

2-(1-Bromo-1-methyl-ethyl)-2-methyl-[1,3]dioxolane

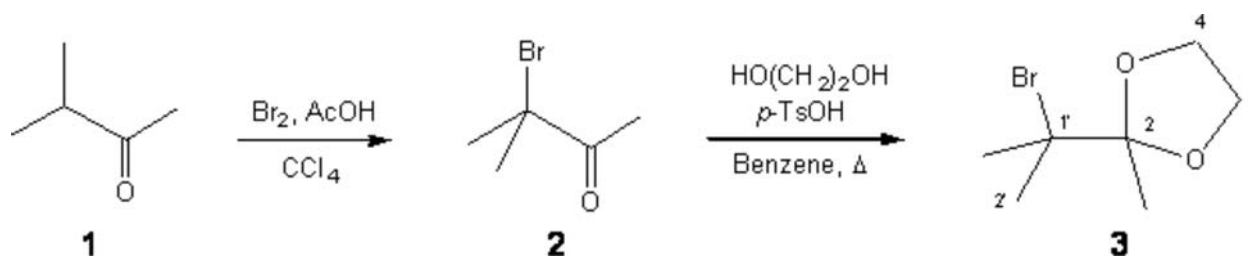
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A solution of bromine (0.3 mL, 5.90 mmol) in CCl_4 (2 mL) was slowly added over a stirred mixture of 3-methyl-butan-2-one (**1**) (505 mg, 5.90 mmol) and AcOH (0.33 mL) at room temperature. After complete addition of bromine it was left reacting for 1 h and then, the reaction was quenched by pouring carefully aqueous NaHSO_3 (25 mL, 40% w/v). The organic layer was washed with 40% NaHSO_3 (25 mL), saturated NaHCO_3 (3 $\times$ 25 mL) and brine (3 $\times$ 25 mL). The organic layer was dried over anhydrous Na_2SO_4 , and 15 mL of MeOH were added to evaporate the azeotrope under reduced pressure. The residue (1.03 g), which contains mainly 3-bromo-3-methyl-butan-2-one (**2**), was resolved in benzene (20 mL) and anhydrous $p\text{-TsOH}$ (171 mg, 1.00 mmol) and ethyleneglycol (928 mg, 14.90 mmol) were added. Then a Dean-Stark trap device was fit and the reaction refluxed for 4.5 h. The crude reaction was worked up by washing with saturated NaHCO_3 (3 $\times$ 25 mL) and brine (4 $\times$ 25 mL) and the organic layer dried over anhydrous Na_2SO_4 , after that, MeOH (15 mL) was added to evaporate the azeotrope under reduced pressure. The residue (811 mg) was purified by reduced pressure distillation (0.15 mmHg, 32 °C) to yield the title compound **3** (770 mg, 3.70 mmol, 62% from **1**) as a colorless liquid.

IR (neat, ν , cm^{-1}): 1161, 1093, 1045, 951 (C-O-C), 649 (C-Br).

^1H NMR (300 MHz, CDCl_3 , d, ppm): 1.52 (3H, s, Me-2), 1.79 (6H, s, 2Me-1'), 4.05 (4H, br s, H-4, H-5).

^{13}C NMR (75 MHz, CDCl_3 , d, ppm): 20.52 (Me-2), 29.51 (C-2', Me-1'), 65.93 (C-4, C-5), 69.99 (C-1'), 111.92 (C-2).

MS (70 eV, m/z): 195 ($[\text{M}+2]^+-\text{Me}$, 1%), 193 (M^+-Me , 2), 129 (M^+-Br , 5), 153 ($\text{C}_3\text{H}_6^{81}\text{Br}^+$, 1), 121

(C₃H₆⁷⁹Br⁺, 1), 114 (M⁺–Br–Me, 6), 99 (M⁺–Br–2Me, 5), 87 (C₄H₇O₂⁺, 98), 69 (9), 57 (22), 43 (100).

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