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A CONVENIENT PREPARATION OF 2-HALOENONES FROM ENONES USING PHENYLSELENIUM HALIDES

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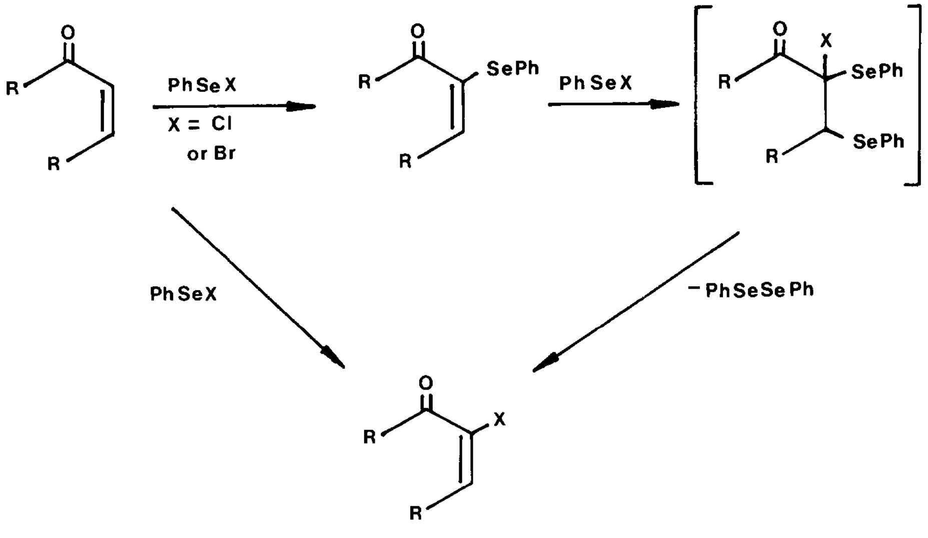
SUMMARY: Enones can be converted in high yield to their corresponding 2-halo analogues by treatment with an excess of phenylselenium halide in methylene chloride/pyridine at 37°C.

In connection with other work we needed supplies of 2-haloenones. As the literature methods[1] to these compounds are inefficient or involve a multistep sequence, we sought a more convenient alternative procedure.

Enones are known to react with phenylselenium chloride to give 2-phenylselenoenones[2] and it seemed reasonable to us that these derivatives might react further with a selenating agent to give adducts which would rapidly disproportionate by loss of diphenyldiselenide[3] to afford the desired halo compounds. Direct halogenation should also be possible by using increased quantities of the phenylselenium halide (Scheme).



SCHEME

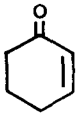
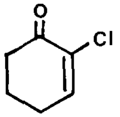
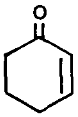
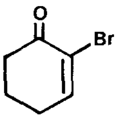
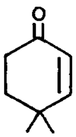
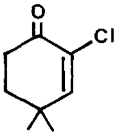
Consequently, by treating a number of enones (or enals) with an excess of phenylselenium chloride (1) or bromide (2) in dry methylene dichloride at 37°C, smooth conversion to the corresponding 2-substituted halo derivative can be achieved in high yield (Table). The products of the reaction were worked up by quenching the cooled reaction mixtures with water and washing the organic phase with dilute hydrochloric acid and water in the usual way Flash chromatography subsequently separated the desired halo compounds from the faster running diphenyldiselenide. The recovered diselenide could be readily transformed back to the starting phenylselenium halides by standard methods.

By following the reactions by t.l c. one can clearly see that these reactions proceed via the prior formation of the 2-phenylseleno enone species.[2] In two experiments (entries 12 and 13 in the Table) 2-phenylseleno substituted enones were separately converted to 2-haloenones by reaction with the appropriate selenium halide.

The lower yields of halo compounds in entries 4 and 7 in the Table were due to the fact that the corresponding 2-phenylseleno derivatives were additionally isolated in 39 and 20% yields respectively and thus indicated incomplete reaction in these examples.

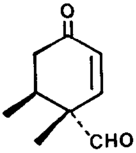
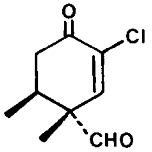
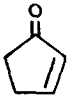
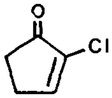
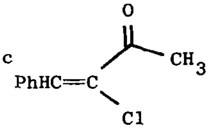
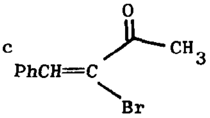
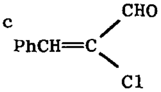
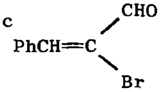
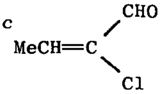
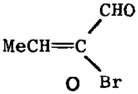
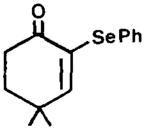
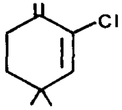
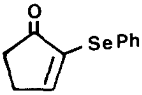
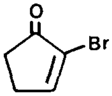
2-Haloenones are potentially useful synthetic intermediates.[4]

TABLE

	STARTING MATERIAL	REAGENTS	PRODUCT[a,b]	TIME h at 37°C	PROPERTIES m.p. °C	YIELD %
1.		(1) 3 equiv. py 3 equiv.		96	71-72	82
2.		(2) 2.5 equiv. py 2.5 equiv.		24[d]	75-76	100
3.		(1) 3 equiv py 3 equiv.		72	oil	92

/continued...

TABLE/continued...

	STARTING MATERIAL	REAGENTS	PRODUCT[a,b]	TIME h at 37°C	PROPERTIES m.p. °C	YIELD %
4.		(1) 3 equiv. py 3 equiv.		48	oil	35
5		(1) 3 equiv. py 3 equiv.		72	oil	52
6.	PhCH═CH CO.CH_3	(1) 3 equiv. py 3 equiv.	[c]  $\mathrm{PhHC{=}C(Cl)COCH_3}$	7 days	oil DNP 218-219°	85
7.	PhCH═CH.CO.CH_3	(1) 3 equiv. py 3 equiv.	[c]  $\mathrm{PhCH{=}C(Br)COCH_3}$	65	30	51
8.	PhCH═CH.CHO	(1) 3 equiv. py 3 equiv.	[c]  $\mathrm{PhCH{=}C(Cl)CHO}$	96	oil	100
9.	PhCH═CH.CHO	(2) 3 equiv. py 3 equiv.	[c]  $\mathrm{PhCH{=}C(Br)CHO}$	7 days	71.5-72	85
10	MeCH═CH.CHO	(1) 3 equiv. py 3 equiv.	[c]  $\mathrm{MeCH{=}C(Cl)CHO}$	12	oil	90
11.	MeCH═CH.CHO	(2) 2.5 equiv. py 2.5 equiv.	[c]  $\mathrm{MeCH{=}C(Br)CHO}$	24[d]	oil	95
12.		(1) 4 equiv. py 3 equiv.		60[d]	oil	95
13.		(2) 1 5 equiv. py 1.5 equiv.		72	38.5-39°	52

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TABLE/continued...

[a] All new compounds were fully characterised by spectroscopic methods and acc. mass and/or microanalysis.

[b] In view of Wender's findings,[4] these compounds should be handled with care owing to their potential vessicant properties. We however have not noticed these unpleasant side-effects with compounds prepared by the above method.

[c] Z/E geometry of these compounds is not yet known.

[d] At room temperature.

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4. Eg. P.A. Wender, C.L. Hillemann, and M.S. Szymonifka, Tetrahedron Lett., 1980, 2205.

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