Solvolysis of Sulphonium Biscarbonyl Ylides

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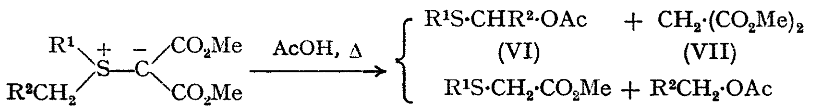
Summary Sulphonium bismethoxycarbonylmethylides react with acids by a Pummerer-type reaction and by nucleophilic substitution on sulphonium salts formed by protonation of the ylides; the product distributions depend on both the ylides and acidity of solvents.

WHILE alkyl- or aryl-sulphonium phenacylides in various solvents have been known to undergo a Pummerer-type[1,2] intramolecular cyclic rearrangement,[3] the reaction of alkylsulphonium biscarbonylmethylides has received little attention. We describe the reactions of alkylsulphonium bismethoxycarbonylmethylides in various acids, which proceed in two different ways depending on the structure of the ylides and the acidities of the acids.

The sulphonium bismethoxycarbonylmethylides (I)—(V), prepared[4,5] by the photolysis of dimethyl diazomalonate with the corresponding sulphides, were heated in acetic acid at 80° for 12 h in sealed tubes. Analysis of the products showed that acetolysis of these ylides may be classified into two categories, depending on the structures of the ylides. Sulphonium bismethoxycarbonylmethylides, (I) and (II), bearing an α-carbonyl group in the sulphonium portion, gave equimolar amounts of alkoxycarbonyl(ethylthio)-methyl acetate (VI) and dimethyl malonate (60—80%). Other ylides (III)—(V), not bearing electron-withdrawing substituents, gave methyl (alkylthio)acetates (VIII) and alkyl acetates (IX) (40—60%).



(I) $R^1 = Et, R^2 = CO_2Me$
(II) $R^1 = Et, R^2 = CO_2Et$
(III) $R^1 = Me, R^2 = H$
(IV) $R^1 = Et, R^2 = Me$
(V) $R^1 = Me, R^2 = Ph$

The former process may be regarded as a type of Pummerer reaction. Thus, in the presence of acid, the starting ylides may be in an equilibrium with the protonated sulphonium salts (A) and the less stable isomeric ylides (B) in which the contribution from the ylene structure (B′) is more important. Nucleophilic attack of AcO⁻ on the ylenic carbon atom would afford the acetate (VI), leaving

TABLE 1

Solvolysis of sulphonium ylide (I) *in various acids at* 110°, 15 *h*

RCO_2H		Pummerer products (%)		Substitution product
R	pK_a	$\mathrm{EtS{\cdot}\underset{O{\cdot}COR}{CH}{\cdot}CO_2Me}$	$CH_2{\cdot}(CO_2Me)_2$	$S{\cdot}(CH_2{\cdot}CO_2Me)_2$
CF_3	0·23	a	Trace	53[b]
$CHCl_2$	1·26	a	Trace	33
CH_2Cl	2·87	8	19	26
$CH_2{\cdot}CH_2Cl$	3·98	25	50	18
Me	4·76	57	54	5
Et	4·87	57	54	4

[a] The corresponding product could not be detected (g.l.c.).
[b] Contained 12% $EtS{\cdot}CH_2{\cdot}CO_2Me$.

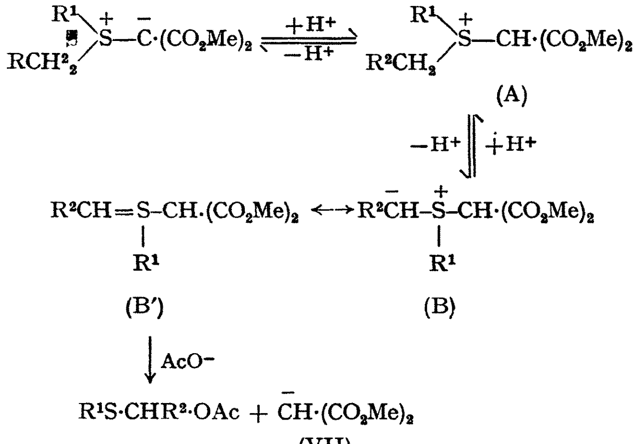
TABLE 2

Solvolysis of sulphonium ylide (III) *in various solvents at* 135°, 6 *h*

RH		Pummerer product (%)		Substitution product
R	pK_a	$MeS{\cdot}CH_2R$	$CH_2{\cdot}(CO_2Me)_2$	$MeS{\cdot}CH_2{\cdot}CO_2Me$
$ClCH_2{\cdot}CH_2{\cdot}CO_2$	3·98	trace	trace	44
$MeCO_2$	4·76	5·4	13	42
$EtCO_2$	4·87	34	31	18
PhO	10·0	a	20	4

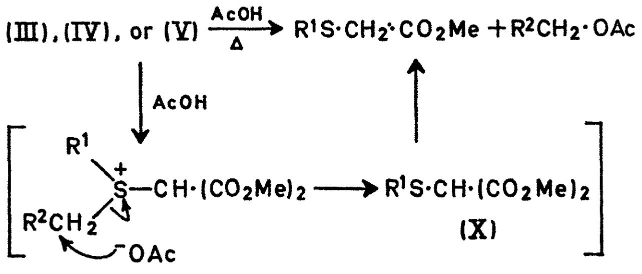
[a] The product corresponding to $MeS{\cdot}CH_2{\cdot}OPh$ could not be detected (g.l.c.).

the carbanion $^{-}CH{\cdot}(CO_2Me)_2$ which is converted into the malonate (VII) (see Scheme 1). Similar attack on the carbanion of the starting ylides may be unfavourable, because the process involves the loss of the poor leaving group $^{-}CH{\cdot}CO_2Me$.



SCHEME 1

The second type of acetolysis may be interpreted by nucleophilic attack of carboxylate anion on sulphonium salts which are formed by protonation of the ylides, giving (alkylthio)malonates (X) which are converted into the (alkylthio)acetates (VIII). Support for these mechanisms is furnished by the nucleophilic reaction of ethylmethylphenylsulphonium perchlorate[6] with acetate which gave methyl and ethyl acetate together with ethyl or methyl phenyl sulphide, and by the loss of one alkoxycarbonyl group from dimethyl (ethylthio)malonate to give methyl (ethylthio)acetate on heating in acetic acid (see Scheme 2).



SCHEME 2

It is obvious that methylene group of R^2CH_2 in the ylides (III)—(V) is less acidic compared with that in the ylides (I) and (II). The concentration of the corresponding less stable ylides (B) is much smaller in acetic acid but the sulphonium salts (A) may be present in considerable concentrations. Consequently, acetolysis of the ylides (III)—(V) occurs by substitution on sulphonium salts. If these rationalizations are correct, the substitution process should occur even with the ylides (I) and (II) in sufficiently strong acids, while in weaker acids the ylides (III)—(V) might afford the Pummerer-type reaction products (see Tables 1 and 2).

As expected, these results show that the Pummerer-type reaction is favoured in weaker acids, and the substitution mechanism in stronger acids.

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