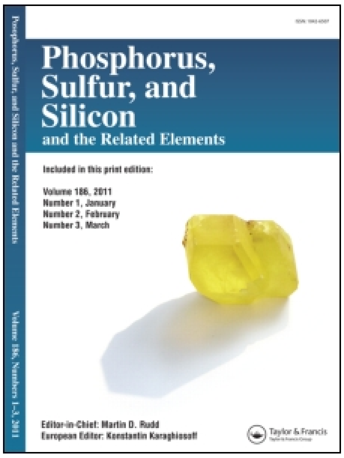

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SYNTHESIS OF 2,2-DISUBSTITUTED-1,3-PROPANE-DITHIOLS

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Notes and Communications

SYNTHESIS OF 2,2-DISUBSTITUTED-1,3-PROPANE-DITHIOLS

by

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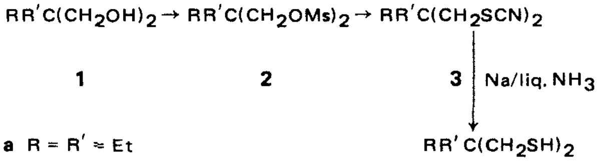
ABSTRACT

A method for the preparation of 2,2-disubstituted-1,3-propanedithiols from the corresponding diols is described. The success of the synthesis is governed by the solvent in which the nucleofilic substitution, dimesylate to dirhodanide, is performed. The proposed reaction sequence is tested out for several diols and the overall yields are very good with respect to the strongly hindered–sterically–neopentyl-structure. All compounds are identified by ^{1}H-nmr.

We wish to report on a convenient method for the preparation of 2,2-disubstituted-1,3-propanedithiols, **4**. Although several methods are described for the formation of thiols from alcohols,[2] little information is available if the compounds to be synthesized are of the neopentyl (RR′R″C CH$_2$X) as is presently the case.

Results and Discussion

The reaction sequence is as follows.



$$\underset{\mathbf{1}}{RR'C(CH_2OH)_2} \rightarrow \underset{\mathbf{2}}{RR'C(CH_2OMs)_2} \rightarrow \underset{\mathbf{3}}{RR'C(CH_2SCN)_2} \xrightarrow{Na/liq.\,NH_3} \underset{\mathbf{4}}{RR'C(CH_2SH)_2}$$

a R = R′ = Et
b R = R′ = $-(CH_2)_4-$
c R = R′ = $-(CH_2)_5-$
d R = Me, R′ = Et
e R = Me, R′ = *n* Pr
f R = Me, R′ = *i* Pr
g R = Me, R′ = *s* Bu

Ms = $-SO_2CH_3$

The first step is without problems, the yields being excellent (90% or better). It is not necessary to purify the dimesylate **2** by recrystallization from methanol, as the yield and reaction time for the subsequent dirhodanide, **3**, formation are mainly determined by the nature of the solvent used during that step. With the several solvents tried, substitution only occurred in HMPT and, faster yet, in DMF at an elevated temperature. The reaction can easily be followed by ^{1}H-nmr ($\delta_{\mathit{CH}_2\mathrm{OMs}} \sim 3$ ppm; $\delta_{\mathrm{CH_2O}\mathit{Ms}} \sim 3.8$ ppm; $\delta_{\mathrm{CH_2S\,CN}} \sim 3.1$ ppm). Reaction times are relatively short and are summarized in Table I, together with the yields (based on diol) of the resulting dithiol. These dithiols are obtained from the dirhodanides through metallic ammonia reduction.

TABLE I

Specific Reaction Time for the Preparation of 3

Compound	Reaction time (hrs)	Yield[a] (%)	BP[a] (°C)
2a	5	58	53/0.1
2b	10	53	123/14
2c	6	55	140/13
2d	7	55	52/0.1
2e	6	57	45/0.05
2f	7	49	107/13
2g	7	51	119/14

[a] Yield and bp of the resulting dithiol (structure checked by ^{1}H-nmr spectroscopy).

Because the experimental procedure is a simple one, the yields are good with respect to the unreactive neopentyl-type structure, and furthermore the purity of the products is excellent, this method appears to be the method of choice for the synthesis of these compounds.

Experimental Section

As a general procedure 0.1 mol of the diol is dissolved in 200 ml of dry pyridine and cooled to −5 to −10°C. Mesyl chloride (0.22 mol) is added while the temperature is kept below −5°. After the complete addition, the resulting mixture is allowed to stand for 12 hr at 0°. The mixture is poured onto 500 ml of ice cold water and extracted with chloroform. The extract is neutralized by washing with 10% HCl and dried over magnesium sulfate. Evaporation of the chloroform affords the dimesylate as the residue which is dissolved in 100 ml of dry dimethylformamide together with 0.22 mol of KSCN. The mixture is heated at 140-150°, while stirring, for several hrs (see Table I). Upon completion of the reaction (^{1}H-nmr) the resulting mixture is allowed to cool, poured onto 500 ml of water, extracted several times with peroxide-free ether and dried over magnesium sulfate. The crude dirhodanide, dissolved in an equal amount of absolute ether, is added dropwise to a solution of 0.2 mol of sodium in liquid ammonia. After evaporation of the ammonia the remaining sodium is destroyed by addition of ethanol and the sodium salt dissolved in water. Recovery of the dithiol can be accomplished by acidifying with 10% HCl, extracting with peroxide-free ether and vacuum distillation under nitrogen atmosphere.

Acknowledgment

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