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2-PHENYL-1,3-BENZODITHIOLYLIUM TRIFLUOROMETHANESULFONATE: A REAGENT FOR THE CONVERSION OF ALCOHOLS INTO BENZYL ETHERS AND BENZOATES UNDER MILD CONDITIONS.

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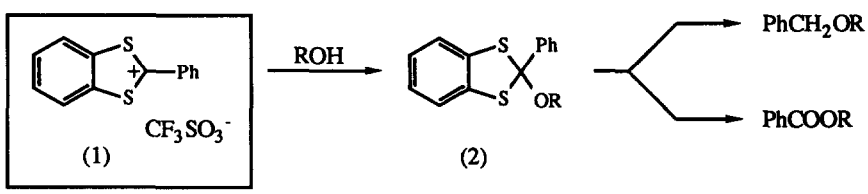
Abstract: 2-Phenyl-1,3-benzodithiolylium trifluoromethanesulfonate, easily prepared from 1,2-benzenedithiol, converts alcohols into dithioorthoesters and, ultimately, benzyl ethers (Bu_3SnH) and benzoates (HgO/HBF_4).

Recently, Ganem reported the conversion of alcohols into benzyl ethers utilizing phenyldiazomethane under mild acidic conditions.[1] As well, Sekine introduced the 2-(methylthio)phenylthiomethyl group for the protection of alcohols, easily removable ($HgCl_2$) or, more interestingly, transformable (Bu_3SnH) into the methyl ether.[2] These two reports have prompted us to communicate our results on the treatment of various alcohols and diols with 2-phenyl-1,3-benzodithiolylium trifluoromethanesulfonate (1), to yield initially dithioorthoesters (2), and ultimately the very useful benzyl ethers and benzoates under mild conditions.



(1) (2)

1,2-Benzenedithiol is available in large amount in two steps from anthranilic acid.[3,4] Treatment of this dithiol with phenyl benzoate in the presence of trifluoromethanesulfonic acid gave the salt (1) as bright yellow plates, indefinitely stable in the absence of moisture. We have found that this salt converts simple alcohols (Table, entries 1-3), and some carbohydrate alcohols (entries 4-6), into the corresponding dithioorthoesters (2). As well, several carbohydrate diols showed good regioselectivity towards the salt (1) with functionalisation occurring preferentially at a primary hydroxyl group (entries 7,9,10).

Reduction of the dithioorthoesters (2) [Bu_3SnH/ AIBN/PhH (↑↓)] generally gave good yields of the corresponding benzyl ethers (entries 4,5,7,8). In some cases where an adjacent hydroxyl group was able to trap the presumed benzylic radical intermediate, unwanted amounts of *O*-benzylidene compounds were formed (entries 7,10). This side reaction could be completely suppressed by functionalisation of the free hydroxyl group before reduction (entry 8), or the use of Raney nickel as reductant (entry 10).

Controlled hydrolysis (HgO/HBF_4) of the dithioorthoesters (2) gave good yields of the corresponding benzoates (entries 4,7,9), but mixtures of regioisomers were obtained when an adjacent hydroxyl group was able to trap the presumed intermediate benzylic carbocation (entry 10).

2-Phenyl-1,3-benzodithiolylium trifluoromethanesulfonate (1)

A mixture of 1,2-benzenedithiol (1.4 g, 10 mmol) and phenyl benzoate (2.0 g, 10 mmol) in trifluoromethanesulfonic acid (2.25 g, 1.5 mL, 15 mmol) was heated (110°, 10 min). The reaction mixture was allowed to cool to room temperature, diluted with acetonitrile (5 mL) and poured into dry ether (100 mL). The precipitate was removed by filtration, washed with dry ether (2 x 25 mL) under nitrogen and dried to give the *salt (1)* (3.63 g, 96%), m.p. 149-151° (MeCN/Et_2O) (Found C, 44.3; H, 2.1. $C_{14}H_9F_3O_3S_3$ requires C, 44.4; H, 2.4%).

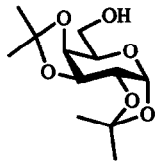
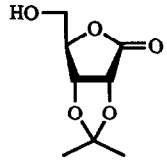
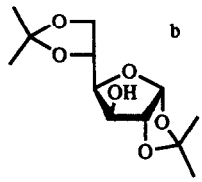
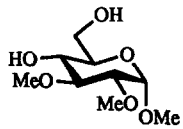
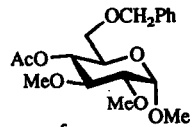
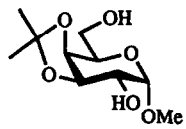
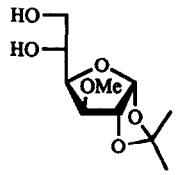
1,2:3,4-Di-O-isopropylidene-6-0-(2-phenyl-1,3-benzodithiol-2-yl)-α-D-galactose

To a solution of 2-phenyl-1,3-benzodithiolylium trifluoromethanesulfonate (380 mg, 1.0 mmol) in acetonitrile (1 mL) was added 1,2:3,4-di-*O*-isopropylidene-α-D-galactose (1.0 mL of 1.0 M in MeCN, 1.0 mmol) and triethylamine (1.0 mL of 1.0 M in MeCN, 1.0 mmol) with stirring (10 min, 25°). The acetonitrile was removed by distillation under reduced pressure. Normal workup of the residue with ether, followed by chromatography (EtOAc/hexanes 2:8), gave *1,2:3,4-di-O-isopropylidene-6-0-(2-phenyl-1,3-benzodithiol-2-yl)-α-D-galactose* (440 mg, 90%) as colourless needles, m.p. 135-136° (hexane), $[\alpha]_D$ -62° (c, 1.3 in $CHCl_3$) (Found: C, 61.6; H, 5.8. $C_{25}H_{28}O_6S_2$ requires C, 61.5; H, 5.7%).

Reduction of 1,2:3,4-di-O-isopropylidene-6-0-(2-phenyl-1,3-benzodithiol-2-yl)-α-D-galactose

To a solution of the above dithioorthoester (310 mg, 0.64 mmol) in benzene was added tributyltin hydride (0.51 mL, 560 mg, 1.9 mmol) and AIBN (20 mg) and the solution heated at reflux under argon (20 h). Evaporation of the solvent, followed by acetonitrile/hexanes partitioning and chromatography (toluene/hexane/EtOAc, 5:4:1), gave 6-*O*-benzyl-1,2:3,4-di-*O*-isopropylidene-α-D-galactose (215 mg, 96%), $[\alpha]_D$ -67° (lit.[5] -65°).

TABLE

Entry	Reactant	Dithioorthoester (2) % (m.p.) {[α]$_D$}	Benzyl ether % {[α]$_D$}	Benzoate %
1	MeOH	84 (53.5-54°)	-	-
2	Pr^{i}OH [a]	66 (110-111°)	-	-
3	Bu^{t}OH [b]	73 (74-75°)	-	-
4		96 (135-136°) {-62°}	96	100
5		-	74 [c]	-
6		74	-	96 [c]
7		90 [d] {+88°}	78 [e] {+102°}	84
8			81 [f] {+112°}	
9		61 [d] (140-142°) {+50°}	-	92
10		90 [d] {-33°}	37 [g] [66 [h]]	100 [i]

(a) Two mole equivalents of the alcohol were used. (b) The alcohol was first converted to the alkoxide. (c) The intermediate dithioorthoester (2) was not purified. (d) Substitution occurred at the primary alcohol. (e) The epimeric 4,6-*O*-benzylidene compounds were also isolated (10%). (f) The dithioorthoester (2) (entry 7) was acetylated before treatment with Bu_3SnH. (g) The epimeric 5,6-*O*-benzylidene compounds were also isolated (43%). (h) The yield obtained using Raney nickel. (i) Obtained as a 1:1 mixture of 5-*O*- and 6-*O*-benzoyl-1,2-*O*-isopropylidene-3-*O*-methyl-α-D-glucofuranose.

Hydrolysis of 1,2:3,4-di-O-isopropylidene-6-0-(2-phenyl-1,3-benzodithiol-2-yl)-α-D-galactose

Aqueous 35% HBF_4 (0.25 mL) was added at room temperature to a suspension of HgO (110 mg, 0.5 mmol) in THF (2 mL). The above dithioorthoester (120 mg, 0.2 mmol) was dissolved in a minimum amount of THF and added in one portion with vigorous stirring (5 min) to the HgO/HBF_4 mixture. The reaction mixture changed colour from orange to yellow, and was then poured into saturated sodium bicarbonate solution (10 mL) and extracted with ether (3 x 15 mL). Evaporation of the ether, followed by chromatography (toluene/hexanes/EtOAc, 5:4:1), gave 6-*O*-benzoyl-1,2:3,4-di-*O*-isopropylidene-α-D-galactose as a clear oil (90 mg, 100%), $[\alpha]_D$ - 58° (c 0.8, $CHCl_3$), identical with a sample prepared by the conventional benzoylation of the starting alcohol.

References and notes

1. Liotta, L.J. and Ganem, B., *Tetrahedron Lett.*, 1989, **30**, 4759.
2. Sekine, M. and Nakanishi, T., *J.Org. Chem.*, 1989, **54**, 5998.
3. Nakayama, J., *Synthesis*, 1975, 38.
4. 2-(3-Methylbutoxy)-1,3-benzodithiole (ref. 3) was treated directly with sodium in liquid ammonia (Degani, I. and Fochi, R., *Synthesis*, 1976, 471).
5. Stanek, J., Sele, A., Jaques, R. and Rossi, A., *Helv. Chim. Acta*, 1972, **55**, 434.

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