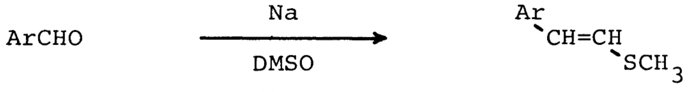
CHEMISTRY LETTERS, pp. 1425-1426, 1978. Published by the Chemical Society of Japan

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

Takakazu KOJIMA and Tamotsu FUJISAWA
Sagami Chemical Research Center,
Nishi-Ohnuma, Sagamihara, Kanagawa 229

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:



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

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

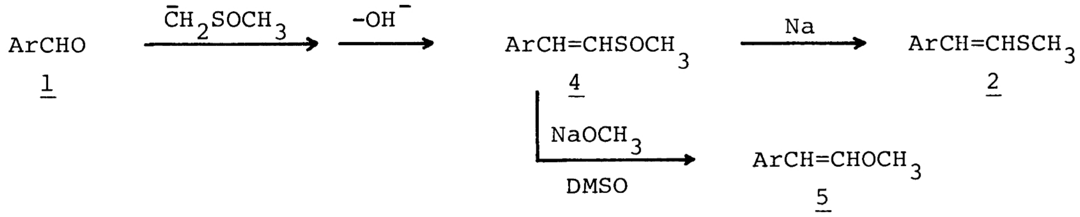
Table 1. Yields and Physical Properties of 2-Arylethenyl Methyl Sulfides (2)

| 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



$$\begin{tikzcd}
\underset{1}{ArCHO} \arrow[r, "\bar{C}H_2SOCH_3"] & {} \arrow[r, "-OH^-"] & \underset{4}{ArCH{=}CHSOCH_3} \arrow[r, "Na"] \arrow[dr, "NaOCH_3"', "DMSO"] & \underset{2}{ArCH{=}CHSCH_3} \\
 & & & \underset{5}{ArCH{=}CHOCH_3}
\end{tikzcd}$$

[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.

## REFERENCES AND NOTE

1) E. J. Corey and J. I. Shulman, J. Org. Chem., 35, 777 (1970).
2) A. J. Mura, Jr., G. Majetich, P. A. Grieco, and T. Cohen, Tetrahedron Lett., 4437 (1975).
3) K. Takaki and T. Agawa, J. Org. Chem., 42, 3303 (1977), and references therein
4) M. C. Caserio, R. E. Pratt, and R. J. Holland, J. Am. Chem. Soc., 88, 5747 (1966).
5) I. Shahak and J. Almog, Synthesis, 170 (1969).
6) The ethylenic protons of these sulfides have a coupling constant of 16 Hz, which is in accord with that of methyl styryl sulfide (2a) of trans structure.[4]
7) G. A. Russel and H.-D. Becker, J. Am. Chem. Soc., 85, 3406 (1963).

(Received September 25, 1978)