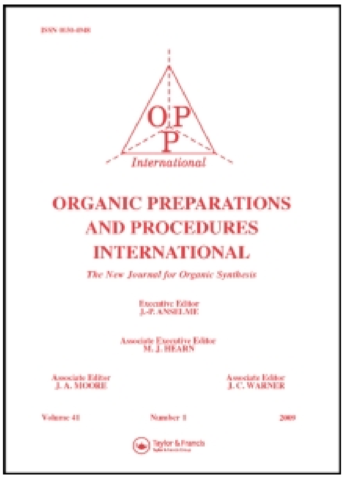

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METHYL AND ETHYL (DIMETHYLSULFURANYLIDENE) ACETATE

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METHYL AND ETHYL (DIMETHYLSULFURANYLIDENE)ACETATE

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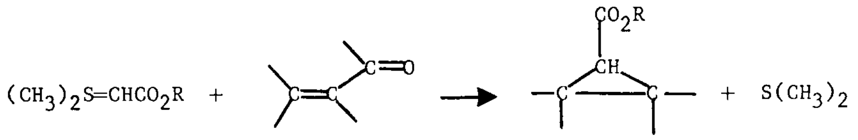
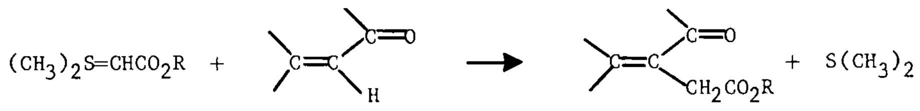
Various resonance-stabilized sulfonium ylides have been studied and their spectral properties have been described[1]. The synthetic usefulness of sulfoniocarboalkoxy ylides has generated increased interest in the chemical properties of these compounds[2,3]. Payne[3a] has recently reported the successful preparation of ethyl (dimethylsulfuranylidene)acetate in aqueous base. An alternate method using potassium *tert*-butoxide has also been described in the preparation of the methyl ester[4].

The ease with which these ylides may be prepared and purified in high yield, their stability during long term storage, and the wide variety of high yield nucleophilic reactions of these compounds characterize them as very useful synthetic intermediates.

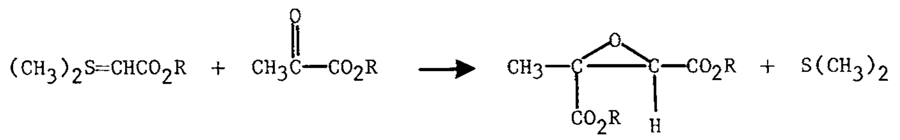
Reactions of the ylides were found to involve Michael attack on α,β-unsaturated compounds to give cyclopropane derivatives in aprotic solvents[3a,4] (eq. 1), acyclic unsaturated products in alcohols[3b,4] (eq. 2), and epoxy esters and other miscellaneous compounds in various solvents[3d], (eq. 3).



(eq. 1)



(eq. 2)



(eq. 3)

Considering their unusual versatility and potential in organic synthesis, useful methods of preparation and purification of these ylides on a preparative scale are recorded here. Both the tosylate and bromide sulfonium salts could be prepared in good yields, although the scheme for the bromide salt is shorter (cf. eq. 4 - 6).

$$HSCH_2COOR \xrightarrow[2)\ (CH_3)_2SO_2]{1)\ \overset{+}{Na}\overset{-}{O}R/ROH} CH_3{-}S{-}CH_2COOR \qquad (52\%) \qquad (eq.\ 4)$$

$$CH_3{-}S{-}CH_2COOR \xrightarrow{CH_3OTs} (CH_3)_2\overset{+}{S}CH_2COOR\ \ {}^{-}OTs \ (91\%) \qquad (eq.\ 5)$$

$$BrCH_2COOR \xrightarrow{S(CH_3)_2} (CH_3)_2\overset{+}{S}CH_2COOR \quad Br^{-} \ (80\text{-}90\%) \qquad (eq.\ 6)$$

Methyl and ethyl esters of both salts generate the corresponding ylides equally well in aqueous base as in potassium *tert*-butoxide (Table I). However, for large scale work the use of an aqueous base[3a] is more satisfactory.

Table I

Results of Ylide Formation

$$\overset{-}{X}\quad (CH_3)_2\overset{+}{S}CH_2COOR \xrightarrow{\text{base}^-} (CH_3)_2S{=}CHCO_2R$$

X	R	Base	Yield
OTs	CH_3	$\overset{+}{K}\ \overset{-}{O}Bu^t/HOBu^t$	77%
OTs	CH_3	12.5N NaOH/Sat'd Na_2CO_3	64%
Br	CH_3	"	51%
Br	C_2H_5	"	88%[a]

[a] Yield reported as 95% in reference 3a.

The ylides were purified by distillation using a continuous falling film molecular still. The methyl ester of the ylide was collected as a clear oil which readily crystallized in the cooled receiving flask (70% yield). The ethyl ester was collected as a clear oil in 80% yield.

Experimental

Methyl-S-methyl Mercaptoacetate. Methyl-S-methyl mercaptoacetate was prepared from methyl mercaptoacetate and dimethyl sulfate, according to earlier procedures[5], 52%, bp 65-68° (18 mm), lit.[6] bp 60-62° (20 mm).

Methyl Dimethylsulfonium Acetate p-Toluenesulfonate. The preparation of this compound from methyl-S-methyl mercaptoacetate and methyl *p*-toluenesulfonate has been described[5]. The salt (91%, mp 71-73°) is sufficiently pure for further use without recrystallization, and is extremely hygroscopic.

Carbomethoxymethyl Dimethylsulfonium Bromide. A solution of 116 g (0.758 mole) of methyl bromoacetate and 59 g (0.923 mole) of dimethyl sulfide in 220 ml of acetone was stored at <-10° for three days. A white solid precipitate was collected and dried, giving 120 g (74%) of the salt, mp 175-177°.

Carbethoxymethyl Dimethylsulfonium Bromide.[7a] Using the same procedure as reported above 105 g (0.63 mole) of ethyl bromoacetate and 45.3 g (0.73 mole) of dimethyl sulfide reacted to yield 116.6 g (81%) of the bromide salt, mp 84-86°, (lit. mp 78-80°,[3a] 85-87° [8]).

Methyl (Dimethylsulfuranylidene)acetate. Method 1. The preparation of this ylid from tosylate salt has been reported[5]. The crude ylidewas a yellow oil (77%) which could be distilled (*vide infra*). Method 2.[3a] A mixture of 65.2 g (0.213 mole) of the tosylate salt in 350 ml of chloroform was cooled to 5-10° (ice bath). While vigorously stirring, 140 ml of saturated potassium carbonate solution and 18 ml of 12.5N sodium hydroxide was added. The reaction mixture was stirred for 15 min at 10°, then allowed to warm up to 20°C and stirred for an additional 15-20 min. The salt formed was filtered and washed with chloroform. The *upper* chloroform layer of the filtrate was separated and dried over sodium sulfate. When the chloroform was removed, 17.7 g (64%) of the ylide remained as a yellow oil.

Using the same procedure as above, 79.3 g (0.368 mole) of the bromide salt was converted to 24.9 g (51%) of the methyl ylide.

Ethyl (Dimethylsulfuranylidene)acetate.[7b] Using Method 2 above, 115 g (0.50 mole) of the bromide salt was converted to 64.9 g (88%) of the ethyl ylide.

Distillation Apparatus. The falling film molecular distillation apparatus used consists of a needle-valve controlled capillary inlet, a degassing chamber, a two foot spiral heated column, and receiving outlets for distilled and undistilled material. The inner core of the spiral column is heated by vapor (acetone or dichloromethane) and the outer wall of the apparatus is cooled by air (room temp.) or cooled nitrogen gas (-10° to room temp.). The distillation is carried out under high vacuum, 0.003 to 0.05 micron.

Distillation

(1) Methyl Ylide. In the distillation flask was placed 11.83 g of the methyl ylide. The inner core was heated to 40° (dichloromethane vapor), while the outer jacket was cooled to 10 ± 5°. The distillate, a clear oil which crystallized in the cooled receiving flask (ice bath) 8.24 g (70%), melted over a 2° to 3° range between 15° and 19°. The undistilled material collected weighed 0.51 g and 3.06 g was left behind on the column. The infrared spectrum showed strong absorption at 1621 cm^{-1} ($C{=}C$). The proton nmr spectrum was both solvent and temperature[4] dependent, 2.77 ppm ($\underset{\sim}{CH_3}S\text{-}$) (s), 2.87 ($-\underset{\sim}{CH}{=}C$) (s), and 3.55 ppm ($-COO\underset{\sim}{CH_3}$) (s) ($C\underset{\sim}{H}Cl_3$) and 2.02 ppm ($\underset{\sim}{CH_3}S\text{-}$ minor isomer) (s), 2.32 ppm ($\underset{\sim}{CH_3}S\text{-}$ major isomer) (s), 3.02 ppm ($-\underset{\sim}{CH}{=}C$) (s), and 3.62 ppm ($-COO\underset{\sim}{CH_3}$) (s) (benzene).

Anal. Cal'd. for $C_5H_{10}O_2S$: C,44.74; H,7.51. Found: C,44.38; H,7.65.

(1) Ethyl Ylide. Starting with 52.47 g of the ethyl ylide using same procedure as above, 42.39 g (80%) of the pure ylide was collected as a clear oil. The undistilled material weighed 6.75 g while that remaining on the column weighed 3.35 g.

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