

**A NOVEL OLEFINATION OF DIAZO-COMPOUNDS WITH CARBONYL COMPOUNDS
MEDIATED BY TRIBUTYLSTIBINE AND CATALYTIC AMOUNT OF Cu(I)I[†]**

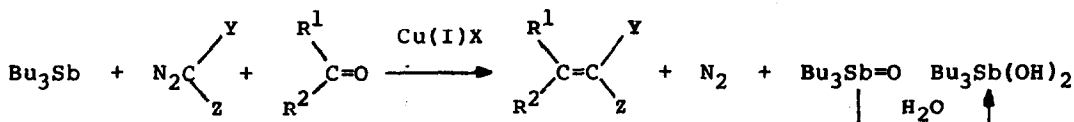
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Abstract. A one-pot reaction of tributylstibine, diazo-compounds including dimethyl diazomalonate, ethyl diazoacetate and diazoacetylacetone, carbonyl compounds and catalytic amount of Cu(I)I resulted in olefination in high yields.

There has been much interest in heteroatom ylides for organic synthesis. However, most research on stibonium ylides has been sporadic. One of the common synthetic routes to heteroatom ylides is from diazo compounds.¹ Lloyd et al. prepared triphenylstibonium tetraphenylcyclopentadienylide, which is the first stibonium ylide and reactive toward arylaldehydes,² and eight stable phenyl ligand-stibonium ylides with strong electron-withdrawing substituents, such as COR, SO₂R etc., in the alkylidene moiety by the diazo method, but found that the stable stibonium ylides were inert even toward 2,4-dinitrobenzaldehyde.³ Diazomalonic esters, including the diazo-derivative from Meldrum's acid, and ethyl diazoacetate etc. did not, however, provide stibonium ylides with triphenylstibine.⁴ On the other hand, tributylstibonium dicarbomethoxymethylide was proposed to be a possible active intermediate for Wittig-type reaction with carbonyl compounds.⁵

We would like to report here a novel olefination of diazo-compounds, including dimethyl diazomalonate, ethyl diazoacetate and a diazoacetylacetone, with carbonyl compounds mediated by tributylstibine and a catalytic amount of Cu(I)X(X= I, Br, Cl).



Y=Z= CO₂Me; Y= H, Z= CO₂Et; Y=Z= COMe. X= I, Br, Cl.

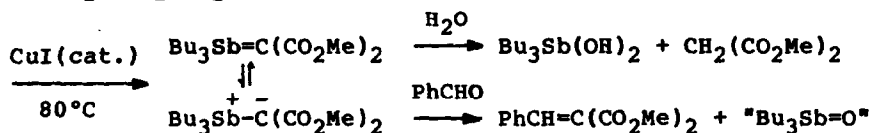
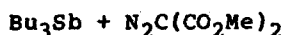
One-pot reactions of dimethyl diazomalonate(2.4mmol), carbonyl compounds (2mmol), tributylstibine(2.4mmol) and CuI(0.1mmol) in benzene(4ml) were carried out at 70-80°C for 4-6 hours until the carbonyl compounds were

converted completely (monitored by TLC). Flash chromatography on silica gel gave the products in high yields. The results are given in Table 1 (entry 1-9).

The reaction is proposed to be through tributylstibonium (dicarbomethoxy) methylyde. In the absence of tributylstibine or CuX catalyst, olefination did not occur at all. Because the alkyl ligand is an electron-donating group while phenyl ligand is an electron-withdrawing group, the lone pairs of electrons of Bu_3Sb are more accessible than those of Ph_3Sb . Thus, Bu_3Sb can react with the carbene from diazo compounds more easily than Ph_3Sb to generate the stibonium ylide. Moreover, the alkyl ligand-stibonium ylide is reactive with carbonyl compounds.

After heating a mixture of an equivalent of Bu_3Sb , $\text{N}_2\text{C}(\text{CO}_2\text{Me})_2$ and a catalytic amount of CuI for two hours, attempts to isolate the ylide by chromatography failed; what we obtained was only dimethyl malonate. To the crude mixture, an equivalent of benzaldehyde was added; the olefination product was also produced (68%) (Scheme 1). This illustrates that the ylide is sensitive to air.

Scheme 1.



Although Lloyd et al. reported that bis(hexafluoroacetylacetonato)copper (II) was the most effective catalyst for preparation of triphenylstibonium ylide from diazo compound,¹ we found cuprous halide Cu(I)X was the most effective catalyst for the preparation of tributylstibonium ylide. This finding is coincident with the reported result that Cu(I)X was the most effective catalyst for the decomposition of diazo compounds.⁶ The efficiency of various catalysts for the reaction of Bu_3Sb , $\text{N}_2\text{C}(\text{CO}_2\text{Me})_2$ and benzaldehyde are shown in Table 2.

Other trapping reagents Bu_3M ($\text{M} = \text{P}, \text{As}, \text{or Bi}$) of group 15 have been investigated. For benzaldehyde as substrate, tributylarsine could also mediate the reaction (84%), tributylphosphine could not, and the reaction mediated by tributylbismuthine was complicated (Table 3).

This one-pot reaction can also be used with ethyl diazoacetate and carbonyl compounds at 40-50°C to give ethyl β -substituted acrylates in high yields. The results are given in Table 1 (entry 10-17). With CuI catalysis the thermal decomposition of ethyl diazoacetate was explosive, so the reaction

Table 1. Olefination of Diazo-compounds with Carbonyl Compounds

Entry	$\overset{1}{R}\overset{2}{R}C=O$	Y	Z	T(°C)	Time(h)	Yields(%) ^a
1	PhCHO	CO ₂ Me	CO ₂ Me	70	4	98
2	p-ClC ₆ H ₄ CHO	CO ₂ Me	CO ₂ Me	70	4	95
3	p-CH ₃ C ₆ H ₄ CHO	CO ₂ Me	CO ₂ Me	80	6	97
4	p-CH ₃ OC ₆ H ₄ CHO	CO ₂ Me	CO ₂ Me	80	6	89
5	PhCH=CHCHO	CO ₂ Me	CO ₂ Me	80	6	81
6	2-Thiofurfural	CO ₂ Me	CO ₂ Me	70	4	94
7	i-PrCHO	CO ₂ Me	CO ₂ Me	70	4	86
8	Citral	CO ₂ Me	CO ₂ Me	70	4	90
9	Cyclohexanone	CO ₂ Me	CO ₂ Me	80	6	62
10	PhCHO	H	CO ₂ Et	40	4	97
11	PhCH=CHCHO	H	CO ₂ Et	50	4	97
12	CH ₃ (CH ₂) ₅ CHO	H	CO ₂ Et	40	4	96
13	2-Furfural	H	CO ₂ Et	40	4	95
14	Cyclopentanone	H	CO ₂ Et	50	6	86
15	Cyclohexanone	H	CO ₂ Et	50	6	88
16	Et ₂ C=O	H	CO ₂ Et	50	6	82
17	Ph ₂ C=O	H	CO ₂ Et	50	10	30 ^b
18	PhCHO	COMe	COMe	80	6	92

a. Isolated yields based on carbonyl compounds. The structures of all products were confirmed by ¹H NMR and IR. b. Unconverted material could be recovered.

Table 2. Efficiency of Various Catalysts^a

Run	Catalyst	Amount (eq.)	T/time (°C/h)	Yield ^b (%)
1	Active Cu ^o	0.2	80/6	40
2	CuCl ₂	0.1	80/4	80
3	CuSO ₄	0.1	80/6	67
4	Cu(OAc) ₂	0.1	80/6	62
5	CuI	0.05	70/4	97
6	CuBr	0.05	80/4	97
7	CuCl	0.1	80/4	97
8	None	--	110/10	0

a. Bu₃Sb: N₂C(CO₂Me)₂: PhCHO, 1.2: 1.2: 1.0 (mmol).

b. Yields determined by ¹H NMR.

Table 3. Reaction mediated by Various R₃M^a

Run	R ₃ M	T(°C)/t(h)	Yield(%) ^b
1	Bu ₃ P	80/10	--
2	Bu ₃ As	80/4	84
3	Bu ₃ Sb	80/4	98
4	Bu ₃ Bi	80/10	20 ^c

a. R₃M: N₂C(CO₂Me)₂: PhCHO: CuI, 1.2: 1.2: 1.0: 0.05 (mmol).

b. Yields determined by ¹H NMR.

c. Accompanied with other products.

was carried out by first diluting the mixture of tributylstibine(1.2mmol), carbonyl compounds(1mmol) and CuI(0.05mmol) with dry benzene(4ml) and then adding the ethyl diazo-acetate(1.2mmol). Ketones as well as aldehydes could be converted to the corresponding products. When aldehydes were used as substrates, the reactions gave the olefins in E configuration. The reaction is also proposed to be through the corresponding stibonium ylide.

Diazo-acetylacetone also reacted with benzaldehyde in the presence of tributylstibine and a catalytic amount of Cu(I)I to give 3-benzylidene-2,4-pentadione(92%)(entry 18).

This new type of reaction is simple, novel and proceeds without base and in high yields. The materials are easy accessible. It is of particular interest in that the tributylstibonium ylides bearing even two strong α -electron-withdrawing groups, such as CO_2R and COMe , were involved in achieving olefination successfully with not only aldehydes but also ketones. These results illustrate that the alkyl ligand-stibonium ylide is more reactive than the phenyl ligand-stibonium ylide and the analogues of phosphonium and arsonium ones. Studies on the synthetic applications of this type reaction and the reactivities of the stibonium ylides are being pursued.

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References and Notes

† This is the 86th reports on the studies of the synthetic applicaton of elemento-organic compounds of 15th and 16th groups.

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