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SOME STABLE STIBONIUM YLIDES. THE USE OF BIS(HEXAFLUOROACETYLACETONATO)COPPER(II) AS A HOMOGENEOUS CATALYST IN THE CONVERSION OF DIAZO-COMPOUNDS INTO YLIDES

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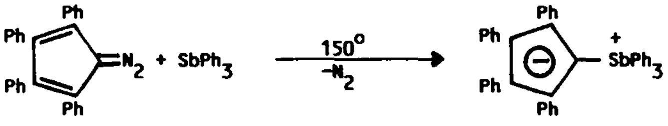
ABSTRACT - Stibonium ylides having α-electron-withdrawing groups have been prepared under mild conditions by reactions between triphenylantimony and an appropriate diazo-compound in the presence of bis(hexafluoroacetylacetonato)-copper(II) as a homogeneous catalyst. Other ylides can be prepared similarly. These stibonium ylides are stable in a dry atmosphere but are slowly solvolysed in protic solvents. Like their arsonium analogues they do not undergo Wittig reactions, even with reactive aldehydes.

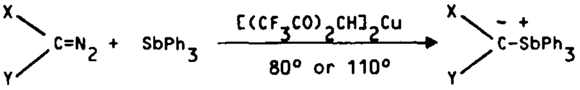
A multitude of phosphonium ylides and a good number of arsonium ylides are known; in contrast the isolation of only one stibonium ylide *(1)* has hitherto been reported[1], although two others have been prepared in solution.[2] Other attempts to prepare stibonium ylides have usually provided at best only impure materials; one problem has been that the methods used to effect the preparations of such ylides have frequently been insufficiently mild to guarantee the survival of the desired ylide.[3] Thus to prepare *(1)* a mixture of diazo-compound and triphenylantimony was melted without solvent and heated to 150 °C[1]:

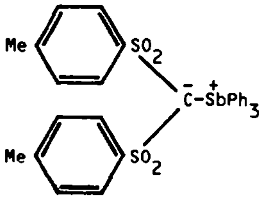


(1)

For similar preparations of arsonium ylides the presence of a catalyst has enabled less vigorous conditions to be used[4,5], and by using bis(acetylacetonato)copper(II) as a homogeneous catalyst it has proved possible to carry out preparations of arsonium ylides in solution in a variety of solvents, at moderate temperatures.[6]

A particularly efficient catalyst for this type of reaction is bis(hexafluoroacetylacetonato)-copper(II)[7], (bis(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)copper(II), $[(CF_3CO)_2CH]_2Cu$). This catalyst has now been used in the preparation of a number of stibonium ylides, which have been isolated in good yield. Reaction of the appropriate diazo-compound with triphenylantimony in boiling dry benzene provided the new stibonium ylides *(2)* - *(6)*; ylide *(7)* was prepared similarly but required a higher temperature for reaction to take place, and boiling toluene was used as solvent. The previously reported stibonium ylide *(1)* has also been prepared by the present method.





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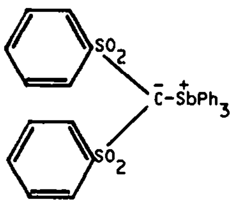

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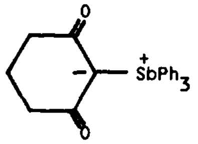

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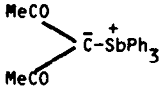

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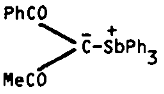

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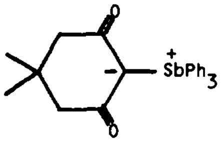


(7)

Diazomalonic esters, including the diazo-derivative from Meldrum's acid, ethyl diazoacetoacetate, diazoacetophenone and ethyl diazoacetate did not however provide stibonium ylides under these conditions. It thus appears that for stibonium ylides to be formed in this reaction it is necessary that the substituent groups on the diazo-compound be strongly electron-withdrawing, and that ester functions cannot fulfil this role.

The role of the catalyst is thought to be as a template for the reaction between triphenylantimony and the diazo-compound, in which the reactants are co-ordinated at *cis* sites in a six--coordinate intermediate (*cf.* ref.6). Only when both the diazo-compound and a carbene acceptor are present together with the catalyst is there any evolution of nitrogen, suggestive of a concerted process at the copper centre. No reaction of any kind is detected if only two of the catalyst, diazo-compound and triphenylantimony are present.

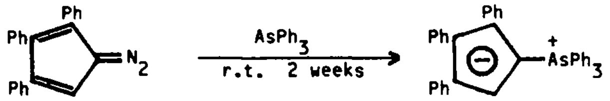
There is much less efficient catalysis by bis(acetylacetonato)copper(II), where the metal atom is of much lower Lewis acidity than in the hexafluoro-analogue (*cf.* also ref.7). (Electron-withdrawing substitutents on acetylacetone ligands in copper(II) complexes have been shown to favour the association of further ligands onto the copper.[8,9]) Whereas ylide *(3)* is formed in 78% yield in 2h using the hexafluoroacetylacetonato catalyst, the acetylacetonato catalyst provides only a 47% yield in 2h, although after 5h this increases to 73%.

There is no catalysis at all by the binuclear rhodium(II) acetate dimer, where the two co--ordination sites are much too far apart. Addition of rhodium acetate to triphenylantimony/diazo--compound mixtures gives no ylide formation. When diazo-compound only is added to rhodium acetate nitrogen is evolved; whenever triphenylantimony is present red solutions are formed, typical[10,11] of the adducts $Rh_2(OAc)_4L_2$, L here being triphenylantimony.

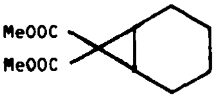
Bis(hexafluoroacetylacetonato)copper(II) is effective as a catalyst not only for the preparation of stibonium ylides. For example the previously described triphenylarsonium bis(phenylsulphonyl)-methylide[4], tetraphenylcyclopentadienylide[12], 2,3,4-triphenylcyclopentadienylide[5,13], and bis-(methoxycarbonyl)methylide[6] have all been prepared using the presently described methodology.

It is of interest to note that the arsonium bis(methoxycarbonyl)methylide could be obtained whereas its stibonium analogue could not, using the same reaction conditions. This may reflect superior co-ordination by arsenic compared to antimony onto the copper catalyst.

With the aid of the present catalyst it also proved possible to effect the conversion of diazo-2,3,4-triphenylcyclopentadiene into the corresponding triphenylarsonium ylide even at room temperature, although reaction was slow and the reaction mixture was kept for a fortnight before work-up.



When dimethyl diazomalonate (which provided an arsonium but not a stibonium ylide) was heated with the catalyst in boiling toluene containing cyclohexene, a low (8%) yield of the bicyclic ester *(8)* [6] resulted. In cyclohexene as solvent the yield rose to 26.5%. The catalyst must be involved also in these reactions, since none of *(8)* is formed in its absence. The lower yield probably reflects the less efficient co-ordination of alkene with copper. From diazodimedone in benzene without any alternative trap present a very small quantity of an adduct, *m/z* = 210, presumed to be *(9)*, was formed. There was never any evidence for the presence of dimer formed by two carbenes reacting together.



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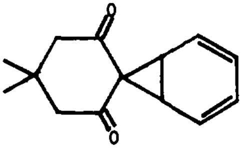


(or valence tautomer)

(9)

The new stibonium ylides are all colourless, or almost so, and appear to be indefinitely stable in a dry atmosphere. They are fairly basic, and are protonated by trifluoroacetic acid. In protic solvents they are slowly cleaved to give triphenylantimony oxide and the corresponding methylene compound, *e.g.*

$$(PhSO_2)_2\bar{C}-\overset{+}{Sb}Ph_3 \longrightarrow (PhSO_2)_2CH_2 + OSbPh_3$$

Their structures are confirmed by elemental analysis, mass, i.r. and n.m.r. spectra and, in the case of *(3)*, by X-ray crystallography.[14]

Like their arsonium analogues[4], the ylides *(2)*, *(3)*, *(4)* and *(6)* do not appear to take part in Wittig reactions even with reactive aldehydes such as 2,4-dinitrobenzaldehyde.

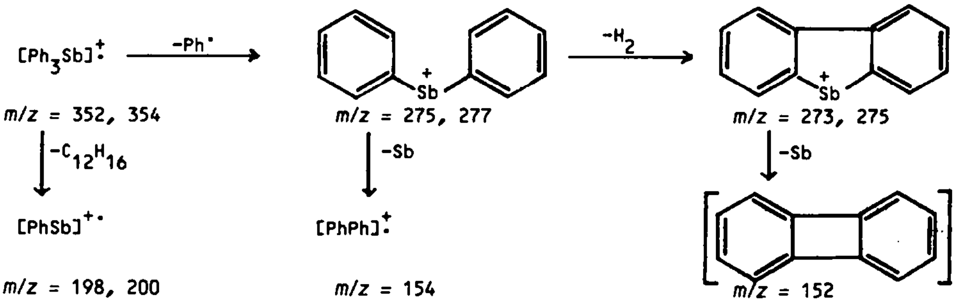
In the infra-red spectra the stretching frequencies associated with the substitutent electron--withdrawing groups, carbonyl or sulphonyl, become steadily lower on going from phosphonium to arsonium to stibonium ylides (see Table), consistent with the corresponding expected increase in polarity of the ylidic bond on going down the periodic table.

Stretching Frequencies of SO_2 and CO in $(PhSO_2)_2CMPh_3$ and $(MeCO)_2CMPh_3$ (M = P, As, Sb) (in Nujol mulls)

	$(PhSO_2)_2CMPh_3$ $\nu(SO_2)/cm^{-1}$	$(MeCO)_2CMPH_3$ $\nu(CO)/cm^{-1}$
M = P[15,16]	1310, 1130	1580, 1545
M = As[4]	1292, 1122	1580, 1510
M = Sb	1280, 1112	1570, 1505

The n.m.r. spectra of these stibonium ylides are very similar to those of their arsonium analogues[4], confirming their similar structures. As in the case of the arsonium ylides there appears to be only one conformer present, likely the *Z,Z* form.

The mass spectra likewise resemble closely those of the arsonium analogues. Molecular ion peaks were observed and, in the case of the acetyl ylides *(5)* and *(6)*, (M + 1) peaks. Fragmentation involves cleavage of the $\overset{+}{Sb}-\overset{-}{C}$ bond; somewhat surprisingly, in view of the probable relative weakness of this ylidic bond, in some cases [*(3)*,*(5)*,*(7)*] the molecular ion peaks are more intense than those due to $[Ph_3Sb]^{+\cdot}$. The ylides may well be stabilised by intramolecular interactions between the positively charged antimony atom and negatively charged oxygen atoms of the α-substituents, for which there is crystallographic evidence in the case of arsonium ylides.[17] Characteristically the $[Ph_3Sb]^{+\cdot}$ fragment breaks down further by the following pattern:



In each spectrum ions arising from loss of characteristic groups from the carbanionic portion of the molecule were also evident.

EXPERIMENTAL

Light petroleum had b.p. 40 - 60°.

Literature methods were used for the synthesis of the diazo-compounds[18-21], bis(hexafluoroacetylacetonato)copper(II)[22], and rhodium(II) acetate[23].

General Procedure for Preparation of Ylides. The diazo-compound (3 mmol), triphenylantimony (6 mmol) and bis(hexafluoroacetylacetonato)copper(II) (0.15 mmol) were dissolved in dry benzene [or in the case of *(7)* in dry toluene] (50 ml) and the mixture was heated under reflux in an atmosphere of nitrogen for times shown below for individual compounds. Evaporation of the solvent *in vacuo* and trituration of the residue with ether and/or hexane gave the ylide as a solid, which was filtered off and washed well with ether. The following new ylides were obtained in this way.

Triphenylstibonium bis(tolyl-*p*-sulphonyl)methylide *(2)*. (6h) (77%), m.p. 192°(dec.) (from benzene-petrol), δ ($CDCl_3$) 2.38 s (6H), 7.70 m (23H), (Found: C, 58.84; H, 4.36. $C_{33}H_{29}O_4S_2Sb$ requires C, 58.68; H, 4.33%.

Triphenylstibonium bis(phenylsulphonyl)methylide *(3)*. (2h) (78%), m.p. 196-198° (from chlorobenzene), δ (CD_2Cl_2) 7.5 m, (Found: C, 57.84; H, 3.88. $C_{31}H_{25}O_4S_2Sb$ requires C, 57.51; H, 3.89%).

Triphenylstibonium 2,6-dioxocyclohexylide *(4)*. (1.5h) (58%), m.p. 169-172° (from ethyl acetate, with charcoal), δ (CD_2Cl_2) 2.05 (quintet) (2H), 2.43 t (4H), 7.48 m (9H), 7.7 m (6H), (Found: C, 62.34; H, 4.56. $C_{24}H_{21}O_2Sb$ requires C, 62.24; H, 4.57%).

Triphenylstibonium diacetylmethylide *(5)*. (1h) (59%), m.p. 186°(dec.) (from benzene), δ (CD_2Cl_2) 1.85 s (6H), 7.4 - 7.75 m (15H), (Found: C, 61.79; H, 4.80; *m/z* = 451.0650. $C_{23}H_{21}O_2Sb$ requires C, 61.23; H, 4.69; $(M + 1)^+$ = 451.0656, for ^{121}Sb).

Triphenylstibonium acetylbenzoylmethylide *(6)*. (1h) (46%), m.p. 148-150°, small adulteration with triphenylantimony oxide, which could not be completely eliminated, (Found: *m/z* = 513.0817; $C_{28}H_{23}O_2Sb$ requires $(M + 1)^+$ = 513.0813, for ^{121}Sb).

Triphenylstibonium 4,4-dimethyl-2,6-dioxocyclohexylide *(7)*. (2h in toluene) (40%), m.p. 162 - 164° (from ethyl acetate), δ ($CDCl_3$) 1.175 s (6H), 2.425 s (4H), 7.75 m (15H), (Found: C, 63.60; H, 5.05. $C_{26}H_{25}O_2Sb$ requires C, 63.57; H, 5.13%). This compound did not solidify on addition of ether and was purified by chromatography on alumina, using light petroleum as eluant to remove excess triphenylantimony followed by benzene/ethyl acetate (1:1) to remove the ylide.

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