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Pseudoesters and Derivatives. Part 37.[1] 1,3-Dipolar Cycloaddition of Diazo Compounds to 2(5*H*)-Furanones Substituted at the 5-Position by Sulfur Bearing Groups

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Abstract: The 1,3 dipolar cycloadditions of diazomethane and ethyl diazoacetate with differently substituted 5-sulfur-2(5*H*)-furanones (**1-6**) are reported. Cycloaddition of diazomethane occurs in a regio- and stereospecific manner to give the expected adducts **9-14**, in good yield. The cycloaddition with ethyl diazoacetate occurs also in a regio- and stereospecific manner, but affords the corresponding 2-pyrazolines **15-19**. © 1998 Elsevier Science Ltd. All rights reserved.

INTRODUCTION

1,3-Dipolar cycloaddition reactions are a valuable method for the synthesis of a variety of five-membered heterocyclic compounds.[2] While the cycloaddition to substituted alkenes and alkynes has been extensively investigated, the use of butenolides as dipolarophiles has been limited to a few reports. Some of the reported examples include the addition of diazo compounds,[3] nitrones,[4] nitrile oxides,[5,3h,3i] arylazides,[6] and azomethine ylide.[7]

Some years ago,[3f] as part of our studies on the reactivity of 5-alkoxy-2(5*H*)-furanones, we have shown that these compounds undergo 1,3-dipolar cycloaddition of diazomethane to afford only one regioisomer as a mixture of the epimeric furopyrazolines, which are valuable intermediates for the synthesis of physiologically interesting molecules.

The exchange of the alkoxy group by a sulfur containing group widens the ability as synthons of 2(5*H*)-furanones. Thus, the presence of this group makes the removal of the proton at 5-position easier, and so 5-ethylthiofuran-2(5*H*)-one was readily converted to its anion, which reacts with a variety of electrophilic reagents in regiospecific maner.[8] Moreover, the presence of a thioether or sulfone group at the 5-position may greatly modify the regio- and the stereochemistry of the cycloaddition reactions.

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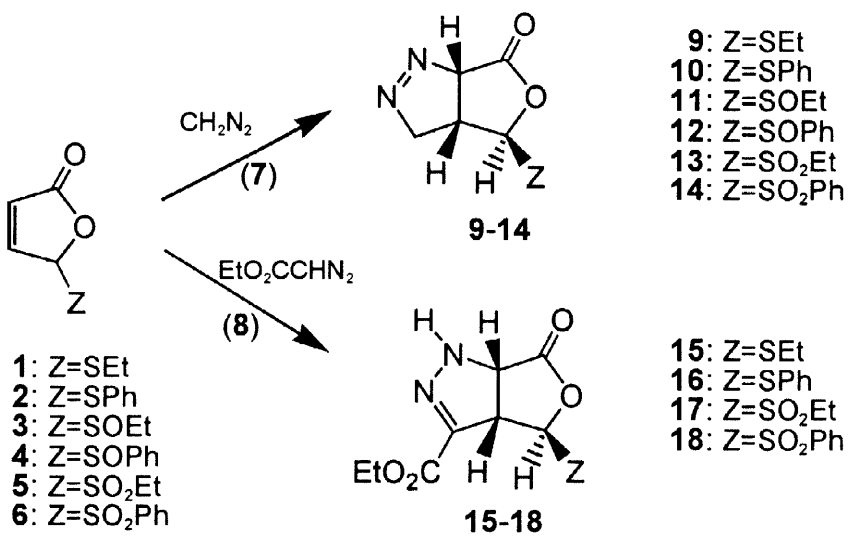
In a recent paper[9] we have reported the cycloaddition of benzo-, aceto- and bromonitrile oxides to 2(5*H*)-furanones substituted at the 5-position by sulfur bearing groups. The cycloaddition with acetonitrile oxide affords only one regioisomer as a mixture of the epimeric furoisoxazolines. However, the reaction with benzo- and bromonitrile oxides affords mixtures of the regio- and stereo-isomer furoisoxazolines.

In the present paper, we study the behaviour of furan-2(5*H*)-ones substituted at the 5-position by sulfur bearing groups such as SEt, SPh, SOEt, SOPh, SO_2Et and SO_2Ph, towards diazo compounds such as diazomethane and ethyl diazoacetate. The reactions have been explored with thioethers, sulfoxides and sulfones to achieve information on the influence of the group at 5-position upon the regio- and stereoselectivity of the cycloaddition.

RESULTS AND DISCUSSION

The preparation of 5-ethylthio- and 5-phenylthiofuran-2(5*H*)-ones (**1**,[10] **2** [11]) and the corresponding sulfoxides **3**,[12] **4**[11] and sulfones **5**[12], **6**[11] used as dipolarophiles has been previously reported by us.

The addition of diazomethane (**7**) to 2(5*H*)-furanones is effected by treatment of the corresponding derivatives of type **1-6** with an excess of ethereal diazomethane at –5°C (Scheme I). The results of these reactions are summarized in Table 1. The reaction was stereo- and regiospecific and led to the corresponding adducts **9-14**, in essentially quantitative yield. The reaction of furanones **3** and **4**, since that are a 1:1 mixture of diastereoisomers, afford mixtures of diastereoisomeric adducts. The ratio of diastereoisomeric adducts **11**,



Scheme I

11' (1:1) **and 12, 12'** (1:1) has been determined by integration of the H-4 proton signal in ^{1}H-NMR spectra.

The direction of the cycloaddition is the expected in accord with the early von Auwers rule[13] and with the results previously obtained by us in the corresponding 5-methoxyfuran-2(5*H*)-ones.[3f] The addition of furanones **2, 4** and **6** takes place at slower rate than those of furanones **1, 3** and **5**.

The cycloadducts from furanones **1, 2, 4, 5, 6,** are stable enough at room temperature, thus allowing their full characterization by analytical and spectral data. In these cases no traces of spontaneous decomposition has been observed. In contrast, the adducts from sulfoxide **3** are unstable at room temperature, thus avoiding the purification of the diastereoisomers, the characterization has only effected on the basis of their ^{1}H-NMR spectra.

Table 1. Cycloaddition of diazomethane to 2 (5*H*)-furanones **1-6**.

Furanone	Z	Time	Yield %	Product
1	SEt	15 h	95	**9**
2	SPh	24 h	90	**10**
3	SOEt	5 h	69	**11**[a]
4	SOPh	72 h	65	**12**[a]
5	SO_2Et	2 h	90	**13**
6	SO_2Ph	9 h	95	**14**

[a] Mixture of diastereoisomers

The structure of the adducts was established on the basis of their spectral data. Thus, the presence of bands approximately at 1780 (C=O) and 1550 (N=N) and the absence of bands over 3000 cm^{-1} (NH) in the IR spectra are indicative of the existence of a saturated δ-lactona and 1-pyrazoline moities.

Table 2. ^{1}H-NMR chemical shifts and coupling constants of adducts **9-14**.

Comp.	Z	H-6a	H-4	H-3	H-3	H-3a	$J_{6a,3a}$	$J_{4,3a}$
9	SEt	5.58	5.10	4.85	4.85	2.86-2.80	9.0	4.6
10	SPh	5.32	5.22	4.86	4.86	3.00-2.87	9.0	4.4
11[a]	SOEt	5.86	4.90	5.22	4.79	3.34-3.26	9.1	1.6
11'[a]	SOEt	5.75	4.89	4.98	4.78	3.20-3.14	9.5	3.4
12[a]	SOPh	5.75	5.47	4.50	4.50	3.08-3.02	9.5	3.3
12'[a]	SOPh	5.86	5.54	5.15	4.91	3.42-3.29	9.4	1.7
13	SO_2Et	5.82	4.88	5.21	4.86	3.50-3.41	9.3	2.3
14	SO_2Ph	6.03	5.84	5.13	5.03	3.50-3.34	9.5	2.4

[a]DMSO-d_6

The regioisomeric assignments could be made from a detailed study of their ^{1}H-NMR spectra (Table 2) and on the basis of the previously reported structure of the adduct isolated in the cycloaddition of the same dipolo to the 5-methoxyfuran-2(5H)-ones.[3f] The *cis* or *trans* relationship between H-4 and H-3a protons, and consequently the *face*-selectivity of the cycloaddition, was assigned from the ^{1}H-NMR data (Table 2). A coupling constant $J_{3a,4}$ =1.7-4.6 Hz suggests a *trans* relationship (*exo* Z group).

Next we studied the cycloaddition of furanones **1, 2, 5** and **6** with ethyl diazoacetate (**8**). The reactions were carried out in dichloromethane at room temperature affording the adducts **15-18** (Scheme I), and the results are summarized in Table 3. The reaction occurs in a regio- and stereospecific manner to afford the 2-pyrazoline with the ester CO group conjugated with the C=N, in accord with previous results reported for 2(5*H*)-furanones.[3d,3h] It should be noted that isomerization to the 2-pyrazoline structure has occurred in the reaction and therefore no 1-pyrazoline isomers were found. However, attempts to cycloaddition reaction of the sulfoxides **3** and **4** failed to afford the expected cycloadducts, presumably due to the easy decomposition of starting sulfoxides.

Table 3. Cycloaddition of ethyl diazoacetate to 2 (5*H*)-furanones **1, 2, 5** and **6**

Furanone	Z	Time	Yield %	Product
1	SEt	20 d[a]	30	**15**
2	SPh	20 d[a]	30	**16**
5	SO_2Et	15 d[b]	30	**17**
6	SO_2Ph	10 d[b]	35	**18**

[a]Time required for a 50% conversion at room temperature.
[b]Time required for a 80% conversion at room temperature

The structure of 2-pyrazolines in adducts **15-18**, was evidence by the presence of bands approximately at 1550 (C=N) and over 3300 cm^{-1} (NH) in the IR spectra and from the ^{1}H-NMR spectra (Table 4) which indicate the presence of NH group (broad singlet at δ 7.00 ppm). Moreover the absence of a coupling constant $J_{3a,4}$ suggests a *trans* relationship (*exo* Z group) between H-4 and H-3a protons.

Table 4. ^{1}H-NMR chemical shifts and coupling constants of adducts **15-18**.

Comp.	Z	NH	H-4	H-6a	H-3a	$J_{6a,3a}$	$J_{4,3a}$
15	SEt	7.17	5.97	4.69	4.02	10.5	-
16	SPh	6.91	6.06	4.15	3.91	10.6	1.1
17	SO_2Et	7.26	5.68	4.82	4.56	10.7	-
18	SO_2Ph	7.18	5.60	4.88	4.72	10.6	-

The regioselectivity observed is in accord with the reported for cycloaddition of the same dipole to 5-methoxyfuran-2(5*H*)-one.[3h] However, the stereoselectivity is bigger than the observed in the above case.

The exclusive formation of the pyrazolines with the sulfur containing group in *exo* arrangement, suggest that the attack of diazo compounds such as diazomethane and ethyl diazoacetate occurs preferentially at the face opposite to the Z group. This result suggests that the nature of the substituents at the 5-position of the 2(5*H*)-furanones plays a significant role, in controlling the regio- and stereoselectivity of the reaction. The furopyrazolines obtained are useful synthon for the synthesis of new fused heterocyclic systems.

EXPERIMENTAL

Melting points were determined with a Kofler hot-stage apparatus and are uncorrected. Microanalyses were performed with a Heraeus analyzer model CHN-O-rapid. 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 analitical tlc, respectively.

Cycloaddition of Diazomethane (8) to furanones 1-6. General Procedure

To a solution of 2(5*H*)-furanone **1-6** (1 mmol) in dichlorometane (7 ml) cooled to –5°C, was added a cold ethereal solution of diazomethane (7) (6 ml, 3 mmol). The reaction mixture was kept at –5°C during the period indicated in Table 1 for each case. The solvent was removed and the residue was analyzed by ^{1}H-NMR. The crude product was purified by column chromatography

***Exo*-4-ethylthio-3*H*,4*H*,3a,6a-dihydrofuro[3,4-c]pyrazol-6-one (9).** From furanone **1** (95%) as a white solid. (Petroleum ether-ethyl acetate, 2:1). M.p. 58-60°C (carbon tetrachloride). Anal. Calcd for $C_7H_{10}N_2O_2S$: C, 45.15; H, 5.41; N, 15.04. Found: C, 45.40; H, 5.45; N, 15.31. IR: 1785, 1555. ^{1}H-NMR: 5.58 (dt, 1H, H-6a, $J_{6a,3}$=2.0 Hz, $J_{6a,3a}$=9.0 Hz); 5.11 (d, 1H, H-4, $J_{4,3a}$=4.6 Hz); 4.87-4.83 (m, 2H, H-3); 2.86-2.80 (m, 1H, H-3a); 2.79-2.64 (m, 2H, S-CH_2); 1.29 (t, 3H, CH_3, J=7.4 Hz). ^{13}C-NMR: 167.3 (C-6); 93.5, 89.1 (C-6a, C-4); 85.1 (C-3); 38.5 (C-3a); 26.1 (CH_2); 14.5 (CH_3). Ms, *m/z*: 187 (M^++1, 2); 186 (M^+, 0.3); 159; 97 (100); 69; 45; 41.

***Exo*-4-phenylthio-3*H*,4*H*,3a,6a-dihydrofuro[3,4-c]pyrazol-6.-one (10).** From furanone **2** (90%) as a white solid. (Petroleum ether-ethyl acetate, 3:1). M.p. 100-102°C. Anal. Calcd for $C_{11}H_{10}N_2O_2S$: C, 56.41; H, 4.27; N, 11.96. Found: C, 56.40; H, 4.33; N, 11.75. IR: 1770, 1560. ^{1}H-NMR: 7.50-7.44 (m, 2H, arom.); 7.37-7.29 (m, 3H, arom.); 5.32 (dt, 1H, H-6a, $J_{6a,3a}$=9.0 Hz, $J_{6a,3}$=2.0 Hz); 5.22 (d, 1H, H-4, $J_{4,3a}$=4.4 Hz); 4.88-4.84 (m, 2H, H-3); 3.00-2.87 (m, 1H, H-3a). ^{13}C-NMR: 167.0 (C-6); 133.4, 130.2, 129.4, 129.1 (arom.); 93.3, 90.7 (C-6a, C-4); 85.2 (C-3); 38.5 (C-3a). Ms, *m/z*: 234 (M^+, 3); 206; 110; 109; 97 (100); 69; 65; 51; 41.

***Exo*-4-ethylsulfinyl-3*H*,4*H*,3a,6a-dihydrofuro[3,4-c]pyrazol-6-one (11)**. From furanone **3** (69%) as a mixture of diastereoisomers **11: 11'** in the ratio 1:1. ^{1}H-NMR (DMSO-d_6): 5.86 (dq, 1H, H-6a, $J_{6a,3a}$=9.1 Hz, $J_{6a,3}$=1.4 Hz, **11**); 5.22 (dd, 1H, H-3, J_{gem}=19.4 Hz, $J_{3,3a}$=9.7 Hz, **11**); 4.90 (d, 1H, H-4, $J_{4,3a}$=1.6 Hz, **11**); 4.79 (dq, 1H, H'-3, $J_{3,3a}$=1.4 Hz, **11**); 3.34-3.26 (m, 1H, H-3a, **11**); 3,05-2.98 (m, 1H, S-CH_2, **11**); 2.85-2.78 (m, 1H, S-CH_2, **11**); 1.32 (t, 3H, CH_3, J=7.6 Hz, **11**). ^{1}H-NMR (DMSO-d_6): 5.75 (dq, 1H, H-6a, $J_{6a,3a}$=9.5 Hz, $J_{6a,3}$=1.3 Hz, **11'**); 4.98 (dd, 1H, H-3, $J_{3,3a}$=9.7 Hz, J_{gem}=19.1 Hz, **11'**); 4.89 (d, 1H, H-4, $J_{4,3a}$=3.4 Hz, **11'**); 4.78 (dq, 1H, H'-3, $J_{3,3a}$=3.3 Hz, **11'**); 3.20-3.14 (m, 1H, H-3a, **11'**); 2.90-2.80 (m, 2H, S-CH_2, **11'**); 1.43 (t, 3H, CH_3, J=7.6 Hz, **11'**).

***Exo*-4-phenylsulfinyl-3*H*,4*H*,3a,6a-dihydrofuro[3,4-c]pyrazol-6-one (12)**. From furanone **4** (65%) as a mixture of diastereoisomers **12**:**12'** in the ratio 1:1.(Chloroform-ethyl acetate, 3:1). Adduct **12**: (33%) as a white solid. M.p. 115-118°C. Anal. Calcd for $C_{11}H_{10}N_2O_3S$: C, 52.80; H, 4.00; N, 11.20. Found: C, 52.84; H, 4.28; N, 10.75. IR: 1780, 1550, 1150, 1090, 1000. ^{1}H-NMR (DMSO-d_6): 7.73-7.62 (m, 5H, arom.); 5.75 (dt, 1H, H-6a, $J_{6a,3a}$=9.5 Hz, $J_{6a,3}$= 1.2 Hz); 5.47 (d, 1H, H-4, $J_{4,3a}$=3.3 Hz); 4.52-4.47 (m, 2H, H-3); 3.08-3.02 (m, 1H, H-3a). ^{13}C-NMR (DMSO-d_6): 167.7 (C-6); 137.6, 131.8, 129.6, 124.6 (arom.); 97.6, 92.7 (C-6a, C-4); 84.7 (C-3); 28.4 (C-3a). Ms, *m/z*: 218 (8); 125; 110; 109; 97 (100); 77; 69; 65; 51; 41. Adduct **12'**: (32%) as a white solid. M.p. 148-150°C. Anal. Calcd for $C_{11}H_{10}N_2O_3S$: C, 52.80; H, 4.00; N, 11.20. Found: C, 53.07; H, 4.32; N, 10.97. IR: 1785, 1585, 1560, 1090, 1050, 1010. ^{1}H-NMR (DMSO-d_6): 7.70-7.56 (m, 5H, arom.); 5.86 (dt, 1H, H-6a, $J_{6a,3a}$=9.4 Hz, $J_{6a,3}$=1.6 Hz); 5.54 (d, 1H, H-4, $J_{4,3a}$=1.7 Hz); 5.15 (dd, 1H, H-3, J_{gem}=19.0 Hz, $J_{3a,3}$=9.9 Hz); 4.91 (ddd, 1H, H'-3, J_{gem}=19.0 Hz, $J_{3,3a}$=2.6 Hz, $J_{6a,3}$=1.6 Hz); 3.42-3.29 (m, 1H, H-3a). ^{13}C-NMR (DMSO-d_6): 167.5 (C-6); 139.1, 131.5, 129.2, 124.9 (arom.); 95.1, 91.1 (C-6a, C-4); 85.7 (C-3); 34.4 (C-3a). Ms, *m/z*: 218 (47); 125; 110; 109 (100); 97; 77; 69; 65; 51; 44; 41.

***Exo*-4-ethylsulfonyl-3*H*,4*H*,3a,6a-dihydrofuro[3,4-c]pyrazol-6-one (13)**. From furanone **5**, the adduct was isolated by filtration (90%) as a yellow solid. M.p. 168-170°C. Anal. Calcd for $C_7H_{10}N_2O_4S$: C, 38.53; H, 4.62; N, 12.84. Found: C, 38.38; H, 4.60; N, 13.00. IR: 1810, 1560, 1320, 1160, 1140. ^{1}H-NMR: 5.82 (ddd, 1H, H-6a, $J_{6a,3}$=1.1 Hz, $J_{6a,3a}$=9.3 Hz, $J_{6a,3}$=1.3 Hz); 5.21 (ddd, 1H, H-3, J_{gem}=19.0 Hz, $J_{3a,3}$=9.8 Hz, $J_{6a,3}$=1.1 Hz); 4.88 (d, 1H, H-4, $J_{4,3a}$=2.3 Hz); 4.92-4.84 (m, 1H, H'-3); 3.50-3.41 (m, 1H, H-3a); 3.17 (q, 2H, S-CH_2); 1.44 (t, 3H, CH_3, J=7.5 Hz). ^{13}C-NMR (DMSO-d_6): 167.3 (C-6); 91.6 (C-6a); 89.7 (C-4); 85.4 (C-3); 44.1 (S-CH_2); 30.0 (C-3a); 5.7 (CH_3). Ms, *m/z*: 218 (M^+, 24), 97, 69, 53; 41 (100).

***Exo*-4-phenylsulfonyl-3*H*,4*H*,3a,6a-dihydrofuro[3,4-c]pyrazol-6-one (14)**. From furanone **6**, the adduct was isolated by filtration (95%) as a yellow solid. M.p. 153-155°C. Anal. Calcd for $C_{11}H_{10}N_2O_4S$: C, 49.62; H, 3.76; N, 10.53. Found C, 49.53; H, 3.92; N, 10.35. IR: 1800, 1585, 1565, 1320, 1165. ^{1}H-NMR (DMSO-d_6): 7.92-7.84 (m, 3H, arom.); 7.77-7.72 (m, 2H, arom.); 6.03 (dt, 1H, H-6a, $J_{6a,3a}$=9.5 Hz, $J_{6a,3}$=1.3 Hz); 5.84 (d, 1H, H-4, $J_{4,3a}$=2.4 Hz); 5.19 (dd, 1H, H-3, J_{gem}=18.9 Hz, $J_{3,3a}$=9.6 Hz); 5.03 (ddd, 1H, H'-3, J_{gem}=18.9 Hz, $J_{3,3a}$=2.5 Hz,

$J_{6a,3}$=1.3 Hz); 3.50-3.34 (m, 1H, H-3a). ^{13}C-NMR (DMSO-d_6): 167.4 (C-6); 135.5, 134.8, 130.1, 129.3 (arom.); 92.4, 91.8 (C-6a, C-4); 85.6 (C-3); 31.3 (C-3a). Ms, *m/z*: 266 (M^+, 0.5); 97 (100); 77; 69; 51; 41.

Cycloaddition of Ethyl Diazoacetate (8) to furanones 1, 2, 5, 6. General Procedure

To a solution of 2(5*H*)-furanone **1**, **2**, **5** and **6** (1 mmol) in dichlorometane (3 ml) was added ethyl diazoacetate (**8**) (0,2 ml, 2 mmol) and the mixture was allowed to stand at room temperature during the period indicated in Table 3 for each case. The solvent was removed, the residue was analyzed by ^{1}H-NMR. The crude product was purified by column chromatography.

***Exo*-4-ethylthio-3-ethoxycarbonyl-1*H*,4*H*,3a,6a-dihydrofuro[3,4-c]pyrazol-6-one (15)**. From furanone **1** (30%) as a white solid. (Petroleum ether-ethyl acetate, 3:1). M.p. 110-112°C (toluene/ hexane). Anal. Calcd for $C_{10}H_{14}N_2O_4S$: C, 46.51; H, 5.43; N, 10.85; S, 12.40. Found: C, 46.80; H, 5.71; N, 10.76; S, 12.34. IR (KBr): 3280, 1790, 1695, 1545. ^{1}H-NMR: 7.17 (s, 1H, NH); 5.97 (s, 1H, H-4); 4.69 (d, 1H, H-6a, $J_{6a,3a}$=10.5 Hz); 4.35-4.28 (m, 2H, $COOCH_2$); 4.02 (d, 1H, H-3a, $J_{6a,3a}$= 10.5 Hz); 2.83-2.74 (m, 2H, S-CH_2); 1.35 (t, 3H, J=7.0 Hz); 1.34 (t, 3H, J=7.5 Hz). ^{13}C-NMR: 174.8 (C-6); 161.7 (COOEt); 140.6 (C-3); 86.7 (C-4); 62.3 (COO-$\underline{C}H_2$-CH_3); 61.9 (C-6a); 52.9 (C-3a); 26.4 (S-CH_2); 15.1, 14.7 (CH_3). Ms, *m/z*: 258 (M^+, 0.3); 214; 170; 168; 154; 141; 139; 125; 113; 111; 95 (100); 83; 69; 55.

***Exo*-4-phenylthio-3-ethoxycarbonyl-1*H*,4*H*,3a,6a-dihydrofuro[3,4-c]pyrazol-6-one (16)**. From furanone **2** (30%) as a yellow solid.(Petroleum ether-ethyl acetate, 3:1). M.p. 92-93°C (toluene/ hexane). Anal. Calcd for $C_{14}H_{14}N_2O_4S$: C, 54.90; H, 4.58; N, 9.15; S, 10.46. Found: C, 55.18; H, 4.80; N, 9.15; S, 10.52. IR (KBr): 3340, 3320, 1780, 1710, 1700, 1550. ^{1}H-NMR: 7.60-7.54 (m, 2H, arom.); 7.40-7.35 (m, 3H, arom.); 6.91 (s, 1H, NH); 6.06 (d, 1H, H-4, $J_{4,3a}$=1.1); 4.31 (q, 2H, $COOCH_2$); 4.15 (d, 1H, H-6a, $J_{6a,3a}$=10.6, Hz); 3.91 (d, 1H, H-3a, $J_{6a,3a}$=10.6 Hz); 1.30 (t, 3H, CH_3, J=7.5 Hz). ^{13}C-NMR: 173.9 (C-6); 161.2 (COOEt); 140.2 (C-3); 135.1, 129.7, 129.5, 129.3 (arom.); 87.9 (C-4); 61.8 (CH_2); 61.1 (C-6a); 53.2 (C-3a); 14.2 (CH_3). Ms, *m/z*: 306 (M^+, 4); 197; 169; 153; 141; 125; 113; 110; 109; 95 (100); 83; 77; 65; 55.

***Exo*-4-ethylsulfonyl-3-ethoxycarbonyl-1*H*,4*H*,3a,6a-dihydrofuro[3,4-c]pyrazol-6-one (17)**. From furanone **5** (30%) as a yellow solid. (Petroleum ether-ethyl acetate, 3:1). M.p. 121-122°C (toluene/ hexane). Anal. Calcd for $C_{10}H_{14}N_2O_6S$: C, 41.38; H, 4.83; N, 9.65; S, 11.03. Found: C, 41.60; H, 5.10; N, 9.44; S, 11.01. IR (KBr): 3330, 1810, 1680, 1555, 1330, 1320, 1150. ^{1}H-NMR: 7.26 (s, 1H, NH); 5.68 (s, 1H, H-4); 4.82 (d, 1H, H-6a, $J_{6a,3a}$=10.7 Hz); 4.56 (d, 1H, H-3a, $J_{6a,3a}$=10.7 Hz); 4.40-4.24 (m, 2H, $COOCH_2$); 3.18 (q, 2H, SOO-CH_2); 1.44 (t, 3H, CH_3, J=7.5 Hz); 1.34 (t, 3H, CH_3, J=7.1 Hz). ^{13}C-NMR: 172.9 (C-6); 161.0 (COOEt); 137.8 (C-3); 87.9 (C-4); 62.0 (CH_2); 60.1 (C-6a); 45.4 (S-CH_2); 44.9 (C-3a); 14.1 (CH_3); 6.0 (CH_3). Ms, *m/z*: 290 (M^+, 2); 245; 197; 167; 141; 123; 113; 95 (100); 83; 68; 55.

***Exo*-4-phenylsulfonyl-3-ethoxycarbonyl-1*H*,4*H*,3a,6a-dihydrofuro[3,4-c]pyrazol-6-one (18).** From furanone **6** (35%) as a yellow solid. (Toluene-ethyl acetate, 8:1). M.p. 149-150°C (toluene/ hexane). Anal. Calcd for $C_{14}H_{14}N_2O_6S$: C, 49.70; H, 4.14; N, 8.28; S, 9.47. Found: C, 49.38; H, 4.13; N, 8.55; S, 9.89. IR (KBr): 3300, 1820, 1710, 1685, 1560, 1335, 1160. ^{1}H-NMR: 7.96-7.91 (m, 2H, arom.); 7.74-7.57 (m, 3H, arom); 7.18 (s, 1H, NH); 5.60 (s, 1H, H-4); 4.88 (d, 1H, H-6a, $J_{6a,3a}$=10.6 Hz); 4.72 (d, 1H, H-3a, $J_{6a,3a}$=10.6 Hz); 4.28-4.25 (m, 2H, CH_2); 1.34 (t, 3H, CH_3, J=7.0 Hz). ^{13}C-NMR: 172.9 (C-6); 160.9 (COOEt); 146.4 (C-3); 135.5, 129.6, 129.4 (arom.); 90.6 (C-4); 61.7 (CH_2); 60.2 (C-6a); 46.3 (C-3a); 14.0 (CH_3). Ms, *m/z*: 338 (M^+, 0,1); 213; 197; 167; 141; 95 (100); 83; 77; 55.

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