A New Route to 2-Bromo-1-alkenes by Hydrobromination of 1-Alkynes with Tetraethylammonium Hydrogen Dibromide

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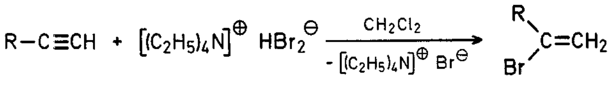
It is well known[1,2,3] that the ionic addition of hydrogen bromide to 1-alkynes is very difficult, the most current reaction being the radical addition that leads to 1-bromo-1-alkenes and 1,2-dibromoalkanes in various amounts. It follows that 2-bromo-1-alkenes are usually obtained by indirect methods: coupling of Grignard reagents with 2,3-dibromopropene[4], addition of hydrogen bromide to 1-trimethylsilyl-1-alkynes[5], reduction of bromovinylic sulphones[6].

Following our previous studies on hydrochlorination of alkynes by means of triethylammonium hydrogen dichloride[7], we now report a new, simple method by which 2-bromo-1-alkenes are obtained by direct hydrobromination of 1-alkynes with tetraethylammonium hydrogen dibromide in dichloromethane.



$$R-C\equiv CH + [(C_2H_5)_4N]^{\oplus}\, HBr_2^{\ominus} \xrightarrow[-\,[(C_2H_5)_4N]^{\oplus}\, Br^{\ominus}]{CH_2Cl_2} \overset{R}{\underset{Br}{>}}C=CH_2$$

Hydrogen bromide can be absorbed by some pure tertiary and quaternary alkylammonium bromides, but the resulting adducts generally are not very stable and loose hydrogen bromide easily at room temperature[8,9]. However, we have found that a dichloromethane solution of tetraethylammonium bromide, or tetra-*n*-butylammonium bromide, can also absorb hydrogen bromide, the final solution retains hydrogen bromide well and can be handled easily. The formation of the hydrogen dibromide ion [$HBr_2^{\ominus}$] in this reaction is deduced from N.M.R. data: the ^{1}H-N.M.R. spectrum of the tetraalkylammonium salt in dichloromethane solution exhibits a sharp singulet at $\delta = 9.8$ ppm when one mol equivalent of hydrogen bromide has been absorbed, this signal being assignable to the $HBr_2^{\ominus}$ ion, in agreement with other studies[10]; this singulet moves upfield with increasing concentration of hydrogen bromide.

The addition reaction is feasible starting from either tetraethylammonium or tetra-*n*-butylammonium bromide, but it is advantageous to use the former: after the reaction, on addition of diethyl ether, the tetraethylammonium salts consisting essentially of the bromide and some hydrogen dibromide, are precipitated, filtered, and heated to drive off excess hydrogen bromide. Tetraethylammonium bromide can thus be nearly quantitatively recovered and recycled; only hydrogen bromide and 1-alkyne are actually required for the reaction to be performed. This treatment is not so simple for the tetra-*n*-butylammonium salt, as the hydrogen dibromide salt is liquid at room temperature.

This addition of hydrogen bromide to 1-alkynes is in accord with Markownikov's rule and leads to the corresponding 2-bromo-1-alkenes in high yields, thus excluding a radical process; a net excess of hydrogen bromide relative to

Table. 2-Bromo-1-alkenes prepared[a]

Product R	Molar ratio $HBr_2^{\ominus}$/alkyne	Reaction time [h]	Yield [%]	b.p. [°C]/torr (Lit. p. [°C]/torr)	Molecular formula[b]	^{1}H-N.M.R. (CCl_4)[e] $\delta_{=CH_2}$ [ppm]
n-C_4H_9	1	3	89	132°/76° (134°/760)[4]	—	5.23–5.4 (m)
n-C_5H_{11}	—	4	80	55°/17 (46°/11)[4]	—	5.3–5.47 (m)
n-C_6H_{13}	—	4	80	62–64°/10	$C_8H_{15}Br$ (191.1)	5.33–5.5 (m)
n-C_7H_{15}	—	5	77	77–78°/11	$C_9H_{17}Br$ (205.1)	5.37–5.53 (m)
	1.5	1.5	90			
HO—CH_2	1.1	4	91[c]	148–150°/760	C_3H_5BrO (137.0)	5.53–5.91 (m)
C_2H_5—CH(OH)—CH_2	—	4	77	74–76°/14	$C_6H_{11}BrO$ (179.1)	5.45–5.67 (m)
HO—$(CH_2)_2$	—	4	83	69–70°/11	C_4H_7BrO (151.0)	5.43–5.63 (m)
C_2H_5O—CH_2	—	24	65[c]	134–136°/760	—[d]	5.48–5.83 (m)

[a] Reaction in dichloromethane at 40 °C.

[b] The microanalyses were in satisfactory agreement with the calculated values (C ± 0.23, H ± 0.29, Br ± 0.42).

[c] Product contains ~9% of the 1-bromo-1-alkene isomer.

[d] Characterized by spectroscopy; satisfactory microanalysis could not be obtained.

[e] For all these spectra it is found: $^2J_{=CH_2} \ddagger {}^4J_{=CH_2-CH_2} \ddagger 1.2$ Hz

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the alkyne makes the reaction faster and may improve the yield, without producing dibrominated compounds. No radical inhibitor is required, and it has been observed, with 1-hexyne, that in the presence of ascaridole, the radical addition is still the minor process. The reaction can be extended to various substrates such as acetylenic alcohols and ethers The data obtained are summarized in the Table.

2-Bromo-1-nonene (R = *n*-C_7H_{15}); Typical Procedure:
A slow stream of dry hydrogen bromide gas (Matheson), which is bubbled through tetrahydronaphthalene and then passed through calcium bromide, is introduced into a saturated solution of tetraethylammonium bromide (11.5 g, 55 mmol) in dichloromethane (50 ml) with stirring and cooling in ice. The absorption of hydrogen bromide makes the tetraethylammonium salt soluble; the desired amount (4.4 g, 55 mmol), absorbed in ~0.5 h, is checked by weighing. The flask is stoppered and the reaction mixture is allowed to warm under stirring to room temperature. 1-Nonyne (6.2 g, 50 mmol) is added at once to this medium and the flask, tightly stoppered, is heated at 40 °C for 5 h. After cooling in ice, diethyl ether (100 ml) is poured into the reaction mixture and the tetraethylammonium salt is filtered off. Distillation gives 2-bromo-1-nonene; yield: 7.8 g (77%); b.p. 77–78 °C/11 torr

$C_9H_{17}Br$	calc.	C 52.69	H 8.35	Br 38.95
(205.1)	found	52.54	8.40	38.53

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