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CHEMISTRY OF SULFUR COMPOUNDS-VI[1]. A NOVEL METHOD FOR THE PREPARATION OF DISULFIDES

Kamel S. Boustany[2] and Alfred B. Sullivan

Monsanto Co., Organic Chemicals Division,
Rubber Chemicals Research Laboratories
Akron, Ohio 44313

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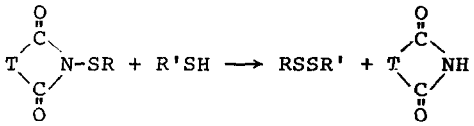
Mukaiyama and Takahashi[3] have recently reported a convenient method for the preparation of unsymmetrical disulfides by reacting thiols with diethyl azodicarboxylate while Lindner and Vitzthum[4] have described a new method for the formation of S-S bonds by reacting carbonyl complexes of metals of Groups VI and VIII with organosulfuryl chlorides in polar solvents. It was found that unsymmetrical and symmetrical disulfides are produced highly pure and in a high yield when a sulfenamide derived from an imide such as phthalimide, succinimide or even maleimide[5] is reacted with a thiol under mild reaction conditions with no catalyst. The general reaction can be depicted as follows:



(I)

T=$(CH_2)_n$, C_6H_4 or (HC=CH) and R ≠ R' = alkyl, cycloalkyl, aryl or aryl alkyl. The reaction took place at a temperature between 20 and 100°C in the presence or absence of solvent. In most cases an inert solvent was used in which the by-product, imide, is insoluble. The precipitation of the imide serves as a driving force for the reaction. It accelerates the complete conversion to the disulfides. The commonly used solvents were aliphatic or aromatic hydrocarbons; however, CCl_4, ether, alcohols or even water can be used. Some of the disulfides obtained by the above described novel method are listed in Table A.

Table A

Disulfides* prepared via thiols and sulfenimides

T	R	R'	Reaction Conditions**	Yields	B.P./Mm or [M.P.]
o-C_6H_4	C_6H_5	C_6H_5	Bz, RT, 2 hr	88%	[59°]
o-C_6H_4	C_6H_{11}	BT$^{(a)}$	Bz, 45°, 1 hr	94	(b)
$(CH_2)_2$	C_6H_{11}	C_6H_5	Hp, 90°, 1.5 hr	89	111-15/0.3$^{(c)}$
o-C_6H_4	C_6H_{11}	p-$CH_3C_6H_4$	Bz, 60°, 5 hr	97.5	159/2.2
o-C_6H_4	C_6H_{11}	o-$CH_3C_6H_4$	C, RF, 5 hr	88	150/1.8
o-C_6H_4	$C(CH_3)_3$	BT	Bz, 70°C, 7 hr	94	[80.5°]$^{(d)}$
o-C_6H_4	$C_6H_5CH_2$	$C_6H_5CH_2$	Bz, RT, 48 hr	92	[68-69°]
o-C_6H_4	n-C_4H_9	$C_6H_5CH_2$	Bz, RT, 48 hr	82	114/1.1$^{(e)}$
CH=CH	C_6H_5	C_6H_5	Bz, RT, 1 hr	84	[60°]
$(CH_2)_2$	C_6H_5	C_6H_5	W, RT, 0.25 hr	96	[59°]

* All compounds obtained were identified by glc and nmr. Glc of the reaction products showed a single peak indicating the disulfides are not mixtures.

** Bz: benzene, Hp: heptane, C: carbon tetrachloride, W: without, RT: room temperature, RF: reflux.

(a):2-benzothiazole; (b) % N calc=4.98, % N found = 4.86, decomposes on distillation; (c): found % C=64.3, % H=7.15, % S=28.6, calc. % C=64.3, % H=7.20, % S=28.6; (d): ref.[6]; (e) % S found=30.12, % S calc.=30.19.

Although the yields reported in the above table do not emphasize this, the reaction in general results in quantitative conversion of the thiomide to the disulfide. In fact, the reaction provides a convenient analytical technique for determining thioimide by back titration of the excess of thiol.

It was also found that thioacids react similarly to thiols. Thus benzoylcyclohexyl disulfide was obtained when thiobenzoic acid was reacted with N-(cyclohexylthio)phthalimide (% S found 25.21, % S calc. 25.45, bp 158°/0.6mm). When a dithiol such as 1,3-dithiopropane was reacted with N-phenylthiosuccinimide the corresponding 1,3-propylene bis(phenyldisulfide) was isolated, and when thiophenol was reacted with 1,6-bis(N-thiophthalimide)-n-hexane, 1,6-bisphenyl-n-hexyldisulfide was isolated (% S found=34.54, % S calc.=35.0). The latter compounds decompose upon heating.

A typical example of synthesis is as follows: 12.4g (0.1 mole) of p-toluene thiol was stirred with 26.2g (0.1 mole) of N-(cyclohexylthio)phthalimide in 100 cc of benzene for 5 hours at 60°C. After cooling, 14.5g of a white solid (phthalimide m.p. measured 234-235°C uncorrected) was recovered by filtration. The solvent is removed by evaporation under reduced pressure, leaving as the residue 23.2g (97.5% yield) of cyclohexyl-p-tolyldisulfide.

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