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PREPARATIVE AND STRUCTURAL STUDIES ON CERTAIN SULPHUR-YLIDES

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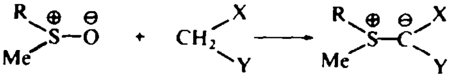
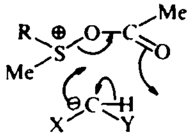
Abstract—A novel route to sulphonium ylides, which consists in condensation of sulphoxides with active methylene compounds, gives stable, crystalline products I–XIII listed in Tables 1 and 2. NMR spectra of these ylides (Figs 1–4) show remarkable temperature-dependence, the implications of which with respect to conformational equilibria have been discussed. Steric and electronic effects of aromatic Me groups of mesitoylmethylide XVI result in an equilibrium XVIA ⇌ XVIB as evidenced by the NMR spectrum (Fig. 5). The pyramidal structure of the sulphur atom in ylides XVII and XVIII is indicated by non-equivalence of two protons of the methylene group attached to the sulphur atom (Figs 6 and 7). Several novel sulphonium phenacylides have been prepared (Table 3) and pairs of these ylides were subjected to exchange. The results of mass spectrometry are summarized in Table 4. The failure to obtain sulphonium ylides in optically active form are discussed on the basis of these findings.

IN CONTINUATION of the work on stable sulphur ylides,[1,2] the condensation of sulphoxides with active methylene compounds has proved a convenient method of obtaining sulphonium ylides. The NMR spectra of compounds I and III thus obtained as well as that of XVI prepared by the published method[1] have aroused interests in assigning possible conformation of compounds of this class.

Condensation of sulphoxides with active methylene compounds.[3,4] In a search for methods of preparing sulphur-ylides under less basic conditions than those previously recorded,[1] the reaction of sulphoxides with active methylene compounds has been found to afford the desired products I–XIII in fair to good yields as listed in Table 1.


I–XIII


XIV

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[1] [a] H. Nozaki, K. Kondô and M. Takaku, *Tetrahedron Letters* 251 (1965); [b] H. Nozaki, M. Takaku and K. Kondô, *Tetrahedron* **22**, 2145 (1966). For analogous findings independently made, see [c] K. W. Ratts and A. N. Yao, *J. Org. Chem.* **31**, 1185 (1966); [d] A. W. Johnson and R. T. Amel, *Tetrahedron Letters* 819 (1966); [e] B. M. Trost, *J. Am. Chem. Soc.* **89**, 138 (1967).

[2] [a] H. Nozaki, D. Tunemoto, S. Matubara and K. Kondô, *Tetrahedron* **23**, 545 (1967). For a review article, see [b] H. Nozaki, M. Takaku, D. Tunemoto, Y. Yamamoto and K. Kondô, *Nippon Kagaku Zasshi* **88**, 1 (1967).

[3] A preliminary account of this part has appeared: H. Nozaki, Z. Morita and K. Kondô, *Tetrahedron Letters* 2913 (1966).

[4] For independent observation on closely related reactions, see [a] W. J. Middleton, E. L. Buhle, J. G. McNally, Jr., and M. Zanger, *J. Org. Chem.* **30**, 2384 (1965); [b] A. Hochrainer and F. Wessely, *Monatsh. Chem.* **97**, 1 (1966); A. Hochrainer, *Ibid.* **97**, 53 (1966); A. Hochrainer, *Oesterreichische Chemiker-Zeitung* **67**, 297 (1966); [c] R. Gompper and H. Euchner, *Chem. Ber.* **99**, 527 (1966); [d] R. Oda and Y. Hayashi, *Nippon Kagaku Zasshi* **87**, 1110 (1966).

The substituents X and Y were keto, ester or nitrile groups and the reaction was effected by either (a) heating the reaction components in acetic anhydride solution under reflux or (b) treating a triethylamine solution of both reactants with phosphorus pentoxide.[5] The respective sulphur ylides were obtained as stable crystalline solids, which showed characteristic frequencies of carbonyl or cyano group shifted ca. 100 cm^{-1} to lower wave number region. The two methods (a and b) were found to be complementary.

TABLE 1. YIELDS AND M.PS OF STABLE YLIDES PREPARED BY THE CONDENSATION OF SULPHOXIDES WITH ACTIVE METHYLENE COMPOUNDS

Compd. No.	R	Substituents X	Y	Method of condensation[a]	Yield (%)	M.p.
I	Me	Ac	Ac	b	13	168–169°
				c	60	
II	Ph	Ac	Ac	a	44	140–141°
				b	12	
III[b]	Me	Ac	Bz	a	40	109–110
IV[c]	Ph	Ac	Bz	a	27	138–139°
				c	20	
V	Ph	–CO$(CH_2)_3$CO–		a	20	124–125°
VI	Me	–$COCH_2C(CH_3)_2CH_2CO$		a	24	172–173°
VII	Ph	–$COCH_2C(CH_3)_2CH_2CO$–		a	27	138–139°
VIII	Me	Ac	COOEt	a	7	64–65°
				c	30	
IX	Ph	Ac	COOEt	a	21	60–61°
				c	10	
X	Me	CN	COOEt	b[d]	14	131–132
				c	21	
XI	Ph	CN	COOEt	b	11	oil
				c	20	
XII[e]	Me	CN	CN	b	11	99–100
XIII[e]	Ph	CN	CN	b	15	77–78°

[a] In the method (a) a mixture of the respective sulphoxide, CH_2XY and Ac_2O was heated at 80–100° In the method (b) a solution of the reactants in Et_3N was treated with P_2O_5 at 100°. In the method (c) a mixture of the corresponding ethoxysulphonium fluoroborate, NaCHXY and $CHCl_3$ was treated with NaH at room temp. See Experimental.

[b] See Ref. 1*d*.

[c] See Ref. 1*a*.

[d] The reaction mixture was vigorously stirred at room temp for 24 hr. At higher temp a black tar was produced.

[e] See Ref. 4*b* and 4*d*.

In the method (a) the principal side reaction was the formation of thiols, as first observed by Pummerer.[6] Another related reaction is the highly selective oxidation

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[5] For sulphilimine synthesis by analogous reaction, see D. S. Tarbell and C. Weaver, *J. Am. Chem. Soc.* **63**, 2939 (1941).

[6] [a] R. Pummerer, *Ber. Dtsch. Chem. Ges.* **43**, 1401 (1910). For the mechanism of the Pummerer reaction, see [b] S. Oae, T. Kitao and Y. Kitaoka, *J. Am. Chem. Soc.* **84**, 3366 (1962); [c] S. Oae, T. Kitao, S. Kawamura and Y. Kitaoka, *Tetrahedron* **19**, 817 (1963). *Cf* also [d] C. R. Johnson and W. G. Phillips, *Tetrahedron Letters* 2101 (1965).

TABLE 2. SPECTRAL AND ANALYTICAL DATA OF NOVEL SULPHONIUM YLIDES

Compd. No.	IR[a] cm^{-1}	UV_{max}^{EtOH} mμ (log ε)	Formula	Found C %	Found H %	Calc. C %	Calc. H %
I	1570	233 (4·05) 270 (4·16)	$C_7H_{12}O_2S$	52·2	7·6	52·5	7·6
II	1582	226 (4·19) 265 (4·08)	$C_{12}H_{14}O_2S$	64·9	6·5	64·9	6·4
V	1565	230 (4·24) 254 (4·34)	$C_{13}H_{14}O_2S$	66·4	6·2	66·7	6·0
VI	1539	258 (4·29)	$C_{10}H_{16}O_2S$	59·8	8·1	60·0	8·1
VII	1572	230 (4·19) 257 (4·29)	$C_{15}H_{18}O_2S$	68·4	6·9	68·7	6·9
VIII	1667 1548	227 (4·02) 258 (4·17)	$C_8H_{15}O_{3.5}S$[b]	48·3	7·7	48·2	7·6
IX	1665 1595	223 (4·29) 247 (4·13)	$C_{13}H_{16}O_3S$	61·6	6·6	61·9	6·4
X	2160 1625	224 (4·08)	$C_7H_{11}NO_2S$	48·3	6·5	48·6	6·4
XI	2180[c] 1660	271 (3·30)	$C_{12}H_{13}NO_2S$	59·8	5·6	61·3	5·6[d]

[a] Unless otherwise stated wave numbers of the characteristically shifted carbonyl and/or cyano group absorptions (Nujol) are given.

[b] The ylide VIII contained a half mole of crystalline water.

[c] IR was taken with a liquid film.

[d] NMR data of the ylides (Ref. 10), which have not been given in figures, are recorded here in the order of the compound number, temp. chemical shift in ppm from TMS (splitting pattern, relative weight, assignment): II, room temp. 2·43 (singlet, 6H, C-Me), 3·36 (singlet, 3H, S-Me), 7·5 (multiplet, 5H, aromatic); II, −20°, 2·43 (doublet with a separation of 6 c/s, 6H, C-Me), 3·38 (singlet, 3H, S-Me), 7·52 (sharp singlet, 5H, aromatic); IV, −62°, 2·48 (broad multiplet of line width of ca. 20 c/s, 3H, C-Me), 3·36 (singlet, 3H, S-Me), 7·5 (multiplet, apparently three sharp singlets, 10 H, aromatic). For NMR of IV at room temp. see Ref. 1*b*.

of alcohols by means of a mixture of DMSO and acetic anhydride.[7] The mechanisms of these two reactions point to the initial formation of acetoxysulphonium ion XIV. The presently observed sulphur-ylide formation also would presumably proceed *via* the attack by XIV on the active methylene compounds or the respective carbanions followed by the loss of acetic acid.

Such mechanistic interpretation has motivated development of the third method ((c) in Table 1), which consists in the condensation of ethoxysulphonium fluoroborates (XV) with the carbanions:

XV

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[7] J. D. Albright and L. Goldman, *J. Am. Chem. Soc.* **87**, 4214 (1965).

The salts XV were prepared by the known method[8] and the condensation was carried out in chloroform solution in the presence of one equivalent of sodium hydride at room temperature. This modification requires the least vigorous reaction conditions, but the yields have not been improved as much as expected.

Attempted condensation of diphenyl sulphoxide did not produce any appreciable amounts of sulphur-ylides. Acid-catalyzed reaction of DMSO and active methylene compounds in the presence of dicyclohexylcarbodiimide[9] also failed to occur in the expected way.

NMR spectra of the stable sulphonium ylides. The NMR spectrum (Fig. 1)[10] of diacetylmethylide I at room temperature showed magnetic equivalence of two acetyl Me groups. The C-Me signal experienced splitting into 1:1 doublet at −60° (Fig. 2), the critical coalescence temperature being ca. −25°. Practically no change was observed with respect to S-Me's at these temperatures.[11] On the basis of previously recorded findings[12] and those of our own,[2b] the most reasonable account for this observation would involve a rapid exchange IA $\rightleftharpoons$ IA′ at room temperature.

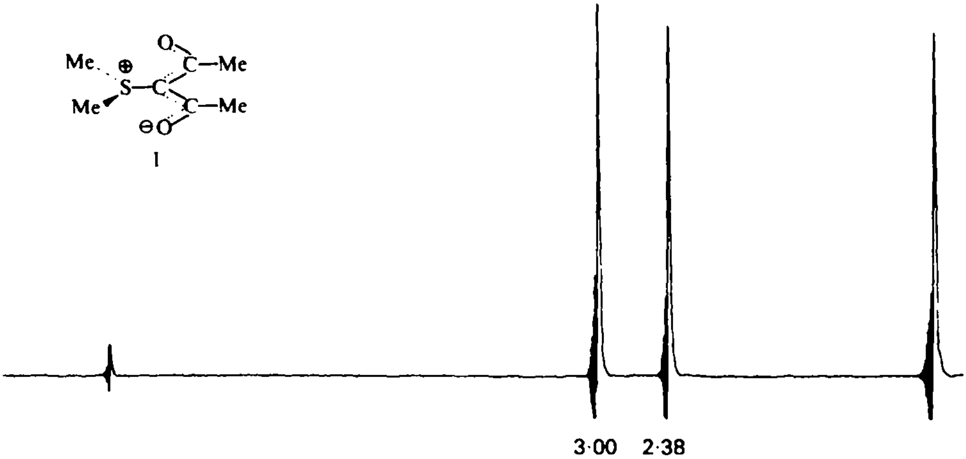


FIG. 1. NMR spectrum of I at room temp

The exchange may occur through either internal rotation around the S-C bond or inversion on the S atom. The latter interpretation seems to be more plausible and will be discussed again in the following section. An alternative explanation might be an exchange IB $\rightleftharpoons$ IB′, *viz.*, the internal rotation of two C—C bonds and the simultaneous inversion at the S atom, which appears to be less likely. The absence of temperature-dependence of S-Me signal rules out the possibility that an extensive exchange IA $\rightleftharpoons$ IB $\rightleftharpoons$ IC etc. is occurring at room temperature.

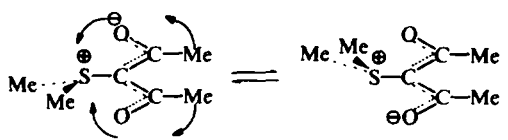
[8] [a] H. Meerwein, E. Battenberg, H. Gold, E. Pfeil and G. Willang, *J. Prakt. Chem.* **154**, 83 (1939); [b] C. R. Johnson and D. McCants, Jr., *J. Am. Chem. Soc.* **87**, 5404 (1965).

[9] [a] K. E. Pfitzner and J. G. Moffatt, *J. Am. Chem. Soc.* **87**, 5661, 5670 (1965); [b] M. G. Burdon and J. G. Moffatt, *Ibid.* **87**, 4656 (1965); [c] K. E. Pfitzner, J. P. Marino and R. A. Olofson, *Ibid.* **87**, 4658 (1965).

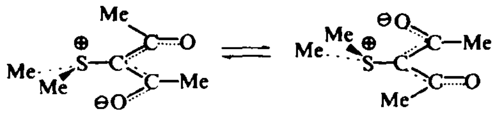
[10] The NMR spectra of this paper were taken on Varian A60 and JEOLCO JNM-3H-60 machines in $CDCl_3$ solns with TMS internal standard unless otherwise stated.

[11] The S-Me signals experienced slight paramagnetic shift at lower temperature. The reason is not clear as yet.

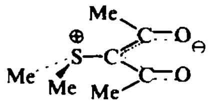
[12] K. W. Ratts, *Tetrahedron Letters* 4707 (1966)



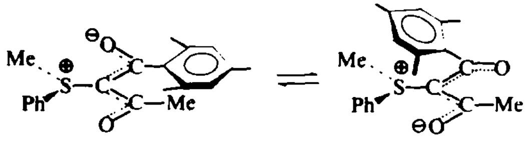
IA (*cis,cis*) IA′



IB (*cis,trans*) IB′



IC (*trans,trans*)



XVIA XVIB

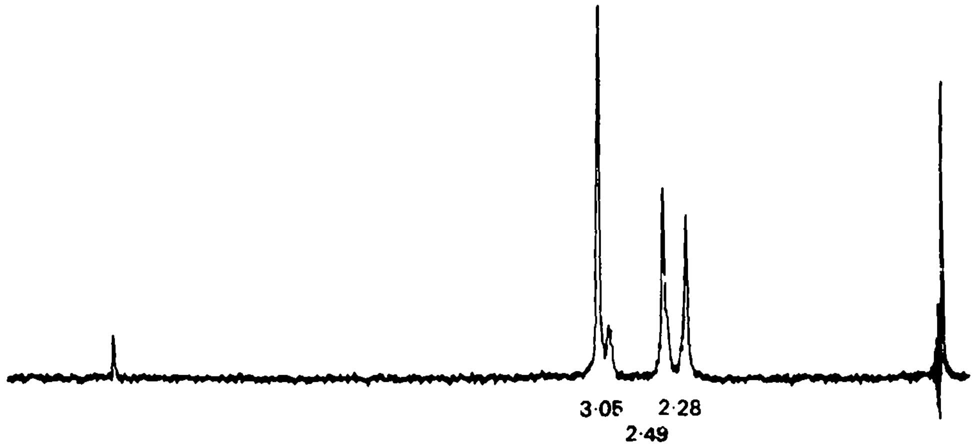


Fig. 2. NMR spectrum of I at −60°.

The existence of van der Waals repulsion between the two C-Me's could be expected to destabilize the *cis,cis* arrangement of the $O\cdots C\cdots C\cdots C\cdots O$ system in IA. The *trans,trans* conformation (IC) is devoid of this strain, but the strong interaction between S- and C-Me's arises instead. In addition, stabilization due to Coulomb interaction[13] between S atom and carbonyl oxygen atoms must be far less important in IC than IA. The conformation IA can be relieved from the steric repulsion between both C-Me's by possible valence angle distortion originating from the Coulomb attraction as indicated in the formula IA and also by slight rotation of two acetyl groups around the ylide carbon to carbonyl carbon bond with respect to each other.

Analogous NMR spectra and temperature dependence have been observed with other diketone-type ylides II–IV. Those of the ylide III have been given in Figs 3 and 4. Notably, the C-Me signals of acetylbenzoylmethylides III and IV showed

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[13] For the significance of this effect established in phosphorus ylides, see A. J. Speziale and K. W Ratts. *J. Am. Chem. Soc.* **87**, 5603 (1965).

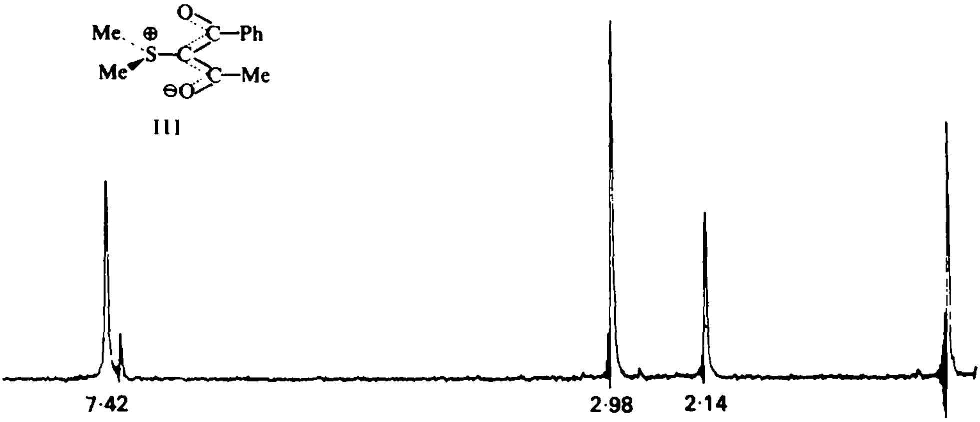

FIG. 3. NMR spectrum of III at room temp.

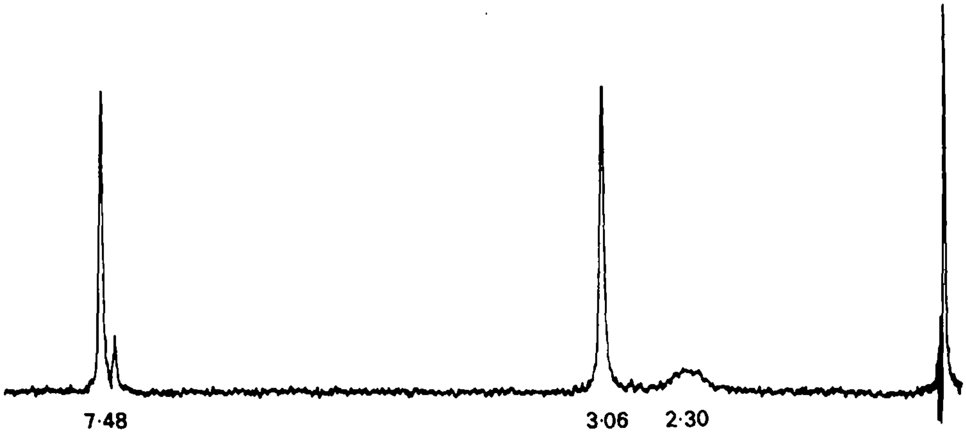

FIG. 4. NMR spectrum of III at −60°.

normal chemical shift values as expected for an acetyl Me group. The NMR spectrum of an acetylmesitoylmethylide XVI (Fig. 5) indicated that this was a 1:1 mixture of conformers XVIA and XVIB. The spectrum remained practically unchanged between +50° and −50°. The anisotropy effect on acetyl Me protons in XVIA is remarkable, whereas the shielding of S-Me group in XVIB is less significant. Such anomalous behaviours of mesitoylmethylide XVI must be ascribed to the steric and electronic effects of ring Me groups.[14] The absence of any appreciable shielding effect on the acetyl Me groups of ylides III and IV would reasonably be explained by means of the skewed *cis,cis* arrangement of O⋯C⋯C⋯C⋯O group with slightly twisted benzoyl benzene ring.

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[14] Probably, the aromatic carbon attached to the carbonyl is electron-rich and the Coulomb attraction between this aromatic carbon and sulphonium S-atom is acting to stabilize the conformer XVIB. Previously recorded stabilization of such *cis,trans* alignment of O⋯C⋯C⋯C⋯O group as XVIB was that analogous to the one of ylides XVII and XVIII (Figs 6 and 7) to be described below. See Refs 1*b* and 2*a*.

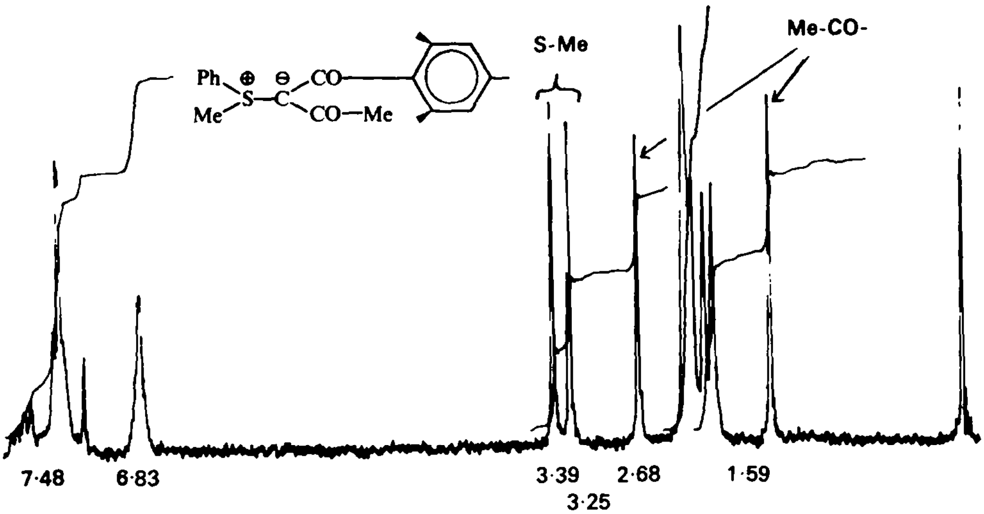

FIG. 5. NMR spectrum of XVI at room temp.

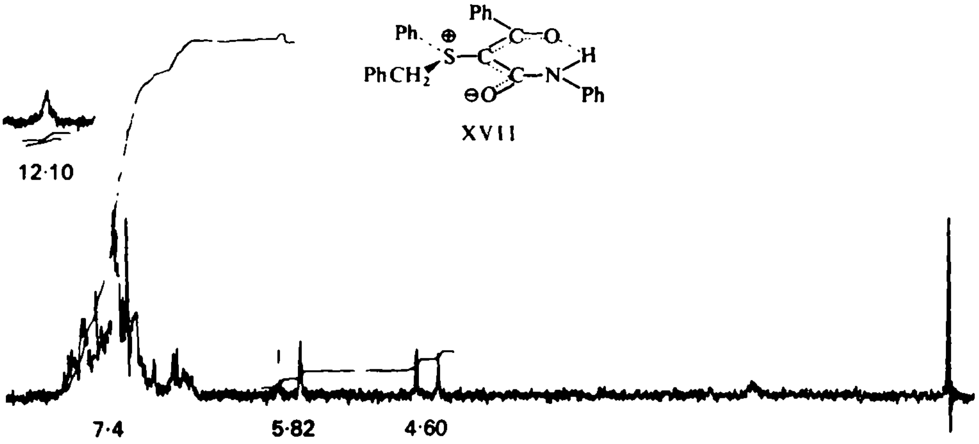

FIG. 6. NMR spectrum of XVII at room temp.

Pyramidal structure of sulphur atom in sulphonium ylides. Failures in resolving sulphonium ylides were recorded previously.[1b] Remarkably, however, the pyramidal structure of trigonal S atom as established in sulphoxides, sulphilimines and sulphonium salts[15] has been confirmed by NMR spectra of novel, crystalline sulphonium ylides XVII and XVIII (Figs 6 and 7). These ylides XVII and XVIII were prepared by carbamoylation of metastable, oily ylides XIX and XX, respectively, *in situ*.[16]

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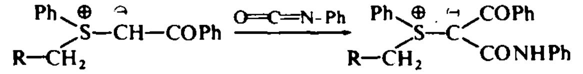
[15] [a] For sulphoxides, see K. Mislow, M. M. Green, P. Laur, J. T. Melillo, T. Simmons and A. L. Ternay, Jr., *J. Am. Chem. Soc.* 87, 1958 (1965). [b] For sulphilimines, see J. Day and D. J. Cram, *Ibid.* 87, 4398 (1965). [c] For sulphonium salts, see M. P. Balfe, J. Kenyon and H. Phillips, *J. Chem. Soc.* 2554 (1930).

[16] Analogous NMR evidences for the pyramidal structure of S atom in sulphonium ylides have been rerecorded very recently by K. W. Ratts (Ref. 12) and also by A. Hochrainer and W. Silhan, *Monatsh. Chem.* 97, 1477 (1966).



R = Ph (XIX), Me (XX) R = Ph (XVII), Me (XVIII)

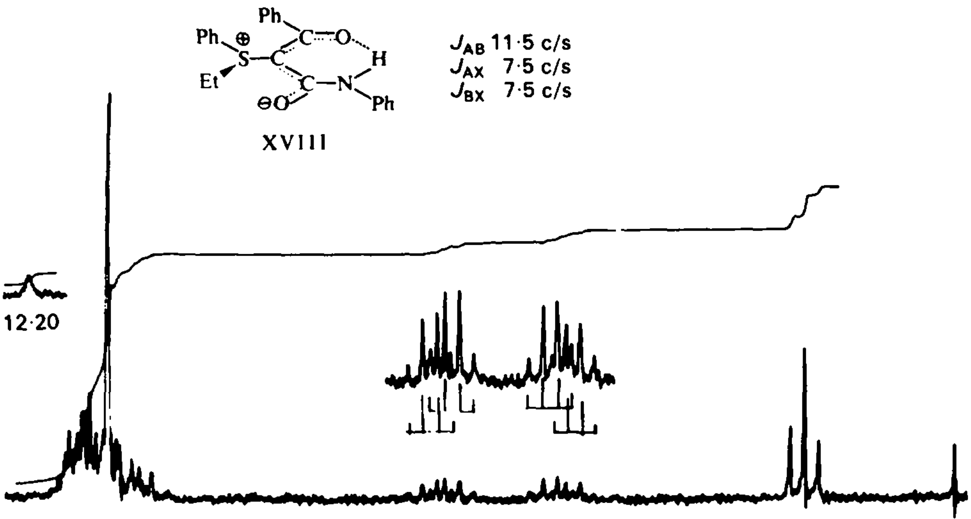
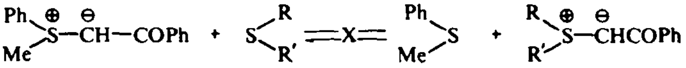
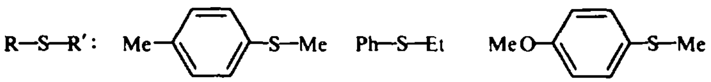


FIG. 7. NMR spectrum of XVIII at room temp.

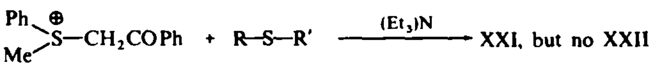
The next problem concerns the facile racemization of phenacylides such as XXI.[1b] The possibility of this occurring through ylide ⇌ carbene equilibrium was excluded by the complete absence of such ylide-sulphide exchange as follows:



XXI XXII

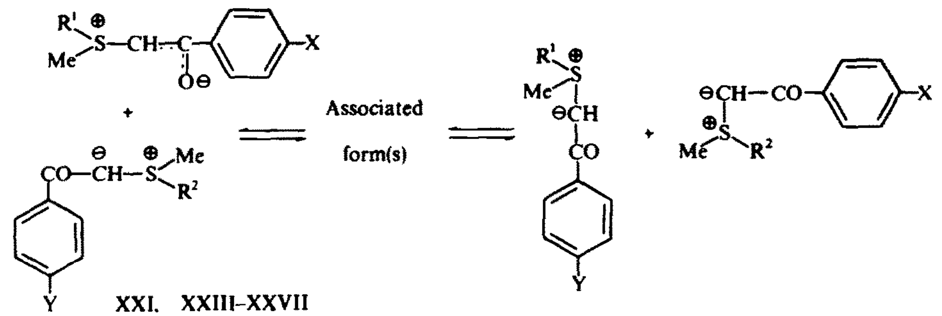


No exchange was again observed in the formation of the ylide XXI from the corresponding sulphonium salt in the presence of added, foreign sulphide (R-S-R'):



$$\mathrm{Ph(Me)\overset{\oplus}{S}{-}CH_2COPh} + \mathrm{R{-}S{-}R'} \xrightarrow{(\mathrm{Et_3})\mathrm{N}} \text{XXI, but no XXII}$$

Certain pairs of ylides listed in Table 3 were subjected to heating or basic treatment and the resulting ylide mixtures were analyzed mass-spectrometrically. The results summarized in Table 4 showed that following ylide-exchange did proceed possibly *via* associated form(s):



XXI, XXIII–XXVII

The exchange may be accompanied with inversion of the configuration at the S atom and accordingly be considered to be one of the possible accounts for the facile racemization. Mol wt determination (cryoscopic in benzene and vapour pressure determination in benzene and in acetone) of the ylide XXI, however, consistently gave values showing that this was nearly monomeric in solutions at room temperature, *viz.*, the concentration of associated species should be low in the equilibrium.

The observed ylide-exchange does not exclude the possibility of simple inversion[17] on the S atom without resource to the associated form(s). This rapid inversion of the configuration of the trigonal S atom would certainly be frozen out at lower temperature as indicated by the NMR spectra mentioned above.[18]

EXPERIMENTAL

All m.ps and b.ps were uncorrected. Microanalyses were performed at the Elemental Analyses Centre of Kyôto University and by Mrs. K. Fujimoto of Prof. K. Sisido's Laboratory.

General methods for the preparation of sulphonium ylides from sulphoxides and active methylene compounds are illustrated by the following 4 examples. The yields and properties of products given in Tables 1 and 2 are not reproduced.

Methylphenylsulphonium diacetylmethylide II *by the method* (a). A mixture of methyl phenyl sulphoxide (1·00 g, 7·14 mmoles), acetylacetone (0·72 g, 7·14 mmoles) and Ac_2O (ca. 20 g, 0·2 mole) was heated at 80–100° for 20 hr. The deep yellow mixture was diluted with 20% NaOH aq at 0° until the soln became basic (pH 10) and then extracted with $CHCl_3$. After drying ($MgSO_4$) the soln was concentrated *in vacuo* to afford a yellow solid, which was recrystallized from a 6:1 mixture of benzene and hexane.

Dimethylsulphonium carboethoxycyanomethylide (X) *by the method* (b). A mixture of DMSO (1·0 g, 12·8 mmoles), ethyl cyanoacetate (1·45 g, 12·8 mmoles), P_2O_5 (1·5 g, 13 mmoles) and Et_3N (20 g, 0·2 mole) was allowed to stand at room temp for 2 hr and another aliquot of P_2O_5 (1·5 g, 12·8 mmoles) was added. After standing for a total of 24 hr at room temp, the solvent was removed by decantation. Work up of the residue gave the ylide X as colourless plates (from EtOH). Other preparations were usually carried out on a boiling water-bath.

Dimethylsulphonium diacetylmethylide (I) *by the method* (c). A $CHCl_3$ (20 ml) suspension of sodioacetylacetone prepared from acetylacetone (1·03 g, 10·3 mmoles) and equivalent amount of NaH[19] was added in one portion to a soln of ethoxydimethylsulphonium fluoroborate[8] (2·0 g, 10 mmoles) in $CHCl_3$ (30 ml). Another equiv of NaH was added and the mixture was stirred for 20 hr at room temp. The mixture was filtered from sodium fluoroborate, the filtrate was concentrated *in vacuo* and the residue was recrystallized from a mixture of benzene and hexane.

Methylphenylsulphonium carboethoxycyanomethylide (XI) *by the method* (c). A $CHCl_3$ soln of ethoxymethylphenylsulphonium fluoroborate prepared from methyl phenyl sulphoxide (1·4 g, 0·01 mole) and

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[17] D. Darwish and G. Tourigny, *J. Am. Chem. Soc.* **88**, 4303 (1966).

[18] Calculation based on the C-methyl signal separation (12 c/s, Fig. 2) indicated that the average life time of each conformer of the ylide I was in the order of 0·02 sec at −25°.

[19] A 50% dispersion of sodium hydride in mineral oil was used without removing the oil.

TABLE 3. NOVEL YLIDES SUBJECTED TO YLIDE-EXCHANGE

Compd No.	R^1 or R^2	X or Y	M.p.	MS mol. wt.	IR^{Nujol} cm^{-1}	UV_{max}^{EtOH} mμ (log ε)	Formula	Found C%	Found H%	Calcd. C%	Calcd. H%
XXIII	*p*-MeC_6H_4	H	111°	256	1590 (m) 1500 (s)	229 (4·35) 310 (4·00)	$C_{16}H_{16}OS$	75·0	6·2	75·0	6·4
XXIV	Ph	Cl	132°	276	1580 (m) 1510 (s)	236 (4·25) 314 (4·09)	$C_{15}H_{13}ClOS$	65·0	4·9	65·1	4·7
XXV	*p*-$MeOC_6H_4$	H	110°	272	1600 (s) 1510 (s)	243 (4·35) 307 (3·96)	$C_{16}H_{16}O_2S$	71·0	6·2	70·6	5·9
XXVI	Ph	OMe	119°	272	1608 (m) 1588 (m), 1500 (s)	253 (4·12) 308 (4·21)	$C_{16}H_{16}O_2S$	70·5	6·0	70·6	5·9
XXVII	*p*-$MeOC_6H_4$	OMe	110°	(302)[b]	1608 (m) 1585 (m), 1500 (s)	247 (4·25) 293 (4·25)	$C_{17}H_{18}O_2S$	67·3	6·3	67·3	6·0

[a] All ylides have been obtained from the respective sulphonium salts by the basic treatment previously reported (Ref. 1).

[b] See footnote *d* of Table 4.

TABLE 4. MASS SPECTROMETRIC DATA ON YLIDE-EXCHANGE

Ylide pair	Treat-ment^{a}	*m/e* (Abundance in % of the base peak)				Base peak (Assignment)
XXIII + XXIV		290	276	256	242	124
	A	(0·67)^{b}	(5·05)	(6·99)	(0·0)	$(PhSMe)^{\oplus}$
	B	(10·4)^{f}	(10·4)	(13·4)	(25·2)^{f}	
	C	(3·66)^{c}	(9·52)	(16·9)	(5·97)^{f}	
XXIV + XXV		306	276	272	242	139
	A	(0·0)	(0·50)	(2·49)	(0·0)	$(COC_6H_4Cl)^{\oplus}$
	B	(0·0)	(0·76)	(1·34)	(0·0)	
	C	(0·14)^{c}	(1·58)	(1·52)	(0·67)^{f}	
XXV + XXVI		302^{d}	272	242		154
	A	(0·0)	(9·68)	(0·0)		$(MeOC_6H_4SMe)^{\oplus}$
	B	(0·0)	(5·87)	(1·26)^{f}		
XXV + XXVI + XXI + XXVII	A^{e}	(0·0)	(1·40)	(1·68)		

[a] Treatment A: an equimolar mixture of the ylides was finely ground together and was introduced into mass spectrometer directly.

Treatment B: a solution of the ylides (0·1 mmole each) in benzene (30 ml) was heated under reflux for 2 hr.

Treatment C: a solution of the ylide (0·1 mmole each), Et_3NHCl (50 mg) and Et_3N (30 mg) in EtOH (20 ml) was stirred at room temp for 2 hr.

[b] An M + 14 peak (256) was also observed in the MS of XXI, whose mass number was 242. The appearance of 290 peak in the run A can not be ascribed to ylide exchange occurring in the mass spectrometer.

[c] Peaks arising from the ylide-exchange products.

[d] The molecular peak 302 was not observed even with the authentic ylide XXVII either.

[e] This is a reference mixture consisting of equimolar amount of the four ylides. The calculated degree of exchange in the sample subjected to treatment B was found to be ca. 8%.

triethyloxonium fluoroborate[8a] (1·9 g, 0·01 mole) was treated with an equiv amount of ethyl sodiocyanoacetate and NaH and the mixture was stirred at room temp for 20 hr. Working up the product, followed by chromatographic separation on a column of basic alumina with a 1:1 mixture of benzene and $CHCl_3$ as an eluant, yielded the ylide XI.

In cases, where difficulties were encountered in separating the product, the elution chromatography on basic alumina proved to be effective.

Methylphenylsulphonium acetylmesitoylmethylide (XVI). To a suspension of methylphenyl(2,4,6-trimethylphenacyl)sulphonium bromide (2·0 g, 5·5 mmoles) in EtOH (100 ml) Et_3N (1·1 g, 11 mmoles) was added under stirring at 0–5°. The mixture was stirred at the same temp for 1 hr, diluted with water and extracted with $CHCl_3$. After drying ($MgSO_4$) and concentrating the extract *in vacuo*, the remaining viscous oil was dissolved in ether-hexane at room temp and then cooled at −70° to afford colourless crystals, which liquified at room temp. Repetition of this procedure 3 times gave an oily sample of *methylphenylsulphonium mesitoylmethylide* (1·33 g or 84%). IR (neat): 1520 cm^{-1}. UV_{max}^{EtOH} (log ε): 248 (4·00), 288 mμ (3·82) (shoulder). Correct analyses have not been obtained yet.

A soln of this oily ylide (0·6 g, 2·1 mmoles) and Ac_2O (0·2 g, 2·0 mmoles) in THF (20 ml) was heated at reflux for 6 hr. The mixture was diluted with water and extracted with $CHCl_3$. The extract was washed with water, dried ($MgSO_4$) and evaporated *in vacuo*. The residue solidified after standing for several hr at 0–5° and was recrystallized from AcOEt to afford 0·3 g (43%) of XVI, m.p. 116–117°. IR (Nujol): 1570 cm^{-1}. UV_{max}^{EtOH} (log ε): 270 mμ (4·22). (Found: C, 73·6; H, 6·6. $C_{20}H_{22}O_2S$ requires: C, 73·6; H, 6·8%.)

Benzylphenylsulphonium benzoyl(N-phenylcarbamoyl)methylide (XVII). To a suspension of benzylphenacylphenylsulphonium fluoroborate (1·0 g, 2·5 mmoles) and phenyl isocyanate (0·3 g, 2·5 mmoles) in THF (10 ml) a soln of Et_3N (0·5 g, 5 mmoles) in THF (7·5 ml) was added dropwise over a 5 min period at room temp. The reaction mixture was then treated with EtOH (0·1 g) in order to destroy unchanged phenyl isocyanate. Work up, followed by recrystallization from THF, afforded an analytical sample of XVII (0·14 g or 13%), m.p. 114–116°. IR (Nujol): 1645, 1630, 1525 cm^{-1}. UV$_{max}^{EtOH}$ (log ε): 238 (4·50), 285 mμ (4·32). (Found: C, 77·1; H, 5·5. $C_{28}H_{23}NO_2S$ requires: C, 76·7; H, 5·3%.)

Ethylphenylsulphonium benzoyl(N:phenylcarbamoyl)methylide (XVIII). This ylide was prepared by analogous treatment of ethylphenacylphenylsulphonium fluoroborate (3·0 g, 8·7 mmoles) with phenyl isocyanate (1·0 g, 8·7 mmoles) dissolved in THF (30 ml) and Et_3N (1·8 g, 18 mmoles) dissolved in THF (20 ml). Recrystallization of the product from THF afforded the ylide XVIII (2·53 g or 77%), m.p. 153–154°. IR (Nujol): 1644, 1596, 1509 cm^{-1}. UV$_{max}^{EtOH}$ (log ε): 239 (4·47), 285 mμ (4·41). (Found: C, 73·3; H, 5·7 $C_{23}H_{21}NO_2S$ requires: C, 73·6; H, 5·7%.)

All sulphonium salts required in the preparation of XVI, XVII and XVIII have been prepared in the standard way and were subjected to the above-mentioned treatment without isolation.

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