Diphosphorus Tetraiodide. A Valuable Reagent in Cyclopropane Chemistry

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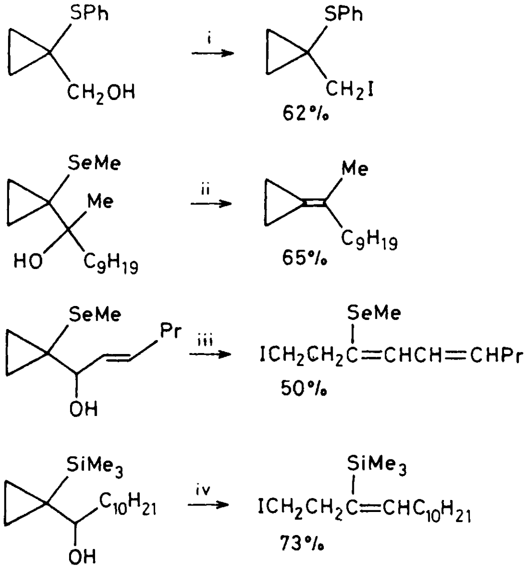
The behaviour of P_2I_4 and PI_3 towards cyclopropyl alcohols, cyclopropyl ketones, α-seleno ketones, and ozonides is reported.

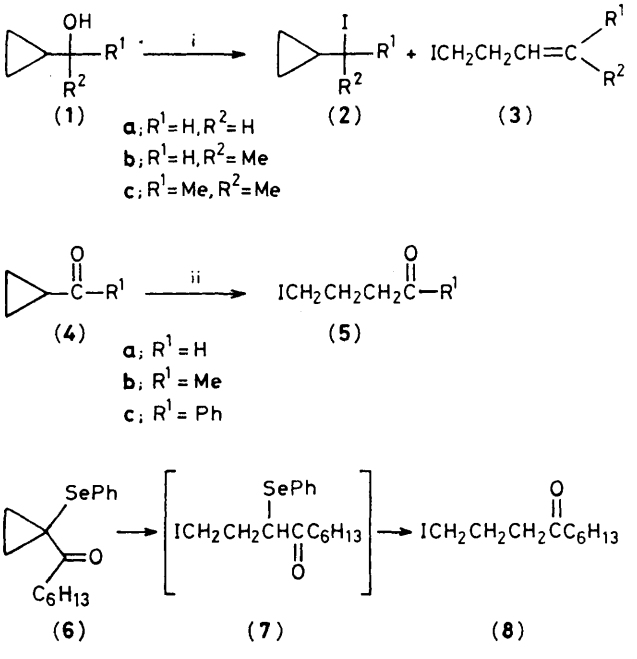
We have recently studied the reactivity of cyclopropyl alcohols having a hetero substituent in the cyclopropane ring with P_2I_4 or PI_3[1-3] and we have found that small structural variations in the starting material lead to a dramatic change in the reaction pathway (Scheme 1).

The variety of results caused us to look in more detail at the reactivity of PI_3 and P_2I_4 with non-functionalized cyclopropyl alcohols.

We found that on reaction with P_2I_4, the primary and secondary cyclopropyl alcohols (**1a**) and (**1b**) produce the corresponding alkyl iodides (**2a**) and (**2b**) (71 and 76% yield, respectively) together with small amounts (4 and 10%, respectively) of homoallyl iodides[3] resulting from opening of the cyclopropane ring (Scheme 2, Table 1). The reaction with the primary alcohol (**1a**) (CH_2Cl_2, 20 °C, 20 h) is quite slow but is



Scheme 1. *Reagents and conditions:* i, P_2I_4–CH_2Cl_2, 55 °C, 24 h (this work); ii, PI_3–Et_3N–CH_2Cl_2, 20 °C, 1 h (ref. 2); iii, PI_3–Et_3N–CH_2Cl_2, 20 °C, 1 h (this work); iv, PI_3–Et_3N–CH_2Cl_2, 0 °C, 0.5 h (ref. 3).



Scheme 2. *Reagents and conditions:* i, P_2I_4 (0.5 mol. equiv.), CH_2Cl_2; ii, P_2I_4 (0.55 mol. equiv.), acetone, 20 °C.

Table 1

Starting material	Conditions		Products	Overall yield, % (ratio)
	Temperature/°C	Time/h		
(1a)	+20	20	**(2a)** + **(3a)**	71 (96/04)
(1b)	−10	1.5	**(2b)** + **(3b)**	76 (90/10)
(1c)	−20	1	**(3c)**	72
(4a)	+20	2	**(5a)**	46
(4b)	+20	1.5	**(5b)**	88
(4c)	+20	2	**(5c)**	89
(6)	+20	1	**(8)**	95

much faster with the secondary alcohol **(1b)** (−10 °C, 1.5 h). The tertiary alcohol **(1c)** reacts even faster (−20 °C, 1 h) but produces the homoallyl iodide **(3c)** exclusively. All attempts to trap the cyclopropyl iodide **(2c)** were unsuccessful. With **(1c)**, the reaction must be performed at low temperatures (−20 °C) since at higher temperatures 2,5-di-iodo-2-methylpentane results from the addition of hydrogen iodide across the carbon–carbon double bond of **(3c)** [2,5-di-iodo-2-methylpentane/**(3c)** ratio 1/4, 2/3, and 1/0 when the reaction is performed at 20 °C for 0.2, 1, or 18 h, respectively]. Cyclopropyl alkyl iodides **(2a)** and **(2b)** are fairly stable at 20 °C but **(2b)** rearranges rapidly on heating to the homoallyl iodide **(3b)** (60 °C, 0.5 h, 100% yield).†

From these results, it appears that the cyclopropane participation increases with increasing stability of the incipient positive charge α to the cyclopropane ring and this seems to be consistent with reported results.[4,5]

One would therefore expect the cyclopropane ring to open when cyclopropyl aldehydes or ketones are treated with P_2I_4 and that proved to be the case.‡

Thus, we found that the cyclopropyl aldehyde **(4a)** and ketones **(4b, c)** (Scheme 2, Table 1) reacted smoothly (20 °C, $\leqslant$2 h) with P_2I_4 (0.5 mol. equiv.), provided acetone is used as the solvent, to produce the corresponding γ-iodo carbonyl compounds **(5)** in good yields.

A higher temperature (80 °C) and longer reaction time (24 h) are required when acetone is replaced by carbon tetrachloride and under these conditions we observed a dramatic lowering in the yield of **(5b)** [47% in the case of **(4b)**].

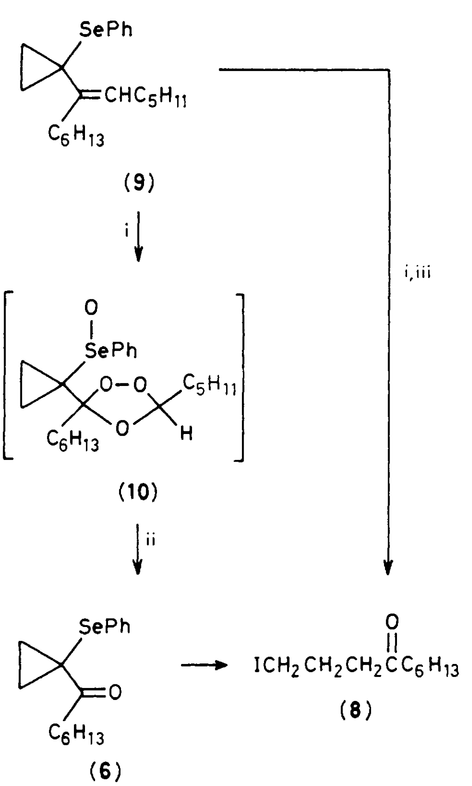
In the course of this work we also examined the reaction of the α-selenocyclopropyl ketone **(6)** with P_2I_4 (1 mol. equiv.). The reaction is fast and occurs at 20 °C in both acetone and methylene dichloride. We were rather surprised to obtain the γ-iodo ketone **(8)** (95 and 93% yield, respectively) in which the selenyl moiety is no longer present (Scheme 2, Table 1).

The mechanism of this reaction was unknown to us. We proposed the γ-iodo α-seleno ketone **(7)** as an intermediate and thus we were interested in the reactivity of P_2I_4 towards aliphatic α-selenoketones.

We observed that 3-methylselenoundecan-2-one and its phenylseleno analogue are readily reduced (20 °C, 0.4 h, $\geqslant$ 80% yield) to the corresponding undecanone (P_2I_4, 0.5 mol. equiv.) in a reaction which parallels the one which we have recently reported for α-halogeno ketones.[7] This is to our knowledge the first reduction of an α-seleno ketone to be described.

All the reactions reported work equally well with PI_3 under similar experimental conditions.

Since PI_3 and P_2I_4 are powerful reagents which react with a large variety of functional groups,[1] we were interested to determine if they show any chemoselection. Our preliminary results are given in Scheme 3.



Scheme 3. *Reagents and conditions:* i, 2 O_3, CH_2Cl_2, −78 °C; ii, 1 mol. equiv. P_2I_4 89% yield of **(6)**, 2 mol. equiv. PI_3 86% yield of **(6)**; iii, 2 mol. equiv. P_2I_4, −78 °C, 0.1 h then 20 °C, 1 h, 'one-pot reaction,' 92% overall yield.

Thus the vinylcyclopropane **(9)** was subjected to the action of ozone. The resulting product **(10)** bearing an ozonide and a selenoxide function was allowed to react further with P_2I_4 or PI_3. Depending upon the conditions used (1 mol. equiv. P_2I_4 at −78 °C, 0.75 h or 2 mol. equiv. of P_2I_4, −78 °C to 20 °C, 1 h), we chemoselectively obtained a high yield of the cyclopropyl ketone **(6)** or the γ-iodo ketone **(8)**.

Moreover this example shows how versatile these phosphorus reagents can be. The following reactions have been performed in a step-wise manner: reduction of an ozonide, reduction of a selenoxide, ring opening of an activated cyclopropane, and reduction of an α-seleno ketone. The interest of the reported reactions is enhanced by the solubility in water of the inorganic by-products containing the phosphorus atom which are easily removed from the organic compounds.

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† The *E* isomer predominates.

‡ During the course of this work, a similar observation was reported (ref. 6) by Miller on the reaction of Me_3SiI with cyclopropyl ketones.