Tetrahedron Letters No. 26, pp 2349 - 2352, 1978.
0040-4039/78/0622-2349$02.00/0

# RING EXPANSION BY SULPHUR MIGRATION:
# SYNTHESIS OF 2-ALKYLIDENE-1,4-BENZODITHIANS AND 1,4-BENZODITHIINS

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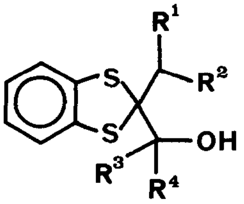
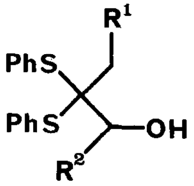
(Received in UK 20 April 1978; accepted for publication 4 May 1978)

Summary. Reaction of 2-(1-hydroxyalkyl)-1,3-benzodithioles (1) with thionyl chloride - triethylamine gives high yields of 2-alkylidene-3-substituted benzodithians, and 2,3-substituted benzodithiins on treatment with acid.

We have described the synthesis of 2-(1-hydroxyalkyl)-1,3-benzodithioles (1).[1] We thought that these novel compounds would be useful synthetic intermediates following the versatile reactions of the analogous α-hydroxydiphenylthioacetals (2) which give α-phenylthioketones (3) with toluene-p-sulphonic acid,[2] dialkylketones (4) with trifluoroacetic acid[3] and the rearranged bissulphides (5) with thionyl chloride in triethylamine.[4]



(1)



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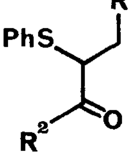

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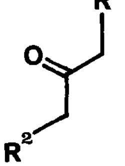

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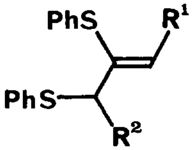
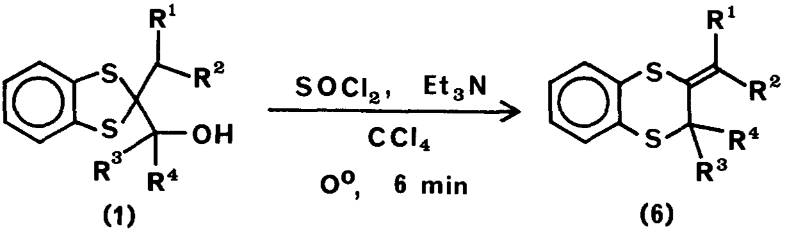
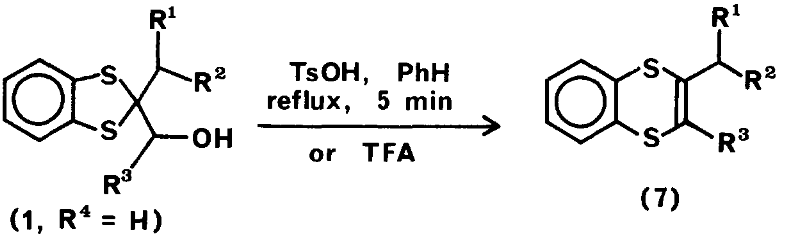


(5)

Reaction of 1,3-benzodithioles (1) with thionyl chloride - triethylamine gives the ring expanded 2-alkylidene-1,4-benzodithians[5] (6) by a [1,2] sulphur migration (Table 1); this reaction is analogous to that of the diphenylthioacetals (2) but does show some differences. The diphenylthioacetals (2) give a mixture of geometrical isomers (5) but the benzodithioles (1) give only single isomers of (6), which on steric grounds might be expected to be the Z-isomers (when $R^2$=H) although the definite geometry has yet to be determined. Also the alkylidene benzodithians (6) are stable in light whilst the analogues (5) rearrange via a [1,3] sulphur shift.



Treatment of the 1,3-benzodithioles (1) with toluene-p-sulphonic acid or trifluoroacetic acid does not give products analogous to those obtained from the diphenylthioacetals (2); instead 1,4-benzodithiins[5] (7) are generally obtained (Table 2). These products are isomeric with the benzodithians (6). Better yields are often obtained using toluene-p-sulphonic rather than trifluoroacetic acid. Obviously with $R^3$ and $R^4$ $\neq$ H this product is not possible and the alkylidene benzodithians (6) or a simple dehydration product is obtained.



In the past,[5] 1,4-benzodithians have been prepared by cyclisation of 1,2-benzenedithiol but this method has not led to any 2-alkylidene-3-substituted derivatives as obtained in the thionyl chloride-triethylamine reaction. The parent 1,4-benodithiin has been prepared by elimination of ethanol from 2-ethoxy-1,4-benzodithian and the 2-substituted derivatives have been obtained by aromatic electrophilic substitutions in the heterocyclic ring but this approach has not led to the 2 or 3 alkyl derivatives we obtained in the toluene-p-sulphonic acid reaction. Thus these ring expansion reactions provide very convenient syntheses of these heterocyclic systems.

## Table 1

### Preparation of benzodithians (6)[a] using $SOCl_2$ - $NEt_3$

| Entry | Benzodithioles (1) | | | | Yield of (6) % |
|---|---|---|---|---|---|
| | $R^1$ | $R^2$ | $R^3$ | $R^4$ | |
| A | H | H | Et | H | 14 |
| B | Me | Me | Ph | H | 85 |
| C | Et | H | Me | H | 91 |
| D | Et | H | 2-Me-$Pr^n$ | H | 78 |
| E | Et | H | Ph | H | 78 |
| F | Et | H | Me | Ph | 73 |
| G | Et | H | -$(CH_2)_5$- | | 92 |

## Table 2

### Preparation of benzodithiins (7)[a] using TsOH or TFA

| Benzodithioles (1) (see Table 1) | Yield of (7) % | | Other product (Yield) |
|---|---|---|---|
| | TsOH | TFA | |
| A | 100 | - | - |
| B | 20 | 69 | (6, 78%) with TsOH |
| C | 99 | - | - |
| D | 95 | 68 | - |
| E | 91 | 80 | - |

[a] Satisfactory spectroscopic and elemental analysis was obtained for all these new compounds.

The following procedures for the rearrangement of the benzodithiole (1, $R^1$= Et, $R^2$ = $R^4$ = H, $R^3$ = Ph, entry E) are typical.

(i) Thionyl chloride (0.04 ml, 0.55 mmol) was added to an ice-cooled solution of the alcohol (65 mg, 0.22 mmol) in carbon tetrachloride (5 ml) and triethylamine (0.25 ml, 1.8 mmol). After stirring for 6 m the mixture was poured into dilute hydrochloric acid and extracted with carbon tetrachloride. The extract was washed with water, dried ($MgSO_4$), and evaporated to give an oil which was purified by preparative t.l.c. (silica, $CCl_4$) to give 3-*phenyl*-2-*n*-*propylidene*-*benzodithian* (48 mg, 78%) $R_F$ 0.45 as a colourless oil.

(ii) Toluene-*p*-sulphonic acid (92 mg, 0.48 mmol) was added to a stirred solution of the alcohol (65 mg, 0.22 mol) heated under reflux in benzene (4 ml). After 5 m, the mixture was cooled, saturated sodium carbonate solution added, and the product extracted with ether. The extract was washed with water, dried and evaporated to give an oil which was purified by preparative t.l.c. (silica, $CCl_4$) to give 3-*phenyl*-2-*n*-*propyl*-*benzodithiin* (56 mg, 91%) $R_F$ 0.46 as a colourless oil.

(iii) Trifluoroacetic acid (3 ml) was added to the alcohol (64 mg, 0.21 mmol) and the mixture stirred with ice-cooling for 5 min. Evaporation in vacuo gave an oil which was purified by preparative t.l.c. (silica, $CCl_4$) to give 3-phenyl-2-n-propyl-benzodithiin (48 mg, 80%), $R_F$ 0.46, as a colourless oil.

We thank the S.R.C. (studentship to P.B.) and the Ministry of Overseas Development (studentship to S.N.) for financial support.

## References

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