Synthesis of 2-Butene-2,3-d_2 and 2-Butene-1,1,1,4,4,4-d_6

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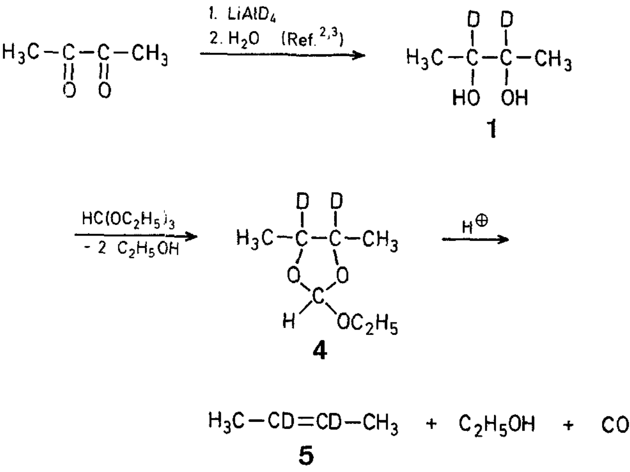
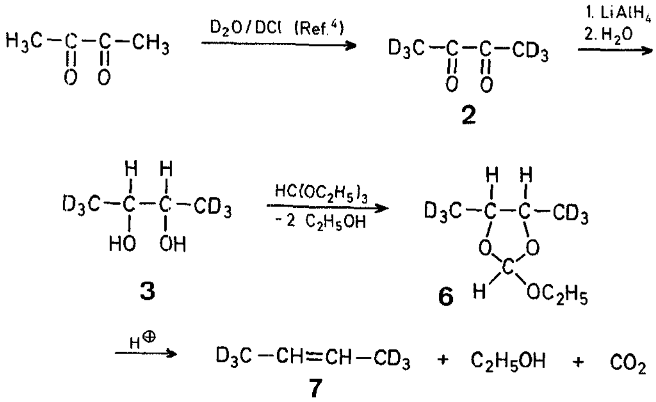
2-Butenes deuterated at C-2 and C-3 or at C-1 and C-4 are of interest for the investigation of the mechanism of the catalytic isomerization of alkenes[1]. The synthesis of such selectively deuterated 2-butenes requires that the position of the double bond be fixed and that the deuterium atoms be introduced only at the desired positions. Alkenes having the C=C double bond at a desired position may be obtained from saturated compounds having suitable functional groups, identical or not, on two vicinal C-atoms. We chose an α-diketone (butanedione) as starting material because it is easy to introduce deuterium atoms into this molecule to obtain selectively deuter-

Sequence A:



Sequence B:



ated α-diols **(1, 3)**. The transformation of the α-diols into the corresponding alkenes **(5, 7)** can be achieved via various cyclic intermediates such as thiocarbonates[5,6], trithiocarbonates[5,7], 2-phenyl-1,3-dioxolane[8,9], or 2-ethoxy 1,3-dioxolane[10]. We found[11] that all these intermediates may be converted into the expected alkene **(5** or **7)**, without formation of isomers. The method involving 2-ethoxy-1,3-dioxolane is by far preferable since it is rapid and gives the best yield of the desired product.

Both reaction sequences A and B are easy to perform and purification of the intermediates **4** or **6**, respectively, is not necessary. The products **5** and **7** are practically not contaminated by impurities except for carbon dioxide which can be easily removed. This is not the case with the products obtained by decomposition of thiocarbonates[12], as sulfur is a well-known poison for a large number of catalysts. Thus, the butenes obtained may be used directly for catalytic reactions, eventually after separation of the *cis*-2-butene from the *trans*-2-butene[1]. This synthesis might be improved by separating the *meso* and *dl* diols, or by separating the corresponding dioxolanes. It would then be possible to obtain pure *cis*- or *trans*-butenes, since the *meso*-diol yields the *cis*-butene and the *dl*-diol the *trans*-butene[11].

The methods described here for the 2-butenes may also be applied to the synthesis of any alkene having a disubstituted double bond and being selectively deuterated in the allylic or vinylic position. It is also applicable to the synthesis of 1-alkenes from 2-oxoalkanoic esters (in place of *vic*-diketones).

G.L.C. analyses of the diols were carried out on an Intersmat IGC 16 gas chromatograph (column 5 ft × 1/8 in packed with 10% LAC-2R-446 on Spherosil X0C-005, temperature 120–170 °C programmed 15 °C/min, carrier gas nitrogen at 20 ml/min). G.L.C. analyses of the butenes were carried out on an Intersmat 120 MB gas chromatograph (catharometer, column 17 ft × 1/8 in packed with 22% BEEA + 8% BEES on Chromosorb P 60/70, temperature 20 °C, carrier gas helium at 10 ml/min). Mass spectra were performed with a Kratos MS-25 mass spectrometer; ^{1}H-N.M.R. and I.R. spectra were recorded on JEOL PMX-60 and Beckman 4250 instruments, respectively.

Sequence A; Synthesis of 2-Butenes-2,3-d_2 (5):

2,3-Butanediol-2,3-d_2 **(1)**: The reaction is carried out in a 500 ml three-necked flask immersed in an ice bath. A solution of butanedione (8.6 g, 0.1 mol) in anhydrous ether (100 ml) is slowly added to a vigorously stirred suspension of lithium aluminum deuteride ($LiAlD_4$; 3.1 g, 0.07 mol) in anhydrous ether (50 ml). The mixture is then refluxed for 2 h, cooled to room temperature, and slowly hydrolyzed by a 30 weight % solution of sodium and potassium tartrate[3] (20 ml). The aqueous layer is extracted continuously with ether for 24 h, the combined organic extract is dried with anhydrous magnesium sulfate, then the diol is purified by distillation; yield: 7.4 g (80%); b.p. 180–181 °C/760 torr; n_D^{22}: 1.4335. The product consists of 70% *meso*-2,3-butanediol-2,3-d_2 and 30% *dl*-2,3-butanediol-2,3-d_2 (according to G.L.C. analysis).

I.R. (CCl_4): $\tilde{\nu} = 3400$ (OH); 2980, 2950, 2880 (CH_3); 2160 (C—D); 1125 (C—O); 1460, 1380 cm^{-1} (CH_3).

^{1}H-N.M.R. (CCl_4/TMS_{int}, 60 MHz): $\delta = 4.1$ (s, 2H, OH); 1.2 ppm (s, 6H, CH_3); no signal at 3.8 ppm corresponding to C$\underline{H}$—OH in the non-deuterated butanediol.

2-Butenes-2,3-d_2 **(5)**: 2,3-Butanediol-2,3-d_2 (**1**; 0.46 g, 0.005 mol) and ethyl orthoformate (0.9 g, 0.006 mol) are introduced into a distillation apparatus consisting of a 50 ml flask equipped with a vertical reflux condenser and a collector. The mixture is heated at 100 °C until the theoretical quantity of ethanol (0.01 mol = 0.46 g) has been recovered in the collector. The dioxolane **(4)** is then decomposed *in situ* by adding traces of acetic acid to the flask and heating the mixture at 140–150 °C until the theoretical quantity of ethanol (0.005 mol = 0.23 g) has been recovered. The butenes **(5)** are collected at the top of the reflux condenser in a gasometer filled with a saturated solution of potassium hydroxide or calcium chloride, depending on whether carbon dioxide is to be removed or not. A typical experiment without elimination of carbon dioxide yields 160 ml of gases: 2-butene-2,3-d_2 (50 mol%) and carbon dioxide (50 mol%) (G.L.C. analysis); yield of 2-butenes-2,3-d_2 **(5)**: 79 ml (70%). The product consists of 70% *cis*-2-butene-2,3-d_2 and 30% *trans*-2-butene-2,3-d_2.

M.S. (10 eV): $m/e = 58$ (M^+, 100%); 59 (4.1); 57 (1.3) [1.98 D per molecule].

^{1}H-N.M.R. (CCl_4/TMS_{int}, 60 MHz) of the 2,3-dibromobutanes prepared by Br_2 addition to each 2-butene isomer separated by G.L.C.: $\delta = 1.8$ ppm (s, —CH_3, *dl* isomer from *cis*-2-butene); 1.9 ppm (s, —CH_3, *meso* isomer from *trans*-2-butene).

Sequence B; Synthesis of 2-Butenes-1,1,1,4,4,4-d_6 (7):

Butanedione-1,1,1,4,4,4-d_6 **(2)**: A mixture of butanedione (30 g, 0.35 mol) and 1 normal DCl/D_2O (10 ml) is refluxed for 24 h in a 100 ml flask fitted with a reflux condenser, and then allowed to cool. The aqueous layer is saturated with sodium chloride and extracted with ether (5 × 5 ml). The combined organic extract is mixed with fresh 1 normal DCl/D_2O (10 ml), and the mixture is refluxed again for 24 h. After 8 exchanges, the deuterated butanedione **(2)** is distilled; yield: 8.0 g (25%); b.p. 90–92 °C/760 torr; n_D^{22}: 1.4118.

M.S. (10 eV): $m/e = 92$ (M^+, 100%); 91 (11.8); 93 (4.4); 90 (0.3) - 5.88 D per molecule.

I.R. (CCl_4): $\tilde{\nu} = 2250$, 2150, 2060 (CD_3); 1040, 960 (CD_3); 1720 cm^{-1} (C=O).

2,3-Butanediol-1,1,1,4,4,4-d_6 **(3)**: Prepared from butanedione-1,1,1,4,4,4-d_6 (**2**; 8.0 g, 0.087 mol) and lithium aluminum hydride ($LiAlH_4$; 2.4 g, 0.06 mol) in essentially the same manner as diol **1**; yield of **3**: 5.8 g (70%); b.p. 183–185 °C/760 torr; n_D^{22}: 1.4354. The product consists of 70% *meso*-diol and 30% *dl*-diol (G.L.C. analysis).

I.R. (CCl_4): $\nu = 3400$ (OH); 2900 (CH); 2220, 2120, 2060 (CD_3); 1125 (C—O); 1035, 965 cm^{-1} (CD_3).

^{1}H-N.M.R. (CCl_4/TMS_{int}, 60 MHz): $\delta = 4.1$ (s, 2H, OH); 3.8 (s, 2H, =CH— *meso*); 3.7 ppm (s, 2H, =CH— *dl*); no signal at 1.1 ppm corresponding to —CH_3 in the non-deuterated butanediol.

2-Butenes-1,1,1,4,4,4-d_6 **(7)**: Prepared from diol **3** (0.48 g, 0.005 mol) and ethyl orthoformate (0.9 g, 0.006 mol) and decomposition of the resultant dioxolane **6** with acetic acid as described for the synthesis of butene **5** in Method A. A typical experiment without elimination of carbon dioxide yields 138 ml of gases: 2-butenes-1,1,1,4,4,4-d_6 (50 mol%) and carbon dioxide (50 mol%) (G.L.C. analysis); yield of butenes **7**: 68 ml (60%). The product consists of 70% *cis*-2-butene-1,1,1,4,4,4-d_6 and 30% *trans*-2-butene-1,1,1,4,4,4-d_6.

M.S. (10 eV): $m/e = 62$ (M^+, 100%); 61 (11.9); 63 (4.4); 60 (0.3) - 5.88 D per molecule.

^{1}H-N.M.R. (CCl_4/TMS_{int}, 60 MHz) of the 2,3-dibromobutanes prepared by Br_2 addition on each 2-butene isomer separated by G.L.C.: $\delta = 4.5$ ppm (s, =CH—, *dl* isomer from *cis*-2-butene); 4.1 ppm (s, =CH—, *meso* isomer from *trans*-2-butene).

The position of the D atoms in the *cis*-2-butene was checked by microwave spectroscopy[13].

2-Butene-d_8:

This compound may be obtained by reduction of butanedione-d_6 (**2**; 6.0 g, 0.065 mol) with lithium aluminum deuteride ($LiAlD_4$; 2.7 g, 0.06 mol); yield: 50%. The product consists of 70% *cis*-2-butene-d_8 and 30% *trans*-2-butene-d_8 (G.L.C. analysis).

M.S. (10 eV): $m/e = 64$ (M^+, 100%); 63 (12.2); 65 (4.4); 62 (0.2) - 7.80 D per molecule.

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