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ONE-STEP SYNTHESIS OF 2-ARYLETHENYL METHYL SULFIDES FROM ARYL ALDEHYDES AND DIMETHYL SULFOXIDE

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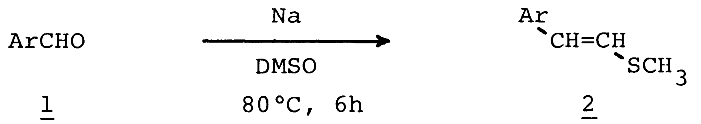
A facile method for preparing *trans*-α,β-unsaturated sulfides has been established by the reaction of aryl aldehydes with dimethyl sulfoxide in the presence of matallic sodium. The reaction proceeds through the selective reduction of an intermediate, 2-arylethenyl methyl sulfoxide, which also gives enol ethers by the reaction with sodium alkoxides.

α,β-Unsaturated sulfides are of value as precursors of aldehydes[1)] and ketones,[2)] and the sulfonium salts derived from them are recently reported to form cyclopropanes and oxiranes.[3)] Although unsaturated sulfides have been prepared from alkynes and thiols,[4)] or aldehydes by Horner-Wittig reaction,[5)] we have found a one-step synthesis of 2-arylethenyl methyl sulfides starting from aryl aldehydes and dimethyl sulfoxide (DMSO) in the presence of metallic sodium, as shown in the following scheme:



$$\underset{1}{\mathrm{ArCHO}} \xrightarrow[\text{DMSO}\\ 80^\circ\text{C, 6h}]{\text{Na}} \underset{2}{\mathrm{Ar{-}CH{=}CH{-}SCH_3}} \qquad [\mathrm{I}]$$

A typical procedure for the preparation of the sulfide (2) is as follows. Benzaldehyde (1a, 2 mmol) in DMSO (40 ml) and tetrahydrofuran (10 ml) was stirred with sodium (8.6 mg-atom) under an atmosphere of argon at 80°C for 6 h. Addition of water was followed by extraction with ether. The organic layer was concentrated under reduced pressure and subjected to a column chromatographic purification using silica gel with n-hexane-benzene (5:1) as an eluant. 2-(Methylthio)ethenylbenzene (2a) was isolated as colorless liquid in a yield of 84%. In the similar precedure, various kinds of the sulfides (2b-2f) were obtained in good yields as shown in Table 1. The yield of 2 depends on the concentration of the starting aldehyde 1. The yield of 2b increased up to 84% in two-fold diluted conditions, while it decreased to 30% in six-fold concentrated ones.

The structure of the products was confirmed by spectroscopic data (UV, IR, NMR, and MS) and elemental analysis. Although Horner-Wittig reaction was reported to give a cis-trans mixture of unsaturated sulfides,[5)] all of the sulfides obtained here have trans (E) configuration as to the carbon-carbon double bond.[6)] No cis isomer was observed in the reaction mixture (NMR). Consequently, the

Table 1. Yields and Physical Properties of 2-Arylethenyl Methyl Sulfides (2)

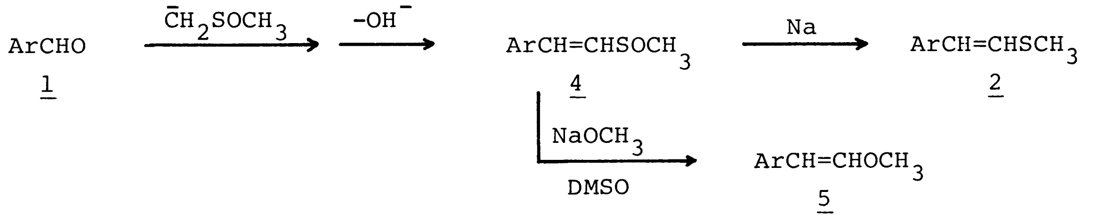
Compd	Ar	Isolated Yield of 2[a]	Mp (bp)
2a	C_6H_5	84%	(140-142°C/35mmHg)[b]
2b	p-$CH_3C_6H_4$	76	35-37°C
2c	p-$CH_3OC_6H_4$	64	72-73[c]
2d	o-$CH_3OC_6H_4$	73	(88-90/1)
2e	2-furyl	66	oil[d]
2f	1-naphthyl	75	(102-104/1)

a) Based on aldehyde (1). b) Lit. 72-76°C/0.5-1.0mmHg.4) c) Lit. 70-71.5°C.4)

d) Diels-Alder reaction with dimethyl acetylenedicarboxylate yielded dimethyl 6-(2-methylthio)ethenyl-3-hydroxyphthalate, which was identified as its 3,5-dinitrobenzoate; mp 171-172°C.

reaction proceeds stereoselectively to the exclusive formation of the trans isomer.

The formation of 2 may be rationalized according to the following scheme [II] via the intermediate 2-arylethenyl methyl sulfoxide (4).7) The unsaturated sulfoxide (4) formed from 1 and methylsulfinyl carbanion is reduced



[II]

chemoselectively to form 2, leaving the carbon-carbon double bond intact. Matallic sodium serves first to form methylsulfinyl carbanion and secondly to reduce 4. The reduction of 4 was confirmed by an independent experiment which actually brought 4 (Ar=Ph) to 2a in DMSO-sodium system (66%). A related compound, α,β-unsaturated ether (5), was also obtained from 4 by apparent substitution of methylsulfinyl group; p-[2-(Methylsulfinyl)ethenyl]toluene (4, Ar= p-Tol) afforded p-[2-(methoxy)ethenyl]toluene (5, Ar= p-Tol) in 60% yield, when treated with sodium methoxide in DMSO at 80°C for 6 h.

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