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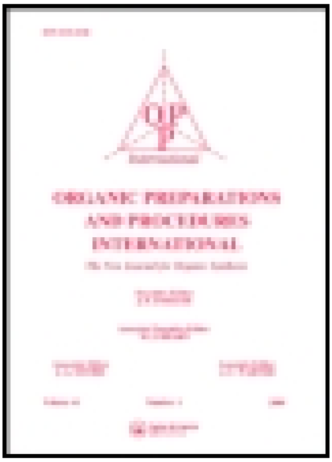

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α,β-UNSATURATED SULFONES BY THE WITTIG REACTION OF STABLE YLIDE WITH ALDEHYDES UNDER MICROWAVE IRRADIATION

Cong Fu [a] , Caiding Xu [a] , Zhi-Zhen Huang [a] & Xian Huang [a]
[a] Department of Chemistry , Hangzhou University , Zhejiang, 310028, PR CHINA
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9. However, ethyl cyanoacetate failed to react with either benzylidene acetophenone or benzylidene acetone under our standard micellar conditions. To understand this unusual result, we are presently investigating these reactions at higher concentration of alkali and micelles.

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Submitted by Cong Fu, Caiding Xu, Zhi-Zhen Huang and Xian Huang[*]
(01/17/96)

Department of Chemistry, Hangzhou University
Zhejiang 310028, *P. R. CHINA*

α,β-Unsaturated sulfones are important intermediates in organic synthesis[1] and may be obtained from the condensation of arylsulfonylacetic acid with aldehydes.[2] Kobayashi *et al.* found that tosyl chloride underwent addition with vinylarenes catalyzed by a ruthenium(II) complex; subsequent dehydrochlorination gave the *trans*-α,β-unsaturated sulfones.[3] The reduction of E-β-iodo-α,β-unsaturated sulfones with zinc in acetic acid afforded Z-tosyl-2-arylethenes.[4] α,β-Unsaturated sulfones may also be obtained from the phase-transfer catalyzed condensation of sulfones with aldehydes.[5] Many reactions, such as the Diels-Alder,[6] Claisen,[6] *ene* reactions,[6] dehydration and nucleophilic substitutions[7] may be conducted safely in commercial microwave ovens with remarkable rate enhancements

$$ArCHO + 4\text{-}CH_3C_6H_4SO_2CH{=}PPh_3 \xrightarrow[\text{Silica gel, 15 min.}]{\text{Microwave}} 4\text{-}CH_3C_6H_4SO_2CH{=}CHAr$$

and dramatic reduction of reaction times compared with conventional heating. Previous papers described the synthesis of ethyl cinnamates and chalcones *via* microwave-induced Wittig reactions,[8] and this paper reports the synthesis of α,β-unsaturated sulfones *via* the Wittig reaction under microwave irradiation.

As is well known, the Wittig reaction of stable ylides proceeds slowly using the conventional methods;[9,10] for example, the condensation of *p*-tosylmethylene triphenylphosphorane with *p*-nitrobenzaldehyde in chloroform required three days at room temperature to give a 53% yield of 1-(*p*-nitrophenyl)-2-(*p*-tosyl)ethylene.[9] Our experiments showed that, *p*-tosylmethylene triphenylphosphorane absorbed on silica gel, underwent the Wittig reaction completely under the irradiation of microwave after 15 min. to afford the *trans* isomer as the sole products. Silica gel was used as an effective support for this reaction, without which the yield of the Wittig reaction decreased dramatically (26%). The *trans* configuration of products was established by ^{1}H NMR spectra in which the coupling constants of vinylic hydrogens were in the range of 15-16Hz. This method was also adapted to aliphatic aldehydes.

TABLE. Synthesis of α,β-Unsaturated Sulfones

Aldehyde	Product	Yield (%)	mp. (°C)	lit. mp. (°C)
C_6H_5CHO	$C_6H_5CH{=}CHTs$	66	120-121	120-121[3]
$4\text{-}NO_2C_6H_4CHo$	$4\text{-}NO_2C_6H_4CH{=}CHTs$	58	182-184	183-184[10]
$4\text{-}ClC_6H_4CHO$	$4\text{-}ClC_6H_4CH{=}CHTs$	63	151-152	151-152[3]
$3\text{-}NO_2C_6H_4CHO$	$3\text{-}NO_2C_6H_4CH{=}CHTs$	57	145-146	146-147[3]
$4\text{-}CH_3C_6H_4CHO$	$4\text{-}CH_3C_6H_4CH{=}CHTs$	70	154-155	154-155[3]
$2.4\text{-}C1_2C_6H_3CHO$	$2,4\text{-}Cl_2C_6H_3CH{=}CHTs$	57	128-129	129-129.5[3]
$(CH_3)_3CCH_2CHO$	$(CH_3)_3CCH_2CH{=}CHTs$	53	oil[a]	oil[11]
$C_6H_5CH_2CHO$	$C_6R_5CH_2CH{=}CHTs$	62	118-120	120[11]

a) ^{1}H NMR ($CDCl_3$): δ 1.0 (s, 9H), 2.2-2.5 (m, 5H), 6.4 (d, 1H, J = 15Hz), 6.8 (d, 1H, J = 15Hz), 7.3-7.8 (m, 4H)

EXPERIMENTAL SECTION

Melting points are uncorrected. ^{1}H NMR spectra were obtained with F 90Q spectrometer in $CDCl_3$ using TMS as internal standard. National NN-5252 domestic microwave oven was used.

Typical Procedure.- A mixture of *p*-tosylmethylene triphenylphosphorane[9] (1mmol), benzaldehyde (1mmol), and silica gel (2g, 200-300 mesh) were introduced into the domestic microwave oven in an open round-bottomed flask irradiated with microwave at an output of about 120w for 15 min. Then 20 mL methylene dichloride was added into the cooled mixture, the extract was concentrated and chromatographed on silica gel (200 mesh), using 10:1 (v/v) benzene-ethyl acetate as eluent to give the product (150mg, 66%) as a yellow solid.

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