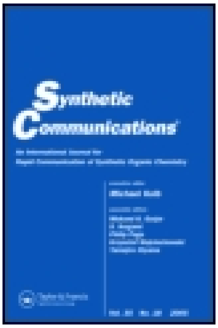

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EFFICIENT PROCEDURES FOR 1-BROMO-1,3-BUTADIENE AND 2-BROMO-1,3-BUTADIENE

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Abstract:

Mixtures of *Z*- and *E*-1-bromo-1,3-butadiene in which the *E*- or *Z*- isomer predominates have been obtained in good yields by treating a mixture of Z- and *E*-1,4-dibromo-2-butene (90% *Z*-isomer) or pure *E*-1,4-dibromo-2-butene, respectively, with powdered potassium hydroxide in high-boiling petroleum. 2-Bromo-1,3-butadiene was obtained in high yields by stirring a mixture of vinylacetylene, concentrated aqueous hydrogen bromide and copper(I) bromide.

1-Bromo-1,3-butadiene and 2-bromo-1,3-butadiene are potentially useful compounds, especially for transition metal-catalyzed cross coupling reactions[1]. Although the methods for their preparation are known[2,3], no satisfactory experimental procedures are available. We have obtained the title compounds as depicted in the schemes.

Treatment of the commercially available Z-1,4-dihydroxy-2-butene with PBr_3 in diethyl ether gave the corresponding 1,4-dibromide. The crude product consisted

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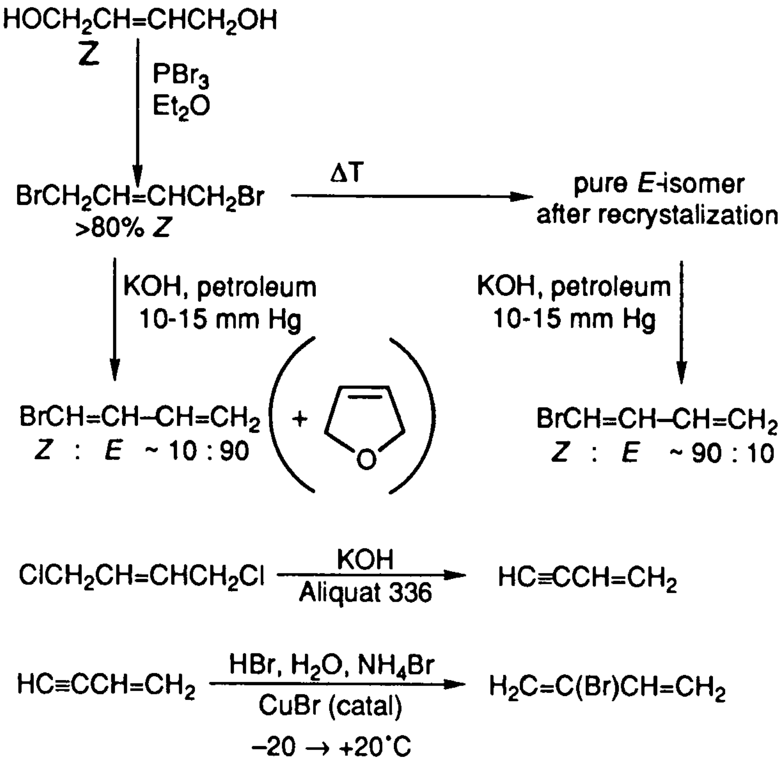

mainly of the Z-isomer (Z / E = 9/1) as estimated from IR- and NMR-spectra. Upon standing, but much faster during distillation, a Z to E isomerization occurred. The *E*-isomer could be easily isolated from a pentane solution of the *E* / *Z*-mixture. Treatment of the freshly prepared, undistilled *E* / *Z*-mixture (Z / *E* = 9/1) with machine-powdered KOH in high-boiling petroleum at elevated temperatures in a vacuum of 10 to 15 mm Hg afforded a mixture consisting for ~85% of *Z*- and *E*-BrCH=CH–CH=CH_2 and ~15% of dihydrofuran. The latter compound could be easily removed by shaking with concentrated aqueous hydrochloric acid. The remaining organic layer consisted of *E*- and Z-BrCH=CH–CH=CH_2 (Z / *E* ratio: ~9).

The crystalline, pure *E*-$BrCH_2$–CH=CH–CH_2Br was dehydrobrominated in a similar way to give mainly Z-BrCH=CH–CH=CH_2 (*E* / *Z* ratio: ~9).

2-Bromo-1,3-butadiene was prepared by stirring a mixture of vinylacetylene[4], 200% excess 48% aqueous HBr, NH_4Br, and ~15 mol% of copper(I)bromide. The initial product, the 1,4-adduct $H_2C=C=CH-CH_2Br$, undergoes a copper(I)-catalyzed rearrangement to 2-bromo-1,3-butadiene[5]. In the absence of copper bromide a mixture consisting of comparable amounts of this allenic bromide and 2-bromo-1,3-butadiene was formed.

Procedures

1,4-Dibromo-2-butene.

Phosphorus tribromide (0.67 mol) was added dropwise over 1.5 h to a (heterogeneous) mixture of 1.00 mol of *Z*-1,4-dihydroxy-2-butene and 250 ml of diethyl ether, while maintaining the temperature (cooling in a bath at –10°C) between 0 and 5°C. After the addition the cooling bath was removed and the temperature allowed to rise to ~20°C. After an additional 2 h the mixture was poured in 500 ml of ice water. After vigorous shaking, (an additional amount of ether was added in order to effect a good separation of the layers) the organic layer was washed three times with a saturated solution of sodium chloride and subsequently dried over $MgSO_4$. After the greater part of the ether had been distilled off on the rotary evaporator (bath temperature not higher than 35°C) the last traces of ether were removed by evaporation with an oil pump (no external heating was applied. The residue was reasonably pure $BrCH_2CH=CHCH_2Br$ (*Z* / *E* ratio about 9), yield ~85%.

1-Bromo-1,3-butadiene (*E* : *Z* ~9).

A 2-l round-bottomed, two-necked flask (vertical necks!) was equipped with an efficient gas-tight mechanical stirrer and a 30-cm Vigreux column. The flask was charged with 250 g (freshly prepared) machine-powdered potassium hydroxide, 150 ml of petroleum (b.p. ≥100°C/15 mm Hg) and 0.20 mol of the freshly prepared mixture (*Z* / *E* ~9) of *Z* and *E* –$BrCH_2CH=CHCH_2Br$ (freed from traces of diethyl ether). The column was connected to a condenser and a receiver cooled in a bath with dry ice and acetone. After evacuation (10 to 15 mm Hg), the vigorously stirred mixture was heated until foaming started. The heating bath was then removed immediately. The volatile bromobutadiene which gave rise to foaming, condensed in the strongly cooled receiver. When the reaction had subsided, external heating was continued for an additional 30 min. During this period a gentle reflux of the petroleum in the lower part of the column was maintained. The contents of the receiver were transferred into a small (contents 50 ml) separating funnel and shaken three times with 10 ml portions of 30 to 36% aqueous hydrochloric acid.

The unwashed lower layer (freed from dihydrofuran by these operations) was transferred into a 250 ml round-bottomed flask containing a few (2 to 3) g of $MgSO_4$. After vigorous shaking, the flask was equipped for a vacuum distillation: 30-cm Vigreux column, condenser and receiver cooled at –75°C. The apparatus was evacuated (water aspirator) and the flask containing the crude bromobutadiene placed in a bath, initially at 15°C, towards the end of the evacuation procedure at 40°C. A very small residue of petroleum remained in the flask. The receiver contained reasonably (≥95% by NMR) pure $BrCH{=}CH{-}CH{=}CH_2$, yield ~65%, *E* : *Z* as estimated from the NMR spectrum: ~9. Distillation of a small sample (~10 g) at normal pressure under nitrogen gave b.p. 90-94°C/760 mm Hg, n^{20}_D 1.512. (lit. [2] gives b.p. 91-91.5°C/756 mm Hg, n^{20}_D 1.5160 for the *E* / *Z* mixture).

The ^1H NMR and ^{13}C NMR (aceton-*d6* Bruker, 200 MHz) spectra gave the following signals for the *E*-isomer

E-1-bromo-1,3-butadiene:

^1H NMR (acetone-*d6*): 6.73 ppm (1 H; qd, ^3J: 13.5 Hz, ^3J: 10.1 Hz, ^4J: 0.6 Hz); 6.35 ppm (1 H; dd, ^3J: 13.5 Hz, ^4J: 0.6 Hz); 6,26 ppm (1 H; td, ^3J: 17.3 Hz, ^3J: 10.4 Hz) ; 5.25 ppm (1 H; td, ^3J: 17.3 Hz, ^3J: 0.6 Hz); 5.14 ppm (1 H; td, ^3J: 10.4 Hz, ^3J: 0.6 Hz).

^{13}C NMR (acetone-*d6*): 138.98 ppm, 135.26 ppm, 118.89 ppm, 110.43 ppm

1-Bromo-1,3-butadiene (*Z* : *E* ~9).

Distillation of the product prepared from Z-$HOCH_2CH{=}CHCH_2OH$ and PBr_3 *in vacuo* (b.p. 85°C/15 mm Hg) gave rise to an appreciable conversion into the *E*-isomer. After standing for one night at –25°C the crystals were filtered off on a sintered-glass funnel and rinsed with cold (–10°C) pentane. Recrystallization from pentane gave the pure *E*-isomer as colourless leaves, m.p. 51-52°C (this compound is also commercially available from Janssen Chimica, Belgium).

The procedure for the preparation of $BrCH{=}CH{-}CH{=}CH_2$ from *E*-$BrCH_2CH{=}CHCH_2Br$ was similar to that described above. As no dihydrofuran was formed, the treatment with concentrated hydrochloric acid was not carried out. A mixture of *Z*- and *E*-$BrCH=CH-CH=CH_2$ (*Z* : *E* ~9 as estimated from the ^1H NMR spectrum) was obtained in ~85% yield. Distillation of a small sample at normal pressure under nitrogen gave a b.p. 90-94°C/ 760 mm Hg, n^{20}_D 1.510. The ^1H NMR and ^{13}C NMR spectra (aceton-*d6*) of the *Z*-isomer gave the following signals:

Z-1-bromo-1,3-butadiene:
^1H NMR (acetone-*d6*): 6.70-6.56 ppm (2 H; m); 6.25-6.12 ppm (1 H; m, ^3J: 5.5 Hz); 5.57-5.32 ppm (2 H; m)
^{13}C NMR (acetone-*d6*): 133.93 ppm, 133.22 ppm, 122.00 ppm, 109.39 ppm

2-Bromo-1,3-butadiene.
A 500-ml three-necked, round-bottomed flask was equipped with an efficient gas-tight mechanical stirrer, a gas inlet and a cold finger, filled with dry ice-acetone mixture. The upper part of this condenser was connected with a cold trap (–78°C). The flask was charged with 250 gram of a 48% aqueous solution of hydrobromic acid, 20 g of copper(I)bromide and 30 g of ammonium bromide. The air in the apparatus was completely replaced by nitrogen, after which the dark mixture was cooled to –25°C (the inlet was replaced by a thermometer). Vinylacetylene (0.50 mol, for the preparation see [4, 5], liquified in a trap cooled at –78°C), was added in one portion and the mixture was vigorously stirred. The cooling bath was removed. The temperature in the flask rose very slowly (in the case of a too vigorous reflux of the vinylacetylene some external cooling should be applied). After ~2 h, when the temperature had risen above 5°C, the intensity of the reflux had decreased considerably, but the conversion appeared to be far from complete. Stirring was therefore continued for an additional 10 hours. The mixture was then poured into 500 ml of ice water and three extractions with portions of 80, 30 and 30 ml of high-boiling (b.p. ≥100°C/15 mm Hg) petroleum were carried out. The combined extracts were washed once with water and subsequently dried over a small amount of $MgSO_4$. The organic solution was transferred into a one-litre round-bottomed flask, which was subsequently equipped for a vacuum distillation: 30-cm Vigreux column, condenser and receiver cooled at –78°C. The apparatus was evacuated (water aspirator) and the temperature of the heating bath gradually raised until the petroleum began to reflux in the lower part of the column. The

receiver contained reasonably (at least 95%) pure $H_2C{=}(Br)CH{=}CH_2$, n^{20}_D 1.498 (lit[3] gives b.p. 42-43°C/165 mm Hg, n^{20}_D 1.4988). Distillation at normal pressure was not carried out.

The ^1H NMR and ^{13}C NMR spectra (chloroform-*d*, Bruker 200MHz) showed the following signals:

E-2-bromo-1,3-butadiene:

^1H NMR (chloroform-*d*): 6.30 ppm (1 H; dd, ^3J: 15.6 Hz, ^3J: 10.3 Hz);5.81 ppm (1 H; d, ^3J: 0.5 Hz); 5.66 ppm (1 H; s) ; 5.59 ppm (1 H; d, ^3J: 15.6 Hz); 5.31 ppm (1 H; d, ^3J: 10.3 Hz).

^{13}C NMR (chloroform-*d*): 134.95 ppm, 130.52 ppm, 120.67 ppm, 120.37 ppm

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