Pergamon

Tetrahedron: Asymmetry, Vol. 7, No. 7, pp. 1943-1950, 1996

0957-4166/96 $15.00 + 0.00

PII: S0957-4166(96)00233-9

(S_S)-5-Ethoxy-3-*p*-Tolylsulfinylfuran-2(5*H*)-ones as Chiral Dipolarophiles: First Asymmetric Cycloaddition of Diazomethane to Vinyl Sulfoxides

Jose L. García Ruano,* Alberto Fraile and M. Rosario Martín.*

Departamento de Química Orgánica, Universidad Autónoma de Madrid, Cantoblanco 28049-Madrid, SPAIN

Abstract: Cycloadditions of diazomethane to (S_S)-5-ethoxy-3-*p*-tolylsulfinylfuran-2(5*H*)-ones **1a-b** and their corresponding 4-methyl derivatives **3a-b**, proceeds in quantitative yields, to give enantiomerically pure 3*H*,6*H*,3a,6a-dihydrofuro[3,4-c]pyrazol-4-ones **2a-b** and **4a-b**, respectively. The sulfinyl group at C-3 strongly increases both the reactivity and the π-facial selectivity. The dipole approach mode is determined by the configuration at the sulfinyl group. Pyrolysis of pyrazolines **2a** or **2b** gives the methyl derivatives **3a** or **3b** in excellent yield. Copyright © 1996 Published by Elsevier Science Ltd

The sulfinyl group has been widely used as a chiral auxiliary in numerous asymmetric transformations,[1] the use of α,β-unsaturated sulfoxides in asymmetric Diels-Alder reactions being one of the best studied due to the efficiency of the sulfinyl group to control both the regioselectivity and the π-facial selectivity of the cycloadditions.[1,2] By contrast, the use of homochiral vinylsulfoxides as dipolarophiles has been less investigated and there are very few examples about 1,3-dipolar cycloaddition on these substrates.[3] Surprisingly, to our knowledge reactions with diazomethane[4] are not included among these examples, despite this reagent is one of the simplest and best known dipoles.

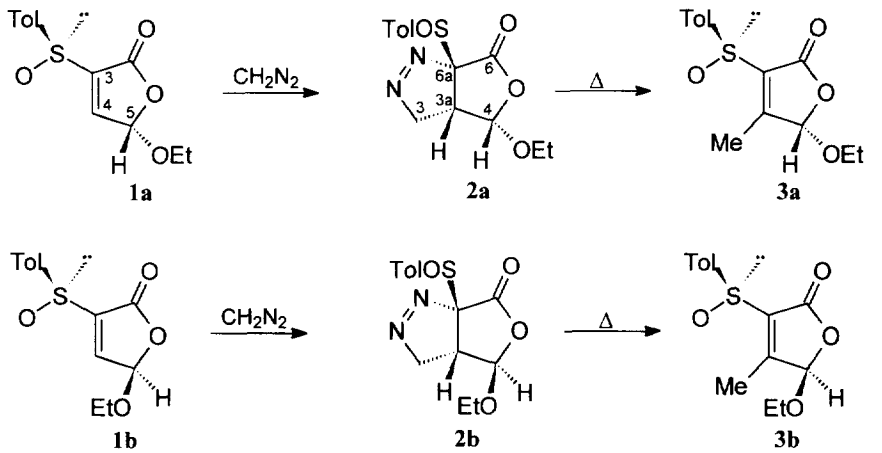
5-Alkoxyfuran-2(5*H*)-ones are valuable synthetic intermediates which have shown to be appropriate dipolarophiles for 1,3-dipolar cycloadditions.[5] The pioneering studies concerning their reactions with diazomethane were reported by Fariña and coworkers, describing its completely regioselective addition to differently substituted racemic 5-methoxyfuran-2(5*H*)-ones.[6] Despite this interest, the use of these dipolarophiles in asymmetric synthesis has only been reported by Feringa,[7] Grigg[8] and Hegedus.[9] The moderate reactivity of the 5-menthyloxyfuran-2(5*H*)-one and its 3-methyl derivative with diazomethane, as well as the low π-facial selectivity of the cycloadditions (d.e.<20%),[7a] strongly decreased their synthetic interest.

Few years ago, we reported the synthesis of the (S_S)-5-ethoxy-3-*p*-tolylsulfinyl-2(5*H*)-furanones and their behaviour in asymmetric Diels-Alder reactions with cyclopentadiene.[10] In this study we found a barely

positive influence of the sulfinyl group on the reactivity. Additionally, its effect on the π-facial selectivity was important but less than that of the configuration at C-5. Now, we consider that these furanones could be interesting substrates to evaluate the influence of the sulfinyl group on the 1,3-dipolar cycloadditions with diazomethane. Moreover, the resulting adduct might offer a quick access to enantiomerically pure functionalized cyclopropanes.[7a] In this paper we report the results obtained in the reactions of diazomethane with the homochiral (S_S)-5-ethoxy-3-*p*-tolylsulfinyl-2(5*H*)-furanones, **1a-b**, which have allowed us to synthesize enantiomerically pure furanones **3a-b**. The behaviour of the latter substrates as dipolarophiles are also reported.

RESULTS AND DISCUSSION

Treatment of sulfinylfuranones **1a** or **1b** with an excess of ethereal diazomethane, at 0 °C for 5 minutes, afforded only compound **2a** or **2b**, in quantitative yield. ^{1}H-NMR analysis of the crude reactions revealed the formation of such compounds as a sole stereoisomer (Scheme 1). Taking into account that the value of the coupling constants $^3J_{3a,4}$ are quite different for the adducts bearing different relative configuration of C-3a and C-4[6,7,11] we have assigned to compounds **2a** and **2b** the stereochemistry depicted in Scheme 1. Thus, $J_{3a,4}$= 6.8 Hz in **2a**, indicating that the *cis*-fused dihydropyrazole ring must exhibit a *cis*-arrangement with respect to the ethoxy group at the lactone moiety, whereas the value of the vicinal coupling constant is only 1.6 Hz in compound **2b**, which implies a *trans* relationship between H-3a and H-4. This stereochemistry has been confirmed by NOESY experiments.



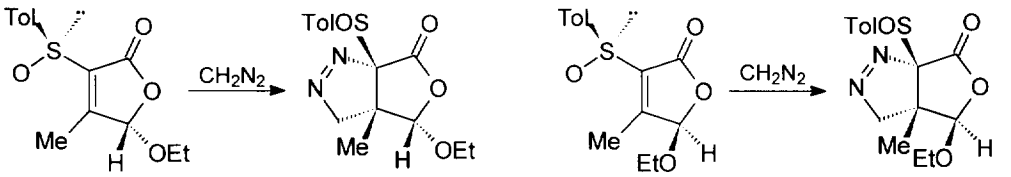
Scheme 1

Several facts come out from these reactions. First of all, the significant stability of the obtained $^1\Delta$-pyrazolines, which remain unaltered for months in the refrigerator, **2a** and **2b** turn out to be the first enantiomerically pure sulfinylpyrazolines that have been fully characterized.[12,13] Second, the complete regio

and stereoselectivity of these cycloadditions, yielding only one isomer is remarkable. According to the results obtained with other furanones,[6,7,14] the high regioselectivity was not unexpected, but the observed high π-facial selectivity contrasts with both the results obtained in previously reported reactions of diazomethane with 5-alkoxyfuranones (d.e <20%),[7a] and those of the Diels-Alder reaction of **1a** and **1b** with cyclopentadiene (similar influence of the configurations at sulfur and C-5 on the π-facial selectivity).[10] It indicates that in these 1,3-dipolar reactions the attack of diazomethane is completely controlled by the configuration at the sulfinyl group. Finally, the third remarkable fact is the substantial increase in the reactivity with diazomethane induced by the sulfinyl group on furan-2(5*H*)-ones. Thus, reactions of **1a** and **1b** are instantaneous at 0°C, whereas other furan-2(5*H*)-ones, lacking of the sulfinyl group, required at least 12 h to be completed. This behaviour also contrasts with the lack of influence that the sulfinyl group has on the reactivity of furan-2(5*H*)-ones with cyclopentadiene.[10]

Pyrolysis of pyrazolines **2a** and **2b**, by heating at 100 °C in toluene, gave the respective 4-methyl substituted furanones **3a** and **3b** (Scheme 1) in excellent yields. It should be noted that cyclopropane derivatives were not detected in these reactions and therefore they provide a convenient method for the introduction a methyl group at the 4-position of 3-sulfinyl-5-alkoxyfuran-2(5*H*)-ones.[15]

1,3-Dipolar cycloaddition of diazomethane to **3a** and **3b** also occurs in a complete regio- and stereoselective manner, yielding a sole adduct (**4a** and **4b**) in very good yields. The structure and relative stereochemistry of these adducts were assigned on the basis of their ^{1}H-NMR spectra and NOESY experiments.

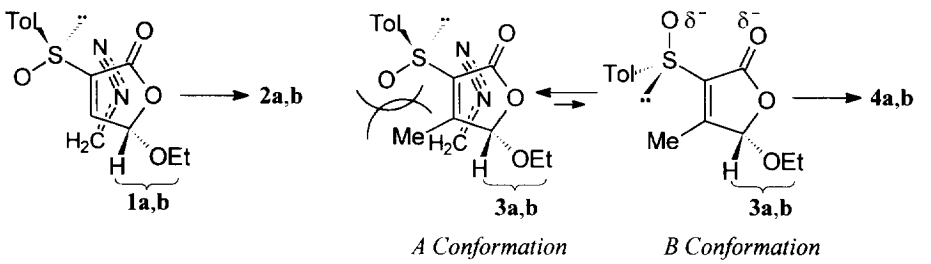


3a **4a** **3b** **4b**

Scheme 2

As we can see in Scheme 2, the π-facial selectivity shown in these cycloadditions seems to be identical to that of the furanones **1a** and **1b**. On the other hand, the lower reactivity of the methylfuranones **3a** and **3b** (they required 1.5-3 h at 0°C) than exhibited by **1a** and **1b** (which only required 5 minutes) was not unexpected taking into account the results reported in the literature for the 3- or 4-methylfuranones.[6,7a] The great influence of the sulfinyl group, increasing the reactivity of furan-2(5*H*)-ones, becomes more evident when **3a** and **3b** are used as dipolarophiles, since the reactions of racemic 5-methoxy-4-methylfuran-2(5*H*)-one requires 540 hours to attain only a partial conversion (ca. 50%).[6]

The stereochemical results evidence a *anti*-facial approach of diazomethane with respect to the ethoxy-substituent in compounds **1b** and **3b**, but an *syn*-facial approach when the reaction takes place on **1a** or **3a**. In the case of dipolarophiles **1a** and **3a**, this behaviour might be explained by assuming an steric approach control of diazomethane from the less hindered face of the sulfinyl group (that displaying the lone electron pair at sulfur) in the most stable (from an electrostatic point of view) and reactive conformation around the C-S bond, which is that exhibiting the sulfinyl oxygen in an *s-cis* arrangement (Scheme 3). The clearly higher effect of the sulfinyl group on the stereoselectivity of the 1,3-dipolar cycloadditions of furan-2(5*H*)-ones, with respect to that observed in their corresponding Diels-Alder reactions with cyclopentadiene, could be a consequence of the fewer steric requirements of diazomethane than those of the cyclopentadiene.[16] Nevertheless, the fact that the same complete π-facial selectivity was observed in reactions from **3a** and **3b**, where the *s-cis* arrangement of the sulfinyl oxygen must be unstabilized by the methyl group (Scheme 3), suggests that electrostatic repulsion in B conformation must be more unstabilizing that steric repulsion in A conformation. Thus the favoured approach must take place on conformations like A. Stabilizing electronic factors involving the sulfinyl group and the nitrogen could contribute to make easier the approach from the face of dipolarophile bearing the electronic pair. This interaction, which must be absent in reactions with cyclopentadiene, could also justify the significant increase in the reactivity of furan-2(5*H*)-ones with diazomethane caused by the sulfinyl group, which was not observed in the Diels-Alder reactions.



Scheme 3

In summary, we have reported herein the first asymmetric 1,3-dipolar cycloaddition of diazomethane with enantiomerically pure vinylsulfoxides, and we have evidenced the highly beneficial effect of the sulfinyl group on both reactivity and π-facial selectivity of these cycloadditions.

We are currently studying the reactions of these dipolarophiles (and other vinylsulfoxides) with 1,3-dipoles different to diazomethane, as well as the effect of Lewis acids on the reactivity and stereoselectivity of these cycloadditions.

EXPERIMENTAL

M.p.s are uncorrected. Microanalyses were performed with a Heraeus analyser. IR spectra were recorded on a Perkin-Elmer model 681 grating spectrophotometer, ν values in cm^{-1}. ^{1}H- and ^{13}C-NMR

spectra were determined with a Bruker AC-200 spectrometer, in $CDCl_3$ solutions. Chemical shifts are reported in p.p.m. (δ) downfield from Me_4Si, J in Hz. Silica gel Merck 60 (230-400 mesh) and DC-Alufolien 60 F_{254} were used for flash column chromatography and analytical t.l.c., respectively. The NOESY experiments of the adducts **2a**,**b** and **4a**,**b** were determined with a Bruker AMX-300 spectrometer, in $CDCl_3$ solutions. Optical rotations were measured with a Perkin-Elmer model 241 polarimeter, at room temperature in $CHCl_3$ solution [1 g/100 mL].

Cycloadditions of diazomethane to (S_5,S_S)- and (R_5,S_S)-ethoxy-3-(*p*-tolylsulfinyl)furan-2(5*H*)-ones (1a and 1b).

General procedure. To a solution of the furanone **1** (521 mg, 1.95 mmol) in diethyl ether (45 mL), at 0 °C, was added an ethereal solution of diazomethane (40 mL, containing 0.6 mmol/mL). The reaction was stirred at 0 °C for 5 min. Disappearance of the starting furanone was monitored by t.l.c. After evaporation of solvent under reduced pressure, the residue was analyzed by ^{1}H NMR.

a) The crude reaction product obtained from **1a** contains pyrazoline **2a** as a sole compound, which was purified by flash column chromatography (hexane/ethyl ether/dichloromethane 35:5:60) to afford **2a** in a 96% yield (578 mg, 1.79 mmol).

b) The crude reaction obtained from **1b** contains **2b** as a sole product, which was purified by flash column chromatography (hexane/ethyl ether/dichloromethane 35:5:60) to afford **2b** in a 97% yield (578 mg, 1.79 mmol).

c) From a 1:1 mixture of furanones **1a** and **1b** the crude reaction obtained contains a 1:1 mixture of the cycloadducts **2a** and **2b**. The pyrazolines were separated and purified by flash column chromatography (hexane/ethyl ether/dichloromethane 35:5:60) to afford **2a** and **2b** in a 49% yield (98% combined yield).

(S_{3a},S_4,R_{6a},S_S)-4-Ethoxy-6a-(p-tolylsulfinyl)-3H,4H-3a,6a-dihydrofuro[3,4-c]pyrazol-6-one (2a)

White solid of m.p. 99-101°C. $[\alpha]_D$: + 258.8. IR (KBr): 1770 (C=O), 1600 (-N=N-). ^{1}H NMR: 1.13 (t, 3H, $CH_2\underline{CH_3}$, J=7.0); 2.45 (s, 3H, CH_3); 3.28 (ddd, 1H, H_{3a}, $J_{3a,3endo}$=3.0, $J_{3a,4}$=6.8, $J_{3a,3exo}$=9.3); 3.46 (m, 1H, $\underline{CH_2}CH_3$,); 3.69 (m, 1H, $\underline{CH_2}CH_3$); 4.66 (dd, 1H, H_{3exo}, $J_{3a,3exo}$=9.3, $J_{3exo,3endo}$=19.0); 4.86 (d, 1H, H_4, $J_{3a,4}$=6.8); 5.29 (dd, 1H, H_{3endo}); 7.40 and 7.62 (AA'BB' system, 4H, arom.). ^{13}C NMR: 14.5 ($CH_2\underline{C}H_3$); 21.5 (CH_3, tolyl); 34.8 (C_{3a}); 66.6 ($\underline{C}H_2CH_3$); 80.8 (C_3); 101.8 (C_4); 121.7 (C_{6a}); 125.0 and 130.5 (CH, tolyl); 134.1 and 143.8 (C, tolyl); 164.0 (C_6). Analysis Calcd for $C_{14}H_{16}O_4N_2S$: C, 54.53; H, 5.23; N, 9.08; S, 10.40. Found: C, 54.74; H, 5.21; N, 8.99; S, 10.27.

(S_{3a},R_4,R_{6a},S_S)-4-Ethoxy-6a-(p-tolylsulfinyl)-3H,4H-3a,6a-dihydrofuro[3,4-c]pyrazol-6-one (2b)

White solid of m.p. 123-125 °C. $[\alpha]_D$: + 118.0. IR (Nujol): 1760 (C=O), 1595 (-N=N-). ^{1}H NMR: 0.86 (t, 3H, $CH_2\underline{CH_3}$, J=7.0); 2.43 (s, 3H, CH_3); 2.97 (ddd, 1H, H_{3a}, $J_{3a,4}$ =1.6, $J_{3a,3endo}$=3.8, $J_{3a,3exo}$=9.7); 3.34 (m, 2H, $\underline{CH_2}CH_3$); 4.82 (dd, 1H, H_{3endo}, $J_{3endo,3exo}$=19.4); 4.97 (d, 1H, H_4, $J_{3a,4}$=1.6); 5.08 (dd, 1H, H_{3exo}); 7.36 and 7.61 (AA'BB' system, 4H, arom.). ^{13}C NMR: 14.4 ($CH_2\underline{C}H_3$); 21.5 (CH_3, tolyl); 37.2 (C_{3a}); 65.6 ($\underline{C}H_2CH_3$);

85.5 (C_3); 107.6 (C_4); 122.4 (C_{6a}); 125.5 and 130.0 (CH, tolyl); 133.9 and 143.3 (C, tolyl); 163.3 (C_6). Analysis Calcd for $C_{14}H_{16}O_4N_2S$: C, 54.53; H, 5.23; N, 9.08; S, 10.40. Found: C, 54.85; H, 5.40; N, 8.88; S, 10.18.

Pyrolysis of 4-Ethoxy-6a-(*p*-tolylsulfinyl)-3*H*,4*H*-3a,6a-dihydrofuro[3,4-c]pyrazol-6-ones.

a) A solution of **2a** (630 mg, 2 mmol) in toluene (70 mL) was heated at 100 °C for 4.5 hours. The evolution of the reaction was followed by t.l.c. The solvent was removed and the purity of the crude compound (monitored by ^{1}H NMR) was suitable for preparative purposes. An analytical sample was obtained, after crystallization of ketone-hexane, in a 92% yield.

(S_S,S_S)-5-Ethoxy-4-methyl-3-(p-tolylsulfinyl)-2(5H)furanone (3a)

White solid of m.p. 130-131°C. $[\alpha]_D$: + 275.5. IR (Nujol): 1760 (C=O), 1645 (C=C). ^{1}H NMR: 1.27 (t, 3H, $CH_2C\underline{H}_3$, J=7.0); 2.40 (s, 3H, CH_3); 2.42 (s, 3H, CH_3); 3.73 (m, 1H, $C\underline{H}_2CH_3$); 3.89 (m, 1H, $C\underline{H}_2CH_3$); 5.58 (s, 1H, H_5); 7.32 and 7.69 (AA'BB' system, 4H, arom.).^{13}C NMR: 11.2 (CH_3); 14.8 (CH_3); 21.4 (CH_3, tolyl); 66.2 ($C\underline{H}_2CH_3$); 103.0 (C_5); 124.7 and 130.1 (CH, tolyl); 132.8; 138.8; 142.3; 164.4 and 165.5 (C) Analysis Calcd. for $C_{14}H_{16}O_4S$: C, 59.98; H, 5.75; S, 11.44. Found: C, 60.20; H, 5.65; S, 11.79.

b) By the above procedure, starting from **2b** (427 mg, 1.38 mmol) in 42 mL of toluene and heating for 3 hours, the crude product **3b** was obtained, which was purified by flash chromatography (hexane/ethyl acetate 3:1) 90% Yield.

(R_S,S_S)-5-Ethoxy-4-methyl-3-(p-toylsulfinyl)furan-2(5H)-one (3b)

White solid m.p. 60-61°C. $[\alpha]_D$: + 127.6. IR (Nujol): 1745 (C=O), 1645 (C=C). ^{1}H NMR: 1.24 (t, 3H, $CH_2C\underline{H}_3$ J=7.1); 2.40 (s, 3H, CH_3); 2.41 (s, 3H, CH_3); 3.78 (m, 2H, $C\underline{H}_2CH_3$); 5.60 (s, 1H, H_5); 7.32 and 7.68 (AA'BB' system, 4H, aromatic).^{13}C NMR: 11.2 (CH_3); 14.8 (CH_3); 21.4 (CH_3, tolyl); 66.5 (($C\underline{H}_2CH_3$); 103.0 (C_5); 124.9 and 130.1 (CH, tolyl); 132.7; 138.9; 142.3; 164.2 and 165.5 (C). Analysis Calcd for $C_{14}H_{16}O_4S$: C, 59.98; H, 5.75; S, 11.44. Found: C, 59.84; H, 5.74; S, 11.49.

Cycloadditions of diazomethane to (S_S,S_S)- and (R_S,S_S)-ethoxy-4-methyl-3-(*p*-tolylsulfinyl)furan-2(5*H*)-ones (3a and 3b).

Following the above cycloaddition procedure, starting from furanones **3a** or **3b**, after 1.5 and 3 hours respectively, the corresponding cycloadducts (**4a** and **4b**) were obtained in quantitative yields.

(S_{3a},S_4,R_{6a},S_S)-4-Ethoxy-3a-methyl-6a-(p-tolylsulfinyl)-3H,4H-3a,6a-dihydrofuro[3,4-c]pyrazol-6-one (4a)

Colourless oil. $[\alpha]_D$: + 348.0. IR (Film): 1775 (C=O), 1595 (-N=N-). ^{1}H NMR: 1.22 (t, 3H, $CH_2C\underline{H}_3$, J=7.1); 1.62 (s, 3H, CH_3); 2.46 (s, 3H, CH_3, tolyl); 3.69 (m, 1H, $C\underline{H}_2CH_3$); 3.86 (m, 1H, $C\underline{H}_2CH_3$); 4.79 (d, 1H, H_{3exo}, $J_{3exo,3endo}$=19.1) 4.97 (d, 1H, H_{3endo}), 5.37 (s, 1H, H_4); 7.41 and 7.73 (AA'BB' system, 4H arom.). ^{13}C NMR: 14.6 and 17.1 (CH_3); 21.5 (CH_3, tolyl); 50.7 (C_{3a}); 67.4 ($\underline{C}H_2CH_3$); 86.8 (C_3); 106.7 (C_4); 111.4 (C_{6a}); 126.6 and 129.4 (CH, tolyl); 133.5 and 143.2 (C, tolyl); 161.3 (C=O). Analysis Calcd. for $C_{15}H_{18}O_4N_2S$: C, 55.89; H, 5.63; N, 8.69; S, 9.94. Found: C, 55.60; H, 5.61; N, 8.51; S, 9.84.

(S_{3a},R_4,R_{6a},S_S)-4-Ethoxy-3a-methyl-6a-(p-tolylsulfinyl)-3H,4H-3a,6a-dihydrofuro[3,4-c]pyrazol-6-one (4b)

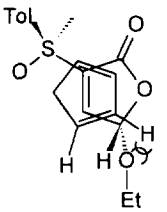
White solid m.p. 133-134°C. $[\alpha]_D$: + 169.6. IR (Nujol): 1770 (C=O), 1595 (-N=N-). ^{1}H NMR: 1.10 (t, 3H, $CH_2C\underline{H}_3$, J=7.0); 1.46 (s, 3H, CH_3); 2.44 (s, 3H, CH_3, tolyl); 3.52 (m, 1H, $C\underline{H}_2CH_3$); 3.75 (m, 1H, $C\underline{H}_2CH_3$); 4.64 (d, 1H, H_{3endo} $J_{3endo,3exo}$=18.9); 5.03 (d, 1H, H_{3exo}); 5.10 (s, 1H, H_4); 7.38 and 7.71 (AA'BB' system, 4H arom.). ^{13}C NMR: 14.4 (CH_3); 14.9 (CH_3); 21.4 (CH_3, tolyl); 50.1 (C_{3a}); 66.1 ($\underline{C}H_2CH_3$); 92.9 (C_3); 105.5 (C_4); 111.4 (C_{6a}); 126.8 and 129.3 (CH, tolyl); 134.4 and 142.8 (C tolyl); 162.4 (C=O). Analysis Calcd. for $C_{15}H_{18}O_4N_2S$: C, 55.89; H, 5.63; N, 8.69; S, 9.94. Found: C, 55.96; H, 5.53; N, 8.70; S, 10.19.

Acknowledgment. We thank Dirección General de Investigación Científica y Técnica (grant PB93-257) and Comunidad Autónoma de Madrid (grants AE00144/94 and AE00244/95) for financial support. A. F. thanks Universidad Autónoma de Madrid for a fellowship.

REFERENCES AND NOTES

1. Carreño, M. C. *Chem. Rev.* **1995**, 95, 1717-1760 and references cited therein.
2. Carreño, M. C.; Garcia Ruano, J. L., Toledo, M. A.; Urbano, A.; Remor, C. Z.; Stefani, W.; Fischer, J. *J. Org. Chem.* **1996**, 61, 503-509 and references cited therein.
3. Takahashi, T.; Fujii, A.; Sugita, J.; Hagi, T.; Kitano, K.; Arai, Y.; Koizumi, T. *Tetrahedron: Asymmetry* **1991**, 2, 1379-1390. b) Louis, C., Hootelé, C. *Tetrahedron: Asymmetry* **1995**, 6, 2149-2152. c) Bravo, P.; Bruché, L.; Farina, A.; Fronza, G.; Meille, S. V.; Merli, A. *Tetrahedron: Asymmetry* **1993**, 4, 2131-2134. d) Takahashi, T.; Kitano, K.; Hagi, T.; Nihonmatsu, H.; Koizumi, T. *Chem. Lett.* **1989**, 597-598. e) Chaigne, F.; Gotteland, J.; Malacria, M. *Tetrahedron Lett.* **1989**, 30, 1803-1806. f) Koizumi, T.; Hirai, H.; Yoshii, E. *J. Org. Chem.* **1982**, 47, 4004-4005. g) Bravo, P.; Bruché, L.; Diliddo, D.; Resnati, G.; *J. Chem. Research (S)*. **1993**, 346-347.
4. Only two reports dealing with the addition of diazomethane to racemic vinyl sulfoxides have been reported (Dean, F. M.; Park, B. K. *Tetrahedron Lett.* **1974**, 4275-4277; Padwa, A.; Meske, M; Rodriguez, A. *Heterocycles* **1995**, 40, 191-204) in which the sulfinylpyrazolines were not isolated.
5. a) Fariña, F.; Martín, M. R.; Martín, M. V.; Martinez, A. *Heterocycles* **1994**, 38, 1307-1316. and references cited therein b) Fariña, F.; Martín, M. V.; Soria, M. L. *An. Quim.* **1995**, 91, 65-73.
6. Fariña, F.; Martín, M. V.; Sanchez, F. *Heterocycles* **1986**, 24, 2587-2592
7. a) de Lange, B.; Feringa, B. L. *Tetrahedron Lett.* 1988, 29, 5317-5320. b) Keller, E.; de Lange, B.; Rispens, M. T.; Feringa, B. L. *Tetrahedron* 1993, 49, 8899-8910.
8. Cooper, D. M.; Grigg, R.; Hargreaves, S.; Kennewell, P.; Reapath, J. *Tetrahedron* **1995**, 51, 7791-7808.
9. Reed, A. D.; Hegedus, L. S. *J. Org. Chem.* 1995, 60, 3787-3794
10. Carretero, J. C.; García Ruano, J. L.; Lorente, A.; Yuste, F. *Tetrahedron: Asymmetry* **1993**, 4, 177-180.

11. Feringa, B. L.; de Lange, B.; de Jong, J. C. *J. Org: Chem.* **1989**, 54, 24712475
12. During the preparation of this manuscript a new reaction of racemic vinyl sulfoxides with diazomethane has been reported (Plancquaert, M.; Redon, M.; Janousek, Z.; Viehe, H. G. *Tetrahedron* **1996**, 52, 4383-4396). This is the first paper containing NMR data of the racemic sulfinylpyrazolines.
13. As a consequence of the high stability of this sulfinylpyrazolines, **2a** and **2b** can be easily separated by chromatography. This separation is much easier than that of the furanones **1a** and **1b**, and therefore, reaction of the **1a** + **1b** mixture with diazomethane and further separation of the obtained pyrazolines, allowed higher yields of **2a** and **2b** (see experimental).
14. Hanessian, S.; Murray, P. J. *J. Org. Chem.* **1987**. 52, 1170-1172.
15. Thermally induced extrusion of nitrogen from 3*H*, 4*H*, 3a,6a-dihydrofuro[3,4-c]pyrazol-6-ones is a known method to obtain 4-methylfuran-2(5*H*)-ones (Jefford, C. W.; Sledeski, A.; Boukouvalas, J. *Helv. Chim. Acta* **1989**, 72, 1362-1370 and Ortuño, R. M.; Bigorra, J.; Font, J. *Tetrahedron* **1987**, 43, 2199-2202 and reference 13).
16. The steric interactions of diene with the substituents at C-5 are more restrictive than those of the diazomethane with such substituents.



(*Received in UK* 10 *April* 1996; *accepted* 13 *May* 1996)