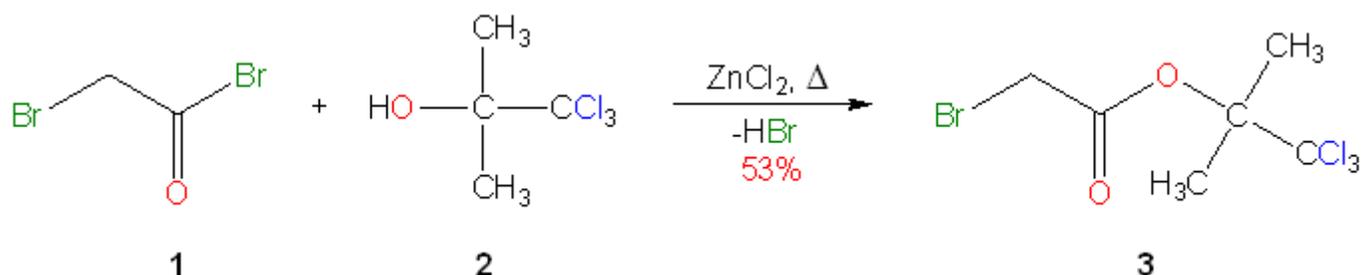


2,2,2-Trichloro-1,1-dimethylethyl bromoacetateLajos Kovács,^{1,*} Péter Forgó², Zoltán Kele¹ and Éva Klement¹¹Department of Medicinal Chemistry,²Department of Organic Chemistry, University of Szeged, Dóm tér 8, H-6720 Szeged, Hungary. Fax: +36-62-54 59 71*E-mail: kovacs@ovrisc.mdche.u-szeged.hu

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In our previous work we have demonstrated the utility of the 2,2,2-trichloro-1,1-dimethylethyl (b, b, b-trichloro-*tert*-butyl, Tcb) group for the protection of carboxylic acids [1]. Herein we would like to describe the preparation of one of their representatives, the title bromoacetate ester. The procedure applied by us is based on the work by Gupta and Srivastava [2].

Experimental: Freshly prepared anhydrous zinc chloride (2.86 g, 20.9 mmol) was chilled in an ice-bath, then bromoacetyl bromide (9.08 mL, 21.10 g, 104.5 mmol) and anhydrous b, b, b-trichloro-*tert*-butanol (12.359 g, 69.6 mmol, prepared by *in vacuo* drying of the commercial hemihydrate over phosphorus pentoxide) were added, each in one portion. The flask was removed from the ice-bath and gently shaken to initiate the evolution of hydrogen bromide. When the gas evolution had subsided the reaction mixture was heated at 100 °C for 2 h. The mixture was diluted with diethyl ether (200 mL), extracted with cold satd. NaHCO₃ solution (3x100 mL) and brine (100 mL), respectively. The organic phase was dried (MgSO₄) and evaporated. The oily residue was subjected to vacuum distillation to afford the product (10.987 g, 53%).

Bp. 120-125 °C/15 kPa.

TLC: light petroleum-ethyl acetate 9:1, R_f 0.68.n_D: 1.5028.Anal. calcd. for C₆H₈BrCl₃O₂ (298.391): C, 24.15; H, 2.70; Br, 26.78%; found C, 24.34; H, 2.76; Br, 26.60%.IR (n, cm⁻¹, neat, KBr): 964s, 1107m, 1156s, 1215m, 1280s, 1371m, 1388m, 1403w, 1421w, 1459w, 1750s, 1754s (n_{C=O}), 2955w, 3005w.

^1H NMR (CDCl_3 , 500 MHz, ppm): 1.94 (s, 6H, $(\text{CH}_3)_2\text{C}$), 3.87 (s, 2H, CH_2).

^{13}C NMR (CDCl_3 , 125 MHz, ppm, assignment based on HMBC and HMQC experiments): 21.09 (CH_3), 26.64 (CH_2), 99.30 ($\text{C}=\text{C}$), 105.01 (CH_3), 165.05 ($\text{C}=\text{O}$).

CI-MS (isobutane, m/z): 303, 301, 299, 297 ($[\text{M}+\text{H}]^+$, isotopic peaks); 267, 265, 263, 261 ($[\text{M}-\text{Cl}]^+$, isotopic peaks). The calculated peak distributions correspond to the expected structure.

References:

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2. I. Gupta, N. P. Srivastava: *Recl. Trav. Chim. Pays-Bas*, **1956**, 75, 48-50.

Sample availability: sample available from the authors.

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