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RETENTION OF CONFIGURATION IN DOUBLE BOND PROTECTION-DEPROTECTION BY BROMINATION-CATHODIC DEBROMINATION

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The double bond can be mildly protected by bromination with PyrHBr$_3$; deprotection is achieved by cathodic reduction at -1.4 V. The overall yields range from 68 to 99 %, the configuration of the double bond is retained with at least 96 %.

The double bond can be protected against oxidation, hydrogenation or electrophilic addition by several methods1). Additionally we have demonstrated that different double bonds in a diene can be selectively monoprotected. Pyridinium hydrobromide perbromide (PyrHBr$_3$) reacts preferentially with the higher alkylated double bond2). For protection of the less alkylated one the tetrabromide is partially reduced by controlled potential electrolysis3). For the protection of acyclic olefins it is important that in this bromination-cathodic debromination the configuration of the double bond is highly retained. For *cis*- and *trans*-2-butene a specific *anti*-addition of bromine has been reported4). With PyrHBr$_3$ the *anti* addition has only been demonstrated for cyclic olefins5). Whilst debromination with Zn6,7), Mg6) or KJ6) is not totally stereospecific, *meso*- or *d,l*-2,3-dibromobutane yields at the mercury cathode pure *cis*- or *trans*-2-butene8). Different acyclic aliphatic alkenes were brominated with PyrHBr$_3$ and the dibromide subsequently reduced at -1.4 V (vs. SCE). The results are summarized in the table.

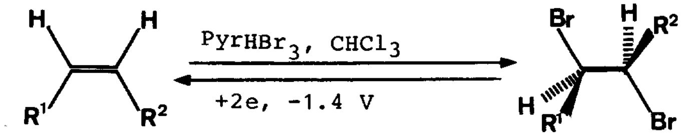

Table: Bromination and cathodic debromination of alkenes; yields and retention of double bond configuration.

Alkene	Yield % Bromination[a]	Yield % Cathodic debromination[b]	Retention of double bond configuration[c] (%)
Oleic acid	99		97.5
Elaidic acid	97	91	100
Linoleic acid	95	85	98
E-4-Heptenol	75[d]	90	96
Z-3-Hexenol	93	81	100

a) Bromination with PyrHBr$_3$ in CHCl$_3$ at -60° to -10° C; b) At -1.4 V (vs. SCE) at a mercury pool (divided cell) in dimethylformamide/TBA·BF$_4$; c) Analysis on configurational isomers by capillary gaschromatography (34m, SE 30); d) The alcohol was first converted into its tetrahydropyranyl ether (94 %), followed by PyrHBr$_3$ addition at -50° C and removal ot the THP-group (80 %).

E-4-Heptenol yields with PyrHBr$_3$ (-60° C) besides 65 % 4,5-Dibromheptanol two cyclization products: 2-(1-Brompropyl)-tetrahydrofuran (31 %) and 3-Brom-2-ethyltetrahydropyran (4 %). Whilst the dibromide is reduced at -1.4 V (vs. SCE) in 88 % yield with only 3-4 % cis-isomerization to E-4-heptanol, the cyclic ethers need the very cathodic reduction potential of -2.5 V (vs. SCE) to be reduced to E-4-Heptenol in the lower yield of 66 % and with 14 % isomerization. This cyclization which necessitates a high cathodic reduction potential for deprotection and such increases the risk to reduce other functional groups of the olefin is prevented by protecting the alcohol as THP-ether (Table).

These results favour a specific anti-addition in the PyrHBr$_3$ bromination and an anti-elimination in the cathodic debromination.

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