Synthesis and Reactions of Bismuthonium Salts and Ylides Bearing an α-Ester Group

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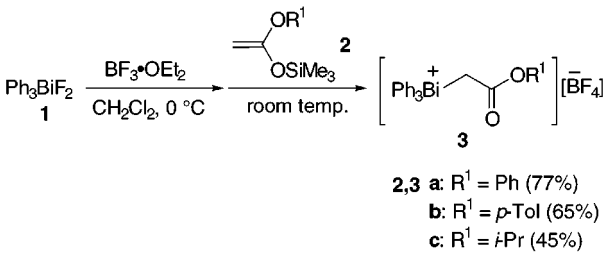
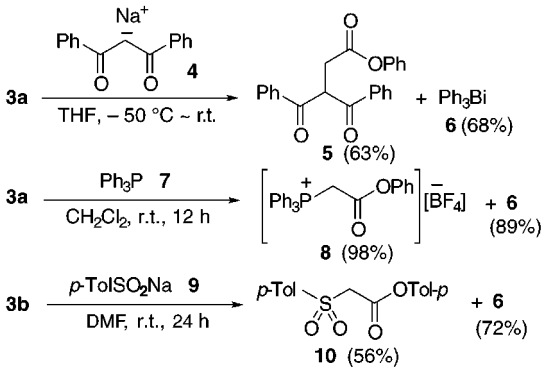
Carbon−carbon bond-forming reactions based on ester ylides of the general form $R_nM{=}CHCO_2R'$ (M = P, As, Sb, S, Se, Te; n = 2, 3) constitute a research area of considerable significance.[1] This class of ylides shows varied reactivity depending on the nature of a heteroatom involved, but their modes of reaction toward the carbonyl function may be classified into two major categories: Wittig-type olefination and Corey−Chaycovsky-type epoxidation. Recently, we have reported that bismuthonium α-keto ylides $Ph_3Bi{=}CHCOR$ (R = alkyl or aryl), generated in situ from the corresponding onium salts,[2] are moderately stabilized and undergo C−C bond-forming reactions with various compounds, which include aldehydes,[3] *N*-sulfonylaldimines,[4] α-keto esters,[5] *o*-quinones,[5] acenaphthenequinone,[6] and benzils.[7] However, no information is available for the α-ester-type bismuthonium ylides, $R_3Bi{=}CHCO_2R'$, due to the lack of general methodology for the synthesis of bismuthonium salt precursors.[8] As a part of our ongoing study on organobismuth(V) chemistry, we report herein the first synthesis and reactions of bismuthonium salts and ylides bearing an ester group at the α-position. Interestingly, this class of bismuthonium ylides has been found to undergo either Corey−Chaycovsky-type epoxidation or carbon-to-oxygen aroyl transposition with carbonyl compounds depending on the structure of the substrates.

Scheme 1



Scheme 2



Treatment of triphenylbismuth difluoride (**1**) with ketene silyl acetals (**2**) in the presence of boron trifluoride etherate ($BF_3{\cdot}OEt_2$) in CH_2Cl_2 at room temperature yielded the corresponding bismuthonium salts bearing an α-ester group (**3**) in 45−77% yield (Scheme 1).[9] No Bi−C bond formation was observed in the absence of the Lewis acid.

Compounds **3** were characterized by spectroscopic methods and elemental analysis. In the ^{1}H NMR spectra, α-methylene protons gave a singlet peak at δ 4.71−4.85 (in $CDCl_3$). In the FAB mass spectra, a strong base ion peak due to $[M^+ - BF_4]$ was observed, and in the IR spectra, broad intense absorptions due to BF_4^- appeared at 1150−950 cm^{-1}. These spectral data are consistent with the onium structure of compounds **3**.

Onium salts **3a**,**b** smoothly underwent the C−C, C−P, and C−S bond formations with sodium enolate **4**, triphenylphosphine **7**, and sodium *p*-toluenesulfinate **9** to give the corresponding α-keto ester **5**, phosphonium salt **8**, and α-sulfonyl ester **10**, respectively, with good recovery of triphenylbismuthine **6** (Scheme 2). Good nucleofugal ability of the triphenylbismuthonio moiety in **3** no doubt plays a key role in these nucleophilic substitutions.

Addition of a base to a colorless suspension of onium salt **3c** in THF at −78 °C produced a yellow solution of ylide **11c**. When this solution was allowed to warm to room temperature, there resulted bismuthine **6** and an *E*/*Z* mixture of olefins **12** (50% based on **3c**) instead of the expected **11c** (Scheme 3). This shows that α-ester bismuthonium ylide **11** is less stabilized and decomposes

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Scheme 3

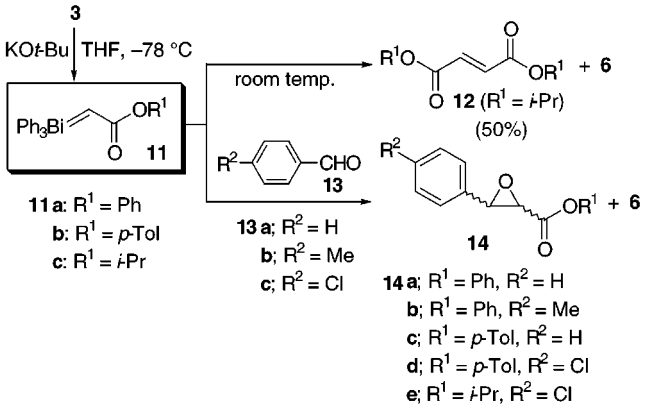


Table 1. Reaction of Bismuthonium Ylides 11 with Aldehydes 13[a]

entry	salt	aldehyde	product	yield/%	cis/trans ratio
1	**3a**	**13a**	**14a**	36	0/100
2	**3a**	**13b**	**14b**	43	0/100
3	**3b**	**13a**	**14c**	35	0/100
4	**3b**	**13c**	**14d**	42	0/100
5	**3c**	**13c**	**14e**	45	36/64

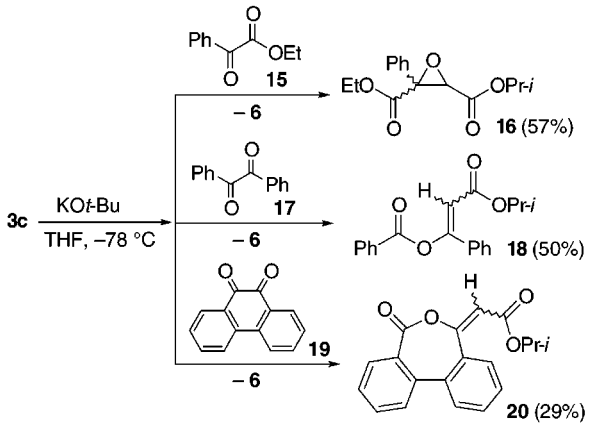
[a] Reactions were carried out in THF at −78 °C. KO-*t*-Bu was used as a base. Triphenylbismuthine was recovered in 74−82% yield.

to **6** and **12** upon warming.[10] In marked contrast, phosphorus analogues $Ph_3P{=}CHCO_2R$ are thermally stabilized and can be handled without decomposition at ambient temperature.[1a]

To examine the reactivity of **11**, the yellow solution generated in situ from bismuthonium salts **3** and a base was treated with carbonyl compounds at −78 °C. Treatment of **3** with aldehydes **13** in the presence of a base gave α,*β*-epoxy esters **14** in 35−45% yield with good recovery of bismuthine **6** (Scheme 3 and Table 1). Among the bases examined, KO-*t*-Bu was found to be the most effective.[11] The cis/trans stereochemistry of epoxides **14** was dependent on the ester portion R^1; the trans isomer was obtained exclusively when R^1 was an aryl group, while a cis/trans isomeric mixture was formed when R^1 was an isopropyl group. Although direct evidence is not yet available, the ester function is likely to perturb the transition-state structure at the C−C bond-forming stage through electronic interaction.

The reaction mode of bismuthonium ylides **11** is different from those of phosphorus, arsenic, and antimony counterparts, which all undergo Wittig-type olefination to give α,*β*-unsaturated esters together with the corresponding pnictogen(V) oxides.[1a−f] This trend has also been predicted from a theoretical study using the model system, $H_3M{=}CH_2 + H_2C{=}O$ (M = P, As, Sb, Bi).[12] The good leaving ability of the triphenylbismuthonio moiety

Scheme 4



coupled with the weaker Bi(V)−$O_{aldehyde}$ interaction should contribute to the unique reactivity of bismuthonium ylides.

Although ylide **11c** failed to react with simple ketones, such as acetophenone and benzophenone, it underwent C−C bond formation with ethyl benzoylformate **15**, benzil **17**, and 9,10-phenanthrenequinone **19** to yield a cis/trans mixture of oxiranes **16**, *O*-benzoyl enolates **18**, and oxepins **20**, respectively (Scheme 4). In all cases, a good yield of bismuthine **6** was recovered. Compounds **16**, **18**, and **20** were characterized by NMR, IR, and MS spectroscopies as well as by elemental analysis. The ^{1}H NMR spectrum of a cis/trans mixture of **16** showed the oxirane ring protons at *δ* 3.57 and 4.11, whereas the olefinic protons of **18** and **20** appeared at *δ* 5.65−6.35. In the IR spectra, double stretching bands of the ester C=O groups were observed at around 1740 cm^{-1} for **16**, 1744−1715 cm^{-1} for **18**, and 1748−1715 cm^{-1} for **20**. Olefins **18** and **20** showed the conjugated C=C stretching band at 1649−1642 and 1667−1662 cm^{-1}, respectively. In the CI mass spectra, **16**, **18**, and **20** showed the parent ion peak due to $[M^+ + 1]$.

Though the oxirane formation is not uncommon in α-ester ylide chemistry,[13] the formation of enolates **18** and **20** is unprecedented and characteristic of bismuthonium ylide **11**. As has been suggested for α-keto ylides,[3] the initial stage of the C−C bond-forming reaction would be nucleophilic addition of the ylidic carbon to the carbonyl function of the substrates. In subsequent step(s), oxiranes **14** and **16** would result from the Corey−Chaycovsky-type bond formation, whereas enolates **18** and **20** may be constructed via the carbon-to-oxygen transposition of the aroyl group.[14] Plausible pathways for the formation of compounds **16** and **18** are illustrated in Scheme 5. In the case of bismuthonium α-keto ylides, benzil behaved similarly, but 9,10-phenanthrenequinone reacted in a different manner to afford 2-acyl-3-hydroxytropone via ring expansion.[5,7]

(10) For thermally stabilized bismuthonium ylides, see: (a) Lloyd, D.; Singer, M. I. C. *J. Chem. Soc., Chem. Commun.* **1967**, 1042. (b) Glidewell, C.; Lloyd, D.; Metcalfe, S. *Synthesis* **1988**, 319. (c) Barton, D. H. R.; Blazejewski, J.-C.; Charpiot, B.; Finet, J.-P.; Motherwell, W. B.; Papoula, M. T. B.; Stanforth, S. P. *J. Chem. Soc., Perkin Trans. 1* **1985**, 2667. (d) Suzuki, H.; Murafuji, T.; Ogawa, T. *Chem. Lett.* **1988**, 847. (e) Ogawa, T.; Murafuji, T.; Suzuki, H. *J. Chem. Soc., Chem. Commun.* **1989**, 1749. (f) Kirij, N. V.; Pasenok, S. V.; Yagupolskii, Y. L.; Naumann, D.; Tyrra, W. *J. Fluorine Chem.* **1994**, *66*, 75.

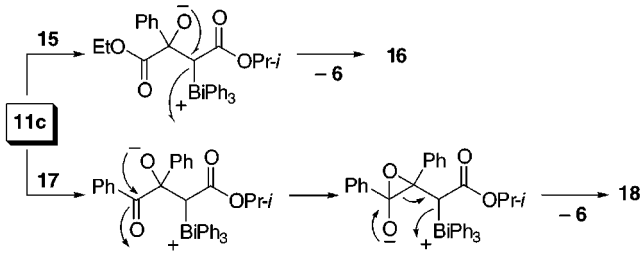
(11) Sodium hydride, lithium bis(trimethylsilyl)amide, LDA, and triethylamine all gave lower yields of **14**.

(12) Naito, T.; Nagase, S.; Yamataka, H. *J. Am. Chem. Soc.* **1994**, *116*, 10080.

(13) Sulfur ylides of the type $Me_2S{=}CRCO_2R'$ undergo Corey−Chaycovsky reaction with aldehydes and dicarbonyl compounds to give oxiranes. (a) Payne, G. B. *J. Org. Chem.* **1968**, *33*, 3517. (b) Trost, B. M.; Arndt, H. C. *J. Org. Chem.* **1973**, *38*, 3140.

(14) Oxiranes **21** and **22**, prepared by the Darzens reaction of isopropyl α-bromoacetate with **17** and **19**, did not isomerize to enolates **18** and **20** under the given reaction conditions.

Scheme 5



In summary, the Lewis-acid-promoted reaction of triphenylbismuth difluoride with ketene silyl acetals provides a general route to bismuthonium salts bearing an α-ester group, which can be readily converted to the corresponding ylides at low temperatures. Bismuthonium α-ester ylides, $Ph_3Bi{=}CHCO_2R$, exhibit unique reactivity toward carbonyl compounds, giving different types of products according to the structure of substrates.

Experimental Section

General Methods. Triphenylbismuth difluoride[15] and ketene silyl acetals[16] were prepared according to the reported procedures. All reactions were carried out under an atmosphere of argon. Column chromatography was performed on silica gel (Wako-gel C200).

(Aryloxycarbonylmethyl)- and (Alkoxycarbonylmethyl)triphenylbismuthonium Tetrafluoroborate (3): General Procedure. To a solution of triphenylbismuth difluoride **1** (2.39 g, 5.0 mmol) in CH_2Cl_2 (25 mL) was added at 0 °C $BF_3{\cdot}OEt_2$ (0.62 mL, 5.0 mmol). After 1 h, silyl ketene acetal **2** (5.0 mmol) was added, and the resulting mixture was stirred for 12 h at room temperature. Evaporation of the solvent under reduced pressure left an oily residue, which was passed through a short silica gel column using CH_2Cl_2 as the eluent. Removal of the solvent under reduced pressure gave a crystalline residue, which was recrystallized from $Et_2O{-}CH_2Cl_2$ (10:1) to afford bismuthonium salt **3**.

(Phenoxycarbonylmethyl)triphenylbismuthonium tetrafluoroborate (3a): mp 165−166 °C; ^{1}H NMR δ 4.85 (s, 2H), 6.69 (d, 2H, J = 6.9 Hz), 7.10−7.30 (m, 3H), 7.50−7.80 (m, 15H); ^{13}C NMR δ 40.5, 121.1, 126.5, 129.5, 132.2, 132.4, 135.8, 138.0, 150.2, 167.7; MS (FAB) m/z 575 ($M^+ - BF_4$), 363, 286, 209; IR (KBr) 1759 (C=O), 1150−1000 (BF_4^-) cm^{-1}. Anal. Calcd for $C_{26}H_{22}BBiF_4O_2$: C, 47.16; H, 3.35. Found: C, 47.27; H, 3.39.

(4-Methylphenoxycarbonylmethyl)triphenylbismuthonium tetrafluoroborate (3b): mp 127−129 °C; ^{1}H NMR δ 2.28 (s, 3H), 4.85 (s, 2H), 6.56 (d, 2H, J = 8.4 Hz), 7.04 (d, 2H, J = 8.4 Hz), 7.50−7.90 (m, 15H); ^{13}C NMR δ 20.8, 40.7, 120.7, 130.0, 132.2, 132.4, 135.9, 136.3, 138.1, 148.0, 167.8; MS (FAB) m/z 589 ($M^+ - BF_4$), 363, 286, 209; IR (KBr) 1759 (C=O), 1150−1000 (BF_4^-) cm^{-1}. Anal. Calcd for $C_{27}H_{24}BBiF_4O_2$: C, 47.95; H, 3.58. Found: C, 48.06; H, 3.34.

(Isopropoxycarbonylmethyl)triphenylbismuthonium tetrafluoroborate (3c): mp 114−115 °C; ^{1}H NMR δ 1.05 (d, 6H, J = 6.3 Hz), 4.71 (s, 2H), 4.83 (sept, 1H, J = 6.3 Hz), 7.52−7.82 (m, 15H); ^{13}C NMR δ 21.4, 41.8, 71.6, 132.1, 132.3, 135.8, 138.1, 168.1; MS (FAB) m/z 541 ($M^+ - BF_4$), 363, 286, 209; IR (KBr) 1732 (C=O), 1200−950 (BF_4^-) cm^{-1}. Anal. Calcd for $C_{23}H_{24}BBiF_4O_2$: C, 43.97; H, 3.85. Found: C, 44.00; H, 3.83.

Reaction of Salt 3a with Sodium Enolate 4. To a suspension of **3a** (662 mg, 1.0 mmol) in THF (5 mL) cooled to −50 °C was added a solution of sodium enolate **4**, generated from NaH (24 mg, 1.0 mmol) and dibenzoylmethane (224 mg, 1.0 mmol) in the same solvent (5 mL). The resulting yellow solution was allowed to warm to room temperature with stirring and then concentrated under reduced pressure. The residue was taken up with Et_2O and evaporated to leave an oil, which was chromatographed on silica gel using hexanes−ethyl acetate as the eluent to afford triphenylbismuthine **6** (300 mg, 68%) and phenyl 3-benzoyl-4-phenyl-4-oxobutanoate **5** (225 mg, 63%): mp 114−115 °C; ^{1}H NMR δ 3.35 (d, 2H, J = 6.5 Hz), 5.87 (t, 1H, J = 6.5 Hz), 7.00−7.80 (m, 15H); MS (EI) m/z 105, 94, 77; IR (KBr) 1748 (C=O), 1690 (C=O), 1676 (C=O) cm^{-1}. Anal. Calcd for $C_{23}H_{18}O_4$: C, 77.08; H, 5.06. Found: C, 76.83; H, 4.98.

Reaction of 3a with Triphenylphosphine 7. A mixture of **3a** (331 mg, 0.50 mmol), triphenylphosphine **7** (131 mg, 0.50 mmol), and CH_2Cl_2 (5 mL) was stirred at room temperature for 12 h. Removal of the solvent and subsequent dilution with Et_2O separated the crystals, which were filtered off, washed with Et_2O, and dried in vacuo to give (phenoxycarbonylmethyl)triphenylphosphonium tetrafluoroborate **8** (238 mg, 98%). The filtrate was concentrated under reduced pressure to leave an oily residue, which was recrystallized from MeOH to give triphenylbismuthine **6** (195 mg, 89%). Compound **8**: mp 160−162 °C; ^{1}H NMR δ 4.99 (d, 2H, J = 13.8 Hz), 6.84 (d, 2H, J = 8 Hz), 7.10−7.30 (m, 3H), 7.60−7.90 (m, 15H); MS (FAB) m/z 397 ($M^+ - BF_4$); IR (KBr) 1744 (C=O), 1200−1000 (BF_4^-) cm^{-1}. Anal. Calcd for $C_{26}H_{22}BF_4O_2P$: C, 64.49; H, 4.58. Found: C, 64.19; H, 4.54.

Reaction of 3b with Sodium *p*-Toluenesulfinate 9. A mixture of **3b** (331 mg, 0.50 mmol), sodium *p*-toluenesulfinate tetrahydrate **9** (1.25 g, 5.0 mmol), and DMF (5 mL) was stirred at room temperature for 24 h and then poured into water (10 mL). The organic layer was extracted with Et_2O (10 mL × 3), and the combined extracts were washed with brine (10 mL × 3), dried over $MgSO_4$, and concentrated under reduced pressure. An oily residue was chromatographed on silica gel using hexanes−ethyl acetate as the eluent to yield triphenylbismuthine **6** (158 mg, 72%) and 4-methylphenyl *p*-toluenesulfonyl acetate **10** (85 mg, 56%): mp 112−113 °C; ^{1}H NMR δ 2.33 (s, 3H), 2.45 (s, 3H), 4.31 (s, 2H), 6.89 (d, 2H, J = 8.6 Hz), 7.15 (d, 2H, J = 8.6 Hz), 7.37 (d, 2H, J = 8.3 Hz), 7.88 (d, 2H, J = 8.3 Hz); MS (EI) m/z 304 (M^+); IR (KBr) 1757 (C=O), 1323 (SO_2), 1167 (SO_2) cm^{-1}. Anal. Calcd for $C_{16}H_{16}O_4S$: C, 63.14; H, 5.30. Found: C, 63.17; H, 5.29.

Generation and Thermal Decomposition of Bismuthonium Ylide 11c. To a suspension of **3c** (628 mg, 1.0 mmol) in THF (10 mL) was added KO-*t*-Bu (112 mg, 1.0 mmol) at −78 °C. After 10 min, the suspension turned to a yellow solution, which was allowed to warm to gradually room temperature. Evaporation of the solvent gave an oily residue that contained triphenylbismuthine **6**, diisopropyl maleate ((*Z*)-**12**), and diisopropyl fumarate ((*E*)-**12**). An *E*/*Z* mixture of **12** was obtained in 50% yield (50 mg; *E*/*Z* = 78/22) by chromatography on silica gel.

Base-Promoted Reaction of 3 with Carbonyl Compounds. Typical Procedure. To a suspension of **3a** (662 mg, 1.0 mmol) in THF (10 mL) was added KO-*t*-Bu (112 mg, 1.0 mmol) at −78 °C. The suspension turned to a yellow solution. After 10 min, benzaldehyde **13a** (0.10 mL, 1.0 mmol) was added, and the resulting mixture was allowed to warm to room temperature. Evaporation of the solvent gave an oily residue, which was taken up with benzene. The benzene solution was concentrated under reduced pressure to leave an oily residue, which was subjected to ^{1}H NMR determination to obtain the isomeric ratio of α,β-epoxy ester **14a**. Triphenylbismuthine **6** (361 mg, 82%) and **14a** (86 mg, 36%) were isolated by column chromatography on silica gel using hexanes−ethyl acetate as the eluent. The stereochemistry of **14** was assigned on the basis of the coupling constants of epoxy ring protons.

The products **16** (isomer ratio = 80/20), **18** (isomer ratio = 78/22), and **20** (isomer ratio = 72/28) were similarly isolated by column chromatography, but their stereochemical assignment was not made.

***trans*-Phenyl 2,3-epoxy-3-phenylpropanoate (14a):** mp 75−76 °C (lit.[17] mp 88−90 °C); ^{1}H NMR δ 3.69 (d, 1H, J = 1.7 Hz), 4.23 (d, 1H, J = 1.7 Hz), 7.10−7.50 (m, 10H); MS (EI) m/z 240 (M^+); IR (KBr) 1752 (C=O) cm^{-1}. Anal. Calcd for $C_{15}H_{12}O_3$: C, 74.99; H, 5.03. Found: C, 74.99; H, 5.03.

***trans*-Phenyl 2,3-epoxy-3-(4-methylphenyl)propanoate (14b):** mp 69−70 °C; ^{1}H NMR δ 2.35 (s, 3H), 3.72 (d, 1H, J = 1.7 Hz), 4.21 (d, 1H, J = 1.7 Hz), 7.10−7.50 (m, 9H); MS (EI)

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m/*z* 197 ($M^+ - 57$); IR (KBr) 1752 (C═O) cm^{-1}. Anal. Calcd for $C_{16}H_{14}O_3$: C, 75.58; H, 5.55. Found: C, 75.35; H, 5.54.

***trans*-4-Methylphenyl 2,3-epoxy-3-phenylpropanoate (14c):** mp 61−62 °C (lit.[18] mp 84−85 °C); ^{1}H NMR δ 2.34 (s, 3H), 3.71 (d, 1H, J = 1.7 Hz), 4.24 (d, 1H, J = 1.7 Hz), 7.04 (d, 2H, J = 8.4 Hz), 7.18 (d, 2H, J = 8.4 Hz), 7.30−7.45 (m, 5H); MS (EI) *m*/*z* 254 (M^+); IR (KBr) 1752 (C═O) cm^{-1}. Anal. Calcd for $C_{16}H_{14}O_3$: C, 75.58; H, 5.55. Found: C, 75.16; H, 5.49.

***trans*-4-Methylphenyl 3-(4-chlorophenyl)-2,3-epoxypropanoate (14d):** ^{1}H NMR δ 2.35 (s, 3H), 3.68 (d, 1H, J = 1.6 Hz), 4.22 (d, 1H, J = 1.6 Hz), 7.03 (d, 2H, J = 8.5 Hz), 7.20 (d, 2H, J = 8.5 Hz), 7.28 (d, 2H, J = 8.6 Hz), 7.38 (d, 2H, J = 8.6 Hz); MS (EI) *m*/*z* 231 ($M^+ - 57$); IR (KBr) 1752 (C═O) cm^{-1}. Anal. Calcd for $C_{16}H_{13}ClO_3$: C, 66.56; H, 4.54. Found: C, 66.34; H, 4.56.

Isopropyl 3-(4-Chlorophenyl)-2,3-epoxypropanoate (14e). This compound was characterized as a mixture of cis/trans isomers: ^{1}H NMR (cis isomer) δ 1.01 (d, 3H, J = 6.1 Hz), 1.04 (d, 3H, J = 6.1 Hz), 3.79 (d, 1H, J = 4.7 Hz), 4.22 (d, 1H, J = 4.7 Hz), 4.87 (sept, 1H, J = 6.1 Hz), 7.25−7.40 (m, 4H); ^{1}H NMR (trans isomer) δ 1.30 (d, 3H, J = 6.2 Hz), 1.32 (d, 3H, J = 6.2 Hz), 3.43 (d, 1H, J = 1.6 Hz), 4.05 (d, 1H, J = 1.6 Hz), 5.14 (sept, 1H, J = 6.2 Hz), 7.25−7.40 (m, 4H); MS (CI) *m*/*z* 241 ($M^+ + 1$). Anal. Calcd for $C_{12}H_{13}ClO_3$: C, 59.88; H, 5.44. Found: C, 60.00; H, 5.45.

Isopropyl Ethyl 3-Phenyl-2,3-epoxysuccinate (16). This compound was characterized as a mixture of cis/trans isomers: ^{1}H NMR (major isomer) δ 1.30 (d, 6H, J = 6.2 Hz), 1.32 (t, 3H, J = 7.2 Hz), 3.57 (s, 1H), 4.28 (q, 2H, J = 7.2 Hz), 5.13 (sept, 1H, J = 6.2 Hz), 7.30−7.60 (m, 5H); ^{1}H NMR (minor isomer) δ 0.81 (d, 3H, J = 6.2 Hz), 1.02 (d, 3H, J = 6.2 Hz), 1.26 (t, 3H, J = 7.2 Hz), 4.11 (s, 1H), 4.25 (q, 2H, J = 7.2 Hz), 4.77 (sept, 1H, J = 6.2 Hz), 7.30−7.60 (m, 5H); MS (CI) *m*/*z* 279 ($M^+ + 1$); IR (neat) 1740−1750 (two C═O) cm^{-1}. Anal. Calcd for $C_{15}H_{18}O_5$: C, 64.73; H, 6.52. Found: C, 65.06; H, 6.78.

Isopropyl 3-benzoyloxy-3-phenylpropenoate 18 (major isomer): mp 85−87 °C; ^{1}H NMR δ 1.14 (d, 6H, J = 6.2 Hz), 5.03 (sept, 1H, J = 6.2 Hz), 6.35 (s, 1H), 7.34−7.74 (m, 8H), 8.23 (d, 2H, J = 7 Hz); MS (CI) *m*/*z* 311 ($M^+ + 1$); IR (KBr) 1744 (C═O), 1715 (C═O), 1642 (C═C) cm^{-1}. Anal. Calcd for $C_{19}H_{18}O_4$: C, 73.53; H, 5.85. Found: C, 73.11; H, 5.84.

Isopropyl 3-benzoyloxy-3-phenylpropenoate 18 (minor isomer): ^{1}H NMR δ 1.17 (d, 6H, J = 6.3 Hz), 5.01 (sept, 1H, J = 6.3 Hz), 6.04 (s, 1H), 7.30−7.70 (m, 8H), 8.09 (d, 2H, J = 7 Hz); MS (CI) *m*/*z* 311 ($M^+ + 1$); IR (KBr) 1744 (C═O), 1721 (C═O), 1649 (C═C) cm^{-1}. Anal. Calcd for $C_{19}H_{18}O_4$: C, 73.53; H, 5.85. Found: C, 73.82; H, 6.04.

Dibenzo[*c*,*e*]-7-isopropoxycarbonylmethylidene-7*H*-oxepin-2-one 20 (major isomer): ^{1}H NMR δ 1.04 (d, 3H, J = 6.3 Hz), 1.08 (d, 3H, J = 6.3 Hz), 4.85 (sept, 1H, J = 6.3 Hz), 6.02 (s, 1H), 7.35−7.75 (m, 7H), 7.92 (d, 1H, J = 7.7 Hz); MS (CI) *m*/*z* 309 ($M^+ + 1$); IR (neat) 1748 (C═O), 1721 (C═O), 1662 (C═C) cm^{-1}. Anal. Calcd for $C_{19}H_{16}O_4$: C, 74.01; H, 5.23. Found: C, 73.69; H, 5.31.

Dibenzo[*c*,*e*]-7-isopropoxycarbonylmethylidene-7*H*-oxepin-2-one 20 (minor isomer): ^{1}H NMR δ 1.29 (d, 6H, J = 6.2 Hz), 5.10 (sept, 1H, J = 6.2 Hz), 5.65 (s, 1H), 7.40−7.75 (m, 7H), 8.00 (d, 1H, J = 8 Hz); MS (CI) *m*/*z* 309 ($M^+ + 1$); IR (neat) 1746 (C═O), 1715 (C═O), 1667 (C═C) cm^{-1}. Anal. Calcd for $C_{19}H_{16}O_4$: C, 74.01; H, 5.23. Found: C, 73.62; H, 5.39.

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