Stibonium and Bismuthonium Ylides. A Comparison with Arsonium and Other Ylides, also including the Crystal Structure of Triphenylarsonium Bis(phenylsulphonyl)methylide and Triphenylarsonium and Triphenylstibonium 4,4-Dimethyl-2,6-dioxocyclohexylides

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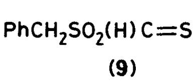
The spectra, dipole moments, *X*-ray structures, and chemistry (stability, hydrolysis, reactivity in Wittig reactions) of a number of stibonium ylides are compared with similar properties of their arsonium analogues. There is a close resemblance between the stibonium and arsonium ylides; this is explained in terms of intramolecular interaction betwen substituent oxygen atoms and the antimony or arsenic atoms. Attempts to prepare stibonium ylides from dichlorotriphenylantimony(v) led always to ylides contaminated with oxybis(triphenylantimony) dichloride. Other oxybis(triphenylantimony) derivatives were obtained from acid hydrolyses of stibonium ylides. Two bismuthonium ylides were also studied. In their case also there appears to be an intramolecular bismuth–oxygen interaction.

The properties of ylides are very dependent on the identity of the heteroatoms. The dipolar and nucleophilic character of the ylides appears to increase and their stability to decrease the lower the heteroatom stands in the Periodic Table;[1,2] see, for example, ylides (**1**)—(**4**). Arsonium ylides have been compared quite extensively with phosphonium ylides,[2,3] but, because until recently only one stibonium ylide (**3**)[4] had been isolated and one other obtained in solution,[5] and only one bismuthonium ylide (**4**) had been described,[6] only one comparative study of stibonium and bismuthonium ylides has been recorded.[1] A recent improvement in the method of preparation of ylides from diazo compounds[7,8] has enabled the preparation and isolation of a number of new stibonium ylides (**5**)—(**12**)[7] and bismuthonium ylides (**13**) and (**14**).[8] (In all the formulae the ylidic bond is represented, for convenience, in the form of a double bond C=X; in all cases this is only one canonical form and other polar forms, such as $\overset{-}{C}$–$\overset{+}{X}$, contribute to a considerable extent to the structure of the ylides, as discussed in the subsequent text.)



(**1**) X = P
(**2**) X = As
(**3**) X = Sb
(**4**) X = Bi

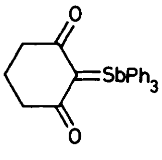
$(PhSO_2)_2C{=}SbPh_3$
(**5**)

$(p\text{-}MeC_6H_4SO_2)_2C{=}SbPh_3$
(**6**)

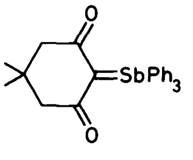
$Ac_2C{=}SbPh_3$
(**7**)

$Ac(PhCO)C{=}SbPh_3$
(**8**)

$PhCH_2SO_2(H)C{=}SbPh_3$
(**9**)



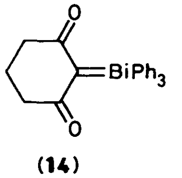
(**10**)



(**11**)

$Ac(PhCH_2SO_2)C{=}SbPh_3$
(**12**)

$(PhSO_2)_2C{=}BiPh_3$
(**13**)



(**14**)

Because of the tendency to increased dipolar and nucleophilic character on going down the Periodic Table it was of interest to investigate the properties of the stibonium and bismuthonium ylides and to compare them with arsonium ylides, which have already been shown to be more dipolar and more reactive than their phosphonium counterparts.[2,3] Their stability, reactivity, spectroscopic properties, dipole moments, and crystal structures are discussed.

Stibonium Ylides.—(a) *General properties and stability.* The new stibonium ylides are all solids which are stable for long periods if kept in a dry atmosphere. They are stable to moderate heat. For example the bis(phenylsulphonyl) ylide (**5**) is recovered unchanged from a solution of it in dry benzene which has been heated for 2 h, but when a sample was recrystallised from chlorobenzene, prolonged heating in this solvent (b.p. 132 °C) resulted in some decomposition of the ylide. Being dipolar molecules these ylides are insoluble in ether or in alkanes, but they are reasonably soluble in chlorinated solvents such as chlorobenzene or dichloromethane and in benzene and ethyl acetate; the bis-sulphonyl ylides (**5**) and (**6**) are the least soluble.

In powdered form the ylides readily gain static and stick to glass surfaces and to spatulae.

In protic solvents the ylides are readily hydrolysed if any moisture is present. For example when a sample of ylide (**5**) was heated in wet ethanol for 5 min it was hydrolysed to give an 87% yield of bis(phenylsulphonyl)methane, plus triphenylstibine oxide [reaction (1)].

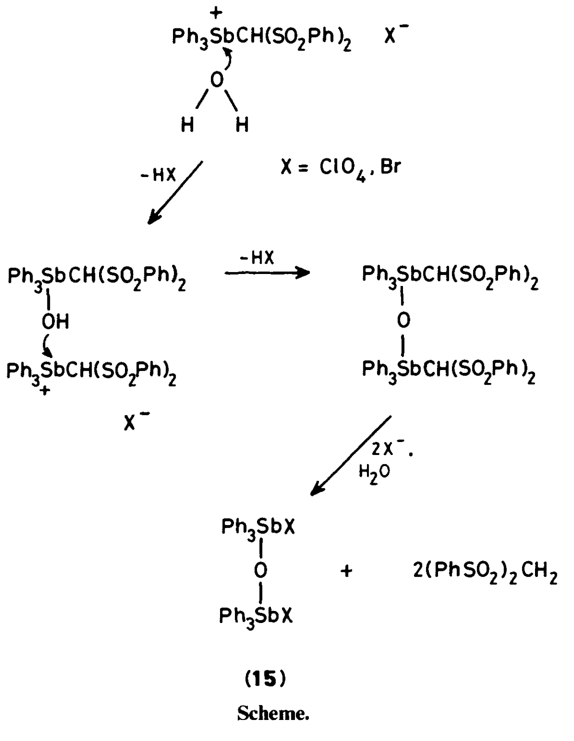
Table 1. Stretching frequencies of SO_2 and CO groups (Nujol mulls)

Ylide	ν/cm^{-1}	ν (As analogue [3])/ cm^{-1}	ν (P analogue)/ cm^{-1}
(5)	1 280, 1 112	1 292, 1 122	1 310, 1 130 [13]
(6)	1 280, 1 112	1 292, 1 120	
(7)	1 570, 1 505	1 580, 1 510	1 580, 1 545 [14]
(8)	1 580, 1 555, 1 495	1 578, 1 555, 1 515	1 560, 1 530 [14]
(9)	1 302, 1 115		
(10)	1 595, 1 570sh, 1 512	1 595, 1 572sh, 1 540	
(11)	1 585, 1 505	1 605, 1 545	
(12)	1 334, 1 130		

$$(PhSO_2)_2C{=}SbPh_3 + H_2O \longrightarrow (PhSO_2)_2CH_2 + \tfrac{1}{2}(Ph_3SbO)_2 \quad (1)$$

There has been much uncertainty about the structures of compounds described as triphenylstibine oxide,[9] but an *X*-ray analysis[10] of the product obtained by hydrolysis of the bis-(*p*-tolylsulphonyl)methylylide (**6**) shows it to be a dimer; its structure is the same as that of a compound obtained by thermal decomposition of tetraphenylstibonium hydroxide.[9] Because of the very low solubility of this dimeric oxide its dipole moment was only obtained with great difficulty, but is found to be $\leqslant$ 0.7 D; this low moment, close to zero, supports a centrosymmetric structure in solution, as well as in the crystal.

(b) *Attempted salt formation: hydrolysis of salts and formation of oxybis(triphenylantimony) derivatives.* Triphenylstibonium tetraphenylcyclopentadienylide (**3**) formed a crystalline salt when treated with perchloric acid, but the salt was readily hydrolysed on attempted recrystallisation from wet ethanol.[1] When ylide (**10**) was dissolved in trifluoroacetic acid the ^{1}H n.m.r. spectrum of the solution indicated that the ylide had been protonated, but attempts to form crystalline perchlorates by treatment with aqueous perchloric acid uniformly failed. Ylides (**5**) and (**7**) dissolved in ethanolic perchloric acid; addition of ether to the solution precipitated the same product in each case. This proved to be oxybis(triphenylantimony) diperchlorate, $[(ClO_4)Ph_3Sb]_2O$ (**15**; X = ClO_4).[11,12]



(15)

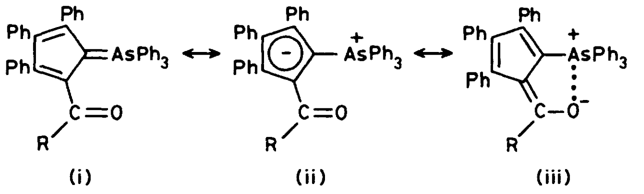
Scheme.

Related oxybis(triphenylantimony) derivatives were also formed instead of the hoped-for products when attempts were made to prepare stibonium ylides either by the salt method or from dichlorotriphenylantimony(v). Thus when a solution of bromobis(phenylsulphonyl)methane and triphenylstibine in benzene was kept at room temperature for 2 days oxybis-(triphenylantimony)dibromide (**15**; X = Br) was formed.

The Scheme presents a reasonable mechanism for the formation of these products from stibonium salts.The last step depends on the fact that $[(PhSO_2)_2CH]^-$, as a very stable delocalised anion, is a very good leaving group.

(c) *Formation of oxybis(triphenylantimony) derivatives in the preparation of stibonium ylides from dichlorotriphenylantimony*(v). The reaction of compounds having reactive methylene groups with dichlorotriphenylphosphorus or dichlorotriphenylarsenic in the presence of triethylamine, was shown to provide phosphonium and arsonium ylides.[13] Attempts to apply this method to the preparation of stibonium ylides from dichlorotriphenylantimony(v) led in some cases, from acetylacetone, benzoylacetone, or cyclohexane-1,3-dione, to the formation of the desired ylide, but it was always accompanied by some oxybis(triphenylantimony) dichloride (**15**; X = Cl).[11] It was difficult to separate this product and the ylide and this devalued the use of this method for making stibonium ylides. The dichloro compound (**15**; X = Cl) is presumably formed from reaction of the dichlorotriphenylantimony(v) with water by a similar mechanism to that given above, and was caused by the presence of moisture in the reaction mixtures. When dimedone, dimethyl malonate, or bis(phenylsulphonyl)methane were used as substrates, no ylide could be isolated, but only the dichloro compound (**15**; X = Cl).

(d) *I.r. spectra.* Table 1 lists the stretching frequencies of the present stibonium ylides and compares them with the values for corresponding arsonium and phosphonium analogues where available. In the case of ylide (**12**) no obvious carbonyl absorption is seen. A similar situation arises in the case of the arsonium ylides (**16**)[15] and (**17**)[16] whose i.r. spectra show no normal carbonyl absorption.[15] This was attributed to large contributions from structure (iii), in which there is strong intramolecular interaction between the arsenic and oxygen atoms. There is similar interaction between antimony and oxygen in suitably structured stibonium ylides, as described later in discussion of *X*-ray structures; the carbonyl absorption of (**12**) may be obscured by a Nujol peak.



(16) R = Me

(17) R = H

In general the stretching frequencies become steadily lower on going from phosphonium to arsonium to stibonium ylides, consistent with an expected increase in polarity of ylides on going down the Periodic Table.

(e) *Electronic spectra.* The electronic spectra of some of the stibonium ylides, together with those of their arsonium analogues, are listed in Table 2. Other stibonium ylides were insufficiently soluble in methanol or were decomposed by protic solvents. The spectra of all the stibonium ylides contain a broad band in the region 240—325 nm associated with intramolecular charge transfer.

The obvious feature is the close similarity between the spectra

Table 2. Electronic spectra of ylides (MeOH)

Ylide	$\lambda_{max.}$/nm (log ε)	$\lambda_{max.}$/nm (log ε) As analogue[3]
(5)	218, 263 (4.46, 3.61)	217, 265, 285 (4.54, 4.03, 3.77)
(7)	221, 271 (4.48, 3.96)	216, 275 (4.41, 4.20)
(10)	220, 264 (4.45, 4.25)	209, 262 (4.30, 4.06)
(11)	224, 266 (4.42, 4.30)	213, 265 (4.40, 4.30)

Table 3. ^{13}C N.m.r. of ylidic carbon atoms δ(50 MHz; solvent CD_2Cl_2; standard Me_4Si)

Ylide	δ (p.p.m.)	δ (p.p.m.) of As analogue
(5)	74.6*	69.8
(10)	95.1	89.6
(11)	93.2	87.9

* There is a slight ambiguity about this signal. There was a detectable level of impurity in the sample and another signal is observable at δ 70.5 p.p.m. However the signal at δ 74.6 p.p.m. has been attributed to the ylide since it provides a consistent Δδ for the As and Sb ylides.

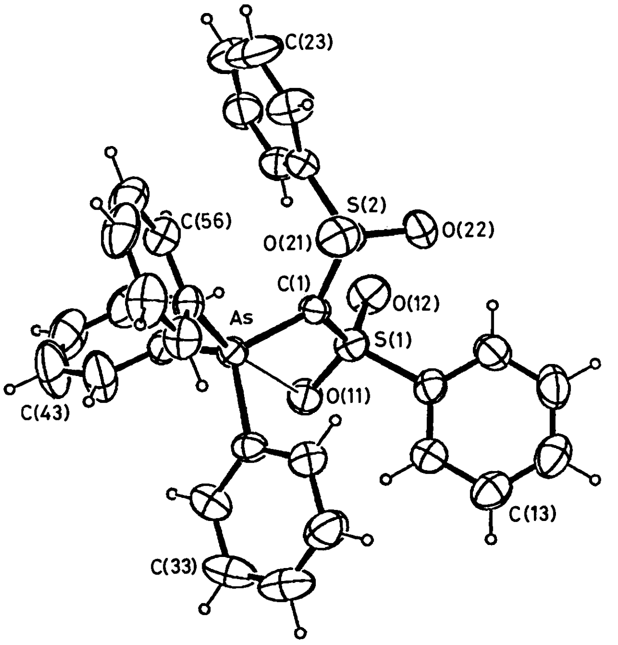


Figure 1. Perspective view of a molecule of (**5A**), showing the atom numbering scheme

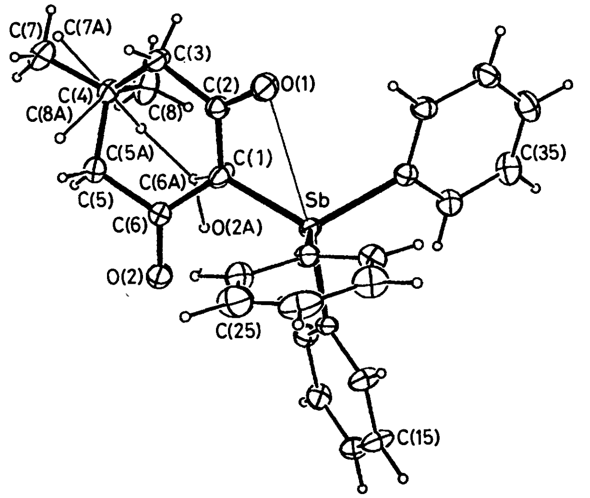


Figure 2. Perspective view of a molecule of (**11**), showing the atom numbering scheme: for the sake of clarity the atoms involved only in the minor conformation are shown as small isotropic atoms bearing no hydrogens

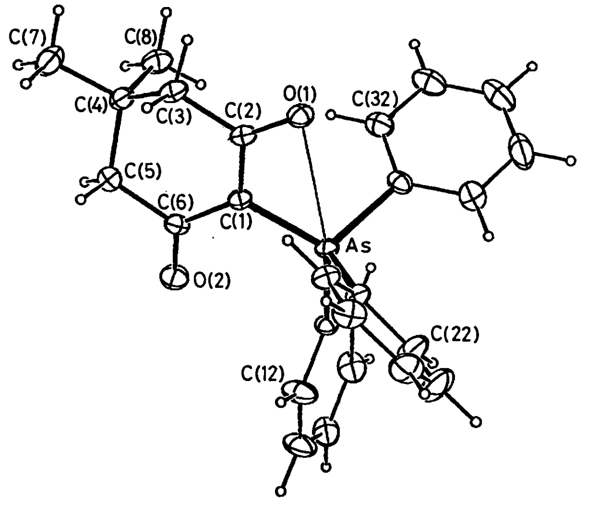


Figure 3. Perspective view of a molecule of (**11A**), showing the atom numbering scheme

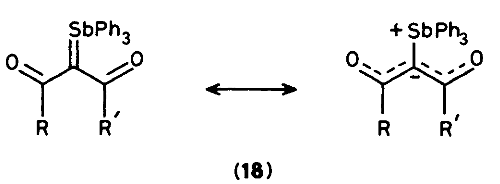
Table 4. Dipole moments

Ylide	μ/D	μ/D of As analogue
(5)	7.79	(**5A**) 7.93
(10)	3.78	(**10A**) 3.62

of the stibonium ylides and their arsonium analogues, which is indicative of very similar electronic structures in both sets of ylides. There is much more difference between $\lambda_{max.}$ of the arsonium and stibonium ylides (**2**) and (**3**),[1] suggesting a bigger difference in their polarity in this case. Ylides (**2**) and (**3**) have no carbonyl or sulphonyl substituents which can interact intramolecularly with the heteroatom and this is probably responsible for the difference between them and the antimony and arsenic ylides listed in Table 2.

Solid-state electronic spectra of ylide (**6**) and its arsonium analogue were virtually identical, with $\lambda_{max.}$ 297 and 300 nm, respectively, implying a close similarity in structure also in the solid state.

(f) ^{1}H *N.m.r. spectra.* The ^{1}H n.m.r. spectra[7] closely resemble those of their arsonium analogues.[1] In particular there is no evidence for the presence of more than one geometric isomer at room temperature. As with arsonium ylides,[1] the most likely structure for the substituents on the ylidic carbon atom is that of the *Z*,*Z*-isomer (**18**), since this allows favourable electrostatic interaction between the antimony and the neighbouring oxygen atoms. This has been confirmed by *X*-ray crystallographic studies of both antimony[17] and arsenic ylides[18] (see also below).



(18)

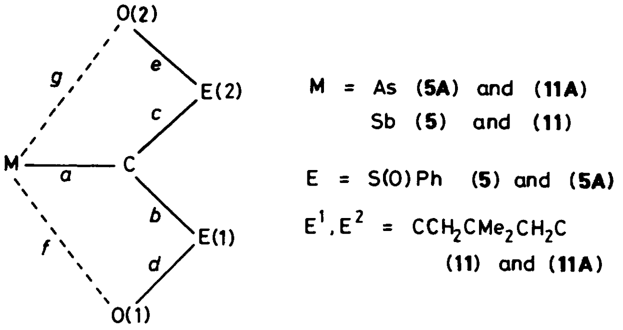
(g) ^{13}C *N.m.r. spectra.* Using routine spectrometers it is difficult to observe signals for the ylidic carbon atom of

Table 5. Details of data collection, and *R* values

	(5A)	**(11)**	**(11A)**
Crystal dimensions (mm)	0.08 × 0.34 × 0.34	0.55 × 0.55 × 0.20	0.30 × 0.35 × 0.36
No. and range of setting reflections	25; $10° \leqslant \theta \leqslant 15°$	25; $10° \leqslant \theta \leqslant 15°$	14; $10° \leqslant \theta \leqslant 15°$
Scan width (°)	$0.6 + 0.35 \tan \theta$	$0.7 + 0.35 \tan \theta$	$0.7 + 0.35 \tan \theta$
$2\theta_{max.}$ (°)	54	54	54
Range of unique *h*	$-14 \longrightarrow +14$	$-14 \longrightarrow 0$	$-14 \longrightarrow +14$
k	$0 \longrightarrow +16$	$-20 \longrightarrow 0$	$-14 \longrightarrow +14$
l	$0 \longrightarrow +23$	$0 \longrightarrow +32$	$0 \longrightarrow +12$
No. reflections measured	6 658	5 580	5 262
No. reflections unique	5 829	4 836	4 749
No. reflections observed	3 149 $[I \geqslant 5\sigma(I)]$	2 859 $[I \geqslant 6\sigma(I)]$	3 391 $[I \geqslant 3\sigma(I)]$
p^a	0.050	0.050	0.060
R	0.028	0.024	0.034
R_w	0.037	0.037	0.043

[a] In weighting scheme $w = 1[\sigma^2(F_o) + p(F_o)^2]$.

Table 6. Selected molecular dimensions for **(5)**, **(5A)**, **(11)**, and **(11A)**



			(11)		
Distances (Å)	**(5)**[a]	**(5A)**	Major conformer	Minor conformer (where different)	**(11A)**
a	2.042(3)	1.868(3)	2.049(4)		1.870(2)
b	1.704(4)	1.710(3)	1.398(5)		1.411(4)
c	1.698(3)	1.704(3)	1.465(6)	1.536(11)	1.430(4)
d	1.454(3)	1.449(2)	1.238(4)		1.246(4)
e	1.435(3)	1.433(2)	1.238(6)	1.240(13)	1.222(4)
f	2.844(3)	2.881(2)	2.835(3)		2.881(2)
g	3.447(3)	3.348(2)	3.347(4)	3.508(9)	3.183(2)
Angles (°)					
$a\hat{}b$	112.0(2)	115.4(2)	109.5(2)		113.1(2)
$a\hat{}c$	123.9(2)	123.3(2)	122.0(3)	124.3(5)	122.1(2)
$b\hat{}d$	103.3(2)	104.2(1)	120.0(3)		122.0(2)
$c\hat{}e$	107.9(2)	110.0(1)	124.4(4)	124.5(9)	125.2(2)

[a] Ref. 17.

arsonium ylides, because of the long relaxation time, but it proved possible to detect such signals by use of a high-performance 360 MHz instrument. The signals for the ylidic carbon atoms of ylides **(5)**, **(10)**, and **(11)** and their arsonium analogues are listed in Table 3.

These results are surprising in that the stibonium ylidic carbon atoms would seem to carry less negative charge than do the ylidic carbon atoms of the arsonium ylides. This appears to be contrary to the concept that ylides become more dipolar the lower the heteroatom is placed in the Periodic Table but, as discussed further below, decreased negative charge on the Sb=C carbon atom may result from significant electrostatic interaction between the antimony atom and oxygen atoms of the substituent groups in the ylide. There is only a very small difference in chemical shift (0.2 p.p.m.) for the *ipso* carbon atoms in the X-phenyl groups when X is changed from As to 5b.

(h) *Dipole moments.* The dipole moments of ylides **(2)**, **(1)**, and their diphenylsulphonium analogue are, respectively, 8.32, 7.75, and 6.69,[19] in accord with expectation of their relative polarities. An unexpectedly low value for **(3)** of 2.2 D was found.[19] Dipole moments have now been determined (Table 4) for ylides **(5)** and **(10)** and their arsonium analogues **(5A)** and **(10A)**. There is thus surprisingly little difference between the values for the As and Sb ylides.

(i) *Attempted Wittig reactions.* Arsonium ylides are more reactive towards carbonyl compounds in the Wittig reaction than are phosphonium ylides.[1-3] The only stibonium ylides hitherto recorded appeared to be yet more reactive.[1,5] Ylides stabilised by electron-withdrawing substituents are much less reactive and a variety of such disubstituted arsonium ylides

Table 7. Least-squares planes for (**11**) and (**11A**)

The equation of the planes takes the form $Ax + By + Cz = D$, where x, y, z are orthogonal Ångstrom co-ordinates

	Atoms forming the plane	*A*	*B*	*C*	*D*	Atom distances from the plane (Å)
(**11A**)	C(1), C(2), C(3), C(5), C(6)	−0.6389	0.3603	−0.6797	−3.2582	C(1), −0.003(3); C(2), 0.005(3); C(3), −0.003(3); C(5), 0.002(3); C(6), 0.000(3); As, 0.013(1); O(1), −0.011(2); O(2), 0.011(2); C(4), 0.627(3)
(**11**)	C(1), C(2), C(3), C(4)	−0.4410	−0.6270	−0.6422	−4.1336	C(1), 0.008(4); C(2), −0.015(3); C(3), 0.014(3); C(4), −0.007(4); Sb, −0.043(1); O(1), −0.035(3); C(5), 0.810(5); C(5A), −0.757(11); C(6), 0.573(5); C(6A), −0.724(11); O(2), 0.816(4); O(2A), −1.031(9)

do not react even with a highly reactive carbonyl compound such as 2,4-dinitrobenzaldehyde.[3] A reason for preparing the currently described stibonium ylides was to see if some might participate in Wittig reactions despite their deactivating substituents. However none of ylides (**5**)—(**11**), not even the monosubstituted ylide (**9**), reacted with 2,4-dinitrobenzaldehyde. Ylide (**6**) also did not react with nitrosobenzene. The fact that there appears to be little difference between the dipole moments of arsonium and stibonium ylides makes it likely that their reactivity towards electrophiles may likewise be similar. Other factors are discussed below in section (k).

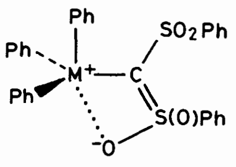
(j) *X-Ray crystal structures.* An *X*-ray crystallographic study of ylides (**5**) and (**11**) and, for comparative purposes, of their arsonium analogues [described here as (**5A**) and (**11A**), respectively], has been made. Details are given in Tables 5—7 for ylides (**11**), (**5A**), and (**11A**); details for ylide (**5**) are already published.[17]

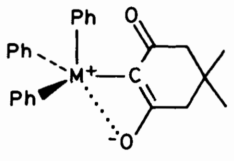
In the two arsonium ylides (**5A**) and (**11A**), the ylidic As–C bond lengths are 1.868(3) and 1.870(2) Å respectively (Table 6), significantly shorter than the corresponding As–C(aryl) distances, whose mean values are 1.920 and 1.919 Å, respectively. These ylidic values compare well with values found for three arsonium acylylides, and signify an appreciable amount of single-bond character and consequently of dipolar character.[18]

Similarly, in the case of the stibonium ylides (**5**) and (**11**) the ylidic Sb–C distances, 2.042(3) and 2.049(4) Å, are significantly shorter than the corresponding Sb–C(aryl) distances, 2.108 and 2.107 Å, respectively. The Sb–C(ylidic) distances fall between the sums of the covalent radii of singly bonded and doubly bonded carbon and antimony (2.18, 1.975 Å),[20] but are significantly nearer to the value for a double bond than is the case for the As–C(ylidic) distances (covalent radii C–As 1.98, C=As 1.775 Å).[20]

For each of the ylides (**5**), (**5A**), (**11**), and (**11A**), there is one M ··· O distance (M = As or Sb) (Table 6) which is significantly less than that of the sum of the van der Waal's radii, 3.4 Å for M = As and 3.6 Å for M = Sb.[21] Associated with these differences in the distances *f* and *g* (Table 6) it is generally found that the S–O or C–O distance *d* is longer than *e*. For both (**11**) and (**11A**) the C–C distances *b* are shorter than *c*, indicating greater double-bond character in bonds *b*. Similarly angles $\widehat{ab}$ and $\widehat{bd}$ are in each case smaller than $\widehat{ac}$ and $\widehat{ce}$, respectively. Similar effects were observed for other arsonium acetylylides.[18]

These observations all indicate an attractive interaction between M and *one* oxygen atom as in the canonical forms (**A**) and (**B**) of [(**5**),(**5A**)] and [(**11**),(**11A**)]. Consistent with this, the geometry of M is intermediate between tetrahedral MC_4 and trigonal bipyramidal MC_4O and similar to that observed in bromotetraphenylstiborane, $BrSbPh_4$.[22]



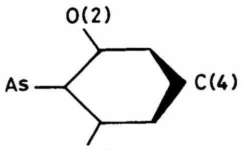


The resemblance between structures (**A**) and (**B**) and the transition state for a Wittig-type reaction may be noted.

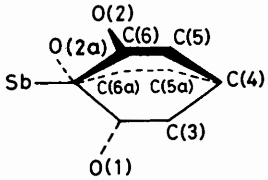
It is particularly noteworthy that the distance $f(\overset{+}{M}\cdots\overset{-}{O})$ is shorter for the two stibonium ylides than it is for their arsonium analogues, despite the greater atomic radius of antimony, while the differences between the two M ··· O distances *f* and *g* are larger in the case of antimony. This indicates a much stronger M ··· O interaction when M = Sb than when M = As.

In the arsonium ylide (**11A**), five atoms C(1)–C(3), C(5), and C(6) of the cyclohexanedione ring are coplanar. The arsenic atom and the two exocyclic oxygen atoms all lie within 0.01 Å of this plane (Table 7 and Figure 3), but the sixth ring atom C(4) is displaced by 0.63 Å, giving an envelope conformation to the ring as a whole (**C**).

In the antimony analogue (**D**), four atoms of the cyclohexanedione ring C(1)–C(4) form a plane, with the antimony atom and one oxygen atom, O(1), very nearly coplanar (Table 7 and Figure 3). The remaining two carbon atoms of the ring, C(5) and C(6), and the other oxygen atom, O(2), are displaced from this plane, and two conformers occur with relative weights 2/3 and 1/3. In each conformer C(5), C(6), and O(2) are displaced from this plane defined by C(1)–C(4), and all lie to one side of the plane in one conformer, and by a similar amount to the other side in the second conformer. The differences between conformations (**C**) and (**D**) presumably arise from the stronger and more lopsided M ··· O bonding when M = Sb.



(**C**)



(**D**)

(k) *Comments on the structure and reactivity of the stibonium ylides.* For many years it has been an article of faith that the stability of ylides decreases and their dipolarity and reactivity generally increases the lower placed the heteroatom is in the Periodic Table.[23] This variation is commonly ascribed to the less efficient *pπ–dπ* overlap between the C-sp^2 orbitals and the increasingly large diffuse *d*-orbitals of X in $(\overset{+}{X}-\overset{-}{C} \longleftrightarrow X{=}C)$ on going down the Periodic Table, together with decreased electrostatic interaction between $\overset{+}{X}$ and $\overset{-}{C}$ consequent upon the increase in size, and decrease in electronegativity, of X. When more polar, more basic, and more reactive in Wittig reactions.

analogous phosphonium and arsonium ylides are compared this faith is generally justified; arsonium ylides are the less stable,

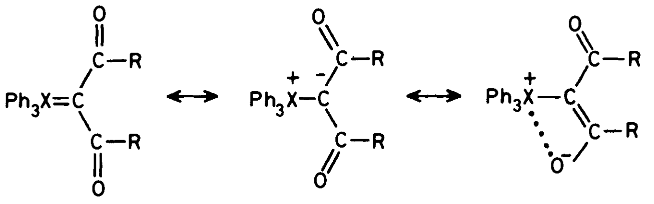
In the case of the previously described stibonium ylide (**3**) these generalisations again appeared to apply. For the currently described stibonium ylides this is less obviously so.

Thus the dipole moment measurements and electronic spectra, the latter in the solid state as well as in solution, are almost identical for arsonium and stibonium ylides. ^{13}C N.m.r. spectra even suggest that there is more negative charge on the ylidic carbon atom in the arsonium ylides than in the stibonium ylides. The lone piece of physical evidence which at first sight appears to indicate greater polarity in the stibonium ylides comes from their i.r. spectra.

Chemically the stibonium ylides are no more reactive in Wittig reactions than arsonium ylides but they are more readily hydrolysed in acid conditions.

The difference between the present stibonium ylides and ylide (**3**) is that the former, but not the latter, have substituent groups, carbonyl or sulphonyl, which can interact intramolecularly with the antimony or arsenic atom, and this interaction is clearly shown by the *X*-ray crystal structures.

In the case of ylides (**1**)—(**4**) the comparative properties depend almost entirely on the nature of the ylidic bond alone; this is no longer so in the case of (**5**)—(**12**) and their arsonium analogues. Here the interaction, and the extent of that interaction, between the heteroatom and substituent oxygen atoms plays a crucial role. Three canonical structures (**E**)—(**G**) must be considered. The *X*-ray studies indicate that structure (**G**) is more important for stibonium than for arsonium ylides. This is presumably because of the greater intrinsic polarity of stibonium ylides. Structures (**E**) contribute little; the increased charge is however dissipated by the contribution of (**G**). The greater dipolarity of the ylide bond, evinced in (**3**) compared with (**1**) and (**2**), no longer obtains. Thus there is little difference in the apparent dipolarity as indicated by physical and chemical properties, between stibonium and arsonium ylides. For the latter the intrinsic polarity is less, but the contribution of structure (**F**) as compared with (**G**) is greater.

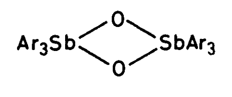

(**E**) (**F**) (**G**)

The one physical feature which suggests greater polarity of the stibonium ylides, namely the i.r. spectra, does so just because it is concerned with the CO or SO groups.

This chelation between substituent carbonyl or sulphonyl groups and the heteroatom clearly contributes to the unreactivity of such ylides towards electrophiles, for example in Wittig reactions, because it leads to a diminished negative charge on the ylidic carbon atom. Furthermore the *X*-ray studies show that these ylides already possess structures closely resembling the transition states for Wittig-type reactions, which will also inhibit their participation in intermolecular Wittig reactions. It may be noted that arsonium ylides having powerful electron-withdrawing groups which, for electronic or steric reasons, will interact less with the arsenic atom [*e.g.* $Ph_3As=C(COOEt)_2$, $Ph_3As=C(CN)_2$] do undergo Wittig reactions.[3] Unfortunately attempts to prepare the stibonium analogues of the latter ylides have so far been unsuccessful.

The stibonium ylides (**5**)—(**12**) are more readily hydrolysed than their arsonium analogues, herein providing the one analogy with ylides (**2**) and (**3**). It is possible (although not proven) that the protonation which is observed takes place on oxygen. This would break the chelation and leave the stibonium ion exposed to hydrolytic attack. A similar mechanism could apply to arsonium keto-ylides but the smaller arsenic atom would be more sterically hindered, and in at least one case it is known that protonation takes place on the ylidic carbon atom, not at oxygen.[24] Protonation of a stibonium keto-ylide on carbon would in any case diminish the antimony–oxygen interaction and facilitate hydrolytic attack.

The strong antimony–oxygen interaction, as observed in the stibonium ylides, also produces the dimeric structure of triphenylantimony oxide (**19**), referred to earlier in this paper. It is interesting to note that the changes in structure of the element M in triarylelement oxide Ar_3MO (M = P, As, or Sb) which may most simply be summarised thus:

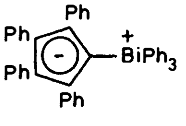


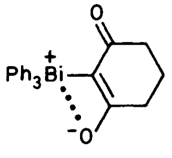
Bismuthonium Ylides.—The one bismuthonium ylide (**4**) hitherto reported[1,6] fulfilled expectations by being markedly less stable than ylides (**1**)—(**3**).

Of the present bismuthonium ylides (**13**) and (**14**), (**13**) decomposes slowly in the solid state to give bis(phenylsulphonyl)methane but (**14**) appears to be fairly stable, remaining unchanged after several months. Both, and especially (**14**), are extremely insoluble in common solvents.

The n.m.r. spectrum of (**14**) was obtained using a solution in [$^2H_5$]pyridine[8] and closely resembles that of its stibonium analogue. This suggests a similar structure for the two ylides.

A striking difference between (**13**), (**14**), and (**4**) is their colour, (**13**) and (**14**) being khaki and (**4**) deep blue and solvatochromic. The electronic spectra of (**4**) in different solvents closely resembled that of its pyridinium analogue,[25] but not those of ylides (**2**)—(**4**); this was attributed to lack of $p\pi$–$d\pi$ overlap in the $\overset{-}{C}$–$\overset{+}{Bi}$ bond (**4a**).


(**4a**)


(**14a**)

The completely different appearance and electronic spectra of (**13**) and (**14**) suggests that they, like their stibonium and arsonium analogues, may be best represented as in (**14a**). The i.r. spectrum of (**14**) is in accord, in that the carbonyl groups provide a broad peak (hexachlorobuta-1,3-diene mull) centred at 1 440 cm^{-1}, at a much lower wavenumber than for the stibonium analogue, indicating a very polarised carbonyl group.

No reaction ensued when (**14**) was heated in benzene with 2,4-dinitrobenzaldehyde for 6 h and the ylide was recovered unchanged. This is in marked contrast to ylide (**4**) which decomposed rapidly and completely in solution.

Experimental

Instruments used for determination of spectra were as follows: electronic, Unicam SP 800; solid-state electronic, edt Research DAs 400 Optoacoustic; i.r., Perkin-Elmer 1310; ^{1}H n.m.r., Brüker WP-80, ^{13}C n.m.r., Varian CFT-20 and Brüker WP-

Table 8. Positional parameters for (**5A**) and their estimated standard deviations

Atom	*x*	*y*	*z*
As	0.803 90(3)	0.205 45(3)	0.013 84(2)
S(1)	0.826 20(7)	0.348 33(6)	−0.113 11(4)
S(2)	0.800 03(7)	0.118 81(6)	−0.145 26(4)
O(11)	0.820 3(2)	0.411 3(2)	−0.048 9(1)
O(12)	0.744 9(2)	0.370 9(2)	−0.179 8(1)
O(21)	0.854 3(2)	0.026 6(2)	−0.108 9(1)
O(22)	0.838 7(2)	0.154 8(2)	−0.209 8(1)
C(1)	0.812 2(3)	0.221 4(2)	−0.085 0(2)
C(11)	0.968 5(3)	0.370 3(2)	−0.132 3(2)
C(12)	1.056 7(3)	0.407 0(3)	−0.076 7(2)
C(13)	1.164 5(3)	0.433 4(3)	−0.092 7(2)
C(14)	1.183 4(3)	0.423 0(3)	−0.163 1(2)
C(15)	1.094 6(3)	0.387 0(3)	−0.218 4(2)
C(16)	0.987 2(3)	0.360 2(3)	−0.203 4(2)
C(21)	0.648 7(3)	0.086 5(3)	−0.172 0(2)
C(22)	0.616 1(4)	−0.017 3(3)	−0.185 2(2)
C(23)	0.497 3(4)	−0.041 3(3)	−0.206 4(3)
C(24)	0.414 1(4)	0.034 9(4)	−0.213 2(2)
C(25)	0.445 5(3)	0.136 5(4)	−0.200 3(2)
C(26)	0.563 3(3)	0.162 9(3)	−0.180 4(2)
C(31)	0.947 7(3)	0.252 2(3)	0.074 5(2)
C(32)	0.951 6(3)	0.320 3(3)	0.132 5(2)
C(33)	1.060 1(4)	0.355 0(3)	0.170 4(2)
C(34)	1.160 9(4)	0.321 5(3)	0.150 9(2)
C(35)	1.158 5(3)	0.251 6(3)	0.094 1(2)
C(36)	1.050 8(3)	0.217 3(3)	0.055 1(2)
C(41)	0.669 5(3)	0.275 0(2)	0.038 6(2)
C(42)	0.651 7(4)	0.271 3(4)	0.109 7(2)
C(43)	0.550 9(4)	0.319 1(4)	0.125 2(2)
C(44)	0.470 8(3)	0.366 7(4)	0.071 9(2)
C(45)	0.488 7(3)	0.368 2(3)	0.002 3(2)
C(46)	0.587 8(3)	0.323 9(3)	−0.015 2(2)
C(51)	0.780 6(3)	0.060 9(2)	0.038 3(2)
C(52)	0.867 6(3)	0.006 6(3)	0.085 1(2)
C(53)	0.847 1(3)	−0.096 8(3)	0.102 9(2)
C(54)	0.743 8(3)	−0.145 2(3)	0.073 3(2)
C(55)	0.657 1(3)	−0.090 6(3)	0.026 5(2)
C(56)	0.674 7(3)	0.012 4(3)	0.009 3(2)

Table 9. Positional parameters for (**11**) and their estimated standard deviations

Atom	*x*	*y*	*z*
Sb	0.102 92(2)	0.127 84(1)	0.148 28(1)
O(1)	−0.061 0(2)	0.256 7(2)	0.118 6(1)
O(2)*	0.271 3(4)	0.137 3(2)	0.038 6(2)
C(1)	0.121 6(3)	0.212 8(2)	0.087 5(1)
C(2)	0.021 7(3)	0.266 4(2)	0.086 3(1)
C(3)	0.015 7(3)	0.334 5(2)	0.044 7(1)
C(4)	0.124 7(3)	0.340 7(2)	0.009 3(1)
C(5)*	0.179 3(5)	0.255 0(3)	−0.005 2(2)
C(6)*	0.196 1(5)	0.194 9(3)	0.041 1(2)
C(7)*	0.111 1(5)	0.391 5(4)	−0.039 3(3)
C(8)*	0.228 5(7)	0.388 4(4)	0.041 8(3)
C(11)	0.250 6(3)	0.046 3(2)	0.160 4(1)
C(12)	0.367 1(3)	0.070 9(2)	0.149 9(1)
C(13)	0.461 5(3)	0.015 6(2)	0.160 3(1)
C(14)	0.440 9(3)	−0.062 1(2)	0.181 2(2)
C(15)	0.324 4(3)	−0.086 7(2)	0.192 3(2)
C(16)	0.231 0(3)	−0.033 3(2)	0.182 1(2)
C(21)	−0.040 0(3)	0.043 8(2)	0.134 5(1)
C(22)	−0.108 3(3)	0.011 4(2)	0.175 8(2)
C(23)	−0.197 4(3)	−0.046 3(3)	0.165 3(2)
C(24)	−0.218 1(3)	−0.073 1(2)	0.114 8(2)
C(25)	−0.152 4(4)	−0.041 8(3)	0.074 7(2)
C(26)	−0.061 6(4)	0.016 6(3)	0.083 6(2)
C(31)	0.080 6(3)	0.180 4(2)	0.224 5(1)
C(32)	−0.020 9(3)	0.228 3(2)	0.237 2(1)
C(33)	−0.030 6(3)	0.262 8(2)	0.287 1(2)
C(34)	0.057 9(4)	0.251 9(3)	0.324 0(2)
C(35)	0.156 9(4)	0.205 6(3)	0.311 5(2)
C(36)	0.168 4(3)	0.169 4(2)	0.262 2(1)
O(2A)†	0.341 6(7)	0.222 2(6)	0.079 3(4)
C(5A)†	0.226 2(10)	0.325 4(7)	0.034 2(4)
C(6A)†	0.241 2(9)	0.253 8(7)	0.071 4(4)
C(7A)†	0.094 7(10)	0.419 6(8)	−0.028 5(6)
C(8A)†	0.080 9(13)	0.264 8(9)	−0.031 3(5)

Atoms marked * and † were assigned occupancies of 2/3 and 1/3 respectively from consideration of electron-density maps.

200SY at the University of Edinburgh (Me_4Si as reference). Elemental analyses were by the Microanalytical Laboratory of the Department of Chemistry, University of St. Andrews.

Light petroleum had b.p. 40—60 °C. Column chromatography was carried out on silica gel Grade M60, aluminium oxide 90.

Stibonium, bismuthonium, and arsonium ylides were prepared as described in refs. 7 and 8.

Hydrolysis of Ylide (**5**) *in Wet Ethanol*.—A solution of the ylide (0.2 g, 0.31 mmol) in ethanol (10 ml) was heated under reflux for 5 min. When cooled, bis(phenylsulphonyl)methane (0.07 g, 76%) precipitated and was filtered off. After removal of solvent from the filtrate, the residue was boiled with water (10 ml) for several minutes and then decanted while hot. More bis(phenylsulphonyl)methane (0.01 g, 11%) precipitated from the cooled solution. The insoluble residue was triphenylstibine oxide,[10] m.p. 200 °C (decomp.).

Reactions of Stibonium Ylides with Aqueous Perchloric Acid.—(a) Perchloric acid (70—73%; 0.05 ml) was added to a suspension of the bis-(*p*-tolylsulphonyl) ylide (**6**) (0.165 g, 0.24 mmol) in ethanol (0.5 ml). The ylide dissolved; addition of ether (5 ml) caused precipitation of bis-(*p*-tolylsulphonyl)methane (0.06 g, 76%), m.p. 130 °C (lit.,[26] 135 °C).

(b) Similar treatment of the bis(phenylsulphonyl) ylide (**5**) or the diacetylmethylide (**7**) gave oxybis(triphenylantimony) diperchlorate (0.21 g, 91%; 0.2 g, 87%), δ(CD_3OD) 7.72—8.20 (m), m.p. 305—307 °C, 307—308 °C (lit.,[11] >300 °C).

Reaction of Triphenylstibine with Bromobis(phenylsulphonyl)-methane.—Bromobis(phenylsulphonyl)methane (0.5 g, 1.33 mmol) and triphenylstibine (0.47 g, 1.33 mmol) were stirred in benzene at room temperature until a clear solution was obtained. After two days at room temperature large crystals had separated out and were filtered off and washed with benzene, followed by ether. The product (0.44 g, 75%), m.p. 248—250 °C (lit.,[11] 252—253 °C; identical i.r. spectrum) was oxybis(triphenylantimony) dibromide (Found: C, 49.65; H, 3.45. Calc. for $C_{36}H_{30}Br_2OSb_2$: C, 49.05; H, 3.45%).

Formation of Stibonium Ylides and of Oxybis(triphenylantimony) Dichloride from Dichlorotriphenylantimony.—(a) A solution of acetylacetone (0.25 g, 2.5 mmol) and triethylamine (0.61 g, 6 mmol) in dry benzene (3 ml) was added to a solution of dichlorotriphenylantimony (1.06 g, 2.5 mmol) in dry benzene (7 ml) and the mixture was heated under reflux for 20 min. The cooled solution was filtered from triethylammonium chloride and oxybis(triphenylantimony) dichloride (0.60 g) and solvent was then evaporated leaving triphenylstibonium diacetylmethylide (0.6 g, 53%), m.p. 166—170 °C [lit.,[7] 186 °C (decomp.)]; i.r. spectra showed this ylide to be contaminated with oxybis(triphenylantimony) dichloride.

(b) When benzoylacetone (0.41 g, 2.5 mmol) replaced acetylacetone the final product (0.52 g) was triphenylstibonium

Table 10. Positional parameters for (**11A**) and their estimated standard deviations

Atom	x	y	z
As	0.326 66(2)	0.308 82(2)	0.233 99(3)
O(1)	0.197 0(2)	0.351 6(2)	0.457 5(2)
O(2)	0.334 5(2)	0.587 3(2)	0.262 5(2)
C(1)	0.267 8(2)	0.463 6(2)	0.356 5(3)
C(2)	0.206 4(2)	0.454 6(2)	0.453 8(3)
C(3)	0.154 7(3)	0.573 7(3)	0.557 4(3)
C(4)	0.114 4(3)	0.700 9(3)	0.501 7(3)
C(5)	0.228 9(3)	0.696 3(3)	0.453 2(3)
C(6)	0.283 0(2)	0.578 2(2)	0.347 7(3)
C(7)	0.083 7(4)	0.812 5(3)	0.625 6(4)
C(8)	−0.011 0(3)	0.718 9(3)	0.371 8(4)
C(11)	0.391 3(2)	0.321 8(2)	0.084 8(3)
C(12)	0.518 6(3)	0.319 8(4)	0.118 2(3)
C(13)	0.564 8(3)	0.329 6(4)	0.010 1(4)
C(14)	0.487 1(3)	0.339 9(3)	−0.129 0(3)
C(15)	0.360 9(3)	0.342 1(3)	−0.163 5(3)
C(16)	0.311 4(3)	0.333 4(3)	−0.056 5(3)
C(21)	0.472 4(2)	0.175 2(2)	0.338 6(3)
C(22)	0.548 8(3)	0.067 4(4)	0.261 3(4)
C(23)	0.651 8(4)	−0.027 7(4)	0.338 0(5)
C(24)	0.681 4(3)	−0.017 2(3)	0.485 7(5)
C(25)	0.608 7(3)	0.090 1(3)	0.562 0(4)
C(26)	0.503 5(3)	0.187 0(3)	0.488 7(3)
C(31)	0.181 6(2)	0.250 8(2)	0.126 2(3)
C(32)	0.053 3(3)	0.340 1(3)	0.099 1(4)
C(33)	−0.051 8(3)	0.303 9(4)	0.010 6(4)
C(34)	−0.030 1(3)—	0.179 9(4)	−0.048 5(4)
C(35)	0.096 1(4)	0.088 8(3)	−0.022 9(5)
C(36)	0.203 2(3)	0.124 1(3)	0.065 4(4)

acetylbenzoylmethylide contaminated with triethylammonium chloride and oxybis(triphenylantimony) dichloride. When this product was washed quickly with ice-cold methanol followed by ether, the ammonium salt was removed but not the oxy compound. The remaining crude ylide (0.34 g, 27%) had m.p. 168—182 °C.

(c) When cyclohexane-1,3-dione (0.28 g, 2.5 mmol) replaced acetylacetone the impure product (0.57 g) was triturated with ether and provided triphenylstibonium 2,6-dioxocyclohexylide contaminated with oxybis(triphenylstibonium) dichloride (0.23 g), m.p. 156—182 °C. To remove the contaminant this product was dissolved in dry dichloromethane and filtered quickly through a layer of neutral alumina supported on Hyflo Supercel. Evaporation of the solvent from the filtrate and trituration of the residue with ether gave the ylide (0.05 g, 4%), m.p. 168—170 °C (lit.,[7] 169—172 °C). Alternatively the initial crude product was dissolved in dichloromethane and the solution was stirred briefly with a small amount of neutral alumina. Removal of the alumina by filtration followed by evaporation of the solvent left ylide (**10**), m.p. 167—169 °C.

Attempted Wittig Reactions using Stibonium and Bismuthonium Ylides.—(a) A solution of triphenylstibonium 2,6-dioxocyclohexylide (**10**) (0.36 g, 0.78 mmol) and 2,4-dinitrobenzaldehyde (0.16 g, 0.78 mmol) in dry benzene (25 ml) was heated under reflux for 5 h. Evaporation of the solvent and trituration with ether provided unchanged ylide (0.33 g). Stibonium ylides (**5**)—(**9**), and (**11**) and bismuthonium ylide (**14**) were similarly recovered unchanged from attempted reactions with 2,4-dinitrobenzaldehyde, as was ylide (**6**) from an attempted reaction with *p*-nitrobenzaldehyde.

(b) A solution of triphenylstibonium bis-(*p*-tolylsulphonyl)-methylide (0.67 g, 1 mmol) and nitrosobenzene (0.11 g, 1 mmol) in dry benzene (30 ml) was heated under reflux for 7 h. After the solvent had been removed, trituration of the residue with ether gave unchanged ylide (0.47 g). Concentration of the ether filtrate provided further ylide (0.06 g).

Table 11. Physical data from dipole moment determinations in benzene solution at the specified temperature

Ylide	t/°C	$w_{max.}$	α_o	$-\beta$	$P_{2\infty}$	R_D	μ/D
(**5**)	30	0.008	10.4	0.548	1 391	171	7.79
(**5A**)	30	0.002	11.7	0.610	1 431	166	7.93
(**10**)	30	0.009	3.66	0.495	412	126	3.78
(**10A**)	30	0.007	3.95	0.550	386	121.5	3.62

X-*Ray Crystallographic Studies.*—Crystals suitable for *X*-ray examination were grown from solvents as follows: triphenylarsonium bis(phenylsulphonium)methylide (**5A**), chlorobenzene; triphenylarsonium and triphenylstibonium 4,4-dimethyl-2,6-dioxocyclohexylides (**11**) and (**11A**), ethyl acetate.

Crystal data. (**5A**), $C_{31}H_{25}AsO_4S_2$, M_r = 600.59. Monoclinic, a = 11.612(2), b = 12.685(3), c = 18.568(5) Å, β = 101.36(2)°, V = 2682(2) Å^3. Space group $P2_1/c$ (No. 14), Z = 4, D_x = 1.49 g cm^{-3}, μ(Mo-K_α) = 14.5 cm^{-1}, λ = 0.710 73 Å, F(000) = 1 232. (**11**), $C_{26}H_{25}O_2Sb$, M_r = 491.24. Orthorhombic, a = 11.120(3), b = 15.815(4), c = 25.254(6) Å, V = 4 441(3) Å^3. Space group $Pbca$ (No. 61), Z = 8, D_x = 1.47 g cm^{-3}, μ(Mo-K_α) = 12.7 cm^{-1}, λ = 0.710 73 Å, F(000) = 1 984. (**11A**), $C_{26}H_{25}AsO_2$, M_r = 444.41. Triclinic, a = 11.489(2), b = 11.517(3), c = 9.785(2) Å, α = 105.12(2), β = 110.09(2), γ = 65.06(2)°, V = 1 092.4(7) Å^3. Space group $P\bar{1}$ (No. 2), Z = 2, D_x = 1.35 g cm^{-3}, μ(Mo-K_α) = 15.7 cm^{-1}, λ = 0.710 73 Å, F(000) = 460.

Data collection. For all three compounds (**5a**), (**11**), and (**11A**) accurate cell dimensions and crystal orientation matrices were determined on a CAD4 diffractometer by least-squares treatment of the setting angles of 25 [14 for (**11A**)] reflections in the range 10° ⩽ θ ⩽ 15°. Data were collected in the ω–2θ scan mode, using graphite-monochromated Mo-K_α radiation. Details of crystal size and reflections measured are in Table 5. Data were corrected for Lorentz and polarisation effects, and for absorption effects. The data were also corrected for secondary extinction:[27] the final refined extinction coefficients were 2 × 10^{-7} for (**5A**) and (**11**), and 6 × 10^{-7} for (**11A**).

Structure solution and refinement. Patterson methods were used to determine the co-ordinates of As and S in (**5A**), of Sb in (**11**), and of As in (**11A**): other non-hydrogen atoms were found by the heavy-atom method. Refinement was by full-matrix least-squares calculations. All non-hydrogen atoms were refined with anisotropic temperature factors: hydrogen atoms were included in calculated positions as riding atoms with C–H = 0.95 Å and B_{iso} of 8.0 Å^2 for methyl hydrogens and 5.0 Å^2 for all others. Parameters p in the weighting scheme $w = 1/[\sigma^2(F_o) + p(F_o)^2]$ and final R factors are in Table 5. All calculations were performed on a PDP 11/73 computer using SDP-Plus;[28] scattering factors and anomalous dispersion corrections were from ref. 29.

Atomic co-ordinates for (**5A**), (**11**), and (**11A**) are in Tables 8—10, respectively. In (**11**), three of the atoms of the cyclohexanedione ring, together with the pendant methyl groups, were found to be disordered over two sites: from electron-density maps the two sets of sites were assigned occupancy factors of 2/3 and 1/3, respectively. Selected molecular dimensions are in Table 6. Figures 1—3 show perspective views of the molecules: the Figures were all prepared using ORTEP-II.[30]

Tables of bond lengths and angles, anistropic temperature factors, and hydrogen atom co-ordinates are deposited with the Cambridge Crystallographic Data Centre.*

Dipole Moment Determinations.—The electric dipole moments were determined in benzene solution at 30.00 ± 0.02 °C by using the well known Debye refractivity method. The total polarisation of the solute, extrapolated to infinite dilution, was calculated from the experimental ratios (2) and (3)[31] where w is the weight fraction of the solute and ε and v are

$$\alpha_o = \lim_{w = 0}\left[\frac{\varepsilon - \varepsilon_1}{w}\right] \quad (2) \qquad \beta = \frac{\Sigma(v - v_1)}{\Sigma w} \quad (3)$$

the dielectric permittivity and specific volume of the solution respectively, and the subscript 1 refers to the pure solvent as used, *i.e.* made up in the same way as the solutions. The α_o value was calculated from the linear function, $\alpha = \alpha_o + \alpha' w$, obtained by the least-squares analysis of the $\varepsilon(w)$ quadratic function.

The distortion polarisation $({}_EP + {}_AP)$ of the solutes was assumed to equal the molecular refraction for sodium D line, calculated from the experimental ratios $\Sigma(n^2 - n_1{}^2)/\Sigma w$ and defined above. The experimental values are in accord (within 3—4 $cm^3 mol^{-1}$) with those calculated from bond refraction increments (from Vogel *et al.*[32] and Gillis[33]); for (**10A**) the (Ph_3As=C) group increment (97.0 $cm^3 mol^{-1}$ [34]) was used.

Techniques used for the measurement of dielectric permittivities specific volumes and refraction indices are described elsewhere.[35,36]

For each solute, the maximal value of $w(w_{max.})$, given to only three decimal places (though it is known to five to six), α_o, $\beta(cm^3 g^{-1})$, P_{20° and R_D (both in $cm^3 mol^{-1}$), and μ (in Debye units; 1 D = 3.3356×10^{-30} C m), are listed in Table 11.

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