

The Reaction of Ozonides from Mono-substituted Alkenes with Stabilized Phosphorus Ylides

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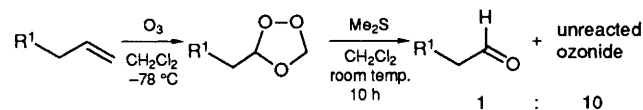
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Ozonides derived from mono-substituted alkenes react with methyl (triphenylphosphoranylidene)acetate or (triphenylphosphoranylidene)acetophenone to form *trans*- α,β -unsaturated esters or ketones, respectively, in high yields.

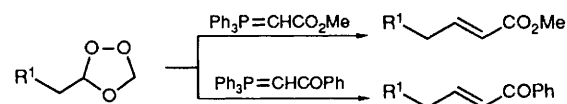
Ozonolysis is an important tool for the cleavage of carbon-carbon double bonds.¹ The intermediate ozonides can be reduced *in situ* to give the corresponding carbonyl compounds or alcohols by treating them with reducing agents, such as methyl sulphide,^{2,3} triphenylphosphine⁴ and sodium borohydride.^{5,6} Occasionally, ozonides are isolated and characterized for the purpose of mechanistic studies.⁷⁻⁹ Nevertheless, little is known about the reactivity of ozonides toward various reagents except as oxidizing and reducing agents.¹

Recently, we found that the ozonides derived from mono-substituted alkenes were reduced to form the aldehydes with difficulty by methyl sulphide in dichloromethane^{3†} (Scheme 1). To our surprise, these ozonides reacted with 1.3 equivalents of methyl (triphenylphosphoranylidene)acetate

($\text{Ph}_3\text{P}=\text{CHCO}_2\text{Me}$) or (triphenylphosphoranylidene)acetophenone ($\text{Ph}_3\text{P}=\text{CHCOPh}$) to give the corresponding α,β -unsaturated esters or ketones, respectively, in high yields (Scheme 2 and Table 1). Furthermore, it was feasible to carry out sequential ozonolysis and Wittig reaction in one flask; the overall yields were comparable with those from the corresponding two-step process (entries 4-7).



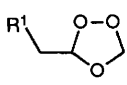
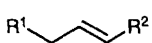
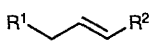
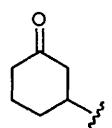
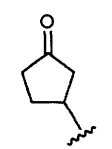
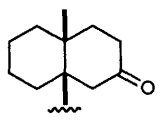
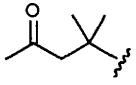
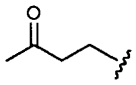
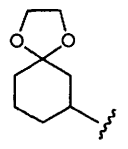
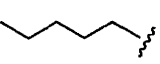
Scheme 1



Scheme 2

[†] After the solvent had been removed under reduced pressure at room temperature, the oily residues were characterized by 200 MHz NMR spectroscopy. The integration ratio is about 10:1 for ozonides to aldehydes.

Table 1 Yields of ozonides, α,β -unsaturated esters and ketones

Entry	R ¹ =	 Yield (%) ^a	 Yield from ozonide (%) ^b	 Yield from one flask reaction (%)
1		95	R ² = CO ₂ Me 85 R ² = COPh 55	—
2		90	R ² = CO ₂ Me 93 R ² = COPh 72	—
3		92	R ² = CO ₂ Me 93 R ² = COPh 62	—
4		93	R ² = CO ₂ Me 92 R ² = COPh 65	R ² = CO ₂ Me 90 R ² = COPh 64
5		93	R ² = CO ₂ Me 91 R ² = COPh 67	R ² = CO ₂ Me 91 R ² = COPh 67
6		94	R ² = CO ₂ Me 92 R ² = COPh 61	R ² = CO ₂ Me 92 R ² = COPh 61
7		90	R ² = CO ₂ Me 90 R ² = COPh 72	R ² = CO ₂ Me 89 R ² = COPh 68

^a All of the ozonides were characterized by IR (1110 and 1060 cm⁻¹), and NMR (¹H, ¹³C, DEPT, 2D-HETCOR) spectroscopy; they were stable at room temperature for several weeks. ^b Only *trans* isomers were obtained, which were identified by their coupling constants (*J* 15–16 Hz). All of the products were characterized by exact mass, IR, and NMR (¹H, ¹³C).

The standard procedure for the sequential ozonolysis and Wittig reaction is as follows. Ozone was introduced into a flask containing a mono-substituted alkene in dichloromethane at -78 °C until the solution turned blue. The excess of ozone was then excluded by nitrogen gas. Methyl (triphenylphosphoranylidene)acetate (1.3 equiv.) was added to the solution, which was warmed up to room temperature. The reaction was complete within 8–12 h.

The results listed in Table 1 indicate that the newly developed method is efficient for the preparation of α,β -unsaturated esters and ketones. The yields for the ester formation were excellent (85–93%). Also, we found that phosphorus ylides (*i.e.*, Ph₃P=CHCO₂Me and Ph₃P=CHCOPh) selectively reacted with the ozonide moiety in the presence of a keto group (entries 1–5). Moreover, only *trans* isomers were generated in these reactions. To the best of our knowledge, this is the first example involving the reaction of ozonides and stabilized ylides to form a carbon–carbon

double bond. The mechanism of this reaction is under investigation in our laboratory.

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