

The Mercury(II) Salt–Halogen Combination $\text{HgX}_2\text{--Hal}_2$: A Versatile Reagent for Stereoselective Addition of Hal-X to Alkenes

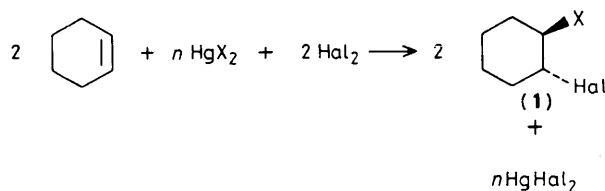
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The reaction of mercury(II) salts (fluoride, chloride, bromide, nitrate, methanesulphonate, toluene-*p*-sulphonate, and toluene-*p*-sulphonate) and halogens (bromine or iodine) with alkenes leads to the corresponding 1,2-bifunctionalized products resulting from the addition of the halogen and the mercury(II) salt anion selectively.

Nearly all methods for the addition of RCO_2Hal ($\text{Hal} = \text{Cl}, \text{Br}, \text{or I}$) or XI ($\text{X} = \text{F}, \text{Cl}, \text{NO}_3, \text{NCO}, \text{or N}_3$) to alkenes have used a mixture of a silver, thallium(I), or copper(II) salt and the corresponding halogen.¹ The use of mercury(II) salts in a process of this type has been described only for mercury(II) acetate.^{†2} We report herein the general addition of $\text{HgX}_2\text{--Hal}_2$ to alkenes.

The reaction of cyclohexene with a mixture of a mercury(II) salt and bromine or iodine led to the *trans*-product (1) stereoselectively (Scheme 1). The stereochemistry of the



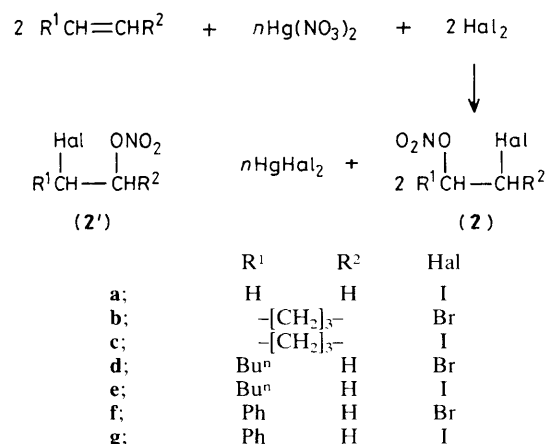
	Hal	X
a;	Br	F
b;	I	Cl
c;	I	Br
d;	Br	NO_3
e;	I	NO_3
f;	Br	MeSO_3
g;	Br	$p\text{-MeC}_6\text{H}_4\text{SO}_2$
h;	I	$p\text{-MeC}_6\text{H}_4\text{SO}_2$
i;	Br	$p\text{-MeC}_6\text{H}_4\text{SO}_3$
j;	I	$p\text{-MeC}_6\text{H}_4\text{SO}_3$

Scheme 1. $\text{Hal} = \text{Br}, n = 2$; $\text{Hal} = \text{I}, n = 1$.

products (1) was determined by comparison of their n.m.r. data with literature data. In the case of bromine an excess of the mercury(II) salt (1:1 molar ratio) was used in order to avoid the formation of *trans*-dibromocyclohexane.

The addition of mercury(II) nitrate–halogen was studied with different alkenes, *e.g.* ethylene, cyclopentene, hex-1-ene, and styrene. In the case of styrene only the expected Markovnikov product (2) was obtained; however, when the reaction was carried out with hex-1-ene the anti-Markovnikov product (2') was obtained (18–25%) together with the expected product (2) (Scheme 2 and Table 1).

In a typical procedure, to a mixture of the mercury(II) salt (5 or 10 mmol, see text and Schemes) and halogen (10 mmol) in dichloromethane (20 ml) was added the corresponding alkene (10 mmol). The mixture was stirred for *ca.* 1 h at room



Scheme 2. $\text{Hal} = \text{Br}, n = 2$; $\text{Hal} = \text{I}, n = 1$.

† Recently we have used mercury(II) tetrafluoroborate to prepare a pyridine complex of iodine tetrafluoroborate for another type of reaction (see ref. 3).

Table 1. Formation of products (1) and (2).

Product	% Yield ^a	B.p., °C; mmHg ^b or m.p., °C	Selected ¹³ C n.m.r. data ^c	
			C-Hal	C-X
(1a)	70	35—38; 15 ^d	52.1 ^e	93.0 ^f
(1b)	89	44—46; 0.1 ^g	36.5	64.5
(1c)	97	63—66; 0.1	37.7	57.8
(1d)	99	35—38; 0.1	50.2	85.2
(1e)	80	69—71; 0.1 ^h	28.4	86.1
(1f)	90	56 (hexane)	53.2	84.7
(1g)	76	Oil	48.2	67.5
(1h)	92	Oil	26.7	68.3
(1i)	78	Oil	52.2	83.7
(1j)	90	Oil	31.1	84.5
(2a)	87	44—47; 0.1	1.9	73.5
(2b)	73	55—57; 0.1	51.6	91.5
(2c)	85	67—69; 0.1	27.8	94.1
(2d)	55 ⁱ	70—72; 0.1	32.4	83.1
(2e)	60 ^j	80—83; 0.1 ^k	5.7	83.4
(2f)	99	67—70; 0.1	31.4	84.5
(2g)	95	83—85; 0.1 ^l	4.5	85.2

^a Isolated yield based on the starting alkene. ^b Distillation temperature range. ^c Neat (SiMe₄ + D₂O capillary); recorded on a Varian FT-80 spectrometer. ^d Lit.⁴ b.p. 30 °C at 13 mmHg. ^e *J*_{CCF} 21.0 Hz. ^f *J*_{CF} 180.4 Hz. ^g Lit.⁵ b.p. 36 °C at 0.2 mmHg. ^h Lit.⁶ b.p. 113 °C at 1.3 mmHg. ⁱ 2-Bromohexyl nitrate (2d') was obtained in 18% yield. ^j 2-Iodohexyl nitrate (2e') was obtained in 25% yield. ^k Lit.⁶ b.p. 80 °C at 0.5 mmHg. ^l Lit.⁶ b.p. 110 °C at 1 mmHg.

temperature and the mercury(II) halide was filtered off; in the case of the iodine derivatives, the filtrate was washed with aqueous Na₂S₂O₃ and KI, dried (MgSO₄), and evaporated. In the case of the bromine derivatives the filtrate was evaporated and the residue was treated with hexane, filtered, and evaporated. The crude products were purified by distillation *in vacuo*.‡

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‡ The products (1) and (2) were fully characterized by their analytical and spectral data (i.r.; ¹H and ¹³C n.m.r.).