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The Reactions of β-Ketosulfonium Salts with Sulfenamide Derivatives

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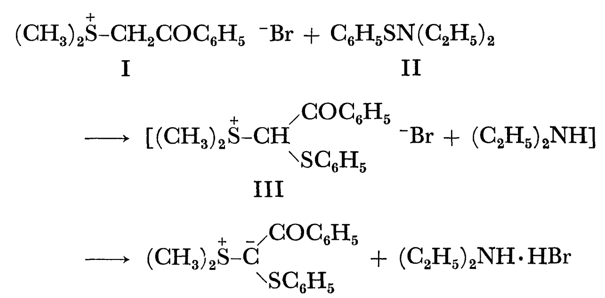
2-Phenylthio-2-(dimethylsulfuranylidene)acetophenone was obtained in good yield by the reaction of dimethylphenacylsulfonium bromide with *N,N*-diethylbenzenesulfenamide. The reaction of dimethyl-α-methylphenacylsulfonium bromide with *N,N*-diethylbenzenesulfenamide gave α-phenylthioacrylophenone in 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 sulfenyl 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 quantitative yields, respectively.



$$\underset{\text{I}}{(CH_3)_2\overset{+}{S}\text{-}CH_2COC_6H_5\ {}^{-}Br} + \underset{\text{II}}{C_6H_5SN(C_2H_5)_2}$$

$$\longrightarrow [\underset{\text{III}}{(CH_3)_2\overset{+}{S}\text{-}CH\genfrac{}{}{0pt}{}{\diagup COC_6H_5}{\diagdown SC_6H_5}}\ {}^{-}Br + (C_2H_5)_2NH]$$

$$\longrightarrow (CH_3)_2\overset{+}{S}\text{-}\overset{-}{C}\genfrac{}{}{0pt}{}{\diagup COC_6H_5}{\diagdown SC_6H_5} + (C_2H_5)_2NH\cdot HBr$$

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

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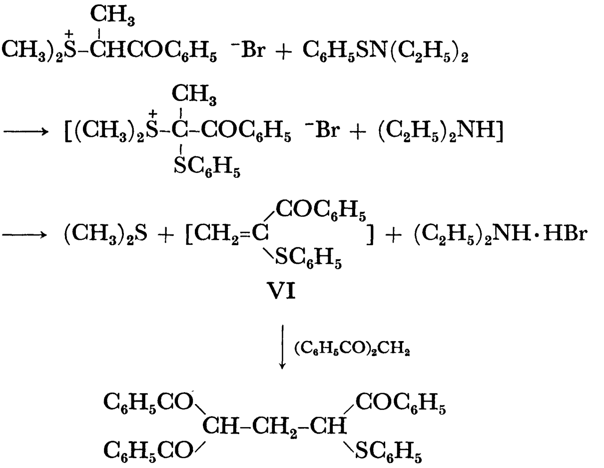
[1] T. Mukaiyama, S. Kobayashi, and T. Kumamoto, *Tetrahedron Lett.*, **1970**, 5115.

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.



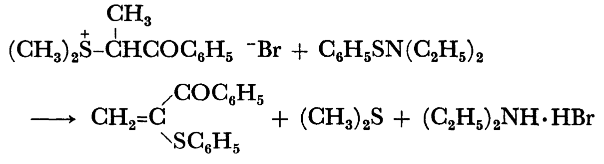
$$(CH_3)_2\overset{+}{S}\text{-}\overset{\overset{CH_3}{|}}{C}HCOC_6H_5\ {}^{-}Br + C_6H_5SN(C_2H_5)_2$$

$$\longrightarrow [(CH_3)_2\overset{+}{S}\text{-}\underset{\underset{SC_6H_5}{|}}{\overset{\overset{CH_3}{|}}{C}}\text{-}COC_6H_5\ {}^{-}Br + (C_2H_5)_2NH]$$

$$\longrightarrow (CH_3)_2S + \underset{VI}{[CH_2{=}C\begin{matrix}\diagup COC_6H_5\\ \diagdown SC_6H_5\end{matrix}]} + (C_2H_5)_2NH\cdot HBr$$

$$\xrightarrow{(C_6H_5CO)_2CH_2} \begin{matrix}C_6H_5CO\diagdown\\ C_6H_5CO\diagup\end{matrix}CH\text{-}CH_2\text{-}CH\begin{matrix}\diagup COC_6H_5\\ \diagdown SC_6H_5\end{matrix}$$

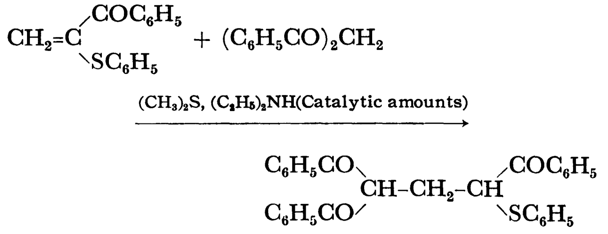
The presumed intermediate, α-phenylthioacrylophenone, was isolated in 98% yield by the reaction of dimethyl-α-methylphenacylsulfonium bromide with *N*, *N*-diethylbenzenesulfenamide, without the addition of dibenzoylmethane, in dichloromethane at room temperature for 4 hr.



$$(CH_3)_2\overset{+}{S}\text{-}\overset{\overset{CH_3}{|}}{C}HCOC_6H_5\ {}^{-}Br + C_6H_5SN(C_2H_5)_2$$

$$\longrightarrow CH_2{=}C\begin{matrix}\diagup COC_6H_5\\ \diagdown SC_6H_5\end{matrix} + (CH_3)_2S + (C_2H_5)_2NH\cdot HBr$$

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.

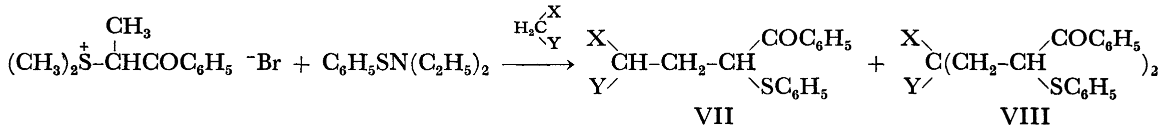


$$CH_2{=}C\begin{matrix}\diagup COC_6H_5\\ \diagdown SC_6H_5\end{matrix} + (C_6H_5CO)_2CH_2$$

$$\xrightarrow{(CH_3)_2S,\ (C_2H_5)_2NH(\text{Catalytic amounts})} \begin{matrix}C_6H_5CO\diagdown\\ C_6H_5CO\diagup\end{matrix}CH\text{-}CH_2\text{-}CH\begin{matrix}\diagup COC_6H_5\\ \diagdown SC_6H_5\end{matrix}$$

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



$$(CH_3)_2\overset{+}{S}\text{-}\overset{\overset{CH_3}{|}}{C}HCOC_6H_5\ {}^{-}Br + C_6H_5SN(C_2H_5)_2 \xrightarrow{H_2C\begin{smallmatrix}\diagup X\\ \diagdown Y\end{smallmatrix}} \underset{VII}{\begin{matrix}X\diagdown\\ Y\diagup\end{matrix}CH\text{-}CH_2\text{-}CH\begin{matrix}\diagup COC_6H_5\\ \diagdown SC_6H_5\end{matrix}} + \underset{VIII}{\begin{matrix}X\diagdown\\ Y\diagup\end{matrix}C(CH_2\text{-}CH\begin{matrix}\diagup COC_6H_5\\ \diagdown SC_6H_5\end{matrix})_2}$$

$CH_2\begin{matrix}\diagup X\\ \diagdown Y\end{matrix}$	VII	VIII	Mp (°C)	Analyses Found (Calcd) (%)			
				C	H	N	S
HSC_6H_5	93%		oil	72.28 (71.99)	5.25 (5.18)		17.24 (17.46)
HSC_2H_5	85%		130 —131[a]	53.31 (53.27)	5.93 (5.65)		22.63[a] (22.41)
$CH_2(COC_6H_5)_2$	70%		123.5—124	77.81 (77.57)	5.37 (5.21)		6.64 (6.89)
$CH_2(CO_2C_2H_5)_2$		63%	178.5—179.5	69.49 (69.36)	5.61 (5.66)		9.91 (9.99)
$CH_2(CN)_2$		75%	132.5—133.0	72.34 (72.51)	4.92 (4.86)	5.35 (5.13)	11.80 (11.71)
$CH_2\begin{matrix}\diagup COCH_3\\ \diagdown CO_2C_2H_5\end{matrix}$	45%		175.5—176	68.32 (68.09)	6.27 (5.99)		8.89 (8.64)

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). Dimethylphenacylsulfonium bromide (I) was prepared from dimethyl sulfide and phenacyl bromide in dry acetone. Similarly, dimethyl-α-methylphenacylsulfonium bromide (IV) was prepared from dimethyl sulfide and α-bromopropiophenone.[3]

Reaction of Dimethylphenacylsulfonium Bromide with N,N-*Diethylbenzenesulfenamide.* A mixture of dimethylphenacylsulfonium bromide (2.61 g, 0.01 mol) and *N,N*-diethylbenzenesufenamide (1.81 g, 0.01 mol) was stirred in dichloromethane (50 m*l*) 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-methylphenacylsulfonium Bromide with N, N-*Diethylbenzenesulfenamide and Dibenzoylmethane.* A mixture of dimethyl-α-methylphenacylsulfonium bromide (1.43 g, 0.005 mol) and *N,N*-diethylbenzenesulfenamide (0.91 g, 0.005 mol) was stirred in dichloromethane (50 m*l*) 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 m*l*). 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-methylphenacylsulfonium 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-methylphenacylsulfonium Bromide with N, N-*Diethylbenzenesulfenamide.* A mixture of dimethyl-α-methylphenacylsulfonium bromide (1.43 g, 0.005 mol) and *N,N*-diethylbenzenesulfenamide (0.91 g, 0.005 mol) was stirred in dichloromethane (50 m*l*) 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 m*l*). 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 m*l*), 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.

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[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.