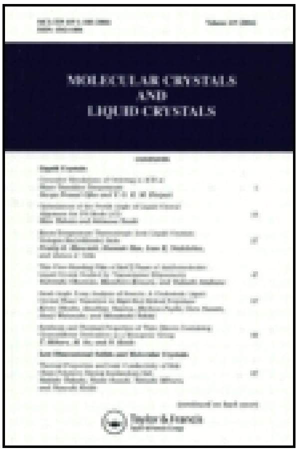

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Oxidizing Power of Aryl Sulfinamides in the Solid State

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To cite this article: Kiyoko Fujiki & Tsutomu Mochizuki (1996): Oxidizing Power of Aryl Sulfinamides in the Solid State, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 277:1, 95-97

To link to this article: http://dx.doi.org/10.1080/10587259608046008

Mol. Cryst. Liq. Cryst., 1996, Vol. 277, pp. 95–97
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OXIDIZING POWER OF ARYL SULFINAMIDES IN THE SOLID STATE

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Abstract Oxidation of thiophenols by aryl sulfinamides without added acid in the solid state is described.

INTRODUCTION

The oxidizing power of the sulfinyl group as in dimethyl sulfoxide has been applied to a wide variety of substrates[1].

Recently we have reported that aryl sulfinamides oxidize iodide ion and thiols to iodine and disulfides respectively[2,3]. In solution the oxidation of thiols by aryl sulfinamides proceeds by initial protonation of the sulfinyl group followed by a series of nucleophilic displacement, the first which gives thiosulfinate and elimination of amine. The more usual reaction with thiosulfinate then gives disulfide, and sulfenic acid as a transitory intermediate, which by reaction with a third mole of thiol yields more disulfide (Series 1–3).

$$\mathrm{PhSO{-}NHPh + Ph'SH \longrightarrow PhNH_2 + PhS(O)SPh'} \quad (1)$$

$$\mathrm{PhS(O)SPh' + Ph'SH \longrightarrow Ph'SSPh' + [PhSOH]} \quad (2)$$

$$\underline{\mathrm{[PhSOH] + Ph'SH \longrightarrow PhSSPh' + H_2O}} \quad (3)$$

$$\mathrm{PhSO{-}NHPh + 3Ph'SH \longrightarrow PhNH_2 + Ph'SSPh' + PhSSPh' + H_2O} \quad (4)$$

Since most biological reactions seem to occur almost in hydrophobic circumstance at their active site, now we have studied the oxidation of thiols in the solid state as a basis for biological applications.

RESULTS AND DISCUSSION

The oxidation of thiophenols in the solid state proceeded readily at a room temperature without added acid at a rate dependent on the acidity of thiols and gave aniline and disulfides by mixing with finely powdered aryl sulfinanilides and irradiating with ultrasonic waves occasionally. For instance, *p*–toluenesulfinanilide / *p*–toluenethiol reaction in which reactant ratio of 1 : 3 gave approximately theoretical yield of di-*p*–tolyl disulfide and aniline according to the Equation (4). It seems the reaction pathway in the solid state is similar to that in solution.

However reaction with lesser amount of *p*–toluenethiol permitted identification of sulfinic acid and thiolsulfonate as an intermediate not thiolsulfinate. Late appearance of thiolsulfonate after rapid appearance of aniline and disulfide characterized the reaction of aryl sulfinanilide with *p*–toluenethiol. Moreover the emergence of diphenyl disulfide in benzenesulfinanilide / *p*–nitrothiophenol reaction also indicates the reaction pathway includes the slightly different course from what we have shown in the Series (1–3). These two experimental findings sggest disproportionation occur from thiolsulfinate to thiolsulfonate. And disulfide mixture and sulfinic acid are given as shown in the Equations (5)[4] and (6).

$$2\,\mathrm{PhS(O)SPh'} \longrightarrow \mathrm{PhSO_2SPh} + \mathrm{Ph'SSPh'} + (\mathrm{PhSSPh}) \qquad (5)$$

$$\mathrm{PhSO_2SPh} + \mathrm{Ph'SH} \longrightarrow \mathrm{PhSO_2H} + \mathrm{PhSSPh'} \qquad (6)$$

The separated reaction of *p*–tolyl–*p*–toluenethiolsulfonate with *p*–nitrothiophenol in the solid state was carried out and gave *p*–toluenesulfinic acid and *p*–nitrophenyl–*p*–tolyl disulfide (Eq 6). Another separated solid reaction of thiolsulfinate with thiol revealed the presence of thiolsulfonate along with disulfide and sulfinic acid in the reaction mixture.

In conclusion the solid oxidation of thiols by aryl sulfinamides can be assumed to have complex pathway {a Series (1–3) including a Series (1), (5) and (6)}

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