Tetrahedron Letters No. 39, pp 3429 - 3432, 1975. Pergamon Press. Printed in Great Britain.

VINYL ACETATES FROM VINYL BROMIDES

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(Received in UK 14 August 1975; accepted for publication 22 August 1975)

Conversion of vinyl halides into enol derivatives and thence into carbonyl compounds is severely hampered by the unreactivity of these substrates, which prevails under conditions of bimolecular substitution[1] as well as under conditions favoring first order ionization[2]. In the absence of cation stabilizing substituents vinyl halides are even inert towards silver salts[2,3]. Hydrolysis to a carbonyl derivative may be accomplished via protonation by strong acid[4]. Recently, a more circuitous route involving bromine/lithium exchange and titanium tetrachloride catalyzed hydrolysis of vinyl thioethers[5] has been described by Seebach and Neumann[6]. Clearly, such procedures may fail with vinyl halides which are acid-sensitive or which permit alternative modes of reaction with organolithiums (e.g., proton abstraction, addition to C=X or to C=C-C=C, elimination of LiX)[7].

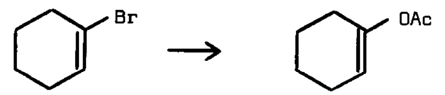
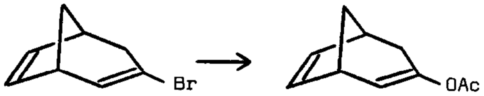
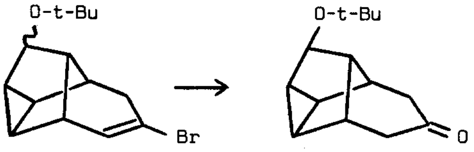
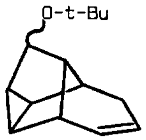
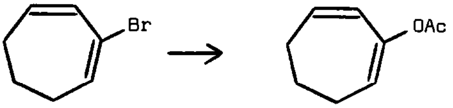
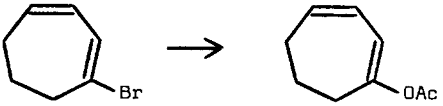
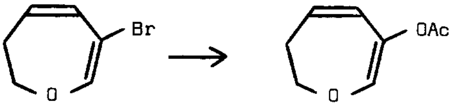
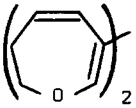
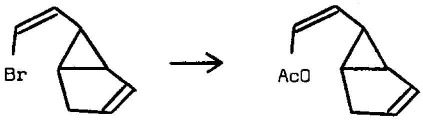
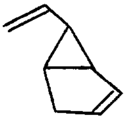
Following the discovery (by H.B.) of the formation of small amounts of ketone in an attempted reduction of a vinyl bromide with the N_2H_4-H_2O_2-Cu(II) acetate system[9] we have found that heating solutions of vinyl bromides under nitrogen with excess Cu(I) acetate provides a mild and simple means for converting them into vinyl acetates, from which carbonyl compounds may then be obtained easily. So far three different sets of reaction conditions have been employed (however, a systematic search for optimum conditions has not yet been carried out):

1. One mole of vinyl bromide is treated with two moles of Cu(I) acetate[10] in acetonitrile at 80-110° for several hours.
2. Cu(I) acetate is prepared by adding one mole of $N_2H_4 \cdot H_2O$ to four moles of $Cu(OAc)_2 \cdot H_2O$ partly dissolved in acetic acid. After the blue-green colour has vanished one mole of vinyl bromide is added and the suspension is stirred at 80° for several hours.
3. Similarly, an excess of Cu(I) acetate is prepared from Cu(II) acetate in diethylene glykol. After adding the vinyl bromide the stirred suspension is heated to 125-185° and kept at this temperature for several hours. Under these conditions ketones are obtained directly from vi-

nyl bromides, presumably through transesterification of the intermediate vinyl acetates followed by isomerisation of the enols.

Table. Vinyl bromides subjected to the Cu(I) acetate reaction

(Transformation; method; T, °C; t, hr; yield, %; by-products, %)

	1; 80; 2; 68[a] 2; 85; 8; 45[a]		
	1; 80; 4; 67[a] 2; 85; 5; 45[a]		
	3; 180; 18; 55[b]		2[b]
	1; 110; 7; 45[b]		
	1; 110; 7; 65[b]		
	1; 80; 10; 14[a]		45[a]
 cis/trans = 62/38 cis/trans = 90/10	1; 85; 2; 41[a]		15[a]

[a] Carried out on g scale; yield determined by distillation.

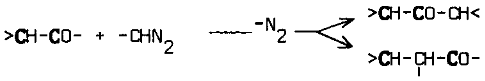
[b] Carried out on mg scale; yield determined by glc.

Vinyl bromides that have been studied are given in the table. A single vinyl chloride tested, (method 1) reacted, too. The reaction is inhibited by t-butyl isocyanide[11].

The mildness of the new synthesis of vinyl acetates[13] is apparent from the vinyl bromides that could be reacted. Most of these substrates would have been isomerized, transformed differently or destroyed by acid and/or by organolithiums. Through its potential generality and ease of execution the reaction lends new importance to the homologisation scheme 1, which lacks several disadvantages (structural limitations, lack of regiospecificity, polyhomologisation) that may beset the more classical alternative of scheme 2. Also, pathways for attachment of -CHO via synthesis of bromomethylene derivatives have now become feasible[18].

(1) $\gt C{=}C\lt + CBr_2 \rightarrow \rightarrow \gt C{=}CBr{-}CH\lt \rightarrow \rightarrow \gt CH{-}CO{-}CH\lt$

(2)



$$\gt CH{-}CO{-} + {-}CHN_2 \xrightarrow{-N_2} \begin{cases} \gt CH{-}CO{-}CH\lt \\ \gt CH{-}\underset{|}{C}H{-}CO{-} \end{cases}$$

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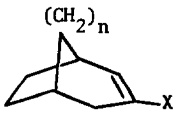
7. An example is provided by bromide A. Unlike several compounds of closely related structure B[8], A does not yield the corresponding ketone on treatment with sulfuric acid, but yields rearranged material, instead[8a].

A



B

8. a) W.R. Moore, W.R. Moser and J.E. LaPrade, J. Org. Chem., 28, 2200 (1963);

   b) B. Waegell and C.W. Jefford, Bull. Soc. Chim. Fr., 1964, 844;

   c) C.W. Jefford, S. Mahajan, J. Waslyn and B. Waegell, J. Amer. Chem. Soc., 87 2183 (1965);

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   e) W. Kraus, G. Klein, H. Sadlo and W. Rothenwöhrer, Synthesis, 1972, 485.

9. The unreactivity of vinyl halides in diimide reductions is known: E.E. van Tamelen, M. Davis and M.F. Deem, Chem. Comm., 1965, 71.

10. Prepared after method "g" of D.A. Edwards and R. Richards, J.C.S. Dalton, 1973, 2463.

11. This finding is of interest, because Saegusa and coworkers have reported that the t-butyl isonitrile ligand enhances the S_N2-reactivity of Cu(I) carboxylates towards alkyl halides[12a]. These workers have also postulated intramolecular substitution of vinylic chlorine by carboxylate in certain 3-chloro-2-alkenoic acids under the influence of Cu$_2$O/isonitrile[12b].

12. a) T. Saegusa, I. Murase and Y. Ito, J. Org. Chem. 38, 1753 (1973);

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13. Although it was stated[14] that cuprous carboxylates (acetate, benzoate, pivalate) react with many types of organic halides and tosylates including vinyl derivatives to give the corresponding esters, no examples from the latter class of compounds were presented. The report[15] that treatment of a mixture of cis- and trans-2-bromo-2-butene with Cu(I) benzoate in diglyme or xylene at 140-160° gave a mixture of enol benzoates (no yield given) therefore represents the only documented example of a reaction closely resembling the one described in this paper. Recently, Commercon et al. have described the formation of vinyl acetates from alkenyl iodides with Cu(I) acetate or Cu(II) acetate[16]. These authors also give a survey of earlier work on Cu(I) relayed substitutions of vinylic halogen. The important applications of lithium dialkyl- and diarylcuprates in such reactions have been reviewed by Posner[17].

14. A.H. Lewin and N.L. Goldberg, Tetrahedron Letters, 1972, 491.

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18. Cf.: G. Köbrich, Angew. Chem., 74, 33 (1962); G. Wittig and M. Schlosser, Chem. Ber., 94, 1373 (1961).