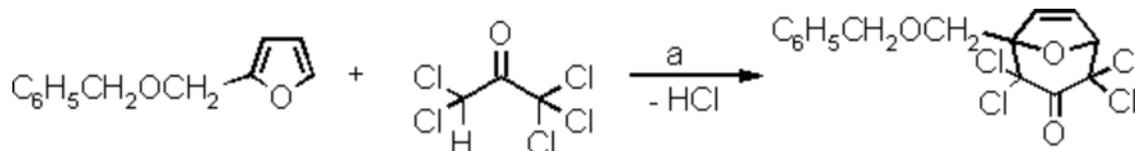


1-Benzyloxymethyl-2,2,4,4-tetrachloro-8-oxabicyclo[3.2.1]oct-6-en-3-one**Günter Kreiselmeier and Baldur Föhlisch***

Institut für Organische Chemie der Universität Stuttgart, Pfaffenwaldring 55, D-70569 Stuttgart, Germany

Fax: (+ 49) 711/6854269;

E-mail: baldur.foehlich@po.uni-stuttgart.de

Received: 8 March 2004 / Accepted: 17 March 2004 / Published: 29 March 2004a: $\text{CF}_3\text{CH}_2\text{ONa} / \text{CF}_3\text{CH}_2\text{OH}$; $0^\circ\text{C} - \text{r.t.}$

A mixture of 2-benzyloxymethylfuran[1] (1.88 g, 10 mmol) and pentachloroacetone[2] (2.30 g, 10 mmol) was cooled in an ice bath. With magnetic stirring, a 1-molar solution of sodium 2,2,2-trifluoroethoxide in 2,2,2-trifluoroethanol[3] (14 mL, 14 mmol) was added dropwise, within 2.5 hours. Sodium chloride precipitated. The ice bath was removed, and stirring was continued for 3 h at room temperature. Then, 25 mL of water was added dropwise; the sodium chloride dissolved, and crystals of the title compound were forming. To complete the crystallization, the mixture was stirred at 0°C for 1 hour. The solid was filtered and washed with water to the point of neutrality[4]. After a final wash with a few mL of ice-cold 50% aqueous ethanol the colourless crystals were dried over P_4O_{10} to yield 2.52 g (66%) with m.p. $99\text{--}99.5^\circ\text{C}$.

TLC (silica, petroleum ether/ethyl acetate, 10:1 v/v): A greenish-brown spot emerged after spraying the sheet with vanillin/sulfuric acid reagent followed by heating with a hot-air gun; $R_f = 0.42$.

$^1\text{H-NMR}$ (250 MHz, CDCl_3): δ 4.19 (center of an AB sub-spectrum with $d_A = 4.27$, $d_B = 4.11$, $J_{AB} = 11.5$ Hz, diastereotopic BnOCH_2), 4.65 (center of an AB sub-spectrum with $d_A = 4.70$, $d_B = 4.59$, $J_{AB} = 12.1$ Hz, diastereotopic PhCH_2), 5.26 (appearing as a 'd', line distance 1.6 Hz, 1H, X part of an ABX sub-spectrum that could not be fully analysed, H-5), 6.48–6.54 (6 lines of the AB part of the ABX sub-spectrum, $J_{AB} = 6.0$ Hz, 2 H, H-6 and H-7), 7.24–7.40 (m, 5 H, C_6H_5).

$^{13}\text{C-NMR/DEPT}$ (62.9 MHz, CDCl_3): δ 67.6 (+, BnOCH_2), 74.05 (+, PhCH_2), 82.2 (C_q , C-4 or C-2), 85.1 (C_q , C-2 or C-4), 87.6 (-, C-5), 94.3 (C_q , C-1), 127.7 (-), 128.0 (-), 128.5 (-), [C-2–C-6 of the phenyl group], 133.2 (-, C-6 or C-7), 136.0 (-, C-7 or C-6), 137.25 (C_q , C-1 of the phenyl group), 184.6 (C_q , C-3).

IR (KBr): 3090, 3075, 3040, 3010 (=C-H), 2960, 2935, 2910 (sh), 2900, 2855 (C-H), 1760, 1740 (C=O), 1595 cm^{-1} (C=C).

Anal. Calcd. for $\text{C}_{15}\text{H}_{12}\text{Cl}_4\text{O}_3$ (382.1): C, 47.16; H, 3.17; Cl, 37.12. Found: C, 47.35; H, 3.30; Cl, 36.98.

References and Notes

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4. This work-up, *i.e.* precipitation by careful addition of water, was also used for the preparation of oxabicyclic compounds from pentachloroacetone and furan (71% yield, m.p. 90–91 °C), 2-methylfuran (63%, m.p. 56–57 °C), 3-methylfuran (88%, m.p. 89–90 °C), 2,5-dimethylfuran (89%, 112–113 °C), and 2-(3-butenyl)-3-methylfuran (86%, m.p. 59–60 °C)[3]. If the products do not crystallize immediately, the oily precipitate becomes solid on scratching with a glass rod. The compounds are pure enough for dechlorination, but may be purified by sublimation *in vacuo*.

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