A New Efficient Method for Direct \( \alpha \)-Alkenylation of \( \beta \)-Dicarbonyl Compounds and Phenols Using Alkenyltriarylbismuthonium Salts

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General experimental information

All reactions were carried out under argon. All melting points are uncorrected. $^1$H and $^{13}$C NMR spectra were recorded using CDCl$_3$ as the solvent. Chemical shifts are reported as the relative value vs. tetramethyldisilane and $J$ values are given in Hz. IR spectra were observed as KBr pellets or neat. MS spectra were measured using $m$-nitrobenzyl alcohol as a matrix. Column chromatography was performed on a fast flow liquid chromatography system fitted with a silica gel column. CH$_2$Cl$_2$ was distilled from CaH$_2$ before use. Toluene was distilled from sodium and stored over molecular sieves 4A. Other reagents were used as commercially received. Alkenylbismuthonium salts 3a-l were prepared from triaryltributonium difluorides 1, alkenylboronic acids 2, and BF$_3$•OEt$_2$ according to the reported procedure. $^1$ Compound 3m was prepared by the BF$_3$•OEt$_2$-promoted reaction of 1a with trimethyl(2-methyl-1-propenyl)stannane. $^2$

Synthesis of alkenylbismuthonium salts. General procedure: $^1$ To a mixture of 1 (1.0 mmol), 2 (1.1 mmol), and CH$_2$Cl$_2$ (20 mL) was added BF$_3$•OEt$_2$ (1.5 mmol) at 0 °C, and the resulting mixture was stirred at room temperature for 2 h. An aqueous solution of NaBF$_4$ (10 mmol) was added to the mixture, and the resulting two-phase solution was stirred vigorously for 15 min. The organic phase was separated, and the water phase was extracted twice with CH$_2$Cl$_2$ (5 mL). The combined organic extracts were dried over MgSO$_4$ and concentrated under reduced pressure to leave a sticky solid, which was then recrystallized from CH$_2$Cl$_2$/Et$_2$O to give 3 as colorless solid.

((E)-Hex-1-enyl)tris(4-methylphenyl)bismuthonium tetrafluoroborate (3a): mp 130–131 °C; $^1$H NMR $\delta$ 0.90 (t, 3H, $J = 7.3$ Hz), 1.34 (tq, 2H, $J = 7.6$, 7.3 Hz), 1.48 (tt, 2H, $J = 7.1$, 7.6 Hz), 2.42 (m, 2H), 2.43 (s, 9H), 6.50 (m, 1H), 7.42 (d, 6H, $J = 8.1$ Hz), 7.58 (d, 6H, $J = 8.1$ Hz), 7.84 (br-d, 1H); $^{13}$C{1H} NMR $\delta$ 13.8, 21.6, 22.3, 30.1, 36.5, 124.2, 132.6, 133.5, 135.5, 142.6, 156.0; IR (KBr) $\nu_{max}$ 2959, 2926, 2872, 1489, 1450, 1393, 1310, 1209, 1188, 1150–950 (BF$_4$–), 799, 538, 521, 478 cm$^{-1}$; MS (FAB) $m/z$ 565 ([M – BF$_4$]$^+$). Anal. Calcd for C$_{27}$H$_{32}$BBiF$_4$ C, 49.71; H, 4.94. Found: C, 49.57; H, 4.79.

((E)-Hex-1-enyl)tris(4-methoxyphenyl)bismuthonium tetrafluoroborate (3c): mp 74–75 °C; $^1$H NMR $\delta$ 0.90 (t, 3H, $J = 7.2$ Hz), 1.30–1.40 (m, 2H), 1.42–1.56 (m, 2H), 2.41 (m, 2H), 3.85 (s, 9H), 6.50 (m, 1H), 7.13 (d, 6H, $J = 8.3$ Hz), 7.61 (d, 6H, $J = 8.3$ Hz), 7.77 (br-d, 1H); $^{13}$C{1H} NMR $\delta$ 13.8,

$^1$ Matano, Y.; Begum, S. A.; Miyamatsu, T.; Suzuki, H. Organometallics 1998, 17, 4332. Compounds 3 can be easily isolated by recrystallization from CH$_2$Cl$_2$/Et$_2$O.

22.3, 30.1, 36.5, 55.6, 117.5, 124.0, 126.9, 137.0, 156.0, 162.3; IR (KBr) ν_{max} 2959, 1580, 1491, 1458, 1398, 1294, 1252, 1178, 1150–950 (BF_{4}^{-}), 820, 787, 584, 513 cm^{-1}; MS (FAB) m/z 613 ([M – BF_{4}]^{+}).
Anal. Calcd for C_{27}H_{32}BBiF_{4}O_{3}: C, 46.31; H, 4.61. Found: C, 46.32; H, 4.54.

((E)-Hex-1-enyl)tris(4-t-butylphenyl)bismuthonium tetrafluoroborate (3d): mp 153–154 °C; ^{1}H NMR δ 0.91 (t, 3H, J = 7.2 Hz), 1.30–1.40 (m, 2H), 1.34 (s, 27H), 1.45–1.55 (m, 2H), 2.42 (dt, 2H, J = 7.1, 6.8 Hz), 6.53 (dt, 1H, J = 15, 7.1 Hz), 7.64 (br-s, 12H), 7.86 (d, 1H, J = 15 Hz); ^{13}C{^{1}H} NMR δ 13.8, 22.3, 30.1, 31.1, 35.2, 36.5, 124.3, 128.9, 133.7, 135.4, 155.5, 155.9; IR (KBr) ν_{max} 3061, 2961, 2870, 1580, 1556, 1487, 1464, 1394, 1364, 1331, 1265, 1204, 1180–900 (BF_{4}^{-}), 820, 762, 719, 629, 546, 517 cm^{-1}; MS (FAB) m/z 691 ([M – BF_{4}]^{+}). Anal. Calcd for C_{36}H_{50}BBiF_{4}: C, 55.54; H, 6.47. Found: C, 55.40; H, 6.52.

((E)-Hex-1-enyl)tris(2-methoxyphenyl)bismuthonium tetrafluoroborate (3e): mp 171–173 °C; ^{1}H NMR δ 0.91 (t, 3H, J = 7.3 Hz), 1.36 (tq, 2H, J = 7.6, 7.3 Hz), 1.48 (tt, 2H, J = 7.1, 7.6 Hz), 2.43 (q, 2H, J = 7.1 Hz), 3.83 (s, 9H), 6.61 (m, 1H), 7.23 (t, 3H, J = 7.6 Hz), 7.28 (d, 3H, J = 8.3 Hz), 7.47 (d, 3H, J = 7.3 Hz), 7.56 (m, 1H), 7.65 (dd, 3H, J = 7.3, 8.3 Hz); ^{13}C{^{1}H} NMR δ 13.8, 22.2, 30.3, 36.1, 56.7, 112.5, 122.8, 124.6, 124.9, 134.4, 135.2, 155.0, 159.9; IR (KBr) ν_{max} 2980, 2965, 1589, 1570, 1472, 1439, 1279, 1244, 1163, 1150–950 (BF_{4}^{-}), 785, 764, 754, 648, 565, 538, 521, 480, 425 cm^{-1}; MS (FAB) m/z 613 ([M – BF_{4}]^{+}). Anal. Calcd for C_{27}H_{32}BBiF_{4}O_{3}: C, 46.31; H, 4.61. Found: C, 45.64; H, 4.50.

((E)-3,3-Dimethylbut-1-enyl)tris(4-methylphenyl)bismuthonium tetrafluoroborate (3f): mp 149–150 °C; ^{1}H NMR δ 1.17 (s, 9H), 2.43 (s, 9H), 6.47 (d, 1H, J = 16 Hz), 7.42 (d, 6H, J = 7.9 Hz), 7.58 (d, 6H, J = 7.9 Hz), 7.82 (br-d, 1H, J = 16 Hz); ^{13}C{^{1}H} NMR δ 21.6, 28.6, 39.4, 121.6, 132.5, 133.8, 135.5, 142.5, 164.7; IR (KBr) ν_{max} 2963, 1489, 1450, 1393, 1367, 1313, 1256, 1209, 1190, 1150–950 (BF_{4}^{-}), 800, 521, 476 cm^{-1}; MS (FAB) m/z 565 ([M – BF_{4}]^{+}). Anal. Calcd for C_{27}H_{32}BBiF_{4} C, 49.71; H, 4.94. Found: C, 49.63; H, 4.86.

Tris(4-methylphenyl)((E)-oct-1-enyl)bismuthonium tetrafluoroborate (3g): sticky solid; ^{1}H NMR δ 0.87 (t, 3H, J = 6.7 Hz), 1.20–1.35 (m, 6H), 1.43–1.55 (m, 2H), 2.37–2.43 (m, 2H), 2.42 (s, 9H), 6.49 (dt, 1H, J = 15, 7.6 Hz), 7.42 (d, 6H, J = 7.9 Hz), 7.58 (d, 6H, J = 7.9 Hz), 7.80 (d, 1H, J = 15 Hz); IR (KBr) ν_{max} 2928, 2856, 1590, 1489, 1453, 1393, 1313, 1283, 1209, 1190, 1150–950 (BF_{4}^{-}), 797, 725 cm^{-1}; MS (FAB) m/z 593 ([M – BF_{4}]^{+}). Anal. Calcd for C_{26}H_{32}BBiF_{4} C, 51.19; H, 5.33. Found: C, 50.89; H, 5.37.

Tris(4-methoxyphenyl)((E)-oct-1-enyl)bismuthonium tetrafluoroborate (3h): sticky solid; ^{1}H
NMR δ 0.87 (t, 3H, J = 6.8 Hz), 1.22–1.38 (m, 6H), 1.45–1.54 (m, 2H), 2.41 (dt, 2H, J = 7.6, 6.8 Hz), 3.85 (s, 9H), 6.48 (m, 1H), 7.12 (d, 6H, J = 8.8 Hz), 7.62 (d, 6H, J = 8.8 Hz), 7.79 (d, 1H, J = 15 Hz); MS (FAB) m/z 641 ([M – BF₄⁺]). Anal. Calcd for C₂₉H₃₆BBiF₄O₃: C, 47.82; H, 4.98. Found: C, 47.55; H, 4.96.

((E)-Oct-1-enyl)tris(4-t-butylphenyl)bismuthonium tetrafluoroborate (3i): mp 105–106 °C; ¹H NMR δ 0.87 (t, 3H, J = 6.8 Hz), 1.22–1.38 (m, 6H), 1.45–1.54 (m, 2H), 2.41 (dt, 2H, J = 7.5, 7.0 Hz), 6.53 (m, 1H), 7.64 (br-s, 12H), 7.85 (br-d, 1H); IR (KBr) νmax 2963, 2868, 1589, 1565, 1472, 1439, 1393, 1364, 1279, 1244, 1163, 1150–950 (BF₄⁻), 816, 760, 752, 548, 521, 480, 426 cm⁻¹; MS (FAB) m/z 719 ([M – BF₄⁺]). Anal. Calcd for C₃₈H₅₄BBiF₄: C, 56.58; H, 6.75. Found: C, 55.92; H, 6.62.

Styryltris(4-methylphenyl)bismuthonium tetrafluoroborate (3j): mp 204–205 °C; ¹H NMR δ 2.44 (s, 9H), 7.25 (d, 1H, J = 15 Hz), 7.33–7.43 (m, 3H), 7.45 (d, 6H, J = 7.9 Hz), 7.56 (dd, 2H, J = 7.3, 1.9 Hz), 7.64 (d, 6H, J = 7.9 Hz), 8.63 (d, 1H, J = 15 Hz); ¹³C{¹H} NMR δ 21.6, 125.2, 127.8, 128.9, 130.5, 132.7, 133.5, 135.3, 135.5, 142.7, 151.2; IR (KBr) νmax 2963, 2868, 1487, 1450, 1391, 1312, 1283, 1209, 1188, 1163, 1150–950 (BF₄⁻), 816, 760, 752, 548, 521, 480, 426 cm⁻¹; MS (FAB) m/z 585 ([M – BF₄⁺]); Anal. Calcd for C₂₉H₂₈BBiF₄: C, 51.81; H, 4.20. Found: C, 51.72; H, 4.23.

Styryltris(2-methoxyphenyl)bismuthonium tetrafluoroborate (3k): mp 155–157 °C; ¹H NMR δ 3.84 (s, 9H), 7.23–7.32 (m, 6H), 7.33–7.46 (m, 4H), 7.53–7.60 (m, 5H), 7.66 (dd, 3H, J = 7.6, 1.2 Hz), 8.31 (br-s, 1H); IR (KBr) νmax 1589, 1568, 1472, 1435, 1298, 1277, 1244, 1163, 1150–950 (BF₄⁻), 787, 758, 735, 538, 521, 480, 428 cm⁻¹; MS (FAB) m/z 633 ([M – BF₄⁺]). Anal. Calcd for C₂₉H₂₈BBiF₄O₃: C, 48.36; H, 3.92. Found: C, 48.07; H, 3.85.

((E)-Prop-1-enyl)tris(4-methylphenyl)bismuthonium tetrafluoroborate (3l): sticky solid; ¹H NMR δ 2.11 (dd, 3H, J = 6.4, 1.2 Hz), 2.43 (s, 9H), 6.55 (br-s, 1H), 7.42 (d, 6H, J = 7.6 Hz), 7.58 (d, 6H, J = 7.6 Hz), 7.83 (br-s, 1H); ¹³C{¹H} NMR δ 21.4, 21.6, 124.9, 132.6, 133.1, 135.4, 142.7, 151.7; IR (KBr) νmax 3000, 2989, 1499, 1390, 1314, 1283, 1208, 1150–900 (BF₄⁻), 841, 793, 700, 635, 569, 519, 473 cm⁻¹; MS (FAB) m/z 523 ([M – BF₄⁺]). Anal. Calcd for C₂₉H₂₆BBiF₄: C, 47.24; H, 4.29. Found: C, 46.95; H, 4.20. The E/Z mixture 3l’ was prepared using an E/Z mixture of the corresponding boronic acid 2l’. The E/Z ratios of 3l’ and 2l’ were determined by ¹H NMR.

**Reaction of 3 with carbonyl compounds in the presence of TMG. General procedure:** To a mixture of 3 (0.50 mmol), carbonyl compound (0.50 mmol), and toluene (5 mL) was added TMG (65
µL, 0.50 mmol) at –50 °C. The resulting mixture was allowed to warm to room temperature with vigorous stirring. Water (5 mL) and Et₂O (5 mL) were added to the mixture, and the organic phase was washed with water (2 mL × 3), dried over MgSO₄, and concentrated under reduced pressure. Adding a suitable amount of MeOH (5–10 mL) to the residue caused precipitation of the bismuthane as a colorless solid. After removal of the bismuthane by filtration, the filtrate was concentrated in vacuo to give an oily residue, which was chromatographed on silica gel using hexane/ethyl acetate as eluents to afford β,γ-unsaturated carbonyl compounds.

**Ethyl 1-((E)-hex-1-enyl)-2-oxocyclohexanecarboxylate (5a):** oil; ¹H NMR δ 0.88 (t, 3H, J = 7.0 Hz), 1.25 (t, 3H, J = 7.0 Hz), 1.31 (m, 4H), 1.85–2.20 (m, 6H), 2.33 (m, 3H), 2.58 (dt, 1H, J = 13.2, 6.8 Hz), 4.15 (q, 2H, J = 7.0 Hz), 5.57 (dd, 1H, J = 15.6, 6.0 Hz), 5.64 (d, 1H, J = 15.6 Hz); IR (neat) νmax 2959, 2930, 1752, 1732, 1459, 1235, 1175, 1145, 1098, 1028, 974 cm⁻¹; MS (FAB) m/z 253 ([M + H]+). A good analytical data for 5a was not obtained, although the spectral data indicated its high state of purity.

**Ethyl 1-((E)-oct-1-enyl)-2-oxocyclohexanecarboxylate (5b):** oil; ¹H NMR δ 0.87 (t, 3H, J = 7.0 Hz), 1.20–1.40 (m, 11H), 1.61–1.84 (m, 4H), 1.94–2.10 (m, 3H), 2.30–2.68 (m, 3H), 4.13–4.26 (m, 2H), 5.52 (dt, 1H, J = 15.9, 6.8 Hz), 5.85 (d, 1H, J = 15.9 Hz); IR (neat) νmax 2930, 2856, 1717, 1453, 1366, 1337, 1238, 1204, 1132, 1088, 1063, 1022, 970, 910, 854 cm⁻¹; MS (FAB) m/z 281 ([M + H]+). Anal. Calcd for C₁₇H₂₈O₃: C, 72.82; H, 10.06. Found: C, 72.97; H, 10.10.

**Ethyl 1-((E)-styryl)-2-oxocyclohexanecarboxylate (5c):** oil; ¹H NMR δ 1.26 (t, 3H, J = 7.0 Hz), 1.65–1.90 (m, 4H), 2.00–2.06 (m, 1H), 2.45–2.57 (m, 2H), 2.72–2.77 (m, 1H), 4.18–4.30 (m, 2H), 6.45 (d, 1H, J = 16.5 Hz), 6.69 (d, 1H, J = 16.5 Hz), 7.23 (t, 1H, J = 7.0 Hz), 7.31 (t, 2H, J = 7.6 Hz), 7.40 (d, 2H, J = 7.0 Hz); MS (FAB) m/z 273 ([M + H]+).

**Ethyl 2-oxo-1-(4-methylphenyl)cyclohexanecarboxylate (6a):** ¹H NMR δ 1.24 (t, 3H, J = 7.0 Hz), 1.65–1.90 (m, 4H), 1.95–2.05 (m, 1H), 2.34 (s, 3H), 2.55–2.60 (m, 2H), 2.70–2.80 (m, 1H), 4.18–4.25 (m, 2H), 7.12 (d, 2H, J = 7.6 Hz), 7.17 (t, 2H, J = 7.6 Hz).

**Ethyl 2-oxo-1-phenylcyclohexanecarboxylate (6b):** ¹H NMR δ 1.25 (t, 3H, J = 7.0 Hz), 1.60–1.90 (m, 4H), 1.95–2.05 (m, 1H), 2.55–2.60 (m, 2H), 2.70–2.80 (m, 1H), 4.18–4.25 (m, 2H), 7.20–7.40 (m, 5H).

**((E)-Hex-1-enyl)bis(4-methylphenyl)bismuthane (8a):** ¹H NMR δ 0.89 (t, 3H, J = 7.1 Hz), 1.20–1.45

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(m, 4H), 2.16 (dt, 2H, J = 6.3, 6.8 Hz), 6.41 (dt, 1H, J = 17.3, 6.3 Hz), 7.18 (d, 4H, J = 7.8 Hz), 7.68 (d, 4H, J = 7.8 Hz), 7.73 (d, 1H, J = 17.3 Hz). Compound 8a was characterized only by $^1$H NMR.

$\text{(E)}$-Hex-1-enyl)diphenylbismuthane (8b): $^1$H NMR $\delta$ 0.90 (t, 3H, J = 7.3 Hz), 1.30–1.50 (m, 4H), 2.17 (dt, 2H, J = 6.3, 6.8 Hz), 6.43 (dt, 1H, J = 17.4, 6.3 Hz), 7.28 (t, 2H, J = 7.3 Hz), 7.36 (t, 4H, J = 7.3 Hz), 7.77 (d, 1H, J = 17.4 Hz), 7.81 (d, 4H, J = 7.3 Hz); IR (neat) $\nu_{\text{max}}$ 2957, 2926, 1570, 1541, 1474, 1429, 1380, 1330, 1215, 1170, 1057, 1015, 997, 978, 723, 695 cm$^{-1}$; MS (FAB) $m/z$ 369, 363, 292, 286, 209. Anal. Calcd for C$_{18}$H$_{21}$Bi: C, 48.44; H, 4.74. Found: C, 48.74; H, 4.58.

(2-Methylprop-1-enyl)diphenylbismuthane (8c): $^1$H NMR $\delta$ 1.86 (s, 3H), 2.01 (s, 3H), 7.27 (dt, 2H, J = 1.2, 7.3 Hz), 7.35 (t, 4H, J = 7.3 Hz), 7.58 (s, 1H), 7.80 (dd, 4H, J = 1.2, 7.8 Hz). Compound 8f was characterized only by $^1$H NMR.

Ethyl 1-((E)-hex-1-enyl)-2-oxocyclopentanecarboxylate (10): oil; $^1$H NMR $\delta$ 1.27 (t, 3H, J = 7.3 Hz), 1.94–2.12 (m, 2H), 2.26–2.50 (m, 3H), 2.72 (dt, 1H, J = 13.2, 6.8 Hz), 4.20 (q, 2H, J = 7.0 Hz), 6.41 (d, 1H, J = 16.3 Hz), 6.51 (d, 1H, J = 16.3 Hz), 7.24 (t, 1H, J = 7.3 Hz), 7.31 (t, 2H, J = 7.3 Hz), 7.39 (d, 2H, J = 7.3 Hz).

(3E)-Ethyl 2-acetyl-4-phenyl-2-styrylbut-3-enoate (12): mp 74–75 °C; $^1$H NMR $\delta$ 1.31 (t, 3H, J = 7.3 Hz), 2.25 (s, 3H), 4.31 (q, 2H, J = 7.3 Hz), 6.47 (d, 2H, J = 16.6 Hz), 6.82 (d, 2H, J = 16.6 Hz), 7.27 (t, 2H, J = 7.3 Hz), 7.33 (t, 4H, J = 7.3 Hz), 7.43 (d, 4H, J = 7.3 Hz); IR (KBr) $\nu_{\text{max}}$ 1740, 1709, 1578, 1499, 1472, 1448, 1352, 1281, 1235, 1180, 1153, 1057, 1015, 995, 858, 768, 747, 689, 598, 538, 494, 471 cm$^{-1}$. Anal. Calcd for C$_{22}$H$_{22}$O$_3$: C, 79.02; H, 6.63. Found: C, 78.79; H, 6.67.

(E)-Ethyl 2-acetyl-2-methyl-4-phenylbut-3-enoate (15): oil; $^1$H NMR $\delta$ 1.30 (t, 3H, J = 7.1 Hz), 1.59 (s, 3H), 2.21 (s, 3H), 4.25 (q, 2H, J = 7.1 Hz), 6.45 (d, 1H, J = 16.5 Hz), 7.26 (t, 1H, J = 7.6 Hz), 7.33 (t, 2H, J = 7.6 Hz), 7.41 (d, 2H, J = 7.3 Hz).

2-((E)-Hex-1-enyl)-2-phenylindan-1,3-dione (17a): oil; $^1$H NMR $\delta$ 0.86 (t, 3H, J = 7.0 Hz), 1.25-1.40 (m, 4H), 2.09 (m, 2H), 5.80 (s, 2H), 7.20-7.35 (m, 5H), 7.88 (m, 2H), 8.05 (m, 2H); IR (neat) $\nu_{\text{max}}$ 3026, 2957, 2928, 1744, 1710, 1597, 1497, 1466, 1447, 1350, 1331, 1256, 1161, 1042, 976, 872, 783, 756, 725, 704, 695 cm$^{-1}$; MS (FAB) $m/z$ 304 (M$^+$). Anal. Calcd for C$_{21}$H$_{20}$O$_2$: C, 82.86; H, 6.62. Found: C, 82.82; H, 6.76.

2-((E)-3,3-Dimethylbut-1-enyl)-2-phenylindan-1,3-dione (17b): mp 108–109 °C; $^1$H NMR $\delta$ 1.01 (s, 9H), 5.73 (d, 1H, J = 16.0 Hz), 5.87 (d, 1H, J = 16.0 Hz), 7.23–7.32 (m, 5H), 7.89 (m, 2H), 8.06 (m, 2H); IR (KBr) $\nu_{\text{max}}$ 2961, 1740, 1709, 1593, 1497, 1460, 1447, 1345, 1327, 1294, 1252, 1202, 1163, 1055, 1034, 978, 883, 787, 756, 725, 706, 694, 623, 550, 538, 494 cm$^{-1}$; MS (FAB) $m/z$ 304 (M$^+$).
Anal. Calcd for C_{21}H_{20}O_{2}: C, 82.86; H, 6.62. Found: C, 82.81; H, 6.55.

2-((E)-Oct-1-enyl)-2-phenylindan-1,3-dione (17c): oil; ^1H NMR δ 0.85 (t, 3H, J = 6.8 Hz), 2.03–2.10 (m, 2H), 7.23–7.33 (m, 5H), 7.89 (m, 2H); IR (neat) ν_{max} 2928, 2855, 1744, 1709, 1597, 1497, 1466, 1447, 1350, 1331, 1256, 1159, 1043, 974, 783, 756, 727, 704, 694 cm⁻¹; MS (FAB) m/z 333 ([M + H]⁺). Anal. Calcd for C_{23}H_{24}O_{2}: C, 83.10; H, 7.28. Found: C, 82.89; H, 7.24.

2-Phenyl-2-((E)-prop-1-enyl)indan-1,3-dione (17d): mp 99–101 °C; ^1H NMR δ 1.74 (d, 3H, J = 4.4 Hz), 5.81 (m, 2H), 7.23–7.35 (m, 5H), 7.87 (dd, 2H, J = 5.8, 3.0 Hz), 8.05 (dd, 2H, J = 5.8, 3.0 Hz); IR (KBr) ν_{max} 1746, 1703, 1597, 1499, 1449, 1352, 1331, 1250, 1048, 976, 868, 812, 781, 758, 731, 704, 613, 544, 494 cm⁻¹; MS (FAB) m/z 263 ([M + H]⁺). Anal. Calcd for C_{18}H_{14}O_{2}: C, 82.42; H, 5.38. Found: C, 82.30; H, 5.53.

2-Phenyl-2-styrylindan-1,3-dione (17e): mp 93–95 °C; ^1H NMR δ 6.54 (d, 1H, J = 16.2 Hz), 6.76 (d, 1H, J = 16.2 Hz), 7.20–7.40 (m, 10H), 7.91 (dd, 2H, J = 5.6, 3.0 Hz), 8.09 (dd, 2H, J = 5.6, 3.0 Hz); IR (KBr) ν_{max} 3027, 1744, 1707, 1595, 1497, 1447, 1350, 1331, 1254, 1159, 1080, 1046, 1030, 970, 895, 878, 824, 785, 747, 729, 695, 627, 596, 520 cm⁻¹; MS (FAB) m/z 324 (M⁺). Anal. Calcd for C_{23}H_{16}O_{2}: C, 85.16; H, 4.97. Found: C, 84.97; H, 4.83.

2-(2-Methylprop-1-enyl)-2-phenylindan-1,3-dione (17f): mp 91–92 °C; ^1H NMR δ 1.42 (d, 3H, J = 1.0 Hz), 1.80 (d, 3H, J = 1.0 Hz), 5.48 (s, 1H), 7.20–7.36 (m, 5H), 7.86 (m, 2H); IR (KBr) ν_{max} 1742, 1707, 1589, 1489, 1448, 1387, 1350, 1256, 1165, 876, 779, 756, 731, 702, 646, 538, 498 cm⁻¹; MS (FAB) m/z 277 ([M + H]⁺). Anal. Calcd for C_{19}H_{16}O_{2}: C, 82.58; H, 5.84. Found: C, 82.35; H, 5.85.

2-(2-Methylprop-1-enyl)-2-phenylindan-1,3-dione (17f): mp 91–92 °C; ^1H NMR δ 1.42 (d, 3H, J = 1.0 Hz), 1.80 (d, 3H, J = 1.0 Hz), 5.48 (s, 1H), 7.20–7.36 (m, 5H), 7.86 (m, 2H); IR (KBr) ν_{max} 1742, 1707, 1589, 1489, 1448, 1387, 1350, 1256, 1165, 876, 779, 756, 731, 702, 646, 538, 498 cm⁻¹; MS (FAB) m/z 277 ([M + H]⁺). Anal. Calcd for C_{19}H_{16}O_{2}: C, 82.58; H, 5.84. Found: C, 82.35; H, 5.85.

2-(2-Methylprop-1-enyl)-2-phenylindan-1,3-dione (17f): mp 91–92 °C; ^1H NMR δ 1.42 (d, 3H, J = 1.0 Hz), 1.80 (d, 3H, J = 1.0 Hz), 5.48 (s, 1H), 7.20–7.36 (m, 5H), 7.86 (m, 2H); IR (KBr) ν_{max} 1742, 1707, 1589, 1489, 1448, 1387, 1350, 1256, 1165, 876, 779, 756, 731, 702, 646, 538, 498 cm⁻¹; MS (FAB) m/z 277 ([M + H]⁺). Anal. Calcd for C_{19}H_{16}O_{2}: C, 82.58; H, 5.84. Found: C, 82.35; H, 5.85.

2-(4-Methylphenyl)-2-phenylindan-1,3-dione (18a): mp 103-105 °C; ^1H NMR δ 2.30 (s, 3H), 7.11 (d, 2H, J = 8.4 Hz), 7.16 (d, 2H, J = 8.4 Hz), 7.23–7.35 (m, 5H), 7.88 (dd, 2H, J = 5.5, 3.0 Hz), 8.08 (dd, 2H, J = 5.5, 3.0 Hz); IR (KBr) ν_{max} 1742, 1732, 1707, 1590, 1510, 1493, 1445, 1352, 1327, 1250, 10884, 850, 808, 795, 770, 752, 706, 691, 668, 610, 507 cm⁻¹. MS (FAB) m/z 312 (M⁺). Anal. Calcd for C_{22}H_{16}O_{2}: C, 84.99; H, 5.16. Found: C, 84.89; H, 5.26.

2,2-Diphenylindan-1,3-dione (18b): mp 126–128 °C (lit., 125 °C); ^1H NMR δ 7.25–7.35 (m, 10H), 7.87–7.94 (m, 2H), 8.07–8.13 (m, 2H).

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2,6-Dimethyl-6-styrylcyclohexa-2,4-dienone (20):^6^ oil; ¹H NMR δ 1.43 (s, 3H), 1.86 (s, 3H), 6.21 (d, 1H, J = 16.2 Hz), 6.24 (dd, 1H, J = 9.7, 6.1 Hz), 6.34 (d, 1H, J = 9.7 Hz), 6.38 (d, 1H, J = 16.2 Hz), 6.84 (dt, 1H, J = 6.1, 1.3 Hz), 7.21 (t, 1H, J = 7.2 Hz), 7.28 (t, 2H, J = 7.3 Hz), 7.33 (d, 2H, J = 7.3 Hz).

1,1-Bis((E)-3,3-dimethylbut-1-enyl)-1H-naphthalen-2-one (22): oil; ¹H NMR δ 0.98 (s, 18H), 5.29 (d, 2H, J = 15.9 Hz), 5.47 (d, 2H, J = 15.9 Hz), 6.08 (d, 1H, J = 10.0 Hz), 7.22 (d, 1H, J = 7.1 Hz), 7.27–7.42 (m, 4H); IR (neat) ν_max 2959, 2903, 2866, 1668, 1566, 1475, 1462, 1394, 1364, 1298, 1267, 1236, 1204, 1128, 974, 851, 827, 758 cm⁻¹; MS (FAB) m/z 309 ([M + H]⁺). Anal. Calcd for C₂₂H₂₈O: C, 85.66; H, 9.15. Found: C, 85.53; H, 9.13.

**Reaction of 3 with TMG.** To a CDCl₃ solution (ca. 0.5 mL) of 3a,f,j (0.02 mmol) was added TMG (0.02 mmol), and the resulting mixture was monitored at room temperature by ¹H NMR spectroscopy. In all cases examined, bismuthane 7a and acetylene 23 were formed in good yields. The products were identified by comparison with authentic specimens. 23a (from 3a): ¹H NMR δ 0.92 (t, 3H, J = 7.0 Hz), 1.35-1.55 (m, 4H), 1.93 (t, 1H, J = 2.6 Hz), 2.19 (dt, 2H, J = 2.6, 7.0 Hz). 23b (from 3f): ¹H NMR δ 1.24 (s, 1H), 2.08 (s, 9H). 23c (from 3j): ¹H NMR δ 3.07 (s, 1H), 7.2–7.5 (m, 5H).

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