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Tributylstibine-Mediated Olefination of Carbonyl Compounds with Bromomalonic Ester and with Dibromomalonic Ester—A Possible Pathway Through a Stibonium Ylide via Halophilic Initiation by Tertiary Stibines†

Chen Chen, Yao-Zeng Huang,* Yanchang Shen, and Yi Liao

Shanghai Institute of Organic Chemistry, Academia Sinica, 345 Lingling Lu, Shanghai, Peoples Republic of China

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ABSTRACT

Tributylstibine can mediate the olefination of carbonyl compounds with bromomalonic ester and with dibromomalonic ester. An initial halophilic attack of tributylstibine on the bromine of bromomalonic or dibromomalonic ester forming an ion pair of bromotributylstibonium cation and malonic (***A***) *or bromomalonic ester carbanion* (***B***)*, respectively, is proposed. These ion pairs react with carbonyl compounds to achieve subsequent olefination. Alternatively, 2 equiv of* ***A*** *collapse, with elimination of malonic ester, to form stiborane* ***D****, and the ion pair* ***B*** *reacts with another equivalent of tributylstibine to form stiborane* ***D****. This last undergoes a Wittig-type reaction with carbonyl compound to achieve olefination.*

In our previous communications, we reported the tributylstibine-mediated olefination reactions of carbonyl compounds with bromoacetates [1], bromoacetamide [2], chloroacetonitrile [3], and α-bromoketones [4]; the reactions of aldehydes with 3-bromobutanone to form β-hydroxyketones [5] and with trichloroacetonitrile to form α,α-dichloro-β-hydroxynitriles [6]; and the reaction of dibromomalonic ester and its analogs with electron-deficient olefins to form cyclopropanes [7]. However, the mechanisms of the tertiary stibine-mediated reactions have hitherto not been clear. Here we would like to report the tributylstibine-mediated olefination of carbonyl compounds with bromomalonic ester and with dibromomalonic ester and discuss the reaction mechanisms thereof.

RESULTS AND DISCUSSION

In the olefination of carbonyl compound (**1**) with bromomalonic ester (**2**) mediated by tributylstibine (**3**) to form **4** or **5**, the best molar ratio of reagents **1**, **2**, and **3** was found to be 1 : 2 : 2. The byproducts were malonic ester and bis(bromotributylantimony) oxide, **6** (Eq. 1):

$$\underset{\mathbf{1}}{R^1R^2C{=}O} + 2\ \underset{\mathbf{2a}:\ R = Me;\ \mathbf{b}:\ R = Et}{BrCH(CO_2R)_2} + 2\ \underset{\mathbf{3}}{Bu_3Sb} \xrightarrow{50^\circ C,\ 0.5\ h} \underset{\mathbf{4}\ R = Me;\ \mathbf{5}\ R = Et}{R^1R^2C{=}C(CO_2R)_2} + \underset{\mathbf{8}}{CH_2(CO_2R)_2} + \underset{\mathbf{6}}{(Bu_3SbBr)_2O} \quad (1)$$

The results are given in Table 1.

In the olefination with dibromomalonic ester (**7**), the best molar ratio of **1**, **7**, and **3** to cause complete conversion of the carbonyl compound

† This paper is the 70th report on the studies of the application of elementoorganic compounds of the 15th and 16th groups in organic synthesis.

* To whom correspondence should be addressed.

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TABLE 1 Olefination of Carbonyl Compounds with Bromomalonic Ester[a]

Compound	R^1	R^2	R	Yield (%)[b]
4a	*i*-Bu	H	Me	97
4b	Ph	H	Me	100[c]
4c	*p*-$O_2NC_6H_4$	H	Me	94
4d	PhCO	Ph	Me	91
5a	Geranyl	H	Et	95
5b	2-Furyl	H	Et	93
5c	Pyridyl	H	Et	97

[a] The reaction was carried out with 2 mmol of carbonyl compound, 4.2 mmol of dialkyl bromomalonate, and 4.2 mmol of tributylstibine at 50°C for 0.5 h.
[b] Isolated yields by flash chromatography on an alumina–silica gel (1 : 1) column.
[c] Determined by NMR.

was 1 : 1 : 2. Bis(bromotributylantimony) oxide (**6**) was the sole byproduct (Eq. 2).

$$\underset{\mathbf{1}}{R^1R^2C{=}O} + \underset{\mathbf{7a}: R = Me \quad \mathbf{b}: R = Et}{Br_2C(CO_2R)_2} + 2\,\underset{\mathbf{3}}{Bu_3Sb} \xrightarrow{\text{room temp., 0.5 h}} \underset{\mathbf{4}\ R = Me \quad \mathbf{5}\ R = Et}{R^1R^2C{=}C(CO_2R)_2} + \underset{\mathbf{6}}{(Bu_3SbBr)_2O} \qquad (2)$$

The results are given in Table 2.

Owing to their strongly nucleophilic character, tertiary phosphines generally react with alkyl halides by an S_N2 mechanism. However, triphenylstibine is inert to alkyl halides with general structure, and the reactions of trialkylstibines with alkyl halides have not been widely investigated.

Hoffmann [8] reported that the organic compounds containing a positively polarized halogen atom reacted with tertiary phosphines either by reductive elimination of the halogen or by formation of phosphonium salts and quasi-phosphonium salts. The reaction can be accelerated by both electron donors and electron acceptors [8]. Accordingly, in our reactions, the tertiary stibine may be behaving the same as these tertiary phosphines. The strong electron acceptors, two carboalkoxy groups, can cause a change in the reactivity of the bromo or dibromo component by polarizing the C—Br bond, giving the bromine atom a partial positive charge and simultaneously stabilizing the remaining carbanion after the removal of the bromine cation. The center of the S_N2 reaction is thus shifted from carbon atom to the bromine. Thus, the reaction of halogen compound with tributylstibine formed an ion pair **A** in the case of bromomalonate and an ion pair **B** in the case of dibromomalonate. Either ion pair reacted with carbonyl compound to achieve further olefination (Schemes 1 and 2). Our studies of the reaction mechanism were based on the ^1H NMR spectral data of the reactions carried out under different conditions. Some data are summarized in Tables 3 and 4.

When tributylstibine and dimethyl bromomalonate (**2a**) were mixed under nitrogen, an exothermic reaction took place. Proton NMR spectrum of the reaction mixture showed it contained dimethyl malonate [δ = 3.20 (s, CH_2), and 3.63 (s, $2CH_3$)], dibromotributylstiborane (**C**) [characterized by the chemical shift of methylene connected to antimony atom, δ = 2.79 (t, J = 7.5 Hz, 3 CH_2)] [9], and compound **D**, which has δ = 3.46 [10] for the methoxy group (Table 3, run 1).

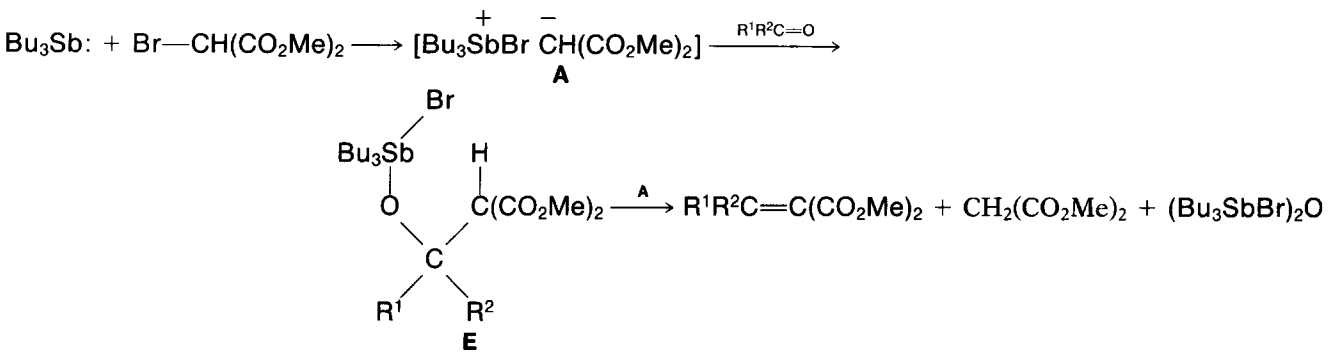
On the other hand, when 2 equiv of tributylstibine and 1 equiv of dimethyl dibromomalonate (**7a**) reacted under nitrogen, the reaction mixture contained dibromotributylstiborane (**C**) and compound **D** with the δ value of the methoxy group also at 3.46 (Table 4, run 1).

Akiba and co-workers have reported that in the reduction of ω-bromoacetophenone with tributylstibine, a stibonium ylide intermediate is formed before protonation [11].

TABLE 2 Olefination of Carbonyl Compounds with Dibromomalonic Ester[a]

Compound	R^1	R^2	R	Yield (%)[b]
4e	2-Thienyl	H	Me	99
4f	—$(CH_2)_5$		Me	90
5d	*n*-Pr	H	Et	96
5e	$MeCHCH_2CH{=}CHCH{=}C$—	H	Et	91
5f	2-(3-Bromothiofuryl)	H	Et	97
5g	2-Pyrrolyl	H	Et	97
5h	Ph	H	Et	86
5i	*p*-$O_2NC_6H_4$	H	Et	89
5j	—$(CH_2)_4$		Et	88
5k	PhCO	Ph	Et	91

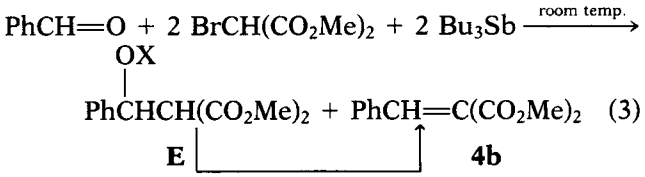
[a] The reaction was carried out with 2 mmol of carbonyl compound, 2.1 mmol of dialkyl dibromomalonate, and 4.2 mmol of tributylstibine at ambient temperature for 0.5 h.
[b] Isolated yields by chromatography.



SCHEME 1

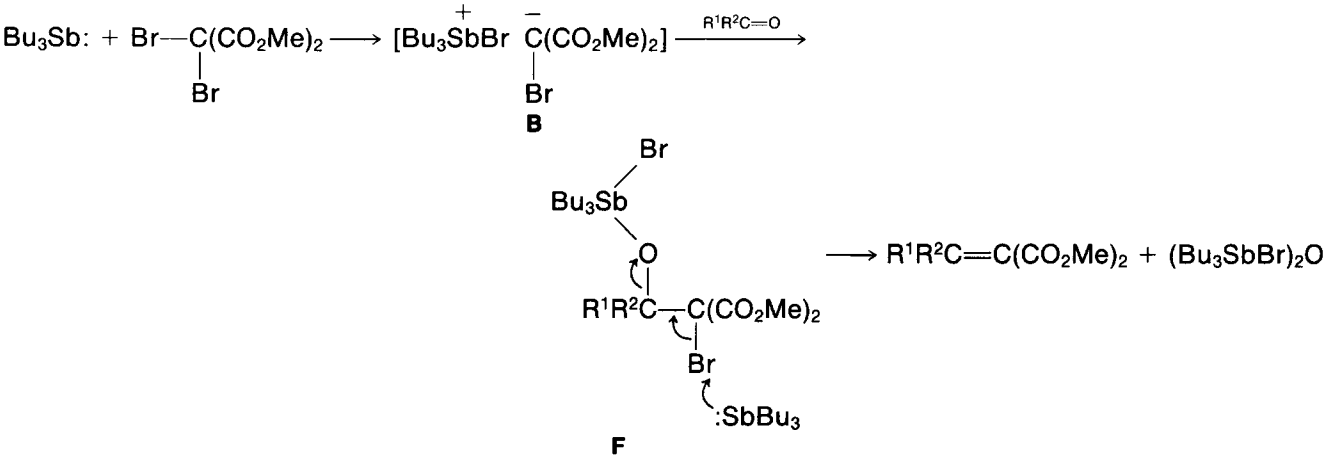
Since the same intermediate **D** was formed from either dimethyl bromomalonate or dimethyl dibromomalonate, it is reasonable to suppose that **D** is di(carbomethoxy)methylenetributylstiborane [12]. Treatment of the intermediates (**C** and **D**) with water gave dimethyl malonate and bis(bromotributylantimony) oxide (Scheme 3). Nevertheless, when the reaction intermediates (**C** and **D**) were treated with methylvinyl ketone, no cyclopropane product formed at all, illustrating that the three-membered ring formation was not through the stibonium ylide pathway [7].

When a mixture of benzaldehyde and dimethyl bromomalonate was treated with tributylstibine in a molar ratio of 1 : 2 : 2 at ambient temperature, an exothermic reaction took place. The ^{1}H NMR spectrum of this reaction mixture showed that, other than the signals of dimethyl benzylidenemalonate [δ = 3.70 (s, Me), 3.73 (s, Me), 7.29 (s, Ph), and 7.53 (s, CH=)], three sets of peaks were discernible [δ = 3.36 (s, 2Me), 5.05 (d, J = 8.0 Hz, CHO), and 7.22 (s, Ph)], their relative intensities were 6 : 1 : 5 (Table 3, run 5). It was appropriate to assign them to the reaction intermediate **E** as the 2,2-dicarbomethoxy-1-phenylethoxy antimony compound (the proton signal of the CH connected to two carbomethoxy groups was not discernible, but the doublet of the benzyl proton was firmly displayed). The ratio of **E** and the olefin (**4b**) was about 1 : 1. The independence of the **E** : **4b** ratio from the amount of benzaldehyde (**1b**) might imply that another pathway was accompanied by an halophilic initiated one in this olefination. This pathway could have involved stibonium ylide **D** (Table 3, runs 5, 6). However, the intermediate **E** was not stable enough; slight heating could cause it to decompose to olefin (Eq. 3) [13].



(3)

where X = Bu_3SbBr.



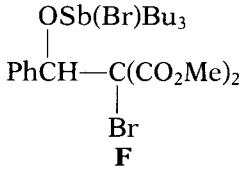
SCHEME 2

TABLE 3 Proton NMR Data of Reaction of Benzaldehyde **(1b)** with Dimethyl Bromomalonate **(2a)** and Tributylstibine **(3)**[a]

	Ratio of:			*of MeO (rel. %)*					*Conversion* **(E/4b)**
Run	***2a***	***3***	***1b***	***E***	***D***	***8***	***4b***	***2a***	(%)
1	1	1	0	—	3.46 (27)	3.63 (53)	—	—	—
2	2	1	0	—	3.42 (6)	3.63 (43)	—	3.75 (48)	—
3	2	1	(1)[b]	—	—	3.63 (46)	3.73 (~5)	3.75 (45)	~5 (—)
4	2	2	(1)[b]	3.36 (8)	—	3.64 (38)	3.70, 3.73 (34)	—	38 (18 : 82)
5	2	2	1	3.36 (13)	—	3.64 (57)	3.70, 3.73 (30)	—	84 (50 : 50)
6	1	1	1	3.36 (13)	—	3.63 (49)	3.70, 3.73 (34)	—	56 (54 : 46)

[a] Reactions were carried out at room temperature for 0.5 h by adding **3** to **2a** or to a mixture of **2a** and **1b.**
[b] Benzaldehyde was added to the intermediate produced from run 1.

On the other hand, benzaldehyde was not completely converted when it reacted with equivalents of dimethyl dibromomalonate and tributylstibine; a byproduct could be detected with ^{1}H NMR. The structure of the reaction intermediate **F** could be assigned according to its chemical shifts [δ = 7.28 (s, Ph), 5.23 (s, CHO), and 3.50 (s, 2MeO)]. Their relative intensities were also 5 : 1 : 6. The ratio of benzaldehyde, compound **F**, and olefin product was roughly 9 : 4 : 5 (Table 4, run 4). Compound **F** is unstable; it decomposes to benzaldehyde and dimethyl bromomalonate in chromatography on silica gel.



F

It is interesting to note that when benzaldehyde (**1b**) is added to the intermediate produced from tributylstibine (**3**) and dimethyl bromomalonate (**2a**) or dibromomalonate (**7a**), olefin **4b** is the product, and **E** or **F** is not detected (Table 3, run 4, and Table 4, run 3). This result strongly supported the formation of the intermediate stibonium ylide **D**, which could give neither **E** nor **F**.

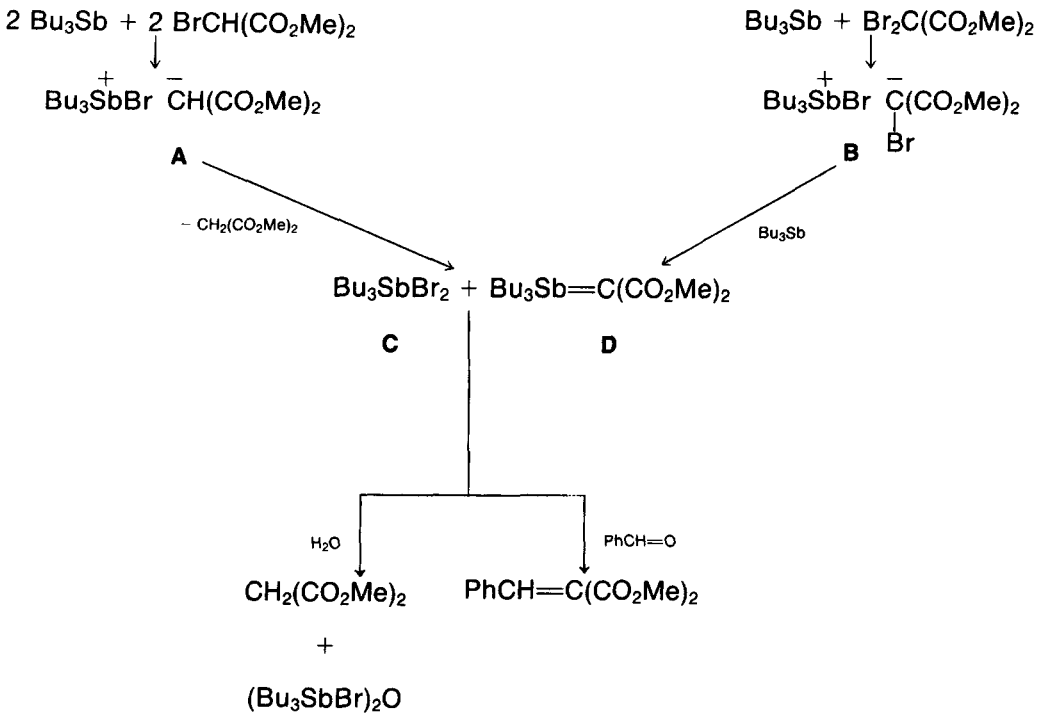
From runs 3 and 4 in Table 3, we found that the formation of **D** was very rare, because **D** could not be tolerated in the presence of excess **2a**, which possesses active hydrogen [14].

Heating was needed to initiate the reaction when the olefination was carried out with triphenylstibine as mediator. For example, triphenylstibine-mediated olfination of benzaldehyde with dimethyl bromomalonate should be performed at 70°C (Eq. 4), in contrast to the tributylstibine-mediated reaction, which could take place even at room temperature.

TABLE 4 Proton NMR Data of Reaction of Benzaldehyde **(1b)** with Dimethyl Dibromomalonate **(7a)** and Tributylstibine **(3)**[a]

	Ratio of:			*of MeO (rel. %)*						*Conversion* **(F/4b)**
Run	***7a***	***3***	***1b***	***D***	***F***	***8***[b]	***4b***	***2a***	***7a***	(%)
1	1	2	0	3.46 (73)	—	3.63 (27)	—	—	—	—
2	1	1	0	3.46 (31)	—	3.63 (8)	—	3.75 (22)	3.84 (39)	—
3	1	2	(1.5)[c]	—	—	3.63 (28)	3.71, 3.74 (72)	—	—	42 (0 : 100)
4	1	1	1	—	3.50 (7)	3.63 (3)	3.73 (27)	3.75 (35)	3.83 (27)	34 (41 : 59)

[a] Reactions were carried out at room temperature for 0.5 h by adding **3** to **7a** or to a mixture of **7a** and **1b.**
[b] The proton might come from moisture in solvent or in workup.
[c] Benzaldehyde was added to the intermediate produced from run 1.

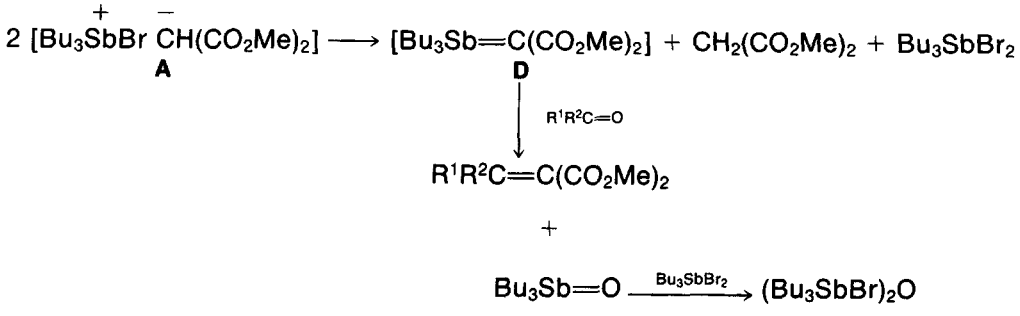


SCHEME 3

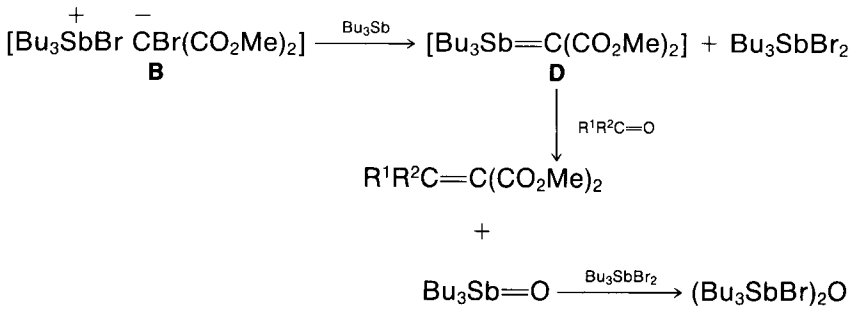
$$PhCHO + 2\ BrCH(CO_2Me)_2 \xrightarrow[70°C,\ 2\ h]{2\ Ph_3Sb} PhCH{=}C(CO_2Me)_2 \quad (4)$$
80%

Lloyd and co-workers have found that triphenyl(diacetylmethylene)stiborane does not undergo Wittig-type reactions and that triphenyl(dicarboalkoxymethylene)stiborane cannot even be prepared by the reaction of triphenylstibine with diazomalonic ester [14]. Furthermore, trialkylstibines have been known to react with alkyl halides [15], whereas triphenylstibine does not [16]. All these facts demonstrate that different substituents on a tertiary stibine greatly influence its reactivity. Obviously, the halophilicity of tributylstibine is greater than that of triphenylstibine. Based on the experiments, the mechanism of the tertiary stibine-mediated reaction of carbonyl compounds with halogeno compounds is most likely initiated by a halophilic attack of the stibine to form an ion pair of the bromotributylstibonium cation and the remaining carbanion. The ion pair undergoes the subsequent olefination reaction (Schemes 1 and 2).

Alternatively, in the case of bromomalonic ester, 2 equiv of ion pair **A** undergo subsequent reaction to form stibonium ylide **D** when substrate is absent, accompanied with malonic ester and dibromotributylstiborane. The stibonium ylide **D** reacts with the carbonyl compound to undergo a typical Wittig-type reaction, which without question, proceeds through a four-membered ring intermediate, and the tributylstibine oxide formed easily combines with dibromotributylstiborane to give bis(bromotributylantimony) oxide [17] as shown in Scheme 4.



SCHEME 4



SCHEME 5

In the case of dibromomalonic ester, ion pair **B** reacts with another equivalent of tributylstibine to form also stibonium ylide **D**, which further reacts with the carbonyl compound to undergo a Wittig reaction as shown in Scheme 5.

CONCLUSION

The mechanisms of the tributylstibine-mediated olefination of carbonyl compounds with bromomalonic ester and dibromomalonic ester are reasonably proposed to be initiated by a halophilic attack of tributylstibine. Ion pair **A** or **B** reacts with a carbonyl compound to achieve olefination. Alternatively, the stibonium ylide could be formed by collapse of 2 equiv of **A** or by reaction of **B** with tributylstibine. The stibonium ylide (**D**) can undergo Wittig-type reactions with carbonyl compounds.

EXPERIMENTAL

Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on Varian-360L instrument in CCl_4 solution with Me_4Si as an internal standard and are reported in δ units. Infrared spectra were taken with an Shimadzu IR-440 infrared spectrophotometer and are reported in cm^{-1} units (neat, unless otherwise stated). Mass spectra were obtained on Finnigan GC-MC 4021 spectrometer.

Materials

Tributylstibine [18], dialkyl bromomalonate [19], and dimethyl and diethyl dibromomalonate [20] were prepared according to methods given in the literature cited.

Olefination with Bromomalonic Ester

General Procedure When 4.2 mmol of tributylstibine were injected into a mixture of 4.2 mmol of dialkyl bromomalonate and 2 mmol of carbonyl compound under nitrogen, an exothermic reaction took place. After being heated at 50°C for 0.5 h, the mixture was chromatographed on an alumina–silica gel (1 : 1) column, ethyl acetate as eluent, to give the product.

Dimethyl isopentylidenemalonate (**4a**)

This compound showed bp 110°C at 2 mmHg; results by ^{1}H NMR, 0.96 (d, 6H, J = 6.0 Hz), 1.36–1.94 (m, 1H), 2.12 (dd, 2H, J = 6.0, 7.0 Hz), 3.72 (s, 6H), 6.85 (t, 1H, J = 7.0 Hz); by IR, 1730vs, 1642m; by MS, m/z (relative intensity), 201 ($M^+ + 1$, 100%), 169 (16), 157 (6), 99 (19); analysis, found, C, 59.95; H, 8.19; calculated for $C_{10}H_{16}O_4$, C, 59.98; H, 8.05%.

Dimethyl 4-nitrobenzylidenemalonate (**4c**)

This compound had mp 135–6°C; result by ^{1}H NMR (CCl_3CN), 3.76 (s, 3H), 3.80 (s, 3H), 7.02 (d, 2H, J = 9.0 Hz), 7.14 (s, 1H), 8.16 (d, 2H, J = 9.0 Hz); by IR (KCl), 1730vs, 1720vs, 1630s; analysis, found, C, 54.11; H, 4.04; N, 5.37; calculated for $C_{12}H_{11}NO_6$, C, 54.34; H, 4.18; N, 5.28%.

Methyl 2-carbomethoxy-3-phenyl-3-benzoylacrylate (**4d**)

This compound has mp 213–6°C; results by ^{1}H NMR, 3.56 (s, 6H), 7.31 (s, 5H), 7.36 (m, 3H), 7.80 (m, 2H); by IR (KCl), 1735vs, 1718vs, 1670s, 1625s; analysis, found, C, 70.53; H, 5.17; calculated for $C_{19}H_{16}O_5$, C, 70.36; H, 4.97%.

Olefination with Dialkyl Dibromomalonate

In a typical procedure, 1220 mg (4.2 mmol) of tributylstibine was slowly injected into a mixture of 224 mg (2.0 mmol) of 2-thiophenecarboxaldehyde and 600 mg (2.1 mmol) of dimethyl dibromomalonate under nitrogen; the reaction was exothermic. The mixture was then stirred at ambient temperature for 0.5 h and poured into an alumina–silica gel (1 : 1) column. Chromatography with ethyl acetate as eluent gave 450 mg of dimethyl 2-thienylmethylenemalonate (**4e**), yield, 99%, a colorless oil, which solidified on standing, mp 44–45°C. Results from ^{1}H NMR, 3.78 (s, 3H), 3.84 (s, 3H), 7.00 (d of d, 1H, J = 4.0, 4.0 Hz), 7.31 (d, 1H, J = 4.0 Hz), 7.45 (d,

1H, J = 4.0 Hz), 7.45 (d, 1H, J = 4.0 Hz); by IR, 1710s (C=O), 1610s (C=C); by MS, m/z (relative intensity), 227 (M^+ + 1, 22%), 226 (M^+, 43), 195 (44), 169 (5), 108 (22), 83 (11), 43 (100); analysis, found, C, 52.96; H, 4.45; calculated for $C_{10}H_{10}O_4S$, C, 53.09, H, 4.46%.

Diethyl 2-methyl-2,4-dihydrobenzylidenemalonate (**5d**). This is a colorless oil; results by ^1H NMR, 0.96 (d, 3H, J = 6.0 Hz), 1.32 (t, 6H, J = 7.0 Hz), 2.60–2.70 (m, 3H), 4.20 (q, 4H, J = 7.0 Hz), 5.83–6.34 (m, 3H), 7.08 (s, 1H); by IR, 1720s, 1665m, 1620m; by MS, m/z (relative intensity), 265 (M^+ + 1, 65%), 264 (M^+, 7), 219 (100), 173 (23), 144 (13), 117 (21); analysis, found, C, 67.81; H, 7.97; calculated for $C_{15}H_{20}O_4$, C, 68.16; H, 7.63%.

Diethyl 2-(3-bromo-2-thienyl)methylenemalonate (**5e**). This is an oil; results by ^1H NMR, 1.30 (t, 3H, J = 7.0 Hz), 1.35 (t, 3H, J = 7.0 Hz), 4.20 (q, 2H, J = 7.0 Hz), 4.27 (q, 2H, J = 7.0 Hz), 6.99 (d, 1H, J = 4.0 Hz), 7.04 (d, 1H, J = 4.0 Hz), 7.54 (s, 1H); by IR, 1720s, 1614s; by MS, m/z (relative intensity), 335, 333 (M^+ + 1, 14%), 334, 332 (M^+, 54), 289, 287 (36), 253 (M^+-Br, 46), 179 (100), 108 (27); analysis found, C, 42.84; H, 3.85; Br, 24.32; calculated for $C_{12}H_{13}BrO_4S$, C, 43.26; H, 3.93; Br, 23.98%.

Dimethyl cyclohexylidenemalonate (**4f**). This compound exhibits bp 120°C at 2 mmHg; results by ^1H NMR, 1.65 (m, 6H), 2.48 (m, 4H), 3.69 (s, 6H); by IR, 1720s, 1632m; analysis, found, C, 62.18; H, 7.88; calculated for $C_{11}H_{16}O_4$, C, 62.25; H, 7.60%.

Bis(bromotributylantimony) oxide (**6**)

Two millimoles of geranial, 4.0 mmol of diethyl bromomalonate, and 4.0 mmol of tributylstibine reacted at room temperature for 0.5 h under nitrogen. The mixture was then treated with light petroleum. White crystals deposited when the solution was allowed to stand overnight. After filtration and drying, 980 mg of bis(bromotributylantimony) oxide was obtained, yield, 46%; mp, 59–62°C [5].

Determination of **D** *with* ^1H *NMR*

In method (a), when 2.0 mmol of tributylstibine was slowly injected into a solution of dimethyl bromomalonate (2.0 mmol) in tetrachloromethane (2 mL) in a capped vessel filled with nitrogen at room temperature, an exothermic reaction took place. After being stirred for half an hour, the mixture was examined with ^1H NMR.

In method (b) 2.0 mmol of **3** and 2.0 mmol of **2a** were worked up as above.

Olefination of Benzaldehyde with **D**

Benzaldehyde was injected into a solution prepared by method (a) or (b) above; the reaction took place exothermally. After half an hour, the mixture was examined with ^1H NMR.

Determination of **E** *and* **F**

Tributylstibine (2.0 mmol) was injected slowly into a solution of dimethyl bromomalonate (2.0 mmol) [or dibromomalonate (1.0 mmol)] and benzaldehyde (1.0 mmol) in tetrachloromethane (2 mL) in a capped vessel at room temperature. Proton NMR spectra of the resulting mixture showed the existence of **E** (or **F**) as discussed in the text.

Acknowledgment

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