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MERCURY IN ORGANIC CHEMISTRY. 31.[1]
PREPARATION OF ALLENIC AND PROPARGYLIC ORGANOMERCURIC HALIDES

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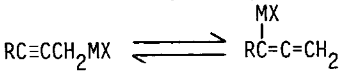
Summary: Propargylic bromides and iodides react with metallic mercury to form the corresponding allenic or propargylic organomercuric halides in high yield.

Propargylic and allenic organometallics are of great current interest, because they possess tremendous potential in synthetic organic chemistry.[2-7] The major problem with these compounds at present is their tendency to equilibrate (eq. 1) or to react so as to



$$RC\equiv CCH_2MX \rightleftharpoons \overset{MX}{\overset{|}{R C}}=C=CH_2 \quad (1)$$

give mixtures of allenic and propargylic products. The likelihood that the corresponding organomercurials might solve such problems has encouraged us to attempt their preparation.

Only one propargylic and one allenic organomercurial have been reported in the literature previously.[8] These compounds were prepared from the corresponding organozinc reagents, thus limiting the types of functional groups which might be accommodated. In 1884, Henry reported that the reaction of propargyl iodide and metallic mercury in sunlight gives propargylmercuric iodide (eq. 2).[9] This approach to the desired organomercurials

$$HC\equiv CCH_2I \; + \; Hg \xrightarrow{h\nu} HC\equiv CCH_2HgI \quad (2)$$

appeared attractive, particularly since it would appear to accommodate a wide range of organic functionality. We have indeed examined this approach and wish now to correct Henry's earlier report and announce that the reaction of propargylic halides and metallic mercury affords a highly convenient route to a variety of allenic and propargylic organomercuric halides.

Our general procedure involves mixing 20 mmol of metallic mercury and 10 mmol of the appropriate propargylic halide in a test tube or similar apparatus, flushing with nitrogen before sealing, shaking the tube until the mercury is finely dispersed and setting the tube in the sunlight for an appropriate amount of time, usually 2 hours. After storing overnight in the refrigerator, the product is dissolved in tetrahydrofuran, the solution filtered, the solvent removed and the resulting crude product recrystallized from a suitable solvent. The results are summarized in Table I.

Some, but not all, propargylic bromides were observed to react. Propargylic iodides are more reactive. Primary, secondary and tertiary halides may be employed. Either allenic or propargylic mercurials are obtained depending on the structure of the starting halide. Terminal alkynes were observed in all cases to afford allenic mercurials. With internal alkynes, primary halides yield propargylic mercurials, while secondary halides (and presumably tertiary halides if they could be easily prepared) afford allenic mercurials. The product from propargyl iodide was quite clearly the allenic mercurial and not the propargylmercurial previously reported. This was easily seen by the presence of a peak at 1926 cm^{-1} (C=C=C) in the infrared spectrum and NMR spectral peaks at δ 4.6 (CH_2) and 5.20 (CHHgI). All other allenic organomercurials exhibited similar IR and NMR spectral data. The propargylic mercurials were characterized by a lack of allenic hydrogens in the NMR spectra and infrared bands at 2197-2420 cm^{-1} ($C{\equiv}C$). Correct spectral and elemental analyses were obtained for all compounds. Mixtures of allenic and propargylic mercurials were never observed. These organometallics do not appear to exist in equilibria. Allenic iodides proved unreactive under our reaction conditions.

We have recently found these propargylic and allenic organomercurials to be quite valuable in organic synthesis and are presently studying possible applications of $CH_3O_2C(CH_2)_3C{\equiv}CCH_2HgI$ in prostaglandin synthesis.

Table I. Synthesis of Allenic and Propargylic Organomercuric Halides

organic halide	organomercuric halide	recrystallization solvent(s)	% isolated yield
$C_6H_5C{\equiv}CCH_2Br$	$C_6H_5C{\equiv}CCH_2HgBr$	EtOH	72
$(CH_3)_2CBrC{\equiv}CH$	$(CH_3)_2C{=}C{=}CHHgBr$	THF/acetone	60
$ICH_2C{\equiv}CH$	$H_2C{=}C{=}CHHgI$	ether	55
$CH_3CHIC{\equiv}CH$	$CH_3CH{=}C{=}CHHgI$	THF/ether	80
$CH_3CHIC{\equiv}CC_6H_5$	$CH_3CH{=}C{=}C(C_6H_5)HgI$	THF/ether	66
$CH_3C{\equiv}CCH_2I$	$CH_3C{\equiv}CCH_2HgI$	THF	83
$C_6H_5C{\equiv}CCH_2I$	$C_6H_5C{\equiv}CCH_2HgI$	acetone	68
$CH_3O_2C(CH_2)_3C{\equiv}CCH_2I$	$CH_3O_2C(CH_2)_3C{\equiv}CCH_2HgI$	THF/ether	80[a]

[a] Yield based on recovered starting iodide.

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