Pergamon

*Tetrahedron*, Vol. 52, No. 41, pp. 13215-13226, 1996

0040-4020/96 $15.00 + 0.00

PII: S0040-4020(96)00796-X

# Reactions of Stabilized Sulfur Ylides with α,β-Unsaturated Alkoxychromiumcarbene Complexes[1]

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*Abstract.* Reaction of stabilized sulfur ylides with α,βunsaturated alkoxychromiumcarbene complexes in MeCN as solvent forms vinylenol ethers **3**, cyclopropanes **4**, and vinylcyclopropanes **5**, depending on the reagent ratio, the temperature and the nature of the ylide. The results obtained in these reactions suggest that factors apart from steric hindrance may control the chemoselectivity of the addition. Less stable ylides would add preferentially to the carbene carbon, 1,4-addition increasing as the stability of the ylide does. For more stable ylides 1,4-addition is preferred and substitution at the β-carbon has little effect in the chemoselectivity. Methoxycarbonylmethylentriphenylphosphorane exclusively add to the carbene carbon while ethyl diazoacetate is unreactive towards α,β-unsaturated alkoxychromium-carbene complexes in the conditions studied.


## INTRODUCTION

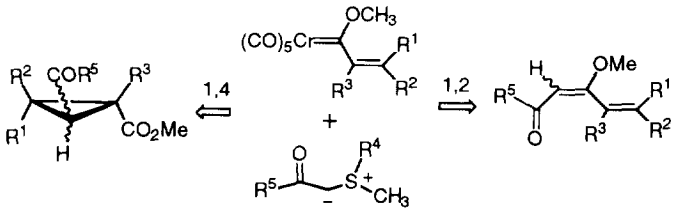
Conjugate additions of nucleophile reagents to an unsaturated system in conjugation with an electron-withdrawing group are of paramount importance in organic synthesis.[2] As a result, an impressive work to understand their scope, mechanism and the factors controlling the chemo- and stereoselectivity of these processes has been made.[3] α,β-Unsaturated chromium carbene complexes may be regarded as an special type of conjugated acceptors in view of the isolobal relationship[4] which makes these complexes the organometallic analogs of α,β-unsaturated esters and amides. However, the presence of the metal introduces severe differences in reactivity and selectivity between both types of compounds. Since Fischer reported[5] the competition between the 1,2- and 1,4- addition of dimethylamine to alkynylcarbene complexes of chromium and tungsten, much has been learned about these reactions[6] and several useful processes for organic synthesis[7] have been reported.[8] However, the factors controlling the chemoselectivity of this class of reactions are not yet well understood. Thus, Casey[9] reported that the conjugate addition of enolate anions to vinylcarbene complexes is controlled mainly by steric effects, while more recent papers[7] described the preferred conjugate addition.

Nevertheless, the decisive influence of the reagent is exemplified by the addition of $ZnEt_2$ and LiAr to alkynyl complexes to form 1,2-adducts exclusively.[10] Finally, heteronucleophiles may form either 1,4- or 1,2-adducts depending on the case.[11]

In this paper we report our findings[1] in the reaction of stabilized sulfur ylides with α,β-unsaturated alkoxychromiumcarbene complexes to form vinylenol ethers, and cyclopropanes.[12] Evidence showing that other factors apart the steric hindrance may control the chemoselectivity of these reactions will be presented.

## RESULTS AND DISCUSSION

The reaction of stabilized sulfur ylides with α,β-unsaturated alkoxychromiumcarbene complexes may, in principle, form two different kind of products. 1,2-Addition of the ylide on the carbene carbon would form enol ethers, as reported by us[13] and others[14] in the reaction of carbene complexes and different types of ylides. The conjugate addition would form cyclopropanes paralleling the reaction of organic esters and sulfur ylides (Scheme 1).[15]



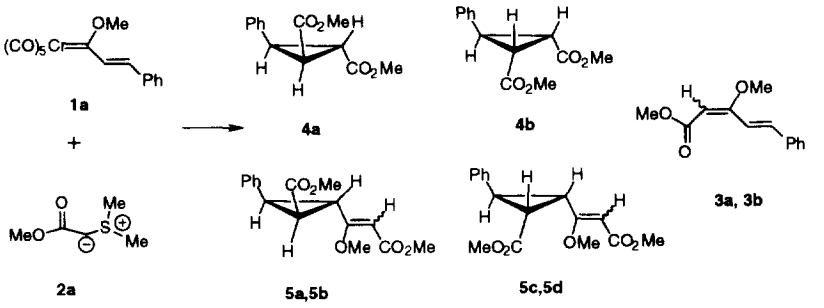

**Scheme 1**

Preliminary studies were carried out by treating pentacarbonyl(methoxystyrylcarbene)chromium(0), **1a**, with sulfur ylide **2a**. The different experiments are collected in Table 1. Depending on the reaction conditions three different types of products were obtained. Vinylenol ethers, **3a-b** were the main products at low temperatures, while raising the temperature resulted in the formation of almost equimolar amounts of diastereomeric cyclopropanes **4a-b** and vinyl ethers **3a-b**. Increasing the amount of ylide did not produce changes in the vinyl ether/cyclopropane ratio but resulted in the formation of a new cyclopropane product instead of compounds **4a-b**. In fact, vinylcyclopropanes **5a-d** were the sole cyclopropane products when an excess of ylide was used. From these results, it can be seen that 1,2-addition is favored, in principle, by low temperatures while the ratio of 1,4-adduct (cyclopropanes **4** or **5**) /1,2-adduct (enol ethers **3**) becomes almost unaltered for temperatures higher than -40 °C.

The stereochemistries of the above compounds were assigned by NMR techniques. It was possible to connect the protons to their corresponding carbons by means of HMQC[16] experiments, which map the connectivities between carbon atoms and their directly bonded protons. The discrimination of most of the signals in the $^{13}C$ NMR spectra was straightforward, since almost all the $^{1}H$ NMR chemical shifts were already known. Only the definitive assignment of the protons to their position in the cyclopropane ring remained to be established. The uncertainty was removed by using an HMBC[17] experiment which shows long-range connectivities between carbon atoms and their coupled protons across 2 or 3 bonds. Using this technique, coupling between the cyclopropane proton attached at the same carbon as the phenyl ring, and the aromatic *ortho*-carbons could be observed for all compounds. In addition, coupling between the cyclopropane

allyl proton and the protonated allylic carbon was also detected in compounds **5**. This coupling left no doubt in the assignment of the remaining proton-carbon pair. Besides, the three bond coupling between a given carbonyl group and its vicinal proton attached to other cyclopropane carbon was also detected. Therefore, the relative stereochemistry of compounds **3**, **4**, and **6** was established.

**Table 1. Reaction of Complex 1a with Ylide 2a.**[a]




| Entry | Molar ratio 1a:2a | T (°C) | 4/5/3[b] | 4a/4b | 5a,5b/5c,5d | (*E*,*E*)3a/ (*Z*,*E*)-3b |
|---|---|---|---|---|---|---|
| 1 | 1:1 | -78 | 15:0:85 | 60:40 | Not formed | 77:23 |
| 2 | 1:1 | -40 | 46:0:54 | 52:48 | Not formed | 72:28 |
| 3 | 1:1 | -20 | 49:0:51 | 59:41 | Not formed | 74:26 |
| 4 | 1:1 | RT | 46:0:54 | 58:42 | Not formed | 72:28 |
| 5 | 1:1 | Δ | 39:0:61 | 54:46 | Not formed | 77:23 |
| 6 | 1:2 | RT | 0:64:36 | Not formed | 59:41 | 75:25 |
| 7 | 1:3 | -78 | 0:21:79 | Not formed | 62:38 | 76:24 |
| 8 | 1:3 | RT | 0:65:35 | Not formed | 63:37 | 67:33 |
| 9 | 1:3 | Δ | 0:46:54 | Not formed | 65:35 | 76:24 |

[a] All experiments were carried out in MeCN as solvent except for those at -78 °C which were performed in THF/MeCN mixtures. Compound ratios were determined by integration of well resolved signals in the $^1$H NMR spectra of the crude reaction mixtures, prior to purification. All experiments were repeated at least twice, and the values on the Table are the media of the two experiments.[b] Almost quantitative yields in organic material were obtained in all cases. Small amounts (< 10 %) of methyl cinnamate were obtained together with compounds **3**-**4** when 1:1 molar ratios were used.

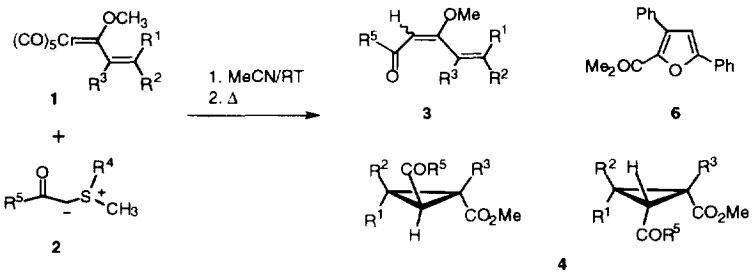
The *E*/*Z* stereochemistry of compounds **3a**-**b** was assigned by NOE experiments. Thus, irradiation of the vinyl proton of *E*-**3a** at 5.14 ppm under NOE conditions produces a 10.5 % increment of the signal corresponding to the MeO group at 3.74 ppm, confirming a *cis*-relationship for both groups. Irradiation under similar conditions of the vinyl proton of the *Z* isomer at 5.37 ppm results in an 4.0 % increment of the signal corresponding to H4 at 6.51 ppm. The double bond stereochemistry of vinylcyclopropanes **5a**-**d** was established analogously by NOE measurements.

With the above results in hand the effect of bulkier ylides was studied. Ylides **2b**-**c** having a *t*-Bu and 2-naphthyl group at the ester and sulfur groups, respectively, were combined with complex **1a** at room temperature and in a 1:1 molar ratio (Table 2, Entries 1-2). The 1,4/1,2-adduct ratio remained mainly

unchanged with ylide **2b**. A slight change in the *E/Z-cis/trans* selectivity of the reaction products, vinyl ethers **3c-d** and cyclopropanes **4c-d**, was the sole difference with respect to the analogous reaction between complex **1a** and ylide **2a**. The outcome of the reaction between complex **1a** and ylide **2c** was drastically different. In this case diastereomeric cyclopropanes **4a-b** were formed almost exclusively. Vinyl ethers **3a-b** were formed in less than 5 % as established by $^1$H NMR analysis of the crude reaction mixtures.

The results above suggested that the chemoselectivity of the addition of sulfur ylides to α,β-unsaturated carbene complexes may be controlled by the steric volume of the ylide substituents. It soon became evident that this is not the sole factor. The reactions of ylide **2c** and complexes **1b-d** resulted in the exclusive formation of enol ethers **3e-j** (Table 2, Entries 3-5). These exclusive 1,2-additions of the bulky ylide **2c** are in clear contrast with the analogous reaction of ketone enolates and other nucleophiles, reported to add exclusively in a conjugate mode with, for example, complex **1b**.[9] Additional evidence against the steric control of these processes is found in the reaction between complex **1b** and ylide **2a** (Table 2, Entry 6). In this case enol ethers **3e-f** were obtained as the sole reaction products, with yields and *E/Z* ratios almost identical to those from the reaction of complex **1b** and ylide **2c**.

**Table 2**




1 + 2 → 3 + 6 + 4

| Entry | 1 | 2 | $R^1$ | $R^2$ | $R^3$ | $R^4$ | $R^5$ | 3/4 ratio[a] | Products 3 | *E*-3/*Z*-3 ratio[a] | Products 4 | 4 ratio[a] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | **1a** | **2b** | H | Ph | H | Me | O*t*-Bu | 52:48 | **3c/3d** | 88:12 | **4c/4d** | 61:39 |
| 2 | **1a** | **2c** | H | Ph | H | α-naphtyl | OMe | >5:95 | **3a/3b** | – | **4a/4b** | 68:32 |
| 3 | **1b** | **2c** | Me | Me | H | α-naphtyl | OMe | 100:0 | **3e/3f** | 37:63 | – | – |
| 4 | **1c** | **2c** | H | $(CH_2)_4$ | | α-naphtyl | OMe | 100:0 | **3g/3h** | 17:83 | – | – |
| 5 | **1d** | **2c** | $(CH_2)_4$ | | H | α-naphtyl | OMe | 100:0 | **3i/3j** | 22:78 | – | – |
| 6 | **1b** | **2a** | Me | Me | H | Me | OMe | 100:0 | **3e/3f** | 37:63 | – | – |
| 7 | **1a** | **2d** | H | Ph | H | Me | Ph | 0:100 | – | – | **4e**[c] | 100:0 |
| 8 | **1b** | **2d** | Me | Me | H | Me | Ph | 10:90 | **3k** | d | **4f/4g** | 68:22 |
| 9 | **1c** | **2d** | H | $(CH_2)_4$ | | Me | Ph | b | – | – | – | – |
| 10 | **1d** | **2d** | $(CH_2)_4$ | | H | Me | Ph | b | – | – | – | – |

[a] Determined by integration of well resolved signals in the $^1$H NMR spectra of the crude reaction mixtures. To ensure reproducibility each reaction was repited twice and the reported data are the media of both experiments.

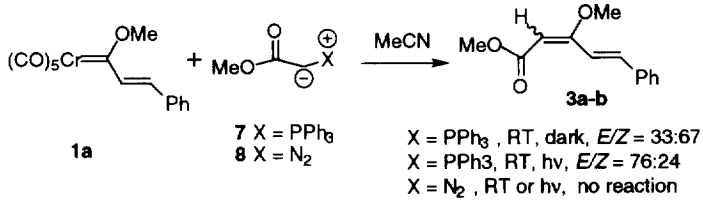
[b] Decomposition to complex mixtures of unknown products was obtained.

[c] 5-(Methoxycarbonyl)-3,4-diphenylfuran, **6**, was obtained (28%, isolated yield) together with cyclopropane **4e**

[d] Not determined.

The stereochemistry of enol ethers **3e-j** was deduced from NOE experiments carried out on compounds **3e** and **3f**. Thus, irradiation of the hydrogen on C4 (δ = 5.71) of compound **3e** resulted on 2.5 %, 3.8 %, and 6.3 % increments of the signals corresponding to H2 (δ = 4.89), OMe (δ = 3.76), and *cis*-Me (δ = 1.86), respectively, which is consistent with a *Z*-configuration for the newly formed double bond. Configurations of enol ethers **3g-j** were assigned by comparation with enol ethers **3e-f**. A *Z*-configuration was assigned to the isomers with the signal corresponding to H4 at higher field and an *E*-configuration for those isomers with H4 at lower fields.

The nature of ylide was the next variable examined. The reactions of complexes **1a-b** and ylide **2d** gave exclusively or predominantly cyclopropane derivatives **4e-g** (Table 2, Entries 7-8) while complexes **1c-d** gave complex reaction mixtures of unknown products (Table 2, Entries 9-10). Furan **6** was isolated from the reaction of complex **1a** and ylide **2d** together with cyclopropane **4e**. This compound may be derived from one of the intermediates in the formation of cyclopropane **4e** as discussed below. Additionally, vinyl cyclopropanes analogous to **5** were not observed in the reaction of carbene complex **1a** and ylide **2d** even in large excesses of ylide, showing the inertia of most stable ylides to add to the carbene carbon. Results in Table 2 show that the nature of the ylide, specially the degree of stabilization, may be the factor controlling the chemoselectivity of the reaction rather than steric factors associated to both the complex or the ylide. To corroborate this statement the reactions of complex **1a** and phosphorous and nitrogen ylides, **7** and **8**, were carried out. Ylide **7** gave exclusively the *E/Z* mixture of enol ethers **3a-b**, while ylide **8** was unreactive (Scheme 2). The sole organic material recovered in the last case was methyl cinnamate formed by oxidation of complex **1a**. This lack of reactivity is noteworthy since the reaction of tungsten and chromium carbenes and simple nitrogen ylides has been reported to yield enol ethers.[14] As can be seen in Scheme 4, the *E/Z* selectivity of the reaction between ylide **7** and carbene complex **1a** can be totally inverted by switching the reaction conditions. The observed differences in the *E/Z* ratio probably arise from isomerization of the new formed double bond under the different conditions used. To ensure this hypothesis, the crude reaction mixture produced from the thermal reaction of complex **1a** and ylide **7** in the dark (*E/Z* ratio 33:67) was irradiated prior to oxidation. The *E/Z* ratio of the resulting mixture was 70:30 nearly equal to that obtained under photochemical conditions (76:24). Furthermore, heating (boiling acetonitrile) of the mixture of olefins obtained at room temperature in the dark, resulted again in isomerization to form a 60:40 *E/Z* mixture. Clearly, both light and temperature are influencing the *E/Z* outcome of the reaction as observed by us in the reaction of other chromium carbene complexes and sulfur ylides.[13]

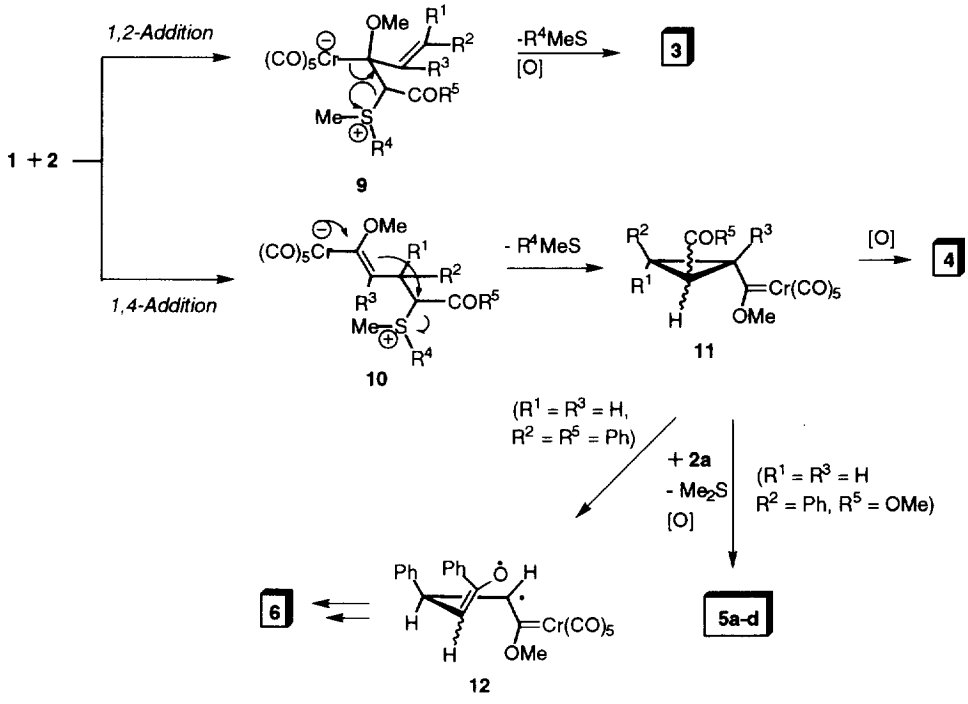



**Scheme 2**

All the results above suggest that factors apart from steric hindrance are involved in the chemoselectivity of these reactions. In fact, less stable ylides would add preferentially to the carbene carbon, with 1,4-addition increasing as the stability of the ylide does. More stable ylides would add preferentially in 1,4-mode with

substitution at the β-position of the complex having little effect in the chemoselectivity. Sulfur ylides having ester substituents add either in 1,2- or 1,4-modes with steric hindrance favoring the 1,4-addition as the bulkiness of the ylide increases.

The reactivity observed may be explained by the reaction pathway in Scheme 3. As discussed, formation of enol ethers **3** and cyclopropanes **4** result from the competitive 1,2- and 1,4-addition to the conjugate system of carbene complexes **1**. Addition on the carbene carbon would form zwitterions **9** which evolve to vinylenol ethers by sulfide loss. Competitive 1,4-addition followed by cyclization would render cyclopropyl complexes **11** through zwitterions **10**. Oxidation of complexes **11** yields cyclopropanes **4**. With excess of ylide a new molecule of ylide would add to the carbene carbon of complexes **11** to form vinylcyclopropanes **5**. This second addition does not take place with stable ylides, even in great excesses of reagent. Finally, furan **6** may be formed through the homolytic cleavage of the cyclopropane ring on complex **11** to form intermediate **12**. This intermediate would evolve to furan **6** by ring closure and oxidation. This rearrangement is related to the well-known carbonylcyclopropane-furane rearrangement.[18]




**Scheme 3**

In conclusion, the reaction of α,β-unsaturated chromiumcarbene complexes and sulfur ylides yields cyclopropanes and/or enol ethers in good yields. The chemoselectivity of the reaction is strongly dependent on the nature of the ylide, specially on its stabilization. The nature of the reagent may overcome the steric hindrance, which has been claimed to be the controlling factor in related processes.[9]

## EXPERIMENTAL SECTION

**General Procedure.** Melting points were taken on a Gallemkamp apparatus and are uncorrected. $^1H$ NMR and $^{13}C$ NMR spectra were recorded in $CDCl_3$, on a Varian XL-300S (300 and 75.43 MHz) and a Bruker 250-AM (250 and 62.5 MHz) spectrometers. Chemical shifts are given in ppm relative to TMS ($^1H$, 0.0 ppm), or $CDCl_3$ ($^{13}C$, 76.9 ppm). IR spectra were taken on a Perkin-Elmer 781 spectrometer in $CHCl_3$ solution. Elemental analyses were obtained from the UCM Microanalysis Service (Facultad de Farmacia, UCM, Madrid). All solvents used in this work were purified by destillation. Tetrahydrofuran (THF) and $Et_2O$ were destilled from Na-benzofenone. Toluene, $CH_2Cl_2$, and $Et_3N$ were destilled from $CaH_2$. Flame-dried glassware and standard Schlenk techniques were use for moisture sensitive reactions. For purification of crude reaction mixtures by flash chromatography, Merck silica-gel (230-400 Mesh) or Florisil were used as the stationary phase. Identification of products was made by TLC (Kiesegel 60F-254). UV light ($\lambda$ = 254 nm) and 5 % phosphomolydic acid solution in 95 % EtOH were use to develop the plates. A 450-W lamp medium-pressure mercury lamp (Applied Photophysic), with a Pyrex filter and Pyrex well was used for irradiations. Except otherwise stated the listed data refers to pure, separated isomers. The following chemicals were prepared according to literature procedures: Pentacarbonyl[(1-cyclohexenyl)methoxycarbene] chromium (0),[19] pentacarbonyl[(styryl)methoxy-carbene] chromium (0),[20] pentacarbonyl[(isobutenyl)methoxycarbene] chromium (0),[21] pentacarbonyl[(cyclopentylidenemethyl)methoxycarbene] chromium (0),[21] methoxycarbonyl methylidenedimethyl sulfurane,[22] terc-butoxycarbonylmethylidenedimethylsulfurane,[23] phenacylidenedimethyl sulfurane,[22] methoxycarbonylmethylidene-(methyl-1-naphthyl)sulfurane.[22]

The stereochemical identity of compounds **3a-b**, **4a-b**, and **5a-d** was stablished by NMR spectrometry using HMQC[16] and HMBC[17] techniques, as follows: The pure absorption one bond proton-carbon correlation experiment was collected in the $^1H$ detection mode using the HMQC pulse sequence and a reverse probe. A data matrix of 256 x 1024 points was used to resolve spectral widths of 25000 and 4000 Hz in F1 and F2; 16 scans were used per increment with a relaxation delay of 1s and a delay corresponding to a J value of 140 Hz. A BIRD pulse was used to minimize the proton signals bonded to $^{12}C$. $^{13}C$ decoupling was achieved by the WALTZ scheme. Prior to FT, squared cosine bell functions were applied in both dimensions and zero filling was used to expand the data to 1K x 2K. The multiple bond proton-carbon correlation experiment was carried out using the HMBC pulse sequence. 64 Scans were used per increment with a relaxation delay of 2s and a pulse delay of 80 ms. The processing was performed in absolute mode in I2.

**General Procedure for the Reactions of Complexes 1 and Ylides 2.** The carbene (1.0 mmol) was dissolved in 15 mL of degassed MeCN (THF/MeCN mixtures were used for temperatures below -40°C) and the solution was placed in a Pyrex flask which was sealed with a rubber septum, evacuated, and purged with argon (three times). A solution of ylide **2** (1-3 mmols depending on the case) in 15 mL of degassed MeCN (THF/MeCN mixtures were used for temperatures below -40 °C) was added and the resulting mixture was stirred until total disappearance of the starting complex (TLC.). The solvent was removed under vacuo. The resulting brown solid residue was dissolved in methyl acetate, filtered through Celite, diluted with one volume of pentane, and air oxidized in an open flask under direct sunlight (usually 10-12 h was required)[24] or in a light box (9 x 20 fluorescent bulbs). Filtration through Celite of the brown precipitate and solvent removal gave crude products. Analytically pure enol ethers and cyclopropanes were obtained by

chromatography using hexane/EtOAc mixtures. In the indicated cases irradiation was used to accelerate the reaction. Once the reaction was completed the work-up was as indicated above.

**Cyclopropanes 4a, 4b. *From ylide 2a.*** Following the general procedure, 338 mg (1 mmol) of carbene **1a** and 138 mg (1 mmol) of ylide **2a** were stirred 2 h at -20ºC. After oxidation of the crude mixture, 65 mg (28 %) of **4a** (colorless oil) and 46 mg (20 %) of **4b** (colorless oil) were obtained. **Dimethyl *t*-3-phenyl-*r*-1,*t*-2-cyclopropanedicarboxylate, 4a.** $^1$H NMR ($CDCl_3$) δ 2.62 (dd, 1H, $J_1$= 5.1 Hz, $J_2$= 10.2 Hz), 2.83 (dd, 1H, $J_1$= 5.1 Hz, $J_2$= 6.6 Hz), 3.06 (dd, 1H, $J_1$= 6.6 Hz, $J_2$= 10.2 Hz), 3.47 (s, 3H), 3.74 (s, 3H), 7.16-7.45 (m, 5H); $^{13}$C NMR ($CDCl_3$) δ 172.0, 168.8, 134.0, 128.8, 128.2, 127.3, 52.3, 51.9, 32.7, 29.8, 25.8; IR ($Cl_3CH$) ν 1730, 1440 cm$^{-1}$; Anal. Calcd. for $C_{13}H_{14}O_4$: C, 66.64; H, 6.03. Found: C, 66.41; H, 6.21. **Dimethyl *t*-3-phenyl-*r*-1,*c*-2-cyclopropanedicarboxylate 4b.** $^1$H NMR ($CDCl_3$) δ 2.38 (d, 2H, J= 6.0 Hz), 3.16 (t, 1H, J= 6.0 Hz), 3.72 (s, 6H), 7.07-7.35 (m, 5H); $^{13}$C NMR ($CDCl_3$) δ 169.5, 137.4, 128.7, 127.2, 126.5, 52.3, 30.0, 29.5; IR ($Cl_3CH$) ν 1730, 1460, 1440 cm$^{-1}$; Anal. Calcd. for $C_{13}H_{14}O_4$: C, 66.64; H, 6.03. Found: C, 66.52; H, 6.14. ***From ylide 2c.*** Following the general procedure, 338 mg (1 mmol) of carbene **1a** and 250 mg (1 mmol) of ylide **2c** were mixed at room temperature. The reaction was instantaneous. After purification of the crude mixture, 117 mg (50%) of **4a** (colorless oil) and46 mg (20%) of **4b** (colorless oil) were obtained.

**Cyclopropanes 4c-4d.** Following the general procedure, 338 mg (1 mmol) of carbene **1a** and 176 mg (1 mmol) of ylide **2b** were stirred 1 h at room temperature. After purification of the crude mixture, 72 mg (26%) of **4c** (colorless oil) and 52 mg (19%) of **4d** (colorless oil) were obtained. ***tert*-Butyl *t*-2-(methoxycarbonyl)-*c*-3-phenyl-*r*-1-cyclopropanecarboxylate, 4c.** $^1$H NMR ($CDCl_3$) δ 1.13 (s, 9H), 2.50 (dd, 1H, $J_1$= 4.8 Hz, $J_2$= 10.5 Hz), 2.76 (dd, 1H, $J_1$= 4.8 Hz, $J_2$= 6.6 Hz), 3.03 (dd, 1H, $J_1$= 6.6 Hz, $J_2$= 10.5 Hz), 3.74 (s, 3H), 7.24 (s, 5H); $^{13}$C NMR ($CDCl_3$) δ 172.2, 167.3, 134.5, 129.1, 128.1, 127.2, 81.2, 52.2, 32.4, 31.0, 25.2 , 27.7; IR ($Cl_3CH$) ν 1720, 1605, 1585, 1500, 1450, 1390 cm$^{-1}$; Anal. calcd. for $C_{16}H_{20}O_4$: C, 69.53; H, 7.30. Found: C, 69.68; H, 7.56. ***tert*-butyl *c*-2-(methoxycarbonyl)-*t*-3-phenyl-*r*-1-cyclopropanecarboxylate, 4d.** $^1$H NMR ($CDCl_3$) δ 1.44 (s, 9H), 2.31 (d, 2H, J= 6.3 Hz), 3.09 (t, 1H, J= 6.3 Hz), 3.71 (s, 3H), 7.10-7.30 (m, 5H); $^{13}$C NMR ($CDCl_3$) δ 169.3, 167.9 138.0, 128.6, 127.0, 126.5, 81.4, 52.0, 31.3, 30.2, 29.0, 28.0; IR ($Cl_3CH$) ν 1730, 1630, 1605 , 1500, 1455, 1440, 1390 cm$^{-1}$; Anal. Calcd. for $C_{16}H_{20}O_4$: C, 69.53; H, 7.30. Found: C, 69.27; H, 7.04.

**Cyclopropane, 4e, and methyl 3,5-diphenyl-2-furoate, 6.** Following the general procedure, 338 mg (1 mmol) of carbene **1a** and 180 mg (1 mmol) of ylide **2d** were stirred 1.5 h at room temperature. After purification of the crude mixture 101 mg (36%) of **4e** (yellow oil) and 78 mg (28%) of furane **6** (yellow oil) were obtained. **Methyl *t*-2-benzoyl-*t*-3-phenyl-*r*-1-cyclopropanecarboxylate, 4e.** $^1$H NMR ($CDCl_3$) δ 3.23 (dd, 1H, $J_1$= 5.1 Hz, $J_2$= 6.3 Hz), 3.35 (dd, 1H, $J_1$= 6.3 Hz, $J_2$= 10.2 Hz), 3.57 (dd, 1H, $J_1$= 5.1 Hz, $J_2$= 10.2 Hz), 3.77 (s, 3H), 7.17 (bs, 5H), 7.36-7.55 (m, 3H), 7.91-7.95 (m, 2H); $^{13}$C NMR ($CDCl_3$) δ 193.1, 172.6, 137.4, 133.6, 133.1, 130.2, 128.7, 128.5, 128.2, 127.2, 52.3, 35.8, 34.9, 25.7; IR ($Cl_3CH$) ν 1730, 1680, 1600, 1580, 1500, 1450 cm$^{-1}$; Anal. calcd. for $C_{18}H_{16}O_3$: C, 77.11; H, 5.76. Found: C, 77.23; H, 6.09. **Methyl 3,5-diphenyl-2-furoate, 6.** $^1$H NMR ($CDCl_3$) δ 3.77 (s, 3H), 6.77 (s, 1H), 7.25-7.38 (m, 6H), 7.52-7.55 (m, 2H), 7.70-7.75 (m, 2H); $^{13}$C NMR ($CDCl_3$) δ 159.6, 155.9, 139.6,

138.7, 136.7, 131.9, 129.2, 129.0, 128.3, 128.0, 124.8, 109.4, 51.7; IR ($Cl_3CH$) ν 1720, 1540, 1500, 1480, 1460, 1400 $cm^{-1}$; Anal. Calcd. for $C_{18}H_{14}O_3$: C, 77.67; H, 5.07. Found: C, 77.81; H, 5.22.

**Vinylcyclopropanes, 5a-d.** Following the general procedure, 338 mg (1 mmol) of carbene **1a** and 402 mg (3 mmol) of ylide **2a** were stirred 15 min. at room temperature. After purification of the crude mixture, 49 mg (17 %) of the mixture of **5a** and **5d** (colorless oil), 52 mg (18 %) of **5b** (colorless oil), and 58 mg (20 %) of **5c** (colorless oil) were obtained. **Methyl *c*-2-[(*E*)-1'-methoxy-2'-methoxycarbonylvinyl]-*t*-3-phenyl-*r*-1-cyclopropanecarboxylate, 5a.** From the mixture of **5a** and **5d**: $^1H$ NMR ($CDCl_3$) δ 2.46 (dd, 1H, $J_1$= 6.0 Hz, $J_2$= 9.0 Hz), 3.17 (dd, 1H, J= 6.0 Hz, $J_2$= 6.9 Hz), 3.29 (ddd, 1H, $J_1$= 0.9 Hz, $J_2$= 6.9 Hz, $J_3$= 9.0 Hz), 3.64 (s, 3H), 3.65 (s, 6H), 5.17 (s, 1H), 7.17 (m, 5H,); $^{13}C$ NMR ($CDCl_3$) δ 170.4, 169.6, 167.7 , 138.8, 128.5, 126.8, 126.6, 93.0, 55.9, 51.8, 50.8, 31.1, 30.9, 29.0. **Methyl *c*-2-[(*Z*)-1'-methoxy-2'-methoxycarbonylvinyl]-*t*-3-phenyl-*r*-1-cyclopropanecarboxylate, 5b.** $^1H$ NMR ($CDCl_3$) δ 2.39 (d, 2H, J= 6.0 Hz), 3.03 (t, 1H, J= 6.0 Hz), 3.66 (s, 3H), 3.72 (s, 3H), 3.91 (s, 3H), 5.22 (s, 1H), 7.16 (m, 2H), 7.31 (m, 3H); $^1H$ NMR ($CD_3COCD_3$) δ 2.52 (dd, 1H, $J_1$= 5.3 Hz, $J_2$= 9.2 Hz), 2.67 (ddd, 1H, $J_1$= 1.2 Hz, $J_2$= 6.9 Hz, $J_3$= 9.2 Hz), 3.00 (dd, 1H, $J_1$= 5.3 Hz, $J_2$ = 6.9 Hz), 3.54 (s, 3H), 3.67 (s, 3H), 3.86 (s, 3H), 5.15 (d, 1H, J= 1.2 Hz), 7.31 (s, 5H); $^{13}C$ NMR ($CDCl_3$) δ 169.5, 165.4, 165.0, 137.3, 128.7, 127.2, 126.5, 97.6, 57.2, 52.2, 50.8, 31.0, 29.7, 29.5; IR ($Cl_3CH$) ν 1730, 1640, 1505, 1480, 1440 $cm^{-1}$; Anal. Calcd. for $C_{16}H_{18}O_5$: C, 66.18; H, 6.25. Found: C, 66.39; H, 5.94. **Methyl *t*-2-[(*Z*)-1'-methoxy-2'-methoxycarbonylvinyl]-*c*-3-phenyl-*r*-1-cyclopropanecarboxylate, 5c.** $^1H$ NMR ($CDCl_3$) δ 2.43 (dd, 1H, $J_1$= 5.4 Hz, $J_2$= 9.6 Hz), 2.80 (dd, 1H, $J_1$= 5.4 Hz, $J_2$= 6.9 Hz), 2.92 (dd, 1H, $J_1$= 6.9 Hz, $J_2$= 9.6 Hz), 3.50 (s, 3H), 3.67 (s, 3H), 3.97 (s, 3H), 5.17 (s, 1H), 7.26-7.27 (m, 5H); $^{13}C$ NMR ($CDCl_3$) δ 169.1, 168.0, 165.4, 134.2, 128.6, 128.2, 127.3, 95.3, 59.0, 51.9, 50.9, 31.5, 28.8, 27.6; IR ($Cl_3CH$) ν 1720, 1635, 1500, 1470, 1450 $cm^{-1}$; Anal. Calcd. for $C_{16}H_{18}O_5$: C, 66.18; H, 6.25. Found: C, 65.89; H, 6.40. **Methyl *t*-2-[(*E*)-1'-methoxy-2'-methoxy-carbonylvinyl]-*c*-3-phenyl-*r*-1-cyclopropanecarboxylate, 5d.** From the mixture of **5a** and **5d**: $^1H$ NMR ($CDCl_3$) δ 2.62 (dd, 1H, $J_1$= 5.4 Hz, $J_2$= 9.9 Hz), 3.00 (dd, 1H, $J_1$= 6.9 Hz, $J_2$= 9.9 Hz), 3.40 (s, 3H), 3.62 (s, 3H), 3.73 (s, 3H), 4.50 (dd, 1H, $J_1$= 5.4 Hz, $J_2$=6.9 Hz), 5.16 (s, 1H), 7.17-7.37 (m, 5H); $^{13}C$ NMR ($CDCl_3$) δ 170.5, 169.7, 168.0, 135.2, 129.2, 128.0, 126.9, 55.7, 51.5, 51.0, 31.9, 28.7, 24.7 .

**Methyl 3-methoxy-5-phenyl-2,4-pentadienoates, 3a and 3b.** Following the general procedure, 338 mg (1 mmol) of carbene **1a** and 134 mg (1 mmol) of ylide **2a** were stirred 1 h at -78 °C. After purification of the crude mixture, 57 mg (26 %) of **3a** (colorless solid, mp 55-56 °C), and 6 mg (12 %) of **3b** (colorless oil) were obtained. ***2E,4E-Isomer*, 3a.** $^1H$ NMR ($CDCl_3$) δ 3.71 (s, 3H), 3,74 (s, 3H), 5.14 (s, 1H), 7.26-7.35 (m, 4H), 7.53 (m, 2H), 8.09 (d, 1H, J= 15.9 Hz); $^{13}C$ NMR ($CDCl_3$) δ 167.8, 166.9, 135.3, 136.1, 128.9, 128.6, 127.6, 120.1, 91.8, 55.4, 51.0; IR ($Cl_3CH$) ν 1705, 1640, 1590, 1575, 1500, 1455, 1445 $cm^{-1}$; Anal. Calcd. for $C_{13}H_{14}O_3$: C, 71.53; H, 6.47. Found: C, 71.38; H, 6.52. ***2Z,4E-Isomer*, 3b.** $^1H$ NMR ($CDCl_3$) δ 3.70 (s, 3H), 3.96 (s, 3H), 5.37 (s, 1H), 6.51 (d, 1H, J= 15.9 Hz), 7.17 (d, 1H, J= 15.9 Hz), 7.31-7.35 (m, 3H), 7.45 (m, 2H); $^{13}C$ NMR ($CDCl_3$) δ 167.0, 165.6, 135.8, 135.5, 129.1, 128.8, 127.3, 123.7, 101.5, 61.2, 51.1; IR ($Cl_3CH$) ν 1705, 1640, 1590, 1580, 1450, 1405 $cm^{-1}$; Anal. calcd. for $C_{13}H_{14}O_3$: C, 71.53; H, 6.47. Found: C, 71.58; H, 6.25.

***tert*-Butyl 3-methoxy-5-phenyl-2,4-pentadienoates, 3c and 3d.** Following the general procedure, 338 mg (1 mmol) of carbene **1a** and 528 mg (3 mmol) of ylide **2b** were stirred 15 min. at room temperature. After oxidation of the crude mixture, 76 mg (30 %) of **3c** (colorless oil) and 100 mg (39 %) of **3d** (colorless oil) were obtained. ***2E,4E-Isomer*, 3c.** $^1$H NMR ($CDCl_3$) δ 1.49 (s, 9H), 3.73 (s, 3H), 5.07 (s, 1H), 7.22-32 (m, 4H), 7.51-7.55 (m, 2H), 8.04 (d, 1H, J= 16.2 Hz); $^{13}$C NMR ($CDCl_3$) δ 166.8, 165.8, 136.4, 134.7, 128.7, 128.6, 127.6, 120.5, 94.4, 79.5, 55.3, 28.4; IR ($Cl_3CH$) ν 1695, 1645, 1590, 1575, 1450, 1440, 1390 cm$^{-1}$; Anal. Calcd. for $C_{16}H_{20}O_3$: C, 73.81; H, 7.75. Found: C, 74.05; H, 7.92. ***2Z,4E-Isomer*, 3d.** $^1$H NMR ($CDCl_3$) δ 1.42 (s, 9H), 3.86 (s, 3H), 5.24 (s, 1H), 6.41 (d, 1H, J= 15.6 Hz), 7.05 (d, 1H, J= 15.6 Hz), 7.17- 7.38 (m, 5H); IR ($Cl_3CH$) ν 1690, 1640, 1595, 1560, 1450, 1420 cm$^{-1}$; Anal. Calcd. for $C_{16}H_{20}O_3$: C, 73.81; H, 7.75. Found: C, 73.62; H, 7.64.

**Methyl 5-Methyl-3-methoxy-2,4-hexadienoates, 3e and 3f.** Following the general procedure, 320 mg (1.1 mmol) of carbene **1b** and 271 mg (1.1 mmol) of ylide **2c** were stirred 2.4 h. at room temperature. After oxidation of the crude mixture, 32 mg (17 %) of **3e** (pale yellow oil) and 54 mg (29 %) of **3f** (pale yellow oil) were obtained after chromatography (hexanes/EtOAc 15:1). ***E-Isomer*, 3e.** Compound **3e** was unstable decomposing within minutes in $CDCl_3$ solution or as net oil. $^1$H NMR: δ 1.91 (s, 6H), 3.61 (s, 6H), 5.01 (s, 1H), 6.77 (s, 1H). ***Z-Isomer*, 3f.** $^1$H NMR: δ 1.88 (s, 3H); 1.89 (s, 3H), 3.68 (s, 3H), 3.76 (s, 3H), 4.89 (s, 1H), 5.71 (m). $^{13}$C NMR: δ 20.2 , 26.5 , 50.8, 57.3, 97.8, 118.7, 144.8, 166.3, 166.8. IR: ν 1740, 1715. Anal. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.62; H, 8.14.

**Methyl (1'-Cyclohexenyl)-3-methoxy-2-propenoates, 3g and 3h.** Following the general procedure, 500 mg (1.1 mmol) of carbene **1c** and 271 mg (1.1 mmol) of ylide **2c** were stirred 15 min. at room temperature. After oxidation of the crude mixture, 137 mg (64 %) of **3h** (colorless oil) was obtained after chromatography (hexanes/EtOAc 20:1). Compound **3g** could not be obtained in pure form. ***E-Isomer*, 3g.** $^1$H NMR (from the mixture of isomers): δ 1.43-1.68 (m, 4H, 2.02-2.17 (m, 4H), 3.61 (s, 3H), 3.65 (s, 3H), 5.21 (s, 1H), 6.32-6.38 (m, 1H). ***Z-Isomer*, 3h.** Colorless oil. Yield 64 %. $^1$H NMR: δ 1.54-1.66 (m, 4H), 2.03-2.11 (m, 4H), 3,58 (s, 6H), 4.92 (s,1H), 5.76-5.79 (m, 1H). $^{13}$C NMR: δ 21.7, 22.5, 25.2, 26.7, 50.9, 55.9, 90.5, 129.7, 134.1, 167.5, 174.6. IR: ν 1715 , 1605. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.51; H, 8.19.

**Methyl 4-cyclopentylidene-3-methoxy-2-propenoates, 3i and 3j.** Following the general procedure, 200 mg (0.63 mmol) of carbene **1d** and 156 mg (0.63 mmol) of ylide **2c** were stirred 2.75 h. at room temperature. After oxidation of the crude mixture, 39 mg (32 %) of **3i** (pale yellow oil) and 39 mg (32 %) of **3j** (pale yellow oil) were obtained after chromatography (hexanes/EtOAc 15:1). ***E-Isomer*, 3i.** Yield 32 %. $^1$H NMR: δ 1.56-1.75 (m, 4H), 2.48 (t, 2H, J= 6.4 Hz), 2.60 (t, 2H, J= 6.4 Hz), 3.68 (s, 6H), 4.96 (s, 1H), 7.20 (t, 1H, J= 2.12 Hz). $^{13}$C NMR: δ 25.6, 27.0, 32.7, 36.7, 50.8, 55.0, 89.2, 113.4, 158.6, 168.2, 169.8. IR: ν 1715, 1640. Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.57; H, 8.30. ***Z-Isomer*, 3j.** Yield 32 %. $^1$H NMR: δ 1.63-1.78 (m, 4H), 2.43 (t, 2H, J= 6.5Hz), 2.52 (t, 2H, J= 6.5 Hz), 3.68 (s, 3H), 3.81 (s, 3H), 5.01 (s, 1H), 5.83 (m, 1H). $^{13}$C NMR: δ 25.5, 27.2, 3.9, 35.4, 50.6, 58.2, 96.9, 114.1, 157.1, 165.1, 167.1. IR: ν 1715, 1620. Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.15; H, 8.35.

**Cyclopropanes 4f-g and vinyl ether 3k.** Reaction time 22 hours (Irradiation was needed in this case). Following the general procedure from 200 mg of complex **1b** (0.69 mmoles) and 130 mg (0.69 mmoles) of ylide **2d**, 90 mg of a mixture of enol ethers **3k** and cyclopropanes **4f-g** (10:90) was obtained. From this mixture pure 11 mg (Yield 7 %) of enol ether **3k** as yellow oil and 53 mg of an inseparable mixture of cyclopropanes **4f-g** (Yield: 33 %), as yellow solid were obtained after chromatography (hexanes/EtOAc 20:1; 2:1). **5-Methyl-3-methoxy-1-phenyl-1,3-butadien-1-one, 3k.** $^1$H NMR: δ 1.56 (s, 6H), 3.78 (s, 3H), 5.61 (d, 1H, J= 0.6 Hz), 6.21 (s, 1H), 7.38-7.45 (m, 4H,), 7.96 (dd, 2H, $J_1$= 6.6Hz, $J_2$= 1.8 Hz). $^{13}$C NMR: δ 27.5, 57.7, 89.9, 92.0, 114.2, 127.9, 128.3, 131.7, 139.9, 165.1, 188.4. IR: ν 1715, 1645. Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 78.02; H, 7.21. ***cis*-Methyl 2-benzoyl-3,3-dimethylcyclopropanecarboxylate 4f.** $^1$H NMR: δ 1.16 (s, 3H), 1.49 (s, 3H), 2.61 (d, 1H, J = 5.7 Hz), 3.16 (d, 1H, J = 5.7 Hz), 3.72 (s, 3H), 7.48 (t, 2H, J = 8.5Hz), 7.58 (t, 1H, J = 9Hz), 7.95 (d, 2H, J = 9Hz). $^{13}$C NMR: δ 20.2, 20.4, 32.9, 33.2, 39.2, 52.0, 128.3, 128.7, 133.2, 137.9, 171.4, 195.9. ***trans*-Methyl 2-benzoyl-3,3-dimethylcyclopropanecarboxylate, 4g.** $^1$H NMR: δ 1.16 (s, 3H), 1.49 (s, 3H,), 2.46 (d, 1H, J= 6 Hz), 3.13 (d, 1H, J= 6 Hz), 3.72 (s, 3H), 7.48 (t, 2H, J = 8.5Hz,), 7.58 (t, 1H, J= 9Hz), 7.95 (d, 2H, J= 9Hz). Anal. Calcd for $C_{14}H_{16}O_3$ (mixture of isomers): C, 72.39; H, 6.94.. Found: C, 72.18; H, 7.07.

**Thermal and Photochemical Reactions of Carbene Complex 1a and Phosphorous Ylide 7.** ***Photochemical Reaction.*** Following an analogous procedure to that used for the reaction with sulfur ylides 100 mg (0.30 mmol) of complex **1a** and 100 mg (0.29 mmol) of ylide **7** were irradiated during 17 h. An *E/Z* mixture (76:24) of enol ethers **3a/3b** was observed in the crude reaction mixture (160 mg) after oxidation. ***Thermal Reaction.*** Carbene complex **1a** (100 mg, 0.30 mmol) and ylide **7** (108 mg, 0.32 mmol) were stirred at 0 °C for 1 h in the dark. After this time the reaction mixture was allowed to reach room temperature and stirred overnigth. An *E/Z* mixture (33:67) of enol ethers **3a/3b** was observed in the crude reaction mixture (170 mg) after oxidation.

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24. Direct sun-light is preferred due to considerably shorter oxidation times.

**Acknowledgments.** Support for this work under grant PB93-0442 (DGYCIT, Spain) is acknowledged. Luis Casarrubios thanks the CAM (Madrid-Spain) for a pre-doctoral grant.

(*Received in UK* 18 *July* 1996; *accepted* 5 *September* 1996)