

BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 2453—2455 (1971)

The Reactions of β -Ketosulfonium Salts with Sulfenamide Derivatives

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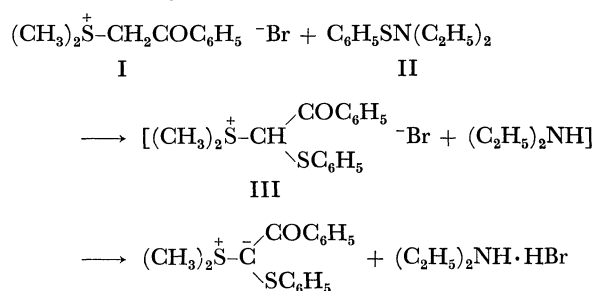
(Received January 28, 1971)

2-Phenylthio-2-(dimethylsulfuranylidene)acetophenone was obtained in good yield by the reaction of dimethylphenacylsulfonium bromide with *N,N*-diethylbenzenesulfenamide. The reaction of dimethyl- α -methylphenacylsulfonium bromide with *N,N*-diethylbenzenesulfenamide gave α -phenylthioacrylophenone in good yield. The reactions of α -phenylthioacrylophenone thus obtained with various active methylene compounds were investigated.

Recently it was reported that sulfenamide derivatives reacted with active methylene compounds to give mono- or di-sulfenylated compounds in good yields. As an example, the reaction of *N,N*-diethylbenzenesulfenamide with acetylacetone in dichloromethane at room temperature gave 3-phenylthio-2,4-pentadione in 77% yield.¹⁾

We studied the equimolar reactions of β -ketosulfonium salts with sulfenamide derivatives with the expectation that α -alkyl or arylthio- β -ketosulfonium salts and amines would be formed as a result of the introduction of sulfonyl group in place of the hydrogen atom attached to the α -carbon of the sulfonium salts. When *N,N*-diethylbenzenesulfenamide was treated with dimethylphenacylsulfonium bromide in dichloromethane at room temperature for an hour, 2-phenylthio-2-(dimethylsulfuranylidene)acetophenone and diethylammonium bromide were obtained in 70% and quanti-

tative yields, respectively.

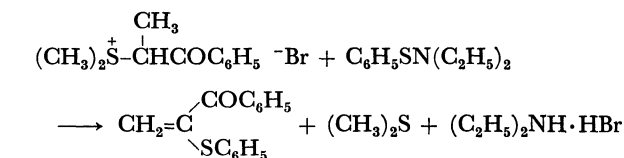
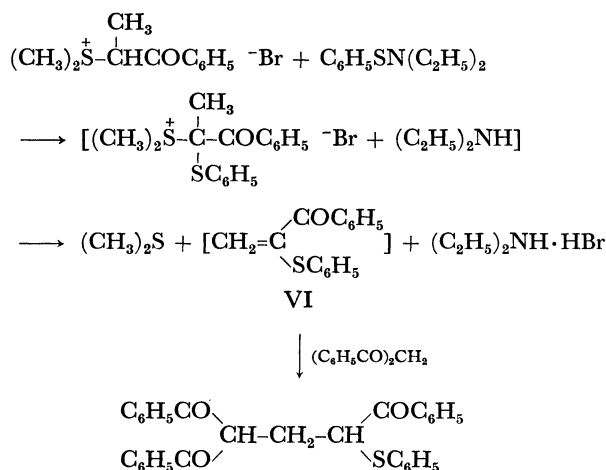


The result is explained as follows. Sulfonium salt (I) reacted with *N,N*-diethylbenzenesulfenamide (II) to form sulfenylated compound (III) and diethylamine as expected. The initially formed sulfonium salt was rapidly converted to 2-phenylthio-2-(dimethylsulfuranylidene)acetophenone by the influence of diethylamine.

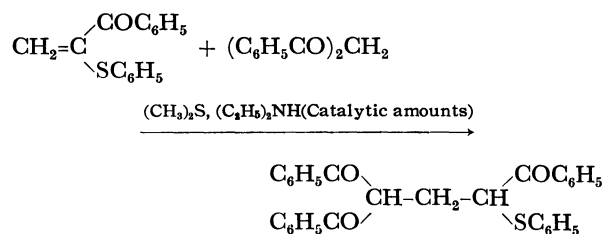
The reactions of dimethyl- α -methylphenacylsulfonium bromide with *N,N*-diethylbenzenesulfenamide and

1) T. Mukaiyama, S. Kobayashi, and T. Kumamoto, *Tetrahedron Lett.*, **1970**, 5115.

active methylene compounds were investigated with the expectation that initially formed dimethyl- α -methyl- α -phenylthiophenacylsulfonium bromide would further react with active methylene compounds to produce condensation products. However, the reaction of dimethyl- α -methylphenacylsulfonium bromide with *N,N*-diethylbenzenesulfenamide in dichloromethane at room temperature for 4 hr and the subsequent addition of dibenzoylmethane in refluxing dichloromethane for 4 hr afforded 2-benzoyl-1,5-diphenyl-4-phenylthio-1,5-pentadione and diethylammonium bromide in 70% and quantitative yields, respectively. The unexpected formation of 2-benzoyl-1,5-diphenyl-4-phenylthio-1,5-pentadione may be explained by considering an initial formation of sulfonium salt (V) and diethylamine from equimolar amounts of dimethyl- α -methylphenacylsulfonium bromide (IV) and *N,N*-diethylbenzenesulfenamide (II). Salt (V) rapidly reacts with diethylamine formed at the same time to give α -phenylthioacrylophenone (VI). The Michael addition of VI and dibenzoylmethane results in the formation of 2-benzoyl-1,5-diphenyl-4-phenylthio-1,5-pentadione.



The α -phenylthioacrylophenone isolated by the above reaction did not react with dibenzoylmethane even when they were refluxed in dichloromethane for 4 hr. However, when the reaction was carried out in the presence of a catalytic amount of diethylamine and an equimolar amount of dimethyl sulfide, 2-benzoyl-1,5-diphenyl-4-phenylthio-1,5-pentadione was obtained in 70% yield.



Similarly, it was established that reactions of dimethyl- α -methylphenacylsulfonium bromide with *N,N*-diethylbenzenesulfenamide and various active hydrogen compounds such as benzenethiol, ethanethiol, ethyl malonate, malononitrile, ethyl acetoacetate, without isolation of α -phenylthioacrylophenone, afforded 1:1 addition compounds or 1:2 addition compounds in good yields (Table 1).

TABLE 1. REACTIONS OF DIMETHYL- α -METHYLPHENACYLSULFONIUM BROMIDE WITH *N,N*-DIETHYLBENZENESULFENAMIDE AND ACTIVE HYDROGEN COMPOUNDS

$(\text{CH}_3)_2\text{S}^+-\text{CH}(\text{COC}_6\text{H}_5)\text{COC}_6\text{H}_5 \text{ } ^-\text{Br} + \text{C}_6\text{H}_5\text{SN}(\text{C}_2\text{H}_5)_2 \xrightarrow{\text{H}_2\text{C}^{\text{X}}_{\text{Y}}} \text{X}\diagdown \text{CH}-\text{CH}_2-\text{CH}\diagup \text{COC}_6\text{H}_5 + \text{X}\diagdown \text{C}(\text{CH}_2-\text{CH}\diagup \text{COC}_6\text{H}_5)_2$							
				VII		VIII	
				VII		VIII	
				Mp (°C)		Analyses Found (Calcd) (%)	
						C	H
						N	
						S	
HSC_6H_5	93%		oil			72.28 (71.99)	5.25 (5.18)
HSC_2H_5	85%		130 —131 ^a)			53.31 (53.27)	5.93 (5.65)
$\text{CH}_2(\text{COC}_6\text{H}_5)_2$	70%		123.5—124			77.81 (77.57)	5.37 (5.21)
$\text{CH}_2(\text{CO}_2\text{C}_2\text{H}_5)_2$		63%	178.5—179.5			69.49 (69.36)	5.61 (5.66)
$\text{CH}_2(\text{CN})_2$		75%	132.5—133.0			72.34 (72.51)	4.92 (4.86)
CH_2COCH_3	45%		175.5—176			68.32 (68.09)	6.27 (5.99)
$\text{CH}_2\text{CO}_2\text{C}_2\text{H}_5$							

a) This was identified by transformation into sulfonium methyl sulfate.

Experimental

Materials. *N,N*-Diethylbenzenesulfenamide (II) was prepared according to the method of Lecher and Holschneider,²⁾ bp 96—97°C/8 mmHg (lit, 90°C/3.5 mmHg). Dimethylphenacysulfonium bromide (I) was prepared from dimethyl sulfide and phenacyl bromide in dry acetone. Similarly, dimethyl- α -methylphenacysulfonium bromide (IV) was prepared from dimethyl sulfide and α -bromopropiophenone.³⁾

Reaction of Dimethylphenacysulfonium Bromide with *N,N*-Diethylbenzenesulfenamide. A mixture of dimethylphenacysulfonium bromide (2.61 g, 0.01 mol) and *N,N*-diethylbenzenesulfenamide (1.81 g, 0.01 mol) was stirred in dichloromethane (50 ml) for an hour at room temperature. The reaction mixture was poured into water to remove diethylammonium bromide and the dichloromethane layer was collected. After the dichloromethane layer was dried with sodium sulfate, the solvent was removed under reduced pressure giving white crystals. The recrystallization from benzene gave 2-phenylthio-2-(dimethylsulfuranylidene)acetophenone,⁴⁾ mp 136—136.5°C, 2.00 g, (70%). (lit, 136°C).

Reaction of Dimethyl- α -methylphenacysulfonium Bromide with *N,N*-Diethylbenzenesulfenamide and Dibenzoylmethane. A mixture of dimethyl- α -methylphenacysulfonium bromide (1.43 g, 0.005 mol) and *N,N*-diethylbenzenesulfenamide (0.91 g, 0.005 mol) was stirred in dichloromethane (50 ml) at room temperature. Evolution of dimethyl sulfide was recognized by its characteristic odor accompanied by disappearance of the crystals of sulfonium salt. After stirring for 4 hr, dibenzoylmethane (1.12 g, 0.005 mol) was added to the reaction mixture and the mixture was refluxed for 4 hr. The solvent was removed under reduced pressure giving oily residue. Fifty milliliters of water was added into the residue and resulting oil was extracted with ether (50 ml). Removal of ether gave

white crystals. Recrystallization from ethanol gave 2-benzoyl-1,5-diphenyl-4-phenylthio-1,5-pentadione, 1.62 g (70%), mp 123—124°C.

Found: C, 77.81; H, 5.37; S, 6.64%. Calcd for $C_{30}H_{24}O_3S$: C, 77.57; H, 5.21; S, 6.89%. The NMR spectrum: τ = 1.7—2.8 (m, 20H), τ = 4.43 (t, 1H), τ = 5.12 (t, 1H), τ = 7.27 (t, 2H).

Similarly, various addition products of active hydrogen compounds, such as benzenethiol, ethanethiol, ethyl malonate, malononitrile or ethyl acetoacetate, and α -phenylthioacrylophenone were obtained from dimethyl- α -methylphenacysulfonium bromide, *N,N*-diethylbenzenesulfenamide and active hydrogen compounds. The results are listed in Table 1. The products were identified by elemental analyses, NMR spectra and IR spectra.

Reaction of Dimethyl- α -methylphenacysulfonium Bromide with *N,N*-Diethylbenzenesulfenamide. A mixture of dimethyl- α -methylphenacysulfonium bromide (1.43 g, 0.005 mol) and *N,N*-diethylbenzenesulfenamide (0.91 g, 0.005 mol) was stirred in dichloromethane (50 ml) for 4 hr at room temperature. The solvent was removed under reduced pressure giving a mixture of crystals and oil. Fifty milliliters of water was added into the mixture and resulting oil was extracted with ether (50 ml). After removal of the solvent, the oil was chromatographed on silica gel and elution with a mixture of petroleum ether (25—30°C) and benzene (1:1) gave α -phenylthioacrylophenone, 0.84 g (70%), mp 106—108°C.

Found: C, 74.82; H, 5.20; S, 13.21%. Calcd for $C_{15}H_{12}SO$: C, 74.99; H, 5.03; S, 13.32%. The NMR spectrum: τ = 1.8—2.8 (m, 10H), τ = 7.55 (S, 1H), τ = 7.65 (S, 1H).

Reaction of α -Phenylthioacrylophenone with Dibenzoylmethane. Into a solution of α -phenylthioacrylophenone (2.40 g, 0.01 mol) and dibenzoylmethane (2.24 g, 0.01 mol) in dichloromethane (50 ml), dimethyl sulfide (0.62 g, 0.01 mol) and a catalytic amount of diethylamine were added under stirring. The mixture was refluxed for 5 hr. After removal of the solvent, the residue was chromatographed on silica gel and elution with mixture of petroleum ether (25—35°C) and benzene (1:1) gave 2-benzoyl-1,5-diphenyl-4-phenylthio-1,5-pentadione, 3.00 g (70%), mp 123°C.

2) H. Lecher and F. Holschneider, *Ber.*, **57**, 757 (1924).

3) T. Mukaiyama, K. Hagio, H. Takei, and K. Saigo, *This Bulletin*, **44**, 161 (1971).

4) Y. Hayasi, M. Takaku, and H. Nozaki, *Tetrahedron Lett.*, **1969**, 3179.