A Gentle Method for the Preparation of a Variety of Ylides (As, Sb, Bi, S, Te, Thiouronium) from Diazo Compounds

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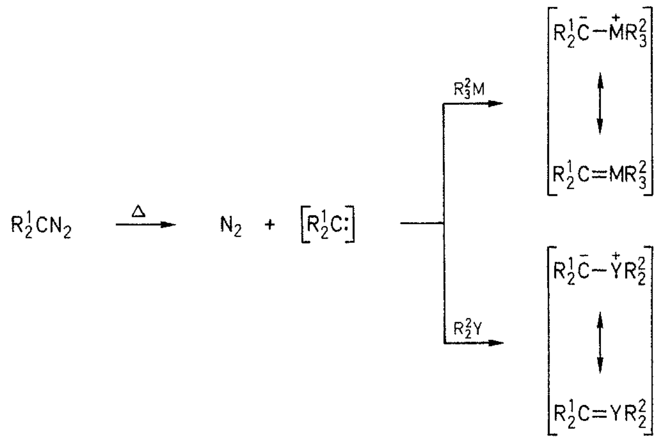
Bis(hexafluoroacetylacetonato)copper(II) is a very effective catalyst for the preparation of ylides from diazo compounds under mild conditions even down to room temperature. It appears that the lower the temperature at which the reaction can be conducted the purer the product which results. Its use in preparing arsonium, stibonium, bismuthonium, sulphonium, telluronium, and thiouronium ylides is described.

Thermal decomposition of diazo compounds, generating carbenes which are trapped by appropriate reagents with available lone pairs of electrons (e.g., R_3M, M=N, As, Sb, Bi; or R_2Y, Y=S, Se, Te), has provided a useful synthetic route to ylides having less usual hetero-atoms.

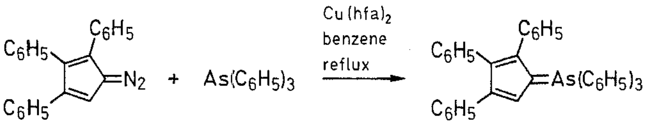


For example, this method provided the first isolated examples of stibonium,[1], bismuthonium,[2] selenonium,[3] and telluronium[4] ylides.

The initial methodology consisted of heating a mixture of the diazo compound with an excess of the trapping agent, without solvent, above the decomposition point of the diazo compound. It was then found that use of copper bronze or copper compounds as a catalyst often improved yields, enabled the reaction to be carried out at lower temperatures, and sometimes allowed reactions to take place which did not do so in the absence of catalyst.[5-7] In particular, the use of catalysts enables reactions to be carried out in solution, in a variety of solvents, at temperatures well below the normal decomposition temperature of the diazo compound.[6,7] A detailed study of a variety of catalysts gave mechanistic information and showed that copper(II) complexes of *β*-diketones were very effective;[7] bis(acetylacetonato)copper(II) has been a popular choice. The function of the catalyst appears to be to bring the reactants into close proximity to each other by their coordination at *cis*-sites at the copper in a six-coordinate intermediate.[7]

In a related reaction between diazotriphenylcyclopentadiene and a pyranthione to form a cyclopentadienylidenepyran,[8] the presence of bis(acetylacetonato)copper(II) only provided a modest improvement.[9] Electron-withdrawing substituents on acetylacetone ligands in copper(II) complexes have been shown to favour the association of further ligands onto the copper.[10,11] This led us to examine the use of bis(hexafluoroacetylacetonato)copper(II), $[Cu(hfa)_2]$.[12] This both increased the yield of cyclopentadienylidenepyran and allowed the reaction to be carried out at lower temperature, in boiling benzene.[9]

Following this success, the use of $Cu(hfa)_2$ as a catalyst for the preparation of ylides from diazo compounds has been investigated. An initial trial made use of the following reaction, using a mole ratio of arsine: diazo compound: catalyst of 2:1:0.04. In refluxing benzene for 2 h, this reaction gave a comparable yield (78 % of purified product) to that obtained previously using bis(acetylacetonato)copper(II)[6] (85 %). It was also found that reaction took place at lower temperatures, although it was much slower; under these conditions a substantially purer product was obtained (Table 1). It is particularly noteworthy that reaction is indeed possible and practicable at room temperature.



1a **2a**

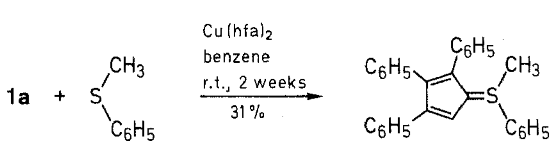
Table 1. Reaction Conditions for the Formation of Triphenyl(2,3,4-triphenylcyclopentadienylidene)arsorane (**2a**)

Reaction Temperature (°C)	Reaction Time (h)	Yield (%)	mp of **2a**[a]
80	2	78	198–202
50	16	45	209–212
50	48	68	210–214
r.t.	312	31	208–212

[a] Lit.[6] mp 198–200 °C.

The efficiency of Cu(hfa)$_2$ at lower temperatures suggested that it might well be useful for making ylides of lower stability, such as those of antimony, bismuth, tellurium, whose preparation in reactions of diazo compounds is spoiled by decomposition of the resultant ylides at the temperatures hitherto needed to effect loss of nitrogen from the diazo compound.

The use of Cu(hfa)$_2$ in preparing ylides with other hetero atoms was investigated. Results are listed in Table 2 and some comments are appended.



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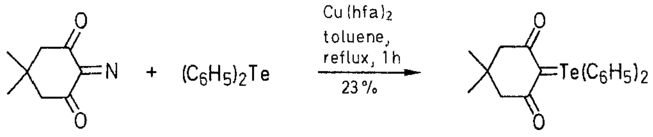
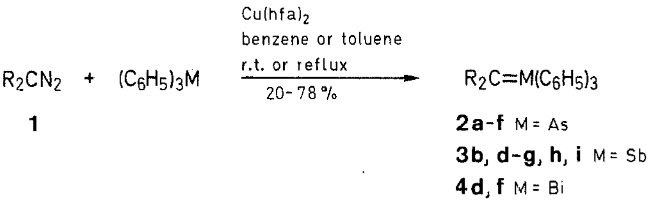
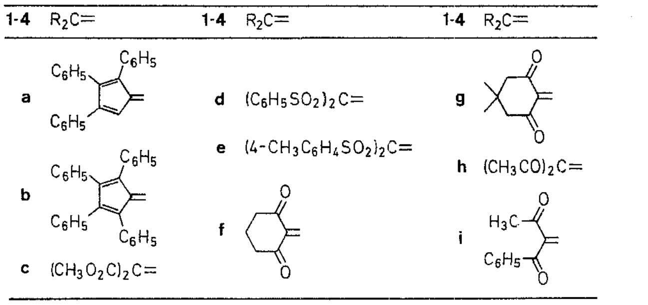
Sulphonium Ylides. Methylphenylsulphonium-2,3,4-triphenylcyclopentadienylide (**5**) had previously been prepared from **1a** in a very impure state.[6] Using (Cu(hfa)$_2$ it could be prepared at room temperature, to give a much purer product.



1g **6**

Telluronium Ylides. Only one telluronium ylide has hitherto been prepared by the diazo method.[4]





Arsonium Ylides: In addition to **2a**, other arsonium ylides have been prepared. Two are new, one other [$(C_6H_5)_3As{=}C(CO_2CH_3)_2$] had been made by an alternative method. $(C_6H_5)_3As{=}C(SO_2C_6H_5)_2$ had been made from the diazo compound at a much higher temperature.

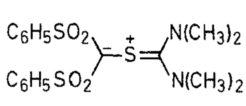
Table 2. Ylides **2**–**7** Prepared

Product	Reaction Conditions		Recrystallization Solvent[a]	Yield (%)	mp (°C)		Earlier Lit.
	Solvent	Temperature (°C), Time			found	reported	
2a	benzene	80, 2 h	benzene/PE	78	198–202	198–200	6,15
	benzene	r.t., 312 h	benzene/PE	31	208–212		
2b	benzene	80, 2 h	nitromethane	66	238–240	204–206	16
2c	toluene	110, 2 h	chlorobenzene	62	178–187	186–188	7
2d	benzene	80, 2 h	chlorobenzene	58	248–250	252–254	5,17
2e	benzene	80, 5.5 h	CH_2Cl_2/PE	69	236–240		new
2f	toluene	110, 1.5 h	CH_2Cl_2/hexane	20	162–164		new
3b	benzene	80, 2 h	–	32	210 (dec)	196–198	1
3d	benzene	80, 2 h	chlorobenzene	78	196–198		18
3e	benzene	80, 6 h	benzene/PE	77	192 (dec)		18
3f	benzene	80, 1.5 h	EtOAc (+charcoal)	58	168–172		18
3g	toluene	110, 2 h	EtOAc	40	162–164		18
3h	benzene	80, 1 h	benzene	59	186 (dec)		18
3i	benzene	80, 1 h	–	46	148–150		18
4d	benzene	80, 2 h	–	22	107–109		new
4f	benzene	80, 2.5 h	–	42	224–228		new
5	benzene	r.t., 2 weeks	benzene/PE	31	140 (dec)	135–138	6
6	toluene	110, 1 h	–	23	154–158	162–163	19
7	benzene	80, 2 h	(washed with MeOH)	65	171–174	170–173	14

[a] PE = petroleum ether.

Stibonium Ylides. Only one stibonium ylide had been isolated[1] before the present work. Attempts to prepare others by thermal decomposition of diazo compounds had failed, seemingly because the ylides had themselves decomposed under the reaction conditions.

Bismuthonium Ylides. Only one bismuthonium ylide has been described.[2] Although reasonably stable as a solid it decomposed rapidly in solution and hence could not be purified. By the use of Cu(hfa)$_2$ as catalyst two new triphenylbismuthonium ylides, both khaki coloured, the bis(phenylsulphonylmethylide) (**4d**) and the 2,6-dioxocyclohexylide (**4f**), have been obtained. Again, neither could be purified satisfactorily because of decomposition ensuing, but spectroscopic evidence strongly supports the proposed structures. The mass spectrum of **4d** contained no molecular-ion peak, but had peaks at m/z values which correspond to fragments in which the ylidic bond is intact. Peaks corresponding to ions formed from the breakdown of $[(C_6H_5)_3Bi]^+$ and the carbanionic moiety were also evident. Ylide **4f** was extremely insoluble in all common solvents and could not be recrystallised. A ^{1}H-NMR spectrum, which closely resembled that of the corresponding arsonium and stibonium ylides, was obtained using a solution in pyridine-d_5.



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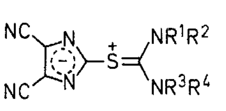

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Thiouronium Ylides. The only thiouronium ylides previously made from diazo compounds were imidazolylide derivatives **8**.[13] Ylide **7**[14] has now been prepared using Cu(hfa)$_2$ as catalyst.

Catalytic decomposition of diazo compounds under mild conditions with Cu(hfa)$_2$ as catalyst thus provides a fertile method for the preparation of a wide variety of ylides and could serve as a useful general method for the preparation of ylides.

Ylides 2–7; General Procedure:

The diazo compound **1** (1 mmol), carbene trapping reagent (2 mmol), and Cu(hfa)$_2$ (11.4 mg, 0.05 mmol) are dissolved in dry benzene or toluene (20 mL) and the mixture is heated under reflux, or allowed to stand for the times shown for individual compounds (Table 2). Evaporation of the solvent *in vacuo* and trituration of the residue with Et$_2$O and/or hexane gives the ylide as a solid, which is filtered off and washed well with Et$_2$O.

Ylides which had been reported previously were all validated by comparing their spectra with those of authentic samples. The following ylides are new (see also Table 2):

Triphenylarsonium Bis(toluene-p-sulphonyl)methylide (Arsorane **2e***):*

$C_{33}H_{29}AsO_4S_2$	calc.	C 63.05	H 4.65
(628.7)	found	62.7	4.65

^{1}H-NMR (CDCl$_3$): $\delta = 2.38$ (s, 6H, 2 CH$_3$); 6.98, 7.08 (half of A$_2$B$_2$ system, 4H, tosyl); 7.25– 7.7 (m, 19H, tosyl and phenyl).

Triphenylarsonium 2,6-Dioxocyclohexylide (Arsorane **2f***):*

$C_{24}H_{21}AsO_2$	calc.	C 69.2	H 5.1
(416.4)	found	69.8	5.1

^{1}H-NMR (CDCl$_3$): $\delta = 2.03$ (quin, 2H, 4-CH$_2$); 2.43 (t, 4H, 3-CH$_2$, 5-CH$_2$); 7.37– 7.70 (m, 15H$_{\text{arom}}$).

^{13}C-NMR (CDCl$_3$): $\delta = 21.5$ (C-4); 38.1 (C-3, C-5); 89.6 (C-1); 128.7, 129.3, 131.8, 133.0 (*ipso-*, *m-*, *p-*, *o-*C$_{\text{arom}}$); 194.1 (C-2, C-6).

Triphenylbismuthonium Bis(phenylsulphonyl)methylide (**4d**):

IR (nujol mull): 1278, 1118 cm^{-1} (SO$_2$).

UV (MeOH): $\lambda_{\text{max}} = 211$ (log $\varepsilon = 4.42$), 258 (3.90), 264 (3.87), 272 nm (3.80).

^{1}H-NMR (CD$_2$Cl$_2$): $\delta = 7.00$–8.20 (m, 15H$_{\text{arom}}$).

Triphenylbismuthonium 2,6-Dioxocyclohexylide (**4f**):

IR (hexachlorobutadiene mull): broad band centred at 1440 cm^{-1} (CO).

UV (MeOH): $\lambda_{\text{max}} = 267$ nm (log $\varepsilon = 4.02$)

^{1}H-NMR (pyridine-d_5): $\delta = 1.82$ (quin, 2H, 4-CH$_2$); 2.45 (t, 4H, 3-CH$_2$, 5-CH$_2$); 7.13–7.68 (m, 15H$_{\text{arom}}$).

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