A New Procedure for the Preparation of β-Chloro-α,β-unsaturated Ketones

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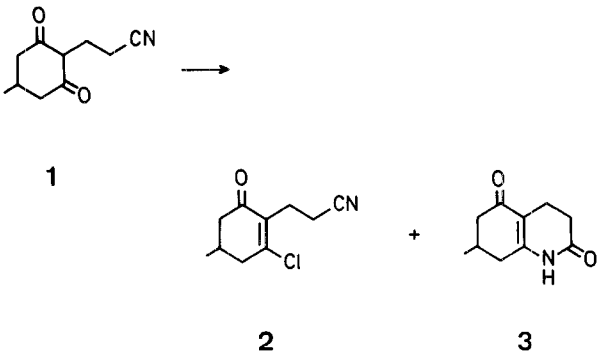
β-Diketones have been converted into β-chloro-α,β-unsaturated ketones by treatment with phosphorus trichloride[1,2,3], phosgene[4], acetyl chloride[5], thionyl chloride[2], and phosphorus oxychloride[1,6]. Reported yields for the conver-

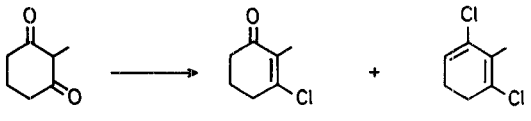
sion using these reagents are in the range 50–70%. We have examined several of the procedures and have found that the yields are often lower, particularly when the β-diketone also contains an acid-sensitive functional group. For example, the diketone **1** reacts with phosphorus trichloride in chloroform to give the chloroenone **2** and the bicyclic lactam **3** in approximately equal amounts.



1 **2** **3**

We have found that oxalyl chloride in benzene or chloroform effectively circumvents this difficulty, affording chloroenone **2** in a distilled yield of 73%; none of the lactam **3** was detected in the reaction product.

In addition, this reagent accomplishes the conversion of several other cyclic β-diketones to the corresponding β-chloro-α,β-unsaturated ketones in much higher yields than are realizable by the literature procedures. For example, 2-methyl-1,3-cyclohexanedione (**4**) reacts with oxalyl chloride in chloroform to give chloroenone **5** in 87% yield. The only by-product is the dichlorodiene **6**, which is produced in 3% yield.



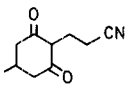
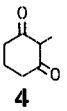
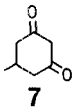
4 **5** **6**

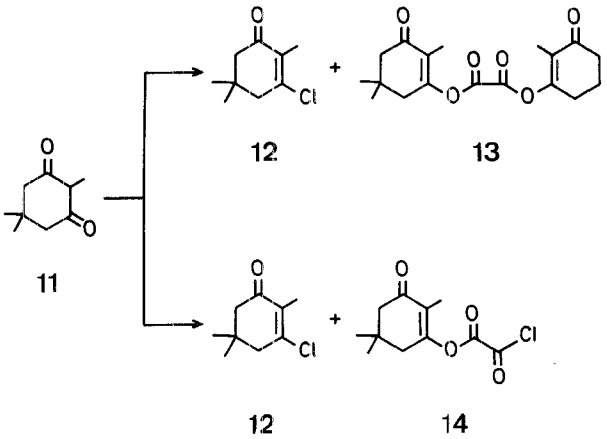
The procedure is simple, as illustrated by the conversion of diketone **4** into chloroenone **5** described below.

Preparation of 5 from 2-Methyl-1,3-cyclohexanedione:
A suspension of diketone (**4**, 10 g) in chloroform (25 ml) is treated with oxalyl chloride (25.2 g). The slurry is heated under reflux for 1 hr, during which time the mixture becomes homogeneous and there is a copious evolution of gas. The solvent is removed at reduced pressure and the crude product distilled to give a slightly colored liquid: yield: 10.20 g. This was shown by ^{1}H-N.M.R. to consist of 97% chloroenone **5** and 3% chlorodiene **6**. In other runs with other diketones, it was found that the reaction time may be shortened to 15 min.

The results which have been obtained with a number of β-diketones are summarized in the Table. 2,5,5-Trimethyl-1,3-cyclohexanedione (**11**) reacts anomalously, giving chloroenone **12** in only 50% yield, accompanied by the oxalate ester **13**. When the reaction is carried out at higher dilution and with a higher concentration of oxalyl chloride to diketone **11**, a mixture of chloroenone **12** and the chlorooxalate ester **14** is formed.

Table. Reaction of Cyclic β-Diketones with Oxalyl Chloride

β-Diketone	Yield (%) of: Chloroenone	Dichlorodiene	B.p.
 **1**	73	0	125°/0.4 torr
 **4**	87	3	62°/2 torr (lit.[7] 84°/7 torr)
 **7**	92	< 1	55°/2 torr
 **8**	91	2	72°/5 torr (lit.[1,2] 110°/14 torr, 105°/20 torr, resp.)
 **9**	78	<1	63°/4 torr (lit.[8,9] 78°/14 torr 104°/24 torr, resp.)
 **10**	73	2.5	42°/1 torr



11 **12** **13** **12** **14**

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