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An Extremely Efficient Way to Prepare Conjugated Carbonyl Compounds from Terminal Alkenes via the Reactions of Ozonides, Triethylamine and Stable Phosphorus Ylides
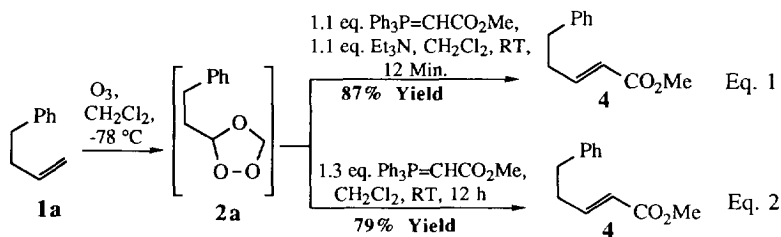
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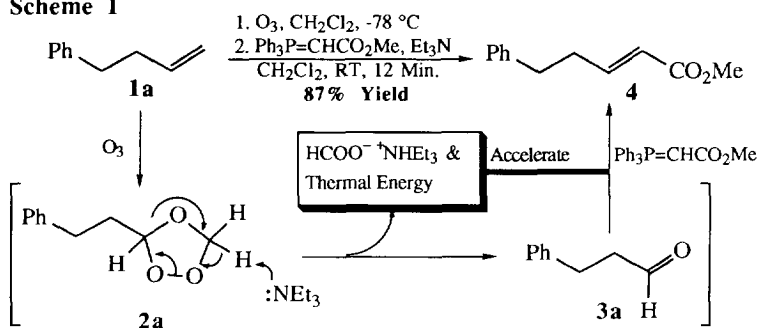Institute of Chemistry, Academia Sinica, Nankang, Taipei, Taiwan 11529, R. O. C.

Abstract: Ozonides derived from mono- and 1,1-di-substituted olefins reacted with triethylamine in the presence of nucleophiles, such as phosphorus ylide or phosphonoacetate to give conjugated carbonyl compounds almost instantaneously in excellent yields. These transformations were accelerated by the by-product (*i.e.* thermal energy and ammonium formate) generated in the reaction.

Simplicity and efficiency are important to synthetic chemistry. Therefore, the development of methods to simplify chemical transformations and minimize manipulations has long been an important mission to synthetic chemists.[1] The by-product in most reactions is usually not useful to the reaction itself. If the by-product could be used in the further transformation in the same flask, this type of reaction will become a very efficient one.[2] We have reported that ozonides derived from mono- and 1,1-di-substituted olefins reacted with secondary amine in the presence of 4Å molecular sieves to afford the tertiary amines in good yield. The ammonium formate, a by-product of the reaction, became a reducing agent in the further transformation. It is a very efficient reaction which involved four sequential transformation in the same flask.[3] We also reported that ozonides derived from mono-substituted alkenes react with $Ph_3P=CHCOOMe$ or $Ph_3P=CHCOPh$ to form *trans-*α,β-unsaturated esters or ketones, respectively, in high yields. This reaction is unique because no reducing agent is needed to reduce the ozonide intermediate. It is also a very efficient reaction which involved three sequential transformations in the same flask.[4] However, it usually took more than 10 h to complete the reaction at room temperature. We tried to improve the efficiency of this reaction by using the concept of the by-product catalysis. In this report, we describe how the by-product (*i.e.* ammonium formate and thermal energy) generated in the same flask affect the reaction rate of the C–C double bond formation.

Since the yield of the ozonide formation from terminal olefins is excellent,[5] the ozonides could be prepared *in situ* at -78 °C and used for the further transformations in the same flask. The mono-substituted ozonide **2a** derived from 3-phenyl-1-butene (**1a**) was treated with a mixture of triethylamine (1.1 mol. equiv.) and $Ph_3P=CHCO_2Me$ (1.1 mol. equiv.) at room temperature to give *trans-*methyl 5-phenyl-2-pentenoate (**4**) in 87% yield in 12 min (Eq. 1). In the absence of triethylamine, it took 12 h to complete the reaction (Eq. 2).[4] The contrast in reaction rates between these two conditions was explained as shown in Scheme 1. The ozonide **2a** generated *in situ* was attacked by triethylamine to give hydrocinnamaldehyde (**3a**)[6], triethylammonium formate and thermal energy. Aldehyde **3a** reacted with phosphorus ylide to give the *trans-*conjugated ester **4**. In the
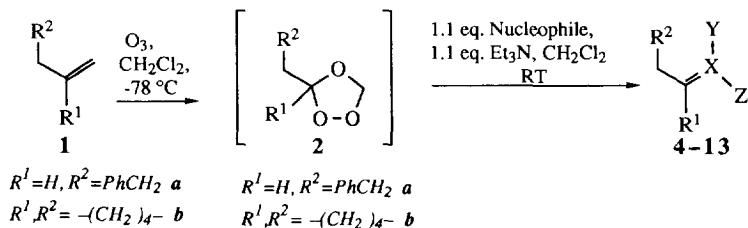
1.1 eq. Ph₃P=CHCO₂Me,
1.1 eq. Et₃N, CH₂Cl₂, RT,
12 Min.

$$\begin{array}{c}\text{1.1 eq. Ph}_3\text{P=CHCO}_2\text{Me,}\\ \text{1.1 eq. Et}_3\text{N, CH}_2\text{Cl}_2\text{, RT,}\\ \underline{\text{12 Min.}}\\ \textbf{87\% Yield}\end{array}$$

Eq. 1

$$\begin{array}{c}\text{1.3 eq. Ph}_3\text{P=CHCO}_2\text{Me,}\\ \underline{\text{CH}_2\text{Cl}_2\text{, RT, 12 h}}\\ \textbf{79\% Yield}\end{array}$$

Eq. 2

Scheme 1

1. O₃, CH₂Cl₂, -78 °C
2. Ph₃P=CHCO₂Me, Et₃N
   CH₂Cl₂, RT, 12 Min.
   87% Yield

HCOO⁻ ⁺NHEt₃ &
Thermal Energy   Accelerate   Ph₃P=CHCO₂Me

Table 1 : Reaction of aldehyde **3a** with Ph₃P=CHCO₂Me in CH₂Cl₂ gave conjugated ester **4** at room temperature.

entry	catalyst	time (h)	yield (%)
1	—	1.5	91
2	1 mol. eq. HCO₂⁻ ⁺NHEt₃	0.5	91
3	1 mol. eq. PhCO₂H	0.5	89
4	0.1 mol. eq. HCO₂⁻ ⁺NHEt₃	0.5	89

entire transformation, three sequential reactions occurred in the same flask. In order to delineate the effects of the ammonium salt and thermal energy on the Wittig reaction, the reaction of aldehyde **3a** and Ph₃P=CHCO₂Me under several reaction conditions were attempted and their results are shown in Table 1. Without catalyst, the Wittig reaction was complete in 1.5 h at room temperature (entry 1). However, in the presence of an acidic catalyst[7] in either a stoichiometric (entries 2 and 3) or catalytic amount (entry 4), all the reactions were complete in 30 min at room temperature. As far as the reaction rates were concerned, the reaction time in Eq. 1 (12 min) is shorter than that of entry 2 of Table 1 (30 min). The only difference of these two conditions was the thermal energy generated from the decomposition of the ozonide by triethylamine. These data clearly indicated the contribution of the thermal energy to the reaction rate. Therefore, both the ammonium formate and thermal energy played important roles to accelerate the Wittig reaction as shown in Scheme 1.

Scheme 2

$$\underset{\mathbf{1}}{\overset{R^2}{\underset{R^1}{\diagup\!\!\diagdown}}} \xrightarrow[-78\,^{\circ}C]{\substack{O_3,\\ CH_2Cl_2,}} \left[\underset{\mathbf{2}}{\overset{R^2}{\underset{R^1}{\diagup\!\!\diagdown}}}\overset{O}{\underset{O-O}{\diagup}}\right] \xrightarrow[\text{RT}]{\substack{1.1\ eq.\ Nucleophile,\\ 1.1\ eq.\ Et_3N,\ CH_2Cl_2}} \underset{\mathbf{4\text{--}13}}{\overset{R^2}{\underset{R^1}{\diagup\!\!\diagdown}}}\overset{Y}{\underset{Z}{\diagup\!\!X}}$$

$R^1=H, R^2=PhCH_2$ **a** $R^1=H, R^2=PhCH_2$ **a**

$R^1,R^2= -(CH_2)_4-$ **b** $R^1,R^2= -(CH_2)_4-$ **b**

Table 2: Reaction of ozonides **2** derived from alkene **1** with triethylamine in the presence of other nucleophiles at room temperature.

entry	starting material	nucleophile	time (h)	product		yield[e] (%)
1	**1a**	$Ph_3P=CHCO_2Me$	1/5	X=C, Y=H, Z=CO$_2$Me	**4**	87
2	**1a**	$Ph_3P=CHCO_2Bu\text{-}t$	1/5	X=C, Y=H, Z=CO$_2$Bu-t	**5**	84
3	**1a**	$Ph_3P=CHCO_2CH_2Ph$	1/5	X=C, Y=H, Z=CO$_2$CH$_2$Ph	**6**	84
4	**1a**	$Ph_3P=CMcCO_2Me$	1/5	X=C, Y=Me, Z=CO$_2$Et	**7**	90
5	**1a**	$Ph_3P=CHCOMe$	1/5	X=C, Y=H, Z=COMe	**8**	79
6	**1a**	$Ph_3P=CHCOPh$	1/5	X=C, Y=H, Z=COPh	**9**	78
7	**1a**	$Ph_3P=CHCHO$	3	X=C, Y=H, Z=CHO	**10**	54[a]
8	**1a**	$(EtO)_2POCHNaCO_2Me$	1/5	X=C, Y=H, Z=CO$_2$Me	**4**	91[b]
9	**1b**	$Ph_3P=CHCO_2Me$	12	X=C,Y=H, Z=CO$_2$Me	**11**	43[c]
10	**1b**	$(EtO)_2POCHNaCO_2Me$	1/5	X=C, Y=H, Z=CO$_2$Me	**11**	89[b]
11	**1a**	$(EtO_2C)_2CH_2$	1/5	X=C, Y=Z=CO$_2$Et	**12**	80[d]
12	**1b**	$TsNHNH_2$	1/5	X,Y=N, Z=NHTs	**13**	93

[a] Refluxing in THF is required. [b] $(EtO)_2POCHNaCO_2Me$ in THF was used. [c] Refluxing in benzene is required. [d] Piperidine instead of triethylamine was used as base. [e] The isolated yields were reported.

The results in Table 2 indicate that many phosphorus ylides can be employed in this newly developed method. Both the α,β-unsaturated esters **4-7** and enones **8-9** were also formed in 12 min. In general, the yields for the ester formation are better than those of the ketone formation (entries 1-4 and 5-6). The yields are relatively insensitive to changes in carboxylate alkoxy substitution. When Ph$_3$P=CHCHO was used in the reaction at room temperature, only aldehyde **3a** was formed. In order to obtain α,β-unsaturated aldehyde **10**, refluxing in tetrahydrofuran for 3 h is needed and 54% yield of the enal **10** was obtained (entry 7).

Interestingly, a mixture of triethylamine and sodium methyl diethylphosphonoacetate in tetrahydrofuran could also afford the conjugated ester **4** in excellent yield (entry 8). For 1,1-di-substituted ozonide, $(EtO)_2POCHNaCO_2Me$ is a better reagent than $Ph_3P=CHCO_2Me$ to form the α,β-unsaturated ester **11** (entries 9 and 10). The stable phosphorus ylide is almost inert to ketone in the absence of catalyst.[7a] The presence of thermal energy and ammonium formate generated in the reaction mixture is not enough to push the reaction forward. Without any additional catalyst, refluxing in benzene is needed to complete the reaction but the yield is only 43% (entry 10). When piperidine instead of triethylamine was utilized to decompose the ozonide (**2a**), diethyl malonate could react with aldehyde to yield the Knoevenagel reaction adduct **12** in a short period of time (entry 11).[8] The yield of the hydrazone **13** formed from methylenecyclohexane is also excellent using our reaction conditions (entries 12).

In summary, the by-product, *i.e.* thermal energy and the triethylammonium formate generated in the reaction of ozonide and triethylamine, played important roles to accelerate the C=C and C=N bond formations. To take advantage of the by-product catalysis concept, our methodology provides an extremely efficient entry to functionalize the mono- and 1,1-di-substituted alkenes.

EXPERIMENTAL

All reactions were carried out under nitrogen. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. Melting points were determined by using a Yanaco micro melting point apparatus and were uncorrected. The ^1H and ^{13}C-NMR spectra were recorded on a Bruker AC 200 spectrometer, and chemical shifts were given in ppm downfield from tetramethylsilane (TMS). IR spectra were taken with a Perkin Elmer 882 spectrophotometer and only noteworthy absorptions were listed. Mass spectra were measured on a VG 70-250S mass spectrometer by electronic impact at 70 eV (unless otherwise indicated).

Standard procedure for reactions of hydrocinnamaldehyde (3a) with phosphorus ylides: To a solution of 115 mg (0.86 mmol) of hydrocinnamaldehyde (**3a**) in 4 mL of dichloromethane was added successively 221 mg (0.94 mmol) of $Ph_3P=CHCO_2Me$ and catalyst (i.e. triethylammonium formate or benzoic acid) at room temperature. The amount of the catalyst used in the reaction, the reaction time and chemical yields are shown in Table 1. The reaction mixtures were concentrated and chromatographed on a silica gel column by elution with EtOAc/hexane (1/20) to give methyl *trans*-5-phenyl-2-pentenoate (**4**) as a colorless oil.

Standard procedure for reactions of ozonides with a mixture of triethylamine and phosphorus ylides: In a 25 mL two-neck flask, equipped with a magnetic stirrer, a drying tube and a gas dispersion tube (with porous fritted tip), were placed 5 mL of dichloromethane and 4-phenyl-1-butene (**1a**) (132.2 mg, 1 mmol). A stream of ozone was bubbled through the solution at -78 °C. Ozone treatment was terminated when the solutions assumed a blue color. Excess ozone was removed by a stream of nitrogen. The reaction mixtures were then allowed to warm up to room temperature. A mixture of Et_3N (111.3 mg, 1.1 mmol) and $Ph_3P=CHCO_2Me$ (368 mg, 1.1 mmol) in 5 mL of dichloromethane was added to the solution. It was an exothermic reaction and the dichloromethane boiled instantaneously. A refluxing condenser was required if a larger scale reaction was carried out. The reaction completed within 12 min. The reaction mixture was concentrated and chromatographed on a silica gel column by elution with EtOAc/hexane (1/20) to give methyl *trans*-5-phenyl-2-pentenoate (**4**) (165.4 mg, 87% yield) as a colorless oil. The results obtained from other phosphorus ylides are listed in Table 2.

Standard procedure for reactions of ozonides with a mixture of triethylamine and sodium phosphonate: Triethylamine (116 mg, 1.15 mmol) was added to a solution of methyl diethylphosphonoacetate (241.7 mg, 1.15 mmol) and NaH (27.6 mg, 1.15 mmol) in 5 mL of THF at 0 °C for 15 min. At room temperature, the resulted solution was added to a solution of ozonide **2a** formed from 4-phenyl-1-butene (**1a**) (132.2 mg, 1 mmol) in dichloromethane. The reaction completed within 12 min. The reaction mixture was concentrated and chromatographed on a silica gel column by elution with EtOAc/hexane (1/20) to give methyl *trans*-5-phenyl-2-pentenoate (**4**) (173.1 mg, 91% yield) as a colorless oil.

Methyl trans-5-phenyl-2-pentenoate (4) Oil; ^{1}H-NMR (CDCl$_3$) δ 2.50–2.58 (m, 2H), 2.78 (t, *J* = 7.4 Hz, 2H), 3.72 (s, 3H), 5.85 (dt, *J* = 15.6 and 1.6 Hz, 1H), 7.01 (dt, *J* = 15.6 and 8.8 Hz, 1H), 7.17–7.33 (m, 5H, Ph-H) ; ^{13}C-NMR (CDCl$_3$) δ 33.84, 34.31, 51.39 (OMe), 121.44 (CH=$\underline{C}$HCO), 126.15, 128.30, 128.45, 140.71, 148.31 ($\underline{C}$H=CHCO), 166.97 (C=O); IR (CH$_2$Cl$_2$) (ν, cm^{-1}): 3029, 2949, 1717, 1653, 1431, 1316, 1256, 1199, 1150; MS (m/z) (60 eV, rel. intensity): 190 (M$^+$, 8), 159 (7), 158 (8), 130 (15), 91 (100); HRMS (m/z): 190.0997 (M$^+$, C$_{12}$H$_{14}$O$_2$, Calcd 190.0994).

tert-Butyl trans-5-phenyl-2-pentenoate (5): Oil; ^{1}H-NMR (CDCl$_3$) δ 1.48 (s, 9H, *tert*-Bu-H), 2.51 (m, 2H), 2.76 (m, 2H, PhCH$_2$), 5.78 (dt, *J* = 15.7 and 1.6 Hz, C=C$\underline{H}$CO), 6.90 (dt, *J* = 15.7 and 6.7 Hz, 1H, CH$_2$C$\underline{H}$=CH), 7.10–7.33 (m, 5H, Ph-H); ^{13}C-NMR (CDCl$_3$) δ 28.14, 33.78, 34.43, 80.08 (O$\underline{C}$Me$_3$), 123.50 ($\underline{C}$H=CHCO), 126.10, 128.30, 128.44, 140.97, 146.74 (C=$\underline{C}$HCO), 165.96 (C=O); IR (CH$_2$Cl$_2$) (ν, cm^{-1}): 3029, 3004, 2977, 2931, 1701, 1648, 1474, 1450, 1389, 1365, 1297, 1144, 847; MS (m/z) (40 eV, rel. intensity): 176 (M$^+$, 20), 159 (20), 130 (15), 91 (100); HRMS (m/z): 176.0833 (M$^+$, C$_{15}$H$_{20}$O$_2$, Calcd 176.0837).

Benzyl trans-5-phenyl-2-pentenoate (6): Oil; ^{1}H-NMR (CDCl$_3$) δ 2.48 (m, 2H), 2.74 (t, *J* = 8.2 Hz, 2H, CH$_2$Ph), 5.15 (s, 2H, OCH$_2$Ph), 5.88 (dt, *J* = 15.7 and 1.5 Hz, 1H), 7.04 (dt, *J* = 15.7 and 6.7 Hz, 1H), 7.12–7.36 (m, 10H, 2 Ph-H); ^{13}C-NMR (CDCl$_3$) δ 33.80, 34.16, 65.90 (O$\underline{C}$H$_2$Ph), 121.41 (CH=$\underline{C}$HCO), 126.06, 128.03, 128.19, 128.38, 136.02, 140.61, 148.62 (CH$_2$$\underline{C}$H=CH), 166.17 (C=O); IR (CH$_2$Cl$_2$) (ν, cm^{-1}): 3055, 3033, 2943, 1715, 1650, 1308, 1250, 1168, 1082, 1019, 979, 695 ; MS (m/z) (33 eV, rel. intensity): 266 (M$^+$, 3), 181 (10), 175 (22), 159 (12), 129 (6), 117 (8), 91 (100); HRMS (m/z): 266.1305 (M$^+$, C$_{18}$H$_{18}$O$_2$, Calcd 266.1307).

Ethyl (3E)-5-phenyl-2-methyl-2-pentenoate (7): Oil; ^{1}H-NMR (CDCl$_3$) δ 1.28 (t, *J* = 7.3 Hz, 3H), 1.78 (s, 3H, Me), 2.48 (q, *J* = 7.3 Hz, 2H), 2.75 (t, *J* = 7.3 Hz, 2H), 4.18 (q, *J* = 7.3 Hz, 2H), 6.80 (t, *J* = 7.3 Hz, 1H), 7.17–7.31 (m, 5H); ^{13}C-NMR (CDCl$_3$) δ 12.24, 14.20, 30.52, 34.67, 35.42, 60.35 (O-$\underline{C}$H$_2$Me), 126.00 (C=$\underline{C}$HCO), 128.26, 128.36, 140.81 (CH$_2$$\underline{C}$H=CH), 141.18, 168.06 (C=O); IR (CH$_2$Cl$_2$) (ν, cm^{-1}): 1700, 1647, 1253, 1173, 1116, 707 ; MS (m/z) (60 eV, rel. intensity): 218 (M$^+$, 20), 173 (10), 144 (5), 117 (5), 91 (100); HRMS (m/z): 218.1302 (M$^+$, C$_{14}$H$_{18}$O$_2$, Calcd 218.1307).

(3E)-6-Phenyl-3-hexene-2-one (8): Oil; ^{1}H-NMR (CDCl$_3$) δ 2.22 (s, 3H), 2.56 (m, 2H), 2.79 (t, *J* = 6.9 Hz, 2H), 6.09 (dt, *J* = 16.0 and 1.4 Hz, 1H), 6.82 (dt, *J* = 16.0 and 6.6 Hz, 1H), 7.15–7.30 (m, 5H); ^{13}C-NMR (CDCl$_3$) δ 26.67 ($\underline{C}$H$_3$CO), 33.88, 34.21, 126.03, 128.13, 128.31, 131.51 (CH=$\underline{C}$HCO), 140.46, 146.84 (CH$_2$$\underline{C}$H=C), 198.26 (C=O); IR (CH$_2$Cl$_2$) (ν, cm^{-1}): 3029, 2939, 1664, 1623, 1492, 1421, 1356, 1313, 1246, 1184, 1086, 974 ; MS (m/z) (60 eV, rel. intensity): 174 (M$^+$, 5), 159 (5), 131 (7), 116 (18), 91 (100); HRMS (m/z): 174.1047 (M$^+$, C$_{12}$H$_{14}$O, Calcd 174.1045).

(2E)-5-Phenyl-2-pentanophenone (9): Oil; ^{1}H-NMR (CDCl$_3$) δ 2.58–2.68 (m, 2H), 2.70–3.00 (m, 2H), 6.85 (d, *J* = 14.2 Hz, 1H), 7.00–7.12 (m, 1H), 7.12–7.44 (m, 5H), 7.45 (m, 3H), 7.86–7.90 (m, 2H); ^{13}C-NMR (CDCl$_3$) δ 34.43, 126.13, 126.52, 128.45, 132.57 (CH=$\underline{C}$HCO), 140.75, 148.34 (CH$_2$$\underline{C}$H=CH), 190.79 (C=O); IR (CH$_2$Cl$_2$) (ν, cm^{-1}): 2985, 2928, 1702, 1647, 1603, 1067, 775; MS (m/z) (60 eV, rel. intensity): 236 (M$^+$, 10), 116 (20), 105 (33), 91 (100), 77 (18); HRMS (m/z): 236.1207 (M$^+$, C$_{17}$H$_{16}$O, Calcd 236.1201).

(2E)-5-Phenyl-pent-2-enal (10): Oil; ^{1}H-NMR (CDCl$_3$) δ 2.67 (q, *J* = 6.3 Hz, 2H), 2.84 (t, *J* = 8.5 Hz, 2H), 6.13 (dd, *J* = 15.5 and 7.9 Hz, 1H), 6.86 (dt, *J* = 15.6 and 6.3 Hz, 1H), 9.49 (d, *J* = 7.9 Hz, 1H); ^{13}C-NMR (CDCl$_3$) δ 34.17, 126.34, 128.28, 128.55, 133.37, 140.22, 157.21, 193.89; IR (CH$_2$Cl$_2$) (ν, cm^{-1}): 2931, 1686, 1490, 1121, 971 ; MS (m/z) (50 eV, rel. intensity): 160 (M$^+$, 8), 142 (5), 116 (20), 91 (100), 77 (5), 65 (18); HRMS (m/z): 160.0895 (M$^+$, C$_{11}$H$_{12}$O, Calcd 160.0888).

Methyl cyclohexylideneacetate (11): Oil; ^{1}H-NMR (CDCl3) δ 1.63 (br, 6H), 2.21 (br, 2H), 2.84 (br, 2H), 3.70 (s, 3H, -OMe), 5.62 (s, 1H); ^{13}C-NMR (CDCl3) δ 26.17, 27.74, 28.55, 29.77, 37.90, 50.65, 112.50, 163.74; IR (CH2Cl2) (v, cm $^{-1}$): 2936, 2857, 1703, 1642, 1434, 1377, 1205, 1158, 696 ; MS (m/z) (70 eV, rel. intensity): 154 (M[+], 100), 139 (12), 123 (75), 111 (51), 95 (65), 79 (53), 67 (52); HRMS (m/z): 154.0982 (M[+], C9H14O2, Calcd 154.0993).

Diethyl 3-phenylpropylidenemalonate (12): Oil; ^{1}H-NMR (CDCl3) δ 1.23–1.34 (m, 6H), 2.50–2.80 (m, 4H), 4.15-4.33 (m, 4H), 7.03 (t, J = 7.6 Hz, 1H), 7.16-7.29 (m, 5H); ^{13}C-NMR (CDCl3) δ 14.06, 31.33, 34.39, 61.22, 126.24, 128.28, 128.50, 135.06, 140.33, 148.07, 163.91 (C=O), 165.30 (C=O); IR (CH2Cl2) (v, cm $^{-1}$): 2981, 1724, 1601, 1370, 1254, 1174, 1092, 1026, 907; MS (m/z) (60 eV, rel. intensity): 276 (M[+], 12), 230 (18), 202 (18), 184 (42), 156 (12), 129 (30), 91 (100); HRMS (m/z): 276.1372 (M[+], C16H20O4, Calcd 276.1362).

Cyclohexanone Tosylhydrazone (13): The ozonide **2a** from 4-phenyl-1-butene (**1a**) (132.2 mg, 1 mmol) in 5 mL of dichloromethane was prepared according to the procedure described above. A mixture of piperidine (93.7 mg, 1.1 mmol) and diethyl malonate (176.2 mg, 1.1 mmol) in 5 mL of dichloromethane was added to the solution. It was an exothermic reaction and the dichloromethane was boiled instantaneously. The reaction completed within 12 min. The reaction mixture was concentrated and chromatographed on a silica gel column by elution with EtOAc/hexane (1/10) to give the desired product **13** (141.1 mg, 80% yield) as a white solid, m. p. 157-158 °C. ^{1}H-NMR (CDCl3) δ 1.5–1.7 (m, 6H), 2.15–2.35 (m, 4H), 2.43 (s, 3H), 7.31 (d, J = 8.3 Hz, 2H), 7.33 (br, 1H, N-H), 7.84 (d, J = 8.3 Hz, 2H); ^{13}C-NMR (CDCl3) δ 21.56, 25.32, 25.62, 26.69, 26.80, 35.23, 128.06, 129.44, 129.91, 143.81, 162.68 (C=N); IR (CH2Cl2) (v, cm $^{-1}$): 3051, 2945, 1603, 1255, 1162, 1090, 712, 689; MS (m/z) (28 eV, rel. intensity): 266 (M[+], 8), 171 (18), 157 (22), 139 (50), 111 (72), 91 (100), 81 (40), 67 (93); HRMS (m/z): 266.1093 (M[+], C13H18N2O2S, Calcd 266.1089).

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