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Reaction of Sulfonium Salts of Formaldehyde Dithioacetals with Aromatic Aldehydes

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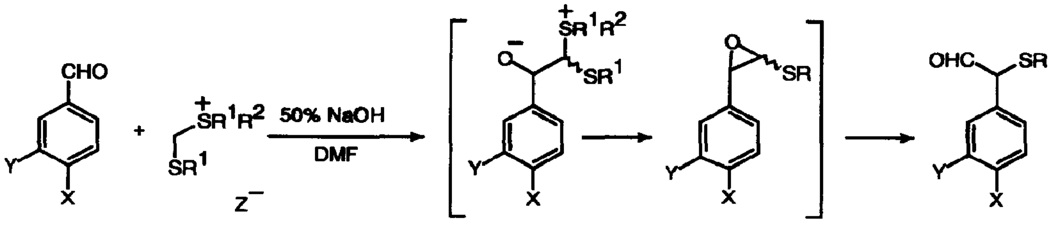
Abstract Aromatic aldehydes react with sulfonium salts of cyclic and chain formaldehyde dithioacetals in presence of aqueous NaOH to give the corresponding oxiranes which rearrange to 2-aryl-2-thioalkylacetaldehydes.

In our previous paper[1] we have described *inter alia* the ring opening vicarious nucleophilic substitution of hydrogen in nitroarenes with the ylide generated from monomethyl sulfonium salt of dithiane **1**. It was quite intriguing that there are no typical reactions of this ylide reported.[2]

Therefore in order to have possibility to compare the reaction of this ylide with nitroarenes and other electrophilic partners we have studied its reaction with aldehydes. It is well known that sulfonium ylides react readily with aldehydes to produce oxiranes *via* addition - intramolecular nucleophilic substitution process.[3] In the case of the ylide generated from **1**, the second step - the intramolecular nucleophilic substitution shall occure with the dithiane ring opening.

Amongst a variety of base-solvent systems applied for the generation and reactions of sulfonium ylides the most convenient and efficient is the two-phase system in which concentrated aqueous NaOH effects on the deprotonation at the interface and the ylide being electrically neutral migrates into the organic phase where it reacts with aldehyde. The reported procedures for the two phase generation and reactions of sulfonium ylides consisted in use as the organic phases such solvents as methylene chloride or toluene.[4] In our hands these solvents were inconvenient, perhaps because of the solubility problems. The best results were obtained using dimethylformamide for this purpose. The reaction carried out at room temperature, under argon, was completed within a few minutes, however the products were not the expected oxiranes but the derivatives of 2-aryl-3,7-dithiaoctanals.[5] Apparently the oxiranes being the initial products of the ring opening intramolecular substitution rearrange rapidly to the aldehydes. Such rearrangements are well known for oxiranes, particularly those containing sulfur substituents at the oxirane ring.[6] Reactions of two other sulfonium salts: methylthiomethyl-dimethylsulfonium chloride **2** [7] and methylthioethyldiethylsulfonium tetrafluoroborate **3** followed the same pathway.

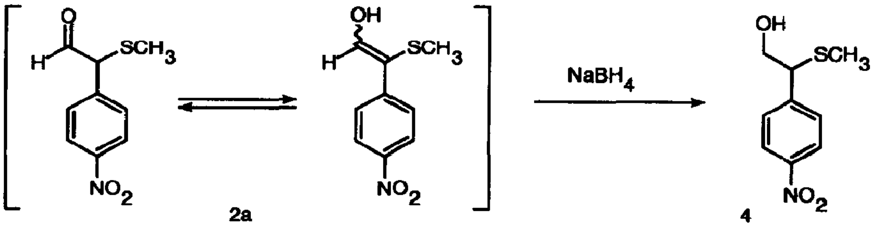


R^1= -$(CH_2)_3$-, R^2= -CH_3 **1**
R^1= -CH_3, R^2= -CH_3 **2**
R^1= -C_2H_5, R^2= -C_2H_5 **3**

R=-$(CH_2)_3SCH_3$, X, Y,: H, NO_2 **1a** 69%; -OCH_3, -H **1b** 67%; -OCH_3, -OCH_3 **1c** 70%; -$N(CH_3)_2$, -H **1d** 84%; R=CH_3, X, Y: -NO_2, -H **2a** 81%; -OCH_3, -H 2b 70%; -$N(CH_3)_2$, -H **2d** 57%; R=C_2H_5, X, Y:-OCH_3, -H **3b** 61%; -OCH_3, -OCH_3 **3c** 62%.

Identification of the aldehydes was initially somewhat difficult because they exist in form of tautomeric keto-enol mixtures, in the NMR and IR spectra features characteristic for both of these form are present and can be identified. At room temp. the equilibration is slow in the NMR time scale and the obtained spectra are superposition of spectra of these tautomers.

In order to have unambiguous confirmation structures of the products one of them, **2a** was reduced with $NaBH_4$ to the alcohol **4**, which was fully identified.[8]



2a
4

References and Notes

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5. Typical Reaction Procedure: To the vigorously stirred solution of sulfonium salt (1 mmol of **1**, **2** or 2 mmol of **3**) and aldehyde **a-d** (1 mmol), under argon, 3 ml of 50 % water solution of NaOH was added. After 5 min reaction mixture was diluted with water and extracted with ethyl acetate. After standard work-up crude product was subjected to column chromatography on silica gel.
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8. All new compounds were characterized by ^{1}H-NMR and elemental analysis.
Selected ^{1}H-NMR data (200 MHz, $CDCl_3$) **1a**: δ= 9.46 (d, *J*=4.2 Hz, 1H), 8.25, 7.55 (AA'XX',4H), 4.44 (d, *J*=4.2 Hz,1H), 2.5-2.8 (m, carbonyl and enolic forms, alifatic protons of **1a**), 2.09 (s,3H), 1.7-2.0 (m, carbonyl and enolic forms, alifatic protons of **1a**); Enolic form of **1a**: δ= 8.19, 7.67 (AA'XX'), 7.37 (d, *J*=14.4 Hz), 6.88 (d, *J*=14.4 Hz).
2a: δ= 9.45 (d, *J*=4.1 Hz, 1H), 8.25, 7.57 (AA'XX',4H), 4.34 (d, *J*=4,1 Hz, 1H), 2.11 (s,3H); Enolic form of **2a**: δ= 8.19, 7.67 (AA'XX'), 7.33 (d, *J*=14.4 Hz), 6.87 (d, *J*=14.4 Hz), 2.09 (s).
4: δ= 8.20, 7.55 (AA'XX',4H), 3.85-4.05 (m,3H), 2.18 (bs,1H), 2.01 (s,3H).

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