PSEUDOESTERS AND DERIVATIVES. PART 38.[1] 1,3-DIPOLAR CYCLOADDITIONS OF ARYL AZIDES AND AN AZIRIDINE, *VIA* AZOMETHINE YLIDE, TO 2(5*H*)-FURANONES SUBSTITUTED AT THE 5-POSITION BY METHOXY AND SULFUR BEARING GROUPS

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Abstract-The behavior of the 2(5*H*)-furanones (**1-3**) towards *p*-methoxy- and *p*-nitrophenyl azides (**4** and **12**) has been investigated, in particular with respect to the regio- and stereoselectivity. The 1,3-dipolar cycloaddition of the azomethine ylide generated by thermal ring opening of dimethyl *trans*-1-(*p*-methoxyphenyl)aziridine-2,3-dicarboxylate (**22**) to 2(5*H*)-furanones (**1-3**) proceeds in good yield and affords functionalized furo[3,4-*c*]pyrrol-3-one derivatives.

INTRODUCTION

The 1,3-dipolar cycloaddition is one of the most useful method for the construction of five-membered heterocyclic rings.[2] While the cycloaddition to substituted alkenes and alkynes has been extensively investigated,[2] the use of butenolides as dipolarophiles has been limited to a few reports. Some of the reported examples include the addition of diazoalkanes,[3] nitrones,[4] nitrile oxides,[5] arylazides[6] and azomethine ylides.[7,3g]

In previous papers, we have reported 1,3-dipolar cycloaddition of diazomethane and nitrile oxides to 5-methoxyfuran-2(5*H*)-one (**1**)[3e,j,5c] and furan-2(5*H*)-ones substituted at the 5-position by sulfur bearing groups such as SEt, SPh, SO_2Et and SO_2Ph[1,5d] as a synthetic route to physiologically interesting molecules. Our results showed the behavior of 2(5*H*)-furanones as dipolarophiles, and the influence of the nature of the substituent at 5-position on the reactivity of the furanone towards diazomethane and nitrile oxides and on the regio- and stereoselectivity of the cycloaddition.

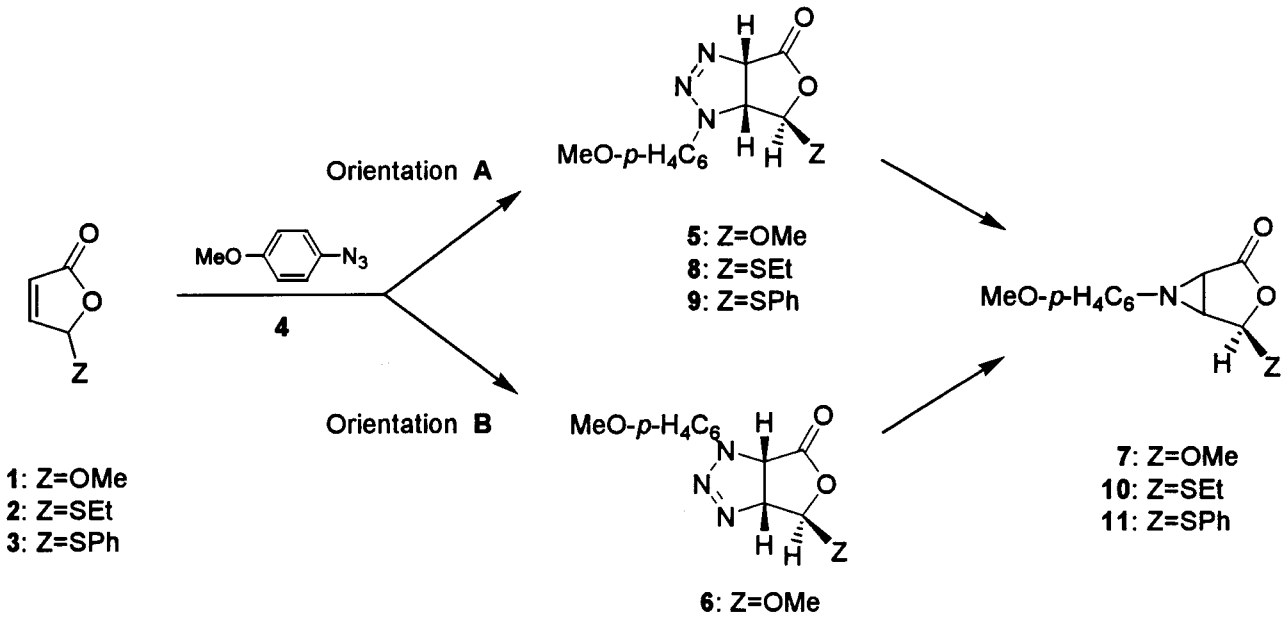
Our interest in 1,3-dipolar cycloadditions to 2(5*H*)-furanone to provide a convenient entry to novel fused heterocyclic systems led us to study the addition of aryl azides and azomethine ylides to 5-

methoxyfuran-2(5*H*)-one (**1**), 5-ethylthio- and 5-phenylthiofuran-2(5*H*)-ones (**2, 3**) as a synthetic route to new fused heterocyclic ring systems. The reactions have been explored with methoxyfuranones and thioethers to acquire information on the influence of the group at 5-position upon the reactivity and the regio- and stereoselectivity of the cycloaddition.

RESULTS AND DISCUSSION

Cycloaddition of *p*-methoxyphenyl azide

The cycloaddition of *p*-methoxyphenyl azide (**4**) with the furanones (**1-3**) has been conducted without solvent at 60 °C in an autoclave, using two fold excess of dipole and the crude reaction mixtures were analysed by ^{1}H-NMR. The results and experimental conditions are summarised in Table I (Scheme I).



Scheme I

The cycloaddition to furanones (**2**) and (**3**) proceeds at a rate slower than that of the methoxyfuranone (**1**). The reaction of 5-methoxyfuran-2(5*H*)-one (**1**) afforded a 78:22 mixture of the regioisomeric cycloadducts (**5** + **6**) (in a ratio 80:20) and the aziridine (**7**). The triazoline (**5**) and the aziridine (**7**) were separated by flash column chromatography, whereas triazoline (**6**) and aziridine (**7**) were obtained as a mixture.

Table I. 1,3- Dipolar Cycloadditions of *p*-Methoxyphenyl Azide (**4**) to Furanones (**1-3**)

Furanone	Z	Time (h)	Conversion (%)	Products[a]		
				Triazoline	Orientation A/B	Aziridine
1	OMe	72	100	**5**+ **6** (78)	80:20	**7** (22)
2	SEt	72	50	**8** (100)	100:0	**10**[b]
3	SPh	96	60	**9** (43)	100:0	**11** (57)

[a] Relative product distribution determined by ^{1}H-NMR. [b] Aziridine was isolated during chromatographic separation.

In contrast, with the thioethers (**2**) and (**3**) the reaction occurs in a regiospecific manner to afford the corresponding triazolines (**8**) and (**9**) as a single regioisomer. In the purification by flash column chromatography of the reaction from thioether (**2**) a second product, the aziridine (**10**) was isolated. Likewise the reaction with thioether (**3**) led a 43:57 mixture of triazoline (**9**) and aziridine (**11**).

Triazoline (**5**) was obtained as crystalline solid, while triazolines (**6**), (**8**) and (**9**) could not be isolated in pure state and the characterisation of which has only been effected on the basis of the spectral data.

The predominant orientation A is in accord with the regiochemistry reported for cycloaddition of *N*-aryl azides to 5-ethoxyfuran-2(5*H*)-one[6a] and α,β–unsaturated lactones.[6b] The structure of the regioisomeric triazolines (**5**) and (**6**) was established on the basis of the chemical shift of the proton coupled with the H-5 one, which in the adducts of type A appears at higher field than in the regioisomer of type B.[8]

The structure of the triazolines could be determined by the spectral data, particularly the ^{1}H-NMR spectra. The magnitude of the coupling constant between the proton (H-6 or H-4) and the adjacent protons (H-6a or H-3a) (J=0-1.1 Hz) suggests that the reaction leads to the triazolines with the Z group in an *exo* arrangement. This fact suggests that the attack of the dipole occurs at the face opposite to the Z group.

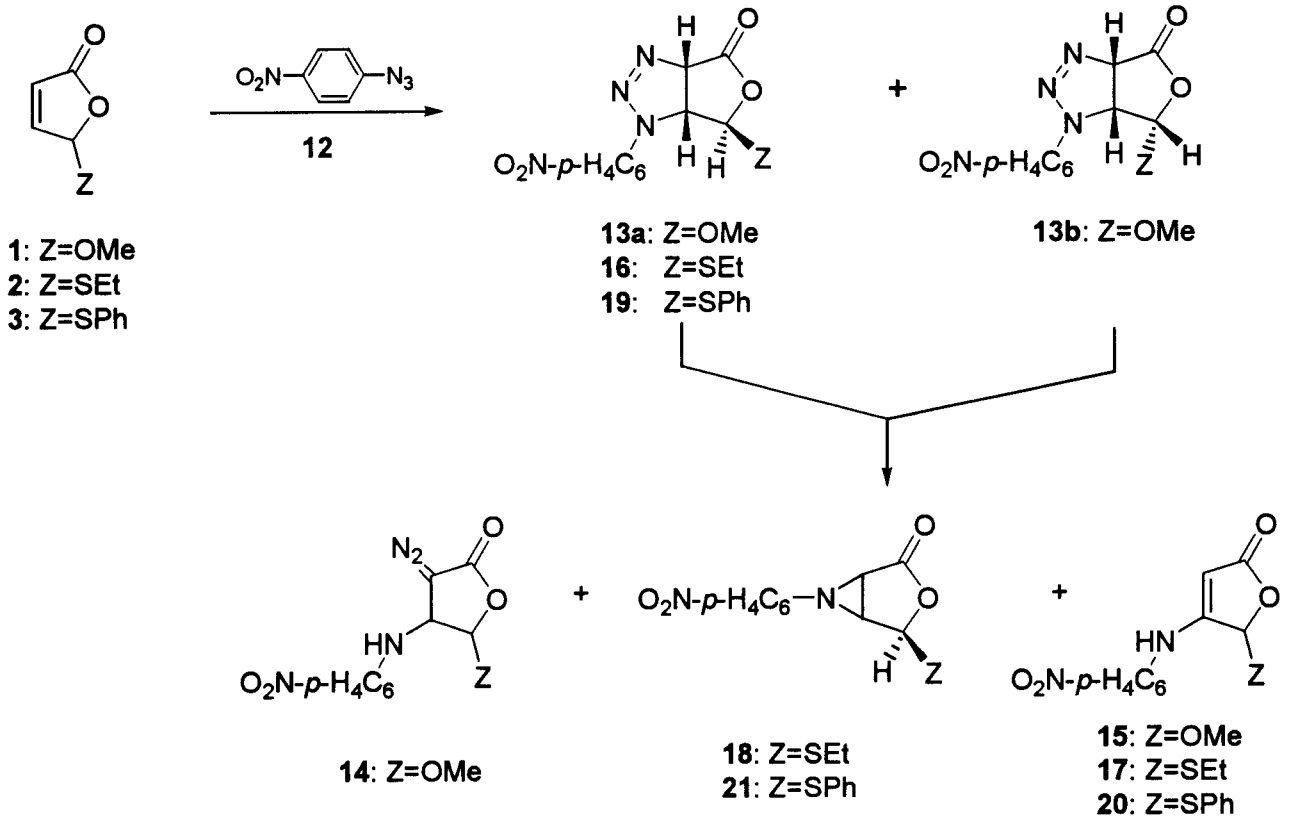
The formation of the aziridine in the reaction can be explained through decomposition of the primary cycloadducts, by ring cleavage with nitrogen expulsion.[8]

The structures of aziridines (**7**), (**10**) and (**11**) were confirmed by their elemental analyses and spectral data. Thus, their ^{1}H-NMR spectra show two doublets (δ 3.45-3.57) and (δ 3.24-3.07) with a coupling constant J=3.7-4.0 Hz, attributable to the H-1a and H-4a protons. Moreover, the absence of the coupling constant between the protons H-4a and H-4 suggests that the Z group is in *exo* arrangement.

Cycloaddition of *p*-nitrophenyl azide

The reaction of *p*-nitrophenyl azide (**12**) with the furanones (**1-3**) has been conducted without solvent at 60 °C in an autoclave, using two fold excess of dipole and the crude reaction mixtures were analysed by ^{1}H-NMR. The results and experimental conditions are summarised in Table II (Scheme II).

The methoxyfuranone (**1**) is much more reactive than the furanones (**2**) and (**3**) in the cycloaddition with *p*-nitrophenyl azide (**12**). This dipole reacts in non-regiospecific manner with 5-methoxyfuran-2(5H)-one (**1**) to afford a 50:50 mixture of the epimeric triazolines (**13a**) and (**13b**). After flash column chromatography, also diazo compound (**14**) and enamine (**15**) were isolated in 6% and 4% yield



Scheme II

respectively. It is noteworthy that the triazoline (**13b**) can not be isolated presumably owing to the easy decomposition during the chromatographic separation and it was characterised by ^{1}H-NMR.

The cycloaddition with the thioethers (**2**) and (**3**) occurs in a regiospecific manner to afford the corresponding triazolines (**16**) and (**19**) as a single isomers. The crude reaction mixture also contained aziridines (**18**) and (**21**), as well as enamines (**17**) and (**20**), respectively.

Table II. 1,3- Dipolar Cycloadditions of *p*-Nitrophenyl Azide (**12**) to Furanones (**1-3**)

Furanone	Z	Time	Conversion (%)	Products[a] Triazoline	Exo/Endo	Aziridine	Enamine
1	OMe	96 h	90	**13a+13b** (100)	50:50	---	**15**[b,c]
2	SEt	14 d	90	**16** (52)	100:0	**18** (27)	**17** (21)
3	SPh	14 d	80	**19** (67)	100:0	**21** (31)	**20** (12)

[a] Relative product distribution determined by ^{1}H-NMR. [b] Enamine was isolated during chromatographic separation.
[c]Diazofuranone (**14**) also was isolated during chromatographic separation.

The structures of cycloadducts (**13a**), (**13b**), (**16**) and (**19**) are supported by the spectral data, particulary the ^{1}H-NMR spectra. The stereochemistry is assigned on the basis of the magnitude of the coupling constant between the proton H-6 and the adjacent protons H-6a. A coupling constant $J_{6,6a}$=0-1.8 Hz indicates that H-6a and H-6 must be *trans* to each other (*exo* Z-group, **13a**, **16** and **19**). Whereas a $J_{6,6a}$=5.0 Hz suggests a *cis* relationship (*endo* OMe group, **13b**).

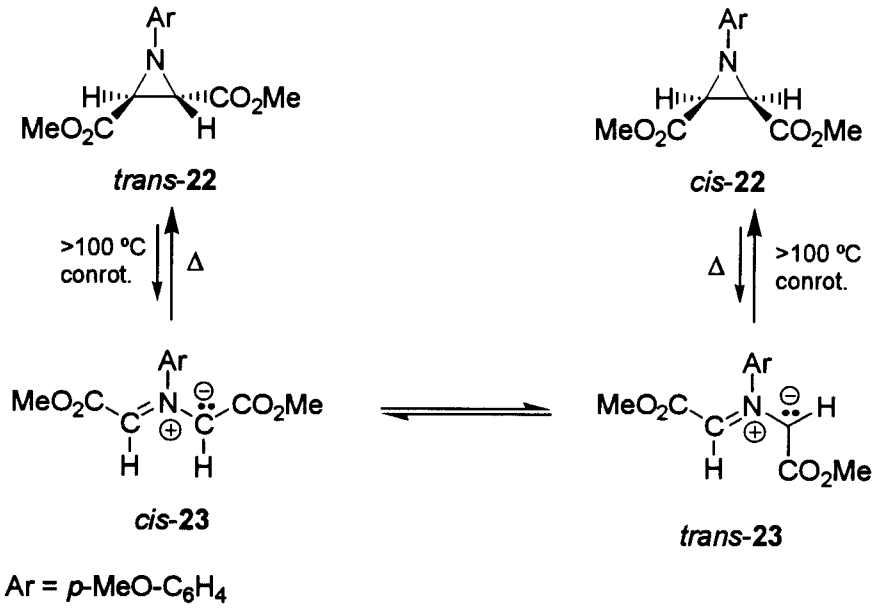
The structures of aziridines (**18**) and (**21**) were confirmed by their elemental analyses and spectral data. Thus, their ^{1}H-NMR spectra show two doublets (δ 3.77-3.73) and (δ 3.25-3.62) with a coupling constant *J*=3.6 Hz, attributable to the H-1a and H-4a protons. Moreover, the magnitude of the coupling constant (*J*=0-0.7 Hz) between the protons H-4a and H-4 suggests that the Z group is in *exo* arrangement.

The structures of diazo compound (**14**) and enamines (**15**), (**17**) and (**20**) were confirmed by their elemental analyses and spectral data. The formation of the decomposition products (**14**), (**15**), (**17**) and (**20**) can be explained by isomerisation of the triazoline to the open-chain diazo compound either spontaneously or under the action of silica gel and subsequent nitrogen expulsion.[8]

Cycloaddition of azomethine ylide

Among the different methods developed for the generation of azomethine ylides[2] we selected the thermal conrotatory ring-opening of aziridines.[9] According to Huisgen[9a] the thermal equilibration at temperatures above 100 °C of aziridines *trans*-**22** and *cis*-**22** takes place *via* the azomethine ylides *cis*-**23** and *trans*-**23** originated by conrotatory ring-opening, as shown in the Scheme III. However, in the presence of a highly active dipolarophile the azomethine ylide *cis*-**23** is trapped to give exclusively the *cis*-adduct and the equilibration *cis*-**23** $\rightleftarrows$ *trans*-**23** is suppressed. If the dipolarophilic activity of the multiple bond system is reduced, *cis*-**23** isomerises in part to *trans*-**23** and mixtures of *cis*- and *trans*-

adducts are obtained.[9c,e] With poor dipolarophiles, the sequence *trans*-**22**→ *cis*-**23**→ *trans*-**23** leads exclusively to the *trans*-adduct.[9f]



Scheme III

The reactions of aziridine *trans*-**22** to 5-methoxyfuran-2(5*H*)-one (**1**) and the thioethers (**2**) and (**3**) have been performed under nitrogen, during the period of time indicate in Table III, in refluxing chlorobenzene. The results of the reactions summarised in Table III indicated that high conversion are obtained under these conditions.

5-Methoxyfuran-2(5*H*)-one (**1**) reacted with aziridine (**22**) giving only one stereoisomeric adduct (**24**), of which structure was determined on the basis of its ^{1}H-NMR spectra (Table IV). The *cis* junction between both rings was corroborated from the magnitude of the coupling constant $J_{2a,5a}$= 9.5 Hz. A coupling constant $J_{5,5a}$=3.8 Hz indicated that the protons H-5 and H-5a must be *trans* to each other (*exo* MeO-group). This fact suggests that the attack of dipole occurs at the face opposite to the OMe group. This observation is in accord with the *face*-selectivity reported previously for the cycloaddition of nitrile oxides to furanone (**1**). It is interesting to note, however that the addition of diazomethane to furanone (**1**) leads to a 30:70 mixture of *endo* and *exo* adducts.

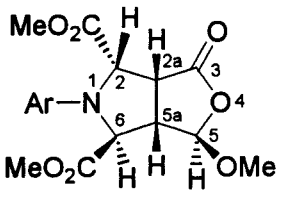
The stereochemical relationship between the methoxycarbonyl groups in the adduct (**24**) could be directly deduced from the magnitude of the coupling constants between H-2 and H-2a, and H-5a and H-6 (Table IV). The *trans* arrangement of the methoxycarbonyl groups was justified by the isomerization process of the *cis*-**23** to *trans*-**23** azomethine ylides, because the furanone (**1**) is not active enough to trap the *cis* isomer and to suppress the equilibration process.

Table III. 1,3-Dipolar Cycloaddition of Azomethine ylide to Furanones (**1-3**)

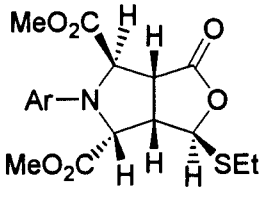
Furanone	Z	Time (h)[a]	Yield %	Product[b]	Exo/Endo
1	OMe	8	79	**24** (100)	100:0
2	SEt	24	70	**25a** (23)+**25b** (71)+ **25c** (6)	23:77
3	SPh	24	75	**26a** (79)+**26b** (21)	79:21

[a] Time required for total conversion. [b] Relative product distribution determined by ^{1}H-NMR.

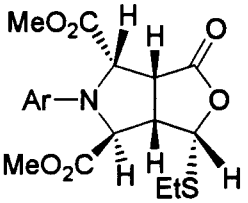
However, the cycloaddition of furanone (**2**) afforded a 23:71:6 mixture of three stereoisomeric adducts (**25a, 25b, 25c**) and these adducts were isolated by flash column chromatography. The structures of the adducts (**25a**), (**25b**) and (**25c**) were assigned on the basis of their ^{1}H-NMR (Table IV). We have assigned the *trans* and *cis* stereochemistry of the methoxycarbonyl group in adducts (**25a**), (**25b**) and (**25c**) on the basis of the magnitude of coupling constants $J_{2,2a}$ and $J_{5a,6}$. The stereochemistry *exo* or *endo* of the above adducts was assigned using arguments similar to those which allowed the assignment of the adduct (**24**). The reaction leads to the adducts with the ethylthio group in the *endo* arrangement as the major group, this fact does not agree with the results previously reported for cycloaddition of diazomethane and nitrile oxides to the same furanone.



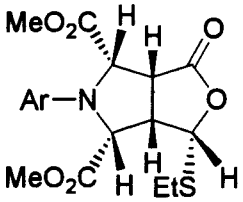
24



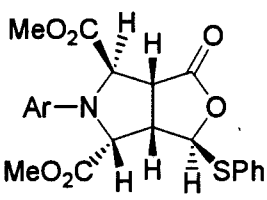
25a



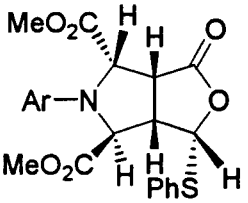
25b



25c



26a



26b

The reaction of phenylthiofuranone (**3**) produced a mixture of two stereoisomeric adducts (**26a** and **26b**) in a 79:21 ratio. These adducts were isolated by flash column chromatography. A *trans* stereochemistry of the methoxycarbonyl group in both adducts could be assigned on the basis of the magnitude of the

coupling constants $J_{2,2a}$ and $J_{5a,6}$ (Table IV). The *cis* or *trans* between H-5 and H-5a and consequently the *face*-selectivity of the cycloaddition were established considering that major stereoisomer (**26a**) displays a coupling constant $J_{5,5a}$ = 2.0 Hz, whereas the minor isomer (**26b**) has a value of 7.8 Hz. These observation are in accord with the *face*-selectivity reported for cycloaddition of diazomethane and nitrile oxide to the furanone (**3**).

Table IV. ^{1}H-NMR Chemical Shifts and Coupling Constants of Pyrrolofuranones (**24-26**).

Comp.	H-2	H-2a	H-5a	H-5	H-6	$J_{2,2a}$	$J_{2a,5a}$	$J_{5a,5}$	$J_{5a,6}$
24	4.83	3.81	3.04	5.49	4.67	9.6	9.5	3.8	2.4
25a	4.82	3.41-3.53	3.41-3.53	5.59	4.79	1.6	9.0	1.1	8.8
25b	4.81	3.72	3.01	5.66	4.64	10.3	9.3	7.9	1.3
25c	4.37	3.68	3.27	5.87	4.36	9.8	9.0	6.8	7.1
26a	4.78	3.14	3.63	5.68	4.84	1.8	8.7	2.0	8.8
26b	4.80	3.68	3.10	5.83	4.70	10.3	9.7	7.8	1.4

In summary, the results described in this study indicate that the 5-ethylthio- and 5-phenylthiofuran-2(5*H*)-ones (**2** and **3**) add regiospecifically to *p*-methoxy- and *p*-nitrophenyl azides (**4** and **12**) and the stereoselectivity rises to 100%. Likewise, the 5-methoxyfuran-2(5*H*)-one (**1**) shows a higher regioselectivity with azide (**4**), whereas the reaction with azide (**12**) occurs in a regiospecific manner and the stereoselectivity rises to 50%. The proportion of the decomposition products of the primary triazolines depends on the nature of the substituent at the 6- or 4-position of the furotriazoline, also the electronic character of an *N*-aryl substituent can play a significant role. The stereoselectivity observed in the cycloaddition with aziridine (**22**) depends on the nature of the substituent Z of the furanone. Moreover, comparison of the observed reaction times (see Tables I-III) shows that the 5-methoxyfuran-2(5*H*)-one (**1**) is more reactive than the 5-ethylthio- and 5-phenylthiofuran-2(5*H*)-ones (**2** and **3**) towards the dipoles (**4**), (**12**) and (**22**).

EXPERIMENTAL

Mps were determined using a Kofler hot-stage apparatus and are uncorrected. Microanalyses were performed with a Heraeus analyser. IR spectra were recorded on a Perkin-Elmer model 681 grating spectrophotometer as nujol mulls, unless otherwise stated, ν values in cm^{-1}. ^{1}H-NMR spectra were

determined with either a Varian Gemini 200, a Bruker AM-200 or a Varian XL-300 spectrometer, in $CDCl_3$ solution, unless otherwise stated. ^{13}C-NMR were determined with either a Varian XL-300 or a Bruker AM-200 in $CDCl_3$ solution, unless otherwise stated. Chemical shifts were reported in ppm (δ) downfield from Me_4Si. Mass spectra were determined on a VG-12-250 spectrometer. Silica gel Merck 60 (70-230 mesh) and DC-alufolien $60F_{254}$ were used for flash column chromatography and analytical TLC, respectively.

The furanones (**1**),[10] (**2**)[11] and (**3**)[12] were prepared according to the literature.

Cycloaddition of *p*-Methoxyphenyl Azide (4). General Procedure

A mixture of furanones (**1-3**) (285 mg, 2.5 mmol) and *p*-methoxyphenyl azide (**4**) (745 mg, 5 mmol) was heated without solvent at 60°C in an autoclave during the period of time indicated in Table I for each case. The crude reaction was analysed by ^{1}H-NMR. The crude product was purified by flash column chromatography on silica gel. The isolated yields are based on consumed furanones.

Addition to 5-methoxyfuran-2(5H)-one (1) afforded 78:22 mixture of adducts regioisomers (**5** and **6**, in a ratio 80:20) and aziridine (**7**). The crude reaction mixture was separated by column chromatography (*n*-hexane-ethyl ether, 3:2) to afford **1-(*p*-methoxyphenyl)-4-*exo*-methoxy-1*H*,4*H*-furo[3,4-*b*]aziridin-2-one (7)** as a white solid (130 mg, 22 %), mp 105-107 °C (from ethyl acetate- *n*-hexane). Anal. Calcd for $C_{12}H_{13}NO_4$: C, 61.22; H, 5.57; N, 5.95. Found: C, 61.62; H, 5.57; N, 5.99. IR: 3060, 1800, 1780, 1240. ^{1}H-NMR: 6.95-6.89 (m, 2H, arom.), 6.83-6.77 (m, 2H arom.), 5.34 (s, 1H, H-4), 3.75 (s, 3H, OCH_3), 3.55 (s, 3H, OCH_3), 3.45 (d, 1H, H-1a, $J_{1a,4a}$= 4.0 Hz), 3.24 (d, 1H, H-4a, $J_{1a,4a}$= 4.0 Hz). ^{13}C-NMR: 170.4, 156.6, 141.2, 121.3, 114.9, 102.6, 56.7, 55.1, 45.0, 39.5. MS, *m/z*: 235 (M^+, 51), 204, 175, 160, 134 (100), 108, 77; a 6:4 mixture of aziridine (**7**) and **1-(*p*-methoxyphenyl)-4-*exo*-methoxy-1*H*,4*H*,3a,6a-dihydrofuro[3,4-*d*]-1,2,3-triazol-6-one (6)** (218 mg). ^{1}H-NMR: 7.51-7.47 (m, 0.8 H arom., **6**), 6.96-6.77 (m, 0.8 H arom.,**6**, 2.4 H arom., **7**), 5.59 (d, 0.4 H, H-4, $J_{3a,4}$= 1.1 Hz, **6**), 5.34 (s, 0.6 H, H-4, **7**), 5.27 (dd, 0.4 H, H-3a, $J_{3a,6a}$= 11.0 Hz, $J_{3a,4}$= 1.1 Hz, **6**), 4.69 (d, 0.4 H, H-6a, $J_{3a,6a}$= 11.0 Hz, **6**), 3.79 (s, 1.2 H, OCH_3, **6**), 3.75 (s, 1.8 H, OCH_3, **7**), 3.61 (s, 1.2 H, Ar-OCH_3, **6**), 3.75 (s, 1.8 H, Ar- OCH_3, **7**), 3.45 (d, 0.6 H, H-1a, $J_{1a,4a}$= 4.0 Hz, **7**), 3.24 (d, 0.6 H, H-4a, $J_{1a,4a}$= 4.0 Hz, **7**) and **1-(*p*-methoxyphenyl)-6-*exo*-methoxy-1*H*,6*H*,3a,6a-dihydrofuro[3,4-*d*]-1,2,3-triazol-4-one (5)** as a white solid (230 mg, 35 %), mp 105-106 °C (from ethyl acetate-*n*-hexane). Anal. Calcd for $C_{12}H_{13}N_3O_4$: C, 54.75; H, 4.98; N, 15.96. Found: C, 54.31; H, 4.86; N, 15.71. IR: 1790, 1515, 1245. ^{1}H-NMR: 7.24-7.19 (m, 2H arom.), 6.98-6.93 (m, 2H arom.), 5.57 (d, 1H, H-3a, $J_{3a,6a}$= 11.1 Hz), 5.29 (s, 1H, H-6), 4.55 (d, 1H, H-6a, $J_{3a,6a}$= 11.1 Hz), 3.82 (s, 3H, OCH_3), 3.60 (s, 3H, OCH_3). ^{13}C-NMR: 168.2, 156.5, 132.1, 116.1, 115.2, 106.7, 80.1, 61.5, 57.5, 55.6. MS, *m/z*: 263 (M^+, 1), 235, 175 (100), 160, 134, 108, 77.

Addition to 5-ethylthiofuran-2(5H)-one (2) afforded unreacted furanone (**2**) and triazoline (**8**). The crude reaction mixture was chromatographed (chloroform) to give **1-(*p*-methoxyphenyl)-6-*exo*-ethylthio-1*H*,6*H*,3a,6a-dihydrofuro[3,4-*d*]-1,2,3-triazol-4-one (8)** as a yellow oil (114 mg, 31%). IR (film): 1790, 1520, 1250. ^{1}H-NMR: 7.28-7.21 (m, 2H, arom.), 6.98-6.90 (m, 2H, arom.), 5.61 (d, 1H, H-6, $J_{6,6a}$= 1.6 Hz), 5.60 (d, 1H, H-3a, $J_{3a,6a}$= 11.2 Hz), 4.56 (dd, 1H, H-6a, $J_{3a,6a}$= 11.2 Hz, $J_{6,6a}$= 1.6 Hz), 3.81 (s, 3H, OCH_3), 2.83 (m, 2H, S-CH_2), 1.34 (t, 3H, CH_3, J=7.4 Hz). ^{13}C-NMR: 168.4, 156.3, 131.8, 116.2, 115.2, 87.6, 80.4, 61.2, 55.5, 25.8, 14.4 and **1-(*p*-methoxyphenyl)-4-*exo*-ethylthio-1*H*,4*H*-furo[3,4-*b*]aziridin-2-one (10)** as a yellow oil (103 mg, 31%). Anal. Calcd for $C_{13}H_{15}NO_3S$: C, 58.85; H, 5.70; N, 5.28; S, 12.08. Found: C, 58.83; H, 5.67; N, 5.27; S, 12.08. IR (film): 3100, 1790, 1760. ^{1}H-NMR: 6.92- 6.88 (m, 2H, arom.), 6.82-6.78 (m, 2H, arom.), 5.58 (s, 1H, H-4), 3.74 (s, 3H, OCH_3), 3.50 (d, 1H, H-1a, $J_{1a,4a}$= 3.7 Hz), 3.35 (d, 1H, H-4a, $J_{1a,4a}$= 3.7 Hz), 2.76 (m, 2H, S-CH_2), 1.32 (t, 3H,CH_3, J=7.9 Hz). ^{13}C-NMR ($CDCl_3$, 50°C): 169.9, 156.5, 121.1, 114.9, 98.3, 82.8, 55.5, 45.6, 40.8, 24.8, 14.8. MS, *m/z* :265 (M^+, 16), 237, 209, 180, 177, 149, 134 (100), 104 , 92, 77.

Addition to 5-phenylthiofuran-2(5H)-one (3) afforded unreacted furanone (**3**) and a 43:57 mixture of triazoline (**9**) and aziridine (**10**). The crude reaction mixture was separated by column chromatography (chloroform) to give **1-(*p*-methoxyphenyl)-6-*exo*-phenylthio-1*H*,6*H*,3a,6a-dihydrofuro[3,4-*d*]-1,2,3-triazol-4-one (9)** as a yellow oil (73 mg, 15%). IR (film): 1810, 1795, 1520, 1260. ^{1}H-NMR: 7.60-7.57 (m, 2H, arom.), 7.44-7.36 (m, 3H, arom.), 7.28-7.25 (m, 2H arom.), 6.98-6.95 (m, 2H arom.), 5.67 (d, 1H, H-6, $J_{6,6a}$= 1.4 Hz), 4.95 (d, 1H, H-3a, $J_{3a,6a}$= 11.1 Hz), 4.70 (dd, 1H, H-6a, $J_{3a,6a}$= 11.1 Hz, $J_{6,6a}$= 1.4 Hz), 3.81 (s, 3H, OCH_3). ^{13}C-NMR: 168.0, 156.6, 135.2, 130.1, 129.9, 129.4, 116.4, 115.3, 114.8, 88.5, 80.1, 62.3, 55.5 and **1-(*p*-methoxyphenyl)-4-*exo*-phenylthio-1*H*,4*H*-furo[3,4-*b*]aziridin-2-one (11)** as a white solid (207 mg, 44%), mp 116-118°C (from *n*-hexane). Anal. Calcd for $C_{17}H_{15}NO_3S$: C, 65.16; H, 4.82; N, 4.47; S, 10.23. Found: C, 64.71; H, 4.86; N, 4.53; S, 9.90. IR: 3075, 1790, 1775, 1510, 1245. ^{1}H-NMR: 7.57-7.51 (m, 2H, arom.), 7.38-7.30 (m, 3H, arom.), 6.89-6.85 (m, 4H, arom.), 5.67 (s, 1H, H-4), 3.73 (s, 3H, OCH_3), 3.57 (d, 1H, H-1a, $J_{1a,4a}$= 3.8 Hz), 3.07 (d, 1H, H-4a, $J_{1a,4a}$= 3.8 Hz). ^{13}C-NMR: 169.7, 156.4, 134.7, 129.4, 129.41, 128.7, 121.0, 114.6, 103.1, 83.6, 55.5, 46.3, 40.6. MS, *m/z*: 313 (M^+, 3), 285, 257, 176, 152, 134 (100), 109, 92, 77.

Cycloaddition of *p*-Nitrophenyl Azide (12). General Procedure

A mixture of furanones (**1-3**) (285 mg, 2.5 mmol) and *p*-nitrophenyl azide (**12**) (745 mg, 5 mmol) was heated without solvent at 60 °C in an autoclave during the period of time indicated in Table II for each case. The crude reaction was analysed by ^{1}H-NMR. The crude product was purified by flash column chromatography on silica gel. The isolated yields are based on consumed furanones.

Addition to 5-methoxyfuran-2(5H)-one (1) afforded unreacted furanone (**1**) and a 50:50 mixture of triazolines (**13a** and **13b**). ^{1}H-NMR: 8.35-8.32 (m, 2H, arom., **13a**, **13b**), 7.41- 7.24 (m, 2H, arom., **13a**, **13b**), 5.76 (d, 0.5H, H-6, $J_{6,6a}$= 5.0 Hz, **13b**), 5.74 (d, 0.5H, H-3a, $J_{3a,6a}$= 10.9 Hz, **13a**), 5.56 (d, 0.5H, H-3a, $J_{3a,6a}$= 11.0 Hz, **13b**), 5.29 (s, 0.5H, H-6, **13a**), 4.92 (dd, 0.5H, H-6a, $J_{3a,6a}$= 11.0 Hz, $J_{6,6a}$= 5.0 Hz, **13b**), 4.60 (d, 0.5H, H-6a, $J_{3a,6a}$= 10.9 Hz, **13a**), 3.63 (s, 3H, OCH_3, **13a**), 3.43 (s, 3H, OCH_3, **13b**). The **1-(p-nitrophenyl)-6-*exo*-methoxy-1H,6H,3a,6a-dihydrofuro[3,4-d]-1,2,3-triazol-4-one (13a)** was isolated by precipitation with chloroform as an orange solid (264 mg, 45 %), mp 162-163 °C. Anal. Calcd for $C_{11}H_{10}N_4O_5$: C, 47.49; H, 3.62; N, 20.14. Found: C, 47.20; H, 3.63; N, 20.31. IR: 1780, 1600,1510, 1335, 1210. ^{1}H-NMR (Acetone-d_6): 8.38-8.34 (m, 2H, arom.), 7.58-7.53 (m, 2H, arom.), 6.01 (d, 1H, H-3a, $J_{3a,6a}$= 10.9 Hz), 5.61 (d, 1H, H-6, $J_{6,6a}$= 1.06 Hz), 4.91(dd, 1H, H-6a, $J_{3a,6a}$= 10.9 Hz, $J_{6,6a}$= 1.06 Hz), 3.67 (s, 3H, OCH_3). ^{13}C-NMR(Acetone-d_6): 168.5, 145.0, 144.1, 126.7, 115.6, 107.9, 83.7, 61.2, 57.9. MS, m/z: 250 (M^+-28, 39); 218, 189, 162, 74 (100). The mother liquor was concentrated and the residue was separated by column chromatography (chloroform) to afford **3-diazo-5-methoxy-4-(*p*-nitroanilino)furan-2(5*H*)-one (14)** as an orange solid (36 mg, 6 %), mp 120-121 °C. Anal. Calcd for $C_{11}H_{10}N_4O_5$: C, 47.49; H, 3.62; N, 20.14. Found: C, 47.54; H, 3.81; N, 20.35. IR: 3360, 2120, 1750, 1610, 1380. ^{1}H-NMR: 8.18-8.14 (m, 2H arom.), 6.71-6.66 (m, 2H arom.), 5.13 (s, 1H, H-5), 5.07 (d, 1H, H-4, $J_{4,NH}$= 8.2 Hz), 4.87 (d, 1H, NH, $J_{4,NH}$= 8.2 Hz), 3.63 (s, 3H, OCH_3). ^{13}C-NMR: 150.0, 140.1, 126.5, 125.2, 119.6, 112.3, 106.4, 65.8, 57.5. MS, *m/z:* 278 (M^+, 3); 250, 218, 189 (100), 162, 123, 116, 89, 53 and **5-methoxy-4-(p-nitroanilino)furan-2(5*H*)-one (15)** as a yellow solid (23mg, 4 %), mp 245-246°C. Anal. Calcd for $C_{11}H_{10}N_2O_5$: C, 52.80; H, 4.03; N, 11.20. Found: C, 52.60; H. 3.74; N, 10.99. IR: 3300, 1730, 1640, 1600, 1330. ^{1}H-NMR: 8.27 (d, AA′ of AA′BB′, 2H arom, J=9.1 Hz), 7.20 (d, BB′ of AA′BB′, 2H arom., J= 9.1 Hz), 6.82 (br s, 1H, NH), 5.76 (s, 1H, H-3), 5.57 (s, 1H, H-5), 3.61 (s, 3H, OCH_3).

Addition to 5-ethylthiofuran-2(5H)-one (2) afforded unreacted furanone (**2**) and a 52:27:21 mixture of triazoline (**16**), aziridine (**18**) and enamine (**17**). ^{1}H-NMR: 8.38-8.18 (m, 2H, arom., **16, 18, 17**), 7.58-7.53 (m, 1.04H, arom., **16**), 7.25-7.08 (m, 0.96H, arom., **18, 17**), 7.20 (br s, 0.21H, NH, **17**), 5.94 (s, 0.21H, H-5, **17**), 5.76 (d, 0.52H, H-3a, $J_{3a,6a}$= 11.0 Hz, **16**), 5.64 (s, 0.21H, H-3, **17**), 5.63 (d, 0.52H, H-6, $J_{6,6a}$= 1.8 Hz, **16**), 5.60 (s, 0.27H, H-4, **18**), 4.60 (dd, 0.52H, H-6a, $J_{3a,6a}$= 11.0 Hz, $J_{6,6a}$= 1.8 Hz, **16**), 3.73 (0.27H, H-1a, $J_{1a,4a}$=3.6 Hz, **18**), 3.62 (0.27H, H-4a, $J_{1a,4a}$=3.6 Hz, **18**), 2.79 (m, 2H, S-CH_2, **16, 18, 17**), 1.28 (t, 2.37H, CH_3, J=7.4 Hz, **16, 18**), 1.30 (t, 0.63H, CH_3, J=7.4 Hz, **17**). The crude mixture was separeted by column chrmatography to give **1-(*p*-nitrophenyl)-4-*exo*-ethylthio-1*H*,4*H*,1a,4a-dihydrofuro[3,4-*b*]aziridin-2-one (18)** (6 mg, 2%). ^{1}H-NMR: 8.23-8.18 (m, 2H arom.), 7,12-7.08 (m, 2H arom.), 5.60 (s, 1H, H-4), 3.73 (d, 1H, H-1a, $J_{1a,4a}$= 3.6 Hz), 3.62 (d, 1H, H-4a, $J_{1a,4a}$= 3.6 Hz), 2.78 (q,

2H, S-CH_2, J=7.4 Hz), 1.28 (t, 3H, CH_3, J=7.4 Hz) and **5-ethylthio-4-(*p*-nitroanilino)furan-2(5*H*)-one (17)** as a yellow solid (58 mg, 15%), mp 191.5-193°C. Anal. Calcd for $C_{12}H_{12}N_2O_4S$: C, 51.42; H, 4.32; N, 9.99; S, 11.44. Found: C, 51.53; H, 4.61; N, 10.03; S, 10.86. IR: 3330, 1780, 1750, 1630, 1600, 1340. ^{1}H-NMR (Acetone-d_6): 9.15 (br s, 1H, NH), 8.32 (d, AA′ of AA′BB′, 2H arom, J=9.2 Hz), 7.61 (d, BB′ of AA′BB′, 2H arom., J= 9.2 Hz), 6.26 (s, 1H, H-5), 5.82 (s, 1H, H-3), 2.68 (q, 2H, S-CH_2, J=7.6 Hz), 1.29 (t, 3H, CH_3). ^{13}C-NMR (Acetone-d_6): 172.3, 160.8, 146.9, 143.7, 126.2, 119.5, 90.6, 83.3, 23.3, 15.2. MS, *m/z*: 280 (M^+, 10), 219 (100), 189, 173, 149, 89, 76.

Addition to 5-phenylthiofuran-2(5H)-one (3) afforded unreacted furanone (**3**) and a 67:31:12 mixture of triazoline (**19**), aziridine (**21**) and enamine (**20**). The crude mixture was separated by column chromatography (chloroform) to give **1-(*p*-nitrophenyl)-6-*exo*-phenylthio-1*H*,6*H*,3a,6a-dihydro-furo[3,4-*d*]-1,2,3-triazol-4-one (19)** as a yellow solid (97 mg, 14%), mp 208-210.5°C. Anal. Calcd for $C_{16}H_{12}N_4O_4S$: C, 53.93; H, 3.39; N, 15.72; S, 9.00. Found: C, 53.64; H, 3.48; N, 15.77; S, 8.98. IR: 1790, 1600, 1510, 1340. ^{1}H-NMR: 8.33 (d, AA′ of AA′BB′, 2H arom, J= 9.2 Hz), 7.63-7.35 (m, 7H, arom.), 5.65 (d, 1H, H-6, $J_{6,6a}$= 1.5 Hz), 5.13 (d, 1H, H-3a, $J_{3a,6a}$= 10.8 Hz), 4.73 (dd, 1H, H-6a, $J_{3a,6a}$= 10.8 Hz, $J_{6,6a}$= 1.5 Hz). ^{13}C-NMR: 166.5, 143.7, 142.9, 135.2, 130.5, 130.1, 129.4, 126.2, 114.5, 88.3, 82.0, 61.0 ; **1-(*p*-nitrophenyl)-4-*exo*-phenylthio-1*H*,4*H*-furo[3,4-*b*]aziridin-2-one (21)** as a white solid (18 mg, 3%), mp 142-142.5 °C. Anal. Calcd for $C_{16}H_{12}N_2O_4S$: C, 58.53; H, 3.68; N, 8.53; S, 9.77. Found: C, 58.22; H, 3.59; N, 8.22; S, 9.47. IR: 3080, 1770, 1590, 1345. ^{1}H-NMR: 8.18-8.13 (m, 2H arom.), 7.56- 7.53 (m, 2H, arom.), 7.41-7.32 (m, 3H, arom.), 7.05-7.00 (m, 2H arom), 5.65 (d, 1H, H-4, $J_{4,4a}$=0.7 Hz), 3.77 (d, 1H, H-1a, $J_{1a,4a}$= 3.6 Hz), 3.25 (dd, 1H, H-4a, $J_{1a,4a}$= 3.6 Hz, $J_{4,4a}$= 0.7 Hz). ^{13}C-NMR: 164.8, 151.8, 144.3, 135.2, 130.0, 129.6, 127.8, 125.6, 120.2, 82.6, 45.9, 40.0. MS, *m/z*: 328 (M^+, 4), 300, 272 (100), 219, 145, 109, 91, 76, 65 and **5-phenylthio-4-(*p*-nitroanilino)furan-2(5*H*)-one (20)** as a yellow solid (80 mg, 13%), mp 209-210 °C. Anal. Calcd for $C_{16}H_{12}N_2O_4S$: C, 58.53; H, 3.68; N, 8.53; S, 9.77. Found: C, 58.29; H, 3.67; N, 8.28; S, 9.41. IR: 3290, 1725, 1630, 1590, 1340. ^{1}H-NMR: (Acetone-d_6): 9.20 (br s, 1H, NH), 8.33-8.27 (m, 2H arom), 7.59-7.36 (m, 7H, arom.), 6.43 (s, 1H, H-5), 5.52 (s, 1H, H-3). ^{13}C-NMR (Acetone-d_6): 171.9, 160.2, 146.9, 144.0, 135.8, 130.4, 130.0, 129.0, 126.2, 119.6, 91.1, 84.5. MS, *m/z*: 328 (M^+, 4), 218 (100), 191,173, 145, 109, 76, 65, 50.

Cycloaddition of Dimethyl *trans*-1-(*p*-Methoxyphenyl)aziridine-2,3-dicarboxylate. General Procedure

To a solution of the furanones (**1-3**) (1 mmol) in chlorobenzene (5 mL) was added a solution of aziridine *trans*-(**22**)[13] (256 mg, 1 mmol) in chlorobenzene (5 mL). The reaction mixture was refluxed under nitrogen during the period of time indicated in Table III for each case. The solvent was removed under

reduced pressure and the residue was analysed by ^{1}H-NMR. The crude product was purified by flash column chromatography on silica gel (*n*-hexane-ether, 3:2).

Addition to 5-methoxyfuran-2(5H)-one (1) afforded **2,6-dimethoxycarbonyl-5-*exo*-methoxy-1-(*p*-methoxyphenyl)-1*H*,5*H*,2,2a,5a,6-tetrahydrofuro[3,4-*c*]pyrrol-3-one (24)** as a white solid (299 mg, 79%), mp 146-147°C (from acetone-petroleum ether). Anal. Cald for $C_{18}H_{21}NO_8$: C, 56.99; H, 5.58; N, 3.69. Found: C, 57.11; H, 5.69; N, 3.77. IR: 1780, 1750, 1725, 1515, 1265. ^{1}H-NMR: 6.81-6.74 (m, 2H, arom.), 6.66-6.58 (m, 2H, arom.), 5.49 (d, 1H, H-5, $J_{5a,5}$= 3.8 Hz), 4.83 (d, 1H, H-2, $J_{2,2a}$= 9.6 Hz), 4.67 (d, 1H, H-6, $J_{6,5a}$= 2.4 Hz), 3.81 (dd, 1H, H-2a, $J_{2,2a}$= 9.6 Hz, $J_{2a,5a}$= 9.5 Hz), 3.71 (s, 3H, OCH_3), 3.68 (s, 3H, OCH_3), 3.60 (s, 3H, OCH_3), 3.57 (s, 3H, OCH_3), 3.04 (ddd, 1H, H-5a, $J_{2a,5a}$= 9.5, $J_{5,5a}$= 3.8 Hz, $J_{5a,6}$= 2.4 Hz).^{13}C-NMR: 172.7, 171.8, 170.7, 154.1, 138.2, 117.0, 114.8, 108.5, 66.3, 64.5, 57.9, 55.4, 52.6, 52.4, 50.7, 47.4. MS, *m/z*: 380 (M^++1, 8); 379 (M^+, 59); 320, 244, 232, 200 (100), 173, 158, 77.

Addition to 5-ethylthiofuran-2(5H)-one (2) afforded a 23:71:6 mixture of **2,6-dimethoxycarbonyl-5-*exo*-ethylthio-1-(*p*-methoxyphenyl)-1*H*,5*H*,2,2a,5a,6-tetrahydrofuro[3,4-*c*]pyrrol-3-one (25a)** as a white solid (43 mg, 11%), mp 144-145 °C (from acetone-petroleum ether). Anal. Calcd for $C_{19}H_{23}NO_7S$: C, 55.73; H, 5.66; N, 3.42; S, 7.83. Found: C, 55.45; H, 5.50; N, 3.23; S, 7.75. IR: 1780, 1760, 1740, 1515, 1250. ^{1}H-NMR: 6.80-6.73 (m, 2H, arom.), 6.56-6.51(m, 2H, arom.), 5.59 (d, 1H, H-5, $J_{5,5a}$= 1.1 Hz), 4.79 (d, 1H, H-6, $J_{5a,6}$=8.8 Hz), 4.82 (d, 1H, H-2, $J_{2,2a}$=1.6 Hz), 3.71 (s, 3H, OCH_3), 3.68 (s, 3H, OCH_3), 3.62 (s, 3H, OCH_3), 3.41-3.53 (m, 2H, H-2a, H-5a), 2.81-2.86 (m, 2H, S-CH_2), 1.34 (t, 3H, CH_3, J=7.4 Hz). ^{13}C-NMR:174.2, 171.9, 171.1, 153.7, 138.2, 116.0, 114.9, 83.8, 64.7, 64.3, 55.5, 52.6, 52.4, 48.0, 47.6, 25.8, 14.6. MS, *m/z*: 410 (M^++1, 9), 409 (M^+, 47), 350, 320, 244, 232 (100), 200, 173, 134, 75; **2,6-dimethoxycarbonyl-5-*endo*-ethylthio-1-(*p*-methoxyphenyl)-1*H*,5*H*,2,2a,5a,6-tetrahydrofuro[3,4-*c*]pyrrol-3-one (25b)** as a white solid (130 mg, 32%), mp 122-124 °C (from acetone-petroleum ether). Anal. Calcd for $C_{19}H_{23}NO_7S$: C, 55.73; H, 5.66; N, 3.42; S, 7.83. Found: C, 55.72; H, 5.65; N, 3.42; S, 7.56. IR: 1785, 1750, 1730, 1515, 1250. ^{1}H-NMR: 6.82-6.74 (m, 2H, arom.), 6.64-6.56 (m, 2H, arom.), 5.66 (d, 1H, H-5, $J_{5,5a}$= 7.9 Hz), 4.81 (d, 1H, H-2, $J_{2,2a}$= 10.3 Hz), 4.64 (dd, 1H, H-6, $J_{5a,6}$= 1.3 Hz, $J_{2a,6}$= 1.3 Hz), 3.72 (ddd, 1H, H-2a, $J_{2,2a}$= 10.3 Hz, $J_{2a,5a}$= 9.3 Hz, $J_{2a,6}$= 1.3 Hz), 3.71 (s, 6H, OCH_3), 3.62 (s, 3H, OCH_3), 3.01 (ddd, 1H, H-5a, $J_{2a,5a}$= 9.3 Hz, $J_{5,5a}$= 7.9 Hz, $J_{5a,6}$= 1.3 Hz), 2.80 (q, 2H, S-CH_2, J=7.4 Hz), 1.34 (t, 3H, CH_3). ^{13}C-NMR: 173.2, 171.7, 171.1, 153.9, 138.2, 116.3, 115.0, 88.3, 66.8, 64.3, 55.5, 52.6, 52.4, 50.7, 47.6, 25.8, 14.6. MS; *m/z*: 410 (M^++1, 13), 409 (M^+, 59), 350, 320, 244, 232 (100), 200, 158, 134, 77, 75 and **2,6-dimethoxycarbonyl-5-*endo*-ethylthio-1-(*p*-methoxyphenyl)-1*H*,5*H*, 2,2a,5a,6-tetrahydrofuro[3,4-*c*]pyrrol-3-one (25c)** as a white solid (25 mg, 6%), mp 165-167 °C (from acetone-petroleum ether). Anal. Calcd for $C_{19}H_{23}NO_7S$: C, 55.73; H, 5.66; N, 3.42; S, 7.83. Found: C, 55.88; H, 5.64; N, 3.41; S, 8.04. IR (KBr): 1780, 1750, 1520, 1250. ^{1}H-NMR: 6.83-6.77 (m, 2H, arom.),

6.69- 6.64 (m, 2H, arom.), 5.87 (d, 1H, H-5, $J_{5,5a}$= 6.8 Hz), 4.37 (dd, 1H, H-2, $J_{2,2a}$= 9.8 Hz, $J_{2,5a}$= 0.9 Hz), 4.36 (dd, 1H, H-6, $J_{5a,6}$= 7.1 Hz, $J_{2a,6}$= 0.9 Hz), 3.76 (s, 3H, OCH_3), 3.73 (s, 3H, OCH_3), 3.72 (s, 3H, OCH_3), 3.68 (dd, 1H, H-2a, $J_{2,2a}$= 9.8 Hz, $J_{2a,5a}$= 9.0 Hz), 3.27 (m, 1H, H-5a, $J_{2a,5a}$= 9.0 Hz, $J_{5,5a}$= 6.8 Hz, $J_{5a,6}$= 7.1 Hz, $J_{2,5a}$= 0.9 Hz), 2.75 (q, 2H, S-CH_2, J=7.4 Hz), 1.31 (t, 3H, CH_3). MS, *m/z*: 410 (M^++1, 16), 409 (M^+, 69), 350, 320, 244, 232 (100), 200, 158, 134, 77, 75.

Addition to 5-phenylthiofuran-2(5H)-one (3) afforded a 79:21 mixture of **2,6-dimethoxycarbonyl-5-*exo*-phenylthio-1-(*p*-methoxyphenyl)-1*H*,5*H*,2,2a,5a,6-tetrahydrofuro[3,4-*c*]pyrrol-3-one (26a)** as a white solid (190 mg, 42%), mp 149-150 °C (from acetone-petroleum ether). Anal. Calcd for $C_{23}H_{23}NO_7S$: C, 60.38; H, 5.07; N, 3.06; S, 7.01. Found: C, 60.87; H, 5.14; N, 3.30; S, 6.87. IR: 1785, 1735, 1520, 1260, 1240. ^{1}H-NMR: 7.55-7.50 (m, 2H, arom.), 7.39-7.33 (m, 3H, arom.), 6.79-6.75(m, 2H, arom.), 6.57-6.52 (m, 2H, arom.), 5.68 (d, 1H, H-5, $J_{5,5a}$= 2.0 Hz), 4.84 (d, 1H, H-6, $J_{5a,6}$= 8.8 Hz), 4.78 (d, 1H, H-2, $J_{2,2a}$= 1.8 Hz), 3.71 (s, 3H, OCH_3), 3.65 (s, 3H, OCH_3), 3.63 (ddd, 1H, H-5a, $J_{2a,5a}$= 8.7, $J_{5,5a}$= 2.0 Hz, $J_{5a,6}$= 8.8 Hz), 3.60 (s, 3H, OCH_3), 3.14 (dd, 1H, H-2a, $J_{2,2a}$= 1.8 Hz, $J_{2a,5a}$= 8.7 Hz). ^{13}C-NMR: 173.9, 171.8, 170.9, 153.9, 138.2, 133.9, 130.4, 129.5, 129.3, 116.3, 114.9, 86.2, 64.9, 64.5, 56.5, 52.5, 52.4, 47.9. MS, *m/z*: 458 (M^++1, 7), 457 (M^+, 70), 398 (100), 320, 244, 232, 200, 123, 109 and **2,6-dimethoxycarbonyl-5-*endo*-phenylthio-1-(*p*-methoxyphenyl)-1*H*,5*H*,2,2a,5a,6-tetrahydrofuro[3,4-c]pyrrol-3-one (26b)** as a white solid (46mg, 10%), mp 145-146 °C (from acetone-petroleum ether). Anal. Calcd for $C_{23}H_{23}NO_7S$: C, 60.38; H, 5.07; N, 3.06; S, 7.01. Found: C, 60.32; H, 5.02; N, 3.10; S, 6.83. IR: 1785, 1755, 1735, 1515, 1210. ^{1}H-NMR: 7.57-7.53 (m, 2H, arom.), 7.37-7.36 (m, 3H, arom.), 6.82-6.79 (m, 2H, arom.), 6.63-6.60 (m, 2H, arom.), 5.83 (d, 1H, H-5, $J_{5,5a}$= 7.8 Hz), 4.80 (d, 1H, H-2, $J_{2,2a}$= 10.3 Hz), 4.70 (d, 1H, H-6, $J_{5a,6}$= 1.4 Hz), 3.72 (s, 3H, OCH_3), 3.71 (s, 3H, OCH_3), 3.68 (dd, 1H, H-2a, $J_{2,2a}$= 10.3 Hz, $J_{2a,5a}$= 9.7 Hz), 3.65 (s, 3H, OCH_3), 3.10 (ddd, 1H, H-5a, $J_{2a,5a}$= 9,7 Hz, $J_{5,5a}$= 7.8 Hz, $J_{5a,6}$= 1.4 Hz). ^{13}C-NMR: 172.9, 171.6, 170.9, 154.0, 138.1, 133.2, 130.8, 129.4, 128.9, 116.31, 114.98, 89.5, 66.2, 64.4, 55.5, 52.8, 52.5, 50.3, 47.7. MS, *m/z*: 458 (M^++1, 23), 457 (M^+, 60), 398, 320, 244, 232 (100), 200, 123, 109, 77.

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