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Flash vacuum pyrolysis of 2,2-dioxo-1*H*,3*H*-pyrrolo[1,2-*c*]thiazoles and 2-vinyl-1*H*-pyrroles

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ABSTRACT

The flash vacuum pyrolysis of new 1,1-dimethyl- and 1-methyl-1*H*,3*H*-pyrrolo[1,2-*c*]thiazole-2,2-dioxides gave penta-substituted 2-vinyl-1*H*-pyrroles via sigmatropic [1,8]-H shift of the corresponding azafulvenium methide intermediates. In some cases these 1*H*-pyrroles underwent rearrangement to 2-allyl-1*H*-pyrroles. Di-substituted 2-vinylpyrroles have also been prepared and their reactivity studied. Under FVP *N*-benzyl-pyrrol-2-ylpropenoates were converted into 3*H*-pyrrolizin-3-ones. On the other hand, microwave-assisted reaction of 1-benzyl-2-vinyl-1*H*-pyrrole gave a 4,5,6,7-tetrahydro-1*H*-indole derivative.

1. Introduction

The study of pericyclic reactions of transient 8π 1,7-dipoles generated by the thermal extrusion of sulfur dioxide from 2,2-dioxo-1*H*,3*H*-pyrrolo[1,2-*c*]thiazoles and 2,2-dioxo-pyrazolo[1,5-*c*]thiazoles is one of our current research interests.[1–4] The intramolecular trapping of azafulvenium methides in pericyclic reactions, namely sigmatropic [1,8]-H shifts and 1,7-electrocyclization, allowed the synthesis of *N*-vinyl-1*H*-pyrroles and 2-vinyl-1*H*-pyrroles, which, under flash vacuum pyrolysis (FVP) conditions, are converted into pyrrolizinones, 4-oxo-1,4-dihydro-1-aza-benzo[*f*]azulenes or 2-allyl-1*H*-pyrroles.[1,3] Diazafulvenium methides unsubstituted at C-7, generated under conventional solution thermolysis conditions, participate in [8π+2π] cycloadditions giving pyrazolo[1,5-*a*]pyridine derivatives resulting from the addition across the 1,7-position. 1-Methyl- and 7,7-dimethyl-diazafulvenium methides undergo intramolecular sigmatropic [1,8]-H shifts giving vinylpyrazoles.[2] Recently we have reported the generation and reactivity of azafulvenium methides and diazafulvenium methides under microwave irradiation.[4] Particularly interesting was to observe that under these reaction conditions both aza- and diazafulvenium methides participate in [8π+2π] cycloadditions.

We observed that 7,7-dimethyl-azafulvenium methides (**1a**–**1c**), derived from 1,1-dimethyl-2,2-dioxo-1*H*,3*H*-pyrrolo[1,2-*c*]thiazoles, undergo sigmatropic [1,8]-H shifts to give 2-vinyl-1*H*-pyrroles (**2a**–**2c**) even in cases where an alternative pericyclic reaction could in principle occur (e.g., 7,7-dimethyl-azafulvenium methide **1b**). Azafulvenium methide **1d**, generated from the corresponding C-3 unsubstituted 1-methyl-2,2-dioxo-1*H*,3*H*-pyrrolo[1,2-*c*]thiazole can only undergo the [1,8]-H shift that leads to the corresponding 2-vinyl-1*H*-pyrrole (**2d**). However, the azafulvenium methide **1e** derived from the corresponding 1,3-dimethyl-2,2-dioxo-1*H*,3*H*-pyrrolo[1,2-*c*]thiazole undergoes the two possible sigmatropic [1,8]-H shifts giving 2-vinyl- and *N*-vinyl-1*H*-pyrroles. Rearrangements of the 2-vinyl-1*H*-pyrroles under flash vacuum pyrolysis conditions afford 5-oxo-5*H*-pyrrolizines (**3**) or functionalized 2-allyl-1*H*-pyrroles (**4**). The 2-allyl-1*H*-pyrroles **4** were obtained directly from the corresponding 2,2-dioxo-1*H*,3*H*-pyrrolo[1,2-*c*]thiazoles by FVP although it was established that 2-vinyl-1*H*-pyrroles are intermediates in this transformation. In fact, the FVP of 1-benzyl-2-isopropenyl-5-methyl-1*H*-pyrrole-3,4-dicarboxylate **2c** affords 5-(2-methyl-1-phenylallyl)-1*H*-pyrrole **4a** (Scheme 1).[3]

The structural feature of the penta-substituted pyrroles, which allows the rearrangement into the 2-allyl-1*H*-pyrroles appears to be the presence of a group of the type $-CH_2R$ (with R=Ph or Me) at N-1 since *N*-methyl-2-isopropenyl-1*H*-pyrrole **2a** and *N*-methyl-2-ethenyl-1*H*-pyrrole **2d** rearrange by a different pathway giving

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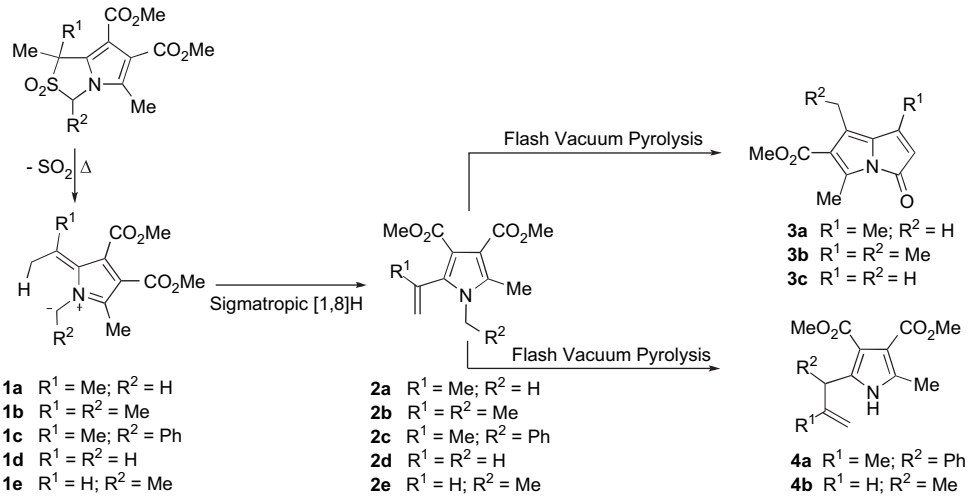


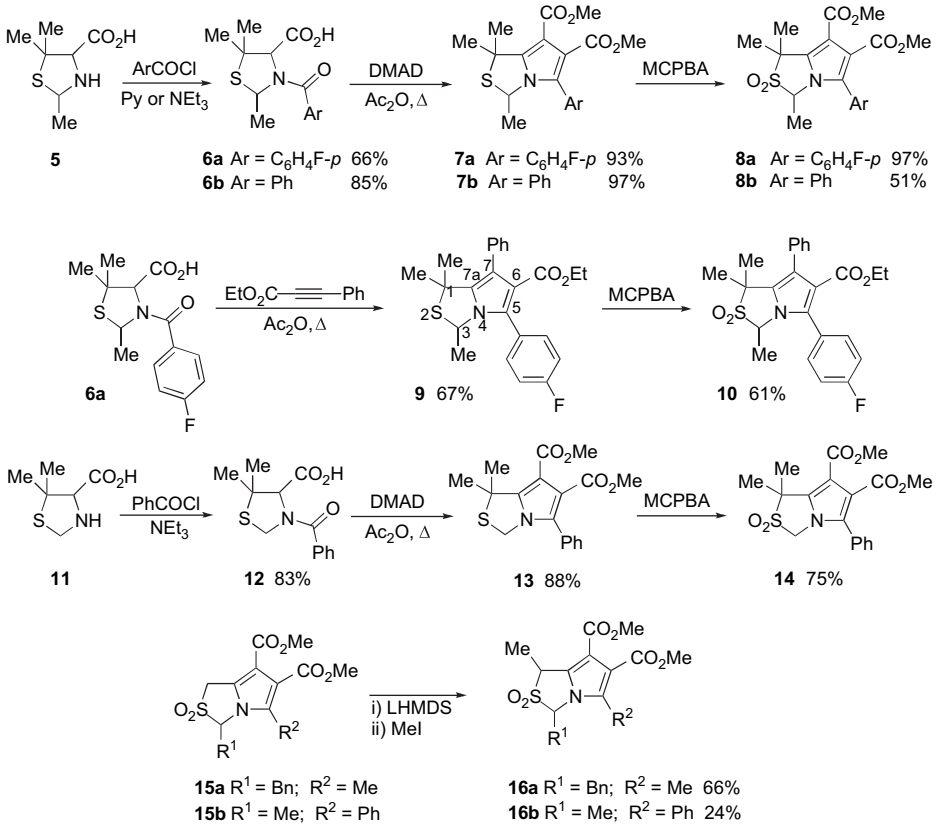
Scheme 1.

5-oxo-5*H*-pyrrolizines. However, in the case of *N*-ethyl-1*H*-pyrroles another structural requirement appears to be needed, the presence of the ethenyl substituent at C-2. In fact, 1*H*-pyrrole **2e** is converted into the 2-allyl-1*H*-pyrrole whereas *N*-ethyl-2-isopropenyl-1*H*-pyrrole **2b** affords 5-oxo-5*H*-pyrrolizines on FVP.

The work has now been extended to the thermolysis of new 1,1-dimethyl- and 1-methyl-1*H*,3*H*-pyrrolo[1,2-*c*]thiazole-2,2-dioxides aiming to get further knowledge on the interesting rearrangement of 2-vinyl-1*H*-pyrroles to 2-allylpyrroles. Disubstituted 2-vinylpyrroles have also been prepared and their reactivity studied.

2. Results and discussion

The 1,1-dimethyl-1*H*,3*H*-pyrrolo[1,2-*c*]thiazole-2,2-dioxides (**8** and **10**) were prepared from 2,5,5-trimethyl-1,3-thiazolidine-4-carboxylic acid[3] (**5**) as outlined in Scheme 2. The N-acylation of the starting thiazolidine with the appropriated acid chloride was carried out following a general procedure previously reported.[5] Heating a solution of the *N*-benzoyl-1,3-thiazolidine-4-carboxylic acid **6** in acetic anhydride in the presence of dimethyl acetylene dicarboxylate afforded the corresponding 1,1,3-trimethyl-1*H*,3*H*-pyrrolo[1,2-*c*]thiazoles (**7**) in high yield (60–93%) via the



Scheme 2.

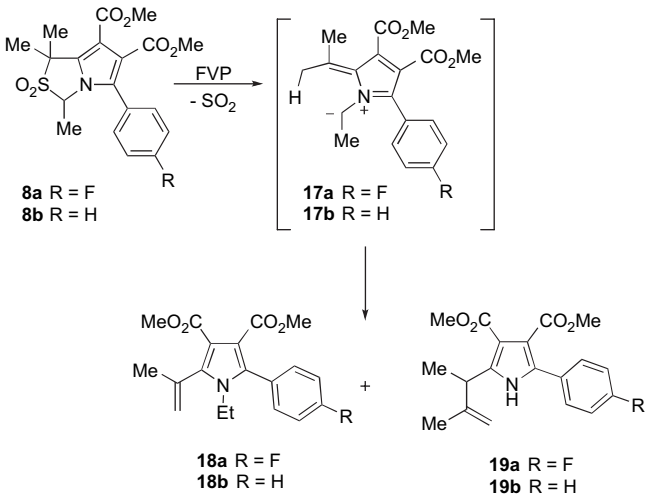
intermolecular dipolar cycloaddition of the in situ generated 5,7,7-trimethyl-3-aryl-5*H*,7*H*-thiazolo[3,4-*c*]oxazol-4-ium-1-olates. Oxidation of the pyrrolo[1,2-*c*]thiazoles **7** with MCPBA afforded sulfones **8**.

Pyrrolo[1,2-*c*]thiazole **9** was regioselectively prepared by the 1,3-dipolar cycloaddition of the thiazolo[3,4-*c*]oxazol-4-ium-1-olate, generated from 3-(4-fluorophenylcarbonyl)-2,5,5-trimethylthiazolidine-4-carboxylic acid **6a**, with phenyl propiolate (Scheme 2). The exclusive formation of **9** is the result of a regioselectivity where the β-carbon of the propiolate combines with the tethered centre of the bicyclic münchnones. The structural assignment of pyrrolo[1,2-*c*]thiazole **9** was based on a NOESY experiment. In fact, in the NOESY spectrum of compound **9**, methyl protons at C-3 show connectivity with the fluorophenyl protons but no connectivity with phenyl protons. On the other hand, the two methyl protons at C-1 show connectivity with the phenyl protons but no correlation was observed with the fluorophenyl protons. Sulfone **10** was also obtained by oxidation of compound **9** with MCPBA.

The 1,1-dimethyl-5-phenyl-1*H*,3*H*-pyrrolo[1,2-*c*]thiazole-2,2-dioxide **14** was also prepared from 5,5-trimethyl-1,3-thiazolidine-4-carboxylic acid[3] (**11**) in good yield. 1-Methylpyrrolo[1,2-*c*]-thiazole-2,2-dioxides **16** were prepared from sulfones **15**[1b] by an alkylation procedure,[6] metallation with LiHMDS and subsequent reaction with iodomethane gave derivatives **16** (Scheme 2).

The FVP of 1,1-dimethyl-1*H*,3*H*-pyrrolo[1,2-*c*]thiazole-2,2-dioxide **8a** leads to the synthesis of 2-vinyl-1*H*-pyrrole **18a** and 2-allyl-1*H*-pyrrole **19a** obtained as a mixture that could only be separated by GC techniques. The best result was obtained by carrying out the pyrolysis at 600 °C/3.5×10^{-2} mbar, which gave the products in 81% overall yield (Scheme 3, Table 1). New 2-vinyl-1*H*-pyrrole **18b** and 2-allyl-1*H*-pyrrole **19b** were also obtained as a mixture on FVP of sulfone **8b**. The FVP of the mixture of pyrroles, either **18a**/**19a** or **18b**/**19b**, led only to recovery of the starting material. However, the mixture is enriched with the 2-vinyl-1*H*-pyrrole indicating the lower stability of the allyl-1*H*-pyrrole derivatives. At higher temperature decomposition of allylpyrrole **19b** occurs (Scheme 3, Table 1). No products could be isolated from the solution thermolysis of sulfones **8** in a sealed tube (255–260 °C). Nevertheless, the results obtained indicate that 2-isopropenyl-1*H*-pyrroles require the presence of an aryl substituent at C-5 or a benzyl group at N-1 in order to rearrange to the corresponding 2-allyl-1*H*-pyrroles.

On flash vacuum pyrolysis conditions (600 °C/3.0×10^{-2} mbar) sulfone **10** undergoes SO_2 extrusion to give 2-vinyl-1*H*-pyrrole **20** as the major product in 40% yield together with the formation of



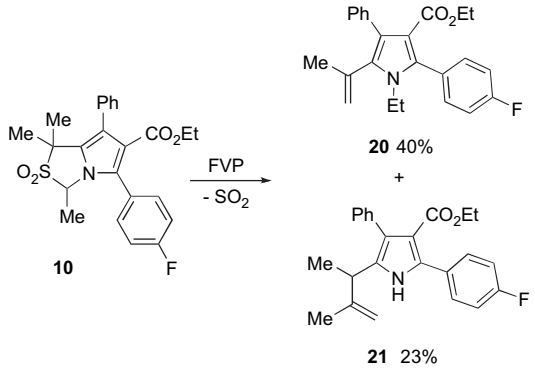
Scheme 3.

Table 1
FVP of compounds **8** and **18**/**19**

Reagents	Conditions	Products (ratio)	Yield (%)
8a	600 °C, 3.5×10^{-2} mbar	**18a**/**19a** (57:43)	81
8a	700 °C, 5.0×10^{-2} mbar	**18a**/**19a** (79:21)	29
8b	500 °C, 2.7×10^{-2} mbar	**18b**/**19b** (49:51)	10[a]
8b	550 °C, 2.7×10^{-2} mbar	**18b**/**19b** (42:58)	8[b]
8b	600 °C, 2.0×10^{-2} mbar	**18b**/**19b** (62:38)	75
8b	650 °C, 2.0×10^{-2} mbar	**18b**/**19b** (56:44)	54
8b	700 °C, 2.7×10^{-2} mbar	**18b**/**19b** (78:22)	45
18a/**19a** (57:43)	650 °C, 2.0×10^{-2} mbar	**18a**/**19a** (67:33)	90
18b/**19b** (56:44)	600 °C, 2.0×10^{-2} mbar	**18b**/**19b** (60:40)	84
18b/**19b** (60:40)	700 °C, 2.7×10^{-2} mbar	**18b**/**19b** (83:17)	22

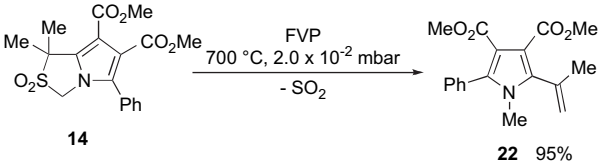
[a] Obtained together with **8b** (48%).
[b] Obtained together with **8b** (23%).

2-allyl-1*H*-pyrrole **21** in 23% yield (Scheme 4). In this case the products could be easily separated. Thus, the presence of two carboxylate groups in the starting 1*H*-pyrrole is not a requirement for the conversion of 2-vinyl-1*H*-pyrroles into 2-allyl-1*H*-pyrroles.



Scheme 4.

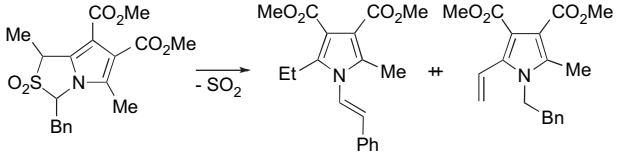
The thermolysis of sulfone **14**, unsubstituted at C-3, was also studied. This compound should lead to a 2-vinyl-1*H*-pyrrole without the substituent of the nitrogen of the type CH_2R. However, we decide to determine if the presence of a phenyl group at C-5 would make possible the rearrangement of **22** to the corresponding 2-allyl-1*H*-pyrrole. It was observed that under FVP (700 °C, 2.0×10^{-2} mbar) sulfone **14** is converted into 2-isopropenyl-1*H*-pyrrole **22** in high yield (Scheme 5). These FVP conditions also allow the synthesis of 2-isopropenyl-1*H*-pyrrole **2a** (70%) from the sulfone analogues to **14** but bearing a methyl group instead of the phenyl group at C-5, although a 5-oxo-5*H*-pyrrolizine derivative is also obtained (5%). Thus, the presence of the phenyl substituent allows the more efficient synthesis of the corresponding 2-vinyl-1*H*-pyrrole derivative. Attempts to carry out the rearrangement of **22** via FVP (700 °C, 2.0×10^{-2} mbar and 800 °C, 2.0×10^{-2} mbar) led only to sublimation of the starting 1*H*-pyrrole.



Scheme 5.

The FVP of 1*H*,3*H*-pyrrolo[1,2-*c*]thiazole-2,2-dioxides **16**, precursors of 2-ethenyl-1*H*-pyrroles, was also studied (Scheme 6). From 2,2-dioxo-1*H*,3*H*-pyrrolo[1,2-*c*]thiazole **16a** the only isolable

products were vinyl-1*H*-pyrroles **23** and **24** obtained in very low yield. In contrast with this result, the flash vacuum pyrolysis of 2,2-dioxo-1*H*,3*H*-pyrrolo[1,2-*c*]thiazole **16b** bearing a phenyl group at C-5 leads to 2-allyl-1*H*-pyrrole **26** in 54% yield as the only product. As previously mentioned, in the case of 2-ethenyl-1*H*-pyrroles the presence of a phenyl group at C-5 is not a structural requirement in order to rearrange to the 2-allyl-1*H*-pyrroles since 1*H*-pyrrole **2e** can be converted into **4b**. However, these results show that the presence of the phenyl group at C-5 allows the selective synthesis of the corresponding 2-allyl-1*H*-pyrrole.

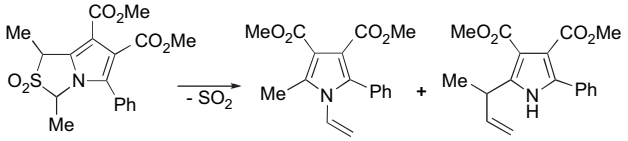


16a **23** **24**

FVP

600 °C, 2.0 x 10^{-2} mbar	6%	7%[a]
650 °C, 2.0 x 10^{-2} mbar	5%	7%[b]
700 °C, 2.0 x 10^{-2} mbar	---	---

[a](23% of **16a**); [b](13% of **16a**)



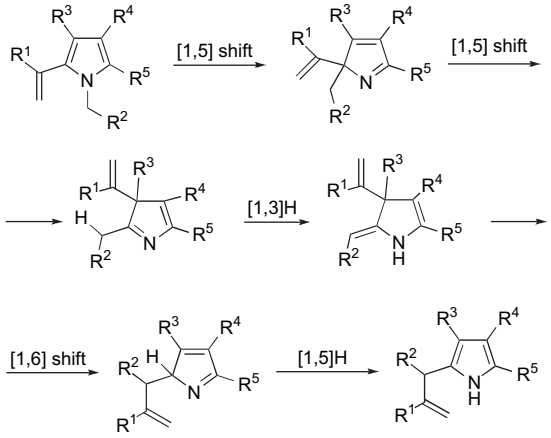
16b **25** **26**

FVP

600 °C, 2.0 x 10^{-2} mbar	---	54%
650 °C, 2.7 x 10^{-2} mbar	4%	20%

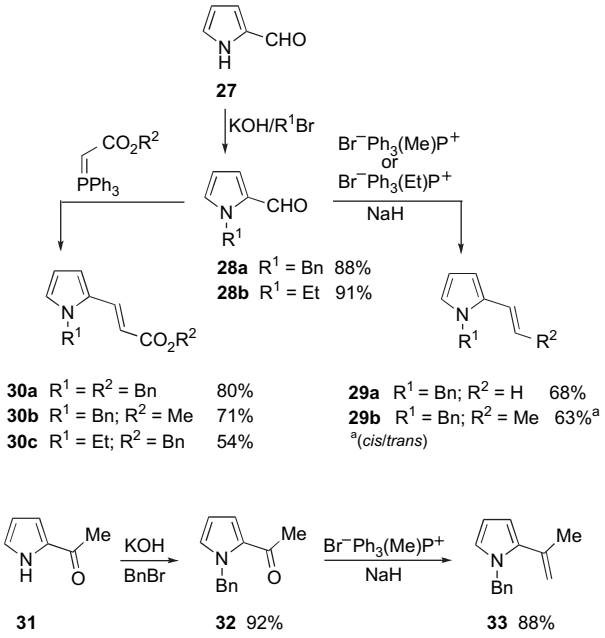
Scheme 6.

The rearrangement of vinylpyrroles to give functionalised allylpyrroles can be explained by a sequence of sigmatropic shifts as shown in Scheme 7. Overall the rearrangement can be regarded as a formal insertion of the R^2CH group in the C–C σ bond involving the pyrrole C-2 carbon and the carbon of the vinylic group.



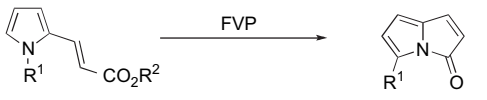
Scheme 7.

We decided to evaluate the possibility of using simple *N*-substituted 2-vinyl-1*H*-pyrroles (**29**, **30** and **33**) for carrying out this rearrangement of 2-vinylpyrroles to 2-allyl-1*H*-pyrroles (Scheme 8). *N*-Benzyl- (**28a**[7a–c]) and *N*-ethylpyrrole-2-carbaldehyde (**28b**[7c,d]) were obtained in high yield from pyrrole-2-carbaldehyde **27** following a known general synthetic procedure.[7a] The Wittig reaction of *N*-benzylpyrrole-2-carbaldehyde **28a** with the phosphorus ylides generated in situ from ethyl- or methyl-triphenylphosphonium bromide in the presence of sodium hydride afforded the 2-vinyl-1*H*-pyrroles **29**.[8a] The reaction of **28a** with triphenylphosphoranylideneacetates gave the corresponding *N*-substituted-pyrrol-2-ylpropenoates **30**.[8b] *N*-Benzyl-2-isopropenyl-1*H*-pyrrole **33** was prepared from 2-acetylpyrrole (**31**) via N-alkylation with benzylbromide followed by the appropriated Wittig reaction.[8c,d]



Scheme 8.

Flash vacuum pyrolysis of *N*-substituted-pyrrol-2-ylpropenoates **30** led to the synthesis of products with an intense red colour typical of pyrrolizinone derivatives (Scheme 9 and Table 2). The same product (**34a**) was obtained in yields ranging from 19 to 21% starting either from 1*H*-pyrrole **30a** or 1*H*-pyrrole **30b**. From the reaction of *N*-ethyl-pyrrol-2-ylpropenoate **30c**, 5-ethyl-3*H*-pyrrolizin-3-one **34b** was obtained in 21% yield.



Scheme 9.

^1H NMR and ^{13}C NMR data of pyrrolizinone **34b** are collected in Table 3. The assignment was supported by two-dimensional COSY, HMQC and HMBC spectra (400 MHz). In the ^{13}C NMR spectrum two quaternary carbons are observed at 136.1 and 141.2 ppm besides the signal at 166.9 ppm corresponding to the carbon of the carbonyl group. In the HMBC spectrum the carbon with the chemical shift 136.1 ppm shows connectivity with H-1, H-2, H-6 and H-7. Thus, this signal was assigned to carbon C-7a. The second quaternary carbon shows connectivity with H-6, H-7, H-8 and H-9 corresponding to carbon C-5. Therefore, the pyrrolizin-3-one must have the ethyl substituent at C-5.

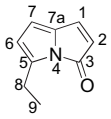
The thermal rearrangement of 1-arylpyrroles to 2-arylpyrroles by sequential [1,5] shifts is known.[9] In fact, under FVP (1000 °C, 0.01 Torr) 1-phenylpyrrole rearranges to 2- and 3-phenylpyrrole.[9a]

Table 2
FVP of compounds **30**

Reagents	Conditions	Products	Yield (%)
30a	600 °C, 2×10^{-2} mbar	**30a**	—[a]
30a	700 °C, 2.7×10^{-2} mbar	**34a**	21
30a	800 °C, 4.0×10^{-2} mbar	**34a**	19
30b	700 °C, 2.0×10^{-2} mbar	**34a**	20
30c	700 °C, 2.0×10^{-2} mbar	**30c**	—[a]
30c	750 °C, 2.0×10^{-2} mbar	**34b**	21
30c	800 °C, 2.0×10^{-2} mbar	**34b**	9

[a] Sublimation of the starting material.

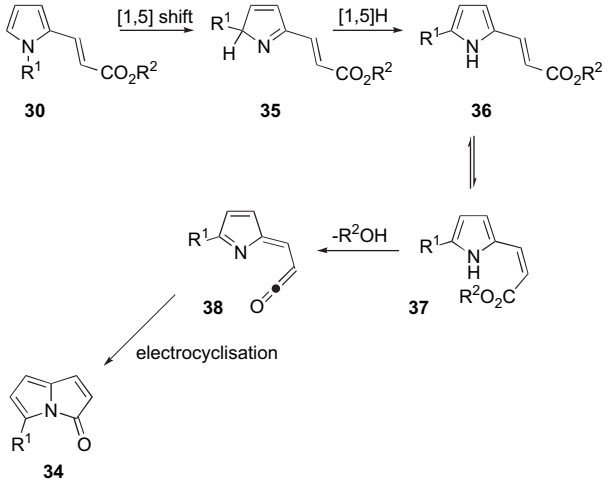
Table 3
^{1}H NMR and ^{13}C NMR data for pyrrolo[1,2-*c*]pyrimidine **34b**



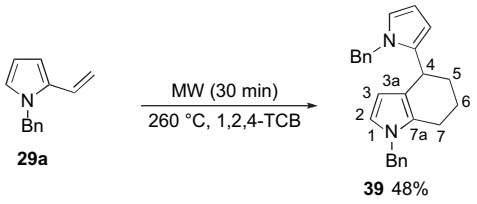
C	^{1}H NMR	^{13}C NMR
C-8	1.23 (3H, t, *J*=7.5 Hz, Et)	11.5
C-9	2.70 (2H, q, *J*=7.5 Hz, Et)	20.0
C-2	5.61 (1H, d, *J*=5.7 Hz)	120.9
C-6	5.67–5.69 (1H, m)	111.4
C-7	5.91 (1H, d, *J*=3.0 Hz)	112.1
C-7a	—	136.1
C-1	7.04 (1H, d, *J*=5.7 Hz)	137.9
C-5	—	141.2
C-3	—	166.9

On the other hand, benzannelated pyrrolizin-3-ones have been prepared from the FVP (925 °C, 0.001 Torr) of 1-(2-methoxycarbonylphenyl)pyrrole by a cascade process involving rate determining 1,5-aryl migration, elimination of methanol and electrocyclization of the ketene intermediate.[9b] MacNab et al. also described that methyl 3-(1-phenylpyrrol-2-yl)propenoate undergoes a 1,5-sigmatropic shift of the phenyl group regiospecifically to the 5-position followed by the conversion into 5-phenylpyrrolizin-3-one in 38% yield.[9c]

The synthesis of pyrrolizin-3-ones **34** can also be explained by the initial rearrangement of 1-substituted pyrroles **30** to 5-substituted derivatives **35** via regiospecific benzyl (R^1=Bn) or ethyl (R^1=Et) 1,5-sigmatropic shift to the 5-position. These compounds undergo concerted elimination of alcohol (methanol or benzyl alcohol) giving pyrrol-2-ylideneketene **38** followed by electrocyclisation to the pyrrolizin-3-ones. Therefore, the synthesis of pyrrolizin-3-ones **34** demonstrate that this cascade process is not



Scheme 10.



Scheme 11.

limited to 3-(1-phenylpyrrol-2-yl)propenoates, and *N*-ethyl and *N*-benzyl derivatives undergo a similar conversion to the corresponding pyrrolizin-3-ones (Scheme 10).

Attempts to carry out the FVP of pyrroles **29a**, **29b** and **33** did not lead to isolable products. Under microwave irradiation, although a similar result was obtained from **29b** and **33**, the reaction of **29a** led to an interesting outcome. In fact, microwave irradiation of 1-benzyl-2-vinyl-1*H*-pyrrole **29a** in 1,2,4-trichlorobenzene for 30 min afforded 4-(1-benzyl-1*H*-pyrrol-2-yl)-4,5,6,7-tetrahydro-1*H*-indole **39** in 48% yield. This heterocycle is the result of a Diels–Alder reaction where 1*H*-pyrrole **29a** acts both as a diene and as a dienophile (Scheme 11).

The structural assignment of 1*H*-pyrrole **39** was supported by two-dimensional COSY, HMQC and HMBC spectra (400 MHz). In the COSY spectrum, H-4 (3.93–3.95 ppm) shows connectivity with protons H-5 (1.57–1.68 ppm), these protons show connectivity with H-6 (1.85–1.91 ppm) and finally protons H-6 are correlated with protons H-7 (2.39–2.42 ppm).

3. Conclusion

In this report we have presented new examples of the rearrangement of 2-vinyl-1*H*-pyrroles to 2-allyl-1*H*-pyrroles. The studied compounds are penta-substituted 1*H*-pyrroles formed by the sigmatropic [1,8]-H shifts of 7,7-dimethyl-azafulvenium methides and 7-methyl-azafulvenium methides, derived from 1,1-dimethyl-2,2-dioxo-1*H*,3*H*-pyrrolo[1,2-*c*]thiazoles and 1-methyl-2,2-dioxo-1*H*,3*H*-pyrrolo[1,2-*c*]thiazoles, respectively. The structural requirement that allows the rearrangement of the penta-substituted pyrroles into 2-allyl-1*H*-pyrroles is the presence of a group of the type $-CH_2R$ (with R=Ph or Me) at N-1. We could conclude that 2-isopropenyl-1*H*-pyrroles require the presence of an aryl substituent at C-5 or a benzyl group at N-1 in order to rearrange to the corresponding 2-allyl-1*H*-pyrroles. This is not the case for the 2-ethenyl-1*H*-pyrroles, although the presence of a phenyl group at C-5 allows the selective synthesis of the corresponding 2-allyl-1*H*-pyrrole. It was also demonstrated that the presence of two carboxylate groups in the starting pyrrole (at C-4 and C5) is not a requirement for carrying out the rearrangement since 1-ethyl-2-(4-fluorophenyl)-5-isopropenyl-4-phenyl-1*H*-pyrrole-3-carboxylate is converted into the corresponding 2-(4-fluorophenyl)-5-(3-methylbut-3-en-2-yl)-4-phenyl-1*H*-pyrrole-3-carboxylate.

No evidence for the rearrangement of 2-vinyl-1*H*-pyrroles to 2-allyl-1*H*-pyrroles starting with di-substituted pyrroles, *N*-benzyl or *N*-ethyl-2-vinyl-1*H*-pyrroles. However, under FVP *N*-benzyl-pyrrol-2-ylpropenoates are converted into 3*H*-pyrrolizin-3-ones. On the other hand, microwave-assisted reaction of 1-benzyl-2-vinyl-1*H*-pyrrole gave the corresponding Diels–Alder cycloadduct, the 4-(1-benzyl-1*H*-pyrrol-2-yl)-4,5,6,7-tetrahydro-1*H*-indole.

4. Experimental

4.1. General

^{1}H NMR spectra were recorded on an instrument operating at 300 MHz or at 400 MHz. ^{13}C NMR spectra were recorded on an

instrument operating at 75.5 MHz or at 100 MHz. The solvent is deuteriochloroform except where indicated otherwise; chemical shifts are expressed in parts per million related to internal TMS, and coupling constants (*J*) are in hertz. Microanalyses were performed using an EA 1108-HNS-O Fisons instrument. Mass spectra were recorded under electron impact (EI) at 70 eV. Thiazolidines **5**[3] and **11**[3] and 2,2-dioxo-1*H*,3*H*-pyrrolo[1,2-*c*]thiazole-6,7-dicarboxylates **15a**[1b] and **15b**[1b] were prepared following procedures described in the literature.

4.2. General procedure for the synthesis of 1*H*,3*H*-pyrrolo-[1,2-*c*]thiazoles

The appropriate 1,3-thiazolidine-4-carboxylic acid (5 mmol), dimethyl acetylene dicarboxylate or phenyl propiolate (0.9 mL, 7.5 mmol) and acetic anhydride (20 mL) were heated at 110–120 °C for 4 h. The reaction mixture was cooled to room temperature and was diluted with CH_2Cl_2 (50 mL). The organic phase was washed with a saturated aqueous solution of $NaHCO_3$ and water, dried ($MgSO_4$) and the solvent evaporated off. The crude product was purified by flash chromatography [hexane/ethyl acetate].

4.2.1. Dimethyl 1,1,3-trimethyl-5-(4-fluorophenyl)-1H,3H-pyrrolo[1,2-c]thiazole-6,7-dicarboxylate ***7a***

Compound **7a** was purified by flash chromatography [ethyl acetate/hexane (1:4)] and obtained as a white solid (1.8 g, 93%), mp 134.3–135.7 °C (from ethyl acetate/hexane). IR (KBr) 1710 cm^{-1}; ^1H NMR (300 MHz) 1.27 (3H, d, *J*=6.2), 1.89 (3H, s), 1.94 (3H, s), 3.69 (3H, s), 3.82 (3H, s), 5.55 (1H, q, *J*=6.2), 7.09–7.16 (2H, m, Ar-H), 7.39–7.44 (2H, m, Ar-H); ^{13}C NMR (75.5 MHz) 25.9, 30.1, 32.3, 51.5, 51.9, 52.2, 58.6, 105.7, 115.8 (d, *J*=21.5), 120.3, 125.9, 126.0, 127.9, 131.3, 131.4, 146.6, 162.8 (d, *J*=247.9), 164.1, 165.6; MS (EI) *m*/*z* 377 (M^+, 51%), 362 (27), 330 (100), 285 (65), 254 (26) and 227 (10); HRMS (EI) *m*/*z* 377.1096 ($C_{19}H_{20}FNO_4S$ [M^+], 377.1097).

4.2.2. Dimethyl 1,1,3-trimethyl-5-phenyl-1H,3H-pyrrolo-[1,2-c]thiazole-6,7-dicarboxylate ***7b***

Compound **7b** was purified by crystallization with diethyl ether/hexane and obtained as a white solid (5.67 g, 97%), mp 91.3–92.8 °C (from diethyl ether/hexane). IR (KBr) 1717, 1441, 1242, 1201, 1170 cm^{-1}; ^1H NMR (300 MHz) 1.25 (3H, d, *J*=6.3), 1.90 (3H, s), 1.95 (3H, s), 3.69 (3H, s), 3.82 (3H, s), 5.61 (1H, q, *J*=6.3), 7.42–7.43 (5H, m, Ar-H); ^{13}C NMR (75.5 MHz) 26.0, 30.0, 32.3, 51.5, 51.9, 52.2, 58.7, 105.6, 120.2, 128.6, 128.7, 128.8, 129.2, 129.9, 146.7, 164.0, 165.8; MS (EI) *m*/*z* 359 (M^+, 46%), 344 (30), 312 (100), 267 (38) and 236 (20). Anal. Calcd for $C_{19}H_{21}NO_4S$: C, 63.49; H, 5.89; N, 3.90. Found: C, 63.26; H, 5.57; N, 3.68.

4.2.3. Ethyl 1,1,3-trimethyl-5-(4-fluorophenyl)-7-phenyl-1H,3H-pyrrolo[1,2-c]thiazole-6-carboxylate ***9***

Compound **9** was purified by flash chromatography [ethyl acetate/hexane (1:6), ethyl acetate/hexane (1:7) and then ethyl acetate/hexane (1:8)] and obtained as oil (1.37 g, 67%). IR (KBr) 1706 cm^{-1}; ^1H NMR (300 MHz) 0.74 (3H, t, *J*=7.1), 1.35 (3H, d, *J*=6.2), 1.49 (3H, s), 1.69 (3H, s), 3.82 (2H, q, *J*=7.1), 5.51 (1H, q, *J*=6.2), 7.10–7.16 (2H, m, Ar-H), 7.25–7.34 (5H, m, Ar-H); ^{13}C NMR (75.5 MHz) 13.9, 26.2, 31.8, 34.6, 51.3, 58.2, 59.5, 115.7 (d, *J*=21.5), 117.7, 118.1, 127.1, 127.8, 128.3, 128.4, 130.8, 131.2, 132.4, 132.5, 135.5, 139.9, 163.1 (d, *J*=246.6), 164.9; MS (EI) *m*/*z* 409 (M^+, 47%), 394 (100), 302 (16), 276 (10) and 261 (11); HRMS (EI) *m*/*z* 409.15109 ($C_{24}H_{24}FNO_2S$ [M^+], 409.15117).

4.2.4. Dimethyl 1,1-dimethyl-5-phenyl-1H,3H-pyrrolo-[1,2-c]thiazole-6,7-dicarboxylate ***13***

Compound **13** was purified by crystallization with ethyl acetate/hexane and obtained as a white solid (2.83 g, 88%), mp 104.5–105.6 °C (from ethyl acetate/hexane). IR (KBr) 1736, 1698, 1440, 1168, 1089 cm^{-1}; ^1H NMR (300 MHz) 1.90 (6H, s), 3.71 (3H, s), 3.82 (3H, s), 4.93 (2H, s), 7.42–7.43 (5H, m, Ar-H); ^{13}C NMR (100 MHz) 29.6, 47.3, 51.6, 52.0, 52.9, 106.2, 119.0, 128.5, 128.8, 129.4, 129.6, 146.6, 164.1, 165.7.

4.3. General procedure for the synthesis of 2,2-dioxo-1*H*,3*H*-pyrrolo[1,2-*c*]thiazoles

To a stirred ice-cold solution of the appropriate 1*H*,3*H*-pyrrolo[1,2-*c*]thiazole-6,7-dicarboxylate (1.0 mmol) in dry dichloromethane (7 mL) was added portionwise 3-chloroperoxybenzoic acid (3.0 mmol) under N_2 atmosphere. The cooling bath was removed and the reaction mixture was allowed to warm to room temperature. After stirring at room temperature for 3 h, the reaction mixture was washed twice with 10% (w/v) aqueous sodium bisulfite solution (2×20 mL) and twice with 10% (w/v) aqueous sodium bicarbonate solution (2×20 mL). The organic fraction was then dried over anhydrous $MgSO_4$ and the solvent evaporated off. The crude product was purified by flash chromatography [hexane/ethyl acetate].

4.3.1. Dimethyl 1,1,3-trimethyl-2,2-dioxo-5-(4-fluorophenyl)-1H,3H-pyrrolo[1,2-c]thiazole-6,7-dicarboxylate ***8a***

Compound **8a** was purified by flash chromatography [ethyl acetate/hexane (1:2)] and obtained as a white solid (0.39 g, 97%), mp 121.9–123.2 °C (from ethyl acetate/hexane). IR (KBr) 1734, 1699, 1327, 1162 cm^{-1}; ^1H NMR (300 MHz) 1.32 (3H, d, *J*=6.8), 1.83 (3H, s), 1.87 (3H, s), 3.69 (3H, s), 3.87 (3H, s), 5.02 (1H, q, *J*=6.8), 7.14–7.19 (2H, m, Ar-H), 7.37–7.41 (2H, m, Ar-H); ^{13}C NMR (75.5 MHz) 17.4, 20.7, 23.5, 51.9, 52.1, 61.4, 69.4, 11.3, 116.1 (d, *J*=21.6), 118.4, 124.8, 124.9, 131.4, 131.5, 131.6, 136.9, 163.3 (d, *J*=249.2), 163.5, 164.8; MS (EI) *m*/*z* 409 (M^+, 22%), 378 (18), 345 (68), 314 (55), 298 (51), 227 (100) and 212 (26). Anal. Calcd for $C_{19}H_{20}FNO_6S$: C, 55.74; H, 4.92; N, 3.42%. Found: C, 55.62; H, 4.92; N, 3.64%.

4.3.2. Dimethyl 1,1,3-trimethyl-2,2-dioxo-5-phenyl-1H,3H-pyrrolo[1,2-c]thiazole-6,7-dicarboxylate ***8b***

This was prepared in the same manner described above, except that 4 equiv of 3-chloroperoxybenzoic acid were used and the reaction was carried at room temperature for 6 h. Compound **8b** was purified by flash chromatography [ethyl acetate/hexane (1:2)] and obtained as a white solid (1.92 g, 51%), mp 148.6–150.0 °C (from diethyl ether). IR (KBr) 1720, 1439, 1321, 1259, 1207, 1169 cm^{-1}; ^1H NMR (300 MHz) 1.29 (3H, d, *J*=6.7), 1.83 (3H, s), 1.87 (3H, s), 3.69 (3H, s), 3.86 (3H, s), 5.09 (1H, q, *J*=6.7), 7.37–7.48 (5H, m, Ar-H); ^{13}C NMR (75.5 MHz) 13.4, 20.6, 23.5, 51.9, 52.1, 61.4, 69.5, 111.1, 118.2, 128.9, 129.4, 129.5, 130.2, 133.7, 136.9, 163.6, 165.1; MS (EI) *m*/*z* 391 (M^+, 33%), 360 (26), 327 (100), 295 (79), 280 (54) and 209 (94). Anal. Calcd for $C_{19}H_{21}NO_6S$: C, 58.39; H, 5.41; N, 3.58. Found: C, 57.91; H, 5.02; N, 3.29.

4.3.3. Ethyl 1,1,3-trimethyl-2,2-dioxo-5-(4-fluorophenyl)-7-phenyl-1H,3H-pyrrolo[1,2-c]thiazole-6-carboxylate ***10***

Compound **10** was purified by flash chromatography [ethyl acetate/hexane (1:6) and ethyl acetate/hexane (1:4)] and obtained as a white solid (0.27 g, 61%), mp 139.6–142.3 °C (from ethyl acetate/hexane). IR (KBr) 1703, 1318, 1180 cm^{-1}; ^1H NMR (300 MHz) 0.76 (3H, t, *J*=7.1), 1.40 (3H, d, *J*=6.7), 1.46 (3H, s), 1.58 (3H, s), 3.84–3.87 (2H, m), 5.01 (1H, q, *J*=6.7), 7.14–7.26 (2H, m, Ar-H), 7.30–7.46 (7H, m, Ar-H); ^{13}C NMR (75.5 MHz) 13.4, 17.2, 22.1, 25.0, 59.6, 60.4, 69.2, 115.6 (d, *J*=21.6), 116.3, 122.4, 126.8, 126.9, 127.3, 127.7, 129.8, 130.5, 132.0, 132.1, 133.7, 133.9, 163.1 (d, *J*=248.1), 163.8; MS (EI) *m*/*z* 441 (M^+, 16%), 377 (54), 330 (94), 316 (100), 289 (28), 275 (21) and 261 (14). Anal. Calcd for $C_{24}H_{24}FNO_4S$: C, 65.29; H, 5.48; N, 3.17%. Found: C, 65.23; H, 5.53; N, 3.39%.

4.3.4. Dimethyl 1,1-dimethyl-2,2-dioxo-5-phenyl-1H,3H-pyrrolo[1,2-c]thiazole-6,7-dicarboxylate ***14***

Compound **14** was purified by crystallization with diethyl ether and obtained as a white solid (2.03 g, 75%), mp 152.9–154.8 °C (from diethyl ether). IR (KBr) 1735, 1708, 1441, 1327, 1167, 1114, 1087 cm^{-1}; ^1H NMR (400 MHz) 1.83 (6H, s), 3.72 (3H, s), 3.87 (3H, s), 4.82 (2H, s), 7.39–7.41 (2H, m, Ar-H), 7.45–7.46 (3H, m, Ar-H); ^{13}C NMR (100 MHz) 20.8, 52.0, 52.2, 61.3, 62.6, 112.3, 117.1, 128.6, 128.8, 129.4, 129.6, 133.1, 137.2, 163.6, 165.0.

4.4. General procedure for the alkylation of 2,2-dioxo-pyrrolo[1,2-*c*]thiazole-2,2-dioxides 15a and 15b

LiHMDS (11.0 mL, 1.0 M in hexanes, 11.0 mmol) was slowly added to a solution of the 2,2-dioxo-1*H*,3*H*-pyrrolo[1,2-*c*][1,3]thiazole-2,2-dioxide (11.0 mmol) in anhydrous THF (230 mL) at −78 °C and the mixture stirred for 1 h. A solution of iodomethane (6.9 mL, 2.0 M, 13.8 mmol, 1.25 equiv) was added slowly and the reaction mixture stirred for 1 h. The reaction mixture was then allowed to warm to room temperature and quenched with saturated aqueous ammonium chloride solution (640 mL). The organic phase was extracted with ethyl acetate, washed with water and brine (50 mL), and dried over anhydrous Na_2SO_4. The solvent was removed in vacuo and the crude was purified by flash chromatography [hexane/ethyl acetate].

4.4.1. Dimethyl 3-benzyl-1,5-dimethyl-2,2-dioxo-1H,3H-pyrrolo[1,2-c]thiazole-6,7-dicarboxylate ***16a***

Compound **16a** was obtained as a white solid (348 mg, 66%), mp 109.2–110.4 °C (from diethyl ether). IR (KBr) 1740, 1706, 1456, 1332, 1308, 1130, 1091 cm^{-1}; ^1H NMR (300 MHz) 1.42 (3H, d, *J*=7.3), 1.94 (3H, s), 3.10 (1H, dd, *J*=7.0 and 14.8), 3.63 (1H, dd, *J*=5.3 and 14.8), 3.82 (3H, s), 3.85 (3H, s), 4.54 (1H, q, *J*=7.3), 5.07 (1H, dd, *J*=5.3 and 7.0), 7.06–7.09 (2H, m, Ar-H), 7.30–7.32 (3H, m, Ar-H); ^{13}C NMR (75.5 MHz) 11.1, 16.6, 39.1, 51.7, 51.8, 57.7, 73.3, 112.0, 115.9, 128.1, 129.2, 129.8, 133.0, 133.1, 133.2, 163.1, 169.4; MS (EI) *m*/*z* 391 (M^+, 28%), 327 (50), 295 (100), 209 (31), 191 (26) and 104 (33). HRMS (EI) *m*/*z* 391.1090 ($C_{19}H_{21}NO_6S$ [M^+], 391.1090).

4.4.2. Dimethyl 1,3-dimethyl-2,2-dioxo-5-phenyl-1H,3H-pyrrolo[1,2-c]thiazole-6,7-dicarboxylate ***16b***

Compound **16b** was obtained as a white solid (1.00 g, 24%), mp 171.2–173.1 °C (from diethyl ether). IR (KBr) 1724, 1704, 1443, 1327, 1249, 1215, 1178, 1138 cm^{-1}; *Minor isomer*: ^1H NMR (300 MHz) 1.25 (3H, d, *J*=6.5), 1.79 (3H, d, *J*=7.1), 3.72 (3H, s), 3.83 (3H, s), 4.63 (1H, q, *J*=7.1), 5.04 (1H, q, *J*=6.5), 7.39–7.48 (5H, m, Ar-H). *Major isomer*: ^1H NMR (300 MHz) 1.36 (3H, d, *J*=7.0), 1.74 (3H, d, *J*=7.4), 3.71 (3H, s), 3.82 (3H, s), 4.71 (1H, q, *J*=7.4), 5.04 (1H, q, *J*=7.0), 7.39–7.48 (5H, m, Ar-H); ^{13}C NMR (75.5 MHz) 14.1, 14.2, 51.9, 52.2, 55.6, 69.5, 111.5, 118.1, 128.8, 128.9, 129.3, 129.5, 133.0, 133.7, 163.1, 165.0. MS (EI) *m*/*z* 377 (M^+, 18%), 313 (100), 280 (67) and 195 (41); HRMS (EI) *m*/*z* 377.0932 ($C_{18}H_{19}NO_6S$ [M^+], 377.0933).

4.5. General procedure for the flash vacuum pyrolysis of 1*H*,3*H*-pyrrolo[1,2-*c*]thiazole-2,2-dioxides

Pyrolysis of the appropriate 1*H*,3*H*-pyrrolo[1,2-*c*]thiazole-2,2-dioxide (0.30–0.90 mmol) or vinyl-1*H*-pyrrole (0.20–0.35 mmol) at 500–700 °C/2×10^{-2} to 5×10^{-2} mbar onto a surface cooled at −196 °C over a period of 0.7–1 h gave a yellowish pyrolysate [the rate of volatilisation of the starting material was controlled by the use of a Kugelrohr oven, which heated the sample at 100–250 °C]. After cooling to room temperature the pyrolysate was removed from the cold finger with dichloromethane and the solvent was removed in vacuo.

4.5.1. Dimethyl 1-ethyl-2-(4-fluorophenyl)-5-isopropenyl-1H-pyrrole-3,4-dicarboxylate ***18a*** *and dimethyl 2-(4-fluorophenyl)-5-(3-methylbut-3-en-2-yl)-1H-pyrrole-3,4-dicarboxylate* ***19a*** *from* ***8a*** *[600 °C/3.5×10^−2 mbar]*

The crude product was purified by flash chromatography [ethyl acetate/hexane (1:2)] to give a mixture of compounds **18a** and **19a** (ratio 57:43) as an oil (0.10 g, 81%). IR (film) 1725, 1643 cm^{-1}. *Major component*: ^1H NMR (300 MHz) 1.00 (3H, t, *J*=7.2), 2.11 (3H, s), 3.80 (3H, s), 3.86 (3H, s), 5.13 (1H, t, *J*=1.5), 5.47 (1H, dd, *J*=1.5), 7.10–7.16 (2H, m, Ar-H), 7.39–7.46 (2H, m, Ar-H). *Minor component*: ^1H NMR (300 MHz) 1.40 (3H, d, *J*=7.1), 1.73 (3H, s), 3.78 (3H, s), 3.79 (3H, s), 4.11 (1H, q, *J*=7.1), 5.01 (1H, app. s), 5.04 (1H, app. d, *J*=1.0), 7.10–7.16 (2H, m, Ar-H), 7.39–7.46 (2H, m, Ar-H), 8.17 (1H, br s). *Major component*: MS (EI) *m*/*z* 345 (M^+, 88%), 314 (86), 298 (60), 227 (100), 212 (28). *Minor component*: MS (EI) *m*/*z* 345 (M^+, 31%), 313 (100), 298 (42), 282 (30), 254 (29).

4.5.2. Dimethyl 1-ethyl-2-isopropenyl-5-phenyl-1H-pyrrole-3,4-dicarboxylate ***18b*** *and dimethyl 2-(1,2-dimethyl-allyl)-5-phenyl-1H-pyrrole-3,4-dicarboxylate* ***19b*** *from* ***8b*** *[600 °C/2.0×10^−2 mbar]*

The crude product was purified by flash chromatography [ethyl acetate/hexane (1:2)] to give a mixture of compounds **18b** and **19b** (ratio 62:38) as an oil (102 mg, 75%). IR (film) 3302, 2949, 1712, 1443, 1212, 766, 700 cm^{-1}. *Major component*: ^1H NMR (300 MHz) 1.00 (3H, t, *J*=7.1), 2.12 (3H, br s), 3.62 (3H, s), 3.80 (3H, s), 3.78–3.86 (2H, m), 5.13–5.14 (1H, m), 5.47–5.49 (1H, m), 7.38–7.44 (5H, m, Ar-H). *Minor component*: ^1H NMR (300 MHz) 1.40 (3H, d, *J*=7.1), 1.73 (3H, br s), 3.81 (3H, s), 3.84 (3H, s), 4.22 (1H, q, *J*=7.1), 5.01–5.02 (1H, m), 5.03–5.04 (1H, m), 7.38–7.44 (5H, m, Ar-H), 8.21 (1H, br s). *Major component*: MS (EI) *m*/*z* 327 (M^+, 29%), 295 (100), 280 (39), 264 (28) and 236 (24). *Minor component*: MS (EI) *m*/*z* 327 (M^+, 100%), 296 (94), 280 (43), 236 (21) and 209 (84); HRMS (EI) *m*/*z* 327.1471 ($C_{19}H_{21}NO_4$ [M^+], 327.1471).

4.5.3. Ethyl 1-ethyl-2-(4-fluorophenyl)-5-isopropenyl-4-phenyl-1H-pyrrole-3-carboxylate ***20*** *and ethyl 2-(4-fluorophenyl)-5-(3-methylbut-3-en-2-yl)-4-phenyl-1H-pyrrole-3-carboxylate* ***21*** *from* ***10*** *[600 °C/3.5×10^−2 mbar]*

The crude product was purified by preparative thin chromatography [ethyl acetate/hexane (1:1)] to give, in order of elution, ethyl 1-ethyl-2-(4-fluorophenyl)-5-isopropenyl-4-phenyl-1*H*-pyrrole-3-carboxylate **20** (35 mg, 40%) and ethyl 5-(1,2-dimethylprop-2-en-1-yl)-2-(4-fluorophenyl)-4-phenyl-1*H*-pyrrole-3-carboxylate **21** (20 mg, 23%), both as solids. *Ethyl 1-ethyl-2-(4-fluorophenyl)-5-isopropenyl-4-phenyl-1H-pyrrole-3-carboxylate* ***20***. Mp 118.8–121.3 °C (from ethyl acetate/hexane). IR (KBr) 1700 cm^{-1}; ^1H NMR (300 MHz) 0.79 (3H, t, *J*=7.1), 1.04 (3H, t, *J*=7.1), 1.76 (3H, s), 3.81–3.88 (4H, m), 5.11 (1H, d, *J*=0.81), 5.38 (1H, t, *J*=1.6), 7.11–7.17 (2H, m, Ar-H), 7.27–7.43 (7H, m, Ar-H); ^{13}C NMR (75.5 MHz) 13.5, 16.7, 24.1, 39.6, 59.16, 112.9, 115.0 (d, *J*=21.4), 120.8, 122.8, 126.1, 127.2, 128.7, 128.8, 130.1, 132.4, 132.5, 132.7, 135.7, 136.2, 136.5, 162.6 (d, *J*=246.1), 164.9; MS (EI) *m*/*z* 377 (M^+, 77%), 330 (100), 316 (100), 304 (54), 289 (32), 275 (27) and 261 (16); HRMS (EI) *m*/*z* 377.1791 ($C_{24}H_{24}FNO_2$ [M^+], 377.1791). *Ethyl 2-(4-fluorophenyl)-5-(3-methylbut-3-en-2-yl)-4-phenyl-1H-pyrrole-3-carboxylate* ***21***. Mp 106.1–108.0 °C (from ethyl acetate/hexane). IR (KBr) 1675 cm^{-1}; ^1H NMR 0.88 (3H, t, *J*=7.1), 1.31 (3H, d, *J*=7.1), 1.66 (3H, s), 3.40 (1H, q), 3.96 (2H, q, *J*=7.1), 4.91 (2H, dd, *J*=3.0 and 1.2), 7.07–7.13 (2H, m, Ar-H), 7.26–7.39 (5H, m, Ar-H), 7.52–7.56 (2H, m, Ar-H), 7.92 (1H, sl, –NH); ^{13}C NMR 13.6, 19.5, 22.5, 36.7, 59.5, 110.3, 111.9, 115.2 (d, *J*=21.4), 123.9, 126.4, 127.6, 128.6, 130.2, 130.6, 130.7, 132.3, 134.1, 135.7, 147.9, 162.6 (d, *J*=246.2), 165.3; MS (EI) *m*/*z* 377 (M^+, 100%), 362 (40), 336 (18), 316 (58), 288 (18), 274 (13) and 262 (12); HRMS (EI) *m*/*z* 377.1795 ($C_{24}H_{24}FNO_2$ [M^+], 377.1791).

*4.5.4. Dimethyl 5-isopropenyl-1-methyl-2-phenyl-1H-pyrrole-3,4-dicarboxylate **22** from **14** [600 °C/2.0×10^{-2} mbar]*

Compound **22** was obtained as a white solid (129 mg, 95%), mp 75.0–76.8 °C (from diethyl ether/hexane). IR (KBr) 2951, 1713, 1218, 1194, 1171 cm^{-1}; ^{1}H NMR (300 MHz) 2.09 (3H, s), 3.33 (3H, s), 3.65 (3H, s), 3.80 (3H, s), 5.12–5.13 (1H, m), 5.48–5.49 (1H, m), 7.36–7.44 (5H, m, Ar-H); ^{13}C NMR (100 MHz) 23.5, 32.6, 51.6, 51.7, 112.3, 114.0, 120.4, 127.2, 128.2, 128.7, 130.4, 130.6, 135.9, 138.8, 165.3, 165.7.

*4.5.5. Dimethyl 2-ethyl-5-methyl-1-styryl-1H-pyrrole-3,4-dicarboxylate **23** and dimethyl 2-methyl-1-phenylethyl-5-vinyl-1H-pyrrole-3,4-dicarboxylate **24** from **16a** [600 °C/2.0×10^{-2} mbar]*

The crude product was purified by flash chromatography [ethyl acetate/hexane (1:3), then ethyl acetate/hexane (1:2)] to give, in order of elution, dimethyl 2-ethyl-5-methyl-1-styryl-1*H*-pyrrole-3,4-dicarboxylate **23** (9 mg, 6%) as a white solid and dimethyl 2-methyl-1-phenylethyl-5-vinyl-1*H*-pyrrole-3,4-dicarboxylate **24** (11 mg, 7%) as an oil. *Dimethyl 2-ethyl-5-methyl-1-styryl-1H-pyrrole-3,4-dicarboxylate **23***. Mp 114.8–116.6 °C (from diethyl ether). IR (KBr) 2943, 1690, 1548, 1440, 1218 cm^{-1}; ^{1}H NMR (300 MHz) 1.16 (3H, t, *J*=7.5), 2.40 (3H, s), 2.83 (2H, q, *J*=7.5), 3.82 (6H, s), 6.66 (1H, d, *J*=14.3), 7.00 (1H, d, *J*=14.3), 7.36–7.48 (5H, m, Ar-H); ^{13}C NMR (75.5 MHz) 12.2, 14.1, 18.9, 51.5, 112.0, 113.0, 122.0, 126.7, 129.0, 132.2, 133.7, 133.8, 139.8, 165.8, 165.9; MS (EI) *m*/*z* 327 (M$^+$, 56%), 295 (100), 280 (91), 263 (59), 209 (43) and 77 (22); HRMS (EI) *m*/*z* 327.1472 ($C_{19}H_{21}NO_4$ [M$^+$], 327.1471). *Dimethyl 2-methyl-1-phenylethyl-5-vinyl-1H-pyrrole-3,4-dicarboxylate **24***. IR (film) 2949, 1705, 1443, 1218, 1162 cm^{-1}; ^{1}H NMR (300 MHz) 2.29 (3H, s), 2.88–2.93 (2H, m), 3.78 (3H, s), 3.84 (3H, s), 4.04–4.09 (2H, m), 5.38 (1H, dd, *J*=1.1 and 11.7), 5.61 (1H, dd, *J*=1.1 and 17.6), 6.55 (1H, dd, *J*=11.7 and 17.6), 7.06–7.09 (2H, m, Ar-H), 7.25–7.30 (3H, m, Ar-H); ^{13}C NMR (75.5 MHz) 10.8, 36.7, 45.6, 51.3, 52.1, 111.3, 115.1, 118.9, 124.1, 127.1, 128.7, 128.8, 130.3, 135.6, 137.2, 165.0, 167.2; MS (EI) *m*/*z* 327 (M$^+$, 100%), 295 (100), 236 (27), 209 (55), 191 (58) and 104 (75); HRMS (EI) *m*/*z* 327.1469 ($C_{19}H_{21}NO_4$ [M$^+$], 327.1471).

*4.5.6. Dimethyl 2-ethyl-5-phenyl-1-vinyl-1H-pyrrole-3,4-dicarboxylate **25** and dimethyl 2-(1-methyl-allyl)-5-phenyl-1H-pyrrole-3,4-dicarboxylate **26** from **16b** [600 °C/4.0×10^{-2} mbar]*

The crude product was purified by preparative thin layer chromatography [ethyl acetate/hexane (1:1)] to give, in order of elution, dimethyl 2-ethyl-5-phenyl-1-vinyl-1*H*-pyrrole-3,4-dicarboxylate **25** (7 mg, 4%) and dimethyl 2-(1-methyl-allyl)-5-phenyl-1*H*-pyrrole-3,4-dicarboxylate **26** (51 mg, 32%), both as oils. *Dimethyl 2-ethyl-5-phenyl-1-vinyl-1H-pyrrole-3,4-dicarboxylate **25***. IR (film) 3302, 2950, 1709, 1444, 1203, 766, 699 cm^{-1}; ^{1}H NMR (300 MHz) 1.23 (3H, t, *J*=7.4), 2.97 (2H, q, *J*=7.4), 3.70 (3H, s), 3.83 (3H, s), 4.98 (1H, dd, *J*=0.7 and 15.9), 5.18 (1H, dd, *J*=0.7 and 8.5), 6.54 (1H, dd, *J*=8.5 and 15.9), 7.33–7.37 (5H, m, Ar-H); ^{13}C NMR (75.5 MHz) 14.0, 18.9, 51.4, 51.9, 111.6, 114.6, 116.1, 128.0, 128.3, 129.9, 130.4, 130.6, 133.6, 141.2, 165.0, 166.3; MS (EI) *m*/*z* 313 (M$^+$, 69%), 281 (97), 266 (100), 194 (45) and 180 (18); HRMS (EI) *m*/*z* 313.1309 ($C_{18}H_{19}NO_4$ [M$^+$], 313.1314). *Dimethyl 2-(1-methyl-allyl)-5-phenyl-1H-pyrrole-3,4-dicarboxylate **26***. IR (film) 3298, 1707, 1456, 1217 cm^{-1}; ^{1}H NMR (300 MHz) 1.40 (3H, d, *J*=7.1), 3.80 (3H, s), 3.82 (3H, s), 4.32–4.37 (1H, m), 5.20–5.26 (2H, m), 6.01–6.12 (1H, m), 7.31–7.47 (5H, m, Ar-H), 8.34 (1H, br s); ^{13}C NMR (75.5 MHz) 18.5, 34.0, 51.3, 52.1, 114.4, 115.6, 124.4, 127.2, 128.2, 128.7, 130.4, 130.8, 139.2, 141.1, 164.7, 166.9; MS (EI) *m*/*z* 313 (M$^+$, 24%), 281 (100), 266 (23), 250 (28), 222 (28), 194 (21) and 180 (17); HRMS (EI) *m*/*z* 313.1308 ($C_{18}H_{19}NO_4$ [M$^+$], 313.1314).

*4.5.7. Dimethyl 2-(1-methyl-allyl)-5-phenyl-1H-pyrrole-3,4-dicarboxylate **26** from **16b** [600 °C/2.0×10^{-2} mbar]*

The crude product was purified by preparative thin layer chromatography [ethyl acetate/hexane (1:2)] to give compound **26** (81 mg, 54%), which was identified by comparison with the specimen previously prepared.

4.6. General procedure for the flash vacuum pyrolysis of 3-(1-substituted-1*H*-pyrrol-2-yl)-acrylates

Pyrolysis of the appropriate 3-(1-substituted-1*H*-pyrrol-2-yl)-acrylates (0.95–1.26 mmol) at 700–750 °C/2×10^{-2} to 2.7×10^{-2} mbar onto a surface cooled at −196 °C over a period of 0.7–1 h gave a red pyrolysate [the rate of volatilisation of the starting material was controlled by the use of a Kugelrohr oven, which heated the sample at 100–230 °C]. After cooling to room temperature the pyrolysate was removed from the cold finger with dichloromethane and the solvent was removed in vacuo.

*4.6.1. 5-Benzyl-pyrrolizin-3-one **34a** from **30b** [700 °C/2.0×10^{-2} mbar]*

The crude product was purified by flash chromatography [ethyl acetate/hexane (1:8), then ethyl acetate/hexane (1:3)] to give **34a** as an intense red oil (61 mg, 20%). IR (KBr) 1728, 1509, 1400, 1238 cm^{-1}; ^{1}H NMR (300 MHz) 4.01 (2H, s), 5.56–5.58 (1H, m), 5.61 (1H, d, *J*=5.7), 5.90 (1H, d, *J*=3.1), 7.04 (1H, d, *J*=5.7), 7.23–7.31 (5H, m, Ar-H); ^{13}C NMR (75.5 MHz) 32.7, 111.8, 113.5, 121.2, 126.6, 128.4, 129.0, 136.3, 137.4, 137.7, 137.8, 166.5; MS (EI) *m*/*z* 209 (M$^+$, 100%), 180 (79), 154 (15) and 132 (41). HRMS (EI) *m*/*z* 209.0841 ($C_{14}H_{11}NO$ [M$^+$], 209.0841).

*4.6.2. 5-Benzyl-pyrrolizin-3-one **34a** from **30a** [700 °C/2.7×10^{-2} mbar]*

The crude product was purified by preparative thin layer chromatography [ethyl acetate/hexane (1:8)] to give **34a** as an intense red oil (41 mg, 21%). Compound **34a** was identified by comparison with the specimen previously prepared.

*4.6.3. 5-Ethyl-pyrrolizin-3-one **34b** from **30c** [750 °C/2.0×10^{-2} mbar]*

The crude product was purified by flash chromatography [ethyl acetate/hexane (1:5)] to give **34b** as an intense red oil (31 mg, 21%). IR (film) 2970, 1730, 1518, 1240, 799 cm^{-1}; ^{1}H NMR (300 MHz) 1.23 (3H, t, *J*=7.5), 2.70 (2H, q, *J*=7.5), 5.61 (1H, d, *J*=5.7), 5.67–5.69 (1H, m), 5.92 (1H, d, *J*=3.0), 7.04 (1H, d, *J*=5.7); ^{13}C NMR (75.5 MHz) 11.5, 20.0, 111.3, 112.0, 121.0, 136.0, 137.7, 141.0, 166.7; MS (EI) *m*/*z* 147 (M$^+$, 53%), 132 (100) and 104 (19); HRMS (EI) *m*/*z* 147.0685 (C_9H_9NO [M$^+$], 147.0684).

*4.6.4. 1-Benzyl-4-(1-benzyl-1H-pyrrol-2-yl)-4,5,6,7-tetrahydro-1H-indole **39***

A solution of 1-benzyl-2-vinyl-1*H*-pyrrole (0.18 g, 0.98 mmol) in 1,2,4-trichlorobenzene (1.2 mL) was irradiated in the microwave reactor with the temperature set to 260 °C for 30 min. After cooling to room temperature, the crude product was purified by flash chromatography in aluminium oxide [hexane] to remove 1,2,4-trichlorobenzene followed by elution with ethyl acetate/hexane (1:8) to give **39** as a colourless oil (84 mg, 47%). IR (film) 3029, 2931, 1495, 1453, 1290, 705 cm^{-1}; ^{1}H NMR (400 MHz) 1.57–1.68 (2H, m), 1.85–1.91 (2H, m), 2.39–2.42 (2H, m), 3.93–3.95 (1H, m), 4.96 (2H, s), 5.13–5.14 (2H, m), 5.84–5.86 (2H, m), 6.12 (1H, dd, *J*=2.8 and 3.4), 6.54 (1H, d, *J*=2.8), 6.60 (1H, dd, *J*=2.8 and 2.0), 6.99–7.02 (4H, m), 7.20–7.37 (6H, m); ^{13}C NMR (100 MHz) 21.4, 21.6, 31.2, 32.4, 50.0, 50.2, 106.6, 106.8, 106.9, 119.7, 120.0, 120.8, 126.3, 126.4, 127.1, 127.2, 128.2, 128.6, 128.7, 137.9, 138.6, 139.0; MS (EI) *m*/*z* 366 (M$^+$, 88%), 338 (42), 275 (25), 247 (17), 209 (33) and 91 (100); HRMS (EI) *m*/*z* 366.2092 ($C_{26}H_{26}N_2$ [M$^+$], 366.2096).

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Supplementary data

Data regarding the synthesis of compounds **6**, **12**, **28**, **29**, **30**, **32** and **33** are provided. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2008.07.079.

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