Azulene-1-azo-2'-thiazoles.[a] Synthesis and Properties

Alexandru C. Razus,[b] Liviu Birzan, Stefania Nae, Mirela Nina Surugiu and Valentin Cimpeanu

Institute of Organic Chemistry, Spl. Independentei 202B, P.O. Box 15-254
060032-Bucharest, Romania
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Several derivatives belonging to a new compound class, namely azulene-1-azo-2'-thiazoles, were prepared by the diazotization of 2-aminothiazoles in the presence of HNO_3/H_3PO_4 followed by the coupling of diazonium salts with azulenes in buffered medium. The reactions proved to be general for this class, the yields are, however, considerably influenced by the substituents at thiazole moiety. For the first time a *N*-oxide provided from an amino substituted five-member nitrogenous heterocycle was diazotized and coupled. The structure of the obtained compounds was assigned and their physico-chemical properties were discussed. The new azulene azo derivatives exhibit a strong bathochromic shift in UV-Vis due to the intense push-pull effect of aromatic system and to the intrinsic properties of thiazole moiety.

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Introduction.

As a part of our continuing interest in the study of synthesis and properties of azulene-1-azoaromatics we have recently investigated the azulene-1-azopyridines derivatives, **1** [1]. Besides the interesting structure and properties of such compounds, it was anticipated that they possess high β hyperpolarizability [2] therefore they can be attractive in the development of various technical fields as dyes and pigments and in the display, storage or transmission of information. Another applicability of azulene-1-azopyridines can be found in electrochemistry, for the generation of an electrically conducting polymer film at the electrode surface [3].

Az-N=N-Py

1

Az = unsubstituted or substituted azulen-1-yl
Py = 2-, 3- or 4 piridyl group, unsubstituted or N-substituted

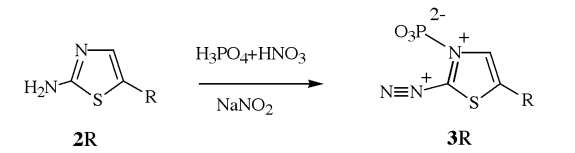
The similarity between the electronic distributions over the pyridine and thiazole systems prompted us to investigate the synthesis and some chemical and optical properties of the new class of azulene-1-azo-2'-thiazole derivatives. Other arguments for our study were the theoretical [4] and experimental works [5,6] which revealed the high β hyperpolarizability for 2-vinyl or 2-azo-thiazoles substituted with NO_2 at C-5.

Synthesis of Azulen-1-azo-2'-thiazoles and their 3'-Oxo derivatives.

A. Azulen-1-azo-2'-thiazoles.

For our study we have chosen the 2-azothiazole derivatives unsubstituted or with different substituents at 5 position provided from stable and accessible corresponding 2-aminothiazoles. Due to increased thiazole stability induced by the phenyl substituted at C-4 these derivatives were also included in this study.

Scheme 1



R	H	Cl	Br	CO_2CH_3	NO_2	SCN	SO_3H	$pCH_3C_6H_4N_2$
recovered **4** (%)	0	3	36	20	32	46	0	-
yield in **5**R (%)	90	88	98	96	67	53	80	5

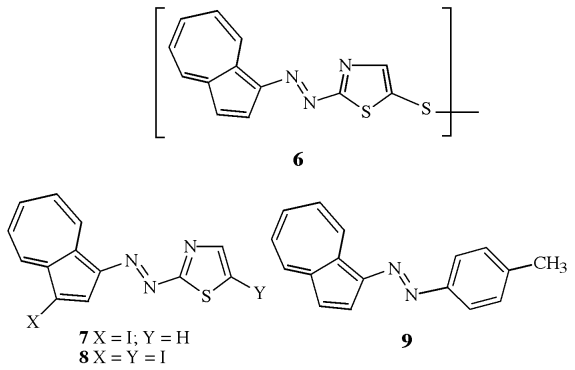
Although the first thiazolamines diazotization followed by azo coupling was already reported in the 19th century [7], some difficulties arose from the low basicity of the thiazolamines or from the possible diazotization reversibility in thermodynamic conditions followed by the nitrosation of coupling substrate [8] (azulene in our case). Therefore, we tried to generate the azulene-1-azo-2'-thiazoles in a similar way as for the corresponding pyridine derivatives [1a].

The diazotization was carried out in a mixture of phosphoric and nitric acids using solid sodium nitrite and the coupling with azulenes was performed in methanol (potassium acetate was used as buffer for a pH about 4-5) (Scheme 1). When groups with small inductive or electromer effect (*e.g.* halogen) were substituted at C-5 in 2-aminothiazoles, the yield in azo product was almost quantitative (Scheme 1); the yield was lower for the strong electron withdrawing functions (*e.g.* NO_2 or SCN). Starting from the **2**SCN, together with the normal coupled azo derivative **5**SCN, disulfide **6** (Scheme 2) resulted in lower yield as a by-product [9]. Using the azo compounds **4***p*$CH_3C_6H_4N_2$, the double coupled compound

5*p*$CH_3C_6H_4N_2$ was obtained in reduced yield together with traces of azo derivative **9**.

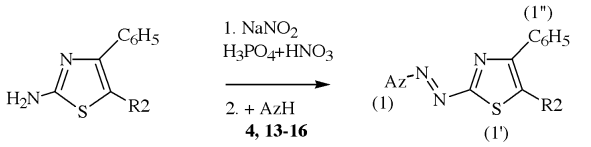
The reaction of the diazonium salt **3I** with azulene does not afford the normal azo products as, for example, in the coupling with phenols [10]; three other products were separated and identified, namely, 1-iodoazulene, **10I** (Scheme 4), 1,3-diiodoazulene [11] and the iodinated azo derivative **7**, in 80 %, 15 % and <5 % yields, respectively (Scheme 2).

Scheme 2



In the attempt to synthesize **5I**, 2-aminothiazole was chloromercuriated at C-5, then diazotised and coupled with azulene. The obtained crude product was treated with iodine in excess for the substitution of HgCl group. Even in this case the compound **5I** was not formed and only the iodo derivatives **7** and **8** were obtained [12].

Scheme 3

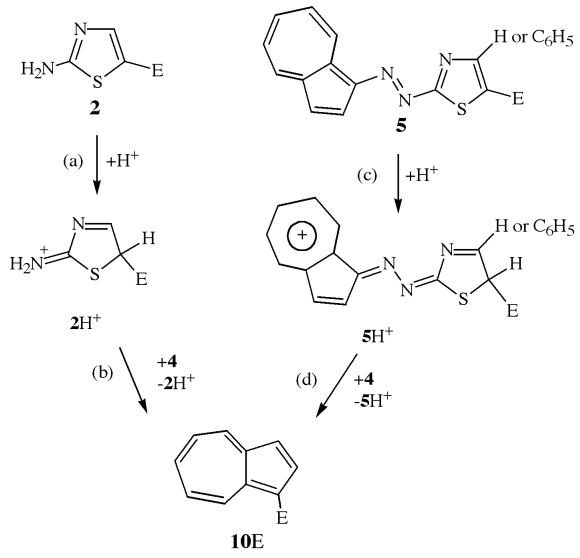


Az	Recovered azulene, %	Yield in products (R2 = H) starting from **11**, %
azulen-1-yl	**4**, 46	**17**, 77
4,8-diMe azulen-1-yl	**13**, 52	**18**, 35
3-t Bu azulen-1-yl	**14**,* 30	**19**, 20
4,6,8-triMe-azulen-1-yl	**15**, 43	**20**, 30
3,8-diMe-5-i-Pr azulen-1-y	**16**, 33	**21**, 36

*__14__ = 1,3-di *tert*-butilazulene

The reaction of 4-phenyl substituted thiazolamine **11** with nitrous acid generally occurs with nitrozation at C-5 [13]. The cyclic nitrogen phosphorylation in a strong acidic medium (as in Scheme 1 for compound **3**R) lowers the electron density at the nucleus directing the NO^+ attack towards the amino group [14] therefore, under the conditions we used, the yields of azo compounds were fairly good

Scheme 4



(Scheme 3). The conversion and the yield of diazotization and coupling are dramatically lower for alkylated azulenes as compared to unsubstituted azulene, possibly, due to the steric influence and to the low stability of some alkylazulenes (*e.g.* guajazulene, **16**).

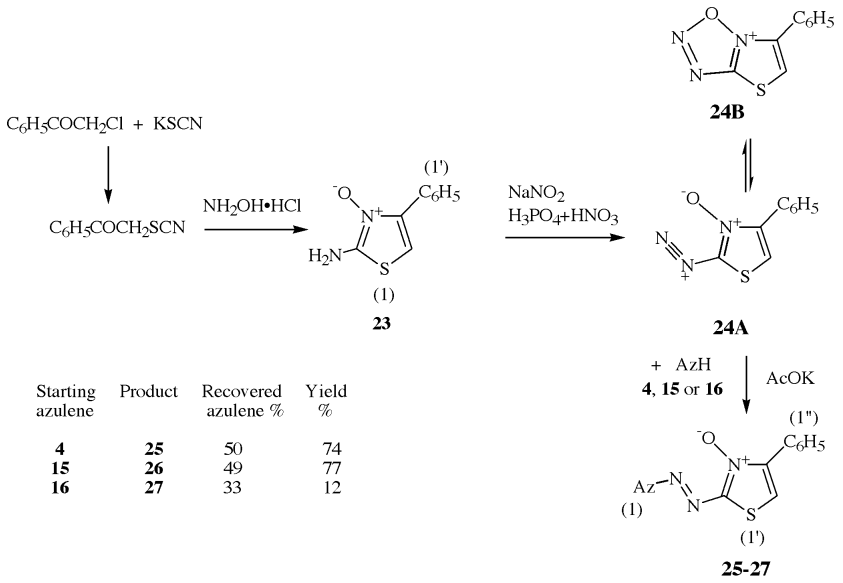
Our attempt to obtain the double coupled thiazole **22** through tandem diazotization of **12** and coupling with azulene, the transfer of a very good electrophilic leaving group, *p*-tolylazo, from the 5-position with the higher electron density in thiazole toward the nucleophilic1-position in azulene was observed. The generation of azo azulene, **9** [15] (8 %), and of the compound without substituent at C-5 in thiazole, **17** (15 %), together with the product **22** (5 %), attest this transfer. There are not arguments to differentiate between the intermolecular (a + b in Scheme 4) or intramolecular route (c + d) of this transfer. The presence of compound **9** at the generation of **5***p*$CH_3C_6H_4N_2$ from the corresponding amine as well as the presence of the iodinated azulenes at the reaction of **2I** can be considered as indications of the generality of this transfer ability.

B. Azulene-1-azo-2'-(3'-oxy-4'-phenylthiazoles).

To the best of our knowledge, no five-atom nitrogenous heterocyclic amine has been diazotized and azo coupled when the cyclic nitrogen was bounded up with oxygen as *N*-oxide. Indeed, although 1-oxy-(aminopyridines) are easily diazotized and coupled in aqueous hydrochloric solutions [1c], only tar is obtained with 3-oxy-2-aminothiazoles. Unlike pyridine *N*-oxides, 3-oxy-2-aminothiazoles are acid sensitive and have a high water solubility that creates difficulties for their synthesis [16] and for use in diazotization + coupling reactions.

The above-mentioned inconveniences were avoided by using a more stable and soluble compound in organic media,

Scheme 5



Starting azulene	Product	Recovered azulene %	Yield %
4	**25**	50	74
15	**26**	49	77
16	**27**	33	12

such as 2-amino-3-oxy-4-phenylthiazole, (Scheme 5) **23** [17].

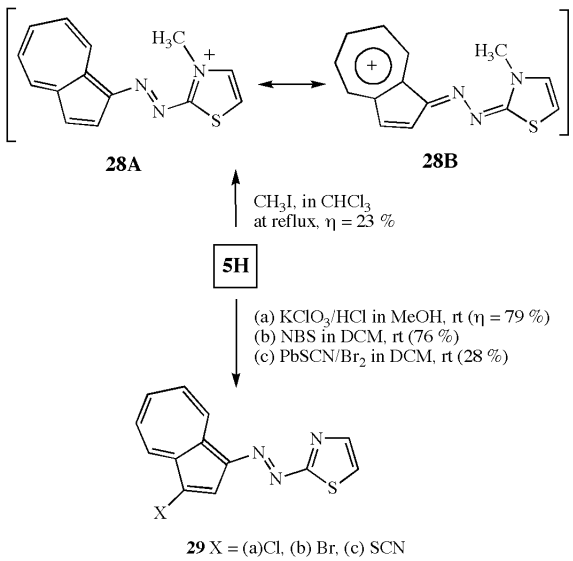
Although compound **23** cannot be diazotized and coupled with azulenes in aqueous media, the reaction occurs in a mixture of concentrated phosphoric and nitric acid. It is possible that the high reaction rate in strong acidic medium hinders the extensive destruction of amine before diazotization. It is puzzling that the yellow-brown color of the diazonium salt solution turns white after a short time, however, the coupling capacity remains unaltered. An explanation for this behavior could be the reversible ring closing of diazonium salt, **24A** to the intermediate **24B** (Scheme 5) [18]. The obtained blue-violet colored azo derivatives **25** – **27** are stable at room temperature. The comparison between the yields of the diazotization and coupling of the aminothiazole and their corresponding 3-oxide is, generally, in favor of the *N*-oxide. This described tandem diazotization + coupling represents the first known example, which starts from five-atom nitrogenous heterocyclic amine with N-oxy group at the ring, opening a way for the generation of other derivatives with interesting properties.

Reactions of Azulene-1-azo-2'-thiazoles.

Based on computational studies [19,20], for 2-substituted thiazole derivatives, the nitrogen is expected to possess the highest negative charge, the next reactive position being at C-5. At the same time, it is known that the azulene moiety is very reactive in orbital controlled reactions due to the presence of a high energy HOMO. Thus, it is expected that hard electrophiles, able to form strong bonds with nitrogen atoms (*e.g.* CH_3I), will react at the thiazolic nitrogen. In contrast, soft electrophiles, without affinity for nitrogen (*e.g.* Br_2) should react at the azulene moiety, although in the last case substitution at C-5 cannot be *a priori* ruled out. The reactions of azulene-1-azo-2'-thiazoles reported here, namely, alkylation with methyl iodide, bromination, chlorination and the reaction with lead thiocyanate, evolve in good agreement with the theoretical anticipation.

The *N*-alkylation of thiazole derivatives, yielding stable compounds that can be used as dyes, is well known [21] however the reported reaction conditions are too severe for the azulene moiety and the characterization and the yields of the products are often absent. To avoid the destruction of azulene moiety during the methylation we used methyl iodide in chloroform at reflux

Scheme 6



(Scheme 6). Even in these conditions, the alkylation of thiazole derivatives took place with lower conversions and yields than those for the corresponding azulene-1-azopyridines. The stability of the C-N bond is sufficiently high [22] to ensure the conservation of the obtained kinetic product by avoiding the rearrangements.

As expected, bromination with *N*-bromosuccinimide, chlorination with a mixture of $KClO_3$/HCl and the reaction with lead thiocyanate take place in good yields at C-3 of azulene moiety (Scheme 6). If the reactant is in excess, subsequent attack to the C-5 in thiazole can also occur, confirming the reactivity sequence of these two positions.

The tendency of azulenes to form a complex with iodine hinders the direct iodination. Therefore the azo compound was halo-mercurated with mercury acetate followed by *in situ* iodine treatment with the generation of mono- and diiodinated compounds, **7** and **8**.

Optical Properties of Azo-thiazols.

From the heterocycle possesing azo compounds, the highest bathochromic effect was reported for the 2-azo thiazoles because “both more excited-state stabilization and less ground-state stabilization participate in the bathochromism of 2-thiazolylazo (as well as of thienylazo) dyes" [23]. As the presence of 1-azulenyl moiety in azo derivatives produces a bathochromic shift in main visible band [24] as well, a dramatic bathochromic effect for the azulene-1-azo-2'-thiazols is expected. Indeed, Table 1 shows a strong shift for azo thiazole, which surpasses with 35 nm and 20 nm the values for the corresponding phenyl- and 4-pyridyl-substituted compounds.

Table 1

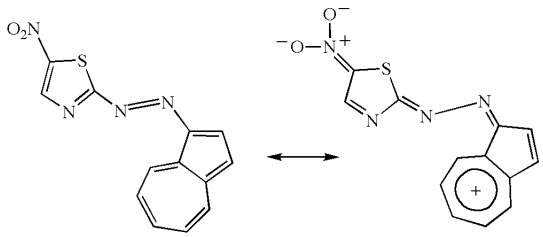
λ_{max} of the Main Visible Band for Azulene-1-azo Aromatics in Cyclohexane

Compound	$\Delta\lambda_{max}$(nm)/logε ($dm^3mol^{-1}cm^{-1}$)
Azulene-1-azobenzene	415/4.30
Azulene-1-azo-4’-pyridine	429/4.39
Azulene-1-azo-2’-thiazole	450/4.42

The bathochromic effect is even larger when the thiazole moiety is substituted at C-5 by an electron withdrawing substituent [23], the most effective being the nitro group. Indeed, as it can be seen from Table 2, the bathochromic shift induced by this group reaches 78 nm. Unfortunately, because of its high light sensitivity, the use of the nitro compound **5**NO_2 in technical purposes is questionable.

The large π and p conjugated electronic system present in the studied neutral azo derivatives can promote different charge distributions depending on the external influence and, as a consequence, different dipole values provided by the possible resonance structures. This fact is well reflected in the solvatochromic effect for azulene-1-azo-2'-thiazoles represented in Table 3. Increasing the solvent polarity, structures with long-range placed charges (as in Scheme 7 structure **5**NO_2**B**) gain in importance inducing a bathochromic effect. For example, at the solvent change from the cyclohexane to dimethylformamide, the value of $\Delta\lambda_{max}$ for the main visible band reaches 61 nm for **5**NO_2 as compared with only 31 nm for **5**H (Table 3). The very small solvatochromic effect of corresponding *N*-oxides reflects the intrinsic polarization of their molecules. The solvatochromic effect is absent, however, for *N*-alkylated salt, **28**, where the positive charge is already spread including the tropylium structure for azulene moiety and the sp^3 hybridization for thiazole nitrogen.

Scheme 7



5NO_2**A** **5**NO_2**B**

Conclusions.

The synthesis and the physico-chemical properties of compounds belonging to a new class of azo derivatives is reported. The obtained azulene-1-azo-2'-thiazoles can be attacked either to the position 3 in azulene or to thiazolic nitrogen depending on the nature of the electrophile. Due to the strong pull-push effect induced by both the azulene moiety and the substituted thiazole, the reported compounds exhibit a very strong bathochromic displacement in UV-Vis and their extended electron conjugated system brings about a solvatochromic effect. These optical properties could be useful in technical aims and in our opinion some from the obtained compounds provided access to materials exhibiting potential valuable optical utilities. The investigations in this respect are in progress.

Table 2

The Difference Between the Values of the Main Visible Band for Unsubstituted and Substituted Azulene-1-azo-2’-thiazoles ($\Delta\lambda_{max}$) in Methanol

Substituent	5-Cl	5-Br	5-NCS	5-CO_2CH_3	N^+-O^-	N^+-CH_3	5-NO_2
Compound	**5**Cl	**5**Br	**5**NCS	**5**CO_2CH_3	**25**	**28**	**5**NO_2
$\Delta\lambda_{max}$	3	19	29	33	46	68	78

Table 3

The Solvent Effect on λ_{max}(nm)/lg ε($dm^3mol^{-1}cm^{-1}$) for the Main Visible Band of Azulene-1-azo-2'-thiazoles

Comp.	Solvent						
	C_6H_{12}	$C_6H_5CH_3$	$(CH_3)_2CO$	CH_3CN	CH_3OH	DMF [a]	H_2O
5H	450(4.42)	466(4.44)	465(4.42)	468(4.40)	475(4.44)	481(4.41)	490(4.44)
5Cl	465(4.41)	484(4.42)	484(4.48)	481(4.48)	488(4.44)	494(4.41)	490(4.44)
5Br	475(4.44)	486(4.45)	486(4.45)	488(4.50)	494(4.47)	498(4.43)	495(4.45)
5SCN	477(4.39)	494(4.41)	494(4.39)	498(4.30)	504(4.39)	506(4.31)	510(4.39)
5CO_2CH_3	472(4.38)	492(4.37)	496(4.39)	496(4.36)	508(4.34)	508(4.39)	514(4.34)
5NO_2	510(4.44)	536(4.45)	546(4.52)	556(4.45)	553(4.50)	571(4.47)	573(4.45)
28	-	576(4.26) [b]	561(4.25)	561(4.30)	561(4.31)	561(4.26)	558(4.26)
25	510(4.40)	521(4.32)	515(4.40)	514(4.28)	521(4.44)	524(4.40)	530(4.40)

[a] DMF: dimethylformamide; [b] not dried.

The presented diazotization of 2-amino-3-oxy-4-phenylthiazole represent the first example of diazonium salts generation starting from a five-atom nitrogenous heterocyclic amine containing N-O bond. Although the *N*-oxides are relatively strong oxidants while azulene derivatives are well known for their sensitivity toward oxidants, the obtained azo derivatives, as well as the corresponding pyridine *N*-oxide derivatives, are stable compounds.

Acknowledgements.

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EXPERIMENTAL

Melting points: Kofler apparatus (Reichert Austria). Elemental analyses: Perkin Elmer CHN 240B. UV spectra: Beckman DK-2A, UV 5240. IR spectra in potassium bromide: Beckman IR 5 A. ^{1}H- and ^{13}C nmr spectra in $CDCl_3$: Bruker WM 300, AC 300, ARX 300 and Gemini 300 (^{1}H: 300 MHz, ^{13}C: 75 MHz), TMS was used as internal standard; when necessary, unequivocal signal assignment was confirmed by ^{1}H-^{1}H COSY and ^{1}H-^{13}C HETCOR experiments (the numbering for the compounds is indicated in Schemes). Mass spectra: Finnigan MAT 311-A/100 MS. Column chromatography: silica gel [70-230 mesh (ASTM)] or basic alumina (activity BII-III (Brockmann)). All eluted solutions were filtered before solvent vaporization. Chloroform was filtered on basic alumina. The dichloromethane (DCM) was distilled over calcium hydride and ethyl acetate over anhydrous sodium carbonate. The reagents were commercial grade. The commercially unavailable 2-aminothiazoles, **2**Cl [25a], **2**CO_2CH_3 [25b], **2**SCN [25c], **2**SO_3H [25d] and **2***p*$CH_3C_5H_4N_2$ [25e], were prepared according to the literature. The nomenclature was obtained using the ACD/I-Lab Web service (ACD/IUPAC Name Free 7.06).

General Procedure for Azo Coupling.

In a flask cooled at 0 °C, phosphoric acid (0.6 ml, 85 %) and nitric acid (0.4 mL, 62 %) were added to 2-aminothiazole (110 mg, 1.1 mmol) and the mixture was stirred until complete dissolution. Then, $NaNO_2$ (crystals), (77 mg, 1.1 mmol) was slowly added, at 0 °C. A very small amount of ice was added to this solution and the mixture was poured at 0 °C in a well-stirred solution of azulene (128 mg, 1 mmol), and potassium acetate (4 g), in methanol, (30 mL). In a short time the color turned red. After 15 min of stirring at 0 °C, aqueous sodium carbonate (20 %) was added for neutralization and the solution was let to reach room temperature. The mixture was extracted with DCM (3 × 25 mL) and the combined organic layers were washed with water, dried (Na_2SO_4) and the solvent was evaporated in vacuum. The residue was separated by column chromatography mainly on silica gel, using *n*-pentane for unreacted azulenes and a mixture of DCM-ethyl acetate as eluents for azo compounds. The conversion and the yields are presented in Schemes 1 and 4. Further particular details for the synthesis of azo compounds **5**SO_3H, **5***p*-$CH_3C_6H_4N_2$, **22** and **25-27** are described below.

2-(Azulen-1-yldiazenyl)-1,3-thiazole, (**5**H).

This compound was obtained as dark brown crystals, mp 80 °C; ir: 740, 780, 790, 845, 885, 1015, 1130, 1200, 1230, 1260, 1300, 1330, 1350, 1380, 1420, 1450, 1480, 1570, 1615, 2370, 3080 cm^{-1}; uv (methanol): λ max (lg ε) 250 (4.24), 291 (4.18), 342 (3.73), 472 (4.36); ^{1}H nmr (300 MHz, $CDCl_3$): δ 7.26 (d, ^3J = 3.3 Hz, 1 H, 5'-H), 7.40 (t, ^3J = 9.7 Hz, 1 H, 5-H), 7.41 (d, ^3J = 4.7 Hz, 1 H, 3-H), 7.52 (t, ^3J = 9,7 Hz, 1 H, 7-H), 7.78 (t, ^3J = 9.7 Hz, 1 H, 6-H), 7.92 (d, ^3J = 3.3 Hz, 1 H, 4'-H), 8.31 (d, ^3J = 9.8 Hz, 1 H, 4-H), 8.36 (d, ^3J = 4.5 Hz, 1 H, 2-H), 9.19 (d, ^3J = 9.8 Hz, 1 H, 8-H); ^{13}C nmr (75 MHz, $CDCl_3$): δ 118.7 (C-5'), 121.9 (C-3), 126.4 (C-2), 128.6 (C-5), 128.7 (C-7), 135.8 (C-8), 138.9 (C-4), 140.2 (C-6), 140.6 (C-8a), 143.1 (C-4'), 143.6 (C-3a), 145.7 (C-1), 179.7 (C-2'). ms: m/z 239 ([M]$^+$, 33.3), 212 (30.3), 167 (13), 166 (19), 154 (15), 128 (77), 101 (100).

Anal. Calcd. for $C_{13}H_9N_3S$: C, 65.26; H, 3.79; N, 17.57; S, 13.37. Found: C, 65.17; H, 3.78; N, 17.61; S, 13.44.

2-(Azulen-1-yldiazenyl)-5-chloro-1,3-thiazole, (**5**Cl).

This compound was obtained as dark brown crystals, mp 191 °C; ir: 740, 785, 885, 1015, 1035, 1130, 1200, 1230, 1270, 1315, 1400, 1420, 1450, 1480, 1570, 1690, 2375 cm^{-1}; uv (methanol): λ max (lg ε) 229 (4.26), 295 (4.18), 347 (3.74), 488 (4.37), 698 (2.80); ^{1}H nmr (300 MHz, $CDCl_3$): δ 7.46 (d, ^3J = 4.7 Hz, 1 H, 3-H), 7.48 (t, ^3J = 9.7 Hz, 1 H, 5-H), 7.60 (t, ^3J = 9.7 Hz, 1 H, 7-H), 8.36 (d, ^3J = 9.8 Hz, 1 H, 4-H), 7.85 (t, ^3J = 9.7 Hz, 1 H, 6-H), 8.35 (d, ^3J = 4.5 Hz, 1 H, 2-H), 7.72 (s, 1 H, 4'-H), 9.19 (d,

1 H, ^3J = 9.8 Hz, 8-H); ^{13}C nmr (75 MHz, $CDCl_3$): δ 122.4 (C-3), 126.7 (C-2), 127.1 (C-5'), 129.1 (C-5), 129.2 (C-7), 135.8 (C-8), 139.1 (C-4), 140.4 (C-6, C-8a), 141.0 (C-4'), 143.6 (C-3a), 146.2 (C-1), 177.2 (C-2'); ms: m/z 275 ([M]$^+$, 15), 273 ([M]$^+$, 48), 246 (51), 244 (63), 210 (23), 166 (21), 155 (20), 153 (31), 140 (61), 127 (100).

Anal. Calcd. for $C_{13}H_8ClN_3S$: C, 56.93; H, 3.31; Cl, 12.76; N, 15.33; S, 11.67. Found: C, 57.10; H, 2.85; Cl, 13.00; N, 15.41; S, 11.64.

2-(Azulen-1-yldiazenyl)-5-bromo-1,3-thiazole, (**5**Br).

This compound was obtained as dark brown crystals, mp 207 °C; ir: 740, 770, 790, 850, 1000, 1015, 1035, 1130, 1200, 1230, 1270, 1310, 1380, 1420, 1450, 1480, 1570, 1700, 2375 cm^{-1}; uv (methanol): λ_{max} (lg ε) 228 (4.20), 293 (4.19), 346 (3.88), 486 (4.35), 694 (2.80). ^{1}H nmr (300 MHz, $CDCl_3$): δ 7.44 (d, ^3J = 4.7 Hz, 1 H, 3-H), 7.47 (t, ^3J = 9.7 Hz, 1 H, 5-H), 7.58 (t, ^3J = 9,7 Hz, 1 H, 7-H), 8.35 (d, ^3J = 9.8 Hz, 1 H, 4-H), 7.83 (t, ^3J = 9.7 Hz, 1 H, 6-H), 8.33 (d, ^3J = 4.5 Hz, 1 H, 2-H), 7.82 (s, 1 H, 4'-H), 9.16 (d, 1 H, ^3J = 9.8 Hz, 8-H); ^{13}C nmr (75 MHz, $CDCl_3$): δ 122.5 (C-3), 126.8 (C-2), 110.2 (C-5'), 129.2 (C-5), 129.3 (C-7), 135.9 (C-8), 139.2 (C-4), 140.5 (C-6, C-8a), 144.2 (C-4'), 143.6 (C-3a), 146.3 (C-1), 175.2 (C-2'); ms: m/z 319 ([M]$^+$, 9), 317 ([M]$^+$, 9), 290 (21), 288 (24), 210 (25), 166 (22), 155 (22), 153 (33), 140 (72), 126 (100).

Anal. Calcd. for $C_{13}H_8BrN_3S$: C, 49.06; H, 2.85; Br, 24.82; N, 13.21; S, 10.06. Found: C, 49.00; H, 2.55; N, 13.15; S, 10.20; Br, 25.10.

Methyl 2-(azulen-1-yldiazenyl)-1,3-thiazole-5-carboxylate, (**5**CO_2CH_3).

This compound was obtained as dark brown crystals, mp 188 °C; ir 740, 775, 805, 860, 1015, 1090, 1140, 1205, 1230, 1245, 1298, 1310, 1400, 1430, 1460, 1480, 1700, 1690, 2375 cm^{-1}; uv (methanol): λ max (lg ε) 226 (4.29), 285 (4.18), 349 (3.74), 500 (4.20). ^{1}H nmr (300 MHz, acetone-d_6): δ 3.88 (s, 3 H, Me), 7.72 (d, ^3J = 4.7 Hz, 1 H, 3-H), 7.84 (t, ^3J = 9.7 Hz, 1 H, 5-H), 7.95 (t, ^3J = 9,7 Hz, 1 H, 7-H), 8.19 (t, ^3J = 9.7 Hz, 1 H, 6-H), 8.26 (d, ^3J = 4.5 Hz, 1 H, 2-H), 8.50 (s, 1 H, 4'-H), 8.74 (d, ^3J = 9.8 Hz, 1 H, 4-H), 9.26 (d, 1 H, ^3J = 9.8 Hz, 8-H); ^{13}C nmr (75 MHz, acetone-d_6): δ 124.3 (C-3), 125.8 (C-2), 125.7 (C-5'), 132.0 (C-5), 132.1 (C-7), 136.2 (C-8), 142.5 (C-8a), 140.9 (C-4), 142.5 (C-6), 148.6 (C-4'), 142.4 (C-3a), 147.3 (C-1), 161.5 (OMe), 182.7 (C-2'); ms m/z: 298 (13), 297 ([M]$^+$, 53), 270 (22), 269 (64), 268 (71), 210 (20), 166 (15), 155 (20), 153 (21), 140 (80), 126 (100).

Anal. Calcd. for $C_{16}H_{11}N_3SO_2$: C, 62.12; H, 3.59; N, 13.59; S, 10.35. Found: C, 62.10; H, 3.50; N, 13.61; S, 10.34.

2-(Azulen-1-yldiazenyl)-5-nitro-1,3-thiazole, (**5**NO_2).

This compound was obtained as dark brown crystals, mp 260 °C; ir 740, 770, 810, 845, 1010, 1115, 1140, 1200, 1230, 1280, 1320, 1340, 1480, 1560, 1615, 1705, 2375, 2860, 2915 cm^{-1}; uv (methanol): λ max (lg ε) 226 (4.25), 291 (4.17), 335 (3.88), 546 (4.20), 698 (2.80); ^{1}H nmr (300 MHz, $CDCl_3$): δ 7.55 (d, ^3J = 4.7 Hz, 1 H, 3-H), 7.70 (t, ^3J = 9.7 Hz, 1 H, 5-H), 7.83 (t, ^3J = 9,7 Hz, 1 H, 7-H), 8.02 (t, ^3J = 9.7 Hz, 1 H, 6-H), 8.38 (d, ^3J = 4.5 Hz, 1 H, 2-H), 8.47 (d, ^3J = 9.8 Hz, 1 H, 4-H), 8.65 (s, 1 H, 4'-H), 9.30 (d, 1 H, ^3J = 9.8 Hz, 8-H); ^{13}C nmr (75 MHz, DMSO-d_6): δ = 126.0 (C-2), 126.5 (C-3), 127.3 (C-5'), 134.3 (C-7), 134.4 (C-5), 137.1 (C-8), 140.6 (C-8a), 141.6 (C-4), 143.3 (C-3a), 143.5 (C-6), 145.3 (C-4'), 149.3 (C-1), 182.2 (C-2'); ms: m/z 285 (1), 284 ([M]$^+$, 8), 255 (22), 210 (33), 166 (4), 155 (10), 153 (11), 140 (42), 127 (100), 113 (38).

Anal. Calcd. for $C_{13}H_8N_4SO_2$: C, 54.92; H, 2.84; N, 19.72; S, 11.26. Found: C, 54.86; H, 2.75; N, 19.81; S, 11.34.

[2-(Azulen-1-yldiazenyl)-1,3-thiazole]-5-yl thiocyanate, (**5**SCN).

This compound was obtained as dark brown crystals, mp 182 °C; ir 755, 785, 845, 890, 1015, 1130, 1215, 1235, 1270, 1315, 1400, 1450, 1570, 2170, 2380, 3030, 3080. cm^{-1}; uv (methanol): λ max (lg ε) 250 (4.31), 291 (4.18), 348 (3.72), 496 (4.47); ^{1}H nmr ($CDCl_3$): δ 7.48 (d, ^3J = 4.7 Hz, 1 H, 3-H), 7.57 (t, ^3J = 9.7 Hz, 1 H, 5-H), 7.69 (t, ^3J = 9,7 Hz, 1 H, 7-H), 7.91 (t, ^3J = 9.7 Hz, 1 H, 6-H), 8.06 (s, 1 H, 4'-H), 8.33 (d, ^3J = 4.5 Hz, 1 H, 2-H), 8.39 (d, ^3J = 9.8 Hz, 1 H, 4-H), 9.20 (d, 1 H, ^3J = 9.8 Hz, 8-H); ^{13}C nmr (75 MHz, $CDCl_3$): δ 113.4 (CN), 144.2 (C-5'), 123.5 (C-3), 126.4 (C-2), 130.4 (C-5), 130.6 (C-7), 136.2 (C-8), 139.6 (C-4), 141.0 (C-6), 141.0 (C-8a), 143.2 (C-3a), 147.4 (C-1), 150.7 (C-4'), 184.6 (C-2'); ms: m/z 296 ([M]$^+$, 4), 267 (14), 210 (20), 166 (5), 155 (4), 153 (5), 140 (22), 127 (100), 113 (23).

Anal. Calcd. for $C_{14}H_8N_4S_2$: C, 56.75; H, 2.72; N, 18.92; S, 21.60. Found: C, 56.69; H, 2.68: N, 18.85: S, 21.78.

Bis[2-(azulen-1-yldiazenyl)-1,3-thiazole-5-thio], (**6**).

Compound **6** is obtained as by product together with compound **5**SCN and is not available in sufficient amount for complete characterization, uv (methanol): λ max (lg ε) 226 (4.60), 288 (4.49), 333 (4.02), 492 (4.68); ^{1}H nmr (300 MHz, $CDCl_3$): δ 7.48 (d, ^3J = 4.7 Hz, 2 H, 3-H), 7.53 (t, ^3J = 9.7 Hz, 2 H, 5-H), 7.56 (t, ^3J = 9,7 Hz, 2 H, 7-H), 7.83 (t, ^3J = 9.7 Hz, 2 H, 6-H), 7.96 (s, 2 H, 4'-H), 8.36 (d, ^3J = 4.5 Hz, 2 H, 2-H), 8.37 (d, ^3J = 9.8 Hz, 2 H, 4-H), 9.22 (d, ^3J = 9.8 Hz, 2 H, 8-H).

Anal. Calcd. for $C_{26}H_{16}N_6S_4$: C, 57.78; H, 2.96; N, 15.56: S, 23.70. Found: C, 57.70; H, 3.04; N, 15.64; S, 23.62.

2-[(4,8-Dimethylazulen-1-yl)diazenyl]-4-phenyl-1,3-thiazole, (**18**).

This compound was obtained as dark-red crystals mp 205 °C; ir 690, 740, 775, 785, 805, 860, 905, 1000, 1020, 1075, 1180, 1210, 1240, 1285, 1300, 1360, 1440, 1455, 1480, 1570, 2380 cm^{-1}; uv (methanol): λ max (lg ε) 231 (4.41), 250 (4.38), 309 (4.12), 333sh (3.76), 492 (4.45); ^{1}H nmr (300 MHz, $CDCl_3$): δ 2.85 (s, 3 H, 4-Me), 3.24 (s, 3 H, 8-Me), 7.30 (d, ^3J = 10.1 Hz, 1 H, 5-H), 7.36 (s, 1 H, 5'-H), 7.37 (tt, ^3J = 8.6 Hz, ^4J = 1.0 Hz, 1 H, 4"-H), 7.38 (d, ^3J = 10.1 Hz, 1 H, 7-H), 7.40 (d, ^3J = 4.9 Hz, 1 H, 3-H), 7.44 (tt, ^3J = 8.6 Hz, ^4J = 1.0 Hz, 2 H, 3"-H, 5"-H), 7.48 (t, ^3J = 10.2 Hz, 1 H, 6-H), 8.02 (dt, ^3J = 8.6 Hz, ^4J = 1.0 Hz, 2 H, 2"-H, 6"-H), 8.35 (d, ^3J = 5.1 Hz, 2-H); ^{13}C nmr (75 MHz, $CDCl_3$): δ 24.55 (Me-4), 29.36 (Me-8), 112.1 (C-5'), 120.2 (C-3), 128.0 (C-2), 124.8 (C-3", C-5"), 126.1 (C-2", C-6"), 128.6 (C-4"), 134.5 (C-1"), 131.8 (C-5), 133.7 (C-7), 149.1 (C-8), 151.8 (C-4), 137.0 (C-6), 137.1 (C-8a), 154.9 (C-4'), 146.9 (C-3a), 144.7 (C-1), 179.7 (C-2'); ms: m/z 343 ([M]$^+$, 23), 315 (28), 314 (27), 300 (29), 168 (100), 153 (100), 128 (58), 77 (67).

Anal. Calcd. for $C_{21}H_{17}N_3S$: C, 73.44; H, 4.99; N, 12.23; S, 9.33. Found: C, 73.25; H, 4.95; N, 12.21, S, 9.59.

2-[(3-*tert*-Butylazulen-1-yl)diazenyl]-4-phenyl-1,3-thiazole, (**19**).

This compound was obtained as red crystals, mp 197 °C; ir 670, 690, 730, 740, 755, 865, 885, 905, 1020, 1035, 1080, 1175, 1190, 1210, 1285, 1305, 1335, 1420, 1455, 1570, 2380, 2850,

2915, 2950 cm^{-1}; uv (methanol) λ_{max} (lg ε): 231 (4.37), 250 (4.36), 298 (4.21), 333 (3.87), 500 (4.45); ^1H nmr (300 MHz, $CDCl_3$): δ 1.59 (s, 3 H, Me), 7.39 (t, ^3J = 10.1 Hz, 1 H, 5-H), 7.45 (s, 1 H, 5'-H), 7.39 (tt, ^3J = 8.6 Hz, ^4J = 1.0 Hz, 1 H, 4"-H), 7.49 (t, ^3J = 10.1 Hz, 1 H, 7-H), 7.45 (tt, ^3J = 8.6 Hz, ^4J = 1.0 Hz, 2 H, 3"-H 5"-H), 7.77 (t, ^3J = 9.8 Hz, 1 H, 6-H), 8.06 (dt, ^3J = 8.6 Hz, ^4J = 1.0 Hz, 2 H, 2"-H, 6"-H), 8.39 (d, ^3J = 5.1 Hz, 2-H), 8.70 (d, ^3J = 9.8 Hz, 1 H, 4-H), 9.23 (d, ^3J = 9.8 Hz, 1 H, 8-H); ^{13}C nmr (75 MHz, $CDCl_3$): δ 112.5 (C-5'), 124.6 (C-3", C-5"), 126.3 (C-2", C-6"), 127.4 (C-3), 127.8 (C-2), 128.5 (C-4"), 128.6 (C-5), 128.7 (C-7), 134.6 (C-1"), 135.5 (C-4), 138.0 (C-8), 140.3 (C-6), 142.3 (C-8a), 143.1 (C-3a), 144.5 (C-1), 155.3 (C-4'), 179.5 (C-2'); ms: m/z 371 ($[M]^+$, 24), 328 (36), 286 (64), 174 (36), 165 (39), 152 (100), 134 (54), 77 (52).

Anal. Calcd. for $C_{23}H_{21}N_3S$: C, 74.36; H, 5.70; N, 11.31; S, 8.63. Found: C, 74.35; H, 5.65; N, 11.41; S, 8.59.

2-[(4,6,8-Trimethylazulen-1-yl)diazenyl]-4-phenyl-1,3-thiazole, (**20**).

This compound was obtained as dark-red crystals mp 214 °C; ir 680, 740, 780, 800, 820, 845, 900, 1020, 1080, 1200, 1230, 1290, 1300, 1310, 1350, 1440, 1450, 1480, 1570, 2370 cm^{-1}; uv (methanol): λ max (lg ε) 234 (4.40), 246sh (4.33), 255sh (4.33), 313 (4.15), 326sh (3.92), 498 (4.37); ^1H nmr (300 MHz, $CDCl_3$): δ 2.67 (s, 3 H, 6-Me), 2.87 (s, 3 H, 4-Me), 3.30 (s, 3 H, 8-Me), 7.33 (d, ^4J = 1.2 Hz, 1 H, 5-H), 7.35 (tt, ^3J = 8.6 Hz, ^4J = 1.0 Hz, 1 H, 4"-H), 7.39 (s, 1 H, 5'-H), 7.40 (d, ^3J = 4.9 Hz, 1 H, 3-H), 7.44 (bs, 1 H, 7-H), 7.45 (tt, ^3J = 8.6 Hz, ^4J = 1.0 Hz, 2 H, 3"-H, 5"-H), 8.06 (dt, ^3J = 8.6 Hz, ^4J = 1.0 Hz, 2 H, 2"-H, 6"-H), 8.31 (d, ^3J = 5.1 Hz, 2-H). ^{13}C nmr (75 MHz, $CDCl_3$): δ 24.44 (Me-4), 28.59 (Me-6), 29.71 (Me-8), 111.9 (C-5'), 120.3 (C-3), 127.9 (C-2), 123.7 (C-3", C-5"), 126.3 (C-2", C-6"), 128.4 (C-4"), 134.6 (C-1"), 133.3 (C-5), 135.7 (C-7), 148.0 (C-8), 150.6 (C-4), 148.9 (C-6), 135.5 (C-8a), 155.0 (C-4'), 147.2 (C-3a), 143.4 (C-1), 179.9 (C-2'); ms: m/z 357 ($[M]^+$, 16), 342 (11), 329 (11), 314 (17), 182 (100), 176 (84), 153 (40), 134 (37), 84 (36).

Anal. Calcd. for $C_{22}H_{19}N_3S$: C, 74.77; H, 5.18; N, 11.37; S, 8.68. Found: C, 74.75; H, 5.15; N, 11.21; S, 8.89.

2[(5-Isopropyl-3,8-dimethylazulen-1-yl)diazenyl]-4-phenyl-1,3-thiazole, (**21**).

This compound was obtained as red crystals, mp 87 °C; ir 685, 735, 775, 810, 860, 900, 960, 1000, 1030, 1100, 1165, 1230, 1290, 1300, 1330, 1440, 1455, 1560, 2380, 2970 cm^{-1}; uv (methanol): λ max (lg ε) 235 (4.39), 259 (4.42), 300 (4.14), 323 (3.86), 517 (4.38); ^1H nmr (300 MHz, $CDCl_3$): δ 1.36 (d, ^3J = 6.9 Hz, 6 H, CH*Me*), 2.54 (s, 3 H, 3-Me), 3.09 (hept, ^3J = 6.9 Hz, 1 H, *CH*Me), 3.20 (s, 3 H, 8-Me), 7.35 (tt, ^3J = 8.6 Hz, ^4J = 1.0 Hz, 1 H, 4"-H), 7.32 (s, 1 H, 5'-H), 7.40 (bd, ^3J = 9.7 Hz, 1 H, 7-H), 7.42 (tt, ^3J = 8.6 Hz, ^4J = 1.0 Hz, 2 H, 3"-H, C5"-H), 7.50 (dt, ^3J = 9.7 Hz, ^4J = 2.0 Hz, 1 H, 6-H), 8.02 (dt, ^3J = 8.6 Hz, ^4J = 1.0 Hz, 2 H, 2"-H, 6"-H), 8.12 (d, ^4J = 1.9 Hz, 4-H), 8.21 (s, 1 H, 2-H); ^{13}C nmr (75 MHz, $CDCl_3$): δ 13.14 (Me3), 24.25 (CH*Me*), 28.58(Me8), 38.16(*CH*Me), 111.6 (C-5'), 126.7 (C-2), 126.3 (C-3", C-5"), 128.2 (C-3),128.5 (C-2", C-6"), 128.9 (C-4"), 131.2 (C-7), 134.6 (C-1"), 135.2 (C-4), 136.7 (C-6), 138.0 (C-8a), 145.5 (C-3a), 144.9 (C-1), 149.3 (C-8), 149.6 (C-5), 154.8 (C-4'), 180.0 (C-2'). MS (m/z): 386 ($[M]^+$+1, 1), 384 ($[M]^+$-1, 1), 358 (1), 356 (1), 211 (7), 176 (100), 134 (98).

Anal. Calcd. for $C_{24}H_{23}N_3S$: C, 74.77; H, 6.01; N, 10.90; S, 8.32. Found: C, 74.79; H, 6.09; N, 10.81; S, 8.31.

2-(Azulen-1-yldiazenyl)-1,3-thiazole-5-sulfonic acid, (**5**SO_3H).

Due to the high solubility of the resulting zwitterion in water, the methanolic solution was evaporated and the solid was continuously extracted with DCM in an extractor. After solvent removal, the obtained red solid was separated by column chromatography on silica gel using *n*-pentane for the unreacted azulene and ethyl acetate:methanol, 4:1, for azo compound **5**SO_3H. This compound was obtained as dark red-brown crystals, mp 235 °C; ir 670, 745, 780, 790, 825, 835, 860, 1015, 1110, 1135, 1200, 1260, 1385, 1450, 1620, 2350, 2900-3600 cm^{-1}; uv (methanol), λ max (lg ε) 229 (4.30), 293 (4.19), 344 (3.72), 488 (4.37), 698 (2.80); ^1H nmr (300 MHz, DMSO-d_6): δ 4.66 (s, 1 H, N^+H), 7.66 (d, ^3J = 4.8 Hz, 1 H, 3-H), 7.73 (t, ^3J = 9.6 Hz, 1 H, 5-H), 7.84 (t, ^3J = 9.6 Hz, 1 H, 7-H), 7.88 (s, 1 H, 4'-H), 8.10 (t, ^3J = 9.6 Hz, 1 H, 6-H), 8.19 (d, ^3J = 4.5 Hz, 1 H, 2-H), 8.67 (d, ^3J = 9.8 Hz, 1 H, 4-H), 9.16 (d, ^3J = 9.6 Hz, 1 H, 8-H); ^{13}C nmr (75 MHz, DMSO-d_6): δ 123.4 (C-3), 125.4 (C-2), 131.0 (C-5, C-7), 135.9 (C-8), 140.4 (C-4'), 140.7 (C-4), 141.1 (C-8a), 142.2 (C-6), 143.0 (C-3a), 143.9 (C-5'), 146.3 (C-1), 178.2 (C-2').

Anal. Calcd. for $C_{13}H_9N_3O_3S_2$: C, 48.89; H, 2.84; N, 13.16; S, 20.08. Found: C, 48.86; H, 2.78; N, 13.25; S, 20.56.

Generation of Double-coupled Thiazols, **22** and **5***p*$CH_3C_6H_4N_2$.

For the generation of **22** and **5***p*$CH_3C_6H_4N_2$ the corresponding aminothiazols **11** and **2**H were first coupled with a diazonium salt obtained from *p*-methylaniline and then the reaction mixture was *in situ* diazotized at thiazole amino group and coupled with azulene. Starting from **11** the intermediate **12** was separated and characterized. This compound (1 g, 3.42 mmole, 10 % excess) was diazotized and coupled with azulene. After work-up, four fractions were obtained by chromatographic separation: fraction 1 (blue), unreacted azulene (cca 6 %), fraction 2 (yellow-green), 1-azulen-1-yl-2-(4-methylphenyl)diazene, **9**, (62 mg, 8 %), fraction 3 (brown), mono coupled compound **17**, (150 mg, 15 %), fraction 4 (violet-blue), double coupled compound **22**, (76 mg, 5 %). Starting from **2**H, the intermediate **5** *p*$CH_3C_6H_4N_2$ was not separated and from the reaction mixture only **5***p*$CH_3C_6H_4N_2$ was separated (in yield under 5 %) and traces of the compound **9** were observed.

5[(4-Methylphenyl)diazenyl]-4-phenyl-1,3-thiazol-2-amine, (**12**).

This compound was obtained as dark yellow crystals, mp 203 °C (lit [23] 200 °C); ^1H nmr (300 MHz, $CDCl_3$): δ 2.34 (s, 3 H, CH_3), 7.29 (d, ^3J = 10.0 Hz, 2 H, 2'-H, 6'-H), 7.37 (tt, ^3J = 6.7 Hz, ^4J = 1.5 Hz, 1 H, 4"-H), 7.51 (t, ^3J = 7.8 Hz, 2 H, 3"-H, 5"-H), 7.55 (t, ^3J = 8.2 Hz, 2 H, 3'-H, 5'-H), 8.21 (dd, ^3J = 8.3 Hz, ^4J = 1.4 Hz, 2 H, 2'-H, 6'-H), 8.34 (s, 2 H, NH_2); ^{13}C nmr (75 MHz, $CDCl_3$): δ 20.89 (Me), 121.8 (C-2', C-6'), 128.5 (C-3', C-5'), 129.5 (C3', C5'), 129.8 (C2", C6"), 129.9 (C4"), 133.8 (C1"), 138.9 (C-4'), 139.9 (C-5), 150.5 (C-1), 154.6 (C-4), 169.3 (C-2); ms: m/z: 294 ($[M]^+$, 63), 293 (100), 133 (17), 91 (65).

2-(Azulen-1-yldiazenyl)-4-phenyl-1,3-thiazole, (**17**).

This compound was obtained as red crystals, mp 163 °C; ir 670, 690, 725, 750, 775, 780, 820, 865, 870, 905, 1020, 1035, 1080, 1175, 1190, 1210, 1275, 1305, 1320, 1365, 1410, 1445, 1560, 1580, 2380 cm^{-1}; uv (methanol): λ max (lg ε) 226 (4.40), 238sh (4.33), 247sh (4.33), 296 (4.24), 336 (3.87), 486 (4.45); ^1H nmr (300 MHz, $CDCl_3$): δ 7.36 (s, 1 H, 5'-H), 7.48 (t, ^3J = 9.7 Hz, 1 H, 5-H), 7.47 (t, ^3J = 7.0 Hz, 2 H, 3"-H, 5"-H), 7.47 (d, ^3J = 4.7 Hz, 1 H, 3-H), 7.47 (t, ^3J = 7.0 Hz, 1 H, 4"-H), 7.60 (t, ^3J = 10.0 Hz, 1 H, 7-H), 7.84 (t, ^3J = 10.0 Hz, 1 H, 6-H), 8.05 (d, ^3J = 8.0

Hz, 2 H, 2"-H, 6"-H), 8.38 (d, ^3J = 9.6 Hz, 1 H, 4-H), 8.46 (d, ^3J = 4.6 Hz, 1H, 2-H), 9.27 (d, 1 H, ^3J = 9.6 Hz, 8-H). ^{13}C nmr (75 MHz, $CDCl_3$): δ 112.7 (C-5'), 122.2 (C-3), 126.8 (C-2), 126.2 (C-3", C-5"), 126.5 (C-2", C-6"), 128.5 (C-4"), 134.5 (C-1"), 128.7 (C-5), 128.8 (C-7), 138.9 (C-8), 135.8 (C-4), 139.2 (C-6), 138.9 (C-8a), 158.3 (C-4'), 144.7 (C-3a), 145.9 (C-1), 177.0 (C-2'); ms: m/z 315 ([M]$^+$, 3), 287 (20), 286 (73), 140 (10), 127 (100).

Anal. Calcd. for $C_{19}H_{13}N_3S$: C, 72.36; H, 4.15; N, 13.32; S, 10.17. Found: C, 72.56; H, 4.25; N, 13.21; S, 9.98.

2-(Azulen-1-yldiazenyl)-4-phenyl-5-[(4-methylphenyl)-diazenyl]-1,3-thiazole, (**22**).

This compound is not available in sufficient amount for the complete characterization: ^{1}H nmr (400 MHz, $CDCl_3$): δ 2.45 (s, 3 H, Me), 7.32 (d, ^{3}J = 8.8 Hz, 2 H, 3'"-H, 5'"-H), 7.47 (t, ^{3}J = 6.8 Hz, 1 H, 4'"-H), 7.52 (d, ^{3}J = 4.8 Hz, 1 H, 3-H), 7.54 (t, ^{3}J = 6.8 Hz, 2 H, 3"-H, 5"-H), 7.55 (t, ^{3}J = 9.6 Hz, 1 H, 5-H), 7.69 (t, ^{3}J =9.8 Hz, 1 H, 7-H), 7.81 (d, ^{3}J = 8.0 Hz, 2 H, 2'"-H, 6'"-H), 7.90 (t, ^{3}J = 10.0 Hz ,1 H, 6-H), 8.41 (d, ^{3}J = 10.0 Hz, 1 H, 4-H), 8.46 (d, ^{3}J = 5.2 Hz, 1 H, 2-H), 8.47 (d, ^{3}J =7.2 Hz, 2 H, 2"-H, 6"-H), 9.34 (d, ^{3}J = 10.0 Hz, 1 H, 8-H); ms: m/z 434 (1), 433 ([M]$^+$, 4), 404 (4), 286 (5), 284 (6), 153 (54), 127 (46), 126 (24), 89 (100), 77 (48).

Anal. Calcd. for $C_{26}H_{19}N_5S$: C, 72.03; H, 4.42; N, 16.16; S, 7.38. Found: C, 72.06: H, 4.56; N, 16.10: S, 7.28.

2-(Azulen-1-yldiazenyl)-5-[(4-methylphenyl)diazenyl]-1,3-thiazole, (**5***p*$CH_3C_6H_4N_2$).

This compound was obtained as black crystals**,** mp 105 °C; uv (methanol): λ max (lg ε) 225 (4.22), 240sh (4.10), 294 (4.05), 350 (3.99), 556 (4.24); ^{1}H nmr (300 MHz, $CDCl_3$): δ 2.45 (s, 3 H, Me), 7.32 (d, ^3J = 8.0 Hz, 2 H, 3"-H, 5"-H); 7.51 (d, ^3J = 4.7 Hz, 1 H, 3-H), 7.54 (t, ^3J = 9.6 Hz, 1 H, 5-H); 7.67 (t, ^3J =9,7 Hz, 1 H, 7-H), 7.81 (d, ^3J = 8.4 Hz, 2 H, 2"-H, 6"-H); 7.90 (t, ^3J = 9.7 Hz, 1 H, 6-H), 8.40 (d, ^3J = 9.8 Hz, 1 H, 4-H), 8.41 (d, ^3J = 4.5 Hz, 1H, 2-H), 8.59 (s, 1H, 4'-H); 9.31 (d, 1 H, ^3J = 9.9 Hz, 8-H); ms: m/z 358 (1), 357 ([M]$^+$, 4), 328 (2), 300 (7), 218 (23), 210 (52), 179 (15), 166 (15), 155 (12), 153 (21), 141 (40), 140 (62), 127 (75), 126 (58), 119 (12), 113 (25), 91 (100).

Anal. Calcd. for $C_{20}H_{15}N_5S$: C, 67.21; H, 4.23; N, 19.61; S, 8.95. Found: C, 67.26: H, 4.30; N, 19.50; S, 8.94.

The Synthesis of Azo Compound, **25**-**27**.

The diazotization of 4-phenyl-1,3-thiazol-2-amine 3-oxide hydrochloride, **23**.HCl, [17] and the coupling with azulenic compounds, **4**, **15** and **16**, were carried out as usual. The solvent removing occurred at room temperature and the chromatography was performed on alumina using as eluent DCM:ethyl acetate 1:1. After the unreacted azulene, the second fraction (blue) contained the azo compound, **25**-**27** (yields in Scheme 5).

2-(Azulen-1-yldiazenyl)-4-phenyl-1,3-thiazole 3-Oxide, (**25**).

This compound was obtained as dark red crystals, mp 141 °C; ir 580, 650, 690, 705, 740, 755, 790, 850, 890, 950, 1010, 1030, 1050, 1150, 1160, 1245, 1250, 1280, 1375, 1435, 1490, 1560, 2380 cm^{-1}; uv (methanol): λ max (lg ε) 229 (4.41), 242sh (4.31), 254 (4.31), 297 (4.17), 364 (3.66), 530 (4.50); ^{1}H nmr (400 MHz, $CDCl_3$): δ 7.32 (s, 1 H, 5'-H), 7.34 (t, ^3J = 9.7 Hz, 1 H, 5-H), 7.47 (t, ^3J = 7.0 Hz, 2 H, 3"-H, 5"-H), 7.46 (d, ^3J = 4.7 Hz, 1 H, 3-H), 7.50 (t, ^3J = 7.0 Hz, 1 H, 4"-H), 7.54 (t, ^3J = 10.0 Hz, 1 H, 7-H), 7.79 (t, ^3J = 10.0 Hz, 1 H, 6-H), 7.97 (d, ^3J = 7.0 Hz, 1 H, 2"-H, 6"-H), (8.30 (d, ^3J = 9.6 Hz, 1 H, 4-H), 8.50 (d, ^3J = 4.6 Hz, 1H, 2-H), 9.12 (d, 1 H, ^3J = 9.6 Hz, 8-H); ^{13}C nmr (100 MHz, $CDCl_3$): δ = 112.6 (C-5'), 123.1 (C-3), 127.7 (C-2), 128.3 (3"), 128.5 (2"), 129.3 (4"), 129.0 (C-1"), 129.3 (C-5), 129.6 (C-7), 136.1 (C-8), 139.0 (C-4), 140.5 (C-6, C-8a), 147.1 (C-4'), 145.6 (C-3a), 146.6 (C-1), 160.5 (C-2'). MS (m/z): 332 (M+1, 1), 288 (69), 286 (100), 284 (51), 260 (7), 205 (11), 205 (11), 143 (15), 126 (94).

Anal. Calcd. for $C_{19}H_{13}N_3SO$: C, 68.86; H, 3.95; N, 12.68; S, 9.67. Found: C, 68.67; H, 3.82, N, 12.71, S, 9.70.

4-Phenyl-2-[(4,6,8-trimethylazulen-1-yl)diazenyl]-1,3-thiazole 3-Oxide, (**26**).

This compound was obtained as dark violet crystals, mp 250 °C; uv (methanol): λ max (lg ε) 235 (4.49), 254sh (4.38), 264sh (4.38), 309 (4.05), 543 (4.52); ^{1}H nmr (400 MHz, $CDCl_3$): δ 2.65 (s, 3 H, 6-Me), 2.84 (s, 3 H, 4-Me), 3.21 (s, 3 H, 8-Me), 7.21 (s, 1 H, 5'-H), 7.32 (bs, 1 H, 5-H), 7.38 (d, ^3J = 5.2 Hz, 1 H, 3-H), 7.40 (bs, 1 H, 7-H), 7.48 (t, ^3J = 7.2 Hz, 1 H, 4"-H), 7.46 (t, ^3J = 7.2 Hz, 2 H, 3"-H, 5"-H), 8.36 (d, ^3J = 4.8 Hz, 1 H, 2-H), 7.97 (d, ^3J = 8.0 Hz, 2 H, 2"-H, 6"-H); ^{13}C nmr (100 MHz, $CDCl_3$): δ 25.45 (Me-4), 28.57 (Me-6), 29.53 (Me-8), 111.4 (C-5'), 121.5 (C-3), 124.8 (C-2), 128.3 (C-3", C-5"), 128.4 (C-2", C-6"), 129.4 (C-4"), 129.2 (C-1"), 134.1 (C-5), 136.4 (C-7), 148.2 (C-8), 149.3 (C-6), 150.9 (C-4), 136.5 (C-8a), 150.9 (C-4'), 146.9 (C-3a), 144.4 (C-1), 149.4 (C-2'); ms: m/z 373 ([M]$^+$, 1), 357 (6), 342 (4), 329 (6), 314 (13), 224 (20), 222 (22), 182 (82), 176 (100), 153 (50), 134 (85).

Anal. Calcd. for $C_{22}H_{19}N_3SO$: C, 70.75; H, 5.13; N, 11.25; S, 8.58. Found: C, 70.67; H, 5.22; N, 11.21; S, 8.50.

2-[(5-Isopropyl-3,8-dimethylazulen-1-yl)diazenyl]-4-phenyl-1,3-thiazole 3-Oxide, (**27**).

This compound was obtained as blue crystals, mp 133 °C (dec.); UV (methanol): λ max (lg ε) 234 (4.45), 246sh (4.43), 305 (4.12), 556 (4.28); ^{1}H nmr (400 MHz, $CDCl_3$): δ 1.38 (d, ^3J = 6.9 Hz, 6 H, CH*Me*), 2.53 (s, 3 H, 3-Me), 3.12 (hept, ^3J = 6.9 Hz, 1 H, C*H*Me), 3.19 (s, 3 H, 8-Me), 7.17 (s, 1 H, 5'-H), 7.44 (bd, ^3J = 9.8 Hz, 1 H, 7-H), 7.45 (m, 3 H, H-3", H-4", H-5"), 7.54 (d, ^3J = 9.8 Hz, 1 H, 6-H), 7.97 (d, ^3J = 4.8 Hz, 2 H, 2"-H, 6"-H), 8.10 (s, 1 H, 2-H), 8.29 (s. 1 H, 4-H); ^{13}C nmr (100 MHz, $CDCl_3$): δ 13.13 (Me3), 24.25 (CH*Me*), 28.38 (Me8), 38.35 (*CH*Me), 110.9 (C-5'), 126.7 (C-2), 127.8 (C-3", C-5"), 128.2 (C-3), 128.6 (C-2", C-6"), 129.4 (C-4"), 131.2 (C-7), 134.6 (C-1"), 135.2 (C-4), 136.7 (C-6), 138.0 (C-8a), 145.5 (C-3a), 144.9 (C-1), 149.3 (C-8), 149.6 (C-5), 150.0 (C-4'), 160.5 (C-2'). MS (m/z): 402 ([M]$^+$, 1), 224 (1), 212 (1), 198 (63), 183 (100).

Anal. Calcd. for $C_{24}H_{23}N_3SO$: C, 71.79; H, 5.77; N, 10.47; S, 7.98. Found: C, 71.68; H, 5.72; N, 10.51; S, 7.99.

Halogenations of the Compound **5**H.

2-[(3-Bromoazulen-1-yl)diazenyl]-1,3-thiazole, (**29**Br).

N-Bromosuccinimide (36 mg, 0.2 mmol) was added to the solution of **5**H, (48 mg, 0.2 mmol) in DCM (3 mL). The reaction mixture was stirred for one hour, the solvent was evaporated to dryness and the residue was separated by chromatography on alumina using DCM as eluent. Three colored fractions were obtained: fraction 1, unidentified products (8 mg), fraction 2, bromo derivative **29**Br, (40 mg, 76 %) and fraction 3 (8 mg unreacted **5**H, 17 %). The compound **29**Br was obtained as dark brown crystals, mp 178 °C (dec); uv (methanol): λ max (lg ε) 212 (4.26), 230 (4.34), 294 (4.24), 345 (3.89), 479 (4.43). ^{1}H nmr

(300 MHz, $CDCl_3$): δ 7.28 (d, ^3J = 3.3 Hz, 1 H, 5'-H), 7.47 (t, ^3J = 9.8 Hz, 1 H, 5-H), 7.52 (t, ^3J = 9,8 Hz, 1 H, 7-H), 7.82 (t, ^3J = 9.8 Hz, 1 H, 6-H), 7.95 (d, ^3J = 3.3 Hz, 2 H, 4'-H), 8.31 (s, 1 H, 2-H), 8.38 (d, ^3J = 9.6 Hz, 1 H, 4-H), 9.10 (d, ^3J = 9.8 Hz, 1 H, 8-H); ^{13}C nmr (75 MHz, $CDCl_3$): δ 111.3 (C-3), 119.1 (C-5'), 127.3 (C-2), 128.6 (C-7), 129.0 (C-5), 136.0 (C-8), 138.4 (C-4), 141.8 (C-6), 139.5 (C-8a), 143.4 (C-4'), 141.0 (C-3a), 141.8 (C-1), 179.1 (C-2'); ms: m/z 319 (7), 317 ($[M]^+$, 7), 290 (8), 288 (8), 210 (58), 207 (19), 205 (19), 140 (38), 126 (100).

Anal. Calcd. for $C_{13}H_8BrN_3S$: C, 49.06; H, 2.85; Br, 24.82; N, 13.21; S, 10.06. Found: C, 49.01; H, 2.90; Br, 24.83; N, 13.24; S, 10.02.

2-[(3-Chloroazulen-1-yl)diazenyl]-1,3-thiazole, (**29**Cl).

To the vigorous stirred solution of **5**H (35 mg, 0.146 mmol) in methanol (3 mL), solid potassium chlorate (8 mg, 0.066 mmol) was added in one portion followed by drop addition of HCl solution (0.1 ml, 36 %) and the reaction mixture was stirred for 2 hours at room temperature. Then DCM (25 mL) was added and the organic extract was neutralized with sodium bicarbonate (20 %), washed with water, dried (Na_2SO_4) and the solvent vaporized to dryness. The residue was separated by chromatography on silica gel using *n*-pentane:DCM (1:1 to 1:4) and three colored fractions were obtained: fraction 1 (pink) unidentified products (3 mg), fraction 2 (brown), chloro derivative **29**Cl (19 mg, 79 %) and fraction 3 (brown) starting material, **5**H (14 mg, recovered 40 %). The compound **29**Cl was obtained as dark brown crystals, mp 192 °C; uv (methanol): λ max (lg ε) 212 (4.21), 230 (4.30), 294 (4.21), 343 (3.87), 477 (4.40). ^{1}H nmr (300 MHz, $CDCl_3$): δ 7.31 (d, ^3J =3.4 Hz, 1 H, 5'-H), 7.49 (t, ^3J = 9.7 Hz, 1 H, 5-H), 7.55 (t, ^3J = 9,7 Hz, 1 H, 7-H), 7.86 (t, ^3J = 9.6 Hz, 1 H, 6-H), 7.96 (d, ^3J = 3.3 Hz, 2H, 4'-H), 8.27 (s, 1H, 2-H), 8.47 (d, ^3J = 9.3 Hz, 1 H, 4-H), 9.19 (d, ^3J = 9.6 Hz, 1 H, 8-H); ^{13}C nmr (75 MHz, $CDCl_3$): δ 119.1 (C-5'), 123.3 (C-3), 124.0 (C-2), 128.4 (C-5), 129.0 (C-7), 136.4 (C-8), 136.8 (C-4), 139.1 (C-8a), 139.5 (C-3a), 140.7 (C-1), 141.6 (C-6), 143.4 (C-4'), 179.2 (C-2'); ms: m/z 275 (6), 273 ($[M]^+$, 18), 246(7), 244 (21), 210 (67), 163 (21), 161 (62), 140 (48), 126 (100).

Anal. Calcd. for $C_{13}H_8ClN_3S$: C, 56.93; H, 3.31; Cl, 12.76; N, 15.33; S, 11.67. Found: C, 56.89; H, 3.25; Cl, 12.83; N, 15.39; S, 11.64.

3-(1,3-Thiazol-2yldiazenyl)azulen-1-yl Thiocyanate, (**29**SCN).

The azo compound **5**H (120 mg, 0.5 mmol) was dissolved in DCM (3 mL) and treated with lead thiocyanide (320 mg, 0.25 mmol) and bromine (160 mg, 0.5 mmol). The reaction mixture was stirred for 30 min. at room temperature, the solvent was vaporized to dryness and the residue was separated by chromatography on alumina with *n*-pentane:DCM (1:1). Four colored fractions were obtained: fraction 1, unidentified products (16 mg), fraction 2, 3-bromoazulene (60 mg, 0.19 mmol), fraction 3, compound **29**SCN (28 mg, 0.094 mmol, 28 %) and the fraction 4, starting material **5**H (32 mg, 0.133 mmol, recovered 67 %). The compound (**29**SCN) was obtained as dark brown crystals, mp 222-; ir 730, 750, 840, 885, 1015, 1130, 1210, 1280, 1305, 1330, 1380, 1420, 1450, 1480, 1570, 2160, 2370 cm^{-1}; UV (methanol): λ max (lg ε) 228 (4.41), 243sh (4.16), 293 (4.20), 340 (3.81), 466 (4.31); ^{1}H nmr (300 MHz, $CDCl_3$: δ 7.35 (d, ^3J = 3.3 Hz, 1 H, 4'-H), 7.70 (t, ^3J = 10.1 Hz, 1 H, 5-H), 7.73 (t, ^3J = 10.1 Hz, 1 H, 7-H), 8.01 (t, ^3J = 9.8 Hz, 1 H, 6-H), 7.99 (d, ^3J = 3.3 Hz, 1 H, 5'-H), 8.53 (s, 1 H, 2-H), 8.71 (d, ^3J = 9.6 Hz, 1 H, 4-H), 9.29 (d, ^3J = 9.8 Hz, 1 H, 8-H); ^{13}C nmr (75 MHz, $CDCl_3$): δ 110.3 (CN), 119.9 (C-5'), 141.2 (C-3), 131.9 (C-2), 130.1 (C-5), 131.0 (C-7), 137.5 (C-8), 137.9 (C-4), 142.3 (C-6), 139.3 (C-8a), 140.7 (C-3a), 143.7 (C-1), 143.7 (C-4'), 179.1 (C-2'); ms: m/z 296 ($[M]^+$, 4), 267 (3), 239 (14), 210 (75), 184 (11), 140 (22), 127 (100).

Anal. Calcd. for $C_{14}H_8N_4S_2$: C, 56.75; H, 2.72; N, 18.92; S, 21.60. Found: C, 56.65: H, 2.76; N, 18.90; S, 21.69.

Iodination of Compound **5**H through Halomercuration.

The azo compound **5**H (48 mg, 0.2 mmol) was dissolved in acetonitrile (6 mL) and treated with mercury acetate (318 mg, 1 mmol). The reaction mixture was stirred for 3 hours at room temperature, then cooled to 0 °C and treated with iodine (200 mg, 0.78 mmol). After 15 min at room temperature, to the mixture DCM (10 mL) was added and washed with water (2 × 25 mL) for mercury salts removing. The organic phase was dried (Na_2SO_4), the solvent was vaporised and the residue was separated on alumina using *n*-pentane:DCM, 1:1. Three coloured fractions were obtained: fraction 1, unidentified products (3 mg), fraction 2, diiododerivative **8**, (38 mg, 0.077 mmol, 39 %), fraction 3, iodoproduct **7** (42 mg, 0.115 mmol, 56 %); starting material conversion was quantitative.

2-[(3-Iodoazulen-1-yl)diazenyl]-1,3-thiazole, (**7**).

This compound was obtained as dark brown crystals, mp 177 °C (dec).; ^{1}H-mr (300 MHz, $CDCl_3$): δ 7.30 (d, ^3J = 3.3 Hz, 1 H, 5'-H), 7.58 (t, ^3J = 9.7 Hz, 1 H, 5-H), 7.63 (t, ^3J = 9,7 Hz, 1 H, 7-H), 7.90 (t, ^3J = 9.7 Hz, 1 H, 6-H), 7.97 (d, ^3J = 3.3 Hz, 1 H, 4'-H), 8.38 (d, ^3J = 9.8 Hz, 1 H, 4-H), 8.58 (s, 1 H, 2-H), 9.19 (d, ^3J = 9.8 Hz, 1 H, 8-H); ^{13}C nmr (75 MHz, $CDCl_3$): δ = 82.73 (C-3), 119.2 (C-5'), 126.2 (C-2), 128.8 (C-7), 129.3 (C-5), 135.5 (C-8), 141.2 (C-4), 141.5 (C-6), 138.8 (C-8a), 143.5 (C-4'), 144.0 (C-3a), 144.5 (C-1), 179.2 (C-2'); ms: m/z 365 ($[M]^+$, 8), 336 (10), 253 (30), 210 (62), 140 (23), 126 (100).

Anal. Calcd. for $C_{13}H_8IN_3S$: C, 42.63; H, 2.48; I, 34.68; N, 11.48; S, 8.74. Found: C, 42.66; H, 2.52: I, 34.57; N, 11.52; S, 8.73.

5-Iodo-2-[(3-iodoazulen-1-yl)diazenyl]-1,3-thiazole, (**8**).

This compound was obtained as dark brown crystals, mp 190 °C; uv (methanol): λ max (lg ε) 226 (4.22), 255 (4.10), 306 (4.20), 360 (3.78), 506 (4.36); ^{1}H nmr (300 MHz, $CDCl_3$): δ 7.96 (s, 1 H, 4'-H), 7.61 (t, ^3J = 9.7 Hz, 1 H, 5-H), 7.62 (t, ^3J = 9,7 Hz, 1 H, 7-H), 7.90 (t, ^3J = 9.7 Hz, 1 H, 6-H), 8.38 (d, ^3J = 9.6 Hz, 1 H, 4-H), 8.53 (s, 1H, 2-H), 9.11 (d, ^3J = 9.9 Hz, 1 H, 8-H); ms: m/z 491 ($[M]^+$, 5), 365 (7), 336 (13), 253 (18), 210 (32), 140 (37), 128 (42), 126 (100).

Anal. Calcd. for $C_{13}H_7I_2N_3S$: C, 31.72; H, 1.64; I, 51.60; N, 8.54; S, 6.50. Found: C, 31.75: H, 1.69: I, 51.41: N, 8.60; S, 6.55.

Methylation of Compound **5**H.

The azo compound **5**H, (48 mg, 0.2 mmol) was dissolved in 10 mL of chloroform and 1.5 mL methyl iodide. The reaction mixture was refluxed with magnetic stirring for 2 hour and a supplementary amount of methyl iodide (1.5 mL) was added after 1 hour to compensate its elimination through evaporation. The reaction mixture was evaporated under vacuum to dryness and the residue was chromatographed on an alumina. Three coloured fractions were collected: the first fraction, eluted with ethyl acetate was the starting material, (13 mg, unreacted compound 27

%); the second fraction was an unidentified yellow product (5 mg) and the third violet fraction, eluted with methanol, was the methylated product **28** (13 mg, 23 %). 2-[Azulen-1-yl)diazenyl]-3-methyl-1,3-thiazol-3-ium iodide, **28**, was obtained as green crystals, mp 272 °C; ir 615, 645, 725, 760, 780, 840, 890, 980, 1020, 1100, 1140, 1210, 1280, 1290, 1325, 1390, 1440, 1515, 1550, 1610, 2350, 2950, 3050 cm^{-1}; uv (methanol): λ max (lg ε) 233 (4.44), 255 (4.12), 298 (3.95), 338 (3.66), 561 (4.40); ^{1}H nmr (300 MHz, DMSO-d_6): δ 4.14 (s, 3 H, Me), 7.84 (d, ^3J = 4.1 Hz, 1 H, 4'-H), 7.90 (d, ^3J = 4.5 Hz, 1 H, 3-H), 8.16 (d, ^3J = 4.3 Hz, 1 H, 5'-H), 8.24 (t, ^3J = 9.7 Hz, 1 H, 5-H), 8.29 (d, ^3J = 4.5 Hz, 1 H, 2-H), 8.34 (t, ^3J = 9,7 Hz, 1 H, 7-H), 8.47 (t, ^3J = 9.8 Hz ,1 H, 6-H), 8.92 (d, ^3J = 9.6 Hz, 1 H, 4-H), 9.28 (d, ^3J = 9.8 Hz,1 H, 8-H); ^{13}C nmr (75 MHz, DMSO-d_6): δ 37.34 (N-Me), 117.4 (C-5'), 125.2 (C-3), 127.0 (C-2), 130.0 (C-5, C-7), 135.4 (C-8), 137.9 (C-4), 138.3 (C-4'), 138.4 (C-8a), 142.7 (C-6), 143.0 (C-3a), 145.1 (C-1), 176.1 (C-2').

Anal. Calcd. for $C_{14}H_{12}IN_3S$: C, 44.10; H, 3.17; I, 33.31; N, 11.03; S, 8.39. Found: C, 44.10; H, 3.18; I, 33.29; N, 11.01; S, 8.42.

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[a] For the sake of simplicity, the trivial names for azo compounds were prefered in the descriptive part of the paper.

[b] Corresponding author: e-mail: acrazus@cco.ro; Fax 0040 213121601.

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