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A NOVEL OLEFINATION OF CARBONYL COMPOUNDS WITH α-BROMOACETIC ESTER MEDIATED BY TRI-n-BUTYLSTIBINE[1]

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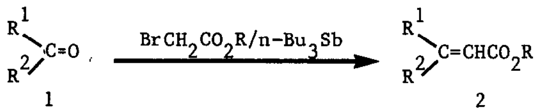
Summary. Tri-n-butylstibine has been found to mediate the olefination of carbonyl compounds by α-bromoacetic ester to give corresponding olefins in good yields.

Olefination of carbonyl compounds has been found widespread application in synthetic organic chemistry especially for the synthesis of natural products and the well known methods to achieve olefination are using Wittig or Phosphoryl reagent. We have found that arsonium ylides bearing an electron-withdrawing substituent in the alkylidene moiety are more reactive than the corresponding phosphonium ylides[2-5]. So far as the stibonium ylide is concerned only a few reports appeared in the literature. Attempt to prepare stibonium salt with triphenylstibine and 9-bromofluorene failed[6] due to its lower nucleophility. Similarly, starting from ω-bromoacetophenone and triphenylstibine or tri-n-butylstibine, no stibonium salt but the debrominated product, acetophenone, was obtained[7]. Preparation of triphenylstiboniummethylide was succeeded but the reaction of methylide with benzophenone led to the formation of rearranged product, diphenylacetaldehyde[8].

We now wish to report a novel olefination of carbonyl compounds with bromoacetic ester mediated by tri-n-butylstibine.



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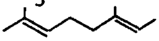
It is noteworthy that the characteristic feature of this reaction is without using any base and the reaction is carried out under neutral condition. The one-pot reaction is quite convenient and the products are stereoselective.

The results are shown in the following Table. All products were characterized by IR, NMR and mass spectroscopy and all the double bondsformed were exclusively in E form.

In addition, this reaction could also take place in the presence of solvents, such as acetonitrile, benzene, THF and n-hexane and the yields were approximately the same. Bromoacetophene, bromomalonic ester and chloroacetonitrile could also be used for olefination. Further study on the application of these compounds in organic synthesis and the mechanism of this reaction is being pursued.

Compound	R^1	R^2	R	Condition		Yield[a]
				Temp.(°C)	Time(h)	(%)
2a	$CH_3CH_2CH_2$	H	C_2H_5	100	2.5	92
2b	$CH_3(CH_2)_9CH_2$	H	C_2H_5	100	3	88
2c	$CH_3CH{=}CH$	H	C_2H_5	100	2.5	84
2d		H	C_2H_5	120	10	82
2e		H	C_2H_5	100	2.5	64
2f	C_6H_5	H	C_2H_5	80	3	96
2g	C_6H_5	H	CH_3	100	6	88
2h	$C_6H_5CH{=}CH$	H	C_2H_5	120	7	86
2i	C_2H_5	C_2H_5	C_2H_5	130	6	10[b]
2j	$-(CH_2)_4-$		C_2H_5	120	6	40
2k	$-(CH_2)_5-$		C_2H_5	130	7	45

[a] isolated yield.

[b] yield determined by NMR.

The typical procedure was as follows:

Benzaldehyde (100 mg, 0.94 mmol) was injected to a solution of 200 mg(1.20 mmol) of ethyl bromoacetate and 320 mg(1.09 mmol) of tri-n-butylstibine under nitrogen. The reaction mixture was stirred at 80°C for 3h in a capped flask and monitored the disappearance of the starting material and the complete formation of the product by NMR. Then the mixture was treated with 2% aqueous sodium hydroxide solution and extracted with ether. The organic layer separated was washed with water, dried and evaporated to remove the solvent. The residue was chromatographed on silica gel eluting with 85:15 petroleum ether(b.p.60-90°C)/ ethyl acetate to give 160 mg(96%) of 2f.

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References and Notes

1. This paper is the 43rd report on the studies of the application of elemento-organic compounds of the fifth and sixth group in organic syntheses.
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