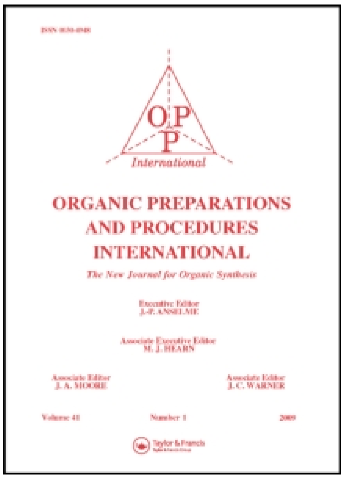

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BIS(2,2,2-TRICHLOROETHYL) SULFITE

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BIS(2,2,2-TRICHLOROETHYL) SULFITE

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Trichloroethyl groups are reported to be easily removable from esters under mild reductive conditions[3]. The introduction of the trichloroethyl group, however, is usually conducted[3] under conditions unsuitable for sensitive molecules (i.e. high temperature, acid-catalysed esterification). We furthermore observed that when basic functions are present in the acid to be esterified, they promote elimination of hydrogen chloride from the 2,2,2-trichloroethanol, thus further complicating the reaction. Hence we decided to use the title compound as a mild esterification reagent, but were unable to prepare it in good yields according to the reported procedure[4]. We therefore developed a new procedure for its preparation in analogy to the method of Iselin and his coworkers[5]. We then demonstrated the usefulness of this reagent by the preparation of 2,2,2-trichloroethyl N-benzyloxycarbonylglycinate.

EXPERIMENTAL

Bis(2,2,2-trichloroethyl) sulfite (I). -Trichloroethanol (Fluka purum, freshly distilled) 12 ml (18 g, 0.12 mole) was dissolved in dry THF (75 ml). Purified[6] thionyl chloride (6.3 ml 10.2 g, 0.06 mole) was added and the mixture cooled with stirring in an ice bath. With thionyl chloride purified less rigourously, yields were lower since the dark crude product necessitated several distillations to give the analytically pure compound. Triethylamine (18 ml, 14.5 g, 0.14 mole) dissolved in THF (45 ml) was then added dropwise over 1.5 hours, and stirring was continued for an additional hour. The precipitated triethylamine hydrochloride was filtered off and the filtrate was poured into ice water (2 lit.). The oil was separated from most of the water by decantation, taken up in dichloromethane (500 ml) and dried ($MgSO_4$). After removal of the solvent distillation in vacuo under argon gave an analytically pure product b.p. 113-118/0.5 mm (9 g, 43%) n_{25}^{D} = 1.5097. The n.m.r. measured on a Varian T-60 instrument showed an AB quartet centered at δ4.79, J_{AB} 12 cps. This compound was stable for several months, when it was kept in the refrigerator under argon, but darkened considerably after a few days at room temperature. Anal. Calcd. for $C_4H_4Cl_6O_3S$: C, 13.93; H, 1.16; Cl, 61.80. Found: C, 14.02; H, 1.01; Cl, 61.40.

2,2,2-Trichloroethyl N-benzyloxycarbonylglycinate. -N-benzyloxycarbonylglycine (418 mg 0.002 mole) was dissolved in dry pyridine (3 ml) and I (0.6 ml, 0.9 g, 0.0026 mole) was added. The mixture was left overnight at room temperature and then poured into 100 ml 1N-HCl. After decantation of the aqueous phase the oil was taken up into dichloromethane (25 ml), washed with sat. $NaHCO_3$ (25 ml) and water (25 ml) and dried ($MgSO_4$). Evaporation of the solvent in vacuo left a viscous syrup that crystallized on prolonged standing at 5°C, and did not melt at room temperature (400 mg, 50% crude). A few crystals were recrystallized from ethyl acetate/petroleum ether, m.p. 49°.

Anal. Calcd. for $C_{12}H_{12}Cl_3NO_4$: C, 42.30; H, 3.62; N, 4.07; Cl, 31.22. Found: C, 42.62; H, 3.34; N, 4.32; Cl, 31.04.

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1. To whom inquiries regarding this work should be sent.

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