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Synthesis of alkenes from tertiary esters utilizing the triphenylphosphine-iodine system

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Abstract—The treatment of tertiary esters with triphenylphosphine and iodine under mild conditions gives the most stable alkene in good yield. Formates, acetates and trifluoroacetates were studied. © 2004 Elsevier Ltd. All rights reserved.

The elimination of carboxylic esters, in which the alkyl group has a β hydrogen, has long been utilized to prepare olefins. However, this method usually involves heating with bases or acids, or pyrolysis, which limits its synthetic usefulness.¹

In a recent paper we have reported that tertiary alcohols undergo regioselective dehydration in the presence of triphenylphosphine and iodine.²

Following our study of the use of this reagent for synthetic purposes we have found that tertiary esters are also converted into the most stable alkenes when they are treated with triphenylphosphine and iodine, under similar conditions to those reported for alcohols. Elimination of some formates, acetates and trifluoroacetates was investigated. The results and conditions are summarized in Table 1. Acetates and formates show a similar degree of reactivity, whereas trifluoroacetates react very slowly (entry 15). Ketoesters 1 and 3 gave the alkenes 2 and 4, respectively (entries 1 and 2). Formates 5 and 7 showed a similar behaviour to that reported for the corresponding alcohols (entries 3 and 4).² Primary acetates do not undergo elimination under these conditions (entries 9 and 10), but the 1,3-diacetate **21** was transformed into the stable diene **22**,² which also resulted from acetoxyalkene **23**. Entry 13 describes a very interesting result: the γ -acetoxyacid **24** and its methyl ester **25** gave isosclareolide (**26**), a very useful synthon,³ in good yield under the reaction conditions. Otherwise, the β -acetoxyester **27** was converted into the β , γ -unsaturated ester **28**. The bis(trifuoroacetate) **29** gave **30** and **31a–b** after 12 h; dienes **31a–b** were the only products when the reaction continued longer (entry 15).

The procedure reported is of great synthetic significance in the case of formates, which can be prepared following our previously reported methodologies, the Baeyer–Villiger rearrangement of tertiary aldehydes⁴ or the thermal rearrangement of ozonides.⁵ The treatment of these formates with triphenylphosphine and iodine, which leads to the most stable alkene, is, from the point of view of regioselectivity, complementary with the elimination of formic acid by heating with collidine, which usually gives the kinetic alkene.⁴ Thus, compounds **1**, **5** and **7** gave predominantly the exocyclic alkene when treated with collidine, whereas **11** gave a 1:1 mixture of the tri- and disubstituted alkenes.

On the whole, as it has been indicated for **11**, elimination of tertiary carboxylic esters with

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Table 1. Reaction of tertiary esters with the $PPh_{3}\!\!-\!\!I_{2}$ system a

Entry	Substrate	Time (h)	Product (%) ^b
1		2	2 (63)
2	у сно	2.5	4 (68)
3	босно 5	3	6 (92)
4	FOCHO 7	2	8 (97)
5	OMe FOCHO 9	2	OMe
6	и	2.5	12 (88)
7	OAc 13	3	14 (94)
8	NHAc ///OAc	2	NHAc
9	OAc VOAc 17	2.5	OAc
10	OAc //OAc 19	2	OAc





^a Reaction conditions: 1 mmol of ester in CH₂Cl₂ (3 mL) and 1.2 equiv of PPh₃-I₂ system in CH₂Cl₂ (5 mL) at room temperature (see Ref. 2).

^b All new compounds were fully characterized.

^c Minor regioisomers were obtained in less than 10%.

triphenylphosphine and iodine are more regioselective than those performed with collidine; when 27 was heated with collidine a 5:3:1 mixture of di-, tetra- and trisubstituted alkenes was obtained.⁶

The surprising transformation of **24** and **25** into lactone **26** prompted us to investigate the use of this reagent to achieve stereoselective lactonizations and other related cyclizations. We are confident that the studies in progress will enable the mechanism of these reactions to be clarified.

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