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CONVENIENT SYNTHESES OF PURE ALLENIC AND ACETYLENIC BROMIDES

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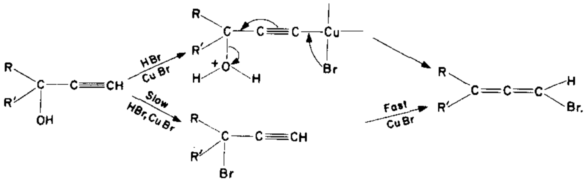
Allenic and acetylenic halides are important intermediates and were required for our synthetic studies. While a limited number of allenic chlorides are now readily available[1] a general source of the more reactive halides was required. We have found that the reaction of concentrated hydrobromic acid with propargylic alcohols in the presence of a cuprous bromide-copper catalyst gives excellent yields of pure 1-bromoallenes from tertiary acetylenic alcohols[2] and 1-bromoallenes mixed with less than 5% of 3-bromoacetylenes (as shown by the vapour phase chromatograms) from secondary acetylenic alcohols. The products (see Table I) gave an exceptionally intense band at 1950 cm^{-1} in the infrared no ultraviolet absorption maximum and identical mixtures of allenic and acetylenic acids were obtained on carbonation of the Grignard derivatives from otherwise identical allenic chlorides and bromides.

Infrared spectra of samples during the course of the reaction showed that propargylic bromides are not formed as the first products[3,4].



We think this points towards an S_Ni' or S_N2' mechanism but a two stage process involving a very fast second stage cannot be excluded on the present evidence.[5] (−)-1-bromo-3,4,4-trimethylpenta-1,2-diene, $[\alpha]_D^{20}$ −32.5° was obtained from (+)-3,4,4-trimethylpent-1-yn-3-ol, $[\alpha]_D^{20}$ + 0.81° indicating a high degree of specificity.[6] However in the absence of cuprous bromide (−)-1-bromo-3,4,4-trimethylpenta-1,2-diene, $[\alpha]_D^{20}$ − 2.7° was obtained from the (−)-3,4,4-trimethylpent-1-yn-3-ol, $[\alpha]_D^{20}$ − 0.76 showing mainly racemisation (SN1 mechanism). The mechanistic implications and the spectroscopic data will be more fully discussed elsewhere.

Table I. R $R^1C=C=CHBr$.

R	R^1	% Yield Crude	% Yield Distilled	B.P. °C/mm.	V.P.C.
H	Me	90	37	61–62/160	5% acetylene
H	Pr^n	82	67	51–52/22	3% acetylene
H	Pr^i	64	43	59–62/35	10% impurity
H	Ph	73	–	– a,b	–
H	$Bu^t - C \equiv C -$	88	–	– c,d	–
Me	Me	71	65	58–60/56	single peak
Me	Et	85	79	59/24	single peak
Me	Bu^t	85	81	59–61/8	single peak
Me	Ph	87	–	– e	–
Pr^i	Pr^i	52	45	61–62/7	20% impurity
Bu^t	Bu^t	84	70	80–81/6	single peak
	= C = CHBr.	63	45	39–41/0.3	–

a. λ max. 267 mμ ; b. m.p. 10–12°; c. prepared by E.S. Pepper; d. λ max. 254 mμ ; e. λ max. 271 mμ .

Equimolar mixtures of primary or secondary acetylenic or allenic alcohols and pyridine react with triphenylphosphite -dibromide[7] to give good yields of bromides (see Table II), the bromine simply replacing the hydroxyl group. In the absence of pyridine considerable quantities of dibromo compounds result from the addition of HBr (evolved during the reaction) to the allenes or acetylene group. This method gives improved and more consistent yields and purer products than the conventional phosphorus tribromide procedure.

Table II.

Bromide	% Yield Crude	% Yield Distilled	B.p. °C/mm.	V.P.C.
$CH_2=C=CH.CH_2Br$	70.0	58.0	62-63/170	single peak
$CH_2=C=CH.CH_2CH_2Br$	80.0	76.0	69-70/70	single peak
$CH\equiv C.CH_2Br$	77.0	72.0	37-38/140	single peak
$CH\equiv C.CH_2OCH_2CH_2Br$	83.0	64.0	34-36/1.0	single peak
$CH_2\equiv CH.CH_2OCH_2CH_2Br$	-	53.0	40-42/6.0	-
$CH\equiv C.CH(CH_3)Br$	78.0	72.0	43-45/100	-
$CH\equiv C.CH(CH_3)OCH_2CH_2Br$	73.0	61.0	37-39/2.3	single peak

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4. cf Hennion and Boisselle *J.Org.Chem.* 1961, 26, 725.
5. Jacobs and Brill, *J. Amer. Chem. Soc.* 1953, 75, 1314 have shown that under similar conditions propargyl bromide rearranges only very slowly only 28% of 1-bromoallene was obtained after six days.
6. Unpublished work by Evans and Landor.
7. cf. Coe, Landor and Rydon, *J. Chem. Soc.* 1954, 2281.