

Oxidative benzylic substitution of azulene-1-azo(4'-methylbenzene)s

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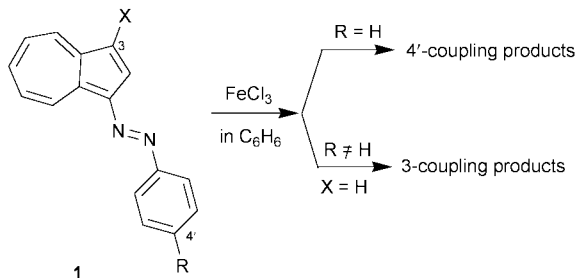
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Treatment of azulene-1-azo(4'-methylbenzene) with position 3 blocked by different substituents X (**2**) or by steric hindrance (**3**), with FeCl₃ in benzene, resulted in the substitution of one or two benzyl hydrogens by phenyl groups. Starting either from **2** (X = CH₃, Cl) or from **3**, triarylmethane derivatives **7** or **10** and corresponding alcohols **9** or **11** are the main separated products while starting from **2** (X = OCH₃), diarylmethanol **8** as well as the related benzophenone and ether, **13** and **14**, respectively, are isolated as major products. Diphenylmethane and triphenylmethane also result from almost all reactions. Conversion of the starting materials was good and the products that were separated and characterised are obtained in 43.5–60.5% overall yields. Single-electron transfer oxidation was thought to be the first reaction step with the generation of the radical cation **2**^{•+}. As a result of the proton and electron transfer or hydrogen atom transfer from **2**^{•+}, the cation **16** with some benzylic character was formed. The cation **16** alkylated benzene in the subsequent reaction and diarylmethane derivatives were formed. A similar reaction pathway can be proposed for triarylmethane products generation.

In a recent study on the azulene-1-azobenzenes **1** oxidation in the presence of ferric chloride in benzene,¹ we have found that the reaction was mainly directed to 4',4' or 3,3 coupling depending on the structure of **1**. Whereas for **1** R = H, the



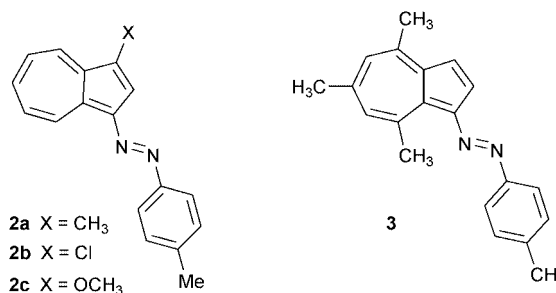
oxidative *p*-phenyl coupling was the major reaction pathway, the dimerisation of **1** R ≠ H occurred mainly on position 3 of the azulene moiety. The compound **1** R = OCH₃ reacted nearly quantitatively and the separated and identified coupling products exceeded 70% yield. Surprisingly, in spite of the good reaction conversion of **1** R = CH₃, the reaction mixture contained 3,3-coupling product only in 14% yield, together with a significant amount of tar. In the complicated ¹H-NMR spectrum of a mixture extracted from this tar, the singlet signal for 4'-methyl protons (at 2.40 ppm) disappears and some small singlets can be observed between 4 and 6 ppm. It seems, therefore, that the azulene-1-azo(4'-methylbenzene) reacted not only at position 3 in the azulene moiety but also at the benzyl methyl to promote the oligomerisation and polymerisation.

The substitution of the benzyl position under oxidative conditions with a nucleophile is one of the important reactions of alkylaromatics from both the practical and the theoretical point of view, and radical cations are proved to be the reaction intermediates.² In most cases, polyalkylated benzenes or anthracenes were substrates and the pyridine bases or other species with N or O functions present in medium were tested as nucleophiles. In the presence of Cu(II)/S₂O₈²⁻,³ Fe(II)/H₂O₂⁴ or tris(phenanthroline)iron tris(hexafluorophosphate),⁵ benzyl alcohols and carbonyl compounds were reported as reaction products. In

our studies on single-electron oxidation of the compounds **1** R = CH₃, in the absence of a classical nucleophile, the reagents which can attack the benzyl position were azulene for **1** X = H and benzene. Based on these results we think we could obtain interesting information on the benzyl substitution from the behaviour of compounds **1** R = CH₃ with the reactive position 3 blocked in order to avoid undesirable reactions.

Results and discussion

The starting substrates were 3-substituted azulene-1-azo(4'-methylbenzenes), **2a–2c**; the effect of steric hindrance of the 3 position as in compound **3** was also considered.



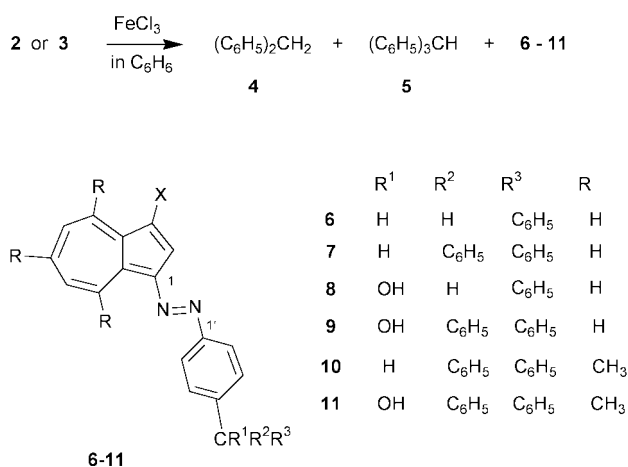
For the synthesis of these compounds, the corresponding substituted azulenes were coupled with the diazonium salt of toluidine (in 90–97% yields).⁶

The oxidation of the azo compounds was carried out in benzene, using ferric chloride in excess (from 4:1 to 6:1 with respect to the azo compound), at room temperature, with stirring. The reaction proceeded slowly and by prolonging the reaction time, modest yields were accompanied by many secondary reactions. After work-up, the products were separated by column chromatography and, when necessary, purified by crystallisation (some chromatographic fractions were contaminated by traces of compounds with aliphatic protons in the ¹H-NMR spectrum). The main reaction products are reported in Scheme 1 and in Table 1.

Table 1 Oxidation of azulene-1-azo(4'-methylbenzenes) **2** and **3** with FeCl₃ in benzene^a

X	Recovered 2 or 3 (%)	Product yield ^{b,c} (%)							
		4	5	6	7	8	9	10	11
CH ₃ (2a)	35	2	3	11	16	0	20	—	—
Cl ^d (2b)	40	4.5	13	2	^e	0	22	—	—
OCH ₃ ^d (2c)	14.5	— ^e	0	0	0	30	0 ^f	—	—
3	23.5	3	11	—	—	—	—	21	17

^a The contact time between the reactants was 48 hours for **2a**, **2b** and **3** and 4 hours for **2c**. ^b Yields in %, based on recovered starting material. ^c For each experiment, the final eluted fraction (with very polar solvents) shows in the aromatic field of the ¹H-NMR spectra complicated signal groups proving the partial oligomerisation of the starting molecules. ^d Other products obtained from **2b** and **2c** will be reported below. ^e Traces of product. ^f After 48 hours and supplementary addition of FeCl₃, the triarylmethanol **9** R = OCH₃ was formed in 6.5% yield only.

**Scheme 1**

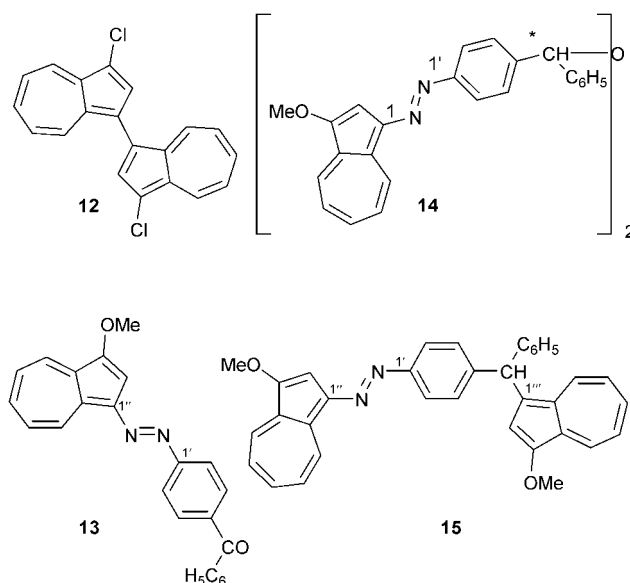
The general features of all products obtained are the similarity in the ¹H-NMR spectra of the azulene moiety proton signals, both in the starting compounds **2** or **3** and in the products, as well as the lack of the proton signal for benzyl CH₃ in the products. For the products **6** X = CH₃ or Cl, a singlet at 4.03 ppm (2 H) characteristic for the CH₂ protons in diarylmethane compounds (for diphenylmethane, 3.96 ppm)⁷ can be observed. The products **7** X = CH₃ or Cl and **10** show, at 5.63 ppm, a singlet (1 H) characteristic for CH in triarylmethane derivatives (for triphenylmethane 5.53 ppm).⁷ The chemical shifts for these proton signals are not influenced by substituents on the azulene moiety. The ratio between the proton signals in the ¹H-NMR spectra, and also the mass spectra, are in agreement with the proposed structures for **6**, **7** and **10**. Diphenylmethane, **4**, and triphenylmethane, **5**, were also separated from almost all reaction mixtures.

The singlet at 5.91 ppm (1 H) in the ¹H-NMR spectrum of the product **8** X = OCH₃ can be assigned to a proton characteristic of a diarylmethanol (for benzhydrol 5.67 ppm) and the IR spectrum indicates, indeed, the presence of an OH function for **8**. The chemical shifts of other proton signals in the ¹H-NMR spectrum and the ratio between them together with the mass spectrum are consistent with the diarylmethanol structure for **8**.

The IR spectra of compounds **9** X = CH₃ or Cl show the OH signal (3580 cm⁻¹, m, in CH₂Cl₂) and in the ¹H-NMR spectra only aromatic (phenyl and azulenyl) proton signals are present. The ¹H-NMR spectra were also recorded in CD₂Cl₂ for accurate phenyl signals integration and the results are in accord with a triarylmethanol structure for **9**. A triarylmethanol structure was also found for compound **11**. The same conclusion concerning the structure of **9** and **11** can be drawn from their mass spectra.

The ¹³C-NMR and elemental analysis for all mentioned products are also consistent with the structure assignments.

Besides the products described in Table 1, the oxidation of **2b** also yields 3,3'-dichloro-1,1'-biazulene, **12**, (6%) and the oxidation of **2c** affords the products **13** (8.5%), **14** (20%) and **15** (2%).



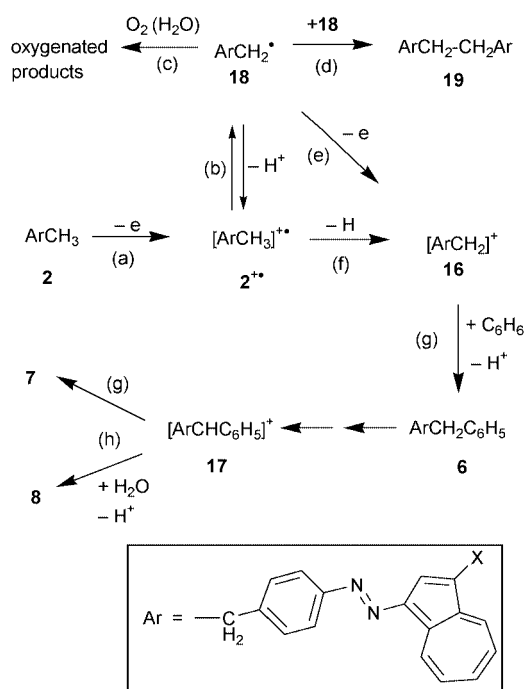
Compound **13** shows in its IR spectrum a carbonyl group band at 1650 cm⁻¹ and the presence of a C=O function is also confirmed by the ¹H-NMR spectrum. Thus, for all studied compounds, including **13**, the AB spin systems for disubstituted phenyl rings showed small changes in chemical shift for protons *vicinal* to the N=N bond (7.8–7.9 ppm). However, the two protons *ortho* to the carbonyl carbon in **13** are strongly shielded (about 0.5 ppm) in comparison with the compounds in which this atom is sp³ hybridised, suggesting the involvement of this carbon atom in a carbonyl bond. The structure assignment for **13** as azulene-1-azo(4'-benzoylbenzene) was also confirmed by other proton signals, by the mass spectrum and by elemental analysis.

The proton chemical shifts in the ¹H-NMR spectrum of **14** are almost identical to those for alcohol **8** X = OCH₃, excepting the chemical shift for the CH benzylic singlet. The hydroxy proton vanished and in the IR spectrum the OH signal was not detected, suggesting an ether structure for **14**. In the mass spectrum of compound **14** the molecular ion (*m/z* = 718) is not detectable, however, the abundance of [M⁺ + 1] is 100%. Another observation is the presence of the peak at 359 (40%) representing M/2. These observations can suggest the tendency of ether **14** for protonation and for transfer of two electrons with the generation of a dication during the mass spectrum recording, and also the low stability of the molecular ion. In the ¹H-NMR spectrum of **14** all proton signals are split with *J ca.* 1 Hz (the split signals have the same ratio in their intensities), although the mass spectrum and elemental analysis seem to

indicate the presence of a single compound. These results are in agreement with the formation of a racemic and *meso* mixture for the ether **14** with two identical asymmetric carbon atoms. The ¹H- and ¹³C-NMR spectra of the side-product **15**, together with COSY and HETCOR experiments, are in agreement with an interesting structure having the benzyl position substituted by both the azulene moiety and phenyl. Structure assignment for the product **15** is based on the data reported in the Experimental section (the purification and complete characterisation of **15** could not be accomplished due to the small amount of product formed).

The structure of the products obtained in the reaction of **2** and **3** indicates that the reaction proceeds exclusively at the benzyl position (in a subsequent reaction the C–azo bond can be broken with the formation of diphenylmethane, **3**, and triphenylmethane, **4**). (a) 3-Methoxy compound **2c** reacted fastest, (b) the overall yield of the separated product decreases in order **2c**, **2a**, **3** and **2b** and in the same order the amount of resulting tar increases and (c) while the oxidation of the compound **2c** affords only diarylmethane compounds (**8** X = OCH₃, **13** and **14**), triarylmethane compounds (**7** X = CH₃ and Cl and **9** X = CH₃ and Cl, or **10** and **11**) are formed as major reaction products starting from **2a** and **2b** or from **3**.

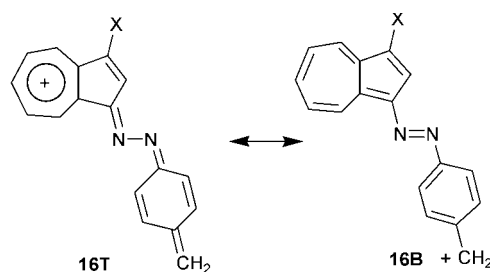
In the previous study concerning the dimerisation of the azulene-1-azoarenes¹ we have explained the product generation by the coupling of two radical cations obtained in an oxidative single-electron transfer from the azo compound to FeCl₃. We suggest a similar oxidation of the compounds **2** or **3** to the corresponding radical cations as the first step in the reported reactions (Scheme 2, step a). However, the subsequent



dimerisation of radical cation $2^{•+}$ (or $3^{•+}$) is hindered because both its reactive positions 3 and 4' are blocked. Therefore, this intermediate must react further by another pathway, a pathway that yields phenyl-substituted products at the benzyl carbon. Benzene alkylation, generally, is an electrophilic reaction and, therefore, cations such as **16** and **17** can be postulated as alkylating reagents.

However, for the benzyl oxidative substitution of radical cations the transfer of the benzyl proton to a base present in the reaction medium, in an acid–base equilibrium,^{2,8} is ordinarily expected to be the favoured pathway (step b) because a radical cation with a proton attached to carbon is often

“superacid”.^{2-5,8-10} The resulting radical **18** can react with oxygen in the air (step c) yielding products with O-containing functions at the benzyl carbon (alcohol, aldehyde, etc.) or has the possibility to dimerise to ethane derivative **19** (step d). Because, generally, the neutral radical is more available for a subsequent single-electron oxidation than its parent compound,¹¹ the radical **18** could be oxidised to the corresponding cation **16** (step e). The structural peculiarities that stabilise the positive charge of the radical cation (for example as a tropylium cation moiety) are expected to weaken its acidity and therefore decrease its aptitude for proton loss.⁸ Therefore, the absence of oxygenated products with an ArCH₂ skeleton and of compounds **19** can be explained by the shifting of the equilibrium (step b) toward $2^{•+}$ and by a higher rate of the single electron oxidation (step e) as compared to the rates of steps c and d (the reversibility of step d can also be considered). Although the benzyl radical cation shows a strong preference for the heterolytic pathway, the alternative path involving a hydrogen atom transfer has sometimes been considered.^{8,10} For the azulenic radical cation $2^{•+}$, with a well stabilised charge, hydrogen atom transfer (step f) could be a favourable alternative reaction route. This pathway allows the direct generation of the stabilised cation **16** and the nonpolar reaction medium seems to favour homolytic C–H bond dissociation. From the possible resonance structures for **16**, only two, the tropylium and benzyl structures, **16(T)** and **16(B)**, respectively, are illustrated because only these



contribute significantly to the stability and reactivity of the formed ion. The attack of **16** towards the benzene (step g) with the generation of diarylmethane product **6** is a well-known electrophilic aromatic benzylation.

From the starting materials investigated, **2c** displays the lowest oxidation potential and, consequently, the best reactivity. While triarylmethane compounds (**7**, **9**, **10** and **11**) were the major products in the oxidation of **2a**, **2b** and **3**, only the diarylmethanol, **8** and the derivatives of this alcohol (benzophenone **13** and ether **14**) were formed in the reaction of **2c**. These results seem to confirm the enhanced stability of carbocation **16** X = OCH₃ in comparison with **16** X = CH₃ or Cl, which reacts again with benzene to produce triarylmethane derivatives. The methyl groups attached to the seven-membered ring in **3** contribute to the stability of the cationic species ($2^{•+}$ and 2^+) and can promote the oxidation (step a). However, in spite of the steric blocking of position 3 in azulene, this position remains partly reactive and can produce polymerisation, a reaction supported by the overall yield diminution.

The oxygenated products can result from the radical reaction with oxygen in the air and the nucleophilic attack of water on the cationic intermediates. The assumption that the benzene alkylation proceeds *via* a heterolytic mechanism suggests that the generation of oxygenated compounds involves the same cation intermediates that attack the benzene.

The reaction of the cationic intermediates with water upon the decomposition of reaction mixture generates the alcohols (step h). However, the presence of the benzophenone **13** seems to indicate that at least some alcohol is generated before the work-up of the reaction mixture (the reaction occurs without protection from the air). Alcoholic compounds could be also obtained from the hydrolysis of the corresponding chloro-compounds generated as intermediates from the carbocations,

however the first pathway seems more probable because in the reaction mixtures halogenated compounds were never found, not even in traces.

The generation of di- and triphenylmethane, **4** and **5** requires that the C–azo bond break. There are two possible pathways for this bond dissociation, a homolytic as well as heterolytic one and two possible breaking positions, azulene–azo or phenyl–azo. Unfortunately, the available experimental evidence does not differentiate between these pathways (the azulene–azulene coupled product **12** would be consistent with a dimerisation of two azulene radicals produced in a homolytic azulene–azo bond break).

In conclusion we have found a system in which the benzyl hydrogen substitution by phenyl occurs to a good extent and generates di- and triarylmethane compounds and their corresponding oxygenated derivatives (alcohols, ether and benzophenone).

Experimental

Melting points: Kofler apparatus (Reichert, Austria). Elemental analyses: Perkin Elmer CHN 240B. UV: Beckman DK-2A, UV 5240. ¹H- and ¹³C-NMR: Bruker WM 300, AC 300, ARX 300, and Gemini 300 (¹H: 300 MHz, ¹³C: 75.47 MHz), *J* values are given in Hz, TMS was used as internal standard in CDCl₃ or CD₂Cl₂ as solvent; signals were assigned on the basis of COSY and HETCOR correlation spectra (the numbering for the compounds was indicated on the structures and in Scheme 1); abbreviations used for ¹³C-NMR: p, primary; s, secondary; t, tertiary; q, quaternary. IR: Beckmann IR 5A. Mass spectra: Finnigan MAT 311-A/100MS. Column chromatography: basic alumina [activity BII-III (Brockmann)] or silica gel [70–230 mesh (ASTM)]. Dichloromethane (DCM) was distilled over calcium hydride, ethyl acetate over anhydrous sodium carbonate and trichloromethane was filtered through basic alumina.

Synthesis of starting azocompounds

For the synthesis of azulene-1-azoarenes we have adapted both the Gerson and the Anderson protocols.⁶ The yields of the azocompounds were above 90% and the resulted compounds were characterised. The synthesis protocol, the yield and the structure assignments for **2b** have been reported in the literature.^{6c}

3-Methylazulene-1-azo(4'-methylbenzene), 2a. Black crystals, mp 131–132 °C (*n*-hexane) (Found: C, 82.99; H, 6.23; N, 10.78. C₁₈H₁₆N₂ requires C, 83.04; H, 6.20; N, 10.76%); λ_{max}(dioxane)/nm 243 (log ε/dm³ mol⁻¹ cm⁻¹ 4.34), 285 (4.32), 338 (4.23), 437 (4.48), 600 sh (2.81); δ_H(CDCl₃) 2.44 (3 H, s, 4'-CH₃), 2.66 (3 H, s, 3-CH₃), 7.20 (1 H, t, *J* 9.8, 5-H), 7.26 (1 H, t, *J* 9.9, 7-H), 7.32 (2 H, d, *J* 8.3, 3'-, 5'-H), 7.64 (1 H, t, *J* 9.9, 6-H), 7.89 (2 H, dt, *J* 8.3 and 1.7, 2'-, 6'-H), 8.15 (1H, s, 2-H), 8.20 (1 H, d, *J* 9.3, 4-H), 9.22 (1 H, d, *J* 9.5, 8-H); δ_C(CDCl₃) 12.89 (p, 3-CH₃), 21.57 (p, 4'-CH₃), 122.20 (t), 125.21 (t), 125.42 (t), 125.73 (t), 128.68 (t), 129.78 (t), 134.99 (t), 10.14%; λ_{max}(dioxane)/nm 256 (log ε/dm³ mol⁻¹ cm⁻¹ 4.25), 292 (4.21), 350 (4.24), 472 (4.41), 493 (4.41); δ_H(CDCl₃) 2.45 (3 H, s, CH₃ in 4'), 4.05 (3 H, s, OCH₃), 6.88 (1 H, t, *J* 9.7, 5-H or 7-H), 6.97 (1 H, t, *J* 9.6, 7-H or 5-H), 7.26 (2 H, dt, *J* 8.8 and 2.2, 3'-, 5'-H), 7.41 (1 H, t, *J* 9.9, 6-H), 7.62 (1 H, s, 2-H), 7.85 (2 H, dt, *J* 8.6 and 2.1, 2'-, 6'-H), 8.15 (1 H, dd, *J* 9.1 and 1.1, 4-H), 9.02 (1-H, d, *J* 9.5, 8-H); δ_C(CDCl₃) 21.52 (p), 57.77 (p), 102.57 (t), 122.09 (t), 124.51 (t), 124.58 (t), 129.75 (t), 131.46 (q), 134.09 (q), 134.25

3-Methoxyazulene-1-azo(4'-methylbenzene) 2c. Black powder, mp 102–103 °C (from CH₂Cl₂, on precipitation with *n*-pentane) (Found: C, 78.12; H, 5.90; N, 10.16. C₁₈H₁₆N₂O requires C, 78.24; H, 5.84; N, 10.14%); λ_{max}(dioxane)/nm 256 (log ε/dm³ mol⁻¹ cm⁻¹ 4.25), 292 (4.21), 350 (4.24), 472 (4.41), 493 (4.41); δ_H(CDCl₃) 2.45 (3 H, s, CH₃ in 4'), 4.05 (3 H, s, OCH₃), 6.88 (1 H, t, *J* 9.7, 5-H or 7-H), 6.97 (1 H, t, *J* 9.6, 7-H or 5-H), 7.26 (2 H, dt, *J* 8.8 and 2.2, 3'-, 5'-H), 7.41 (1 H, t, *J* 9.9, 6-H), 7.62 (1 H, s, 2-H), 7.85 (2 H, dt, *J* 8.6 and 2.1, 2'-, 6'-H), 8.15 (1 H, dd, *J* 9.1 and 1.1, 4-H), 9.02 (1-H, d, *J* 9.5, 8-H); δ_C(CDCl₃) 21.52 (p), 57.77 (p), 102.57 (t), 122.09 (t), 124.51 (t), 124.58 (t), 129.75 (t), 131.46 (q), 134.09 (q), 134.25

(t), 136.07 (t), 139.08 (q), 140.47 (q), 140.76 (t), 152.48 (q), 152.66 (q); *m/z* (70 eV) 276 (M⁺, 3%), 275 (M⁺ – 1, 2.7), 261 (M⁺ – 15, 2), 157 (C₁₀H₆OCH₃⁺, 19), 142 (13), 128 (4.5), 127 (4.5), 115 (9), 114 (100), 91 (C₇H₇⁺, 51.5), 88 (22.5), 65 (47.5).

4,6,8-Trimethylazulene-1-azo(4'-methylbenzene), 3. Brown-black microcrystalline powder, mp 155–156 °C (from ethyl ether on precipitation with *n*-pentane) (Found: C, 83.37; H, 6.94; N, 9.69. C₂₀H₂₀N₂ requires C, 83.30; H, 6.99; N, 9.71%); λ_{max}(dioxane)/nm 245 (log ε/dm³ mol⁻¹ cm⁻¹ 4.33) 292 (4.26), 325 (4.12), 440 (4.39); δ_H(CDCl₃) 2.41 (3 H, s, 4'-CH₃), 2.59 (3 H, s, 6-CH₃), 2.83 (3 H, s, 4-CH₃), 3.33 (3 H, s, 8-CH₃), 7.12 (1 H, s, 5-H), 7.23 (1 H, s, 7-H), 7.27 (2 H, d, *J* 8.2, 3'-, 5'-H), 7.33 (1 H, d, *J* 4.5, 3-H), 7.77 (2 H, d, *J* 8.5, 2'-, 6'-H), 8.12 (1 H, d, *J* 4.8, 2-H); δ_C(CDCl₃) 21.41 (p), 25.30 (p), 28.54 (p), 29.64 (p), 117.83 (t), 122.01 (t), 122.28 (t), 129.62 (t), 130.38 (t), 132.67 (t), 133.40 (q), 138.82 (q), 140.31 (q), 146.95 (q), 147.41 (q), 147.50 (q), 149.61 (q), 152.49 (q); *m/z* (70 eV) 289 (M⁺ + 1, 2%), 288 (M⁺, 9.5), 287 (M⁺ – 1, 7.0), 273 (M⁺ – CH₃, 13), 182 (100).

Oxidation with ferric chloride—general procedure

In a round-bottomed flask, to a magnetically stirred solution of 1 mmol azocompound **2** or **3** in 25 cm³ benzene, anhydrous ferric chloride was added at room temperature, without air protection (the azocompound:FeCl₃ molar ratio will be indicated for each azocompound). From time to time the separated viscous oily product was mechanically removed from the flask wall for better contact between the reactants. The reaction was monitored by TLC (homogenous samples were collected, washed with a saturated sodium hydrogen carbonate solution and dried) and it was stopped when the spot of the starting compound had vanished or maintained a constant intensity (the reaction time will be indicated for each azo compound). The reaction mixture was quenched in a saturated sodium hydrogen carbonate solution and the majority of the benzene was evaporated *in vacuo*. The suspension was extracted three times with 200 cm³ DCM, the organic extracts were washed once with water, dried (Na₂SO₄) and the solvent was evaporated *in vacuo*. The residue was separated by column chromatography under the conditions described below.

Reaction of 3-methylazulene-1-azo(4'-methylbenzene), 2a. The azocompound:FeCl₃ ratio = 1 : 4; reaction time = 48 hours. The resulting residue on work-up (290 mg) was separated by chromatography on silica gel, eluent DCM–*n*-pentane (4 : 1); *fraction 1* (173 mg) was again separated on alumina; *fraction 2* (4 mg), indefinite pink-coloured compound or mixture (with complicated ¹H-NMR spectrum and a proton signal above 10 ppm); *fraction 3* (9 mg), complex mixture of components with very close R_F; *fraction 4* (64 mg, 0.15 mmol) triarylmethanol **9** X = CH₃. Chromatography of *fraction 1* was carried out on alumina with *n*-pentane–ethyl acetate (50 : 1): *fraction 1.1* (3 mg), green oily unidentified mixture; *fraction 1.2* (7 mg) mixture of diphenylmethane, **4**, and triphenylmethane, **5**,¹² in molar ratio 1 : 1.5 (from ¹H-NMR spectrum), yields 3% and 2%, respectively; *fraction 1.3* (90 mg, 35 mmol) starting azocompound, **2a**, and *fraction 1.4* (66 mg), mixture of compounds **6** X = CH₃ and **7** X = CH₃ molar ratio 1 : 1.45 (from ¹H-NMR spectrum). The product **7** X = CH₃ was separated from the *fraction 1.4* by chromatography on alumina with *n*-pentane–ethyl acetate (100 : 1).

3-Methylazulene-1-azo[4'-(diphenylmethyl)benzene], 7 X = CH₃. Yield 16%, black microcrystalline powder, mp 141–142 °C (from DCM on precipitation with *n*-pentane) (Found: C, 87.19; H, 5.92; N, 6.89. C₃₀H₂₄N₂ requires C, 87.35; H, 5.86; N, 6.79%); δ_H(CD₂Cl₂) 2.66 (3 H, s, 3-CH₃), 5.63 (1 H, s, (C₆H₅)₂CH-), 7.13–7.35 (14 H, m, 5-, 7-, 3'-, 5'-H and 2 C₆H₅), 7.64 (1 H, t, *J* 9.9, 6-H), 7.87 (2 H, dt, *J* 9.2 and 1.0, 2'-, 6'-H), 8.13 (1 H, s, 2-H), 8.21 (1 H, d, *J* 9.6, 4-H), 9.18 (1 H, d, *J* 9.8,

8-H); $\delta_{\text{C}}(\text{CD}_2\text{Cl}_2)$ 12.78 (p, 3- CH_3), 55.77 (t, $(\text{C}_6\text{H}_5)_2\text{CH}-$), 122.10 (t), 125.28 (t), 125.45 (t), 125.83 (t), 126.46 (t), 128.42 (t), 128.70 (q), 129.55 (t), 130.12 (t), 134.94 (t), 135.10 (t), 139.08 (q), 139.33 (t), 141.48 (q), 142.68 (q), 143.81 (q), 145.02 (q), 152.88 (q); m/z (70 eV) 414 ($\text{M}^+ + 2$, 2%), 413 ($\text{M}^+ + 1$, 8), 412 (M^+ , 35), 411 ($\text{M}^+ - 1$, 39), 397 ($\text{M}^+ - \text{CH}_3$, 3), 141 (100), 115 (92).

3-Methylazulene-1-azo[4'-(phenylmethyl)benzene], 6 $X = \text{CH}_3$. Yield 11% (from $^1\text{H-NMR}$ spectrum), contaminated with **7** $X = \text{CH}_3$, black powder; $\delta_{\text{H}}(\text{CD}_2\text{Cl}_2)$ 2.63 (3 H, s, 3- CH_3), 4.03 (0.8 H, s, $(\text{C}_6\text{H}_5)_2\text{CH}_2$ - in **6**), 5.63 (0.6 H, s, $(\text{C}_6\text{H}_5)_2\text{CH}-$ in **7**); the signals in the aromatic field are common for **6** and **7**: 7.15–7.35 (m, 3'-, 5'-, 7-, 5-H and C_6H_5), 7.65 (1 H, t, J 9.9, 6-H), 7.86 (2 H, dt, J 8.8 and 1.9 Hz, 2'-, 6'-H), 8.10 (1 H, s, 2-H), 8.21 (1 H, d, J 9.3, 4-H), 9.17 (1 H, d, J 9.8, 8-H); m/z (FD) 415 ($\text{M}^+ + 3$, 4%), 414 ($\text{M}^+ + 2$, 8), 413 ($\text{M}^+ + 1$, 100), 412 (M^+ , 15) for **7** and 339 ($\text{M}^+ + 3$, 2), 338 ($\text{M}^+ + 2$, 5), 337 ($\text{M}^+ + 1$, 36), 336 (M^+ , 2) for **6**.

3-Methylazulene-1-azo[4'-(diphenylhydroxymethyl)benzene], 9 $X = \text{CH}_3$. Yield 20%, brown-black crystals, mp 123–124 °C (from DCM on precipitation with *n*-pentane) (Found: C, 83.10; H, 5.71; N, 6.22. $\text{C}_{30}\text{H}_{24}\text{N}_2\text{O}$ requires C, 83.07; H, 5.65; N, 6.54%; λ_{max} (dioxane)/nm 240 (log $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 4.35), 286 (4.30), 340 (4.42), 441 (4.50), 600 sh (2.88); $\nu_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$ 3580 (OH); $\delta_{\text{H}}(\text{CD}_2\text{Cl}_2)$ 2.66 (3 H, s, 3- CH_3), 2.98 (1 H, s, OH), 7.28 (1 H, t, J 9.7, 5-H), 7.27–7.36 (11 H, m, 7-H and 2 C_6H_5), 7.32 (2 H, dt, J 8.6 and 1.8, 3'-, 5'-H), 7.70 (1 H, t, J 9.9, 6-H), 7.88 (2 H, dt, J 8.8 and 1.9, 2'-, 6'-H), 8.11 (1 H, s, 2-H), 8.27 (1 H, d, J 9.4, 4-H), 9.20 (1 H, d, J 9.5, 8-H); $\delta_{\text{C}}(\text{CD}_2\text{Cl}_2)$ 13.27 (p, 3- CH_3), 86.62 (q), 122.23 (t), 125.85 (t), 126.41 (t), 126.91 (t), 128.11 (t), 128.66 (t), 128.77 (t), 129.40 (t), 129.80 (q), 135.57 (t), 136.12 (t), 140.02 (q), 140.33 (t), 142.35 (q), 143.33 (q), 147.65 (q), 148.44 (q), 154.05 (q); m/z (FD) 430 ($\text{M}^+ + 2$, 7.5%), 429 ($\text{M}^+ + 1$, 42), 428 (M^+ , 100); m/z (70 eV) 430 ($\text{M}^+ + 2$, 4%), 429 ($\text{M}^+ + 1$, 20), 428 (M^+ , 65), 427 ($\text{M}^+ - 1$, 11), 141 (100), 115 (46).

Reaction of 3-chloroazulene-1-azo(4'-methylbenzene), 2b.

Ferric chloride was added in two portions, 4 mmol at the beginning of the stirring and 2 mmol after three hours (addition in only one portion lowers the yield); the total reaction time was 48 hours. The resulting residue on work-up (340 mg) was separated on silica gel, eluent *n*-pentane–ethyl acetate (from 20:1 to 1:1): *fraction 1* (150 mg) and *fraction 2* (12 mg) were again chromatographed; *fraction 3* (23 mg), was a complex unidentified mixture; *fraction 4* (59 mg, 0.13 mmol), triarylmethanol **9** $X = \text{Cl}$; *fraction 5* (20 mg), a mixture of oligomers with complex signals in the aromatic field of $^1\text{H-NMR}$ spectrum. *Fraction 1* was separated on silica gel with *n*-pentane: *fraction 1.1* (6 mg, 0.02 mmol) 3,3'-dichloro-1,1'-biazulene, **12**; *fraction 1.2* (25.5 mg), mixture of diphenylmethane, **4**, and triphenylmethane, **5**,¹² molar ratio 1:3 (from $^1\text{H-NMR}$), yields 4.5% and 13%, respectively; *fraction 1.3* (6.5 mg), uncharacterised complex mixture; *fraction 1.4* (112 mg, 0.4 mmol) starting material, **2b**. *Fraction 2* was separated on silica gel with *n*-pentane–DCM 2:1: *fraction 2.1* (4.5 mg), uncharacterised mixture, *fraction 2.2* (6 mg), mixture of **6** $X = \text{Cl}$, and **7** $X = \text{Cl}$, molar ratio 1:4 (from $^1\text{H-NMR}$), yields 2% and >1%, respectively, and *fraction 2.3* (1.5 mg), complex unidentified mixture. It cannot be claimed that analysis of the spectra of *fraction 2.2* allows unequivocal structure assignment for the compounds **6** $X = \text{Cl}$ and **7** $X = \text{Cl}$. However, the chemical shifts of many signals in the recorded spectra of *fraction 2.2* are similar to those present in the spectra of other compounds **6** and **7** (for example the aliphatic proton signals for $\text{C}_6\text{H}_5\text{CH}_2-$ or for $(\text{C}_6\text{H}_5)_2\text{CH}-$). GCMS is not useful in this case because of the very low volatility of the products.

3,3'-Dichloro-1,1'-biazulene, 12. Yield 6%, green needles, mp 143–144 °C (from diethyl ether on precipitation with *n*-pentane) (Found: C, 74.30; H, 3.71; Cl, 21.99. $\text{C}_{20}\text{H}_{12}\text{Cl}_2$ requires C, 74.32; H, 3.74; Cl, 21.94%; λ_{max} (dioxane)/nm 246 sh (log ϵ/dm^3

$\text{mol}^{-1} \text{ cm}^{-1}$ 4.48), 270 (4.67), 301 sh (4.45), 313 (4.54), 334 sh (3.92), 395 (4.16), 638 (2.86); $\delta_{\text{H}}(\text{CDCl}_3)$ 7.07 (2 H, t, J 9.8, 7-, 7'-H), 7.19 (2 H, t, J 9.7, 5-, 5'-H), 7.61 (2 H, t, J 9.8, 6-, 6'-H), 7.92 (2 H, s, 2-, 2'-H), 8.24 (2 H, d, J 9.4, 8-, 8'-H), 8.42 (2 H, d, J 9.8, 4-, 4'-H); $\delta_{\text{C}}(\text{CDCl}_3)$ 76.59 (q), 77.02 (q), 77.44 (q), 116.53 (q), 123.13 (t, C-5), 123.74 (t, C-7), 135.00 (t, C-4), 135.79 (t, C-2), 136.96 (t, C-8), 139.79 (t, C-6); m/z (70 eV) 327 ($\text{M}^+ + 4$, 3%), 326 ($\text{M}^+ + 3$, 13), 325 ($\text{M}^+ + 2$, 16), 324 ($\text{M}^+ + 1$, 77), 323 (M^+ , 26), 322 ($\text{M}^+ - 1$, 100), 161 (13).

3-Chloroazulene-1-azo[4'-(diphenylmethyl)benzene], 7 $X = \text{Cl}$, in a mixture with 3-chloroazulene-1-azo[4'-(phenylmethyl)benzene], **6** $X = \text{Cl}$. Black powder, $\delta_{\text{H}}(\text{CDCl}_3)$ 4.05 (0.30 H, s, $(\text{C}_6\text{H}_5)_2\text{CH}_2-$ in **6** $X = \text{Cl}$), 5.62 (0.85 H, s, $(\text{C}_6\text{H}_5)_2\text{CH}-$ in **7** $X = \text{Cl}$), the protons signals in aromatic field for **6** and **7** are common: 7.13–7.41 (12 H, m, 3-, 7-H and phenyl protons), 7.86 (2-H, dt, J 8.5 and 2.0, 2'-, 6'-H), 8.19 (1 H, s, 2-H), 8.41 (1 H, d, J 9.4, 4-H), 9.24 (1 H, d, J 9.9, 8-H); $\delta_{\text{C}}(\text{CDCl}_3)$ 56.71 (s), 120.98 (t), 122.22 (t), 122.86 (t), 126.20 (t), 126.44 (t), 126.65 (q), 128.38 (t), 128.52 (t), 128.69 (t), 129.46 (t), 130.11 (q), 136.05 (t), 136.18 (q), 137.41 (q), 140.83 (q), 143.60 (t), 145.68 (q), 152.40 (q); m/z (15 eV) 434/432 ($\text{M}(\mathbf{7})^+ + 35/100\%$), 435/433 ($\text{M}(\mathbf{7})^+ + 1$, 8.5/37), 431 (39), 397 ($\text{M}(\mathbf{7})^+ - 35$, 8.5), 379 (14.5%), 378/376 ($\text{M}(\mathbf{6})^+ + 60/100$), 377 (45), 375 (41), 358 (12), 356 (43), 341 (10), 189 (11.5), 166 (12), 163 (28.5), 161 (82).

3-Chloroazulene-1-azo[4'-(diphenylhydroxymethyl)benzene], 9 $X = \text{Cl}$. Yield 22%, black powder, mp above 260 °C (at 250 °C slight decomp., from DCM on precipitation with *n*-pentane) (Found: C, 77.30; H, 4.85; N, 6.39; Cl, 7.90. $\text{C}_{29}\text{H}_{21}\text{ClN}_2\text{O}$ requires C, 77.59; H, 4.71; N, 6.24; Cl, 7.89%; λ_{max} (dioxane)/nm 287 (log $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 4.32), 336 (4.26), 436 (4.47), 455 sh (4.40), 600 sh (2.96), 675 sh (2.76); $\nu_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$ 3580 m (OH); $\delta_{\text{H}}(\text{CDCl}_3)$ 2.90 (1 H, s, OH), 7.25–7.38 (12 H, m, 5-, 7-H and 2 C_6H_5), 7.42 (2 H, dt, J 8.7 and 2.0, 3'-, 5'-H), 7.74 (1 H, t, J 9.8, 6-H), 7.87 (2 H, dt, J 8.7 and 2.0, 2'-, 6'-H), 8.19 (1 H, s, 2-H), 8.40 (1 H, d, J 9.3, 4-H), 9.23 (1 H, d, J 9.6, 8-H); $\delta_{\text{C}}(\text{CDCl}_3)$ 82.01 (q), 121.75 (t), 122.84 (t), 126.33 (t), 126.80 (t), 127.38 (t), 127.91 (t), 128.00 (t), 128.62 (t), 135.30 (q), 136.03 (t), 136.20 (t), 137.26 (q), 137.52 (q), 140.86 (t), 141.19 (q), 146.65 (q), 148.14 (q), 152.84 (q); m/z (70 eV) 450/448 (M^+ , 25/75%), 160 (100).

Reaction of 3-methoxyazulene-1-azo(4'-methylbenzene), 2c.

The azocompound:FeCl₃ ratio = 1:4; the reaction time = 4 hours. The resulting residue on work-up (320 mg) was separated on silica gel with *n*-pentane–ethyl acetate (5:1): *fraction 1* (3 mg) in the $^1\text{H-NMR}$ spectrum shows the signals of diphenylmethane, **4**, and triphenylmethane, **5**,¹² *fraction 2* (40 mg, 0.15 mmol), starting compound, **2c**; *fraction 3* (27 mg, 0.074 mmol), ketone **13**; *fraction 4* (62 mg, 0.086 mmol), ether **14**; *fraction 5* (12 mg) was again chromatographed; *fraction 6* (94 mg, 0.26 mmol), diarylmethanol **8** $X = \text{OCH}_3$; *fraction 5* was separated on silica gel, eluent DCM–*n*-pentane (3:1): *fraction 5.1* (4 mg, 0.008 mmol), compound **15** and *fraction 5.2* (6 mg), unidentified mixture.

3-Methoxyazulene-1-azo[4'-(phenylhydroxymethyl)benzene], 8 $X = \text{OCH}_3$. Yield 30%, black powder, mp 59–61 °C (from DCM on precipitation with *n*-pentane) (Found: C, 78.93; H, 5.38; N, 7.51. $\text{C}_{24}\text{H}_{20}\text{N}_2\text{O}_2$ requires C, 78.24; H, 5.47; N, 7.60%; λ_{max} (dioxane)/nm 250 (log $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 4.42), 292 (4.35), 350 (4.36), 471 (4.41), 492 (4.41); $\nu_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$ 3585 m (OH); $\delta_{\text{H}}(\text{CDCl}_3)$ 4.06 (3 H, s, OCH_3), 5.91 (1 H, s, CH in **4**'), 7.02 (1 H, t, J 9.6, 5- or 7-H), 7.09 (1 H, t, J 9.9, 7- or 5-H), 7.23–7.28 (1 H, m, 4''-H), 7.35 (2 H, t, J 7.6, 3''-, 5''-H), 7.42 (2 H, d, J 7.2, 2''-, 6''-H), 7.49 (2 H, dt, J 8.5 and 1.7, 3'-, 5'-H), 7.54 (1 H, t, J 9.9, 6-H), 7.65 (1 H, s, 2-H), 7.90 (2 H, dt, J 8.6 and 2.0, 2'-, 6'-H), 8.25 (1 H, dd, J 9.1, and 1.3, 4-H), 9.08 (1 H, d, J 9.9, 8-H); $\delta_{\text{C}}(\text{CDCl}_3)$ 57.73 (p), 75.94 (t), 102.43 (t), 122.04 (t), 124.77 (t), 124.88 (t), 126.62 (t), 127.17 (t), 127.55 (t), 128.47 (t), 131.68 (q), 134.33 (t), 134.51 (q), 136.03 (t), 140.45 (q), 140.81 (t), 143.80 (q), 144.39 (q),

152.74 (q), 153.68 (q); m/z (25 eV) 370 ($M^+ + 2$, 2.5%), 369 ($M^+ + 1$, 19), 368 (M^+ , 88), 367 ($M^+ - 1$, 80), 353 ($M^+ - 15$, 2), 352 (52.5), 351 (51), 337 (12), 218 (9), 165 (20), 157 (100), 143 (14), 142 (37), 137 (22), 136 (24), 135 (12), 123 (17), 121 (24), 115 (10), 114 (59).

4-(3''-Methoxyazulene-1''-azo)benzophenone, **13**. Yield 8.5%, black powder, mp 147 °C (from ether on precipitation with *n*-pentane) (Found: C, 78.03; H, 4.90; N, 7.55. $C_{24}H_{18}N_2O$ requires C, 78.67; H, 4.95; N, 7.64%); λ_{max} (dioxane) 245 nm (log $\epsilon/dm^3 mol^{-1} cm^{-1}$ 4.17), 290 (4.06), 356 (3.98), 500 (4.14), 690 sh (2.71); $\nu_{max}(CCl_4)/cm^{-1}$ 1650 m (C=O); $\delta_H(CDCl_3)$ 4.08 (3 H, s, OCH₃), 7.11 (1 H, t, *J* 9.9, 7''-H or 5''-H), 7.20 (1 H, t, *J* 9.9, 5''-H or 7''-H), 7.48–7.58 (3 H, m, 3-, 4-, 5-H), 7.61 (1 H, t, *J* 9.6, 6''-H), 7.66 (1 H, s, 2''-H), 7.83 (2 H, d, *J* 7.7, 2-, 6-H), 7.93 (2 H, d_{AB}, *J* 8.6, 3'-, 5'-H or 2'-, 6'-H), 7.96 (2 H, d_{AB}, *J* 8.6, 2'-, 6'-H or 3'-, 5'-H), 8.3 (1 H, d, *J* 9.4, 4''-H), 9.14 (1 H, d, *J* 9.9, 8''-H); m/z (15 eV) 369 ($M^+ + 3$, 2%), 368 ($M^+ + 2$, 8), 367 ($M^+ + 1$, 26), 366 (M^+ , 100), 365 ($M^+ - 1$, 67), 351 ($M^+ - 15$, 14), 341 (4), 157 (52), 136 (68), 123 (40), 121 (44), 109 (34).

meso- and (RS)-Bis[(3-methoxyazulene-1-azophenyl)-(phenyl)methyl] ether, **14**. Yield 20%, black powder (not definite mp) (Found C, 79.97; H, 5.41; N, 7.70. $C_{24}H_{18}N_2O_3$ requires C, 80.20; H, 5.33; N, 7.79; λ_{max} (dioxane)/nm 290 (log $\epsilon/dm^3 mol^{-1} cm^{-1}$ 4.11), 292 (4.03), 349 (3.97), 487 (4.12); $\delta_H(CDCl_3)$ 4.050 and 4.055 (3 H, 2 s, integral ratio ca. 0.7:2.3, OCH₃), 5.51 (1 H, s, OCH), 6.99 and 7.00 (1 H, 2 t, *J* 9.9, 7-H or 5-H), 7.06 and 7.08 (1 H, 2 t, *J* 9.9, 5-H or 7-H), 7.24 and 7.31 (1H, m, 4''-H), 7.34 and 7.35 (2 H, 2 t, *J* 7.0, 3''-, 5''-H), 7.43 (2 H, d, *J* 7.1, 2''-, 6''-H), 7.49 (2 H, d, *J* 8.3, 3'-, 5'-H), 7.52 and 7.53 (1 H, 2 t, *J* 9.9, 6-H), 7.647 and 7.654 (1 H, 2 s, 2-H), 7.89 and 7.90 (2 H, 2 d, *J* 8.3, 2'-, 6'-H), 8.23 and 8.24 (1 H, 2 d, *J* 9.8, 4-H), 9.07 and 9.08 (1 H, 2 d, *J* 9.9, 8-H); $\delta_C(CDCl_3)$ 57.75 (p, OCH₃), 79.98 (t, O-CH), 122.07 (t), 124.51 (t), 124.56 (t), 124.73 (t), 124.82 (t), 124.85 (t), 127.29 (t), 127.34 (t), 127.96 (q), 128.01 (t), 128.41 (t), 128.44 (t), 131.69 br (q), 134.31 (t), 134.50 br (q), 136.07 (t), 140.50 (q), 140.52 (q), 140.80 (t), 142.07 (q), 142.61 (q), 142.71 (q), 142.98 (q), 152.74 br (q), 153.79 (q), 153.82 (q); m/z (FD): ($M^+ + 3$, 33%), ($M^+ + 2$, 83), ($M^+ + 1$, 100), (M^{2+} , 40).

[4'-(3''-Methoxyazulene-1''-azo)phenyl](3'''-methoxyazulene-1-phenyl)methane, **15**. Yield 2%, black powder; $\delta_H(CDCl_3)$ 3.94 (3 H, s, OCH₃), 4.08 (3 H, s, OCH₃), 6.19 (1 H, s, C₆H₅CH), 6.67 (1 H, t, *J* 9.6, 7'''-H or 5'''-H), 6.75 (1 H, t, *J* 9.6, 5'''-H or 7'''-H), 7.02 (1 H, t, *J* 9.7, 5''-H), 7.04 (1 H, s, 2''-H), 7.08 (1 H, t, *J* 9.7, 7''-H), 7.19 (2 H, d, *J* 7.2, 2-, 6-H), 7.26 (2 H, d_{AB}, *J* 8.4, 2'-, 6'-H), 7.27–7.32 (3 H, m, 3-, 4-, 5-H), 7.34 (1 H, t, *J* 10, 6'''-H), 7.54 (1 H, t, *J* 10.0, 6''-H), 7.67 (1 H, s, 2''-H), 7.87 (2 H, d_{AB}, *J* 8.4, 3'-, 5'-H), 8.04 (1 H, d, *J* 9.6, 4''-H or 8'''-H), 8.19 (1 H, d, *J* 9.6, 8''-H or 4''-H), 8.25 (1 H, d, *J* 9.2, 4''-H), 9.08 (1 H, d, *J* 9.6, 8''-H).

Reaction of 4,6,8-trimethylazulene-1-azo(4'-methylbenzene), 3. The ratio azocompound:FeCl₃ = 1:4; the reaction time 48 hours. The resulting residue on work-up (267 mg), was chromatographed on silica gel with DCM–ethyl acetate (from 1:0 to 100:1): fraction 1 (15 mg), diphenylmethane **4** and triphenylmethane **5**,¹² molar ratio 0.15:1; fraction 2 (150 mg) was once more separated; fraction 3 (75 mg) was, also, again separated; fraction 4 (12 mg) mixture of oligomers. Fraction 2 was chromatographed on alumina with *n*-pentane–ethyl ether (from 20:1 to 1:1): fraction 2.1 (59 mg), mixture of **4**, **5** and starting material **3**, molar ratio 1:2:12.5 (molar, from ¹H-NMR signals), fraction 2.2, 33 mg, mixture of **3** and triarylmethane **10**, ratio 1.8:1 (from ¹H-NMR) and fraction 2.3 (56 mg), triarylmethane **10**. Fraction 3 was chromatographed on silica gel, eluent DCM–ethyl acetate (40:1): fraction 3.1, 12 mg complex unidentified mixture and fraction 3.2 (60 mg), triarylmethanol **11**.

4,6,8-Trimethylazulene-1-azo[4'-(diphenylmethyl)benzene], **10**. Yield 21%, brown microcrystalline powder, mp 208–209 °C

(from trichloromethane on precipitation with *n*-pentane) (Found: C, 87.30; H, 6.41; N, 6.29. $C_{32}H_{28}N_2$ requires C, 87.22; H, 6.42; N, 6.36%); λ_{max} (dioxane) 245 nm (log $\epsilon/dm^3 mol^{-1} cm^{-1}$ 4.42), 295 (4.16), 328 (4.19), 442 (4.49); $\delta_H(CDCl_3)$ 2.61 (s, 3 H, CH₃), 2.85 (3 H, s, CH₃), 3.32 (3 H, s, CH₃), 5.61 (1 H, s, (C₆H₅)₂CH-), 7.15 (1 H, s, 5-H or 7-H), 7.17 (4 H, d, *J* 7.0, 2''-, 6''-H), 7.23 (2 H, d, *J* 8.3, 3'-, 5'-H), 7.26 (1 H, s, 7-H or 5-H), 7.20–7.30 (2 H, m, 4''-H), 7.31 (4 H, t, *J* 7.4, 3''-, 5''-H), 7.34 (1 H, d, *J* 5.0, 3-H), 7.80 (2 H, d, *J* 8.5, 2'-, 6'-H), 8.12 (1 H, d, *J* 4.7, 2-H); $\delta_C(CDCl_3)$ 25.33 (p, CH₃), 28.54 (p, CH₃), 29.64 (p, CH₃), 56.78 (t), 117.95 (t), 122.04 (t), 122.28 (t), 126.42 (t), 128.39 (t), 129.53 (t), 130.06 (t), 130.56 (t), 132.87 (t), 133.60 (q), 140.49 (q), 143.86 (q), 144.60 (q), 147.06 (q), 147.62 (q), 149.67 (q), 152.87 (q); m/z (70 eV) 441 ($M^+ + 1$, 4.5%), 440 (M^+ , 11), 439 ($M^+ - 1$, 10), 425 ($M^+ - CH_3$, 15.5), 182 (100), 181 (73.5).

4,6,8-Trimethylazulene-1-azo[4'-(diphenylhydroxymethyl)benzene], **11**. Yield 17%, brown crystalline powder, mp 144–146 °C (from trichloromethane on precipitation with *n*-pentane) (Found: C, 84.25; H, 6.14; N, 6.10. $C_{31}H_{28}N_2O$ requires C, 84.17; H, 6.19; N, 6.12%); λ_{max} (dioxane) 246 nm (log $\epsilon/dm^3 mol^{-1} cm^{-1}$ 4.31), 293 (4.06), 324 (4.07), 440 (4.33); $\nu_{max}(CH_2Cl_2)$ 3580 cm^{-1} m (OH); $\delta_H(CDCl_3)$ 8.12 (2 H, d, *J* 5.0, 2-H), 7.80 (2 H, d, *J* 8.6, 2'-, 6'-H), 7.39 (2 H, d, *J* 8.6, 3'-, 5'-H), 7.27–7.35 (10 H, m, 2 C₆H₅), 3.32 (3 H, s, CH₃), 2.85 (3 H, s, CH₃), 2.61 (3 H, s, CH₃); $\delta_C(CDCl_3)$ 25.33 (p, CH₃), 28.54 (p, CH₃), 29.64 (p, CH₃), 82.07 (q, C-OH), 118.06 (t), 121.81 (t), 122.05 (t), 127.35 (t), 128.00 (t), 128.65 (t), 130.73 (t), 133.04 (t), 133.83 (q), 140.67 (q), 146.88 (q), 147.17 (q), 147.55 (q), 147.70 (q), 148.93 (q), 149.72 (q), 153.36 (q); m/z (70 eV) 457 ($M^+ + 1$, 3%), 456 (M^+ , 8.4), 455 ($M^+ - 1$, 13), 441 ($M^+ - CH_3$, 18.7), 182 (89.0), 181 (100).

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