

1,3-Dioxane (formaldehyde trimethylene acetal) [505-22-6] $C_4H_8O_2$, M 88.1, m -45° , b $104.5^\circ/751\text{mm}$, $105\text{-}106^\circ/\text{atm}$, d_4^{20} 1.040, n_D^{20} 1.417. Dry the dioxane with Na and fractionally distil it. [*Beilstein* 19/1 V 11.] **1,4-Dioxane (Dioxane, diethylene oxide)** [123-91-1] has m $10\text{-}12^\circ$, 11.8° , b $12^\circ/20\text{mm}$, $34^\circ/60\text{mm}$, $45^\circ/100\text{mm}$, $82^\circ/400\text{mm}$, $101.1^\circ/760\text{mm}$, $100\text{-}102^\circ/\text{atm}$, $101.3^\circ/\text{atm}$, d_4^{25} 1.0292, n_D^{15} 1.4236, n_D^{25} 1.42025. It is prepared commercially either by dehydration of ethylene glycol with H_2SO_4 and heating ethylene oxide or bis(β -chloroethyl)ether with NaOH. The usual impurities are acetaldehyde, ethylene acetal, acetic acid, water and peroxides. Peroxides can be removed (and the aldehyde content decreased) by percolation through a column of activated alumina (80g per 100-200ml solvent), by refluxing with $NaBH_4$ or anhydrous stannous chloride and distilling, or by acidification with concentrated HCl, shaking with ferrous sulfate and leaving in contact with it for 24 hours before filtering and purifying further. Hess and Frahm [*Chem Ber* 71 2627 1938, DOI: 10.1002/cber.19380711234] refluxed 2L of dioxane with 27ml concentrated HCl and 200ml water for 12 hours with slow passage of nitrogen to remove acetaldehyde. After cooling the solution, KOH pellets were added slowly and with shaking until no more would dissolve and a second layer had separated. The dioxane was decanted, treated with fresh KOH pellets to remove any aqueous phase, then transferred to a clean flask where it was refluxed for 6-12 hours with sodium, then distilled from it. *Alternatively*, Kraus and Vinge [*J Am Chem Soc* 56 511 1934, DOI: 10.1021/ja01318a004] heated it on a steam bath with solid KOH until fresh addition of KOH gave no more resin (due to acetaldehyde). After filtering through paper, the dioxane was refluxed over sodium until the surface of the metal was not further discoloured during several hours. It was then distilled from sodium.

The acetal (**b 82.5°**) is removed during fractional distillation. Traces of *benzene, if present, can be removed as the *benzene/MeOH azeotrope by distillation in the presence of MeOH. Distillation from $LiAlH_4$ removes aldehydes, peroxides and water. Dioxane can be dried using Linde type 4X molecular sieves. Other purification procedures include distillation from excess C_2H_5MgBr , refluxing with PbO_2 to remove peroxides, fractional crystallisation by partial freezing and the addition of KI to dioxane acidified with aqueous HCl. Dioxane should be stored out of contact with air, preferably under N_2 .

A detailed purification procedure is as follows: Dioxane is stood over ferrous sulfate for at least 2 days, under nitrogen. Then water (100ml) and conc HCl (14ml)/ litre of dioxane are added (giving a pale yellow colour). After refluxing for 8-12 hours with vigorous N_2 bubbling, pellets of KOH are added to the warm solution to form two layers and to discharge the colour. The solution is cooled rapidly with more KOH pellets being added (magnetic stirring) until no more dissolved in the cooled solution. After 4-12 hours, if the lower phase is not black, the upper phase is decanted rapidly into a clean flask containing sodium, and refluxed over sodium (until freshly added sodium remained bright) for 1 hour. The middle fraction is collected (and checked for minimum absorbency below 250nm). The distillate is fractionally frozen three times by cooling in a refrigerator, with occasional shaking or stirring. This material is stored in a refrigerator. Before use it is thawed, refluxed over sodium for 48 hours, and distilled into a container. All joints are clad with Teflon tape.

Coetzee and Chang [*Pure Appl Chem* 57 633 1985, DOI: org/10.1351/pac198557040633] dried the solvent by passing it slowly through a column (20g/L) of 3A molecular sieves activated by heating at 250° for 24 hours. Impurities (including peroxides) are removed by passing the effluent slowly through a column packed with type NaX zeolite (pellets ground to 0.1mm size) activated by heating at 400° for 24 hours or chromatographic grade basic Al_2O_3 activated by heating at 250° for 24 hours. After removal of peroxides the

effluent is refluxed for several hours over sodium wire, excluding moisture, distilled under nitrogen or argon and stored in the dark. One of the best tests of purity of dioxane is the formation of the purple *disodium benzophenone complex* during reflux and its persistence on cooling. (Benzophenone is better than fluorenone for this purpose and for storing the solvent.) [Carter et al. *Trans Faraday Soc* **56** 343 1960, DOI: 10.1039/TF9605600343; *Beilstein* **19** V 16.] **TOXIC — do not inhale vapour.**

Rapid purification: Check for peroxides (see Chapter 1 and Chapter 2 for test under ethers). Pre-dry with CaCl_2 or better over Na wire. Then reflux the pre-dried solvent over Na (1% w/v) and benzophenone (0.2% w/v) under an inert atmosphere until the blue colour of the benzophenone ketyl radical anion persists. Distil, and store it over 4A molecular sieves in the dark.