

Reduction of Organic Halides with Diethyl Phosphonate and Triethylamine

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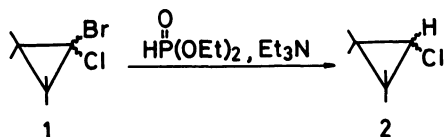
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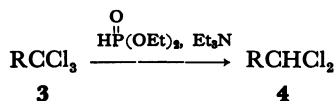
Synopsis. Reduction of organic halides [*gem*-bromochlorocyclopropanes, 1,1,1-trichloromethane derivatives, 1,1-dibromo-2-benzyloxyethylene, methyl α -bromocinnamate, α , β -dibromoacetophenone, and (1,2-dibromoethyl)benzene] with diethyl phosphonate and triethylamine is surveyed.

We have developed a novel method for reduction of *gem*-dibromocyclopropanes and *gem*-dibromoalkenes with diethyl phosphonate and triethylamine into the corresponding monobromides, respectively.¹⁾ Furthermore, α -bromo- α , β -unsaturated ketones or 1,1-dibromo-2-trimethylsiloxy-cyclopropanes are shown to be converted to β , γ -unsaturated ketones with diethyl phosphonate and triethylamine.²⁾ These findings suggest a versatility of diethyl phosphonate-triethylamine as a reducing agent. Now we wish to extend the generality of reduction with diethyl phosphonate-triethylamine.

Treatment of *gem*-bromochlorocyclopropanes **1** with diethyl phosphonate and triethylamine gave the corresponding chlorocyclopropanes **2** exclusively, without formation of bromocyclopropanes (Table 1).

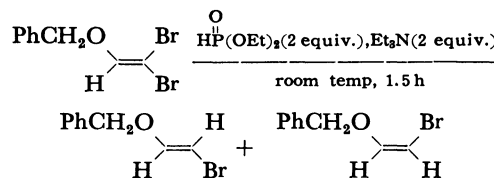


One of the chlorine atoms of the trichloromethane derivatives **3** was, however, reduced to yield the dichloromethane ones **4**, which were inert under the present reaction conditions, giving no further reduced compounds³⁾ (Table 1).

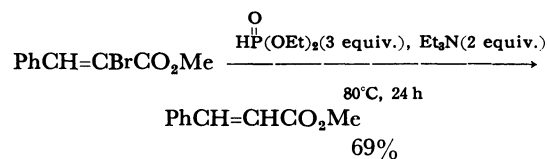


These results are considered to indicate that only activated halogen atom is reactive towards reduction. The following observation also supports this reactivity. Reduction of α -bromostyrene and (*E*)- β -bromostyrene

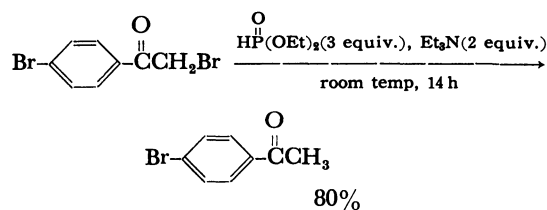
was not achieved even at a high reaction temperature (80 °C), though β , β -dibromostyrene is reduced to (*E*)- β -bromostyrene.¹⁾ The present method is effective for reduction of 1,1-dibromo-2-benzyloxyethylene, producing (*E*)- and (*Z*)-1-bromo-2-benzyloxyethylene in 29 and 51% yields, respectively.



It is of interest to note that methyl α -bromocinnamate was allowed to be reduced into methyl cinnamate in 69% yield, which is in contrast with addition of diethyl phosphonate to methyl cinnamate.⁴⁾



Furthermore, the α -bromine atom of ketones is reduced, as exemplified in the transformation of α , β -bromoacetophenone into β -bromoacetophenone. In the special cases, the similar kinds of reduction have been reported.⁵⁾

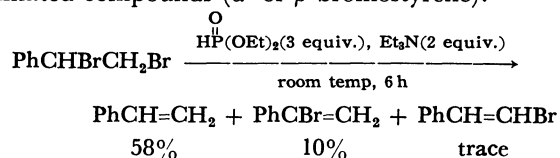


(1,2-Dibromoethyl)benzene was treated with diethyl phosphonate and triethylamine to give styrene as a main product. Since α - and β -bromostyrene were not subjected to reduction as mentioned above, styrene is presumably derived by direct debromination of (1,2-dibromoethyl)benzene, not reduction of the dehydro-

TABLE 1. REDUCTION OF **1** AND **3** WITH DIETHYL PHOSPHONATE AND TRIETHYLAMINE

1 or 3	O HP(OEt) ₂ (equiv.)	Et ₃ N (equiv.)	Reaction conditions		2 or 4 (Isolated yield/%)
			Temp/°C	Time/h	
	4	2	90	20	(76)
	4	2	90	22	(52)
$\text{Cl}_3\text{CCMe}_2\text{OH}$	4	3	80	12	$\text{Cl}_2\text{CHCMe}_2\text{OH}$ (73)
PhCCl_3	3	2	80	8	PhCHCl_2 (86)

brominated compounds (α - or β -bromostyrene).



The attack of diethyl phosphonate or its anion on the bromine or chlorine atom is assumed to be the first step in the reduction reaction.⁶⁾ The present procedure provides a convenient and selective method for reduction of activated halogenated compounds.

Experimental

Materials. *gem*-Bromochlorocyclopropanes,⁷⁾ α -bromostyrene,⁸⁾ methyl α -bromocinnamate,⁹⁾ and (1,2-dibromoethyl)benzene¹⁰⁾ were prepared by the reported methods. 1,1-Dibromo-2-benzyloxyethylene was obtained by the reaction of dibromocarbene with benzyl formate.¹¹⁾ The other reagents are commercially available and purified by usual methods before use.

Reduction of 1-Bromo-1-chloro-2-phenylcyclopropane. To a mixture of diethyl phosphonate (1.10 g, 8 mmol) and triethylamine (0.40 g, 4 mmol) was added 1-bromo-1-chloro-2-phenylcyclopropane (0.46 g, 2 mmol) dropwise at room temperature. The resultant mixture was stirred at 90 °C for 20 h. The reaction proceeded with deposition of $\text{Et}_3\text{N} \cdot \text{HBr}$, which was filtered off and washed with ether. Upon evaporation of the filtrate *in vacuo*, the residue was chromatographed on a silica-gel column to give 0.23 g (76%) of 1-chloro-2-phenylcyclopropane. This product was identified by comparison of the IR and NMR spectra with those of the authentic sample.¹²⁾

Reduction of other organic halides was carried out in the similar manner as mentioned above. The molar ratio of

diethyl phosphonate or triethylamine, and reaction conditions are shown in Table 1 or equations.

Debromination of (1,2-Dibromoethyl)benzene. A mixture of (1,2-dibromoethyl)benzene (1.32 g, 5 mmol), diethyl phosphonate (2.07 g, 15 mmol) and triethylamine (1.01 g, 10 mmol) was stirred at room temperature for 6 h. The salt was filtered off and washed with ether. Upon concentration of the filtrate *in vacuo*, the residue was chromatographed on a silica-gel column to give 0.30 g (58%) of styrene, 0.09 g (10%) of α -bromostyrene, and a trace amount of β -bromostyrene.

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