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Reduction of Organic Halides with Diethyl Phosphonate and Triethylamine

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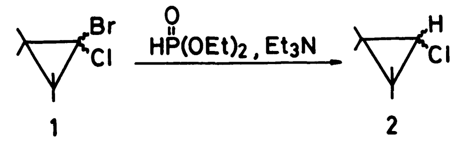
Synopsis. Reduction of organic halides [*gem*-bromochlorocyclopropanes, 1,1,1-trichloromethane derivatives, 1,1-dibromo-2-benzyloxyethylene, methyl α-bromocinnamate, α,*p*-dibromoacetophenone, and (1,2-dibromoethyl)benzene] with diethyl phosphonate and triethylamine is surveyed.

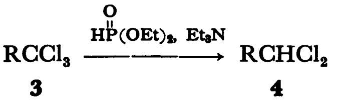
We have developed a novel method for reduction of *gem*-dibromocyclopropanes and *gem*-dibromoalkenes with diethyl phosphonate and triethylamine into the corresponding monobromides, respectively.[1] Furthermore, α-bromo-α,β-unsaturated ketones or 1,1-dibromo-2-trimethylsiloxycyclopropanes are shown to 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).



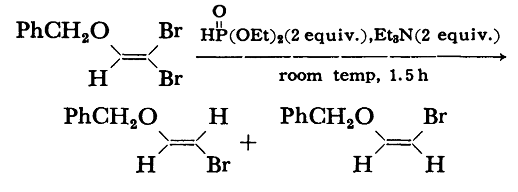
1 **2**

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 compounds[3] (Table 1).

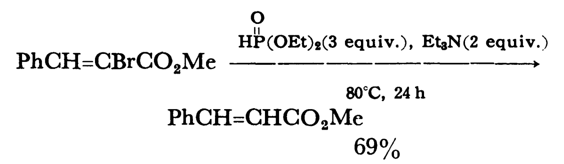


$$\underset{\mathbf{3}}{RCCl_3} \xrightarrow{H\overset{O}{\overset{\|}{P}}(OEt)_2,\ Et_3N} \underset{\mathbf{4}}{RCHCl_2}$$

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.

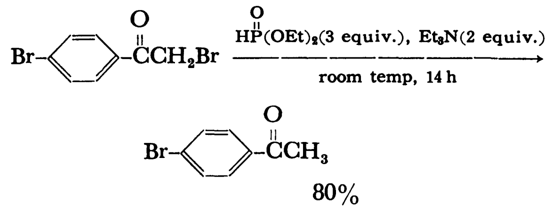


It is of interest to note that methyl α-bromocinnamate was allowed to be reduced into methyl cinnamate in 69% yield, which is in contrast with addition of diethyl phosphonate to methyl cinnamate.[4]



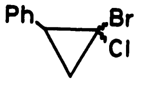
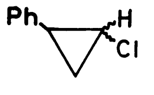
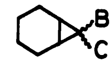
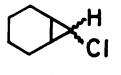
$$PhCH{=}CBrCO_2Me \xrightarrow[80^{\circ}C,\ 24\,h]{H\overset{O}{\overset{\|}{P}}(OEt)_2(3\ equiv.),\ Et_3N(2\ equiv.)} \underset{69\%}{PhCH{=}CHCO_2Me}$$

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

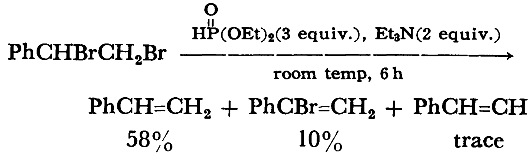


(1,2-Dibromoethyl)benzene was treated with diethyl phosphonate and triethylamine to give styrene as a main product. Since α- and β-bromostyrene were not subjected to reduction as mentioned above, styrene is presumably derived by direct debromination of (1,2-dibromoethyl)benzene, not reduction of the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

Table 1. Reduction of **1** and **3** with diethyl phosphonate and triethylamine

1 or **3**	$H\overset{O}{\overset{\|}{P}}(OEt)_2$ (equiv.)	Et_3N (equiv.)	Reaction conditions Temp/°C	Time/h	**2** or **4** (Isolated yield/%)
	4	2	90	20	 (76)
	4	2	90	22	 (52)
Cl_3CCMe_2OH	4	3	80	12	Cl_2CHCMe_2OH (73)
$PhCCl_3$	3	2	80	8	$PhCHCl_2$(86)

brominated compounds (α- or β-bromostyrene).



$$\mathrm{PhCHBrCH_2Br} \xrightarrow[\text{room temp, 6 h}]{\overset{\mathrm{O}}{\overset{\|}{\mathrm{HP}}}\mathrm{(OEt)_2(3\ equiv.),\ Et_3N(2\ equiv.)}} \underset{58\%}{\mathrm{PhCH{=}CH_2}} + \underset{10\%}{\mathrm{PhCBr{=}CH_2}} + \underset{\text{trace}}{\mathrm{PhCH{=}CHBr}}$$

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 $Et_3N \cdot HBr$, 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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