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TRIBUTYLSTIBINE MEDIATED SYNTHESIS OF 1,1,2-TRI-SUBSTITUTED CYCLOPROPANES[1]

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Abstract-- A novel method for the synthesis of 1,1,2-tri-substituted cyclopropanes is reported which involves the reaction of electron-deficient olefins with dibromomalonic ester, dibromocyanoacetic or dibromobenzeneacetic ester promoted by tri-n-butylstibine. The reaction was carried out under mild conditions to give the cyclopropane derivatives in moderate to good yields. Other R_3M (M= As,Sb,Bi) reagents as promoter for this reaction have been studied and seem to be less effective than tributylstibine.

In the last three decades much attention has been centered on the organometallics toward organic synthesis. However, relatively rare report has appeared in the literature by means of organoantimony compounds. Recently we reported that the trialkylstibine could promote the carbon-carbon bond formation feasibly by the reactions of α-halo- acetic ester,[2a] methyl ketone,[2b,2c] acetonitrile[2d,2e] and allylic halide[2f] with carbonyl compounds. In a preliminary communication we have reported trialkylstibine mediated synthesis of cyclopropanes with 1,1,2-three electron-withdrawing substituents (Eq.1).[2g]

(1)

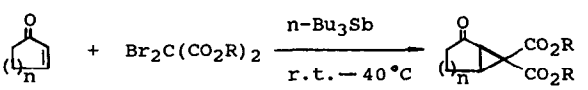
1 E = CHO,CN,$COCH_3$,CO_2Et 2

3 R=Me
4 R=Et

Cyclopropane derivatives activated by two electron-withdrawing substituents at geminal position are called electrophilic cyclopropanes and have been recognized as useful intermediates in organic synthesis.[3] Their inter- and intra-molecular ring opening reactions by various nucleophiles have been studied intensively and applied to the synthesis of several natural products.[3] Cyclopropanes with 1,1,2-three electron-withdrawing substituents have been synthesized by the reactions of α-chloroacrylate and α-chloroacrylonitrile with active methylene compounds by means of cuprous oxide-isocyanide complex.[4] Alternatively, they can be obtained from the reaction of ethyl dibromomalonate and olefins in DMSO promoted by copper.[5]

Results and Discussion

Our approach to the title compounds is by means of organoantimony compounds as shown in Eq.1. The reaction took place easily under mild conditions and gave the



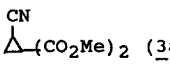
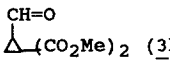
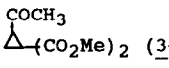
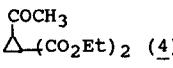
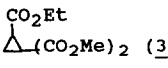
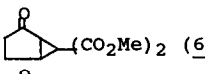
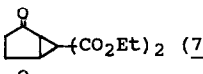
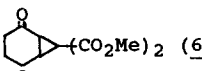
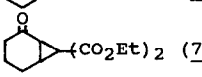
(2)

5 n=1,2

6 R=Me, 7 R=Et

cyclopropane derivatives in high yields. We found that besides the terminal olefins such as methyl vinyl ketone, acrolein, acrylonitrile and acrylic esters, cyclic α,β-unsaturated ketones such as 2-cyclopentenone and 2-cyclohexenone can also react

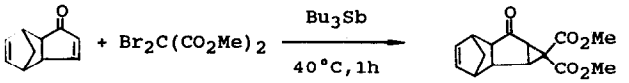
Table 1. Cyclopropanes from Dibromomalonate and Electron Deficient Olefins[a]

Entry	Olefin	R (in $Br_2C(CO_2R)_2$)	Product	Yield(%)[b]
1	CH_2=CH-CN (1a)	Me	 (3a)	88
2	CH_2=CHCHO (1b)	Me	 (3b)	86
3	CH_2=CHCOCH$_3$ (1c)	Me	 (3c)	84
4	1c	Et	 (4)	89
5	CH_2=CHCO$_2$Et (1d)	Me	 (3d)	43
6	 (5a)	Me	 (6a)	78
7	5a	Et	 (7a)	80[c]
8	 (5b)	Me	 (6b)	86
9	5b	Et	 (7b)	84

a) Reactions were carried out with 3.6mmol of olefin, 3.0mmol of $Br_2C(CO_2R)_2$ and 3.3mmol of tri-n-butylstibine at r.t. for 0.5 hr; b) Isolated yield by column chromatography, based on $Br_2C(CO_2R)_2$; c) Reaction was carried out at 40°C for 1 hr.

with dibromomalonate to give bicyclic compounds(Eq.2). Table 1 shows the results.

Dimethyl dibromomalonate reacted with 1-dicyclopentadienone(8) promoted by tributylstibine to give tetracyclo[4,4,$1^{7,10}$,$0^{3,5}$,0]-4,4-dimethoxycarbonylundec-8-en-2-one(9) (Eq.3).



8 9 72% (3)

Despite that dibromomalonate could react with carbonyl compounds,[6] the above mentioned results showed that with the less hindered olefinic aldehyde or ketone, the reaction took place preferentially at double bond. Under the same conditions, acryloamide, cinnamic ester, crotonic ester, β-ionone, p-chlorochalcone, styrene, maleic anhydride, diethyl maleate and fumarate did not react with dimethyl dibromomalonate. When one of the latter two compounds was used as substrate, the main product isolated was tetracarbomethoxyethylene(10) as shown in Eq 4.

$$2\ Br_2C(CO_2Me) + 2\ Bu_3Sb \xrightarrow{60°C,4h} (MeO_2C)_2C{=}C(CO_2Me)_2 + 2\ Bu_3SbBr_2 \qquad (4)$$

10 83%

When triethylstibine, triphenylstibine, tri-n-butylarsine, or tri-n-butylbithmuthine was used as a promoter instead of tributylstibine for the reaction of dimethyl dibromomalonate with methyl vinyl ketone or acrylonitrile, cyclopropane derivatives were also obtained. But experiments showed that the trialkylstibine is the most effective reagent (Table 2).

This reaction could be carried out without solvent. In some solvents such as tetrahydrofuran, acetonitrile, benzene and petroleum ether, the results are also good.

Table 2. Results of the Reaction of Dimethyl Dibromomalonate with the Olefins Promoted by Various R_3M Reagents[a]

Entry	Olefin	R_3M	Conditions(°C/hr)	Product	Yield(%)[b]
1	CH_2=CHCOCH$_3$	n-Bu_3Sb	r.t./0.5	3c	84
2		Et_3Sb	r.t./0.5	"	86[c]
3		Ph_3Sb	80/2	"	62[c]
4		n-Bu_3As	70/1	"	40[c]
5		n-Bu_3Bi	r.t./0.5	"	10[d]
6	CH_2=CHCN	n-Bu_3Bi	r.t./0.5	3a	53

a) Reactions were carried out with methyl vinyl ketone or acrylonitrile (2.4mmol), dimethyl dibromomalonate(2.0mmol) and R_3M(2.2mmol) under the prescribed conditions; b) Isolated yield, based on $Br_2C(CO_2Me)_2$; c) Determined by ^1H NMR analysis of the reaction mixture after removal of the organoantimony by-product, and were based on $Br_2C(CO_2Me)_2$; d) Accompanied with methyl 2-methoxycarbonyl-3-methylpenta-2,4-dienate and other complicated products.

$$R'CH{=}CH{-}E + Br_2C(CN)CO_2Et \xrightarrow[r.t.,0.5h]{n\text{-}Bu_3Sb} \underset{\underline{11}}{\text{R'-cyclopropane(E, CN, CO}_2\text{Et)}} \quad (5)$$

Dibromocyanoacetic ester reacted with electron deficient olefins equally well as dibromo-malonic ester to give the title compounds (Eq.5). The results are shown in Table 3.

Table 3. Cyclopropanes from Ethyl Dibromocyanoacetate and Electron Deficient Olefins Mediated by Tri-n-butylstibine[a]

Entry	Olefin	Product[b]	Yield(%)[c]
1	CH_2=CHCN	Ethyl 1,2-dicyanocyclopropanecarboxylate (11a)	59[d]
2	CH_2=CHCOCH$_3$	Ethyl 1-cyano-2-acetylcyclopropanecarboxylate (11b)	60
3	CH_2=CHCO$_2$Me	Ethyl 1-cyano-2-carbomethoxycyclopropanecarboxylate (11c)	68
4	CH_2CH_2CH=CHCO	Bicyclo[3,1,0]-6-cyano-6-carboethoxyhexan-2-one (11d)	76
5	$CH_2(CH_2)_2CH$=CHCO	Bicyclo[4,1,0]-7-cyano-7-carboethoxyheptan-2-one (11e)	74

a) Reactions were carried out with 3.6mmol of olefin, 3.0mmol of $Br_2C(CN)CO_2Et$ and 3.3mmol of tri-n-butylstibine at r.t. for 0.5hr; b) Only one isomer was obtained; c) Isolated yield, based on $Br_2C(CN)CO_2Et$; d) 62:38 mixture of E and Z isomers was obtained, determined by GLC analysis.

In the reaction of ethyl dibromocyanoacetate with acrylic ester, besides the main product, cyclopropane, we also isolated two reduced products as shown in Eq.6.

$$CH_2{=}CHCO_2Me + Br_2C(CN)CO_2Et \xrightarrow{n\text{-}Bu_3Sb} \underset{68\%}{\text{cyclopropane(CO}_2\text{Me, CN, CO}_2\text{Et)}} + \underset{6\%}{BrCH(CN)CO_2Et} + \underset{20\%}{CH_2(CN)CO_2Et} \quad (6)$$

Two isomers of the cyclopropane derivative were obtained from acrylonitrile. The E to Z isomer ratio is 62:38, determined by GLC analysis. The relative configuration was assigned on the basis of their ^1H NMR data.[7] The E:Z isomer ratio

seemed to reflect the thermodynamic stability of the cyclopropane product. However, GLC analysis of the products from other substrates showed only one peak. ^{1}H NMR spectra of the isolated cyclopropane derivatives did not clearly indicate the presence of stereoisomers. So the new reaction is useful for the synthesis of electrophilic cyclopropane derivatives in a stereospecific way from the electron-deficient olefins other than acrylonitrile.

Reaction of ethyl α,α-dibromobenzeneacetate with electron-deficient olefins gave cyclopropanes in low to moderate yields (Eq.7). The yields and the ratio of E to Z isomer are shown in Table 4.

$$R'CH{=}CHE + C_6H_5CBr_2CO_2Et + Bu_3Sb \xrightarrow{r.t.} \underset{\underline{12}}{\text{R'-cyclopropane(E, C}_6\text{H}_5\text{, CO}_2\text{Et)}} + Bu_3SbBr_2 \qquad (7)$$

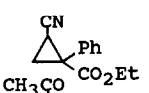
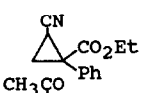
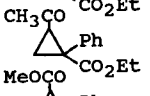
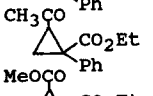
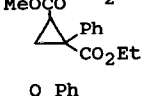
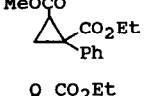
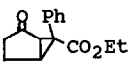
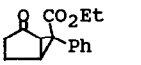
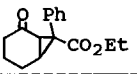
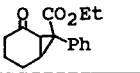
The reason for the lower yield has been demonstrated to be due to the side-reaction occurred simultaneously, forming two reduced products as well as a coupling compound (Eq. 8).

$$CH_2{=}CHCOCH_3 + PhCBr_2CO_2Et \xrightarrow[r.t.,0.5hr]{n\text{-}Bu_3Sb} \underset{50\%}{\text{cyclopropane(COCH}_3\text{, Ph, CO}_2\text{Et)}} + PhCHBrCO_2Et + PhCH_2CO_2Et + EtO_2C(Ph)C{=}C(Ph)CO_2Et \qquad (8)$$

16% 7% 11%

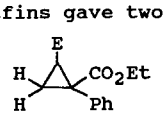
Attempts to improve the yield of cyclopropane have not been successful.

Table 4. Cyclopropanes from Ethyl Dibromobenzeneacetate and Olefins[a]

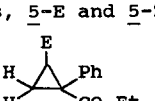
Entry	Olefin	Product E	Product Z		Yield(%)[b]	Ratio(E/Z)[c]
1	$CH_2{=}CHCN$			(12a)	60	45:55 (49:51)
2	$CH_2{=}CHCOCH_3$			(12b)	53	70:30 (71:29)
3	$CH_2{=}CHCO_2Me$			(12c)	47	74:26 (79:21)
4				(12d)	31	-[d] (89:11)
5				(12e)	40	80:20 (74:26)

a) Reactions were carried out with Br_2CPhCO_2Et(3.0mmol), olefin(3.6mmol) and tri-n-butylstibine(3.3mmol) at r.t. for 0.5hr; b) Isolated yield by column chromatography, and were based on Br_2CPhCO_2Et; c) The ratio was estimated by ^{1}H NMR data. The results of GLC analysis are given in parentheses; d) Indistinguishable on ^{1}H NMR.

The cyclopropanes formed from the reaction of α,α-dibromobenzeneacetate with electron-deficient olefins gave two stereoisomers, 5-E and 5-Z. They have different

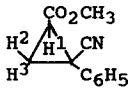


5-Z

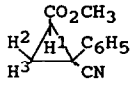


5-E

chemical shifts in ^1H NMR. This is coincident with that of ethyl 2-cyano-2-phenylpropanecarboxylate 13 reported in the literature.[4]



13-Z

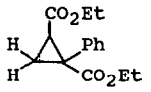


13-E

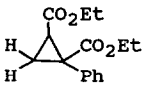
Chemical Shifts of the Isomer 13

Isomer	δ Value			
	C_6H_5	OCH_3	H^1	H^2,H^3
i	7.31	3.42	2.75	~2.10
ii	7.35	3.82	2.30	~2.00

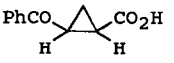
Although the assignment of the two structures was not given by Saegusa,[4] Schmidt determined the E/Z ratio of diethyl 1-phenyl-1,2-cyclopropanedicarboxylate (14) according to the difference of the cis and trans isomers of 2-benzoylcyclopropanecarboxylic acid(15) in ^1H NMR.[8] Based on these analyses, isomer 13-i could be assigned to E isomer.



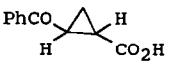
14-E



14-Z



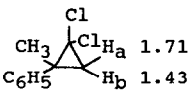
15-cis



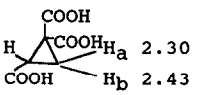
15-trans

The characteristic of ^1H NMR data of 13-E is that H^1 has larger δ value, and OCH_3, smaller, than that of corresponding Z isomer.

On the other hand, the influence of phenyl and carboxylic groups upon the chemical shifts of ring proton is in different manner.[9] The following data may be useful for explanation.



16



17

Ring proton located at the same side with phenyl group appeared at upfield on ^1H NMR (H_b in 16). Just reverse is true, ring proton located at the same side with carboxylic group has great δ value (H_b in 17), while at different side has small one. Theoretical consideration predicted the cis oriented substituents is located in the diamagnetic shielding cone of the aryl ring.[10]

In regarding to these results of the ^1H NMR analysis, we determined the ratio of E/Z, combining with GLC analysis(Tabl 4).

When dimethyl dibromomalonate was refluxed in benzene with triphenylstibine in the absence of olefin substrate, bromomalonate and hydroxy-bromo-triphenylstiborane resulted almost quantitatively as shown in Eq.9, instead of corresponding pentavalent organoantimony salt like its phosphonium analogs.[11]

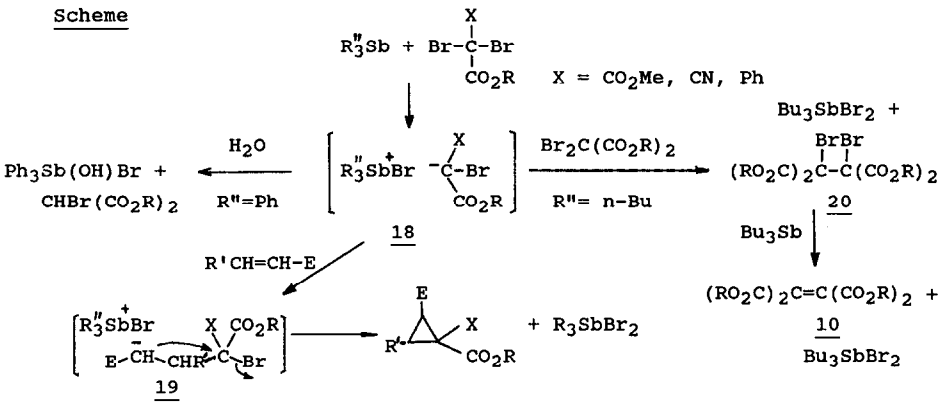
$$Br_2C(CO_2Me)_2 + Ph_3Sb \xrightarrow[\text{reflux,2h}]{C_6H_6} Ph_3Sb(OH)Br + CHBr(CO_2Me)_2 \quad (9)$$

~100%

While with inactive substrate such as ethyl maleate, coupling product was formed by tributylstibine (see Eq.4).

Lloyd and coworkers have reported that some stibonium ylides with gem-electron-withdrawing groups at α-position did not undergo Wittig reaction even with reactive aldehyde.[12] Accordingly, a mechanism involving Michael type addition of the carbanion of bromoacetate derivative induced by halophilic procedure may be plausible for the reaction.[13] Following Scheme gives the possible pathway.

Scheme



Trialkylstibine underwent halophilic attack to bromine atom of dibromoacetate derivative like tertiary-phosphine,[14] the ion pair 18 with bromostibonium cation and bromoacetate anion could be destroyed by protonation,or attack another halogeno compound to form coupling product 20, which is easily debrominated by tri-n-butyl-stibine[15] to give olefin 10. In the presence of substrate,the addition of carbanion 18 to polar double bond by nucleophilic attack form a new anion 19 associated with the electron-withdrawing group(E). This anion underwent intramolecular nucleophilic substitution to give cyclopropane derivative and tri-n-butylstibine dibromide.

This reaction of α-substituted dibromoacetic esters with active olefins mediated by trialkylstibine could be used for the synthesis of the title compounds with simple procedure, mild reaction conditions and good yields.

Experimental

^{1}H NMR spectra were recorded on Varian Model EM-360A or XL-200 spectrometer in CCl_4 using TMS as internal standard other than noted. IR spectra were recorded on an IR-440 grating spectrophotometer. Mass spectra were obtained on a Finnigan 4021 and Varian MA1211 mass spectrometer. GLC analysis was performed by a GC-102 gas chromatograph equipped with a OV-1 column.

Materials: Tri-n-butyl-arsine,[16] stibine,[17] bithmuthine,[18] triethylstibine,[19] triphenylstibine[20] and ethyl cyanodibromoacetate[21] were prepared according to the literature methods. Dimethyl and diethyl dibromomalonate were prepared by bromination of the correspounding malonate initiated by heating, instead of by light in the literature.[22] Ethyl α,α-dibromobenzeneacetate was synthesized by refluxing ethyl benzeneacetate(0.1mole) and N-Bromosuccinamide(0.2mole) in tetrachloromethane (70ml) for 5 days. Yield: 60%. B.p. 107°C/2Torr (Lit. 88-90°C/0.02Torr[23]). Olefins were commercially available and were distilled before use. Other chemicals were purified by standard method.

REACTION OF DIBROMOMALONATE WITH OLEFINS AND TRIBUTYLSTIBINE.

General procedure: 3.1mmol of tri-n-butylstibine was injected into a mixture of 3.0mmol of diethyl dibromomalonate and 3.1-3.3mmol of the olefin. After the exothermic reaction took place and being stirred at r.t. for 0.5h,the reaction mixture was submitted to chromatography on an alumina-silica gel (1:1) column, eluting with ethyl acetate. Products were further purified by distillation if necessary.

Dimethyl 2-cyano-1,1-cyclopropanedicarboxylate 3a: oil; ^{1}H NMR: 1.61(dd,J_{gem}=4.5Hz, J_{cis}=9.5Hz,1H), 1.97(dd, J_{gem}=4.5Hz, J_{trans}=7.0Hz,1H), 2.49(dd, J_{cis}=9.5Hz, J_{trans}= 7.0Hz,1H), 3.75(s,3H), 3.82(s,3H); IR(neat): 3020(w), 2220(w), 1730(vs), 880(m);

MS m/e(rel.%): 184(M^++1,7), 183(M^+,11), 178(2), 152(92),151(48),124(11),120(44), 92 (15),65(26),59(100); Found: C,52.73; H,5.08; N,7.87%. Calcd for $C_8H_9NO_4$: C,52.46; H,4.95; N,7.65%.

Dimethyl 2-formyl-1,1-cyclopropanedicarboxylate 3b: b.p. 93°C/10Torr; ^{1}H NMR: 1.67 (dd,J_{gem}=4.2Hz, J_{cis}=9.0Hz,1H), 1.96(dd,J_{gem}=4.2Hz, J_{trans}=7.0Hz,1H), 2.62(dd,J_{cis}= 9.0Hz, J_{trans}=7.0Hz, J=4.0Hz,1H), 3.69(s,3H),3.73(s,3H), 9.21(d,J=4.0Hz,); IR(neat): 3000(w),1710(vs),1280(vs); MS m/e(rel.%): 186(M^+,7),185(M^+-1,82),157(13), 153(33),59(100); Found: C,51.33; H,5.17%. Calcd for $C_8H_{10}O_5$: C,51.61; H,5.41%.

Dimethyl 2-acetyl-1,1-cyclopropanedicarboxylate 3c: colorless oil; ^{1}H NMR: 1.49(dd, J_{gem}=4.2Hz, J_{cis}=8.0Hz,1H), 1.88(dd, J_{gem}=4.2Hz, J_{trans}=5.5Hz,1H), 2.33(s,3H), 2.78 (dd,J_{cis}=8.0Hz, J_{trans}=5.5Hz,1H), 3.63(s,3H), 3.73(s,3H); IR(neat): 3000(w), 1730 (vs), 1708(s), 880(w); MS m/e(rel.%): 200(M^+,7), 185(100), 169(61),157(11),141(7), 126(31),59(84); Found: C,53.88; H,5.79%. Calcd for $C_9H_{12}O_5$: C,54.00; H,6.04%.

Dimethyl 2-carboethoxy-1,1-cyclopropanedicarboxylate 3d: oil; ^{1}H NMR: 1.25(t, J= 7.0Hz,3H), 1.52(dd,J_{gem}=4.0Hz, J_{cis}=9.0Hz,1H), 1.83(dd,J_{gem}=4.0Hz,J_{trans}=6.0Hz,1H), 2.42(dd, J_{cis}=9.0Hz, J_{trans}=6.0Hz,1H),3.70(s,3H), 3.72(s,3H), 4.06(t, J=7.0Hz, 2H); IR(neat): 3000(w), 1725(vs), 865(m); MS m/e(rel.%): 230(M^+,8), 199(46), 185(100), 171(90), 157(43),142(37),126(37),97(43),83(22),67(57); Found: C,52.12; H,6.39%. Calcd for $C_{10}H_{14}O_6$: C,52.17; H,6.13%.

Bicyclo[3,1,0]-6,6-dicarbomethoxyhexan-2-one 6a: 88°C/1Torr; ^{1}H NMR: 1.57-2.80(m, 6H), 3.77(s,6H); IR(neat): 2985(m),1740(vs),860(m); MS m/e(rel.%): 213(M^++1,85), 184(31),181(86),156(100),153(42),125(16),97(13),66(13); Found: 212.0628. Calcd for $C_{10}H_{12}O_5$: 212.2018.

Bicyclo[4,1,0]-7,7-dicarbomethoxyheptan-2-one 6b: oil; ^{1}H NMR: 1.50-2.50(m, 8H), 3.73(s,3H), 3.80(s,3H); IR(neat): 2985(m),1720(s); Found: C,58.29; H,5.95%. Calcd for $C_{11}H_{14}O_5$: C,58.40; H,6.24%.

Diethyl 2-acetyl-1,1-cyclopropanedicarboxylate 4: b.p. 115°C/1Torr(Lit.90.5-92.5 C/ 0.08-0.05Torr[24]); ^{1}H NMR: 1.20(t, J=7.0Hz,3H), 1.26(t,J=7.0Hz,3H), 1.44(dd,J_{gem}= 4.0Hz, J_{cis}=8.5Hz, 1H), 1.80(dd, J_{gem}=4.0Hz, J_{trans}=7.0Hz,1H), 2.30(s,3H), 2.72(dd, J_{trans}=7.0Hz, J_{cis}=8.5Hz,1H), 4.03(q,J=7.0Hz,2H), 4.12(q,J=7.0Hz,2H); IR(neat): 3000(m), 1740(s), 1715(s), 862(m).

Bicyclo[3,1,0]-6,6-dicarboethoxyhexan-2-one 7a: oil; ^{1}H NMR: 1.28(t,J=7.0Hz,6H), 1.60-2.83(m,6H), 4.18(q,J=7.0Hz,4H); IR(neat): 2990(m), 1740(vs), 860(m); MS m/e (rel.%): 241(M^++1,16),240(M^+,6), 212(32),195(50),184(45),167(62),165(100), 139(40). 111(20),66(98); Found: C,59.63; H,6.77%. Calcd for $C_{12}H_{16}O_5$: C,59.90, H, 6.71%.

Bicyclo[4,1,0]-7,7-dicarboethoxyheptan-2-one 7b: b.p. 98°C/2Torr; ^{1}H NMR: 1.28 (t,J=7.0Hz,6H), 1.53-2.53(m, 8H), 4.14(q,J=7.0Hz,4H); IR(neat): 2990(m), 1720(vs), 860(m); MS(EI) m/e(rel.%): 255(M^++1, 57.6), 226(24.6), 209(64), 208(31), 180(54) 163(100),153(83),134(50),125(52); Found: 254.1961. Calcd for $C_{13}H_{18}O_5$: 254.2822.

Tetracyclo[4,4,0,$1^{7,10}$,$0^{3,5}$]-4,4-dimethoxycarbonyl-undec-8-en-2-one 9: colourless oil; ^{1}H NMR: 1.50(m,2H), 2.10-2.46(m,2H), 3.10(m,4H), 3.70(s,3H), 3.77(s,3H), 6.12(brs, 2H); IR(neat): 2990(m), 1730(vs), 850(m); MS m/e(rel.%): 276(M^+,16),245(15),217 (11), 211(60), 185(14), 179(100). Found: C,64.84; H,5.66%. Calcd for $C_{15}H_{16}O_5$: C, 65.21; H,5.84%.

REACTION OF ETHYL DIBROMOCYANOACETATE WITH OLEFINS AND TRIBUTYLSTIBINE.
Typical Procedure: 960mg(3.3mmol) of tri-n-butylstibine was injected into a mixture of 810mg(3.0mmol) of ethyl dibromocyanoacetate and 280mg(3.3mmol) of methyl acrylate in a capped vessel under nitrogen, an exothermic reaction took place. After being stirred for half an hour at r.t., the reaction mixture was chromatographed on an alumina-silica gel(1:1) column, eluting with ethyl acetate.The eluent was evaporated and the residue was then chromatographed on silica gel,eluting with petroleum ether-ethyl acetate(9:1,v/v), giving (1), 68mg of ethyl cyanoacetate(20%); (2),34mg of ethyl bromocyanoacetate(6%); and (3),402mg of ethyl 1-cyano-2-carbomethoxycyclopropanecarboxylate(11c)(68%).

Ethyl 1,2-dicyanocyclopropanecarboxylate 11a:[7] b.p. 122°C/1Torr; ^{1}H NMR(TMS/$CDCl_3$) (mixture of E and Z): 1.46(t,J=7.0Hz,3H), 1.80-2.67(m,3H), 4.43(q,J=7.0Hz,2H); IR (neat): 2992(m), 2240(m), 1760(vs),850(m); MS m/e(rel.%): 165(M^++1,100), 137(28), 136(11), 119(17), 91(5), 64(6).

Ethyl 1-cyano-2-acetylcyclopropanecarboxylate 11b: b.p. 130°C/1Torr: ^{1}H NMR: 1.34 (t, J=7.0Hz,3H), 1.63-2.26(m, 2H), 2.40(s, 3H), 2.84(dd, J=8.0,8.0Hz,1H), 4.21(q,J=7.0Hz,2H); IR(neat): 3000(m),2260(m),1730(s),860(m); MS m/e(rel.%): 182(M^++1,100), 181(M^+,3), 166(10), 154(13), 136(7), 109(12), 82(4), 67(1); Found: C,59.61; H,6.11; N,8.00%. Calcd for $C_9H_{11}NO_3$: C,59.66; H,6.12; N,7.73%.

Ethyl 1-cyano-2-carbomethoxycyclopropanecarboxylate 11c: b.p. 80°C/1Torr; ^{1}H NMR: 1.37(t,J=7.0Hz,3H), 1.83(dd,J_{gem}=4.0Hz, J_{cis}=8.5Hz,1H), 2.03(dd,J_{gem}=4.0Hz, J_{trans}=7.5Hz, 1H), 2.57(dd, J_{cis}=8.5Hz, J_{trans}=7.5Hz, 1H), 3.78(s,3H), 4.27(q,J=7.0Hz,2H); IR(neat): 2980(m),2245(m), 1750(vs),1730(vs),850(m); MS m/e(rel.%): 198(M^++1,100), 170(14), 166(27), 152(16), 138(8), 123(12), 110(10), 93(6), 67(5); Found: C,54.19; H,5.79; N,7.33%. Calcd for $C_9H_{11}NO_4$: C,54.82; H,5.62; N,7.10%.

Bicyclo[3,1,0]-6-cyano-6-carboethoxyhexan-2-one 11d: oil; ^{1}H NMR: 1.37(t,J=7.0Hz, 3H), 1.90-2.93(m,6H), 4.24(q,J=7.0Hz,2H); IR(neat): 2990(m),2245(m),1750(vs),1735 (vs),860(m); MS m/e(rel.%): 193(M^+,19),165(10),148(15),137(28), 124(100), 120(41), 92(55). Found: C,62.46; H,5.62; N,7.02%. Calcd for $C_{10}H_{11}NO_3$: C,62.17; H,5.74; N, 7.15%.

Bicyclo[4,1,0]-7-cyano-7-carboethoxyheptan-2-one 11e: b.p.128-130°C/1Torr; ^{1}H NMR: 1.34(t,J=7.0Hz,3H), 1.67-2.96(m,8H), 4.20(q,J=7.0Hz,2H); IR(neat): 2970(m),2240(m), 1740(vs), 1710(vs), 850(m); MS m/e(rel.%): 208(M^++1,54), 207(M^+,24), 179(13), 162 (35), 151(22), 134(31), 124(100), 106(65). Found: C,63.54; H,6.28; N,6.98. Calcd for $C_{11}H_{13}NO_3$: C,63.75; H,6.32, N,6.75.

REACTION OF ETHYL α,α-DIBROMOBENZENEACETATE WITH OLEFINS AND TRIBUTYLSTIBINE.
Typical procedure: 644mg (2.0mmol) of ethyl α,α-dibromobenzeneacetate was injected into a capped vessel containing 640mg (2.2mmol) of tri-n-butylstibine and 200mg (2.8mmol) of methyl vinyl ketone, an exothermic reaction took place. After being stirred for 0.5 h at room temperature, the reaction mixture was chromatographed on an alumina-silica gel (1:1) column, eluting with ethyl acetate. This procedure can separate organoantimony from other products. The eluent was, after evaporation, chromatographed on silica gel, eluting with petroleum ether-ethyl acetate (9:1) and the following products were obtained: (1), 20mg of ethyl benzeneacetate(6%); (2), 40mg of ethyl α-bromobenzeneacetate(8%); (3), 150mg of diethyl 2,3-diphenylbutenate (11%); and (4), 245mg of ethyl 1-phenyl-2-acetylcyclopropanecarboxylate(53%). All of the products were characterized by ^{1}H NMR, IR, MS or microanalyses.

Ethyl 1-phenyl-2-cyano-cyclopropanecarboxylate 12a: 102°C/1Torr; ^{1}H NMR: 1.06(t,J=7.0Hz,1.35H,E), 1.17(t,J=7.0Hz, 1.65H,Z), 1.36-2.50(m,3H), 3.97(q,J=7.0Hz, 0.9H,E), 4.06(q,J=7.0Hz, 1.1H,Z), 7.18(s,2.75H,Z), 7.24(s,2.25H,E): IR(neat): 3000(m),2200(m),1730(sh),1720(s),1600(w),1495(w),855(m); MS m/e(rel.%): 215(M^++1,8),214(M^+,44), 187(37), 170(22), 160(40), 142(54), 116(90), 115(100); Found: C,72.27; H,6.12; N,6.61%. Calcd for $C_{13}H_{13}NO_2$: C,72.54; H,6.09; N,6.51%.

Ethyl 1-phenyl-2-acetylcyclopropanecarboxylate 12b: 115°C/1Torr; ^{1}H NMR(TMS/$CDCl_3$-CCl_4): (E) 1.160(t, J=7.12Hz,3H), 1.784(m,1H), 2.064(m, 1H), 2.096(s,3H), 2.98(dd, J_{cis}=8.10Hz, J_{trans}=6.74Hz,1H), 4.094(q,J=7.12Hz,2H), 7.234(m,5H); (Z) 1.190(t,J=7.12Hz,3H), 1.784(m,1H), 2.064((m,1H), 2.096(s,3H), 2.368(m,1H), 4.118(q, J=7.12Hz, 2H),7.177(m,5H); IR(neat):3000(w),1715(vs),1600(w),1495(m),855(m); MS m/e(rel.%): 233(M^++1,23), 232(M^+,1), 187(57), 159(100); Found: C,72.29; H,6.66%. Calcd for $C_{14}H_{16}O_3$: C,72.39; H,6.94%.

Ethyl 1-phenyl-2-carbomethoxycyclopropanecarboxylate 12c: oil; ^{1}H NMR: 1.06(t,J=7.0Hz, 2.22H,E), 1.09(t,J=7.0Hz, 0.78H,Z), 1.47-2.20(m,2.26H,), 2.55(dd,J_{cis}=8.0Hz, J_{trans}=6.0Hz, 0.74H,E), 3.27(s,2.22H,E), 3.49(s,0.78H,Z), 3.96(q, J=7.0Hz,2H), 7.11(s,5H); IR(neat): 3000(m),1720(s),1600(w),1495(w),860(w); MS m/e(rel.%): 249(M^++1,43), 248(M^+,62), 217(23), 203(34), 115(100); Found: C,67.63; H,6.44%. Calcd for $C_{14}H_{16}O_4$: C,67.73; H,6.50%.

Bicyclo[3,1,0]-6-carboethoxy-6-phenylhexan-2-one 12d: oil; ^{1}H NMR: 1.06(t,J=7.0Hz, 3H), 1.40-2.85(m,6H), 3.94(q,J=7.0Hz,2H), 7.21(s,5H); IR(neat): 3050(w), 1720(s), 1605(w),1495(w),855(w); MS m/e(rel.%): 244(M^+,25),202(15),199(8),188(13),173(18), 143(18),129(100),128(99),115(43); Found: C,73.27; H,6.29%. Calcd for $C_{15}H_{16}O_3$: C,73.75; H, 6.60%.

Bicyclo[4,1,0]-7-carboethoxy-7-phenylheptan-2-one 12e: oil; ^{1}H NMR: 1.04(t,J=7.0Hz, 2.4H,E), 1.16(t,J=7.0Hz,0.6H,Z), 1.40-2.50(m,8H), 3.95(q,J=7.0Hz,2H), 7.18(s,4H,E), 7.29(s,1H,Z); IR(neat): 3000(w),1720(s),1600(w),1495(m),860(m); MS m/e(rel.%): 259(M^++1,100), 258(M^+,7),230(16), 212(76),185(31); Found: C,74.58; H,7.01%. Calcd for $C_{16}H_{18}O_3$: C,74.40; H,7.02%.

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References and Notes

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