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BIS(DIISOBUTYLALUMINUM) 1,2-ETHANEDITHIOLATE: A REAGENT IN THE CONVERSION OF OXYACETALS TO THIOACETALS[1)]

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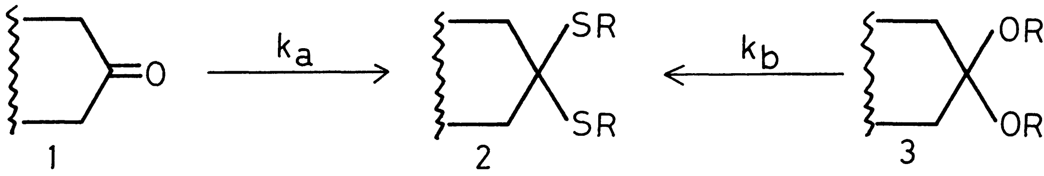
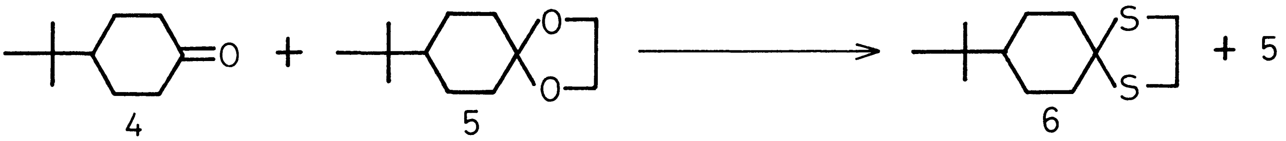
Bis(diisobutylaluminum) 1,2-ethanedithiolate (9) made from diisobutylaluminum hydride and ethanedithiol in benzene is useful to convert oxyacetals into thioacetals, however not effective to ketones.

In organic synthesis, functional group differentiation is one of the most important problem. Thioacetalization of a ketone (1)[2)] or an oxyacetal (3)[3)] is usually carried out by treatment of these compounds with alkylthiol and BF_3-OEt_2 in an appropriate solvent at room temperature. Under these conditions, the thioacetalization of ketones are usually faster than that of oxyacetals ($k_a \geqq k_b$).



For example, the equal mixture of 4-tert-butylcyclohexanone (4) and its ethyleneoxyacetal (5) in CH_2Cl_2 was treated with ethanedithiol and catalytic amount of BF_3-OEt_2 at room temperature to give thioacetal (6) and small amount of starting oxyacetal (5). In this case k_a and k_b are almost equal.



In this communication we wish to report a reagent for the transformation of only oxyacetal to thioacetal from a mixture of ketones and oxyacetal. This reaction complements the usual condition using BF_3-OEt_2 and thiols.

Bis(dimethylaluminum) 1,2-ethanedithiolate (7)[4] and bis(dimethylaluminum) 1,3-propanedithiolate (8)[5] were known to be used for protection of carbonyl groups of

$$(CH_3)_2AlS(CH_2)_2SAl(CH_3)_2$$

7

$$(CH_3)_2AlS(CH_2)_3SAl\ (CH_3)_2$$

8

$$(iso\text{-}C_4H_9)_2AlS(CH_2)_2SAl(iso\text{-}C_4H_9)_2$$

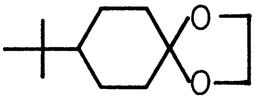
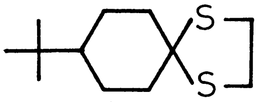
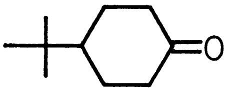
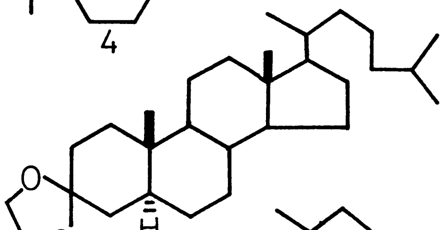
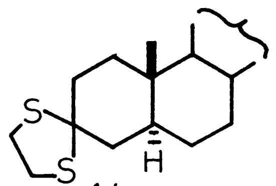
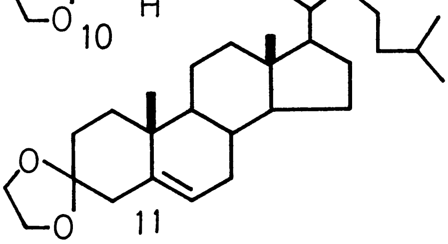
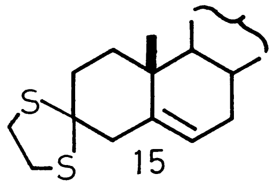
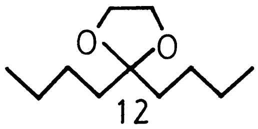
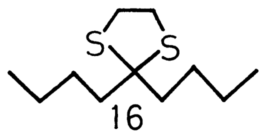
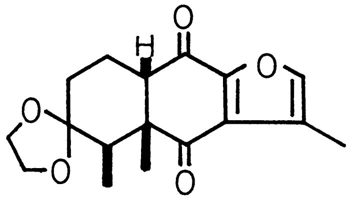
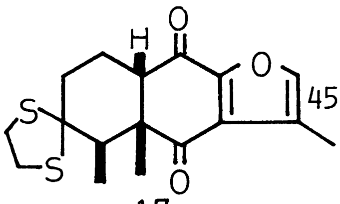
9

lactones and esters or conversion of esters to unsaturated aldehyde and ketones, respectively, by Corey *et al.* Various kinds of other alkylaluminium thiolates for functional group transformation are also reported.[6] In our studies bis(diisobutylaluminum) 1,2-ethanedithiolate (9) was used for our purpose because diisobutylaluminum hydride (DIBAL-H)[7] is most easily available alkylaluminium reagent.

Bis(diisobutylaluminum) 1,2-ethanedithiolate (9) is made simply by adding ethanedithiol (1 eq) to DIBAL-H (2 eq) in benzene at 0°C. After vigorous hydrogen gas evolution, the colorless solution is used immediately. As shown in Table 1, various kinds of oxyacetals were converted to thioacetals in modest to good yield. It is worth noting that ketone (4) does not undergo this transformation at all (see entry 1 and 2). In ethanedithiol-BF_3-OEt_2 system, it is almost impossible to get thioacetal (2) from oxyacetal (3) in the presence of ketone (1). As usually $k_a \geqq k_b$ mixture of 1 and 3 give 2 and 3 or only 2. In contrast to the ethanedithiol-BF_3-OEt_2 system, treatment of the mixture of equal amount of 4 and 5 with the reagent (9) gave thioacetal (6) and unreacted 4 in good yield.

General procedure: All reaction were conducted in dry apparatus with good stirring. To a solution of diisobutylaluminum hydride (1.0 mmol) in 1 ml of dry benzene in a 20 ml flame dry flask was added ethanedithiol (0.5 mmol; in some cases excess amount (2 mmol) of ethanedithiol gave slightly better yield) dropwise at 0°C. After the evolution of hydrogen gas ceased in about 10 min, a solution of oxyacetal (0.5 mmol) in small amount of benzene was added to the aluminumdithiolate solution. The reaction mixture was stirred at room temperature for 15 min to 2.5 h. The reaction mixture was diluted with ether and the solution was washed with aq. NH_4Cl or 3M-HCl and the excess of thanedithiol was removed by washing with 10% NaOH follow-

Table 1

Entry	Oxyacetal	Time	Thioacetal	Yield[a]
1	 5	30 min	 6	80 %
2	 4	30 min		0 %[b]
3	 10	45 min	 14	75 %
4	 11	2.5 h	 15	18 %[c]
5	 12	15 min	 16	89 %
6	 13	2 h	 17	45 %

a. Isolated yields of pure material. All the thioacetals were confirmed by comparison with the authentic samples.

b. Starting ketone (4) (85% yield) was recovered after work-up.

c. Reaction was sluggish and after 2.5 h some amount of 11 was still present.

ed by brine. The organic layer was dried over Na_2SO_4 and then the solvent was evaporated. The crude thioacetal was purified by silica gel column chromatography.

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References

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7) DIBAL-H is supplied from Mitsuwa Pure Chemicals and is 1.75 M in hexane.

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