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# 1,3-BENZODITHIOLIUM ION MEDIATED ANNULATIONS

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Summary: A mild and selective method for cyclizations onto aromatic systems using 1,3-benzodithiolium ions is described.

The Friedel-Crafts reaction continues to play an important role in annulation chemistry.[1] The utility of this reaction, however, is sometimes limited by the strongly acidic reaction conditions which are often employed.[1a] Recently, a number of novel methods have been published which address this problem.[1c,d]

We wish to report the results of a study in connection with another project which features a particularly mild cyclization protocol mediated by the 1,3-benzodithiolium carbocation.[2,3] Typically, several crystals (10 mg) of p-toluenesulfonic acid are added to a solution of ketene dithioacetal 1a-f[4] (2.0 mmol) in dry acetonitrile (10 ml). The resulting solution is stored at 0°C for approximately 24 hr at which time the crystals of benzodithiole 2a-f are filtered off. (see Table I)

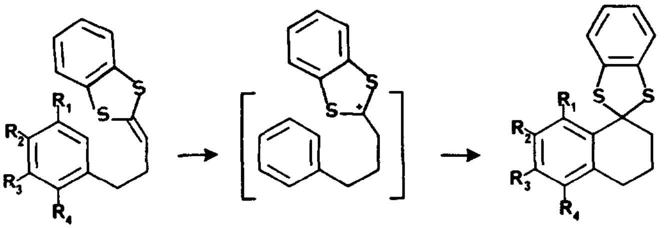

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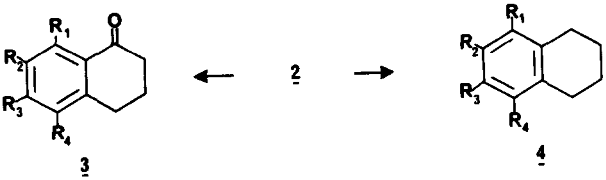
TABLE I

| Ketenedithioacetal[a] | Benzodithiole,[a] yield(mp) | Tetralone,[a] yield(mp) | Tetralin,[a] yield |
|---|---|---|---|
| 1a) $R_2,R_3$=OMe | 76%(141-142°C)[c] | 60%(98-100°C)lit[6a] 99-100°C | 69%(55-57°C) |
| 1b) $R_3,R_4$=OMe | 56%(132°-133°C) | 55%(104°C)lit[6b]104-105°C | 75% |
| 1c) $R_2,R_3$=-OCH$_2$- | 75%(135°-136°C)[c] | 55%(77°C) | 91%(41-45°C) |
| 1d) $R_3$=OMe | 77%(130°-131°C)[c] | 62%(76-78°C)lit[6c]77-79°C | 95% |
| 1e) $R_1$-$R_4$=H | 70%[d] | 62%[b] | - |
| 1f) $R_2$=OMe | 74%(95°-97°C)[d] | 56%(61°C)lit[6c]61-63°C | - |
| 1g) $R_1,R_4$=OMe | - | - | - |

a) The $^1$H NMR, CMR, IR, and MS of these compounds were completely consistent with the assigned structure. b) $^1$H NMR and IR were identical to those of the authentic material c) None of the other possible regioisomer was observed. d) Approximately twice the normal quantity of p-TsOH was required for efficient cyclization.

The benzodithioles obtained from this exceptionally mild process are versatile intermediates which can be hydrolyzed to the corresponding tetralones 3a-f ($HgO/BF_3 \cdot Et_2O$/aqTHF)[5] or desulfurized with Raney-Nickel (W-2) to the related tetralins 4a-d.



The regioselectivity exhibited by this reaction is particularly noteworthy since only one of two possible isomers was obtained with ketenedithioacetals 1a,c,d. In addition, entry 1g did not yield any cyclized product even under forcing conditions. This selectivity for bond formation remote to ortho substituents is probably steric in nature. It is also interesting that the relatively electron poor system 1e cyclizes surprisingly well. We are currently applying this annulation process to more complex systems encountered in several classes of natural products.

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References and Notes

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4. These ketenedithioacetals are prepared in excellent yields (95%-98%) from the corresponding aldehyde[7] and 2-lithio-2-diethoxy phosphinyl-1,3-benzodithiole: K. Akiba, K. Ishikawa, N. Inamoto, *Bull. Chem. Soc., Japan*, 51, 2674 (1978).
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7. The aldehyde precursors are prepared from the corresponding benzaldehyde and the anion of triethyl phosphonoacetate followed by reduction with lithium aluminum hydride and pyridinium chlorochromate oxidation.

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