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NOVEL REDUCTION OF α-BROMO-α,β-UNSATURATED KETONES. SELECTIVE SYNTHESIS OF β,γ-UNSATURATED KETONES

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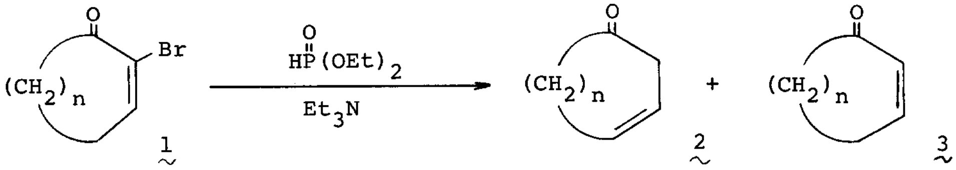
Summary: Treatment of α-bromo-α,β-unsaturated ketones or 1,1-dibromo-2-trimethylsiloxycyclopropanes with diethyl phosphite and triethylamine affords β,γ-unsaturated ketones selectively.

In our preceding paper,[1] diethyl phosphite-triethylamine is proven to be a versatile reagent for reduction of gem-dibromocyclopropanes and gem-dibromoalkenes to the corresponding monobromo derivatives, respectively. We describe herein that the reaction of α-bromo-α,β-unsaturated ketones with diethyl phosphite and triethylamine gives β,γ-unsaturated ketones selectively. This process comprises reduction of the bromide and deconjugation of an olefinic moiety.



Typical procedure is as follows. To a solution of 0.945 g (5.0 mmol) of 2-bromo-2-cycloheptenone and 0.829 g (6.0 mmol) of diethyl phosphite was added 0.607 g (6.0 mmol) of triethylamine at room temperature, and the mixture was stirred for 15 h. Ether (50 mL) was added and filtered to remove $Et_3N \cdot HBr$. After concentration of the filtrate, the residue was chromatographed on a silica gel column eluting with benzene to produce 0.350 g of 3-cycloheptenone (2a) in 64% yield. A small amount of 2-cycloheptenone (3a) was separated as a by-product. Some results are summarized in Table 1.

The present reaction was applicable to acyclic α-bromo-α,β-unsaturated ketones. For example, 5-bromo-4-decen-6-one[2] was treated with diethyl phosphite and triethylamine at room temperature for 16 h to yield (E)-3-decen-6-one (61%), being contaminated with (E)-4-decen-6-one (3%). Another important characteristic is stereoselctivity of the olefin geometry of β,γ-unsaturated ketones; in the reaction of 2-bromo-2-cycloundecenone[2] or 5-bromo-4-decen-6-one, the corresponding (E)-β,γ-unsaturated ketone was produced.

Table 1. Preparation of β,γ-Unsaturated Ketones

1	$HP(O)(OEt)_2$ (equiv.)	Et_3N (equiv.)	Reaction Temp.	Reaction Time	Products % **2** + **3**
2-bromo-2-cycloheptenone	1.2	1.2	rt	15 h	66 (96:4)
2-bromo-5-methyl-2-cycloheptenone	1.2	1.2	rt	20	41 (91:9)
2-bromo-2-cyclooctenone	3	1.5	80°C	3.5	47 (81:19)
2-bromo-2-cycloundecenone[a]	3	2	80°C	1	84[b] (90:10)

a. The olefin geometry was not determined. b. An E isomer of **2** or **3** was produced.

α-Bromo-α,β-unsaturated ketones were given by treatment of 1,1-dibromo-2-siloxycyclopropanes with diethyl phosphite. The reaction of 7,7-dibromo-1-trimethylsiloxybicyclo[4.1.0]heptane (**4a**) with diethyl phosphite at 50°C for 2 h produced 2-bromo-2-cycloheptenone (**1a**) in 90% yield. The same elimination in pyrolysis or in the presence of acid was reported.[3] This finding made it possible to prepare β,γ-unsaturated ketones from 1,1-dibromo-2-siloxycyclopropanes in one step. Treatment of **4a** with 4 equiv. of diethyl phosphite and 3 equiv. of triethylamine at room temperature for 5 days gave **2a** and **3a** in 37% yield (**2a**:**3a**=78:22), though the selectivity and yield of **2a** were low.

The mechanism of the present conversion has not been clarified. Isomerization between **2a** and **3a** was not observed in contact with diethyl phosphite and triethylamine at room temperature. As one of the plausible reaction paths, the α-bromo-β,γ-unsaturated ketone, arising from the intervention of the dienol, is subjected to debromination with diethyl phosphite and triethylamine to yield the β,γ-unsaturated ketone **2**.

α-Bromo-α,β-unsaturated ketones are alternatively prepared from gem-dibromocyclopropanes.[4] The present process provides a convenient method for the preparation of β,γ-unsaturated ketones. A full scope of this reaction is being investigated.

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References and Note

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