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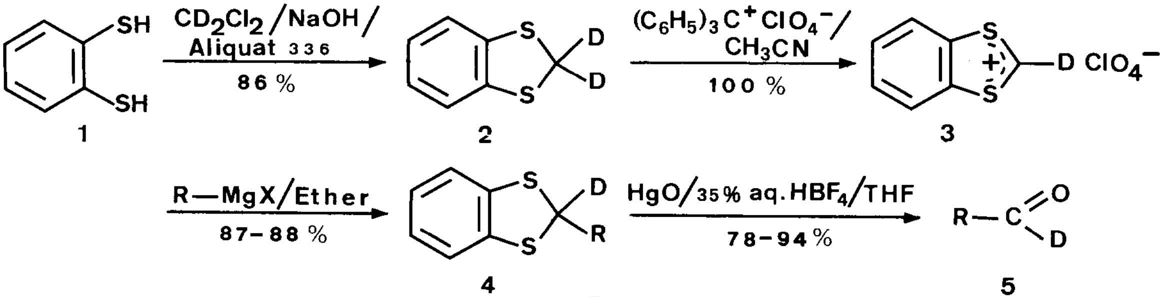
2-DEUTERIO-1,3-BENZODITHIOLIUM PERCHLORATE: A USEFUL SYNTHON FOR THE PREPARATION OF ALDEHYDES-1-d[1]

Iacopo Degani, Rita Fochi and Valeria Regondi
Istituto di Chimica Organica dell' Università, I-10125 Torino, Italy

Summary: 2-Deuterio-1,3-benzodithiolium perchlorate reacted with Grignard reagents to give 2-alkyl or 2-aryl-2-deuterio-1,3-benzodithioles, which in turn could be hydrolysed to corresponding aldehydes-1-d.

Among the several methods for the preparation of aldehydes-1-d[2,3], to our knowledge no procedure involving the direct introduction of a real or potential deuterated formyl group has been reported.

As part of a program aimed at evaluating the synthetic potential of 1,3-benzodithiolium salts[2,4-6], we have solved the above problem according to the following scheme:



The conversion of 1,2-benzenedithiol[7] (1) to 2,2-dideuterio-1,3-benzodithiole (2) was achieved under phase transfer conditions by adding dropwise over a period of 4 hours, a solution of 1 (50 mmol) in sodium hydroxide (125 mmol) and water (25 ml) to a stirred slightly refluxing mixture of water (10 ml), CD_2Cl_2 (8.5 ml, 11.56 g;>99.5 Atom % D, from Fluka) and Aliquat 336 (0.5 g). Stirring and refluxing were continued for an additional 4 hours; the excess of CD_2Cl_2 was recovered by distillation (5.34 g; it had the same isotopic purity as the starting reagent) and the residue was extracted with petroleum ether and filtered through silica gel to eliminate the catalyst. The yield of product 2 was 86 %, based on 1 (61 % based on the consumed CD_2Cl_2); m.p. 23-24°C, identical to that of the unlabelled compound[4]; ^{1}H-N.M.R.(CCl_4): δ = 6.80-7.20 p.p.m. (m, H arom.); the band at δ = 4.42[8] due to protons at C-2 was absent.

2-Deuterio-1,3-benzodithiolium perchlorate (3) was then obtained in quantitative yield from 2 (10 mmol), by deuteride ion exchange with trityl perchlorate (10 mmol) in acetonitrile (5 ml), according to the literature[2]; m.p. 182°C (exp.), identical to that of the unlabelled compound[5,8]; ^{1}H-N.M.R. (CF_3COOD): δ = 8.00-8.32 and 8.70-9.00 p.p.m. (2m, 1:1, H arom.); the band at δ = 11.67[9] due to the proton at C-2 was absent.

Salt 3 proved to be an efficient synthon for the preparation of aldehydes-1-d, which were obtained by reaction of 3 with Grignard reagents under the same conditions reported in the case of the unlabelled salt 3[4], and subsequent hydrolysis of 2-substituted 2-deuterio-1,3-benzodithioles (4) by a mixture of HgO, 35 % aqueous HBF_4 and tetrahydrofuran, according to a general procedure recently developed by us for the hydrolysis of sulfurized precursors of carbonyl compounds[10].

In all the steps the yields were high (see scheme and table) and the isotopic purity was maintained unaltered as compared with the starting CD_2Cl_2.

Table - 2-Substituted 2-Deuterio-1,3-benzodithioles (4) and Aldehydes-1-d (5)

R	Yield (%)[a] of 4	m.p.°C or b.p.°C/torr[2]	Yield (%)[b] of 5	b.p.°C/760[2]
C_6H_5	87	72-73	94	178-179
$4\text{-}H_3CO\text{-}C_6H_4$	87	71-72	94	247-248
$n\text{-}C_9H_{19}$	88	164-165/0.2	78	207-209

[a] Yield after isolation by column chromatography. [b] Yield of isolated pure aldehyde-1-d (purity control by ^{1}H-N.M.R., I.R., T.L.C., G.L.C.).

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