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Selective Activation of Primary Carboxylic Acids by Electron-rich Triarylbi-muthanes. Application to Amide and Ester Synthesis under Neutral Conditions

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On being heated in benzene in the presence of tris(methoxyphenyl)bismuthanes **1b–1e**, primary carboxylic acids are selectively activated to couple with amines and alcohols to produce the corresponding amides and esters in satisfactory yields, while secondary, tertiary and aromatic carboxylic acids remain unaffected. 2-Benzylmalonic acid is similarly converted into its corresponding diamides and diesters, but 2,2-dibenzylmalonic acid suffers extensive decarboxylation and, in the presence of aromatic olefins, it undergoes a novel [3 + 2]-type cycloaddition reaction to form 4-substituted 2,2-dibenzyl-4-butanolides in low to fair yields.

In recent years bismuth compounds have received considerable attention as reagents for organic synthesis:¹ in 1978, Barton and co-workers reported that pentavalent bismuth compounds can be used as selective oxidizing reagents for various organic compounds.¹ⁱ Arylation reactions with trivalent and pentavalent organobismuth compounds have been studied extensively by Barton and co-workers.^{1a,b} The Barbier-type reactions of allyl halides with activated bismuth metal have been reported by Wada and co-workers.^{1a}

As part of our continuing study on organobismuth compounds, we report herein that some electron-rich triaryl-bismuthanes such as tris-(2-methoxyphenyl)bismuthane **1b** and tris-(2,6-dimethoxyphenyl)bismuthane **1d** can be used as highly structure-dependent reagents for the coupling of carboxylic acids with amines and alcohols; primary carboxylic acids are apparently activated by these bismuthanes, while secondary, tertiary and aromatic carboxylic acids are not (Scheme 1). We also report the bismuthane-induced decarb-

phenyl)bismuthane **1d** was found to be most effective in promoting the coupling (Table 1); within a reasonable reaction time (*ca.* 6 h), yields of amide as high as an 94% were obtained. A highly susceptible functional group such as an epoxide can be tolerated under the reaction conditions employed; epoxyoleic acid reacted with 2-phenylethylamine in the presence of the bismuthane **1d** to give *N*-(2-phenylethyl)epoxyoleamide in 35% isolated yield. Unusually high basicity of tris-(2,6-dimethoxyphenyl)pnictogenides has recently been disclosed by Wada *et al.*,² but the potentials of these compounds as reagents in organic synthesis remain unexplored.

- a; R¹ = R² = R³ = R⁴ = H
- b; R¹ = OMe, R² = R³ = R⁴ = H
- c; R¹ = R² = R⁴ = H, R³ = OMe
- d; R¹ = R⁴ = OMe, R² = R³ = H
- e; R¹ = R² = R³ = OMe, R⁴ = H

Scheme 1 Reagents and conditions: i, bismuthane **1**, PhH, reflux, 12 h

oxylative [3 + 2]-type cycloaddition reaction of 2,2-dibenzylmalonic acid with aromatic olefins to yield substituted butanolides.

Results and discussion

When phenoxyacetic acid, 2-phenylethylamine and tris-(2-methoxyphenyl)bismuthane **1b** were taken up in benzene in 3:3:1 molar proportions and heated under gentle reflux for 12 h, the coupling occurred smoothly to afford *N*-(2-phenylethyl)phenoxyacetamide in 78% isolated yield, together with anisole and a bismuth-containing insoluble substance. A similar reaction carried out in the absence of solvent led to an increase in yield up to 88%. Tris-(4-methoxyphenyl)bismuthane **1c** and tris-(2,3,4-trimethoxyphenyl)bismuthane **1e** showed a similar efficacy for coupling, but the replacement of these bismuthanes by the parent triphenylbismuthane **1a** resulted only in the recovery of starting materials. Among several alkoxylated triarylbi-muthanes examined, tris-(2,6-dimethoxy

The most prominent feature of the present reaction is that only primary carboxylic acids can couple with the amino or hydroxylic nucleophiles smoothly; attempted reactions with secondary, tertiary and aromatic carboxylic acids failed completely. The unique selectivity of the present reaction was well demonstrated by a competition experiment; heating of an equimolar mixture of benzoic acid, phenoxyacetic acid, 2-phenylethylamine and the bismuthane **1b** in benzene for 21 h followed by usual work-up afforded only *N*-(2-phenylethyl)-phenoxyacetamide (yield > 95%) as the condensation product, and benzoic acid was recovered mostly unchanged.

The acylation by the bismuthane **1b** proceeded with a secondary amine and an alcohol also; the phenoxyacetylation of morpholine afforded the corresponding amide in 70% isolated yield, and that of butan-2-ol gave the ester in 30% yield. However, attempted reaction with a tertiary alcohol, 2-methylpropan-2-ol, led only to recovery of the starting materials under the same conditions.

Chemoselectivity of the present acylation for the amino *versus* hydroxy groups was also satisfactory. When 2-aminoethanol was treated with phenoxyacetic acid in the presence of the bismuthane **1d**, only the *N*-acylated compound was obtained, the hydroxy group remaining intact. However, the reaction failed to differentiate a primary alcoholic function

Table 1 Bismuthane-mediated reaction of carboxylic acids with amines and alcohols (Scheme 1)^a

Carboxylic acid R ¹	Amine or Alcohol		Bismuthane	Time (t/h)	Product yield ^b (%)
	R ²	R ³			
	<i>Amines</i>				<i>Amides</i>
PhOCH ₂	PhCH ₂ CH ₂	H	1a	12	0 ^c
PhOCH ₂	PhCH ₂ CH ₂	H	1b	12	78
PhOCH ₂	PhCH ₂ CH ₂	H	1b	12	88 ^d
PhOCH ₂	PhCH ₂ CH ₂	H	1c	12	76
PhOCH ₂	PhCH ₂ CH ₂	H	1d	6	94
PhOCH ₂	PhCH ₂ CH ₂	H	1e	12	76
PhOCH ₂	Ph	H	1b	12	56
PhOCH ₂	Ph	H	1e	20	58
PhOCH ₂	CH ₂ CH ₂ OCH ₂ CH ₂	H	1b	12	70
n-C ₇ H ₁₅	PhCH ₂ CH ₂	H	1b	12	61
n-C ₇ H ₁₅	Ph	H	1b	12	44
Ph	PhCH ₂ CH ₂	H	1b	12	0 ^c
2,4,6-Me ₃ C ₆ H ₂	PhCH ₂ CH ₂	H	1b	12	0 ^c
Bu ^f	PhCH ₂ CH ₂	H	1b	12	0 ^c
PhCH ₂ (Et)CH	PhCH ₂ CH ₂	H	1b	12	0 ^c
Et ₂ CH	PhCH ₂ CH ₂	H	1b	12	0 ^c
PhOCH ₂	HO[CH ₂] ₂	H	1d	12	65 ^e
epoxyOL ^f	PhCH ₂ CH ₂	H	1d	12	35
	<i>Alcohols</i>				<i>Esters</i>
PhOCH ₂	Et		1b	12	75
PhOCH ₂	Et		1d	12	37
PhOCH ₂	PhCH ₂		1b	12	73
PhOCH ₂	Et(Me)CH		1b	12	31
PhOCH ₂	Me ₃ C		1b	12	0 ^c
n-C ₇ H ₁₅	PhCH ₂		1b	12	86
PhOCH ₂	EtCH(OH)CH ₂		1b	12	40 ^g

^a Reactions were performed in benzene at reflux temperature under nitrogen unless otherwise noted. ^b Isolated yields, not optimized. ^c Starting materials were recovered. ^d The reaction was carried out at 80 °C in the absence of solvent. ^e A similar reaction with ethyl-(2-hydroxyethyl)amine gave the corresponding secondary amide in 43% yield. ^f epoxyOL stands for epoxyoleic acid. ^g Accompanied by 19% of 2-*O*-acyl and 8% of 1,2-di-*O*-acyl derivatives.

from a secondary one; the acylation of butane-1,2-diol with phenoxyacetic acid under the above conditions afforded a mixture of 1-*O*-acyl (40%), 2-*O*-acyl (19%) and 1,2-di-*O*-acyl (8%) derivatives.

The present condensation also occurred smoothly with a dicarboxylic acid. Thus, when 2-benzylmalonic acid (**2a**; R = H) and 2-phenylethylamine were heated together in benzene in a 1:2 molar ratio in the presence of the bismuthane **1b**, 2-benzyl-*N,N'*-bis-(2-phenylethyl)malondiamide **3** was obtained in 60% yield. However, when 2,2-dibenzylmalonic acid (**2b**, R = PhCH₂) was similarly treated, decarboxylation occurred extensively to afford 2-benzyl-3-phenylpropanoic acid **4** in 70% isolated yield (Scheme 2).

In order to check for possible intermediacy of a ketene in this highly selective condensation of primary carboxylic acids with amines and alcohols, a trapping experiment for the presumed ketene intermediate by some activated alkenes was attempted. However, no cycloaddition product could be obtained from the reaction of phenoxyacetic acid with the bismuthane **1b** in the presence of aromatic olefins. During the attempts, an unexpected product **5** arose from the bismuthane-mediated reaction of 2,2-dibenzylmalonic acid **2b** with aromatic 1-alkenes. Thus, when compound **2b** was heated with an excess of phenylethene in benzene for 12 h in the presence of the bismuthane **1b**, 2,2-dibenzyl-4-phenyl-4-butanolide (**5a**; R³ = Ph, R⁴ = H) was isolated in 27% yield (Scheme 2). Additional examples of butanolide formation are summarized in Table 2. Attempted reactions of compound **2b** with oct-1-ene, dimethyl fumarate, ethyl acrylate, ethyl vinyl ether, and 1,1-diethoxyethene under the same conditions afforded no butanolides. In every case, 2-benzyl-3-phenylpropanoic acid was obtained as a by-product in 50–60% yield.

Scheme 2 Reagents and conditions: i, bismuthane **1b**, PhH, reflux, 12 h

Although a mechanistic study of the butanolide-formation reaction has not yet been made, one of the possible pathways is shown in Scheme 3. The formation of bismuth diacylate **6** by ligand exchange³ is followed by loss of carbon dioxide from this intermediate to yield a diradical species **7**, which is trapped by an alkene and then couples at the oxygen atom of the resulting intermediate **8** to give butanolide derivative **5**.

Table 2 Butanolide formation from 2,2-dibenzylmalonic acid **2b** and aromatic olefins in the presence of bismuthanes **1**^a

Alkene		Bismuthane	Solvent	Butanolide 5 Yield (%) ^b
R ³	R ⁴			
H	Ph	1b	PhH	27
H	Ph	1d	PhH	12
Ph	Ph	1d	PhH	6
Ph	Me	1d	PhH	18
Ph	Me	1d	Et ₂ O	5
Ph	Me	1d	THF ^c	3
Ph	Me	1d	CH ₂ Cl ₂	4
Ph	Me	1d	DME ^d	10
Ph	Me	1d	DMF ^e	2

^a Reactions were carried out in the given solvent under reflux for 12 h, with molar proportions of malonic acid:alkene:bismuthane 1:3:1.

^b Isolated yield, not optimized. In every case, 2-benzyl-3-phenylpropanoic acid **4** was isolated in 50–60% yield as a by-product.

^c Tetrahydrofuran. ^d 1,2-Dimethoxyethane. ^e Dimethylformamide.

Acetylation of amines and alcohols by bismuth triacetate at high temperatures (~180 °C) was previously reported by Reese *et al.*⁴ However, the direct acylation of amines and alcohols by other bismuth triacylates was found to be less effective than the present acylation methodology. When bismuth tris(phenoxyacetate) was heated with 2-phenylethylamine in benzene for 24 h, *N*-(2-phenylethyl)phenoxyacetamide was obtained in only 38% yield. In contrast, the triarylbismuthane-mediated reaction of phenoxyacetic acid with the same amine afforded the expected amide in 76–94% isolated yield within a much shorter reaction time (Table 1).

The time-courses of the product distributions in the reaction of phenoxyacetic acid with 2-phenylethylamine in the presence of bismuthane **1b** were followed by HPLC under several reaction conditions: (A) When a benzene solution (6 cm³) of the acid (2.4 mmol) and the bismuthane (2.4 mmol) was heated in an oil-bath (95 °C), a clear solution was obtained after a few

Fig. 1 Time courses of phenoxyacetylation of 2-phenylethylamine in the presence of the bismuthane **1b** in benzene at reflux temperature: (A) 2-Phenylethylamine (2.4 mmol) was added to a refluxing benzene solution (6 cm³) of phenoxyacetic acid (2.4 mmol) and the bismuthane **1b** (2.4 mmol). (B) 2-Phenylethylamine (2.4 mmol) was added to a refluxing benzene solution (6 cm³) of phenoxyacetic acid (2.4 mmol) and the bismuthane **1b** (0.8 mmol). (C) A benzene solution (6 cm³) of phenylethylamine (2.4 mmol), phenoxyacetic acid (2.4 mmol), and the bismuthane **1b** (0.8 mmol) prepared at room temperature was heated to reflux.

minutes and 2.4 mmol of anisole was detected by HPLC. To this solution was added the amine (2.4 mmol) and the quantity of the products was followed by HPLC of aliquots (Fig. 1, A). After ca. 10 h, 2.2 mmol of the amide and 3.8 mmol of anisole were detected by HPLC and ~1 mmol of the bismuthane **1b** was isolated from the reaction mixture. The recovery of the triarylbismuthane strongly suggests that not only a diarylbismuth acylate but also an arylbismuth diacylate and/or a bismuth triacylate were formed by the reaction of the triarylbismuthane with an equimolar amount of the acid.

(B) When the acid (2.4 mmol) and the bismuthane (0.8 mmol) were heated under the same conditions, only 1.7 mmol of anisole were determined by HPLC from the clear solution. After addition of more amine (2.4 mmol), the amount of anisole gradually increased as the reaction proceeded and after ca. 10 h 2.4 mmol of anisole and 2.0 mmol of the amide were produced (Fig. 1, B).

(C) When a benzene suspension (6 cm³) of the acid (2.4 mmol), the amine (2.4 mmol) and the bismuthane (0.8 mmol) prepared at room temperature was heated in an oil-bath (95 °C), the reaction proceeded more slowly than that performed under conditions (B), and no anisole nor amide was detected until ca. 4 h. After ca. 10 h, 1.8 mmol of anisole and 1.8 mmol of the amide were produced. Since no amide was produced when no anisole was detected, we can reasonably surmise that some kind of bismuth acylate is involved in the reactions.

From these results we concluded that the most probable mechanism for the bismuthane-mediated coupling reactions of carboxylic acid with amines or alcohols would involve the direct acylation of these nucleophiles by an *in situ*-generated mixture of diarylbismuth acylate, arylbismuth diacylate, and bismuth triacylate. Although we could not determine quantitatively the differences in reactivity among these bismuth acylates, the diarylbismuth acylate and/or the arylbismuth diacylate may be more reactive than the bismuth triacylates seeing that the reaction performed under conditions (A) proceeded significantly more quickly than did that under conditions (B) in which a lesser amount of diarylbismuth acylate and/or arylbismuth diacylate was expected to be formed. From molecular orbital calculations based on the

Table 3 The calculated charge on the carboxy group carbon atom of carboxylic acids, their esters, bismuth triacylates, and diarylbismuth carboxylates^a

R	R-H	R-Et	R ₃ Bi	Ar ₂ Bi-R ^b
PhOCH ₂ C(=O)O	0.3721	0.3669	0.3983	0.4103
PhC(=O)O	0.4311	0.4251	0.4512	0.4659
EtC(=O)O	0.3756	0.3710	0.4154	0.4214

^a Calculation was performed by PM3 in MOPAC Ver. 6.01.¹⁰ ^b Ar = 2-MeOC₆H₄.

Fig. 2 Molecular models of (a) bis-(2-methoxyphenyl)bismuth 2,2-dimethylpropionate and (b) bis-(2-methoxyphenyl)bismuth phenoxyacetate optimized by PM3 in MOPAC Ver. 6.01¹⁰

premise that charges on the carboxylic carbon of the diarylbismuth acylate are the most positive among the acylates compared (see Table 3), we can reasonably anticipate that it is the most reactive toward nucleophiles, followed by bismuth triacylate and ethyl acylate.

The origin of the unique selectivity for primary carboxylic acids may now be sought for steric requirements. As shown visually by the molecular modellings in Fig. 2, the carboxylic carbon of the diarylbismuth acylate is considerably hindered by the bismuth atom of a large Van der Waals radius. If the carbon atom alpha to the carboxylate function is multiply substituted as is the case with a tertiary carboxylic [Fig. 2(a)], nucleophiles could hardly attack on the carboxylic carbon atom of the diarylbismuth acylate.

Bismuthane-mediated dehydration of alcohols themselves by similar reaction conditions was attempted in vain; the alcohols were recovered almost quantitatively and no detectable amounts of the corresponding ethers were formed. Attempted preparation of organyl iodides from alcohols under the similar conditions in the presence of tetrabutylammonium iodide also gave recovered starting alcohols. Such a difficulty of coupling reactions of alcohols might be attributed to the lower acidity of the alcohols. If bismuth alkoxide could be formed efficiently *in situ*, the attempted substitution reactions might proceed.^{1a}

The present bismuthane-mediated coupling reaction provides a novel methodology for the selective amide/ester synthesis from carboxylic acids under completely neutral conditions. Although a variety of mild procedures are available for the condensation of carboxylic acids with amines and alcohols,⁵ no reagents appear to our knowledge to be able to differentiate effectively between branched carboxylic acids and unbranched ones. The procedure is straightforward; gentle heating of the starting materials in benzene followed by removal of insoluble substance by filtration and subsequent evaporation of the filtrate under reduced pressure gives the condensation product almost in pure form in moderate to good yields.

Experimental

M.p.s were determined with a YANACO MP apparatus and are uncorrected. IR spectra were determined on a Hitachi 260-10 spectrophotometer. ¹H NMR spectra were recorded on a JEOL JNM-HM60 or a JEOL JNM-GX270 instrument for solutions in CDCl₃ with tetramethylsilane as an internal standard. Coupling constants *J* are given in Hz. Mass spectra were determined on an ESCO EMD-05 or a Hitachi M-80B instrument at 20 or 70 eV. TLC was performed by using Merck silica gel 60 precoated sheets F₂₅₄ and spots were visualized under 254 nm UV light or with the aid of iodine. We thank the Advanced Instrumentation Center for Chemical Analysis, Ehime University, for elemental analyses. Commercially available bismuth(III) chloride was used without further purification. Triaryl bismuthanes were prepared by the arylation of bismuth(III) chloride with the corresponding arylmagnesium bromides or aryllithiums. Carboxylic acids, alcohols and amines were all commercial products and were purified by recrystallization or distillation before use. Solvents were dried with calcium hydride or sodium benzophenone ketyl and distilled prior to use.

General Procedure for Reactions of Carboxylic Acids with Alcohols and Amines in the Presence of a Triaryl bismuthane 1.—A mixture of carboxylic acid (1.2 mmol), an alcohol or an alkylamine (1.2 mmol), tris(methoxyphenyl)bismuthane **1** (0.4 mmol) and benzene (3 cm³) was heated under reflux for 12 h. A precipitated solid was filtered off and the solvent, together with the anisole formed, was evaporated under reduced pressure to leave a crude ester or amide, which was purified by chromatography over silica gel or by recrystallization from CH₂Cl₂–hexane.

N-(2-Phenylethyl)phenoxyacetamide: m.p. 76–77 °C; δ_{H} 2.81 (2 H, t, *J* 6.0), 3.61 (2 H, dt, *J* 6.0 and 6.0), 4.44 (2 H, s), 6.45–7.46 (10 H, m) and 8.06 (1 H, br s); ν_{max} (KBr)/cm⁻¹ 3325, 1655, 1595 and 1540 (Found: C, 75.6; H, 6.8; N, 5.7. C₁₆H₁₇NO₂ requires C, 75.3; H, 6.7; N, 5.5%).

N-Phenylphenoxyacetamide: m.p. 104–106 °C [lit.,⁶ 101.5 °C]; δ_{H} 4.62 (2 H, s), 6.95–7.55 (10 H, m) and 8.32 (1 H, br s); ν_{max} (KBr)/cm⁻¹ 3180, 1660, 1598 and 1555 (Found: C, 73.9; H, 5.8; N, 6.1. C₁₄H₁₃NO₂ requires C, 74.0; H, 5.8; N, 6.2%).

N-(Phenoxyacetyl)morpholine: m.p. 94–96 °C; δ_{H} 3.6 (8 H, m), 4.66 (2 H, s), 6.9 (3 H, m) and 7.2 (2 H, m); ν_{max} (KBr)/cm⁻¹ 1640, 1585, 1575, 1480, 1210 and 1110; *m/z* 221 (74%, M⁺), 128 (56) and 114 (100) (Found: C, 64.9; H, 6.9; N, 6.4. C₁₂H₁₅NO₃ requires C, 65.1; H, 6.8; N, 6.3%).

N-(2-Phenylethyl)octanamide: m.p. 59–61 °C; δ_{H} 0.85–0.90 (3 H, m), 1.26–1.71 (10 H, m), 2.11 (2 H, t, *J* 7.0), 2.81 (2 H, t, *J* 6.0), 3.52 (2 H, dt, *J* 6.0 and 6.0), 5.44 (1 H, br s) and 7.18–7.34 (5 H, m); ν_{max} (KBr)/cm⁻¹ 3275, 2895, 1630 and 1535 (Found: C, 77.4; H, 10.2; N, 5.7. C₁₆H₂₅NO requires C, 77.7; H, 10.2; N, 5.7%).

N-Phenyl octanamide: m.p. 55–57 °C [lit.,⁷ 57 °C]; δ_{H} 0.88 (3 H, t, *J* 6.0), 1.29–2.17 (10 H, m), 2.35 (2 H, t, *J* 6.0), 7.05–7.59 (5 H, m) and 7.82 (1 H, br s); ν_{max} (KBr)/cm⁻¹ 3295, 2910, 1655 and 1595.

Ethyl phenoxyacetate: oil [lit.,⁸ b.p. 251 °C]; δ_{H} 1.27 (3 H, t, *J* 7.2), 4.26 (2 H, q, *J* 7.8), 4.60 (2 H, s) and 6.83–7.44 (5 H, m); ν_{max} (NaCl)/cm⁻¹ 2960, 1740, 1590, 1480, 1440, 1375, 1280, 1190, 1080, 1020, 750 and 685; *m/z* 180 (99%, M⁺), 135 (10), 107 (100), 93 (40) and 77 (69) (Found: C, 66.6; H, 6.7. C₁₀H₁₂O₃ requires C, 66.7; H, 6.7%).

Benzyl phenoxyacetate: oil; δ_{H} 4.60 (2 H, s), 5.18 (2 H, s) and 6.93–7.30 (10 H, m); ν_{max} (NaCl)/cm⁻¹ 1755, 1595, 1585, 1490, 1440, 1275, 1190, 1142, 750 and 690; *m/z* 242 (8%, M⁺), 107 (72), 105 (16), 91 (100) and 77 (41) (Found: C, 74.2; H, 5.8. C₁₅H₁₄O₃ requires C, 74.4; H, 5.8%).

Butan-2-yl phenoxyacetate: oil; δ_{H} 0.88 (3 H, t, *J* 7.3), 1.24 (3

H, d, *J* 6.1), 1.50–1.65 (2 H, m), 4.61 (2 H, s), 4.98 (1 H, m), 6.9–7.0 (3 H, m) and 7.25–7.35 (2 H, m); $\nu_{\max}(\text{NaCl})/\text{cm}^{-1}$ 1740, 1720, 1590, 1485, 1280 and 1190; *m/z* 208 (100%, M^+) and 107 (99) (Found: C, 68.8; H, 7.8. $\text{C}_{12}\text{H}_{16}\text{O}_3$ requires C, 69.2; H, 7.7%).

Benzyl octanoate: oil; δ_{H} 0.84–0.89 (3 H, m), 1.27–1.66 (10 H, m), 2.34 (2 H, t, *J* 7.6), 5.10 (2 H, s) and 7.23–7.35 (5 H, m); $\nu_{\max}(\text{NaCl})/\text{cm}^{-1}$ 2920, 2850, 1740, 1500, 1460, 1380, 1250, 1210, 1160, 1105, 760 and 695; *m/z* 234 (14%, M^+), 125 (28), 108 (96) and 91 (100).

N-(2-Hydroxyethyl)phenoxyacetamide: m.p. 52–54 °C; δ_{H} 3.03–3.86 (6 H, m), 4.46 (2 H, s) and 6.83–7.32 (5 H, m); $\nu_{\max}(\text{NaCl})/\text{cm}^{-1}$ 3350, 2920, 1650 and 1590; *m/z* 195 (100%, M^+), 177 (18), 152 (74), 107 (97) and 77 (74) (Found: C, 61.4; H, 6.6; N, 7.1. $\text{C}_{10}\text{H}_{13}\text{NO}_3$ requires C, 61.5; H, 6.7; N, 7.2%).

N-Ethyl-N-(2-hydroxyethyl)phenoxyacetamide: oil; δ_{H} 1.19 (3 H, t, *J* 7.0), 3.24–3.66 (7 H, m), 4.70 (2 H, s) and 6.87–7.40 (5 H, m); $\nu_{\max}(\text{NaCl})/\text{cm}^{-1}$ 3350, 2920, 1645 and 1595; *m/z* 223 (54%, M^+), 192 (34), 180 (30), 164 (46), 116 (48), 107 (100), 88 (45) and 77 (27) (Found: C, 64.7; H, 7.8; N, 5.9. $\text{C}_{12}\text{H}_{17}\text{NO}_3$ requires C, 64.6; H, 7.7; N, 6.3%).

N-(2-Phenylethyl)-9,10-epoxyoctadecanamide: m.p. 65–67 °C; δ_{H} 0.87–0.91 (3 H, m), 1.27–1.61 (26 H, m), 2.11 (2 H, t, *J* 7.0), 2.84 (2 H, t, *J* 7.0), 2.89 (2 H, br s), 3.52 (2 H, q, *J* 7.0), 5.41 (1 H, br s) and 7.18–7.34 (5 H, m); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3300, 2910, 1640 and 1550; *m/z* 402 (0.8%, M^+), 383 (5), 292 (8), 274 (13), 176 (15), 163 (23), 155 (8), 122 (24), 105 (37) and 104 (100) (Found: C, 77.4; H, 10.4; N, 3.5. $\text{C}_{26}\text{H}_{43}\text{NO}_2$ requires C, 77.8; H, 10.8; N, 3.5%).

Condensation of Phenoxyacetic Acid with Butane-1,2-diol in the Presence of a Triarylbismuthane 1.—Reaction of phenoxyacetic acid, butane-1,2-diol and the bismuthane **1b** in 3:3:2 molar proportions under conditions similar to those described in the preceding section afforded a 2:1 mixture of 2-hydroxybutyl phenoxyacetate and (1-hydroxymethyl)propyl phenoxyacetate (59%), and 1,2-bis(phenoxyacetoxy)butane (8%). The monoester mixture was inseparable by chromatography and so was analysed as such.

Reaction of phenoxyacetic acid, butane-1,2-diol and the bismuthane **1b** in 3:3:1 molar proportions under similar conditions to those denoted above afforded a 2:1 mixture of 2-hydroxybutyl phenoxyacetate and (1-hydroxymethyl)propyl phenoxyacetate (50%) and 1,2-bis(phenoxyacetoxy)butane (6%).

A mixture of 2-hydroxybutyl phenoxyacetate and 1-(hydroxymethyl)propyl phenoxyacetate: oil; δ_{H} 0.87 (t, *J* 7.5), 0.93 (t, *J* 7.0), 1.46 (quintet, *J* 7.5), 1.60 (quintet, *J* 7.0), 3.54–3.68 (m), 3.71–3.74 (m), 4.04–4.24 (m), 4.65 (s), 4.93–4.97 (m) and 6.88–7.30 (m); $\nu_{\max}(\text{NaCl})/\text{cm}^{-1}$ 3400, 2925, 1740, 1595, 1490, 1430, 1380, 1270, 1190, 1080 and 750; *m/z* 224 (72%, M^+), 166 (31), 152 (29), 107 (100) and 77 (43) (Found: C, 64.0; H, 7.3. $\text{C}_{12}\text{H}_{16}\text{O}_4$ requires C, 64.3; H, 7.2%).

1,2-Bis(phenoxyacetoxy)butane: oil; δ_{H} 0.90 (3 H, t, *J* 7.5), 1.62 (2 H, quintet, *J* 7.5), 4.12 (1 H, dABq, *J* 12.1 and 6.9), 4.46 (1 H, dABq, *J* 12.1 and 2.9), 4.58 (2 H, s), 4.59 (2 H, s), 5.13–5.18 (1 H, m) and 6.87–7.31 (10 H, m); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1750, 1600, 1490, 1290, 1190, 1090, 760 and 695; *m/z* 358 (100%, M^+), 207 (70), 179 (14), 152 (20), 107 (100) and 77 (50) (Found: C, 66.7; H, 6.3. $\text{C}_{20}\text{H}_{22}\text{O}_6$ requires C, 67.0; H, 6.2%).

Condensation of 2-Benzylmalonic Acid 2a with 2-Phenylethylamine in the Presence of a Triarylbismuthane 1.—When 2-benzylmalonic acid **2a** (194 mg, 1.0 mmol) was treated with 2-phenylethylamine (266 mg, 2.2 mmol) in the presence of the bismuthane **1b** (371 mg, 0.7 mmol) in benzene (10 cm³) under gentle reflux for 10 h, 2-benzyl-N,N'-bis-(2-phenylethyl)malondi-

amide **3a** was isolated in 60% yield as crystals, m.p. 153.5–154.0 °C; δ_{H} 2.58–2.73 (4 H, m), 2.98–3.09 (3 H, m), 3.36–3.46 (4 H, m) and 7.02–7.32 (15 H, m); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3260, 1650, 1625 and 1520; *m/z* 400 (52%, M^+), 309 (65), 296 (21), 281 (21) and 280 (100) (Found: C, 78.0; H, 7.05; N, 7.0. $\text{C}_{26}\text{H}_{28}\text{N}_2\text{O}_2$ requires C, 77.5; H, 7.1; N, 7.0%).

Reaction of 2,2-Dibenzylmalonic Acid 2b with Aromatic Olefins in the Presence of a Triarylbismuthane 1.—A mixture of 2,2-dibenzylmalonic acid **2b** (284 mg, 1.0 mmol), the bismuthane **1b** (530 mg, 1.0 mmol), phenylethene (312 mg, 3.0 mmol) and benzene (10 cm³) was gently heated for 12 h under argon. A precipitated black solid was filtered off and a product obtained after removal of the solvent was chromatographed on silica gel with CH_2Cl_2 -hexane (from 0:100 to 100:0) as eluent. Recrystallization from CH_2Cl_2 -hexane gave 2,2-dibenzyl-4-phenyl-4-butanolide **5a** as crystals (92 mg, 27%); m.p. 121–123 °C; δ_{H} 2.18 (1 H, dABq, *J* 13.5 and 9.5), 2.43 (1 H, dABq, *J* 13.5 and 7.3), 2.80 (2 H, d, *J* 13.1), 3.28 (1 H, d, *J* 13.1), 3.37 (1 H, d, *J* 13.4), 4.04 (1 H, dd, *J* 7.32 and 9.46) and 6.55–7.35 (15 H, m); δ_{C} 38.00 (CH_2), 43.68 (CH_2), 44.62 (CH_2), 52.30 (C), 78.46 (CH), 125.62 (CH), 127.02 (CH), 127.45 (CH), 128.17 (CH), 128.38 (CH), 128.63 (CH), 128.77 (CH), 129.93 (CH), 130.63 (CH), 136.29 (C), 136.67 (C), 139.66 (C) and 180.56 (C=O); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1755, 1182 and 702; *m/z* 342 (49%, M^+), 251 (100), 205 (94), 173 (65), 129 (98), 105 (99) and 91 (100) (Found: C, 83.8; H, 6.6. $\text{C}_{24}\text{H}_{22}\text{O}_2$ requires C, 84.2; H, 6.5%).

A similar reaction with 1-methyl-1-phenylethene afforded 2, 2-dibenzyl-4-methyl-4-phenyl-4-butanolide, m.p. 139–141 °C; δ_{H} 0.95 (3 H, s), 2.33 (1 H, ABq, *J* 13.0), 2.53 (1 H, ABq, *J* 13.0), 2.69 (2 H, *J* 13.0), 2.93 (1 H, d, *J* 13.0), 3.32 (1 H, d, *J* 13.0) and 6.86–7.35 (15 H, m); δ_{C} 30.96 (Me), 41.28 (CH_2), 43.28 (CH_2), 44.28 (CH_2), 52.73 (C), 83.53 (C), 123.41 (CH), 126.70 (CH), 126.91 (CH), 127.13 (CH), 128.14 (CH), 128.24 (CH), 128.57 (CH), 130.42 (CH), 130.66 (CH), 135.72 (C), 136.86 (C), 146.14 (C) and 180.24 (C=O); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1755, 1230, 760 and 695; *m/z* 356 (15%, M^+), 341 (15), 264 (32), 238 (41), 219 (18), 208 (27), 194 (6), 149 (19), 131 (14), 129 (18), 121 (23), 118 (59) and 105 (100) (Found: C, 83.9; H, 6.8. $\text{C}_{25}\text{H}_{24}\text{O}_2$ requires C, 84.2; H, 6.8%).

A similar reaction with 1,1-diphenylethene afforded 2,2-dibenzyl-4,4-diphenyl-4-butanolide, m.p. 162–165 °C; δ_{H} 2.73 (2 H, *J* 13.0), 2.88 (2 H, s), 2.99 (2 H, d, *J* 13.0) and 6.99–7.38 (20 H, m); δ_{C} 41.80 (CH_2), 42.37 (CH_2), 51.73 (C), 86.64 (C), 125.77 (CH), 1226.99 (CH), 127.53 (CH), 128.27 (CH), 128.32 (CH), 130.77 (CH), 136.17 (C), 143.98 (C), 179.76 (C=O); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1760, 1445, 1195, 1170, 970, 760 and 695; *m/z* 418 (28%, M^+), 341 (8), 327 (44), 283 (15), 281 (20), 249 (6), 194 (5), 180 (100), 152 (12), 281 (20), 249 (6), 194 (5), 180 (100), 152 (12), 117 (36) and 105 (97) (Found: C, 86.4; H, 6.3. $\text{C}_{30}\text{H}_{26}\text{O}_2$ requires C, 86.1; H, 6.3%).

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