

Formation of Dithianes and Dithiolanes catalysed by Clay. An Unexpected Functional Selectivity

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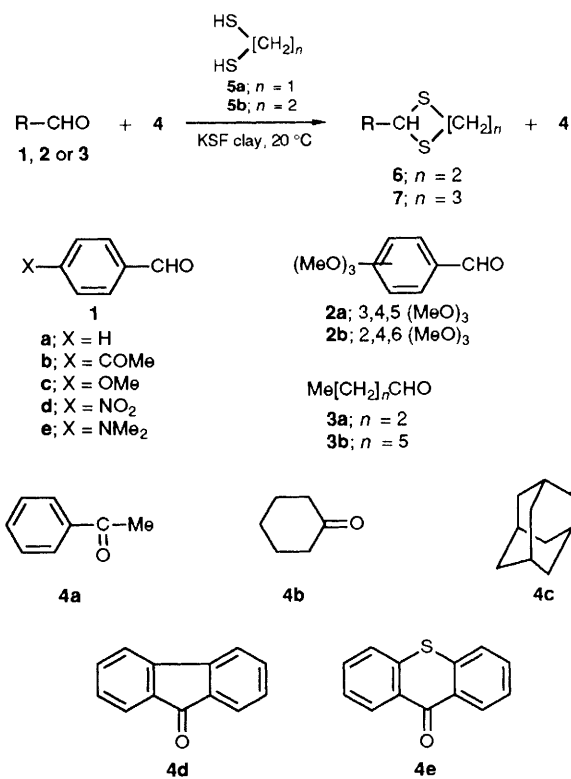
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Montmorillonite KSF at room temperature without solvent catalyses the synthesis of dithiolanes and dithianes from carbonyl compounds; chemoselectivity in dithiane and dithiolane formation is observed between aromatic aldehydes and ketones and between aromatic and aliphatic aldehydes.

We have reported the formation of a wide variety of useful organosulfur compounds^{1,2} (dithiolanes, dithianes, thioketals, thiochromanes, enol thioethers) by the reaction of carbonyl compounds with thiols catalysed by the clay KSF in refluxing toluene. KSF clay is inexpensive and offers several advantages over the classical acids: strong acidity ($H_0 = -8$ to -9), no corrosive action, selectivity and easy work-up. In these reactions, the clay acts as a solid Brønsted acid catalyst. We report herein that aldehydes react with one equivalent of dithiols (HSCH₂CH₂SH or HSCH₂CH₂CH₂SH) simply by adsorption on montmorillonite KSF at room temperature without solvent.

The yields of dithianes or dithiolanes are excellent. In contrast with the results obtained in the homogeneous acidic phase, yields are also good with sensitive aldehydes such as dimethylaminobenzaldehyde **1e** (yield 90%) or thiophene-2-carbaldehyde (85%). The reaction is fast with aromatic aldehydes (15–60 min), but slower with aliphatic aldehydes and with ketones. Dithiane and dithiolane derivatives are useful for the protection of carbonyl compounds⁷ (dithiolane) or for polarity inversion (Umpolung)⁸ (dithiane).

Qualitative kinetic results suggest the possibility of chemoselectivity. In a typical competitive experiment, an equimolar mixture (5 mmol) of benzaldehyde **1a**, acetophenone **4a**, and ethane-1,2-dithiol was adsorbed on KSF clay (2 g) at room temperature. After 24 h, the products were extracted with methylene chloride or acetonitrile (30 ml) and the solvent was removed by evaporation *in vacuo*. Only the dithiolane derivative of benzaldehyde was formed, in quantitative yield. When the molecule contains several different carbonyl



groups, as in 4-acetylbenzaldehyde **1b**, the only dithiane or dithiolane derivative formed with one equivalent of dithiol is that of the aromatic aldehyde.

The results obtained for the synthesis of dithiolanes are reported in Table 1. Similar results were obtained with propane-1,3-dithiol for the formation of dithianes.

Table 1 Selectivity in competition reactions between carbonyl compounds (A and B) in formation of dithiolanes (A' derived from A, B' from B) (yield of dithiolanes 95–99%)^a

A	B	A' (%)	B' (%)
1a	4a	100	0
1a	1c	48	52
1a	1d	73	27
1a	3a	100	0
1a	3b	100	0
2b	2a	52	48
1a	4b	100	0
1a	4d	100	0
1a	4e	100	0
4a	4b	100	0
4a	4c	100	0
4c	4b	95 ^b	5 ^b
4d	4b	100	0
4e	4b	100	0

^a Equimolar quantities of the solid carbonyl compounds were dissolved in the minimum volume of methylene chloride mixed with ethane-1,2-dithiol and adsorbed on to clay. The solvent was removed by evaporation *in vacuo*. All products were characterized by elemental analysis and their IR and ¹H NMR spectra. Yields of products were determined by ¹H NMR spectroscopy or gas chromatography. Montmorillonite KSF is commercially available from Fluka, Aldrich and Süd Chemie (München). ^b The yield was only 50% after 24 h.

Chemoselectivity between aldehydes and ketones was reported by Hojo⁴ using thionyl chloride-impregnated silica gel, by Miranda⁵ with boron trifluoride and by Perni⁶ with Amberlyst A15. We also observed chemoselectivity between aromatic and aliphatic aldehydes: only the aromatic dithiane derivative was formed in competition reactions. Competition reactions between the aromatic aldehydes (**1a** and **1c**; **1a** and **1d**) show that electron-donor groups accelerate the reaction. Competition reaction between **2a** and **2b** gave a mixture of dithiolanes although **2b** is sterically hindered. The aromatic ketones (**4a**, **4d** and **4e**) reacted more rapidly than aliphatic ketones.

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