2-Substituted (Azulen-1-yl)ethenes

Alexandru C. Razus,*[a] Carmen Nitu,[a] Victorita Tecuceanu,[b] and Valentin Cimpeanu[b]

Keywords: C−C coupling / Nitrogen heterocycles / Schiff bases / Solvent-free synthesis

An easy and efficient solvent-free synthesis of 1-(azulen-1-yl)-2-aryl- and heteroarylethenes is described. The reaction was performed simply by melting solid mixtures of azulenic Schiff bases and arylacetic acids, the crude products being purified by column chromatography. Limitations of the method were established by study of a large range of aryl and heteroarylacetic acids and also by examination of various azulenic Schiff bases. The same reaction was observed with other active methylene compounds, such as malonic acid and its derivatives or 1,3-diketones.

Introduction

During our continuing researches on 1-substituted azulenes with double bonds, compounds **1**, we have studied the synthesis and the physicochemical, electrochemical and optical properties of azo azulene **1** ($X = Y = N$)[1] and of the corresponding Schiff bases **1** ($X = CH$ and $Y = N$).[2] From the synthetic point of view the reported compounds are important because they are the building blocks for the generation of complex molecular structures.[3] Recently, azulene derivatives, especially compounds belonging to these two classes, have been receiving increasing attention because of their valuable optical and electrochemical properties: as dyes,[4] for the elaboration of nonlinear optical (NLO) materials[5] or for the generation of chemically modified electrodes with polymeric films on their surfaces.[6] The results encouraged us to extend our investigations on the corresponding alkenes 1 ($X = Y = CH$). Although these conjugated systems exhibit high hyperpolarizability, offering candidates for NLO systems,[7] and although they are also useful for synthetically purposes, no simple and efficient synthesis for this class of compounds has been mentioned in the literature until now.

$Az–X = Y–Ar$

1

$X = Y = N$ or $X = CH$ and $Y = N$

Az = substituted or unsubstituted 1-azulenyl
Ar = substituted or unsubstituted aryl or heteroaryl

Previously employed methods for the generation of vinylazulenes followed classical routes generally used for substituted alkenes.[8] The Wittig reaction (starting from azulene carbaldehydes or azulene ylides, in the presence of strong bases) seems to be the most widely used, and the obtained yields are satisfactory to good.[7d,9,10] Reductive condensation of azulenecarbaldehydes with low-valent titanium (the McMurry reaction[9b]) also proceeds with good results [yields between 40 and 70 %, with only (*E*) geometry]. Application of this method, however, is limited by the exclusive generation of symmetrically substituted ethenes, the lack of reproducibility and the incompatibility of many substrates with Ti^0. The Siegrist condensation[11] and the Heck reaction[12] have also been used for a few particular products.

Some examples of the construction of a C=C bond starting from aromatic azomethines (obtained mainly from ketones) and from compounds with activated methylene groups, such as malononitrile, cyanoacetic acid, cyanoacetamide and nitroalkanes, have also been described in the literature.[13,14] Usually the condensation is performed in solution and/or in the presence of strong bases or acids as catalysts, but in most reported examples[14,15] only addition to the double bond C=N was observed, without subsequent amine elimination. Interest in this method ceased and compounds with C=O groups were preferred for condensations.

Results and Discussion

The very simple availability of azulenic Schiff bases,[2] their ease of handling and the difficulties occurring in the synthetic procedures described above suggested that we could attempt the development of a versatile route for the generation of vinylazulenes through condensations between these bases and compounds containing activated methylene groups, starting from aryl- and heteroarylacetic acids.

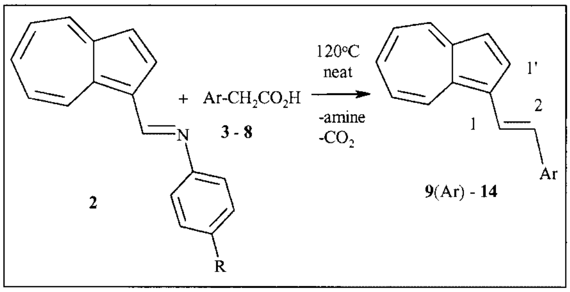
---

[a] Technical University Darmstadt, Institute of Organic Chemistry,
Petersenstr. 22, 64287 Darmstadt, Germany
[b] Romanian Academy, Institute of Organic Chemistry,
Spl. Independentei 202B, 060023 Bucuresti 15, P. O. Box 254, Romania,
E-mail: acrazus@cco.ro

Supporting information for this article is available on the WWW under http://www.eurjoc.org or from the author.

In attempts to carry out the condensation in solvents such as xylene at reflux (6 h) or in acetic acid (heating for 5 h) we recovered the starting reagents **2** and **3** almost quantitatively.

An attractive procedure currently widely used in modern synthesis eliminates the use of the solvent as reaction medium. We therefore studied the possibility of condensing the two reagents by heating them in the absence of any solvent or catalyst, and the results were very good. Preliminary experiments were carried out in order to establish the most favourable reaction conditions. For this purpose, the cheap and commercially available phenylacetic acid **3**(H) was condensed with different Schiff bases **2** (starting with **2**(OCH_3), see Scheme 1).



	2(OCH_3)	**2**($N(CH_3)_2$)	**2**(CH_3)	**2**(H)	**2**(CN)	**2**(NO_2)
R	OCH_3	$N(CH_3)_2$	CH_3	H	CN	NO_2

	3(H)	**3**(pNO_2)	**3**(oNO_2)	**3**(pCl)
Ar	C_6H_5	$pC_6H_4NO_2$	$oC_6H_4NO_2$	pC_6H_4Cl

	4α	**4β**	**5**	**6**	**7**
Ar	1-naphthyl	2-naphthyl	2-thienyl	4-pyridyl	1-azulenyl

8 = (5-methoxy-2-methyl-1*H*-inden-3-yl)acetic acid

Starting acid	**3**(H)	**3**(pNO_2)	**3**(oNO_2)	**3**(pCl)	**4α**	**4β**	**5**	**6**	**7**	**8**
Obtained alkene	**9**(H)	**9**(pNO_2)	**9**(oNO_2)	**9**(pCl)	**10α**	**10β**	**11**	**12**	**13**	**14**

Scheme 1

The reaction was performed in a flask protected against humidity. The temperature was maintained above 100 °C, at which the mixture of reagents was liquid (under this temperature the reaction either occurred slowly or failed). After 10 min of heating, CO_2 began to evolve vigorously from the melted reaction mixture. At the top of the flask, *para*-anisidine sublimed progressively and at the end of the reaction time, the sublimed anisidine could be washed and removed with a small amount of solvent. The workup of the reaction mixture consisted only of chromatographic separation. From the condensation conditions reported in Table 1, it can be seen that the use of both a molar ratio of **2**(OCH_3)/**3**(H), 1:1 and a reaction time of 4 h (Table 1, Entry 1) are satisfactory for a good conversion of Schiff base and a high yield of 1-styrylazulene [**9**(H)] (above 80 % and 95 %, accordingly).

The 1-styrylazulene [**9**(H)] proved to be formed exclusively in the (*E*) geometry; this feature was generally encountered for the obtained ethenes. In certain cases the generation of dimers **15** or **16** (in yields 10−15 %) at longer reaction condensation times is worth mentioning (Scheme 2).

We also investigated the limitations of the procedure, enlarging the field of Schiff bases **2** and arylacetic acids used and maintaining the reaction conditions described above. The results, as listed in Table 2, show a dramatic decrease in reactivity, correlated with electron-donating ability in the series: $OCH_3 \approx N(CH_3)_2 > CH_3 > H > CN$. The presence of the CN group strongly lowers both the degree of conversion and the yield, while that of NO_2 completely hinders the condensation and produces only tar. Syntheses of ethenes from Schiff bases with various substituents at the azulene five- or seven-membered rings are currently under investigation.

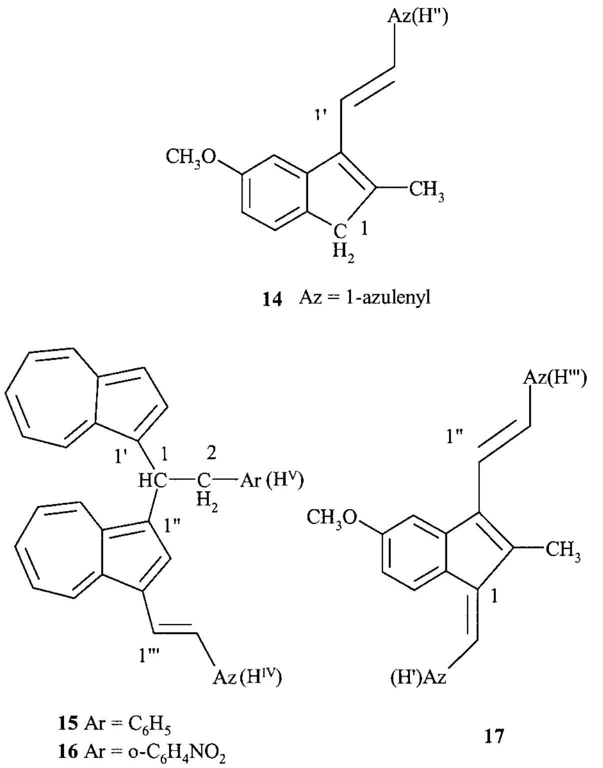
As would be expected, the structures of the arylacetic acids play an important role in the condensation, so a large number of acetic acid derivatives (**3**−**8**) were condensed with the Schiff base **2**(OCH_3)[16] (see Table 3).

The reactivities of the phenylacetic acids **3** increase with the withdrawing strength of the *para* substituent in the order $Cl < H < NO_2$. The reaction occurred rapidly and almost quantitatively for the *ortho*- and *para*-nitrophe-

Table 1. Condensations between Schiff base **2**(OCH_3) and phenylacetic acid **3**(H)

Entry	Reaction conditions			Recovered **2**(OCH_3) (%)	Yield in **9**(H) (%)
	Molar ratio **2**/**3**	Time (h)	Other conditions		
1	1:1	4	120 °C[a] (melted mixture)	18	95[b]
2	1:1	4	grinding the mixture of **2** and **3**, then 120 °C (melt.)	20	95[b]
3	1:1.5	4	135 °C (melted mixture)	12	70[b]
4	1:1	6	120 °C (melted mixture)	20	79[b]
5	1:1.5	6	120 °C (melted mixture)	25	35[c]
6	1:2	6	120 °C (melted mixture)	18	37[c]
7	1:1	4.5	toluene at reflux	100	–
8	1:1	7	xylene at reflux	100	–
9	1:1	4.5	acetic acid at reflux	100	–

[a] Temperature in the oil bath. [b] Together with alkene, its dimer **15** was separated in a yield of under 1%. [c] The yield of dimer **15** was between 10 and 15%; the rest of the obtained material remained at the start of the chromatographic column.



14 Az = 1-azulenyl

15 Ar = C_6H_5
16 Ar = o-$C_6H_4NO_2$

17

Scheme 2

Table 2. Condensations between Schiff bases **2**(R) and phenylacetic acid **3**(H)

R[a]	OCH_3	$N(CH_3)_2$	CH_3	H	CN	NO_2[b]
Recovered **2**(R) (%)	18	15	21	39	45	30
Yield in **9**(H) (%)	95	95	95	85	50	0[c]

[a] The reactions were carried out at 120 °C in the melted mixture, the ratio **2**(R):**3**(H) = 1:1 and the reaction time was 4 h. [b] After heating for 6.5 h. [c] Only unchanged reagent and tar were obtained.

nylacetic acids **3**(oNO$_2$) and **3**(pNO$_2$) and for thienylacetic acid **5**, and good results were also obtained from the condensation of 4-pyridineacetic acid hydrochloride **6**·HCl. The described condensation provides a convenient method for the preparation of compounds **9**(oNO$_2$), **9**(pNO$_2$) or **10**, as well as for other 1-(azulen-1-yl)-2-arylethenes − which are difficult or even impossible to obtain in other ways. The reaction between 1-azuleneacetic acid (**7**) and **2**(OCH_3) occurs in good yield, although the availability of the acid limits the importance of this method in comparison with other syntheses of 1,2-diazulenylethene (**13**).[9b] The stereocontrolled pathway of the reaction may explain the better results in the condensation of β-naphthaleneacetic acid **4**β in comparison with its α isomer **4**α. Steric hindrance is strong in the condensation between phenylacetic acid and the Schiff base with the 4,6,8-trimethylazulene moiety; in this case only azulenic hydrocarbon could be separated from the reaction mixture.

In the condensation of acid **8**, together with the "normal" condensation product **14**, another product, **17** − unexpectedly condensed at the indene methylene − was generated (Scheme 2).

Attempts to perform the condensation of Schiff bases with chloroacetic or diphenylacetic acid failed, as did treatment of phenylacetic acids with the bases obtained from the ketones such as 1-acetylazulene.

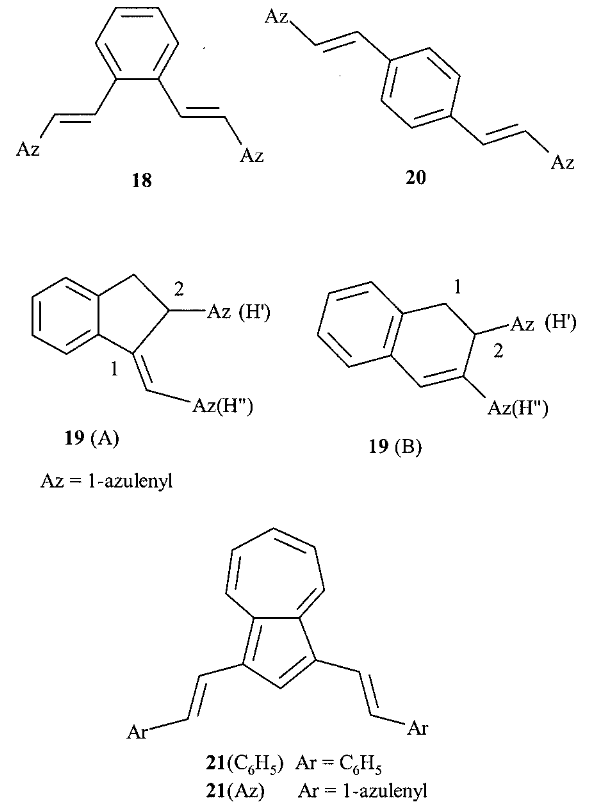
Since the proposed condensation procedure is straightforward and high-yielding, we used it for the synthesis of polycyclic linear or cyclic compounds containing alternating benzenoid moieties, azulene moieties and double bonds. As starting reagents we considered compounds with at least two reacting groups (CH_2CO_2H or CH=Nar).

Thus, by condensation of 1,2- and 1,4-phenylenediacetic acids or 1,3-azulenediacetic acid with two equivalents of Schiff base **2**(OCH_3), we obtained the polycyclic compounds **18**, **20** or **21**(Az) with highly extended electronic conjugation (Scheme 3).

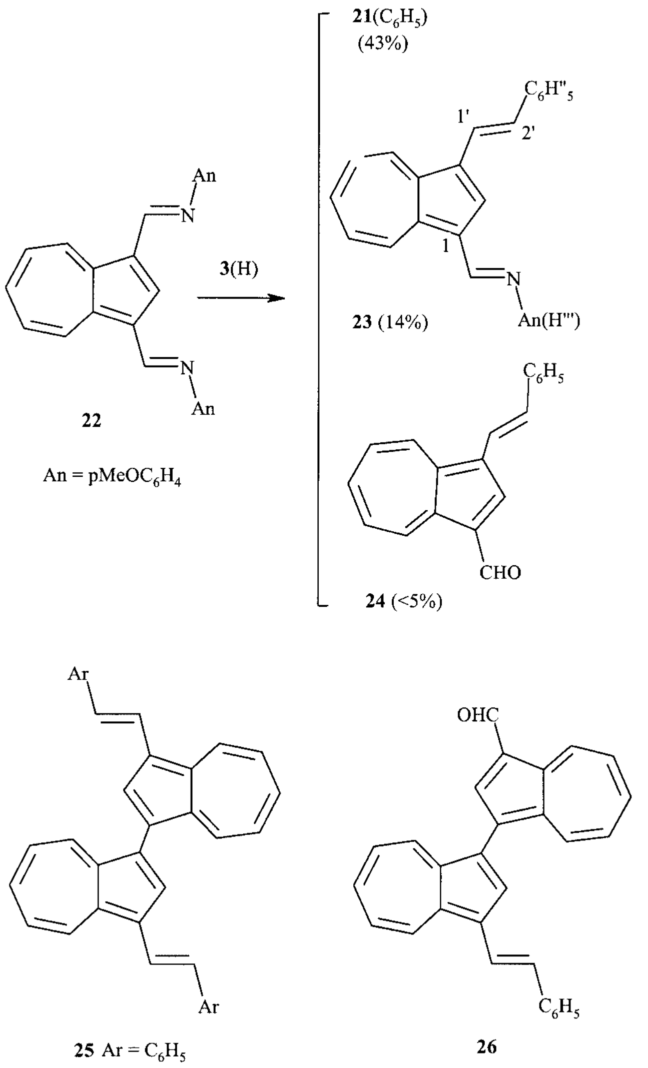
Table 3. Condensations between Schiff base **2**(OCH_3) and arylacetic acids **3**(Ar)-**8**

Acid[a]	Obtained ethylene[b]	Reaction conditions	Recovered **2**(OCH_3), (%)	Yield (%)
3(H)	**9**(H)	240 min	18	95
3(pNO$_2$)	**9**(pNO$_2$)	30 min	3	95
3(oNO$_2$)	**9**(oNO$_2$)	120 min	17	90[c]
3(pCl)	**9**(pCl)	240 min	13	94
4α	**10**α	240 min	32	76
4β	**10**β	60 min	15	86
5	**11**	15 min	9	98
6[d]	**12**	5 min, ratio **2**(OCH_3)/**6** (1:1)	32	25[e]
		60 min, ratio **2**(OCH_3)/**6** (1:2), 100 °C	26	82
7	**13**[f]	240 min	40	81
8	**14**	8 h	62	[g]

[a] The reactions were carried out at 120 °C in the melted mixture, the molar ratio **2**(OCH_3)/**3**−**8** = 1:1. [b] The structures of the resulting ethylene and of the starting arylacetic acids are presented in Scheme 1. [c] Together with alkene, its dimer **16** was separated in a yield of about 7%. [d] **6**·HCl was used. [e] 4-Picoline was detected in the reaction mixture; the tendency for decarboxylation to 4-picoline became important when the reaction temperature was high (>120 °C) or when the reaction time was prolonged.[f] Reported yields of **13**[9b] are 55% and 68% for Wittig and for McMurry approaches, respectively.[g] The yield of product **14** was under 6% and of the double condensation product **17**, about 20% (the structures of these products are shown in Scheme 2).



Scheme 3



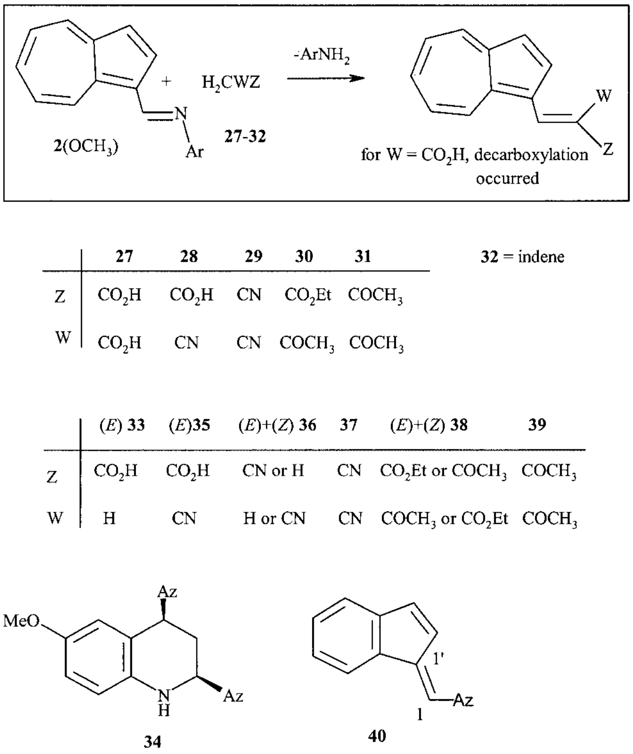
Scheme 4

Although the condensation of 1,4-phenylenediacetic acid to provide compound **20** occurred in good yield based on reacted Schiff base, a large amount of starting compounds remained unchanged even after a long reaction time (increasing amount of *para*-xylene was detected in the reaction mixture), probably due to the very high melting point of the acid. The low condensation yield of the 1,2-phenylenediacetic acid can be attributed to the steric and chemical interactions between the *ortho* groups in the starting acid or in the resulting dialkene. The product **18** (as the *trans-trans* isomer)[17] was thus obtained in 10 % yield after 2 h at 148 °C [recovered **2**(OCH_3), 30 %], together with an interesting cyclic compound, **19**(A), separated in 7 % yield (Scheme 3). When starting from 1,3-azulenediacetic acid[18] and **2**(OCH_3), the compound **21**(Az) with three azulene moieties, separated by two double bonds, was generated in about 40 % yield [recovered **2**(OCH_3) 35 %].

Condensations between the azulenic 1,3-bis(imino) compound **22** and two mol of arylacetic acids occurred with satisfactory results. A mixture of 1,3-distyrylazulene [**21**(C_6H_5)][9d] (43 %), the monocondensation product **23** (14 %) and its hydrolysis derivative, compound **24** (< 5 %), was obtained (Scheme 4) and was separated without difficulties on an alumina column. The 3,3′-bis(imino)-1,1′-biazulene[2] showed the same behaviour and the distyryl-substituted product **25** (Scheme 3) was obtained together with the hydrolysed monocondensed product **26**.

These results obtained from the condensation of aryl- or heteroarylacetic acids encouraged us to extend the solvent-free condensation of azulenic Schiff bases to other active methylene compounds. The few results reported until now[13,15,19] relating to the condensation of aromatic imines with various methylene compounds are rather ambiguous and generally refer to the reaction in solution.

The methylenic compounds **27**−**32** considered (Scheme 5), with different hydrogen mobility,[20,21] reacted with Schiff base **2**(OCH_3) under conditions similar to those used for arylacetic acids; the results are reported in Table 4. With increasing hydrogen mobility in the series − indene **32**, arylacetic acids, malonic acid **27**, cyanoacetic acid **28** and malononitrile **29** − an augmentation in reactivity can be observed. The unexpectedly slow condensation of ethyl acetoacetate (**30**) and especially acetylacetone (**31**), and the moderate yields obtained can be explained by the high enolization tendencies of the reagents. Another interesting feature of the condensation lies in the difference between the



	27	28	29	30	31	32 = indene
Z	CO_2H	CO_2H	CN	CO_2Et	$COCH_3$	
W	CO_2H	CN	CN	$COCH_3$	$COCH_3$	

	(*E*) 33	(*E*)35	(*E*)+(*Z*) 36	37	(*E*)+(*Z*) 38	39
Z	CO_2H	CO_2H	CN or H	CN	CO_2Et or $COCH_3$	$COCH_3$
W	H	CN	H or CN	CN	$COCH_3$ or CO_2Et	$COCH_3$

Scheme 5

exclusive generation of (*E*) isomers for the arylacetic acids and isomer mixtures for other methylenic compounds.

Although low yields are obtained in some cases for the condensations of methylenic derivatives, the above procedure represents a valuable method for the syntheses of various functionalized vinylazulenes and, sometimes, a unique way to generate them.

It is more difficult to establish the solvent-free reaction mechanism than in the case of reactions occurring in solution because very often only spectral measurements (when possible), together with the structures of starting materials and of products, are the sole arguments for the proposal of a reaction route.[22] We consider that our results are far from allowing us to propose a coherent reaction pathway. Other attempts are in progress and may eventually support a mechanism suggestion.

Product Characterisation[23,24]

The structural assignment of 1-azulene-2-arylethenes does not give rise to any major problems.[25] For these compounds the presence of the AB group with coupling constants of about 16 Hz [characteristic of two ethylene protons in (*E*) geometry] at low field must be signalled. However, the structure peculiarities of the by-products **15**, **16**, **17** and **19** produced together with the ethenes is described more thoroughly.

For the dimers **15** and **16** (Scheme 2) the problem lies in the position of the second azulene moiety in the ethane skeleton. The *gem* relationship of the two azulenes was confirmed by the NOE responses of 8′-H and 8′′-H on the irradiation of 1-H. Another interesting feature of compounds **15** or **16** is represented by the nonequivalence of the two protons at C-2; bulk substituents at C-1 are likely to hinder the free rotation about the (C-1)−(C-2) bond.

A NOE experiment between 2-CH_3 and H_{exo} was also used to establish the methylene geometry at C-1 in compound **17**.

In the condensation of 1,2-phenylenediacetic acid, two structures **19**(A) or **19**(B) may be generated by the intramolecular cyclization of **18**.[26] The ^1H NMR spectrum of **19** shows one doublet at $\delta = 7.87$ ppm ($J = 1.8$ Hz) for a vinylic proton coupled with an allylic proton and one dd at $\delta = 3.03$ ppm ($J = 16.0, 1.8$ Hz), one dd at $\delta = 3.75$ ppm ($J = 16.0$ and 8.4 Hz) and one dt at $\delta = 5.23$ ppm ($J = 8.6$ and 1.8 Hz) for the sequence $-CH_2-CH$(azulenyl)-. The coupling constants show that the aliphatic sequence belongs to a rigid five- or six-membered cyclic structure, **19**(A) or **19**(B), respectively (see Scheme 3). From a 2D-long-range correlation experiment (HMBC) showing a three-bond distance between the vinylic hydrogen and C-2 in azulene, structure (A) was proposed. No NOE was observed between the H_{exo} protons and 2-H, indicating a possible *syn* relationship of the H_{exo} and phenyl.

Of products **33**−**40**, only for **34** and **35** does the structural assignment seem to be more difficult (most of the analytical data for these compounds are reported in the ESI).

For compound **34**, the sequence $-AzC^2H-C^3H_2-C^4Haz-$ and the *cis* relationship of the azulene moieties is attested to by the chemical shifts of the protons (four dis-

Table 4. Condensation reactions between azulene Schiff bases **2**(OCH_3) and methylene compounds

Z−CH_2−W (starting reagent) Z	W	Product	Reaction conditions: time, molar ratio[a] **2**(OCH_3)/CH_2ZW	Recovered **2**(OCH_3) (%)	Yield (%)
CO_2H	CO_2H (**27**)	**33**	60 min, 1	10	47[b]
CO_2H	CN (**28**)	**35**	30 min, 1	0	68[c]
CN	CN (**29**)	**37**	10 min, 1	0	100[d]
CH_3CO	$CO_2C_2H_5$ (**30**)	**38**	4 h, 0.5	24	57[e]
CH_3CO	CH_3CO (**31**)	**39**	4 h, 0.5	77	32
Indene (**32**)		**40**	30 h, 1	87	54

[a] The reaction temperature was 120 °C. [b] The first eluted fraction on column separation, blue-green coloured, probably contains 1-vinylazulene that polymerises before analysis; tetrahydroquinoline derivative **34** (Scheme 5) was also obtained in moderate yield. [c] (*E*) and (*Z*)-**35**, (*E*)-and (*Z*)-**36** also resulted in 12.5% and 6% yield, respectively. [d] Asato[7a] reported the synthesis of compound **37** characterized by ^1H NMR spectroscopy without a preparation procedure or yield. [e] A mixture of (*E*) and (*Z*) isomers was obtained.

tinct protons), the signal multiplicity and the values of the *gem*, *cis* and *trans* coupling constants.

For the correct geometry assignment of compound **35**, we recorded ^{1}H NMR spectra in the presence of increasing concentrations of [Eu(fod)$_3$] and we noted the displacement of the chemical shift belonging to the olefinic protons towards low field. This attests to the (*Z*) geometry of hydrogen and CO_2H.

Conclusions

This study has two main points of interest. The former concerns the smooth, efficient and reproducible synthesis of 2-substituted 1-(azulen-1-yl)ethenes. Condensations between the Schiff bases and the methylenic compounds were accomplished without catalyst or solvent; this means simplicity in process and handling, reduced pollution and lower costs. The lack of any requirement for a catalyst, the high or almost quantitative conversion of starting reagents and the good product yields allow a very simple workup of the reaction mixture with the separation of the pure products.

The generality of the proposed syntheses, enabling access to various interesting azulene compounds, represents the second point of interest. Thus, a very large range of substituents (such as benzenoid aryls, non-benzenoid aryls, heteroaryls and other similar groups) can be attached to the double bond of vinylazulene. Investigations into the hyperpolarizabilities of these compounds and into their electrochemical properties are in progress. The procedure also allows the synthesis of derivatives with two or more double bonds in the molecule in alternation with azulene and/or aryl moieties, with the potential for use in other syntheses. The obtained hydrocarbons can subsequently be activated by substitution (e.g., Vilsmeier carbonylation) and the obtained compounds can be used as synthons in other reactions. Research in this area is in progress and the results will be reported. 3-Azulenylacrylic acid and its derivatives are also obtained in good yields by the proposed synthetic method.

Experimental Section

Melting points: Kofler apparatus (Reichert, Austria). Elemental analyses: Perkin−Elmer CHN 240B. ^{1}H and ^{13}C NMR: Bruker ARX 500 (^{1}H: 500 MHz, ^{13}C: 125.75 MHz), Bruker Avance DRX4 (^{1}H: 400 MHz, ^{13}C: 100.62 MHz) Bruker WM 300, AC 300 and Gemini 300 (^{1}H: 300 MHz, ^{13}C: 75.47 MHz), *J* values are given in Hz, TMS was used as internal standard in $CDCl_3$ or [D$_6$]DMSO as solvent; signals were assigned on the basis of COSY and HETCOR correlation spectra (the numbering for the compounds is indicated in the Schemes). Mass spectra: Finnigan MAT 311-A/100MS or Carlo Erba QMD 1000 (EI+, 70 eV); for compounds of low volatility the MS were recorded in the solid state. Column chromatography: basic alumina [activity BII-III (Brockmann)] or silica gel [70−230 mesh (ASTM)]. Dichloromethane (DCM) was distilled from over calcium hydride and ethyl acetate over anhydrous sodium carbonate.

The elemental analyses and the physical characteristics of compounds **2**[N(CH$_3$)$_2$], **2**(CN), **9**(H), **9**(*o*NO$_2$), **9**(*p*Cl), **10**−**12**, **14**, **16**, **17**, **21**(C$_6$H$_5$)−**24**, **26**, **33**, **34**, **36** and **38** [(*E*) and (*Z*)], **39** and **40** are described in the electronic supplementary information (ESI). The nomenclature was obtained by use of the ACD/I-Lab Web service (ACD/IUPAC Name Free 7.06).

Synthesis of Schiff Bases: All the Schiff bases have been described by us,[2] except for the compounds **2**[N(CH$_3$)$_2$], **2**(CN) and **22**, synthesized by the known procedure[2] (the results are reported in Table 5).

Table 5. Schiff base synthesis[2]

Schiff base	M.p.[a] (°C)	Yield (%)
2[N(CH$_3$)$_2$]	85−87	100
2(CN)	129−130	83
22	125−127	78

[a] From ethanol and after good drying on P_2O_5.

General Procedure for Condensation of Schiff Bases and Arylacetic Acids: A mixture of equimolar amounts of the arylacetic acid and the Schiff base, in a flask protected against air humidity, was heated at 120 °C (oil bath temperature), for the time indicated in Table 2 and 3. In all cases, the arylacetic acid dissolved in the melted Schiff base, although at the end of the reaction time most of the reaction mixture became solid. After cooling, the resulting amine, condensed on the top wall of the flask, was carefully recovered by washing with DCM. The reaction mixture was then dissolved in DCM. Before the workup, the mixture was analysed by TLC and if the degree of conversion was low, the organic solution was washed with a 5 % cold solution of NaOH, then with ice water, and dried (Na_2SO_4). The mixture of compounds was separated by column chromatography on silica gel or alumina. All fractions were filtered, and the solvents were evaporated at reduced pressure. In almost all cases the first fraction was the generated alkene, followed by the starting Schiff base and some amide obtained from the eliminated amine and the arylacetic acid. A small amount of aldehyde and amine corresponding to the Schiff base may be formed during chromatography. The degree of conversion of the starting material was calculated from the integrals of the characteristic proton signals (with the same multiplicity, mainly singlets) in the ^{1}H NMR spectra of the fractions collected after the alkene. The yields are reported to the reacted Schiff base. Tables 1−3 report both the degrees of conversion of the starting materials and the product yields. For analytical purposes the products were additionally separated by column chromatography and washed with boiling hexane.

The particular reaction conditions or separation procedures are discussed below for each alkene. A typical example for the properties of the obtained alkenes is described for **9**(*p*-NO$_2$).

1-[(*E*)-2-Phenylvinyl]azulene [9(H)]: The reaction mixture was separated on silica gel. The first fraction, compound **9**(H), was eluted with benzene and the second with DCM/ethyl acetate (1:1). The second fraction contained a mixture of Schiff base, *p*-anisyl-phenylacetamide and *p*-anisidine, molar ratio 3.4:3.7:1.0. A very small amount (under 1 %) of the dimer **15** was always eluted, after the alkene [the amount of the **15** increased with increasing of the excess of **3**(H)].

1-(1-Azulen-1-yl-2-phenylethyl)-3-[(*E*)-2-phenylvinyl]azulene (15): Green crystals, m.p. 70−75 °C. $C_{36}H_{28}$: calcd. C 93.87, H 6.13; found C 93.79, H 6.15. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ =

3.66 [dd, $^{2}J_{H,H}$ = 14.5, $^{3}J_{H,H}$ = 7.5 Hz, 1 H, C(2)-H$_{A}$], 3.69 [dd, $^{2}J_{H,H}$ = 14.5, $^{3}J_{H,H}$ = 7.5 Hz, 1 H, C(2)-H$_{B}$], 5.48 [t, $^{3}J_{H,H}$ = 7.5 Hz, 1 H, C(1)-H], 6.79 [t, $^{3}J_{H,H}$ = 10.0 Hz, 1 H, C(7′)- or C(7′′)-H], 6.90 [t, $^{3}J_{H,H}$ = 10.0 Hz, 1 H, C(7′)- or C(7′′)-H], 6.94 [t, $^{3}J_{H,H}$ = 10.0 Hz, 1 H, C(5′)- or C(5′′)-H], 6.97 [d, $^{3}J_{H,H}$ = 7.3 Hz, 2 H, C(2^{V})-, C(6^{V})-H], 7.01 [t, $^{3}J_{H,H}$ = 10.0 Hz, 1 H, C(5′)- or C(5′′)-H], 7.04−7.08 [m, 3 H, C(3^{V})-, C(4^{V})-, C(5^{V})-H], 7.12 [d, $^{3}J_{H,H}$ = 16.0 Hz, 1 H, C(2′′′)-H], 7.20 [t, $^{3}J_{H,H}$ = 7.4 Hz, 1 H, C(4^{IV})-H], 7.33−7.37 [m, 4 H, C(3′)-, C(6′ or 6′′)-, C(3^{IV})-, C(5^{IV})-H], 7.43 [t, $^{3}J_{H,H}$ = 10.0 Hz, 1 H, C(6′)- or C(6′′)-H], 7.55 [d, $^{3}J_{H,H}$ = 7.3 Hz, 2 H, C(2^{IV})-, C(6^{IV})-H], 7.65 [d, $^{3}J_{H,H}$ = 16.0 Hz, 1 H, C(1′′′)-H], 7.92 [d, $^{3}J_{H,H}$ = 4.0 Hz, 1 H, C(2′)-H], 8.00 [d, $^{3}J_{H,H}$ = 9.3 Hz, 1 H, C(8′)- or C(8′′)-H], 8.11 [d, $^{3}J_{H,H}$ = 9.8 Hz, 1 H, C(8′)- or C(8′′)-H], 8.22 [d, $^{3}J_{H,H}$ = 9.4 Hz, 1 H, C(4′)- or C(4′′)-H], 8.24 [s, 1 H, C(2′′)-H], 8.36 [d, $^{3}J_{H,H}$ = 10.0 Hz, 1 H, C(4′)- or C(4′′)-H] ppm. ^{13}C NMR (125.75 MHz, $CDCl_3$, 25 °C): δ = 38.48 (C-1), 44.90 (C-2), 116.94 (C-3′), 120.53 (C-1′′′), 121.72 (C-7′ or -7′′), 122.19 (C-5′ or -5′′), 122.31 (C-5′ or -5′′), 122.81 (C-7′ or -7′′), 125.82 [(C-3^{V}, -5^{V}) or C-4^{V}], 125.88 (q), 125.98 (C-2^{IV}, -6^{IV}), 126.32 (C-2′′′), 126.73 (C-4^{IV}), 128.02 [(C-3^{V}, -5^{V}) or C-4^{V}], 128.64 (C-3^{IV},-5^{IV}), 128.96 (C-2^{V}, -6^{V}), 132.24 (C-2′′), 133.11 (C-8′ or -8′′), 133.25 (C-8′ or -8′′), 133.34 (q), 133.37 (C-4′ or -4′′), 134.96 (q), 135.00 (q), 135.04 (q), 136.09 (q), 136.16 (C-2′), 136.57 (C-4′ or -4′′), 137.23 (C-6′ or -6′′), 138.12 (C-6′ or -6′′), 138.45 (q), 138.46 (q), 140.79 (q) ppm. EI MS: *m*/*z* (%) = 460 (2%) [M^{+}], 369 (25), 269 (2), 268 (33), 267 (100), 266 (12), 265 (33), 252 (17), 230 (27), 202 (6), 189 (2), 152 (6), 97 (8), 69 (10), 57 (17) FD MS: *m*/*z* (%) = 463 (1) [M^{+} + 3], 462 (54) [M^{+} + 2], 461 (38) [M^{+} + 1], 460 (100) [M^{+}].

1-[(*E*)-2-(2-Nitrophenyl)vinyl]azulene and 1-[(*E*)-2-(4-Nitrophenyl)-vinyl]azulene [9(*o*NO$_2$) and 9(*p*NO$_2$)]: The reaction mixture was directly separated on alumina with DCM/*n*-pentane (1:2) and the alkene was eluted as the first fraction, followed by a fraction containing the alkene dimer **16** and finally by a fraction containing azulenecarbaldehyde from the hydrolysis of the Schiff base **2**(OCH_3). The generation of dimer for the *para*-nitro derivative failed even with an excess of acid.

1-[(*E*)-2-(4-Nitrophenyl)vinyl]azulene 9(*p*NO$_2$): Brown crystals, m.p. 191−192 °C. $C_{18}H_{13}NO_2$: calcd. C 78.53, H 4.76, N 5.09; found C 78.12, H 4.69, N 5.15. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.18 [t, $^{3}J_{H,H}$ = 10.0 Hz, 1 H, C(5′)-H], 7.19 [d, $^{3}J_{H,H}$ = 16.0 Hz, 1 H, C(2)-H], 7.23 [t, $^{3}J_{H,H}$ = 10.0 Hz, 1 H, C(7′)-H], 7.43 [d, $^{3}J_{H,H}$ = 4.0 Hz, 1 H, C(3′)-H], 7.61 [t, $^{3}J_{H,H}$ = 10.0 Hz, 1 H, C(6′)-H], 7.65 [d, $^{3}J_{H,H}$ = 8.9 Hz, 2 H, C(2′′)-, C(6′′)-H], 7.87 [d, $^{3}J_{H,H}$ = 16.0 Hz, 1 H, C(1)-H], 8.21 [d, $^{3}J_{H,H}$ = 8.9 Hz, 2 H, C(3′′)-, C(5′′)-H], 8.27 [d, $^{3}J_{H,H}$ = 4.0 Hz, 1 H, C(2′)-H], 8.27 [d, $^{3}J_{H,H}$ = 10.0 Hz, 1 H, C(4′)-H], 8.53 [d, $^{3}J_{H,H}$ = 10.0 Hz, 1 H, C(8′)-H] ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$, 25 °C): δ = 119.71 (C-3′), 123.61 (C-7′), 123.83 (C-5′), 124.24 (C-2), 124.91 (C-3′′,-5′′), 125.09 (C-1), 126.02 (C-2′′, -6′′), 126.35 (q), 133.59 (C-8′), 133.64 (C-2′), 136.80 (q), 137.26 (C-4′), 138.71 (C-6′), 143.69 (q), 145.13 (q), 145.88 (q) ppm. EI MS (in the solid state): *m*/*z* (%) = 277 (6) [M^{+} + 2], 276 (17) [M^{+} + 1], 275 (23) [M^{+}], 274 (13) [M^{+} − 1], 245 (7), 230 (12), 229 (21), 228 (20), 227 (20), 226 (20), 215 (18.5), 202 (20), 189 (20), 176 (20), 163 (18), 153 (24), 152 (24), 128 (24), 126 (25), 113 (100), 108 (16), 101 (85), 95 (24), 88 (31), 76 (27), 75 (27), 63 (24.5).

1-[(*E*)-2-(4-Chlorophenyl)vinyl]azulene [9(*p*Cl)]: The reaction mixture was separated on silica gel with benzene and the alkene **9**(*p*Cl) was eluted as the first fraction, followed by a fraction containing a mixture of 1-azulenecarbaldehyde and Schiff base.

1-[(*E*)-2-(1-Naphthyl)vinyl]azulene and 1-[(*E*)-2-(2-naphthyl)vinyl]-azulene (10α and 10β): The reaction mixture was separated on alumina with benzene/*n*-pentane (1:1), and the alkene was eluted as the first fraction, followed by unchanged **2**(OCH_3).

2-[(*E*)-2-Azulen-1-ylvinyl]thiophene (11): The reaction mixture was separated on silica gel with benzene and the alkene was separated as the first fraction, followed by a fraction containing unchanged **2**(OCH_3).

4-[(*E*)-2-Azulen-1-ylvinyl]pyridine (12): The mixture of Schiff base and 4-pyridylacetic acid hydrochloride was heated for 1 h at 100 °C. The solution in DCM was washed with a solution of NaOH (2 N) to obtain the free base. The mixture was separated on alumina with DCM/*n*-pentane (2:1) and three fractions were collected: *fraction 1* contained 4-picoline, resulting from decarboxylation of 4-pyridylacetic acid, *fraction 2* a mixture of unchanged **2**(OCH_3) and 1-azulenecarboxaldehyde, molar ratio 5.2:1, and *fraction 3* the product **12**.

1-[(*E*)-2-Azulen-1-ylvinyl]azulene (13): The reaction mixture was separated on alumina with DCM/*n*-pentane (1:5). Alkene **13** (with the same characteristics as described in the ref.[9b]) was separated as the first fraction, followed by a fraction containing a mixture of **2**(OCH_3) and azulenecarbaldehyde.

Condensation between (5-Methoxy-2-methyl-1*H*-inden-3-yl)acetic Acid[27] (8) and 2(OCH$_3$): The reaction mixture obtained from 1.5 mmols of reagents was separated after workup on alumina with benzene/*n*-pentane (1:1). Three fractions were collected: *fraction 1*, 1-[(*E*)-2-(5-methoxy-2-methyl-1*H*-indene-3-yl)vinyl]azulene (**14**, 10 mg, 0.032 mmol, yield 5.6 %), *fraction 2*, (1*Z*)-1-(azulen-1-ylmethylene)-3-[(*E*)-2-(azulen-1-yl)vinyl]-2-methyl-1*H*-inden-5-yl methyl ether (**17**, 56 mg, 0.124 mmol, yield 44 %), and *fraction 3* (256 mg), a mixture of unchanged **2**(OCH_3), 1-azulenecarbaldehyde and *p*-anisidine, molar ratio 4.0:1:1.4, conversion of **2**(OCH_3) 38 %.

Condensation between 1,2-Phenylenediacetic Acid and 2(OCH$_3$): A mixture of Schiff base and 1,2-phenylenediacetic acid (2 mmol:1 mmol) was heated at 147−149 °C for 2 h. After workup the reaction mixture was separated on alumina with *n*-pentane/benzene (5:1) and three fractions were collected: *fraction 1* compound **18** (19 mg, 0.049 mmol, yield 7 %), *fraction 2* compound **19** (27 mg, 0.07 mmol, yield 10 %), and *fraction 3* unchanged **2**(OCH_3) (156 mg, 0.59 mmol, 30 %, eluted with benzene).

1,2-Bis[(*E*)-2-(azulen-1-yl)vinyl]benzene (18): Green crystals, m.p. 195−197 °C. $C_{30}H_{22}$: calcd. C 94.20, H 5.80: found C 94.01, H 5.82. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.07 [t, $^{3}J_{H,H}$ = 10.0 Hz, 4 H, C(5′′)-, C(7′′)-H], 7.30 [m, 2 H, C(4)-, C(5)-H], 7.41 [d, $^{3}J_{H,H}$ = 4.1 Hz, 2 H, C(3′′)-H], 7.51 [t, $^{3}J_{H,H}$ = 10.0 Hz, 2 H, C(6′′)-H], 7.61 [d, $^{3}J_{H,H}$ = 16.0 Hz, 2 H, C(1′)-H], 7.64 [d, $^{3}J_{H,H}$ = 16.0 Hz, 2 H, C(2′)-H], 7.72 [m, 2 H, C(3)-, C(6)-H], 8.21 [d, $^{3}J_{H,H}$ = 9.2 Hz, 2 H, C(4′′)-H], 8.29 [d, $^{3}J_{H,H}$ = 4.2 Hz, 2 H, C(2′′)-H], 8.47 [d, $^{3}J_{H,H}$ = 10.0 Hz, 2 H, C(8′′)-H] ppm. ^{13}C NMR (125.75 MHz, $CDCl_3$, 25 °C): δ = 119.02 (C-3′′), 122.80 (C-5′′ or -7′′), 123.17 (C-2′), 123.88 (C-5′′ or -7′′), 93 (C-1′), 126.43 (C-3, -6), 127.06 (C-4, -5), 129.17 (q), 133.64 (C-2′′), 133.71 (C-8′′), 136.77 (C-4′′), 136.90 (q), 137.73 (q), 138.25 (C-6′′), 144.31 (q) ppm. EI MS: *m*/*z* (%) = 384 (6) [M^{+} + 2], 383 (35) [M^{+} + 1], 382 (100) [M^{+}], 381 (31) [M^{+} − 1], 365 (17), 352 (10), 339 (6), 303 (7), 289 (14), 267 (59), 265 (27), 254 (87), 253 (75), 252 (65), 239 (39), 228 (33), 215 (10), 202 (6), 191 (14), 176 (10), 165 (7), 152 (16), 141 (92), 130 (30), 115 (20). FD MS: *m*/*z* (%) = 383 (32) [M^{+} + 1], 382 (100) [M^{+}], 78 (50), 261 (3).

1-[(*E*)-(2-(Azulen-1-yl)-2,3-dihydro-1*H*-inden-1-ylidene)methyl]-azulene (19): (Structure A − Scheme 3). Green crystals, m.p.

177−178 °C. $C_{30}H_{22}$: calcd. C, 94.20, H 5.80; found C 94.10, H 5.85. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 3.03 [dd, $^{3}J_{H,H}$ = 16.0, 1.8 Hz, 1 H, C(3)-H], 3.75 [dd, $^{3}J_{H,H}$ = 16.0, 8.4 Hz, 1 H, C(3)-H], 5.23 [dt, $^{3}J_{H,H}$ = 16.0, 1.8 Hz, 1 H, C(2)-H], 6.98 [t, $^{3}J_{H,H}$ = 10.0 Hz, 1 H, C(5′)-H], 6.99 [d, $^{3}J_{H,H}$ = 4.0 Hz, 1 H, C(3′)-H], 7.07−7.12 [m, 3 H, C(7′′)-, C(5′′)-, C(3′′)-H], 7.16−7.21 [m, 3 H, C(4)-, C(5)-, C(7′)-H], 7.34 [t, $^{3}J_{H,H}$ = 7.6 Hz, 1 H, C(6)-H], 7.44 [d, $^{3}J_{H,H}$ = 4.0 Hz, 1 H, C(2′)-H], 7.51 [t, $^{3}J_{H,H}$ = 10.0 Hz, 1 H, C(6′′)-H], 7.61 [d, $^{3}J_{H,H}$ = 3.6 Hz, 1 H, C(2′′)-H], 7.62 [t, $^{3}J_{H,H}$ = 10.0 Hz, 1 H, C(6′)-H], 7.87 (d, $^{3}J_{H,H}$ = 1.8 Hz, 1 H, H_{exo}), 7.91 [d, $^{3}J_{H,H}$ = 7.6 Hz, 1 H, C(7)-H], 8.07 [d, $^{3}J_{H,H}$ = 9.2 Hz, 1 H, C(4′)-H], 8.22 [d, $^{3}J_{H,H}$ = 9.6 Hz, 1 H, C(4′′)-H], 8.54 [d, $^{3}J_{H,H}$ = 10.0 Hz, 1 H, C(8′)-H], 8.58 [d, $^{3}J_{H,H}$ = 10.0 Hz, 1 H, C(8′′)-H] ppm. ^{13}C NMR (125.75 MHz, $CDCl_3$, 25 °C): δ = 41.43 (C-2), 42.34 (C-3), 112.94 (CH_{exo}), 116.90 (C-3′′), 119.01 (C-3′), 119.93 (C-7), 121.59 (C-7′), 122.27 (C-7′′ or -5′′), 122.33 (C-7′′ or -5′′), 123.38 (C-5′), 125.60 (C-4 or -5), 126.10 (q), 126.84 (C-6), 127.71 (C-5 or -4), 133.07 (C-8′), 133.51 (C-8′′), 133.94 (q), 135.40 (q), 136.16 (C-2′, -2′′), 136.20 (C-4′′), 136.44 (C-4′), 136.65 (q), 137.15 (C-6′), 137.98 (C-6′′), 141.85 (q), 141.39 (q), 143.29 (q), 143.65 (q), 143.70 (q) ppm. EI MS: *m/z* (%) = 384 (7) [M^{+} + 2], 383 (43) [M^{+} + 1], 382 (100) [M^{+}], 381 (17) [M^{+} − 1], 365 (17), 352 (6), 253 (51), 254 (32), 252 (35), 241 (17), 191 (8), 141 (64), 128 (10). FD MS: *m/z* (%) = 384 (5) [M^{+} + 2], 383 (24) [M^{+} + 1], 382 (100) [M^{+}].

Condensation between 1,4-Phenylenediacetic Acid and 2(OCH_3): The 1,4-phenylenediacetic acid (1 mmol) was added to an excess of melted **2**(OCH_3) (2.5 mmol) and the mixture was then maintained at 120 °C (oil bath) for 10 h. The solubility of the product **20** was very low, so the resulting mixture was triturated with DCM and filtered. The solution contained unchanged **2**(OCH_3); only 0.50 mmols had reacted. The precipitate was dissolved in a large excess of ethyl acetate and filtered through a pad of alumina. After solvent removal, the product **20** proved to be analytical pure in 91 % yield.

1,4-Bis[(*E*)-2-(azulen-1-yl)vinyl]benzene (20): Brown crystals, very slightly soluble in most solvents. The compound did not melt until 260 °C. ($C_{30}H_{22}$: calcd. C 94.20, H 5.80; found C 93.89, H 5.90). ^{1}H NMR (400 MHz, [D_6]DMSO, 25 °C): δ = 7.16 [t, $^{3}J_{H,H}$ = 9.4 Hz, 2 H, C(5′′)-H], 7.19 [t, $^{3}J_{H,H}$ = 9.4 Hz, 2 H, C(7′′)-H], 7.30 [d, $^{3}J_{H,H}$ = 16.0 Hz, 2 H, C(1′)-H], 7.48 [d, $^{3}J_{H,H}$ = 4.2 Hz, 2 H, C(3′′)-H], 7.64 [t, $^{3}J_{H,H}$ = 10.0 Hz, 2 H, C(6′′)-H], 7.72 [s, 4 H, C(2)-, C(3)-, C(5)-, C(6)-H], 7.94 [d, $^{3}J_{H,H}$ = 16.0 Hz, 1 H, C(2′)-H], 8.30 [d, $^{3}J_{H,H}$ = 9.4 Hz, 2 H, C(4′′)-H], 8.38 [d, $^{3}J_{H,H}$ = 4.4 Hz, 2 H, C(2′′)-H], 8.79 [d, $^{3}J_{H,H}$ = 9.6 Hz, 2 H, C(8′′)-H] ppm. EI MS (solid state): *m/z* (%) = 384 (5) [M^{+} + 2], 383 (31) [M^{+} + 1], 382 (53) [M^{+}], 365 (7), 252 (33), 239 (15), 228 (39), 215 (12), 202 (27), 191 (1/2 M^{+}, 100), 183 (45), 176 (36), 153 (57), 152 (50), 141 (42), 128 (40), 115 (26), 102 (13), 77 (13), 63 (6), 49 (19), 39 (10).

Condensation between *N*-({3-[(4-Methoxyphenylimino)methyl]azulene-1-yl}methylene)-4-methoxyaniline (22) and Phenylacetic Acid [3(H)]: A mixture of **22** and **3**(H) (1 mmol:2 mmol) was heated for 6 h at 120 °C and after workup the reaction mixture was separated on silica with benzene/*n*-pentane (1:1). Three fractions were collected: *fraction 1*, 1,3-distyrylazulene, **21**(C_6H_5) (144 mg, 0.432 mmol, yield 43.2 %), *fraction 2*, the product of reaction only at one imino group (**23**, 15 mg, 0.041 mmol), and *fraction 3*, containing a mixture of **23** and its hydrolysis product, the aldehyde **24**, in a molar ratio 1.85:1 (the ratio between the two compounds was calculated from the signal integrals of -CHO and -CH=N-protons in ^{1}H NMR spectrum, 49 mg). The yields of **23** and in **24** were 14 % and 5 %, respectively. The products **23** and **24** were not analytically purified. The structure of **23** was assigned on the basis of ^{1}H NMR and MS data for the *fraction 2*. The characteristic ^{1}H NMR signals for aldehyde **24** were obtained from the mixture of **23** and **24** (the results are reported in the ESI). No starting material was obtained by chromatographic separation.

Condensation between *N*-({3′-[(4-Methoxyphenylimino)methyl]-1,1′-biazulen-3-yl}methylene)-4-methoxyaniline and Phenylacetic Acid [3(H)]: A mixture of the 3,3′-bis(Schiff base) of 1,1′-bis(azulene)[2] and phenylacetic acid **3**(H) (1 mmol:3 mmol) was heated for 4 h at 140 °C and worked up as described. The mixture was separated on alumina with DCM/*n*-pentane (1:4) and three fractions were separated: *fraction 1,* 3,3′-bis[(*E*)-2-phenylvinyl]-1,1′-biazulene (**25**, 84 mg, 0.18 mmol, yield 19 %), *fraction 2,* 3′-[(*E*)-2-phenylvinyl]-1,1′-biazulene-3-carbaldehyde (**26**, 98 mg, 0.26 mmol, yield 28 %), and *fraction 3,* containing the starting material with one hydrolysed azomethine group (22 mg, 0.053 mmol). All attempts to obtain an analytical sample of compound **26** failed because of contamination by the half-hydrolysed starting material (^{1}H NMR spectrum of the compound **26** is reported in ESI).

3,3′-Bis[(*E*)-2-phenylvinyl]-1,1′-biazulene (25): Dark yellow crystals, m.p. 176−177 °C. ($C_{36}H_{26}$: calcd. C 94.28, H 5.71; found C 94.18, H 5.75). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 6.99 [t, $^{3}J_{H,H}$ = 10.0 Hz, 2 H, C(5)-, C(5′)-H], 7.10 [t, $^{3}J_{H,H}$ = 10.0 Hz, 2 H, C(7)-, C(7′)-H], 7.23 [t, $^{3}J_{H,H}$ = 7.5 Hz, 2 H, C(4′′′)-H], 7.26 [d, $^{3}J_{H,H}$ = 15.8 Hz, 2 H, C(2′′)-H], 7.38 [t, $^{3}J_{H,H}$ = 7.5 Hz, 4 H, C(3′′′)-, C(5′′′)-H], 7.51 [t, $^{3}J_{H,H}$ = 9.8 Hz, 2 H, C(6)-, C(6′)-H], 7.60 [d, $^{3}J_{H,H}$ = 7.5 Hz, 4 H, C(2′′′)-, C(6′′′)-H], 7.78 [d, $^{3}J_{H,H}$ = 16.0 Hz, 2 H, C(1′′)-H], 8.20 [d, $^{3}J_{H,H}$ = 9.4 Hz, 2 H, C(4)-, C(4′)-H], 8.39 [s, 2 H, C(2)-, C(2′)-H], 8.52 [d, $^{3}J_{H,H}$ = 9.8 Hz, 2 H, C(8)-, C(8′)-H] ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$, 25 °C): δ = 120.38 (C-1′′), 122.88 (C-7, -7′), 124.02 (C-5, -5′), 126.09 (C-2′′′, -6′′′), 126.58 (q, C-1, -1′), 126.66 (q, C-3, -3′), 126.92 (C-2′′), 126.97 (C-4′′′), 128.69 (C-3′′′, -5′′′), 133.95 (C-8, -8′), 134.64 (C-2, -2′), 136.38 (C-4, -4′), 136.66 (q, C-8a, -8a′), 138.34 (q, C-1′′′), 139.06 (C-6, -6′), 140.13 (q, C-3a, -3a′) ppm.

Condensation between 1,3-Azulenediacetic Acid and 2(OCH_3): The mixture of **2**(OCH_3) and 1,3-azulenediacetic acid[18] (2 mmol:1 mmol) was maintained at 120 °C for 6 h and worked up as described. The reaction mixture was separated by column chromatography on silica, eluent DCM/*n*-pentane (1:1), and the alkene **21**(Az) was separated as the first fraction (275 mg, 0.636 mmol, yield 48 %), followed by a fraction (110 mg, 0.705 mmol), eluted with DCM/ethyl acetate (1:1), containing 1-azulenecarbaldehyde [from hydrolyse of **2**(OCH_3)], degree of conversion of starting material, 65 %.

1,3-Bis[(*E*)-2-(azulen-1-yl)vinyl)azulene [21(Az)]: Brown crystals; the compound did not melt until 260 °C. ($C_{34}H_{24}$: calcd. C 94.41, H 5.59; found C 94.52, H 5.41). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 6.85−7.14 [m, 6 H, C(5)-, C(7)-, C(5′′)-, C(7′′)-H], 7.38 [t, $^{3}J_{H,H}$ = 10.0 Hz, 1 H, C(6)-H], 7.43 [d, $^{3}J_{H,H}$ = 4.0 Hz, 2 H, C(3′′)-H], 7.49 [t, $^{3}J_{H,H}$ = 10.0 Hz, 2 H, C(6′′)-H], 7.70 [2 H, d, $^{3}J_{H,H}$ = 16.0, C(1′)-H], 7.85−7.89 [2 H, m, C(2′)-H], 8.17 [d, $^{3}J_{H,H}$ = 10.0 Hz, 2 H, C(4′′)-H], 8.31 [d, $^{3}J_{H,H}$ = 10.0 Hz, 2 H, C(4)-, C(8)-H], 8.36 [d, $^{3}J_{H,H}$ = 4.0 Hz, 2 H, C(2′′)-H], 8.56 [d, $^{3}J_{H,H}$ = 10.0 Hz, 2 H, C(8′′)-H], 8.74 [s, 1 H, C(2)-H] ppm. EI MS: *m/z* (%) = 434 (8) [M^{+} + 2], 433 (37) [M^{+} + 1], 432 (100) [M^{+}], 303 (37), 302 (60), 276 (44), 265 (24), 252 (22), 213 (27), 207 (45), 200 (36), 165 (28), 153 (52), 152 (92), 151 (53), 141 (90), 139 (43), 128 (99), 127 (35), 115 (50), 102 (24), 77 (30), 44 (49).

Condensations between Schiff Bases and other Compounds with Active Methylene: The molar ratios between the reagents and the reaction conditions are reported in Table 4. The workup and the separation procedures are discussed for each condensation.

Condensation between Malonic Acid (27) and 2(OCH$_3$): After condensation between 1 mmol of each reagent, the resulting *para*-anisidine was removed as already described and the reaction mixture was treated with NaOH solution (2 N). The aqueous layer was extracted with DCM. The solvent was evaporated, and the resulting mixture contained, together with the product **34**, traces of anisidine, unchanged **2**(OCH$_3$) and 1-azulenecarbaldehyde.[28] The tetrahydroquinoline **34** was separated from the aldehyde by filtration through an alumina bed (eluent *n*-pentane/DCM). All attempts to separate traces of anisidine from the product failed, so the product was not completely characterised (only mass and NMR spectra were recorded). After neutralisation with HCl solution (2 N), the aqueous layer was extracted with DCM (2 × 50 mL), the organic layer was dried (Na$_2$SO$_4$), and the solvent was removed in vacuo to afford pure (*E*)-3-(azulen-1-yl)acrylic acid (**33**, 93 mg, 0.47 mmol, yield 47 %).

Condensation between Cyanoacetic Acid (28) and 2(OCH$_3$): The workup of the reaction mixture obtained after condensation of 1 mmol of each reagent followed the same procedure as for malonic condensation. The residue from the organic layer was separated on silica with DCM/*n*-pentane (1:2) and two fractions were collected: *fraction 1*, (2*Z*)-3-(azulen-1-yl)acrylonitrile [(*Z*)-**36**, 10 mg, 0.06 mmol, yield 6 %] and *fraction 2*, (*E*)- **36**, (22 mg, 0.12 mmol, yield 12.5 %). From the aqueous layer, (2*E*)-3-(azulen-1-yl)-2-cyanoacrylic acid (**35**), was obtained in 68 % yield (152 mg, 0.68 mmol). No starting material was recovered.

(2*E*)-3-(Azulen-1-yl)-2-cyanoacrylic Acid (35): Dark red crystals, m.p. > 350 °C. (C$_{14}$H$_9$NO$_2$: calcd. C 75.33, H 4.06, N 6.28; found C 75.18, H 4.00, N 6.31). ^{1}H NMR (500 MHz, [D$_6$]DMSO, 25 °C): δ = 7.70 [d, $^3J_{H,H}$ = 4.0 Hz, 1 H, C(3′)-H], 7.73 [1 H, t, $^3J_{H,H}$ = 10.0, C(5′)-H], 7.76 [1 H, t, $^3J_{H,H}$ = 10.0, C(7′)-H], 8.10 [1 H, d, $^3J_{H,H}$ = 10.0, C(6′)-H], 8.72 [d, $^3J_{H,H}$ = 10.0 Hz, 1 H, C(4′)-H], 8.80 [s, 1 H, C(1)-H], 8.85 [d, $^3J_{H,H}$ = 4.0 Hz, 1 H, C(2′)-H], 9.00 [d, $^3J_{H,H}$ = 10.0 Hz, 1 H, C(8′)-H] ppm. ^{13}H NMR (125.75 MHz, [D$_6$]DMSO, 25 °C): δ = 94.32 (q), 118.47 (q), 120.53 (q), 122.14 (t), 128.96 (t), 129.69 (t), 135.29 (t), 135.57 (t), 139.54 (t), 141.22 (t), 142.58 (q), 143.39 (t), 145.27 (q), 165.00 (q) ppm. EI MS: *m*/*z* (%) = 224 (11) [M$^+$ + 1], 223 (100) [M$^+$], 222 (5) [M$^+$ − 1], 206 (4), 179 (15), 178 (25), 177 (20), 151 (20), 150 (15), 126 (3), 108 (2), 89 (1), 76 (5), 63 (4). FD MS: *m*/*z* (%) = 226 (2) [M$^+$ + 3], 225 (4) [M$^+$ + 2], 224 (18) [M$^+$ + 1], 223 (100) [M$^+$], 113 (4).

Condensation between Malononitrile (29) and 2(OCH$_3$): The obtained reaction mixture was triturated with a small amount of warm *n*-pentane and after drying in vacuo, pure (azulen-1-ylmethylene)malononitrile (**37**[7a]) was obtained in 100 % yield. No starting material was recovered.

Condensation between Ethyl Acetoacetate (30) and 2(OCH$_3$): The reagents were allowed to react in a flask under a reflux condenser, under inert atmosphere. At the end, the resulting *para*-anisidine and a quantity of unchanged ethyl acetoacetate were removed from the top wall of the flask. The reaction mixture was separated on silica with ethyl acetate/*n*-pentane (1:4) and the ethyl 2-acetyl-3-(azulen-1-yl)acrylate [**38**, a mixture of (*E*) and (*Z*) isomers with unassigned structures, in molar ratio 3.6:1] was separated as the first fraction (115 mg, 0.429 mmol, yield 57 %), followed by a fraction of 105 mg, containing a mixture of **30** and 1-azulenecarbaldehyde, molar ratio 2:1.

Condensation between Acetylacetone (31) and 2(OCH$_3$): The reaction and the workup were performed as for the condensation between **30** and **2**(OCH$_3$). The reaction mixture was separated on alumina: *fraction 1,* eluent benzene, a mixture of Schiff base and the corresponding aldehyde (molar ratio 2:1), and *fraction 2*, eluent DCM, alkene **39** and traces of acetylacetone (the separation of a pure analytical sample of **39** from the mixture failed).

Condensation between 1-*H*-Indene (32) and 2(OCH$_3$): The reaction and the workup were performed as for the condensation between **30** and **2**(OCH$_3$). The reaction mixture was separated on silica with benzene (1:4) and the alkene **40** was separated as the first fraction followed by a mixture of Schiff base and aldehyde. The compound **40** is stable over time only in solution, so the NMR and mass spectra were recorded for structure assignment.

Acknowledgments

A. C. R. and C. N. gratefully acknowledge the Alexander von Humboldt Foundation for their fellowship granted by the Stability Pact for Southeast Europe, which allowed this work to be accomplished. The project was carried out in the working group of Prof. Klaus Hafner (T. U. Darmstadt, Germany), whom the authors A. C. R. and C. N. wish to thank for valuable discussions and helpful suggestions and for partial financial support. The Ministry of Education and Research, Romania, provided a part of the financial support.

---

[1] [1a] A. C. Razus, L. Birzan, S. A. Razus, V. Horga, *Rev. Roum. Chim.* **1999**, *44*, 235−248. [1b] A. C. Razus, *J. Chem. Soc., Perkin Trans. 1* **2000**, 981−988. [1c] A. C. Razus, L. Birzan, S. Nae, S. A. Razus, V. Cimpeanu, C. Stanciu, *Synth. Commun.* **2001**, *32*, 825−837.

[2] A. C. Razus, C. Nitu, S. Carvaci, L. Birzan, S. A. Razus, M. Pop, L. Tarko, *J. Chem. Soc., Perkin Trans. 1* **2001**, 1227−1233.

[3] A. C. Razus, L. Birzan, S. Nae, C. Nitu, V. Tecuceanu, V. Cimpeanu, *Arkivoc* **2002**, 142−153.

[4] A. C. Razus, L. Birzan, S. Nae, L. Cristian, F. Chiraleu, V. Cimpeanu, *Dyes Pigm.* **2003**, *57*, 223−233.

[5] P. G. Lacroix, I. Malfant, G. Iftime, A. C. Razus, K. Nakatani, J. A. Delaire, *Chem. Eur. J.* **2000**, *6*, 2599−2608.

[6] N. D. Totir, A. C. Razus, C. Lete, C. Nitu, S. Lupu, 81st Bunsen-Kolloquium, Dresden (Germany), September **2002**.

[7] [7a] A. E. Asato, R. S. H. Liu, V. P. Rao, Y. M. Cai, *Tetrahedron Lett.* **1996**, *37*, 419−422. [7b] P. Wang, P. Zhu, C. Ye, A. E. Asato, R. S. H. Liu, *J. Phys. Chem.* **1999**, *103*, 7076−7082. [7c] R. Herrmann, B. Pedersen, G. Wagner, J.-H. Youn, *J. Organomet. Chem.* **1998**, *571*, 261−266. [7d] G. Iftime, P. G. Lacroix, K. Nakatani, A. C. Razus, *Tetrahedron Lett.* **1998**, *39*, 6853−6856.

[8] A short review of the syntheses of different vinylazulenes was presented by: K.-P. Zeller, in *Methoden der Organischen Chemie* (Houben-Weyl), B. V/2c, Georg Thieme Verlag, Stuttgart, New York, **1985**.

[9] [9a] R. N. McDonald, W. S. Stewart, *J. Org. Chem.* **1965**, *30*, 270−273. [9b] S. Hunig, B. Ort, *Liebigs Ann. Chem.* **1984**, 1905−1935. [9c] K. Hafner, G. L. Knaup, H. J. Lindner, *Bull. Chem. Soc. Jpn.* **1988**, *61*, 155−163. [9d] J. O. Currie, R. A. LaBar, R. D. Breazeale, A. G. Anderson, *Org. Prep. & Proced.* **1976**, *8*, 169−177. [9e] M. Saito, T. Morita, K. Takase, *Chem. Lett.* **1974**, 289−292. [9f] M. Saito, T. Morita, K. Takase, *Bull. Chem. Soc. Jpn.* **1980**, *53*, 3276−3278.

[10] For the synthesis of 1-(azulen-1-yl)-2-phenylethene [**9**(H)] we applied a Wittig procedure in the presence of *n*-butyllithium

This resulted in, together with unchanged 1-azulenecarbaldehyde (20 %), a mixture of (*Z*)- and (*E*)-**9**(H) (in yields of 44.5 % and 7.5 %, respectively).

[11] A. E. Siegrist, *Helv. Chim. Acta* **1967**, *50*, 907−957; A. E. Siegrist, H. R. Meyer, *Helv. Chim. Acta* **1969**, *52*, 1282−1323; A. E. Siegrist, P. Liechti, H. R. Meyer, K. Weber, *Helv. Chim. Acta* **1969**, *52*, 2521−2553; A. E. Siegrist, *Helv. Chim. Acta* **1981**, *64*, 662−685.

[12] H. Horino, T. Asao, N. Inoue, *Bull. Chem. Soc. Jpn.* **1991**, *64*, 183−190.

[13] G. Charles, *Bull. Soc. Chim. France* **1963**, 1559−1565; 1566−1572; 1573−1578; 1578−1583.

[14] K. Harada, in *The Chemistry of C=N bond* (Ed.: S. Patay), Interscience Publisher Wiley & Sons, London, New York, Sidney, **1970**, p. 262 and following.

[15] T. I. Bieber, R. Sites, Y. Chiang, *J. Org. Chem.* **1958**, *23*, 300−301.

[16] For synthetic purposes, of the two Schiff bases with the highest reactivity, we preferred **2**(OCH_3) obtained from *para*-anisidine, an amine that is more stable and less harmful.

[17] An alternative synthesis of the compound **18** was performed by the authors by use of a Wittig reaction between *ortho*-phenylenediylide and two equivalents of azulenecarbaldehyde. A complex mixture of *trans*-*trans, cis*-*cis* and *cis*-*trans* isomers of **18**, together with internal cyclization compounds, was obtained. The results will be published.

[18] V. A. Nefedov, L. K. Tarygina, *Zh. Org. Khim.* **1994**, *30*, 1639−1643.

[19] V. M. Rodionov, E. V. Yavorskaya, *Zh. Obschei. Khim.* **1953**, *23*, 983−986; *Zh. Obschei. Khim.* **1955**, *25*, 2147−2150.

[20] R. G. Pearson, R. L. Dillon, *J. Am. Chem. Soc.* **1953**, *75*, 2439−2443.

[21] S. Patay, J. Zabicky, *J. Chem. Soc.* **1960**, 2030−2038.

[22] K. Tanaka, F. Toda, *Chem. Rev.* **2000**, *100*, 1025−1074.

[23] Of the previously reported alkenes − **9**(H),[9a] **13**,[9b] **21**(C_6H_5),[9d] and **37**[7a] − only **13** was completely characterized.

[24] The UV/Vis spectra will be reported and commented on in another paper in preparation.

[25] In Exp. Sect. we report the NMR spectra only for the compound **9**(p-NO_2); other spectra are reported in the electronic Supporting Information; for details see also the footnote on the first page of this article.

[26] The diethene **18** and the compound **19** have the same molecular ion signal in their mass spectra.

[27] Compound **8** was a gift from Prof. Klaus Hafner.

[28] The ratio of these components, established from the ^{1}H NMR spectrum of the mixture, showed that about 10 % of **2**(OCH_3) remained unchanged and the compound **34** was produced in about 20 % yield.

Received June 10, 2003