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# Reactivity of α-Oxophosphonium Ylides: A Contribution to the Mechanistics

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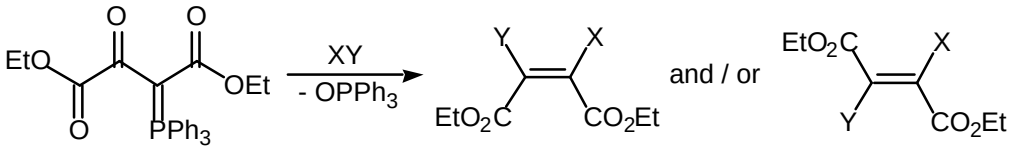
**Abstract:** Ylides **1f** and **1g** react with chlorine, with bromine and with *N*-chlorosuccinimide in the presence of a range of nucleophiles. The 2,3-disubstitutedbutenedioates obtained in this way allow us to gather more information about the mechanism involved. Ylide **1c** was also studied showing similar reactivity and leading to the highly selective synthesis of 2,3-disubstituted-3-phenylpropenoates.

**Keywords:** phosphorus ylides, tetrasubstituted alkenes.

## Introduction

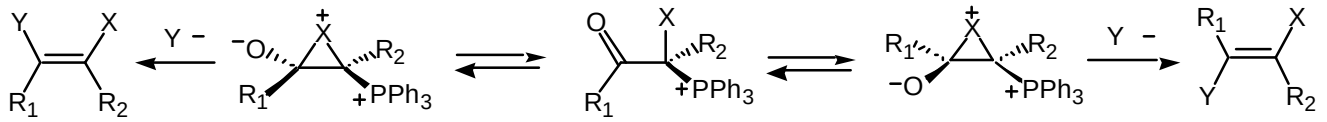
We have previously studied the reactivity of diethyl 2-oxo-3-triphenylphosphoranylidene-butanedioate **1a** with chlorine and bromine in the presence of a range of nucleophiles [1]. Triphenylphosphine oxide was eliminated and 2,3-disubstituted diethyl butenedioates were formed (Scheme 1). The reaction of *N*-bromosuccinimide and *N*-chlorosuccinimide in methanol also gave 2,3-disubstituted diethylbutenedioates. Several of the reactions were highly stereoselective whereas others gave both (*E*) and (*Z*) isomers. The method offers a route to some simple tetrasubstituted alkenes of a type that was poorly represented in the literature.




**1a**

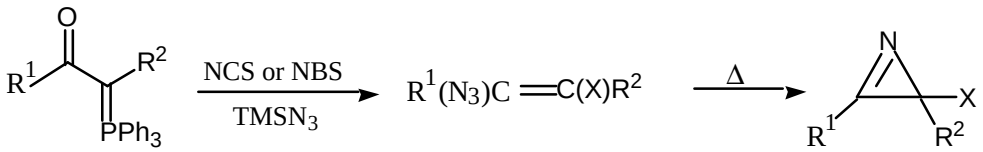
**Scheme 1.**

The formation of the observed products was explained by postulating isomeric halonium ions as intermediates. These halonium ions could interconvert by way of an acyclic cation (Scheme 2). The opening of the two halonium ions by a nucleophile would lead to the isomeric alkenes after the elimination of triphenylphosphine oxide.




**Scheme 2.**

α-Oxophosphonium ylides (**1a**–**1e**) also react with *N*-chlorosuccinimide and *N*-bromosuccinimide in the presence of azidotrimethylsilane giving the corresponding haloazidoalkenes (**2**) with elimination of triphenylphosphine oxide [1,2]. These compounds were completely converted into the corresponding *2H*-azirines **3** on heating in heptane (Scheme 3) [2].




**1** **2** **3**

**1a** $R^1 = R^2 = CO_2Et$
**1b** $R^1 = R^2 = CO_2Me$
**1c** $R^1 = Ph$; $R^2 = CO_2Et$
**1d** $R^1 = CO_2Me$; $R^2 = COPh$
**1e** $R^1 = Me$; $R^2 = CO_2Me$

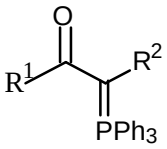
**Scheme 3.**

Abell et al [3] has also described the reaction of α-oxophosphonium ylides, bearing a terminal carboxylic acid group acting as the nucleophile, with $Br_2$ or $SOCl_2$ and $NEt_3$ which leads to the formation of *E*- and *Z*-halo enol lactones. The cyclization proceeds via a halophosphonium salt followed by loss of triphenylphosphine oxide.

## Results and Discussion

We decided to investigate this type of reactions with ylides with the general structure **1** where $R^1$ and $R^2$ are ester groups, the ylides **1f** and **1g**. These compounds should show a reactivity similar to **1a** in the reaction with halogens and *N*-chlorosuccinimide in the presence of nucleophiles. However, since ylides **1f** and **1g** have $R^1 \neq R^2$ the study of these reactions with a reagent system XY (electrophile/nucleophile), where $X \neq Y$, could allow the gathering of more information concerning the proposed mechanism.

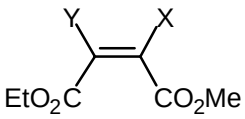
The stabilized ylides 3-oxo-2-triphenylphosphoranylidinebutanedioates **1f** and **1g** were prepared and their reactions studied. The comparision of the product obtained from **1a** [1] with those from **1f** and **1g** allowed us to establish their stereochemistry.



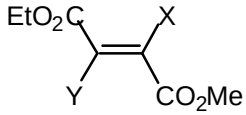

**1f** $R^1 = CO_2Et$; $R^2 = CO_2Me$
**1g** $R^1 = CO_2Me$; $R^2 = CO_2Et$

**Figure 1.**

Ylide **1f** reacted with chlorine giving, after 5 minutes, the ethyl methyl (*Z*)-2,3-dichlorobutenedioate (*Z*)-**4** in 72% yield (Table 1). The reaction of **1f** with hypobromous acid and acetic acid was a stereoselective process giving, after 24 hours, the isomer (*Z*)-**5** in 78% yield. On the other hand, the reaction with hipochlorous acid and acetic acid gave a mixture of isomers (*Z*)-**6** and (*E*)-**6** (49:51) in 49% overall yield. Ylide **1f** also reacted with chlorine in methanol giving the alkene (*E*)-**7** in 44% yield.




(*Z*)-**4** – (*Z*)-**7**



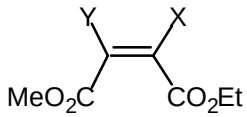

(*E*)-**4** – (*E*)-**7**

**Figure 2.**

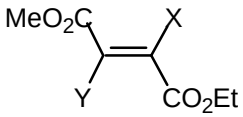
**Table 1.** Products obtained from the ylide **1f**.

| Reagents | X | Y | Products | Yield (%) |
|---|---|---|---|---|
| $Cl_2$ | Cl | Cl | (*Z*)-**4** | 72 |
| HOBr/AcOH | Br | OAc | (*Z*)-**5** | 78 |
| HOCl/AcOH | Cl | OAc | (*Z*)-**6**, (*E*)-**6** (49:51) | 49 |
| $Cl_2$/MeOH | Cl | OMe | (*E*)-**7** | 44 |

Table 2 shows the results obtained with ylide **1g**. The reaction with hypobromous acid and acetic acid gave this time a mixture of isomers (*Z*)-**8** and (*E*)-**8** being the Z isomer the major component (78:22) in 88% overall yield. The reaction with hypochlorous acid and acetic acid gave a mixture of isomers (*Z*)-**9** and (*E*)-**9** in 50% yield. Ylide **1g** also reacted with *N*-chlorosuccinimide in the presence of methanol giving alkene (*E*)-**10** in 44% yield.




(*Z*)-**8** – (*Z*)-**10**




(*Z*)-**8** – (*Z*)-**10**

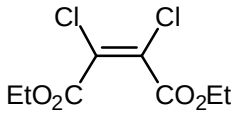
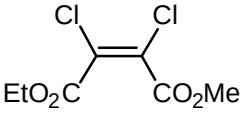
**Figure 3.**

**Table 2.** Products obtained from the ylide **1g**.

| Reagents | X | Y | Products | Yield (%) |
|---|---|---|---|---|
| HOBr/AcOH | Br | OAc | (*Z*)-**8**, (*E*)-**8** (78:22) | 88 |
| HOCl/AcOH | Cl | OAc | (*Z*)-**9**, (*E*)-**9** (47:53) | 50 |
| NCS / MeOH | Cl | OMe | (*E*)-**10** | 44 |

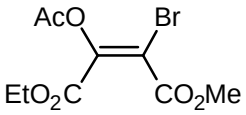
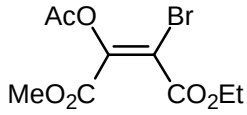
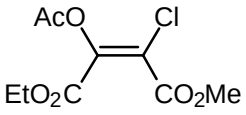
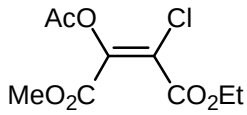
On the basis of the $^{13}C$ nmr analysis it was possible to determine the regioisomers obtained in the reactions of ylides **1f** and **1g**. From the $^{13}C$ nmr of diethyl (*Z*)-2,3-dichlorobutenedioate and of ethyl methyl (*Z*)-2,3-dichlorobutenedioate (*Z*)-**4** we could determine the effect of the substitution of an ethyl ester group by a methyl ester group (Table 3). This substitution leads to a decrease of the chemical shift of the α carbon ($\Delta\delta$ = - 0.43) and an increase of the chemical shift of the β carbon ($\Delta\delta$ = + 0.31).

**Table 3.** $^{13}C$ chemical shifts (ppm) of diethyl (*Z*)-2,3-dichloro-butenedioate [1] and ethyl methyl (*Z*)-2,3-dichlorobutenedioate (*Z*)-**4**.

| | C=O | C=C |
|---|---|---|
|   | 161.17 | 130.50 |
|   | 161.12<br>161.74 | 130.07<br>130.81 |

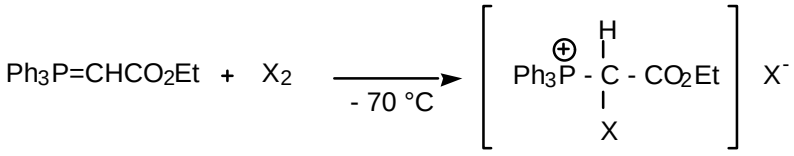
The values for the chemical shifts of double bond carbons of alkenes **4**-**10** were estimated by adding these increments to the chemical shifts of the corresponding diethyl esters. Table 4 shows the results of this analysis for the products (the *Z* isomers) of the reactions of ylides **1f** and **1g** with hypobromous and hypochlorous acids in the presence of acetic acid. The comparison of the estimated values with the experimental values allow us to define the regioisomers obtained in each case. The same analysis was carried out with the other alkenes.

**Table 4.** $^{13}C$ chemical shifts (ppm).*

| | Estimated values | | Exp.values | |
|---|---|---|---|---|
| | C-3 | C-2 | C-3 | C-2 |
|  (*Z*)-**5** | 115.04 | 141.31 | 115.12 | 141.25 |
|  (*Z*)-**8** | 115.78 | 140.57 | 115.71 | 140.63 |
|  (*Z*)-**6** | 124.49 | 139.95 | 124.54 | 139.82 |
|  (*Z*)-**9** | 125.23 | 139.20 | 125.24 | 139.49 |

* Diethyl (Z)-2-acetoxy-3-bromobutenedioate: 115.47 (C-3) and 141.00 (C-2); Diethyl (Z)-2-acetoxy-3-chlorobutenedioate 124.92 (C-3) and 139.64 (C-2) [1].

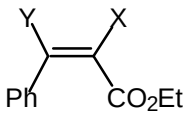
These results show that the electrophile attacks the carbon of the triphenylphosphoranylidene group of the starting ylide as postulated in Scheme 2. This fact is in agreement with the known halogenation of α-oxophosphonium ylides which gives the salt **11** [4] (Scheme 4).



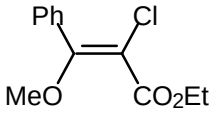

**11**

**Scheme 4.**

The reactivity of ylide **1c** was also studied. We have previously described the reaction of this ylide with NCS or NBS in the presence of azidotrimethylsilane leading to the corresponding haloazidoalkene with high selectivity [2] (Scheme 3) The reaction of the same ylide with chlorine led to the formation of dichloroalkene **12** with elimination of triphenylphosphine oxide. By analogy with the reactivity of the previously studied ylides we concluded that **12** was the *Z* isomer and was obtained in 69% yield (Table 5). The reaction with hipobromous acid and acetic acid gave **13** (60% yield) and the reaction with *N*-chlorosuccinimide in methanol gave alkene **14** in 98% yield. In all cases the reactions showed high stereoselectivity.




**12** X = Y = Cl
**13** X = Br = OAc




**14**

**Figure 4.**

**Table 5.** Products obtained from the ylide **1c**.

| Reagents | X | Y | Products | Yield (%) |
|---|---|---|---|---|
| $Cl_2$ | Cl | Cl | **12** | 69 |
| HOBr/AcOH | Br | OAc | **13** | 60 |
| NCS/MeOH | Cl | OMe | **14** | 98 |

## Conclusion

The results obtained from the study of the reactivity of ylides **1f**, **1g** and **1c** clearly indicate that the reactions studied follow the mechanism described in Scheme 2, where the halogen binds exclusively to the carbon of the phosphoranylidene group of the starting ylide and the oxygen which is eliminated in the process is from the keto carbonyl group.

This work allowed the synthesis of a range of tetrasubstituted alkenes, 2,3-disubstituted-butenedioates (**4**-**10**) and 2,3-disubstituted-3-phenylpropenoates (**12**-**14**).

## Experimental

*General*

Unless otherwise indicated all common reagents and solvents were used as obtained from

commercial suppliers without further purification. IR spectra were recorded on a Perkin Elmer 1720X FTIR spectrometer. $^{1}H$ and $^{13}C$ NMR spectra were recorded in deuteriochloroform on a Bruker AMX300 spectrometer. Mass spectra were recorded on a VG Micromass 7070E instrument by chemical ionisation (CI) with isobutane (except where indicated otherwise) or where indicated under electron impact. M.p.'s were recorded on a Leitz Wetzlar 799 hot stage and are uncorrected. Flash column chromatography was performed with Merck 9385 silica as the stationary phase.

*1-Ethyl 4-methyl 2-oxo-3-triphenylphosphoranylidenebutanedioate (***1f***)*

Methyl triphenylphosphoranylideneacetate [6] (10.93 g, 32.7 mmol) was dissolved in toluene (80 mL) and the resulting solution was cooled at 5–10 °C. Ethyl oxalyl chloride (3.6 mL, 32.83 mmol) was added dropwise. The reaction mixture was stirred at 5–10 °C for 5 min then at room temperature for 30 min. Diethyl ether (80 mL) was added and an oil separated out. The solution was decanted from the oil and the solvent was removed under reduced pressure. The residue was triturated with ether to give a colourless solid which was isolated by filtration. Water was added to the oil separated by decantation and the resulting solution was extracted with chloroform. After evaporating the solvent and addition of ether, more solid was obtained, giving altogether 8.66 g (70%).

Mp 170 - 172 $^{o}$C (lit. [7], 173 - 174$^{o}$C).

$^{1}H$ NMR δ: 1.37 (t, 3H, $C\underline{H}_3CH_2$), 3.32 (s, 3H, $CH_3$), 4.33 (q, 2H, $CH_3C\underline{H}_2$), 7.27 - 7.73 (m, 15H, Ar-H).

$^{13}C$ NMR δ: 14.05, 50.13, 60.84, 122.95, 124.80, 128.52, 128.77, 132.41, 132.36, 133.39, 133.59, 154.39, 154.51, 167.22, 167.41, 184.59, 184.51.

IR (KBr) cm$^{-1}$ 2920, 1730, 1665.

*4-Ethyl 1-methyl 2-oxo-3-triphenylphosphoranylidenebutanedioate (***1g***)*

Ethyl triphenylphosphoranylideneacetate [6] (10.39 g, 29.84 mmol) was dissolved in toluene (75 mL) and the resulting solution was cooled at 5–10 °C. Methyl oxalyl chloride (2.1 mL, 29.96 mmol) was added dropwise. The reaction mixture was stirred at 5–10 °C for 5 min then at room temperature for 30 min. Diethyl ether (70 mL) was added and an oil separated out. The solution was decanted from the oil and the solvent was removed under reduced pressure. The residue was triturated with ether to give a colourless solid which was isolated by filtration. Water was added to the oil separated by decantation and the resulting solution was extracted with chloroform. After evaporating the solvent and addition of ether, more solid was obtained, giving altogether 7.46 g (62%).

Mp 110 $^{o}$C (lit. [7], 115 - 118$^{o}$C).

$^{1}H$ NMR δ: 0.76 (t, 3H, $C\underline{H}_3CH_2$), 3.82 (q, 2H, $CH_3C\underline{H}_2$), 3.85 (s, 3H, $OC\underline{H}_3$), 7.47 - 7.86 (m, 15H, Ar-H).

IR (KBr) cm$^{-1}$ 2980, 1724, 1674.

*Ethyl 3-oxo-3-phenyl-2-triphenylphosphoranylidenepropanoate [5] (***1c***)*

Ethyl triphenylphosphoranylideneacetate [6] (5 g, 14.4 mmol) was dissolved in dry THF (50 mL) and $NEt_3$ was added (2 ml, 19.4 mmol). Benzoyl chloride (2 g, 16 mmol) was added dropwise. The reaction mixture was stirred under nitrogen at room temperature for 19 hours. The solution was filtered and the solid was washed with THF. The solvent was removed under reduced pressure and the residue was dissolved in chlroform. The organic phase was washed with water and dried over $MgSO_4$. The residue obtained upon removal of the solvent was purified by crystallization [ethyl acetate–hexane (2:1)] leading to **1c**, as a white solid (4.5 g, 72%).

Mp 94.3 - 97 $^oC$.

$^1H$ NMR δ: 0.58 (t, 3H, $C\underline{H}_3CH_2$), 3.67 (q, 2H, $CH_3C\underline{H}_2$), 7.30 - 7.36 (m, 3H, Ar-H), 7.43 - 7.56 (m, 9H, Ar-H), 7.67 - 7.70 (m, 2H, Ar-H),7.73 - 7.81 (m, 6H, Ar-H).

IR (KBr) $cm^{-1}$ 3051, 1671, 1530.

MS (EI) *m/z* (%) 452 (100), 423 (23), 379 (64), 347 (30), 77 (65).

Anal. Calc. for $C_{29}H_{25}PO_3$: C, 76.96; H, 5.57. Found: C, 76.34; H, 5.46.

*Ethyl methyl (Z)-2,3-dichlorobutenedioate (Z)-***4**

The ylide **1f** (5.82 g, 13.35 mmol) was dissolved in chloroform (120 mL) and a solutions of chlorine (1 g, 14.1 mmol) in chloroform (120 mL) was added The mixture was stirred at room temperature for 5 min. The organic phase was washed with an aqueous solution of sodium bisulfite and dried over $MgSO_4$. The residue obtained upon removal of the solvent was purified by column chromatography [ethyl acetate–hexane (2:1)] leading to the separation of triphenylphosphine oxide and isolation of the diester (*Z*)-**4**, an oil, that was purified by distillation at 73 °C/0.1.7 Torr (2.18 g, 72%).

$^1H$ NMR δ: 1.35 (t, 3H, $C\underline{H}_3CH_2$), 3.88 (t, 3H, $CH_3$) and 4.34 (q, 2H, $CH_3C\underline{H}_2$)..

$^{13}C$ NMR δ: 13.81 (q), 53.45 (q), 63.25 (t), 130.06 (s), 130.81 (s), 161.12 (s),161.72 (s).

IR (film) $cm^{-1}$ 1745, 1600

MS (CI) *m/z* (%) 227 [M($^{35}Cl$) + $H^+$] (17), 191 (25), 181 (55), 167 (12).

*1-Ethyl 4-methyl (Z)-2-acetoxy-3-bromobutenedioate (Z)-***5**

The ylide **1f** (3.87 g, 8.9 mmol) was dissolved in a mixture of acetic acid (35 mL) and chloroform (75 mL) and solutions of bromine (1.17 g, 7.3 mmol) and sodium bicarbonate (0.87 g, 10.3 mmol) in water (75 mL) were added. The reaction mixture was stirred at room temperature for 24 h and the organic phase was washed with an aqueous solution of sodium bisulfite and dried over $MgSO_4$. The residue obtained upon removal of the solvent was purified by column chromatography [ethyl acetate–hexane (2:1)] leading to the separation of triphenylphosphine oxide and isolation of the diester (*Z*)-**5**, an oil, that was purified by distillation at 112.5 °C/0.1.7 Torr (2.04 g, 78%).

$^1$H NMR δ: 1.32 (t, 3H, C$\underline{H}_3$CH$_2$), 2.25 (s, 3H, $\underline{CH}_3$CO), 2.32 (s, 3H, CO$_2\underline{CH}_3$), 4.29 (q, 2H, CH$_3$C$\underline{H}_2$).

$^{13}$C NMR δ: 13.71, 20.11, 53.51, 62.64, 115.12 (3-C), 141.25 (2-C), 159.07, 163.10, 165.17

IR (film) cm$^{-1}$ 2986, 1762, 1736

MS (CI) *m/z* (%) 295 [M($^{79}$Br) + H$^+$] (82), 279 (12), 265 (22), 221 (29).

*1-Ethyl 4-methyl (Z)- and (E)-2-acetoxy-3-chlorobutenedioate (Z)-***6** */ (E)-***6**

The ylide **1f** (5.82 g, 13.35 mmol) was dissolved in a mixture of acetic acid (52.5 mL) and chloroform (110 mL) and a solution of chlorine (7.8 g, 10.95 mmol) and sodium bicarbonate (1.32 g, 15.45 mmol) in water (110 mL) was added. The reaction mixture was stirred at room temperature for 24 h and the organic phase was then washed with an aqueous solution of sodium bisulfite and dried over $MgSO_4$. The residue obtained upon removal of the solvent was purified by column chromatography [ethyl acetate–hexane (2:1)] leading to the separation of triphenylphosphine oxide and the isolation of a mixture of the alkenes (*Z*)-**6** and (*E*)-**6** (49:51) (1.76 g, 49%) as an oil

$^1$H NMR (*Z*)-**6** δ: 1.26 (t, 3H, C$\underline{H}_3$CH$_2$), 2.24 (s, 3H, CO$\underline{CH}_3$), 3.87 (s, 3H, CO$_2\underline{CH}_3$), 4.27 (q, 2H, CH$_3$C$\underline{H}_2$).

$^{13}$C NMR (*Z*)-**6** δ: 13.62, 19.94, 53.40, 62.52, 124.54 (3-C), 139.82 (2-C), 159.48, 161.41, 166.88

$^1$H NMR (*E*)-**6** δ: 1.34 (t, 3H, C$\underline{H}_3$CH$_2$), 2.30 (s, 3H, CO$\underline{CH}_3$), 3.89 (s, 3H, CO$_2\underline{CH}_3$), 4.34 (q, 2H, CH$_3$C$\underline{H}_2$).

$^{13}$C NMR (*E*)-**6** δ 13.75, 19.94, 53.40, 62.41, 122.28 (3-C), 141.32 (2-C), 159.94, 162.23, 167.72.

IR (film) cm$^{-1}$ 2995, 2980, 1785, 1740, 1640.

MS (CI) *m/z* (%) 251 [M($^{35}$Cl) + H$^+$] (84), 221 (12), 177 (10).

*4-Ethyl 1-methyl 2-chloro-3-methoxybutenedioate (E)-***7**

The ylide **1f** (5.82 g, 13.35 mmol) was dissolved in chloroform (60 mL) and a solution of chlorine (2.55 g, 36 mmol) in methanol (45 mL) was added. The reaction was complete after 5 min at room temperature. The organic phase was washed with an aqueous solution of sodium bisulfite and dried over $MgSO_4$. The residue obtained upon removal of the solvent was purified by column chromatography [ethyl acetate–hexane (2:1)] leading to the separation of triphenylphosphine oxide and the isolation of the enol ether (*E*)-**7** (1.33 g, 44%) as an oil.

$^1$H NMR δ: 1.39 (t, 3H, C$\underline{H}_3$CH$_2$), 3.80 (s, 3H, CH$_3$O), 3.89 (s, 3H, CO$_2\underline{CH}_3$), 4.40 (q, 2H, CH$_3$C$\underline{H}_2$).

$^{13}$C NMR δ: 13.83, 52.80, 58.20, 62.74, 105.20 (2-C), 156.01 (3-C), 161.73, 163.22.

IR (film) cm$^{-1}$ 2955, 1742, 1612.

MS (CI) *m/z* (%) 223 [M($^{35}$Cl) + H$^+$] (88), 177 (100), 163 (31), 149 (70).

*4-Ethyl 1-methyl (Z)-2-acetoxy-3-bromobutenedioate (Z)*-**8** / *(E)*-**8**

The ylide **1c** (3.87 g, 8.9 mmol) was dissolved in a mixture of acetic acid (35 mL) and chloroform (75 mL) and solutions of bromine (1.17 g, 7.3 mmol) and sodium bicarbonate (0.87 g, 10.3 mmol) in water (75 mL) were added. The reaction mixture was stirred at room temperature for 24 h and the organic phase was washed with an aqueous solution of sodium bisulfite and dried over $MgSO_4$. The residue obtained upon removal of the solvent was purified by column chromatography [ethyl acetate–hexane (2:1)] leading to the separation of triphenylphosphine oxide and isolation of the mixture (*Z*)-**8** / (*E*)-**8** (78:22), an oil, that was purified by distillation at 112 °C/1.7 Torr (2.31 g, 88%).

$^1$H NMR (*Z*)-**8** δ: 1.36 (t, 3 H, C$\underline{H}_3$CH$_2$), 2.31 (s, 3 H, $\underline{CH}_3$CO), 3.81 (s, 3 H, CO$_2\underline{CH}_3$), 4.35 (q, 2 H, CH$_3$C$\underline{H}_2$).

$^{13}$C NMR (*Z*)-**8** δ: 13.79, 20.17, 53.11, 63.04, 116.97 (3-C), 140.84 (2-C), 159.77, 162.59 and 167.68.

$^1$H NMR (*E*)-**8** δ: 1.34 (t, 3 H, C$\underline{H}_3$CH$_2$), 2.23 (s, 3 H, $\underline{CH}_3$CO), 2.86 (s, 3 H, CO$_2\underline{CH}_3$), 4.32 (q, 2 H, CH$_3$C$\underline{H}_2$).

$^{13}$C NMR (*E*)-**8** δ:13.94, 20.06, 52.99, 62.95, 111.37 (3-C), 140.83 (2-C), 160.83, 161.79 and 167.33.

IR (film) cm$^{-1}$ 3000, 1782, 1738, 1638

MS (CI-CH$_4$) *m/z* (%) 296 [M($^{81}$Br)] (100), 262 (8) and 252 (55).

Anal. Calc. for $C_9H_{11}BrO_6$: C, 36.63; H, 3,76. Found: C, 36.69; H, 3.73.

*4-Ethyl 1-methyl (Z)- and (E)-2-acetoxy-3-chlorobutenedioate (Z)*-**9** / *(E)*-**9**

The ylide **1g** (5.82 g, 13.35 mmol) was dissolved in a mixture of acetic acid (52.5 mL) and chloroform (110 mL) and a solution of chlorine (7.8 g, 10.95 mmol) and sodium bicarbonate (1.32 g, 15.45 mmol) in water (110 mL) was added. The reaction mixture was stirred at room temperature for 24 h and the organic phase was then washed with an aqueous solution of sodium bisulfite and dried over $MgSO_4$. The residue obtained upon removal of the solvent was purified by column chromatography [ethyl acetate–hexane (2:1)] leading to the separation of triphenylphosphine oxide and the isolation of a mixture of the alkenes (*Z*)-**9** and (*E*)-**9** (1.67 g, 50%) as an oil, that was purified by distillation at 133 °C/1.7 Torr**.**

$^1$H NMR (*Z*)-**9** δ: 1.24 (t, 3H, C$\underline{H}_3$CH$_2$), 2.26 (s, 3H, CO$\underline{CH}_3$), 3.74 (s, 3H, CO$_2\underline{CH}_3$), 4.13 (q, 2H, CH$_3$C$\underline{H}_2$).

$^{13}$C NMR (*Z*)-**9** δ: 13.92, 20.08, 53.08, 62.96, 125.23 (3-C), 139.82 (2-C), 160.24, 161.05, 167.41.

$^1$H NMR (*E*)-**9** δ: 1.31 (t, 3H, C$\underline{H}_3$CH$_2$), 2.20 (s, 3H, CO$\underline{CH}_3$), 3.77 (s, 3H, CO$_2\underline{CH}_3$), 4.34 (q, 2H, CH$_3$C$\underline{H}_2$).

$^{13}$C NMR (*E*)-**9** δ:14.00, 20.08, 53.02, 62.81, 123.28 (3-C), 140.71 (2-C), 160.63, 161.79 and 167.04.

IR (film) $cm^{-1}$ 2988, 1741, 1636.

MS (EI) *m/z* (%) 250 $[M(^{35}Cl)]^+$ (53), 218 (8) and 156 (26).

*4-Ethyl 1-methyl 3-chloro-2-methoxybutenedioate (E)*-**10**

The ylide **1g** (3.84 g, 8.8 mmol) was dissolved in chloroform (40 mL) and a solution of *N*-chlorosuccinimide (1.2 g, 8.8 mmol) in methanol (64 mL) was added. The reaction was complete after 5 min at room temperature. The organic phase was washed with an aqueous solution of sodium bisulfite and dried over $MgSO_4$. The residue obtained upon removal of the solvent was purified by column chromatography [ethyl acetate–hexane (2:1)] leading to the separation of triphenylphosphine oxide and the isolation of the enol ether (*E*)-**10** (1.33 g, 44%) as an oil, that was purified by distillation at 119 °C/1.7 Torr**.**

$^1H$ NMR δ: 1.33 (t, 3H, $C\underline{H}_3CH_2$), 3.87 (s, 3H, $OCH_3$), 3.92 (s, 3H, $OCH_3$), 4.24 (q, 2H, $CH_3C\underline{H}_2$).

$^{13}C$ NMR δ: 13.68, 52.83, 58.01, 61.81, 105.54 (3-C), 155.30 (2-C), 161.98, 162.34.

IR (film) $cm^{-1}$ 2957, 1744, 1613.

MS (EI) *m/z* (%) 222 $[M(^{35}Cl)]^+$ (30), 207 (10), 163 (28) and 59 (100).

*Ethyl (Z)-2,3-dichloro-3-phenylpropenoate (***12***)*

The ylide **1c** (4.0 g, 8.82 mmol) was dissolved in chloroform (82 mL) and a solutions of chlorine (3.3 g, 47 mmol) in chloroform (80 mL) was added The mixture was stirred at room temperature for 1 h. The organic phase was washed with an aqueous solution of sodium bisulfite and dried over $MgSO_4$. The residue obtained upon removal of the solvent was purified by column chromatography [ethyl acetate–hexane (1:1)] leading to the separation of triphenylphosphine oxide and isolation of **12**, an oil, that was purified by distillation at 23 °C / 2.5 Torr (1.5 g, 69%).

$^1H$ NMR δ: 1.17 (t, 3H, $C\underline{H}_3CH_2$), 4.31 (q, 2H, $CH_3C\underline{H}_2$), 7.45 - 7.50 (m, 2H, Ar-H), 7.59 - 7.64 (m, 1H, Ar-H), 8.02 - 8.05 (m, 2H, Ar-H).

$^{13}C$ NMR δ: 13.49, 64.68, 82.01 (2-C), 128.74, 129.97, 130.85, 134.30, 163.90 (3-C), 183.09.

IR (film) $cm^{-1}$ 1765, 1689, 1250.

*Ethyl (Z)-3-acetoxy-2-bromo-3-phenylpropenoate (***13***)*

The ylide **1c** (2.0 g, 4.45 mmol) was dissolved in a mixture of acetic acid (17.5 mL) and chloroform (37.5 mL) and solutions of bromine (0.23 ml, 4.45 mmol) and sodium bicarbonate (0.528 g, 6.59 mmol) in water (45.5 mL) were added. The reaction mixture was stirred at room temperature for 20 h and the organic phase was washed with an aqueous solution of sodium bisulfite and dried over $MgSO_4$. The residue obtained upon removal of the solvent was purified by column chromatography [ethyl

acetate–hexane (1:1)] leading to the separation of triphenylphosphine oxide and isolation of **13**, an oil, that was purified by distillation at 82.5°C/1.5 Torr (0.84 g, 60%).

$^1$H NMR δ: 1.14 (t, 3 H, C<u>H</u>$_3$CH$_2$), 2.25 (s, 3 H, AcO), 4.29 (q, 2 H, CH$_3$C<u>H</u>$_2$), 7.42 - 7.48 (m, 2 H, Ar-H), 7.57 - 7.62 (m, 1 H, Ar-H), 8.04 - 8.06 (m, 2 H, Ar-H).

$^{13}$C NMR δ: 13.49, 20.79, 64.68, 105.87 (2-C), 128.21, 128.58, 130.07 (3-C), 130.59, 133.94, 155.42 and 182.95..

IR (film) cm$^{-1}$ 2985, 1728, 1707, 1694.

MS (CI-CH4) *m/z* (%) 313 [M($^{79}$Br) + H$^+$] (28), 253 (42) and 233 (100).

*Ethyl (E)-2-chloro-3-methoxy-3-phenylpropenoate (***14***)*

The ylide **1c** (0.5 g, 1.1 mmol) was dissolved in chloroform (5 mL) and a solution of *N*-chlorosuccinimide (0.15 g, 1.1 mmol) in methanol (8 mL) was added. The reaction was complete after 10 min at room temperature. The organic phase was washed with an aqueous solution of sodium bisulfite and dried over $MgSO_4$. The residue obtained upon removal of the solvent was purified by column chromatography [ethyl acetate–hexane (3:1)] leading to the separation of triphenylphosphine oxide and the isolation of **14** (0.26 g, 98%) as an oil, that was purified by distillation at 91.7 °C/1.5 Torr**.**

$^1$H NMR δ: 1.37 (t, 3H, C<u>H</u>$_3$CH$_2$), 3.51 (s, 3H, OMe), 4.39 (q, 2H, CH$_3$C<u>H</u>$_2$), 7.44 - 7.49 (m, 2H, Ar-H), 7.59 - 7.62 (m, 1H, Ar-H), 8.02 - 8.05 (m, 2H, Ar-H).

$^{13}$C NMR δ: 13.48, 58.95, 64.61, 81.85 (2-C), 128.59, 129.99, 130.78, 134.16, 163.96 (3-C), 183.12.

IR (film) cm$^{-1}$ 2986, 1767, 1715, 1646.

MS (EI) *m/z* (%) 240 [M($^{35}$Cl)]$^+$ (3), 195 (3), 153 (2), 77 (45).

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*Samples Availability*: Samples available from the authors.