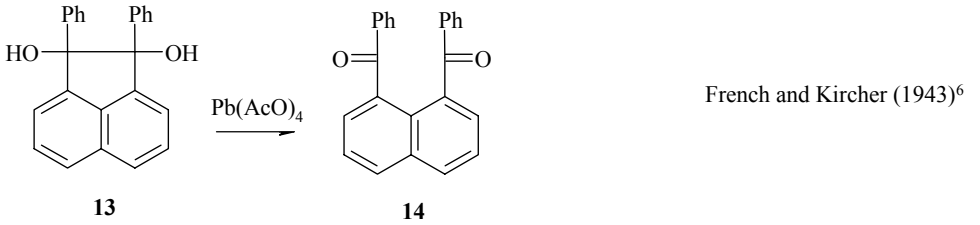
The well-known reaction between aromatic compounds and phthalic anhydride or the corresponding acid dichloride in the presence of Lewis acids results in the formation of phthalide (3,3-diaryl-3H-isobenzofuran-1-one); using more severe reaction conditions an intramolecular cycloacylation was observed. When acid dichloride was the starting compound, 3,3-dichloro-3H-isobenzofuran-1-one was separated as intermediate in the phthalide generation.[2]

The reaction mechanism seems to be more controversial when derivatives of naphthalic acid are used. The Scheme 3 resumes the results found in the literature. Thus, Mason[3] reported that the acid **10** was generated by reaction of dichloride **8** with 1 equivalent of benzene, in the presence of $AlCl_3$ and with an excess of benzene, only tar was obtained. Surprisingly, with toluene in excess the compound **11** was formed. The author was not however able to demonstrate if the last product possesses a cyclic or an open structure. At the

reproduction of this work, French and Kircher[4] obtained together with the acid **10** the lactone **12**[5] and two non-identified products. From the obtained results they postulated that before the reaction, the acid dichloride was isomerized to *gem*-dichloro-lactone. The structure of acid **10** was also a subject of discussions[6,7] because an equilibrium could be established between its open and close structures (an open structure was determined in non-polar solvents).[8] Anyway, until now the only route for generation of the 1,8-diaroylated product (e.g., compound **14**) seems to be the oxidation of corresponding diol.[6]



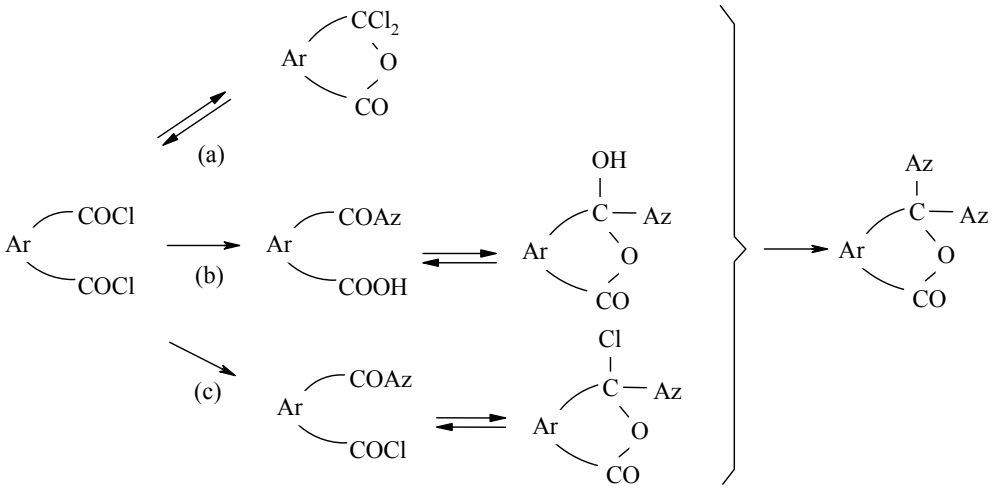




Scheme 3

From the reactions of the same acid derivatives and azulenes we have obtained and unambiguously characterized the azulenyl substituted products similar to those described in the above analyzed papers,

namely, lactones **4**, **9**, diketones **5**, **10** and aroylated acids **6**, **11**. Obviously, the diketones as well as the acids were obtained by the normal electrophilic acylation of azulenes. The lactones however can result on several routes, namely (a) the izomerization of acid dichlorides to dichloro-lactones which react with azulene, (b) the cyclization of aroylated acids to lactols and the subsequent substitution of OH group by azulenes or (c) the cyclization of acid chloride of acylated acids and the substitution of chlorine atom by azulenes. In the aim to discriminate between these possibilities we have separated the obtained aroylated acids **6** and **11** and we have treated them with azulene in the presence of catalysts. Because almost all quantity of starting reagents remained unreacted, a small contribution of route (b) can be considered. Between route (a) and (c) the choice is more complicated. Because no trace of the intermediates formed in route (c) was found along the products[9] we consider that this route is also unimportant. We have thought that the ratio lactone (**4** or **9**) : (diketone and/or aroylated acid) results from the equilibration of closed and open dihalogenated intermediates, route (a). From the high amount of obtained lactones it seems that a reduced time is necessary for the equilibration of dichloro intermediates and also that the reaction of *gem*-dichloro-lactones occurred rapidly. The ring closure occurred more difficultly for naphthalene series due to the enhanced energy required for the closure of the almost co-planar six membered cycle as compared to the energy necessary to generate the five membered cycle. Therefore, while for phthalic dichloride only the strong Lewis acid, $AlCl_3$, generates the open product **5** both Lewis acids are active for naphthalic dichloride.



Scheme 4

Correlation between structural features of compounds and their NMR-spectra.

The equivalence of the protons chemical shifts for the two azulene in phthalide **4a** and **4b** (Table 2) and the values similar to those of unsubstituted azulene, **3a**, show that these moieties conserve sufficient mobility in the molecular structure and are placed rather outside of the phenyl magnetic field. The surprise arises from the ^{1}H-NMR spectrum of the trimethylated compound **4c** where the azulene protons are deshielded comparing with **4a** and **4b** and all signals (each for 2 H) are doubled. For each of doubled signal the two belonging signals are equivalent. Two signals with the same integrals are obtained also for each of the three methyl groups attached to the azulene. That means that the two azulene moieties in **4c** are differently placed towards the phenyl ring due to their forbidden rotation. Another effect of relatively fix and different positions of azulenes in molecule results in the anisotropy of phenyl magnetic field exerted on the azulenes protons. Thus, the difference, which can surpass 1 ppm, between the chemical shifts of the protons at the same position (*e.g.*, 5'-H and 5''-H) indicates the different position for the two azulene groups.

The anisotropy of some azulene protons in the magnetic field of naphthalene can be also signaled for the compound **9**. As shown in Figure 1, at room temperature the azulene ^{1}H-signals at 8-, 2- and 3-positions are broad singlets. With the temperature rise the energy barrier for the rotation around azulene-six membered ring bonds is surpassed and the signals become sharp doublets.

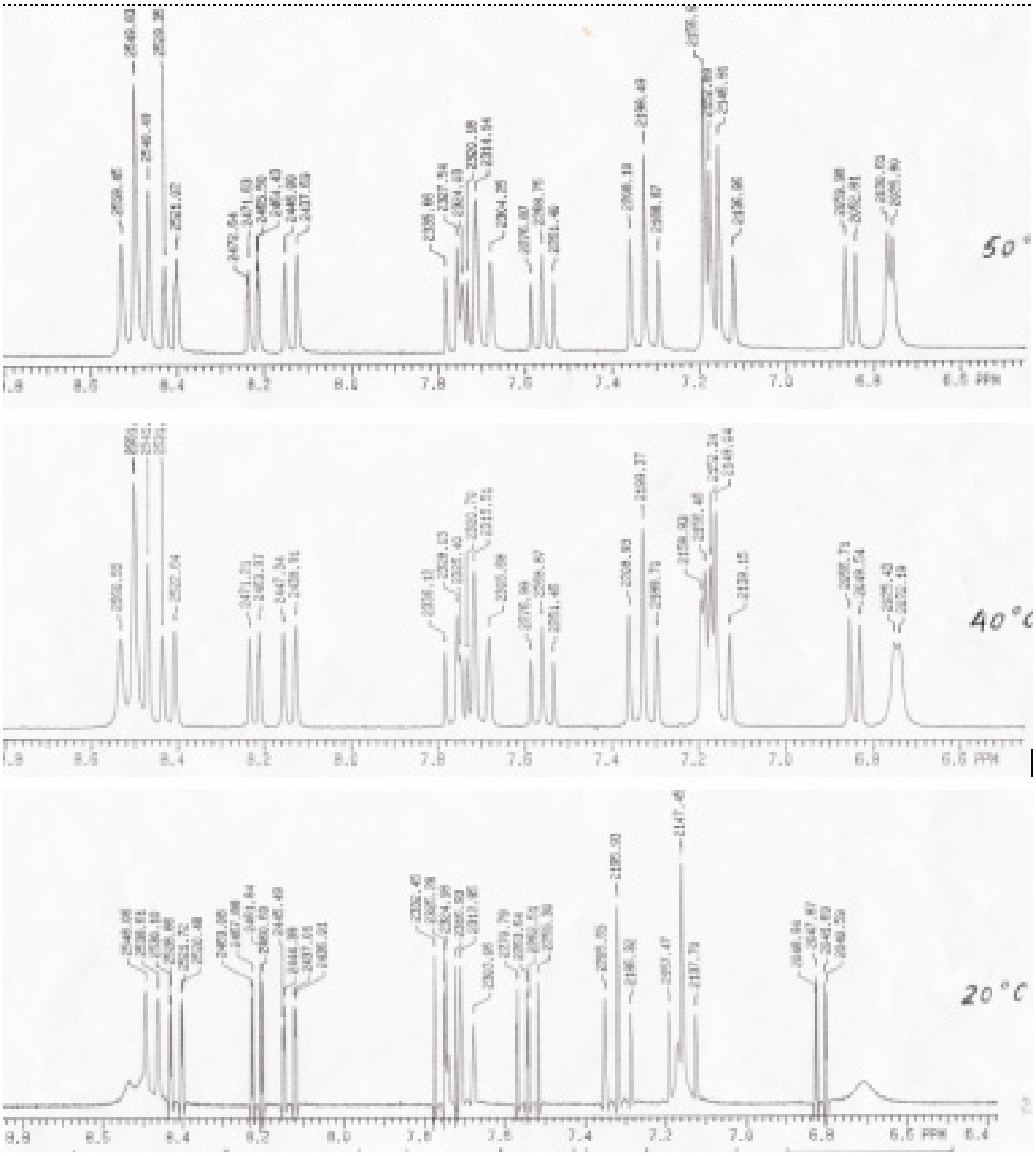


Fig. 1 – ^{1}H-NMR spectra of compound **9** at various temperatures.

As expected, similar chemical shifts of azulene protons for the diketones **5a,** 5c**, 5d** and **10** can be observed; the same is valuable for the azulene protons in acids **6a** and **11** (methyl ester).

The correct assignment of all proton signals for phenyl or mainly naphthyl moieties failed despite the carefully NMR experiments undertaken (COSY, HETCOR or HMBC) because the complex multiplicity and the similar chemical shifts of these protons. The ^{13}C-NMR spectra are presented in the experimental part and for the almost all positions the signal assignments are determined.

In conclusion, despite the rather low yields obtained for diketones, the synthesis starting from acid dichlorides consists the only way to access toward this useful synthones. The obtained lactones are also interesting structures and can be used in valuable technical purposes. Along with these results we have proposed an explanation of the reaction route by which the products are generated. Our investigations show that the used anhydrides are inert or with very low reactivity.

Table 2

^{1}H-Chemical shifts for the azulene protons, (at 25 ^{0}C, in $CDCl_3$, δ in ppm)

Comp.	Protons position						
	2'(2")	4'(4")	8'(8")	6'(6")	3'(3")	5'(5")	7'(7")
3a	7.81	8.23	8.23	7.45	7.30	7.07	7.07
4a	7.70	8.17	8.33	7.52	7.26	7.16	6.92
4b	7.46	7.96	8.12	7.35	-	6.97	6.71
4c[a]	6.90 and 7.20	-	-	-	6.28 and 6.20	5.52 and 6.55	6.65 and 7.02
5a	7.89	8.24	9.12	7.55	7.13	7.26	7.19
5c	7.50	-	-	-	7.03	7.07	7.17
5d	7.48	8.14	-	7.41	-	-	7.56
6a	7.57	8.60	9.73	7.96	7.23	7.59	7.67
9[b]	7.18	8.50 and 8.48[b]		7.71	6.74	7.32 and 7.15[b]	
10	7.42	8.09	9.37	7.45	6.85	7.15	7.20
11[d]	8.12	8.53	9.88	7.87	7.31	7.54	7.65

[a] All the azulene signals are doubled; the integral ratio between the protons of two signal series = 1. [b]The spectrum was recorded at 40 ^{0}C in DMSO-d_6. [c]The unequivocal signal attributions failed. [d]Characterized as methyl ester.

EXPERIMENTAL PART

Melting points: Kofler apparatus (Reichert Austria). Elemental analyses: Perkin Elmer CHN 240B. ^{1}H- and ^{13}C-NMR: Bruker Avance DRX4 (^{1}H: 400 MHz, ^{13}C: 100.62 MHz) and Gemini 300 (^{1}H: 300 MHz, ^{13}C: 75.47 MHz), *J* values are given in Hz, TMS was used as internal standard in $CDCl_3$ or DMSO-d_6 as solvent; COSY and HETCOR correlation experiments were used for the structure assignment. Mass spectra: JEOL JMS-DX303 spectrometer coupled to analytical gas-chromatograph Shimadzu GC-14B with a DB-1 capillary column and C-R6A integrator and Finnigan MAT 311-A/100 MS; for the spectra recording in solid state Carlo Erba QMD 1000 (EI+, 70 eV) device was used. Column chromatography: basic alumina (BII-III). All eluted solutions were filtered before concentration. The DCM (DCM) was distilled over calcium hydride and ethyl acetate over anhydrous sodium carbonate. The numbering for the positions in the below characterized compounds were presented in Scheme 1 and 2. The nomenclature was obtained by use of the ACD/I-Lab web service (ACD/IUPAC Name Free 7.06).

General procedure for the reaction with $SnCl_4$. To a stirred mixture of azulene (1.2 mmol) and acid dichloride (0.6 mmol) in CCl_4 (90 mL), protected against air humidity, $SnCl_4$ (1 mL) was added. Then the mixture was refluxed the time indicated in the Scheme 2 and 3, was cooled and poured in an aqueous saturated solution of ammonium chloride. The organic layer was separated and the aqueous solution was extracted once with ethyl acetate. The organic extracts were washed twice with water, and dried on Na_2SO_4. The solvent was removed in vacuum and the residue was separated on alumina with a mixture of DCM and ethyl acetate as eluent (with gradient in ester till pure ester). Generally, the first eluted fraction was the unreacted azulene, followed by cyclic diazulenyl derivatives and finally by diketones. When the reaction mixture contained the acidic compound, this compound was eluted only with ethyl acetate and long time after the other products. The obtained results are shown in Scheme 2 and 3.

General procedure for the reaction with $AlCl_3$. To a mixture of azulene (2.0 mmol) and acid dichloride (1.0 mmol) in DCM (50 mL), protected against air humidity, stirred and cooled at 0 ^{0}C, $AlCl_3$ (294 mg, 2.2 mmol) was added and the stirring and cooling was maintained for the time showed in Schemes 2 and 3. When acid dichloride was added on the mixture of the other starting materials in DCM, the yield in products was lower despite the small amount of recovered azulenes. The same work-up as above was also used for this reaction mixture. The results are reported in Schemes 2 and 3.

Products characterization. For the compounds **4a,b, 5a,c,d** and **10** the chemical shifts of the two azulene-1-yl groups are identically (namely, δ for 2' ≡ δ for 2" etc.). The spectra were recorded at room temperature in $CDCl_3$ excepting for the compound **9** which was dissolved in DMSO-d_6 and the sample temperature was 40 ^{0}C.

3,3-Di-azulen-1-yl-3H-isobenzofuran-1-one, ***4a***. Brown powder, m.p. 212-213 °C; ^{1}H NMR δ 6.92 (t, *J* = 9.8 and 9.4 Hz, 2H, 7'-H), 7.16 (t, *J* = 9.7 Hz, 2H, 5'H), 7.26 (d, *J* = 4.0 Hz, 2H, 3'H), 7.52 (t, *J* = 9.9 and 9.4 Hz, 2H, 6'H), 7.52-7.56 (m, 1H, 4-H), 7.59-7.65 (m, 2H, 5-, 6-H), 7.70 (d, *J* = 4.0 Hz, 2H, 2'-H), 8.00 (d, *J* = 7.5 Hz, 1H, 7-H), 8.17 (d, *J* = 9.8 Hz, 2H, 4'-H), 8.33 (d, *J* =9.6 Hz, 2H, 8'H), ^{13}C NMR δ 90.1 (C-Az), 116.19 (C-3'), 123.80+123.78 (C-5' + C-7'), 123.88 (C-6), 125.34 (C-3a), 126.00 (C-7), 127.94 (C-1'), 129.01 (C-4), 133.83 (C-5, -6), 135.99 (C-8'a), 136.29 (C-4'), 136.65 (C-2'), 137.78 (C-8'), 138.18 (C-6'), 142.58 (C-3'a), 154.23 (C-7a), 170.69 (C-1); ; *m/z*: 387 (100 %) [M+1], 388 (38 %) [M+2]. Anal. Calcd. for $C_{28}H_{18}O_2$: C, 87.02; H, 4.69. Found: C, 86.83; H, 4.80.

3,3-Di-(3-methylazulen-1-yl)-3H-isobenzofuran-1-one, ***4b***. Brown powder, decomp. above 300 °C; ^{1}H NMR δ 2.50 (s, 3H, C*H*$_3$), 6.71 (t, *J* = 10.0 Hz, 2H, 7'-H), 6.97 (t, *J* = 9.6 Hz, 2H, 5'-H), 7.35 (t, *J* = 9.6 and 10.0 Hz, 2H, 6'-H), 7.42-7.48 (m, 1H, 6-H), 7.46 (s, 2H, 2'-H), 7.52-7.58 (m, 2H, 4-, 5-H), 7.90 (d, *J* = 7.6 Hz, 1H, 7-H), 7.96 (d, *J* = 9.6 Hz, 2H, 4'-H), 8.12 (d, *J* = 9.6 Hz, 2H, 8'-H), ^{13}C NMR δ 12.63 (*C*H$_3$), 90.14 (C-Az), 122.21 (C-5'), 122.93 (C-7'), 123.74 (C-4 or -5), 123.98 (q), 125.25 (q), 125.95 (C-7), 126.20 (q), 128.92 (C-2'), 133.78 (C-5 or -4), 134.54 (C-8'), 135.71 (C-4'), 136.09 (q), 137.71 (C-6), 138.00 (C-6'), 138.66 (q), 154.38 (q), 170.72 (C-1); *m/z*: 415 (100 %) [M+1], 416 (19 %) [M+2]. Anal. Calcd. for $C_{30}H_{22}O_2$: C, 86.93; H, 5.35. Found: C, 86.85; H, 5.42.

3,3-Di-(4,6,8-trimethylazulen-1-yl)-3H-isobenzofuran-1-one, ***4c***. Brown powder, decomp. above 300 °C; ^{1}H NMR δ 1.03, 1.28, 2.23, 2.36, 2.63 and 2.80 (6 s, each for 3H, 6xC*H*$_3$), 5.52, 6.55, 6.65 and 7.02 (4 s, each for 1H, 5'-, 5"-, 7'H and 7"), 6.28 and 6.72 (2d, *J* = 5.2 Hz, each for 1H, 2'-, 3'-H), 6.90 and 7.20 (2d, *J* = 4.6 Hz, each for 1H, 2"-, 3"-H), 7.47 (td, *J* = 7.6 and 1.2, 1H, H-6), 7.49 (d, J = 8.0, 1H, H-4), 7.66 (td, J = 7.5 and 1.2 Hz, 1H, H-5), 8.05 (dd, *J* = 7.6 and 1.2 Hz, 1H, H-7), *m/z*: 471 (100 %) [M+1], 472 (10 %) [M+2]. Anal. Calcd. for $C_{34}H_{30}O_2$: C, 86.77; H, 6.43. Found: C, 86.60; H, 6.20.

[2-(Azulene-1-carbonyl)-phenyl]-azulen-1-yl-methanone, ***5a***. Brown powder, m.p. 148-150 ^{o}C; ^{1}H NMR δ 7.13 (d, *J* = 4.1 Hz, 2H, 3'-H), 7.19 (t, *J* = 10.0 and 9.6 Hz, 2H, 7'-H), 7.26 (t, *J* = 10.0 Hz, 2H, 5'-H), 7.55 (t, *J* = 10.0; 9.6 Hz, 2H, 6'-H), 7.59-7.65 (m, 2H, 4-H and 5-H), 7.72-7.77 (m, 2H, 3-H and 6-H), 7.89 (d, *J* = 4.4 Hz, 2H, 2'-H), 8.24 (d, *J* = 9.6 Hz, 2H, 4'-H), 9.12 (d, *J* = 9.6 Hz, 2H, 8'-H), ^{13}C NMR δ 117.75 (C-3'), 126.56 (q), 127.13 (C-7'), 128.82 (C-5'), 128.98 (C-3 and C-6), 129.69 (C-4 and C-5), 138.11 (C-4'), 138.82 (C-8'), 138.98 (C-6'), 140.42 (q), 142.18 (C-2'), 142.61 (q), 145.40 (q), 192.99 (C=O); *m/z*: 387 (100 %) [M+1], 388 (22 %) [M+2]. Anal. Calcd. for $C_{28}H_{18}O_2$: C, 87.02; H, 4.69. Found: C, 87.25; H, 4.44.

[2-(4,6,8-Trimethylazulene-1-carbonyl)-phenyl]-(4,6,8-trimethylazulen-1-yl)-methanone, ***5c***. Brown powder, m.p. 242-247 ^{o}C; ^{1}H NMR δ 2.32 (C_4- or C_6-C*H*$_3$), 2.54 (C_6- or C_4-C*H*$_3$), 2.80 (C_8-C*H*$_3$), 7.03 (d, *J* = 4.4 Hz, 2H, 3'H), 7.07 (t, *J* = 9.6 Hz, 2H, 5'-H), 7.17 (t, *J* = 9.6 Hz, 2H, 7'-H), 7.50 (d, *J* = 4.4 Hz, 2H, 2'-H), 7.56-7.61 (m, 2H, 4-, 5-H), 7.72- 7.77 (m, 2H, 3-, 6-H), ^{13}C NMR δ 25.81 (*C*H$_3$), 28.08 (*C*H$_3$), 28.26 (*C*H$_3$), 114.67 (C-3'), 129.94 and 129.98 (4 C_{phenyl}), 130.54 (q), 130.77 (C-7'), 132.77 (C-5'), 135.55 (q), 140.57 (C-2'), 141.93 (q), 143.02 (q), 146.72 (q), 147.24 (q), 151.16 (q),; *m/z*: 471 (100 %) [M+1], 472 (32 %) [M+2]. Anal. Calcd. for $C_{34}H_{30}O_2$: C, 86.77; H, 6.43. Found: C, 86.64; H, 6.56.

[2-(5-iso-Propyl-3,8-dimethylazulene-1-carbonyl)-phenyl]-azulen-1-yl-methanone, ***5d***. Brown powder, m.p. 217-220 ^{o}C; ^{1}H NMR δ 1.32 (d, 12H, *J* = 6.8 Hz, C*H*$_3$-*i*Pr), 2.28 (s, 6H, 3'-C*H*$_3$), 2.47 (s, 6H, 8'-C*H*$_3$), 3.06 (m, 2H, *J* = 6.8 Hz, C*H*-*i*Pr), 7.41 (dd, 2H, *J* = 10.9 and 2 Hz, 6'-H), 7.48 (s, 2H, 2'-H), 7.56 (d, 2H, *J* = 10.8 Hz, 7'-H), 7.57-7.63 (m, 2H, 4-, 5-H), 7.71-7.77 (m, 2H, 3-, 6-H), ^{13}C NMR δ 12.70 (8'-*C*H$_3$), 24.47 (*i*Pr *C*H$_3$), 27.23 (3'-*C*H$_3$), 37.93 (*i*Pr *C*H), 123.91 (q), 127.08 (q), 129.70 and 129.84 (C_{phenyl}), 132.02 (C-7'), 134.03 (C-4'), 135.94 (C-6'), 137.15 (q), 141.86 (q), 143.15 (q), 143.33 (C-2'), 144.72 (q), 149.85 (q), 191.98 (C=O).; *m/z*: 527 (100 %) [M+1], 528 (25 %) [M+2]. Anal. Calcd. for $C_{38}H_{38}O_2$: C, 86.65; H, 7.27. Found: C, 86.62; H, 6.22.

2-(Azulene-1-carbonyl)-benzoic acid, ***6a***. Brown powder, m.p. 251-254 ^{o}C; ^{1}H NMR δ 7.18-7.24 (m, 1H, 4-H), 7.23 (d, *J* = 4.0 Hz, 1H, 3'-H), 7.40-7.48 (m, 2H, 3- and, 5-H), 7.57 (d, *J* = 4.0 Hz, 1H, 2'-H), 7.59 (t, *J* = 10.0 Hz, 1H, 5'-H), 7.67 (t, *J* = 10.0 Hz, 1H, 7'-H), 7.96 (t, *J* = 10.0 Hz, 1H, 6'-H), 7.97-8.03 (m, 2H, 1- and 2-H), 8.60 (d, *J* = 9.6 Hz, 1H, 4'-H), 9.73 (d, *J* = 10.0 Hz, 1H, 8'-H), ^{13}C NMR δ 117.23 (C-3'), 125.69 (C-4), 125.94 (q), 127.18 (C-3), 127.53 (C-5'), 128.19 (C-7'), 128.74 (C-5), 129.62 (C-2), 136.77 (q), 138.19 (C-8'), 138.61 (C-4'), 138.76 (q), 139.62 (C-6'), 141.70 (C-2'), 143.41 (q), 144.18 (q), 170.86 (CO_2), 194.63 (C=O).; *m/z*: 277 (100 %) [M+1]. Anal. Calcd. for $C_{18}H_{12}O_3$: C, 78.25; H, 4.38. Found: C, 78.62; H, 4.70.

3,3 Di-azule-1-yl-3H-benzo[de]isochromen-1-one, ***9***. Brown powder, m.p. 251-253 ^{o}C; ^{1}H NMR δ 6.74 (d, *J* = 4.1 Hz, 2H, H-3', -3''), 6.84 (dd, *J* = 8.3 and 1.0 Hz, 1H, 4-H), 7.15 (t, *J* = 9.8 Hz, 2H, 7'-, 7''-H or 5'-, 5''-H), 7.18 (d, *J* = 4.2 Hz, 2H, 2'-, 2''- H), 7.32 (t, *J* = 9.7 Hz, 2H, 5'-, 5''- H or 7'-,7''-H), 7.56 (dd, *J* = 7.2 and 8.3 Hz, 1H, 5-H), 7.71 (t, *J* = 9.8 Hz, 2H, 6'-, 6''-H), 7.75 (dd, *J* = 7.2 and 8.3 Hz, 1H, 8-H), 8.14 (dd, *J* = 8.4 and 1.1 Hz, 1H, 6-H), 8.22 (dd, *J* = 8.5 and 1.2 Hz, 1H, 7-H), 8.42 (dd, *J* = 8.3 and 1.2 Hz, 1H, 9-H), 8.48 (d, *J* = 9.5 Hz, 2H, 4'-, 4''-H or 8'-, 8''- H), 8.50 (d, *J* = 9.8 Hz, 2H, 8'-, -8''-H or 4'-, -4''-H), ^{13}C NMR δ 88.17 q (C-3), 115.58 (C-2', -2''),[10] 121.06 q (C-9a), 123.74 (C-7',-7'' or C-5', -5''), 124.39 (C-5', -5'' or C-7', -7''), 125.62 (C-4), 126.48 (C-5), 126.57 (C-8), 127.89 (C-6), 128.00 q (C-9b), 128.97 (C-7), 132.14 (C-6a), 134.35 (C-9), 135.18 q (C-3'a and -8'a), 135.95 q (C-3a), 137.18 (C-4', -4''or C-8', -8''), 138.29 (C-8', -8'' or C-4', -4''),, 138.73 (C-6', -6''), 142.00 (C-1', -1''), 164.53 q (C-1). Anal. Calcd. for $C_{32}H_{20}O_2$: C, 88.05; H, 4.62. Found: C, 87.85; H, 4.76.

[8-(Azulene-1-carbonyl)-naphthyl]-azulen-1-yl-methanone, ***10***. Brown powder, decomp. at storage; ^{1}H NMR δ 6.85 (d, *J* = 4.0 Hz, 2H, 3'-H), 7.15 (t, *J* = 10.0 Hz, 2H, 7'-H), 7.17, (t, *J* = 10.0 Hz, 2H, 5'-H), 7.42 (d, *J* = 4.0 Hz, 2H, 2'-H), 7.45 (t, *J* = 10.0 Hz, 2H, 6'-H), 7.60 (dd, *J* = 7.8 and 6.8 Hz, 2H, 3- and 6-H), 7.68 (dd, *J* = 6.8 and 1.6 Hz, 2H, 4- and 5-H), 8.05 (dd, *J* = 8.4 and 1.6 Hz, 2H, 2- and 7-H), 8.09 (d, *J* = 9.6 Hz, 2H, 4'-H), 9.37 (d, *J* = 9.6 Hz, 2H, 8'-H),^{13}C NMR δ 117. 20 (C-3'), 124.97 (C-3 and -6), 125.39 (C-1'), 126.94 (C-5'), 128.72 (C-8a), 128.84 (C-4 and-5), 128.87 (C-7'), 130.79 (C-2 and-7), 134.54 (C-4a), 137.56 (C-4'), 138.49 (C-6'), 139.19 (C-8'), 140.16 (C-1 and-8), 140.54 (C-8'a), 142.67 (C-2'), 144.79 (C-3'a), 192.97 (C=O), *m/z* . Anal. Calcd. for $C_{32}H_{20}O_2$: C, 88.05; H, 4.62. Found: C, 88.35; H, 4.26.

8-(Azulene-1-carbonyl)-naphthoic acid, **11**. In NMR spectra of acid **11** several signals are present as unresolved multiplets. Therefore we have characterized this acid as *methyl ester*. The ester was ordinary obtained from the acid with ethereal solution of diazomethane. Brown powder, m.p. 212-213 ^{o}C; ^{1}H-NMR (400 MHz. $CDCl_3$) δ: 3.18 (s, 3H, CH_3) 7.31 (d, *J* = 4.2 Hz, 1H, 3'-H), 7.54 and 7.56 (t, *J* = 8 Hz and 7.2 Hz, 2H, 6-H and 3-H), 7.54 (t, *J* = 9.6 Hz, 1H, 5'-H), 7.65 (t, *J* = 10 Hz, 1H, 7'- H), 7.77 (d, *J* = 6.4 Hz, 1H, 5-H), 7.87 (t, *J* = 9.8 Hz, 1H, 6'-H), 7.92 (d, *J* = 7.2 Hz, 1H, 4-H), 8.00 (d, *J* = 8.0 Hz, 1H, 7-H), 8.05 (d, *J* = 8.4 Hz, 1H, 2-H), 8.12 (d, *J* = 4 Hz, 1H, 2'-H), 8.53 (d, *J* = 9.6 Hz, 1H, 4'-H), 9.88 (d, *J* = 10.00 Hz, 1H, 8'-H); ^{13}C-NMR ($CDCl_3$) δ: 51.32 (CH_3), 117.90 (C-3'), 124.94 (C-3 or -6), 125.26 (C-6 or -3), 125.27 (q), 127.67 (C-5'), 127.97 (q), 129.27 (C-7'), 129.90 (C-4 or C-5), 129.97 (C-5 or C-4), 130.37 (q), 131.06 (C-7), 132.37 (C-2), 134.60 (q), 138.60 (C-4'), 139.34 (C-6'), 139.49 (q), 139.53 (C-8'), 141.57 (q), 142.85 (C-2'), 145.62 (q), 169.45 (CO_2), 193.44 (C=O). Anal. Calcd. for $C_{23}H_{16}O_3$: C, 81.16; H. 4.74. Found: C, 81.01; H, 4.81.

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