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2,2,2-Trichloro-1,1-dimethylethyl 4-methylbenzoate

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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 aromatic ester. This compound was mentioned by Gupta and Srivastava [2] but it was not described in detail.

Experimental: Freshly prepared anhydrous zinc chloride (1.90 g, 13.9 mmol) was chilled in an ice-bath, then 4-methylbenzoyl chloride (10.75 g, 69.5 mmol) and anhydrous b, b, b-trichloro-*tert*-butanol (8.225 g, 46.3 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 chloride. 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 solidified upon standing (13.167 g, 96%, TLC: slightly contaminated) and it was recrystallized from ethanol (15 mL) to afford the product (9.088 g, 66%).

Mp. 84.6-86.3 °C (lit. [2] 85 °C).

TLC: light petroleum-ethyl acetate 95:5, Rf: 0.55.

Anal. calcd. for C12H13Cl3O2 (295.589): C, 48.76; H, 4.43; Cl, 35.98%; found C, 48.90; H, 4.37; Cl, 35.72%.

¹H NMR (CDCl₃, 500 MHz, ppm): 2.04 (s, 6H, (C<u>H</u>₃)₂C), 2.42 (s, 3H, arom. CH₃), 7.25 (d, 2H, *J*=8.3 Hz, arom. CH_s), 7.95 (d, 2H, *J*=8.3 Hz, arom. CH_s).

¹³C NMR (CDCl₃, 125 MHz, ppm, assignment based on HMBC and HMQC experiments, asterisks denote interchangeable assignments): 21.41 ((\underline{C} H₃)₂C^{*}), 21.66 (arom. \underline{C} H₃^{*}), 88.98 (\underline{C} Cl₃), 106.54 ((CH₃)₂C), 127.94 (C-4), 129.16 (arom. CHs), 129.85 (arom. CHs), 143.94 (C-1), 164.52 (\underline{C} OO).

CI-MS (isobutane, m/z): 297, 295 ($[M+H]^+$, isotopic peaks), 263, 261 ($[M-Cl]^+$, isotopic peaks). The calculated peak distributions correspond to the expected structure.

References:

1. L. Kovács, P. Forgó, Z. Kele: *Fourth International Electronic Conference on Synthetic Organic Chemistry*, abstr. no. a0076 (http://www.unibas.ch/mdpi/ecsoc-4/a0076/a0076.htm).

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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