

SUPPORTING INFORMATION

A Mild Synthesis of Vinyl Halides and *gem*-Dihalides Using Triphenyl Phosphite–Halogen-based Reagents.

Alberto Spaggiari, Daniele Vaccari, Paolo Davoli, Giovanni Torre, and Fabio Prati*

*Dipartimento di Chimica, Università di Modena e Reggio Emilia
via Campi 183, 41100 Modena, Italy*

prati.fabio@unimore.it

fax: +39.059.373543

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General.

Ketones **1–3** and **5–13** and aldehydes **15** and **16** were purchased from commercial sources and used without further purification. Ketone **4** was prepared from the corresponding 3-acetylphenylboronic under standard conditions.¹ Commercially available phenyl acetaldehyde **14** was distilled immediately prior to use. Dichloromethane and chloroform were dried according to standard methods and all glassware was oven-dried at 110 °C and assembled under argon atmosphere.

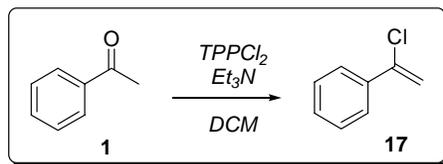
¹H and ¹³C NMR spectra were recorded in CDCl₃ solution on a 200 MHz instrument. Geometric configuration of compounds **18a-b** and **34** was assigned by comparison with literature data, whereas a NOESY experiment on a 400 MHz instrument was utilized to aid in the assignment of *E/Z* configuration of compounds **24a-b** and **40a-b**. Multiplicity is given as s = singlet, d = doublet, t = triplet q = quartet, quintet and m = multiplet, and chemical shifts (δ) are reported in ppm downfield from TMS as internal standard. Coupling constants (*J*) are given in Hz. GC analysis were performed using a DB capillary column (1.5 μ m, 30 \times 0.53 mm i.d.). MS determinations were performed in the EI mode (70 eV).

Gaschromatographic yields were calculated using the internal standard method, by spiking samples with a known amount of ketone **7** or **13**, so that the concentration of internal standard was comparable to that of the target product.

Chromatographic purification of compounds was performed on silica gel (60–200 μ m) using light petroleum/diethyl ether 9:1 as the eluant.

¹ Morandi, S.; Caselli, E.; Forni, A.; Bucciarelli, M.; Torre, G.; Prati, F. *Tetrahedron: Asymmetry* **2005**, *16*, 2918.

1-Chlorovinylbenzene (**17**)²



Acetophenone **1** (770 mg, 6.4 mmol) was added to a freshly prepared solution of TPPCl₂ in anhydrous dichloromethane at -21 °C. The mixture was stirred for 18 h, allowing the cold bath to reach rt, and finally refluxed for 2 h. Column chromatography of crude residue afforded vinyl chloride **17** as a pale yellow oil (772 mg, 87%).

¹H NMR (200 MHz): δ = 5.56 (1 H, d, J = 1.7 Hz, CH₂), 5.80 (1 H, d, J = 1.7 Hz, CH₂), 7.43–7.35 (3 H, m, H-arom), 7.72–7.62 (2 H, m, H-arom).

¹³C NMR (50 MHz): δ = 112.7, 126.5, 128.4, 129.2, 131.5, 140.0.

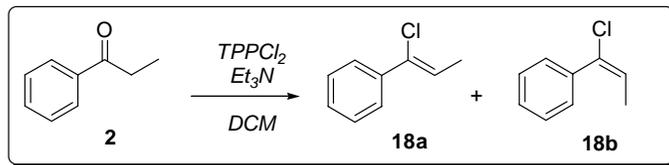
MS (ED): m/z (%) = 138–140 (M⁺, 40), 103 (100), 77 (80).

Anal. Calcd. for C₈H₇Cl: C, 69.33; H, 5.09.

Found: C, 69.39; H, 5.13.

² Kagan, J.; Arora, S. K.; Bryzgis, M.; Dhawan, S. N.; Singh, S. P.; Tow, L. *J. Org. Chem.* **1983**, *48*, 703.

(Z)-1-Chloropropenylbenzene (18a) and (E)-1-chloropropenylbenzene (18b)³



Propiophenone **2** (859 mg, 6.4 mmol) was added to a freshly prepared solution of TPPCl₂ in anhydrous dichloromethane at -21 °C. The mixture was stirred for 18 h, allowing the cold bath to reach rt, and finally refluxed for 2 h. Column chromatography of the crude residue afforded an inseparable mixture of vinyl chlorides **18a** and **18b** in a 95:5 ratio (by ¹H NMR analysis), as a pale yellow oil (757 mg, 78%). The *E/Z* configuration was assigned by comparison with literature data.⁴

¹H NMR (200 MHz): δ = 1.80 (3 H, d, J = 7.3 Hz, **18b** H-3), 2.01 (3 H, d, J = 6.7 Hz, **18a** H-3), 6.12 (1 H, q, J = 7.3 Hz, **18b** H-2), 6.26 (1 H, q, J = 6.7 Hz, **18a** H-2), 7.35–7.82 (5 H, m, **18b** H-arom; 5 H, m, **18a** H-arom).

¹³C NMR (50 MHz): δ = 10.4, 15.1, 122.4, 126.2, 126.3, 128.1, 128.2, 128.3, 128.9, 131.1, 133.8, 138.5, 142.8.

MS (EI): **18a** m/z (%) = 152–154 (M⁺, 61), 117 (100), 91 (13).

18b m/z (%) = 152–154 (M⁺, 59), 117 (100), 91 (10).

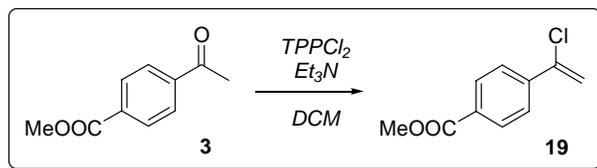
Anal. Calcd. for C₉H₉Cl: C, 70.83; H, 5.94.

Found: C, 70.59; H, 6.01.

³ Fahey, R.C.; Schubert, C. *J. Am. Chem. Soc.* **1965**, *87*, 5172.

⁴ Kropp, P.J.; Crawford, S.D. *J. Org. Chem.* **1994**, *59*, 3102.

Methyl 4-(1-chlorovinyl)benzoate (**19**)



Methyl 4-acetylbenzoate **3** (1.14 g, 6.4 mmol) was added to a freshly prepared solution of TPPCl₂ in anhyd dichloromethane at -21 °C. The mixture was stirred for 18 h, allowing the cold bath to reach rt, and finally refluxed for 2 h. Column chromatography of crude residue afforded **19** as a yellowish deliquescent waxy solid (mp 38.1–39.9 °C; 1.08 mg, 86%).

¹H NMR (200 MHz): δ = 3.91 (3 H, s, Me), 5.61 (1 H, d, J = 1.9 Hz, =CH₂), 5.86 (1 H, d, J = 1.9 Hz, =CH₂), 7.65–7.70 (2 H, m, H-arom), 7.99–8.03 (2 H, m, H-arom).

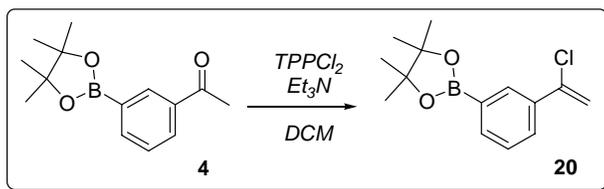
¹³C NMR (50 MHz): δ = 52.2, 114.7, 126.3, 129.6, 130.5, 139.0, 140.9, 166.4.

MS (EI): m/z (%) = 196–198 (M⁺, 53), 165 (100), 137 (20), 102 (24).

Anal. Calcd. for C₁₀H₉ClO₂: C, 61.08; H, 6.61.

Found: C, 61.32; H, 6.50.

Pinacol 3-(1-chlorovinyl)phenylboronate(**20**)



Pinacol 3-acetylphenylboronate **4** (1.17 g, 6.4 mmol) was added to a freshly prepared solution of TPPCl₂ in anhyd dichloromethane at -21 °C. The mixture was stirred for 18 h, allowing the cold bath to reach rt, and finally refluxed for 2 h. Column chromatography of crude residue afforded the title compound **20** as a colorless oil (957 mg, 76%).

¹H NMR (200 MHz): δ = 1.38 (12 H, s, Me), 5.55 (1 H, d, J = 1.6 Hz, =CH₂), 5.83 (1 H, d, J = 1.6 Hz, =CH₂), 7.41–8.10 (4 H, m, H-arom).

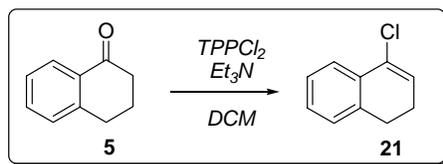
¹³C NMR (50 MHz): δ = 24.9, 84.0, 112.9, 127.8, 129.3, 132.5, 135.5, 136.4, 140.0 (C–B not seen).

MS (EI): m/z (%) = 264–266 (M⁺, 53), 249 (49), 178 (100), 165 (59).

Anal. Calcd. for C₁₄H₁₈BClO₂: C, 63.56; H, 6.86.

Found: C, 62.39; H, 6.78.

1-Chloro-3,4-dihydronaphthalene (**21**)⁵



α -Tetralone **5** (934 mg, 6.4 mmol) was reacted with a freshly prepared solution of TPPCl₂ in anhydrous dichloromethane at $-20\text{ }^{\circ}\text{C}$. The mixture was stirred for 18 h, allowing the cold bath to reach rt and then refluxed for 2 h. Column chromatography of crude residue afforded the title product (**21**) as a yellowish oil (955 mg, 91%).

¹H NMR (200 MHz): δ = 2.41 (1 H, ddd, J = 0.6, 8.2, 4.8 Hz, H-3), 2.44 (1 H, dd, J = 8.2, 4.8, H-3), 2.87 (2 H, t, J = 8.2 Hz, H-4), 6.21 (1 H, t, J = 4.8 Hz, H-2), 7.33–7.13 (3 H, m, H-5, H-6 and H-7), 7.64–7.59 (1 H, m, H-8).

¹³C NMR (50 MHz): δ = 24.2, 27.6, 124.1, 126.0, 126.7, 127.3, 128.3, 130.6, 132.4, 136.4.

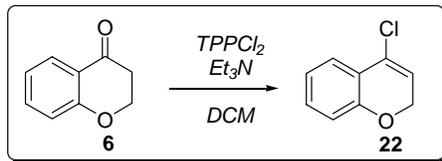
MS (ED): m/z (%) = 164–166 (M^+ , 46), 129 (100).

Anal. Calcd. for C₁₀H₉Cl: C, 72.96; H, 5.51.

Found: C, 73.13; H, 5.45.

⁵ Fleming, I.; Pearce, A. *J. Chem. Soc., Perkin Trans. 1* **1980**, 2485.

4-Chloro-2*H*-chromene (**22**)⁶



4-Chromanone **5** (945 mg, 6.4 mmol) was reacted with a freshly prepared solution of TPPCl₂ in anhyd dichloromethane at -20 °C. The mixture was stirred for 18 h, allowing the cold bath to reach rt and then refluxed for 2 h. Column chromatography of the crude residue afforded the title product **22** as a yellowish oil (872 mg, 83%) that quickly darkened upon storage.

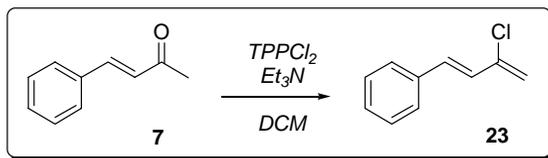
¹H NMR (200 MHz): δ = 4.86 (2 H, d, J = 3.9 Hz, H-2), 5.91 (1 H, t, J = 3.9 Hz, H-3), 6.82–6.87 (1 H, dd, J = 1.1, 7.7 Hz, H-8), 6.94–7.03 (1 H, dt, J = 1.1, 7.7 Hz, H-6), 7.18–7.27 (1 H, dt, J = 1.7, 7.7 Hz, H-7), 7.44–7.49 (1 H, J = 1.7, 7.7 Hz, H-5).

¹³C NMR (50 MHz): δ = 66.1, 115.8, 118.9, 121.2, 121.6, 124.6, 128.1, 130.6, 154.5.

MS (EI): m/z (%) = 165–167 ($M^+ - 1$, 100), 131 (89).

⁶ Ariamala, G.; Balasubramanian, K.K. *Tetrahedron* **1989**, *45*, 309.

3-Chloro-1-phenylbutadiene (**23**)⁷



Cinnamyl-methyl ketone **7** (943 mg, 6.4 mmol) was added to a freshly prepared solution of TPPCl₂ in anhyd dichloromethane at -20 °C. The mixture was stirred for 18 h, allowing the cold bath to reach rt. After refluxing for 2 h GC analysis showed complete conversion and 96% yield (calculated using **13** as internal standard). For analytical purposes, a pure sample was obtained by column chromatography, affording **23** as a lightly-brown sticky oil that quickly blackened in the flask upon storage.

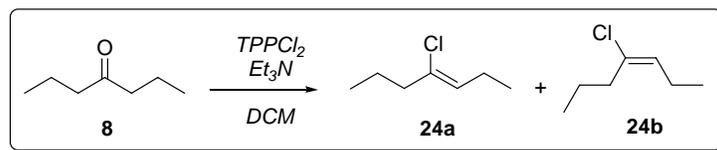
¹H NMR (200 MHz): δ = 5.50 (2 H, dd, J = 3.2, 0.5 Hz, H-4), 6.85 (1 H, dd, J = 15.4, 0.5 Hz, H-2), 7.05 (1 H, d, J = 15.4 Hz, H-1), 7.61–7.27 (5 H, m, H-arom).

¹³C NMR (50 MHz): δ = 116.0, 125.5, 127.1, 128.5, 128.8, 132.1, 133.5, 150.8.

MS (EI): m/z (%) = 164–166 (M⁺, 17), 129 (100), 102 (9), 77 (8).

⁷ Ma, S.; Wang, G. *Tetrahedron Lett.* **2002**, 43, 5723.

(Z)-4-Chlorohept-3-ene (24a) and (E)-4-chlorohept-3-ene (24b)⁸



4-Heptanone **8** (738 mg, 6.4 mmol) was added to a freshly prepared solution of TPPCl₂ in anhydrous dichloromethane at -24 °C. The mixture was stirred for 18 h, allowing the cold bath to reach rt. The mixture was then refluxed for 2 h. GC analysis showed complete conversion and 94% yield of **24a** and **24b** in a 60:40 ratio (calculated with GC analysis using **13** as the internal standard). For analytical purposes the crude residue was purified by column chromatography to afford an inseparable mixture of **24a** and **24b** as a colorless oil. For the configurational assignment, a NOESY experiment was utilized.

¹H NMR (400 MHz): δ = 0.94 (3 H, t, J = 7.5 Hz, **24a** H-7), 0.96 (3 H, t, J = 7.8 Hz, **24b** H-7), 1.01–1.05 (m, 3 H, **24a** H-1 and 3 H, **24b** H-1), 1.58–1.77 (m, 2 H, **24a** H-6 and 2 H, **24b** H-6), 2.10 (2 H, quintet, J = 7.6 Hz, **24b** H-2), 2.19–2.24 (2 H, m, **24a** H-2), 2.31 (2 H, t, J = 7.3 Hz, **24a** H-5), 2.36 (2 H, t, J = 7.2 Hz, **24b** H-5), 5.48 (1 H, t, J = 6.9 Hz, **24a** H-3), 5.65 (1 H, t, J = 7.7 Hz, **24b** H-3).

¹³C NMR (100 MHz): δ = 13.0, 13.1, 13.2, 14.1, 20.5, 20.6, 21.9, 22.0, 35.4, 41.4, 127.1, 129.7, 133.4, 133.9.

MS (EI): **24a** m/z (%) = 132–134 (M⁺, 30), 97 (49), 55 (100).

24b m/z (%) = 132–134 (M⁺, 43), 97 (50), 55 (100).

Elemental analysis (as a mixture of **24a** and **24b**): Anal. Calcd. for C₇H₁₃Cl: C, 63.39; H, 9.88.

Found: C, 63.13; H, 9.78.

When the reaction was performed in the absence of triethylamine, analysis of the crude reaction mixture after 4 hrs by ¹H and ¹³C NMR spectroscopy revealed the presence of a conspicuous amount of an additional compound, along with the expected reaction product 4-chlorohept-3-ene (as

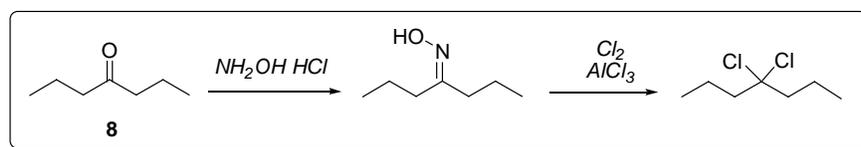
⁸ Georgoulis, C.; Meyet, J.; Smadja, W. *J. Organomet. Chem.* **1976**, *121*, 271.

a mixture of *E/Z* stereoisomers). By means of HSQC and HMBC experiments, δ_{H} and δ_{C} values for the additional product were assigned unambiguously and found to match perfectly with those of 4,4-dichloroheptane prepared independently (see below) from 4-heptanone oxime by treatment with chlorine.⁹

¹H NMR (400 MHz): δ = 1.01–1.05 (6 H, m, H-1 and H-7), 1.67–1.77 (4 H, m, H-2 and H-6), 2.21–2.26 (4 H, m, H-3 and H-5).

¹³C NMR (100 MHz): δ = 13.6, 18.7, 50.1, 95.4 (C-4).¹⁰

4,4-Dichloroheptane⁹



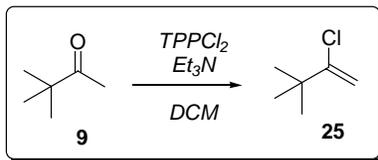
4-Heptanone **8** was converted into the corresponding oxime by a standard procedure.¹¹ 4-Heptanone oxime (520 mg, 4.0 mmol) was then dissolved in anhyd dichloromethane (20 mL) and AlCl_3 (256 mg, 1.9 mmol) was added. The suspension was cooled with an ice bath and chlorine was bubbled under magnetic stirring. The solution turned brilliant blue, and bubbling was continued until the color vanished. The reaction mixture was then diluted with dichloromethane (20 mL), poured over ice and water (30 mL), and the organic layer was washed with 5% hydrochloric acid, 20% sodium hydrogen carbonate solution, brine and dried over magnesium sulfate. Evaporation of the solvent under reduced pressure afforded 4,4-dichloroheptane as a colorless liquid (582 mg, 86%).

⁹ Tordeux, M.; Boumizane, K.; Wakselman, C. *J. Org. Chem.* **1993**, *58*, 1939.

¹⁰ The δ_{C} value for quaternary carbon atom (C-4) was wrongly assigned at 90.1 ppm in the original publication.⁹

¹¹ Furniss, B. S.; Hannaford, A. J.; Smith, P. W. G.; Tatchell, A. R. *Vogel's Textbook of Practical Organic Chemistry*, 5th ed.; Longman: Harlow, 1989.

2-Chloro-3,3-dimethylbutene (**25**)¹²



Pinacolone **9** (640 mg, 6.4 mmol) was added to a freshly prepared solution of TPPCl₂ in anhyd dichloromethane at $-22\text{ }^{\circ}\text{C}$. The mixture was left to stir over a 18 h period, allowing the cold bath to reach rt. The mixture was then refluxed for 2 h, until GC analysis showed 100% conversion and 96% yield (using ketone **7** as the internal standard). For analytical purposes, the reaction mixture was gently concentrated at normal pressure and the residue distilled to afford pure **25** as mint-smelling colorless oil (bp $85\text{--}88\text{ }^{\circ}\text{C}$, 760 mmHg).

¹H NMR (200 MHz): $\delta = 1.15$ (9 H, s, *tert*-Bu), 5.07 (1 H, d, $J = 1.6$ Hz, H-1), 5.11 (1 H, d, $J = 1.6$ Hz, H-1).

¹³C NMR (50 MHz): $\delta = 28.5, 39.1, 109.1, 116.1$.

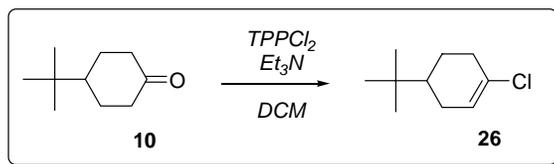
MS (EI): m/z (%) = 118–120 (M^+ , 18), 103–105 (46), 83 (100), 57 (22).

Anal. Calcd. for C₆H₁₁Cl: C, 60.76; H, 9.35.

Found: C, 60.86; H, 9.42.

¹² Binnerwitz, R. J.; Klingerberger, H. W.; Welter, R. P. P. *Chem. Ber.* **1983**, *116*, 1271.

4-*tert*-Butyl-1-chlorocyclohexene (**26**)¹³



4-*tert*-Butylcyclohexanone **10** (987 mg, 6.4 mmol) was added to a freshly prepared solution of TPPCl₂ in anhyd dichloromethane at -21 °C. The mixture was stirred for 18 h, allowing the cold bath to reach rt. The mixture was then refluxed for 2 h and the crude residue was purified by column chromatography to afford **26** as apple-scented waxy colorless crystals (885 mg, 80%).

¹H NMR (200 MHz): δ = 0.89 (9 H, s, *tert*-Bu), 1.47–1.38 (2 H, m, H-5), 1.95–1.83 (2 H, m, H-3), 2.12–2.07 (1 H, m, H-4), 2.38–2.32 (2 H, m, H-6), 5.79 (1 H, m, H-2).

¹³C NMR (50 MHz): δ = 25.1, 27.2, 27.6, 32.0, 34.0, 43.1, 124.5, 131.6.

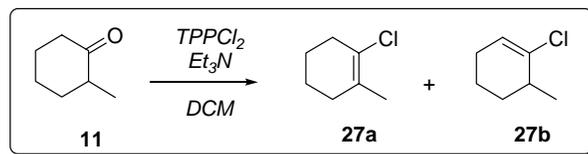
MS (EI): m/z (%) = 172–174 (M⁺, 18), 116–118 (10), 79 (25), 57 (100).

Anal. Calcd. for C₁₀H₁₇Cl: C, 69.55; H, 9.92.

Found: C, 69.40; H, 9.76.

¹³ Ochiai, M.; Sumi, K.; Takaoka, Y.; Kunishima, M.; Nagao, Y.; Shiro, M.; Fujita, E. *Tetrahedron* **1988**, *44*, 4112.

1-Chloro-2-methylcyclohexene (**27a**) and 1-chloro-6-methylcyclohexene (**27b**)¹⁴



2-Methyl-cyclohexanone **6** (717 mg, 6.4 mmol) was added to a freshly prepared solution of TPPCl₂ in anhyd dichloromethane at -24 °C. The mixture was stirred for 18 h, allowing the cold bath to reach rt. The mixture was then refluxed for 2 h, until GC analysis showed complete conversion. Distillation of the solvent at normal pressure and purification of the crude residue by column chromatography gave an inseparable mixture of **27a** and **27b** in a 55:45 ratio (determined by ¹H NMR) as an apple-smelling colorless waxy solid (677 mg, 81% overall yield).

¹H NMR (200 MHz): δ = 1.17 (3 H, d, J = 5.8 Hz, **27b** Me-6), 1.76–1.48 (6 H, m, **27b** H-3, H-4 and H-5), 1.74 (3 H, m, **27a** Me-2), 2.12–2.02 (m, 4 H, **27a** H-4, H-5 and 1 H, **27b** H-6), 2.32 (4 H, m, **27a** H-3, H-6), 5.74 (1 H, dt, J = 1.4, 4.1 Hz, **27b** H-2).

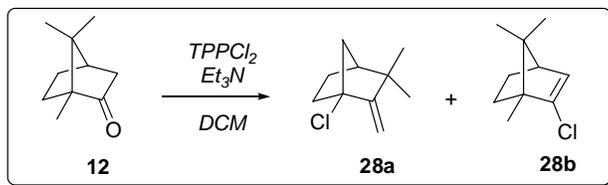
¹³C NMR (50 MHz): δ = 19.0, 19.4, 20.0, 22.6, 24.2, 26.5, 31.7, 32.1, 33.6, 35.6, 124.7, 131.8, 133.0, 141.8.

MS (EI): **27a** m/z (%) = 130–132 (M⁺, 30), 95 (100), 79 (45);
27b m/z (%) = 130–132 (M⁺, 27), 95 (100), 79 (41).

Elemental analysis (as a mixture of **27a** and **27b**): Anal. Calcd. for C₇H₁₁Cl: C, 64.37; H, 8.49.
Found: C, 64.42; H, 8.59.

¹⁴ Bottini, A. T.; Carson, F. P.; Fitzgerald, R.; Frost, K. A. *Tetrahedron* **1972**, 28, 4883.

1-Chloro-3,3-dimethyl-2-methylene-bicyclo[2.2.1]heptane (28a) and 2-chloro-1,7,7-trimethyl-bicyclo[2.2.1]hept-2-ene (28b)¹⁵



(+)-Camphor **12** (974 mg, 6.4 mmol) was added to a fresh solution of TPPCl₂ in anhydrous dichloromethane at -21 °C. The mixture was stirred for 18 h, allowing the cold bath to reach room temperature and finally refluxed for 2 h. Column chromatography of crude residue afforded an inseparable mixture of **28a** and **28b** in a 65:35 ratio (determined by GC analysis) as a mint-smelling colorless waxy solid (898 mg, 82%).

¹H NMR (200 MHz): δ = 0.81 (3 H, s, **28b** Me-7), 0.88 (3 H, s, **28b** Me-7), 1.02 (3 H, s, **28b** Me-1), 1.11 (3 H, s, **28a** Me-3), 1.13 (3 H, s, **28a** Me-3), 2.12–1.55 (m, 4 H, **28a** H-5, H-6 and 4 H, **28b** H-5, H-6), 2.34 (1 H, t, J = 3.5 Hz, **28b** H-4), 5.14 (1 H, s, **28a** =CH₂), 4.77 (1 H, s, **28a** =CH₂), 5.83 (1 H, d, J = 3.5 Hz, **28b** H-3).

¹³C NMR (50 MHz): δ = 11.0, 19.3, 20.0, 25.6, 25.7, 26.3, 29.8, 30.9, 37.9, 43.1, 44.9, 46.0, 51.7, 56.5, 101.3, 128.7, 143.1, 163.0.

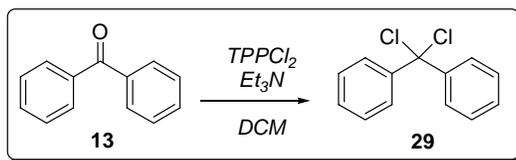
MS (ED): **28a** m/z (%) = 170–172 (M⁺, 17), 127 (100), 91 (60);
28b m/z (%) = 170–172 (M⁺, 39), 155 (67), 127 (67), 91 (100).

Elemental analysis (as a mixture of **28a** and **28b**): Anal. Calcd. for C₁₀H₁₅Cl: C, 70.37; H, 8.86.

Found: C, 70.25; H, 8.69.

¹⁵ Paukstelis, J. V.; Macharia, B. W. *J. Org. Chem.* **1973**, *33*, 646.

1,1-Dichloro-1,1-diphenylmethane (**29**)¹⁶



Benzophenone **13** (1.17 g, 6.4 mmol) was treated with a freshly prepared solution of TPPCl₂ in anhyd dichloromethane at -20 °C and stirred for 5 h. The reaction was then refluxed for 16 h. The solvent was removed under reduced pressure and dry ether (25 mL) was slowly added to the crude residue to precipitate ammonium salts, which were separated by centrifugation. The solvent was evaporated and the crude oily residue was distilled under reduced pressure (bp 109–113 °C, 0.5 mmHg) to yield **29** as a colorless and odorless oil (1.43 g, 94%).

¹H NMR (200 MHz): δ = 7.87–7.35 (10 H, m, H-arom).

¹³C NMR (50 MHz): δ = 92.0, 127.5, 128.1, 129.1, 144.1.

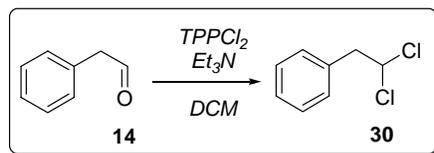
MS (EI): m/z (%) = 236–238 (M⁺, 1), 201–203 (100), 165 (85).

Anal. Calcd. for C₁₃H₁₀Cl₂ : C, 65.85; H, 4.25.

Found: C, 65.77; H, 4.16.

¹⁶ Newman, M. S.; Sujeeth, P. K. *J. Org. Chem.*, **1978**, 22, 4367.

(2,2-Dichloroethyl)-benzene (30)¹⁷



Freshly distilled phenyl acetaldehyde **14** (770 mg, 6.4 mmol) was added to a solution of TPPCl₂ in anhyd dichloromethane at -21 °C. The mixture was stirred for 18 h, allowing the cold bath to reach rt, and finally refluxed for 2 h. Column chromatography of crude residue afforded **30** as a stinky colorless oil (843 mg, 80%).

¹H NMR (200 MHz): δ = 3.62 (2 H, d, J = 6.4 Hz, H-1), 5.99 (1 H, t, J = 6.4 Hz, H-2), 7.60–7.38 (5 H, m, H-arom).

¹³C NMR (50 MHz): δ = 49.8, 73.2, 127.8, 128.7, 129.9, 135.3.

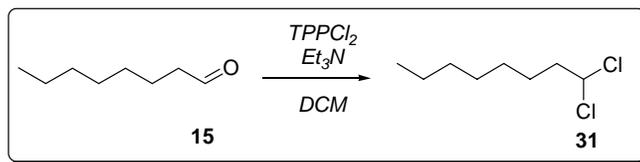
MS (EI): m/z (%) = 174–176 (M^+ , 11), 139–141 (3), 91 (100), 77 (10).

Anal. Calcd. for C₈H₈Cl₂: C, 54.89; H, 4.61.

Found: C, 54.99; H, 4.73.

¹⁷ Martinez, A. G.; Fernandez, A. H.; Alvarez, M. R.; Fraile, A. G.; Calderon, J. B.; Borcina, J. O. *Synthesis* **1986**, 1076.

1,1-Dichlorooctane (**31**)¹⁸



Octanal **15** (821 mg, 6.4 mmol) was added to a freshly prepared solution of TPPCl₂ in anhydrous dichloromethane at $-20\text{ }^{\circ}\text{C}$. The mixture was stirred for 18 h, allowing to reach rt, and finally refluxed for 2 h. Column chromatography of the crude residue afforded **31** as a colorless oil (869 mg, 75%).

¹H NMR (200 MHz): δ = 0.91 (3 H, t, J = 5.6 Hz, H-8), 1.59–1.26 (10 H, m, H-3, H-4, H-5, H-6 and H-7), 2.20 (2 H, m, H-2), 5.93 (1 H, t, J = 6.0 Hz, H-1).

¹³C NMR (50 MHz): δ = 14.0, 22.6, 26.0, 28.5, 29.0, 31.6, 43.7, 73.6.

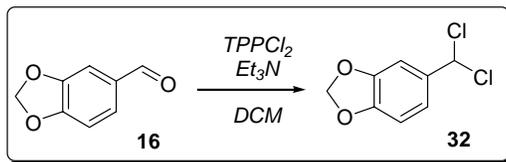
MS (ED): m/z (%) = 182–184 (M^+ , 100).

Anal. Calcd. for C₈H₁₆Cl₂: C, 52.47; H, 8.81.

Found: C, 52.36; H, 8.70.

¹⁸ Villieras, J.; Tarhouni, R.; Kirschleger, R.; Ramboud, M. *Bull. Soc. Chim. Fr.* **1985**, 5, 825.

Piperonyl dichloride (**32**)¹⁹



Piperonal **16** (1.00 g, 6.7 mmol) was added to a freshly prepared solution of TPPCl_2 in anhydrous dichloromethane at $-22\text{ }^\circ\text{C}$. The mixture was stirred for 18 h, allowing to reach rt. The mixture was then refluxed for 2 h. The solvent was then removed and the residue distilled under reduced pressure (bp $85\text{--}87\text{ }^\circ\text{C}$, 0.3 mmHg), yielding **32** (1.22 g, 93%) as an almond-smelling waxy solid that decomposed on standing.

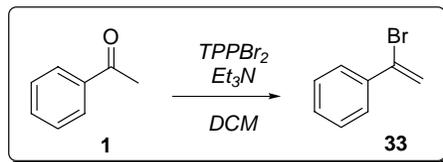
^1H NMR (200 MHz): $\delta = 6.01$ (2 H, s, O- CH_2 -O), 6.65 (1 H, s, $\text{Cl}_2\text{C-H}$), 6.77 (1 H, d, $J = 8.0$ Hz, H-5), 6.97 (1 H, ddd, $J = 0.3, 8.0, 1.9$ Hz, H-6), 7.15 (1 H, d, $J = 1.9$ Hz, H-2).

^{13}C NMR (50 MHz): $\delta = 71.8, 101.7, 106.8, 107.7, 119.9, 134.4, 148.2, 148.9$.

MS (EI): m/z (%) = 204–206 (M^+ , 11), 169–171 (100), 139 (8).

¹⁹Harada, K.; Masashi, F.; Furuya, T.; Kuroda, N. U.S. Patent 5,696,301, 1997.

1-Bromovinylbenzene (**33**)²⁰



Acetophenone **1** (773 mg, 6.4 mmol) was added to a freshly prepared solution of TPPBr₂ in anhydrous dichloromethane at $-60\text{ }^{\circ}\text{C}$. The mixture was stirred for 18 h, allowing to reach rt, and finally refluxed for 2 h. Column chromatography of crude residue yielded vinyl bromide **33** as a brown oil (1.00 g, 86%).

¹H NMR (200 MHz): $\delta = 5.86$ (1 H, d, $J = 2.0$ Hz, H-2), 6.19 (1 H, d, $J = 2.0$ Hz, H-2), $7.45\text{--}7.38$ (3 H, m, H-*meta* and H-*para*), $7.89\text{--}7.84$ (2 H, m, H-*ortho*).

¹³C NMR (50 MHz): $\delta = 117.7, 127.4, 128.4, 129.2, 131.1, 138.6$.

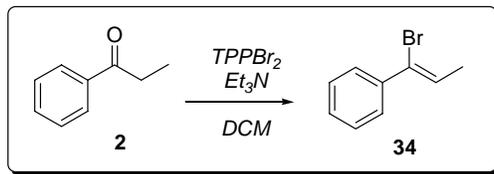
MS (EI): m/z (%) = 182–184 (M^+ , 12), 103 (100), 77 (30).

Anal. Calcd. for C₈H₇Br: C, 52.49; H, 3.85.

Found: C, 52.60; H, 3.98.

²⁰ Soderquist, J. A.; Hassener, A. *J. Org. Chem.* **1983**, *48*, 1801.

(Z)-1-Bromopropenylbenzene (34)²¹



Propiophenone **2** (858 mg, 6.4 mmol) was added to a freshly prepared solution of TPPBr₂ in anhyd dichloromethane at -60 °C. The mixture was stirred for 18 h, allowing the cold bath to reach rt, and finally refluxed for 2 h. Column chromatography of crude residue afforded vinyl bromide **34** as a pale yellow oil (958 mg, 76%); the *Z* configuration was assigned by comparison with literature data.⁴ The *E*-isomer was detected only in traces by GC-MS analysis.

¹H NMR (200 MHz): δ = 1.96 (3 H, d, J = 6.6 Hz, H-3), 6.29 (1 H, q, J = 6.6 Hz, H-2), 7.27–7.56 (5 H, m, H-arom).

¹³C NMR (50 MHz): δ = 16.3, 123.9, 126.2, 128.3, 128.4, 134.7, 140.5.

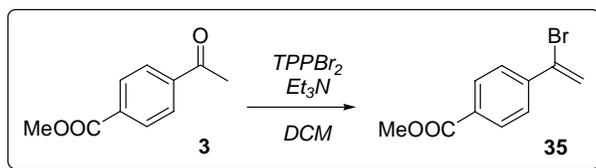
MS (EI): m/z (%) = 196–198 (M⁺, 55), 117 (100).

Anal. Calcd. for C₉H₉Br: C, 54.85; H, 4.60.

Found: C, 55.04; H, 4.71.

²¹ Napolitano, E.; Fiaschi, R.; Mastrorilli, E. *Synthesis* **1986**, 122.

Methyl 4-(1-bromovinyl)benzoate (**35**)



Methyl 4-acetylbenzoate **3** (1.14 g, 6.4 mmol) was added to a freshly prepared solution of TPPBr₂ in anhyd dichloromethane at $-60\text{ }^{\circ}\text{C}$. The mixture was stirred for 18 h, allowing the cold bath to reach rt, and finally refluxed for 2 h. Column chromatography of crude residue afforded **35** as a lightly yellow waxy solid (mp $70.3\text{--}72.2\text{ }^{\circ}\text{C}$; 940 mg, 61%).

¹H NMR (200 MHz): δ = 3.92 (3 H, s, Me), 5.87 (1 H, d, J = 2.2 Hz, =CH₂), 6.21 (1 H, d, J = 2.2 Hz, =CH₂), 7.62–7.68 (2 H, m, H-arom), 7.99–8.03 (2 H, m, H-arom).

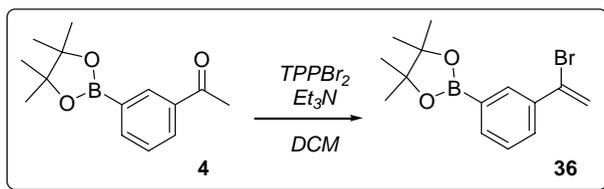
¹³C NMR (50 MHz): δ = 52.3, 119.6, 127.3, 129.6, 129.7, 130.5, 142.5, 166.4.

MS (EI): m/z (%) = 240–241 (M^+ , 15), 209 (10), 161 (100).

Anal. Calcd. for C₁₀H₉BrO₂: C, 49.82; H, 3.76.

Found: C, 50.03; H, 3.82.

Pinacol 3-(1-bromovinyl)boronate (**36**)



Pinacol 3-acetylphenylboronate **4** (986 g, 4.0 mmol) was added to a freshly prepared solution of TPPBr₂ in anhyd dichloromethane at -60 °C. The mixture was stirred for 18 h, allowing the cold bath to reach rt, and finally refluxed for 2 h. Column chromatography of crude residue afforded **36** as a colorless oil (803 mg, 65%).

¹H NMR (200 MHz): δ = 1.37 (12 H, s, Me), 5.80 (1 H, d, J = 2.0 Hz, =CH₂), 6.16 (1 H, d, J = 2.0 Hz, =CH₂), 7.37–8.06 (4 H, m, H-arom).

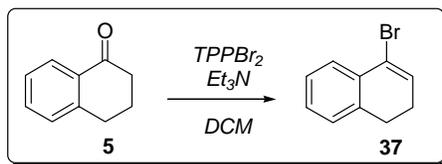
¹³C NMR (50 MHz): δ = 24.9, 84.0, 117.8, 127.7, 130.3, 131.0, 133.2, 135.5, 138.0 (C–B not seen).

MS (EI): m/z (%) = 308–310 (M⁺, 25), 293–295 (17), 229 (75), 222–224 (55), 129 (100).

Anal. Calcd. for C₁₄H₁₈BBrO₂: C, 54.42; H, 5.87.

Found: C, 54.52; H, 5.99.

1-Bromo-3,4-dihydronaphthalene (**37**)²¹



α-Tetralone **5** (936 mg, 6.4 mmol) was added to a freshly prepared solution of TPPBr₂ in anhydrous dichloromethane at -60 °C. The mixture was stirred for 18 h, allowing to reach rt, and then refluxed for 2 h. Column chromatography of crude residue afforded **37** as a dark orange oil (1.28 g, 96%).

¹H NMR (200 MHz): δ = 2.37 (1 H, dd, *J* = 4.8, 8.5 Hz, H-3), 2.40 (1 H, dd, *J* = 4.8, 8.5 Hz, H-3), 2.86 (2 H, t, *J* = 8.5 Hz, H-4), 6.46 (1 H, t, *J* = 4.8 Hz, H-2), 7.08–7.59 (4 H, m, H-arom).

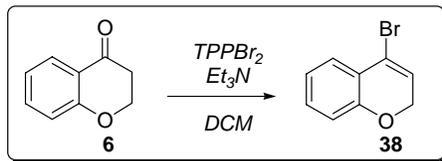
¹³C NMR (50 MHz): δ = 25.4, 27.6, 121.4, 126.5, 126.8, 127.2, 128.2, 130.7, 133.1, 136.3.

MS (EI): *m/z* (%) = 208–210 (M⁺, 27), 129 (100).

Anal. Calcd. for C₁₀H₉Br: C, 57.44; H, 4.34

Found: C, 57.36; H, 4.31.

4-Bromo-2H-chromene (38)⁶



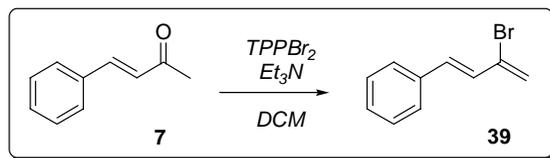
4-Chromanone **5** (942 mg, 6.4 mmol) was reacted with a freshly prepared solution of TPPBr₂ in anhyd dichloromethane at -20 °C. The mixture was stirred for 18 h, allowing the cold bath to reach rt and then refluxed for 2 h. Column chromatography of crude residue afforded **38** as a yellow oil (1.02 g, 76%) that darkened upon storage.

¹H NMR (200 MHz): δ = 4.80 (2 H, d, J = 4.0 Hz, H-2), 6.16 (1 H, t, J = 4.0 Hz, H-3), 6.78–6.83 (1 H, dd, J = 1.2, 7.7 Hz, H-8), 6.93–7.01 (1 H, dt, J = 1.2, 7.7 Hz, H-6), 7.16–7.24 (1 H, dt, J = 1.7, 7.7 Hz, H-7), 7.40–7.44 (1 H, dd, J = 1.7, 7.7 Hz, H-5).

¹³C NMR (50 MHz): δ = 66.7, 115.8, 118.1, 121.7, 121.9, 123.5, 127.0, 130.6, 154.3.

MS (EI): m/z (%) = 210–212 (M⁺, 51), 131 (100).

3-Bromo-1-phenylbutadiene (**39**)⁷



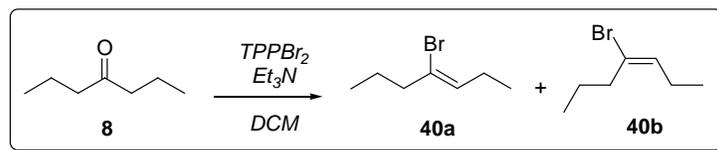
Cinnamyl-methyl ketone **7** (940 mg, 6.4 mmol) was reacted with TPPBr₂ in anhyd dichloromethane at $-60\text{ }^{\circ}\text{C}$. The mixture was stirred for 18 h, allowing to reach rt. After refluxing for 2 h GC analysis showed complete conversion and 99% yield (calculated using **13** as internal standard). For analytical purposes, a pure sample was obtained by column chromatography, affording **39** as a lightly-brown sticky oil that quickly darkened in the flask.

¹H NMR (200 MHz): $\delta = 5.72$ (1 H, d, $J = 0.7$ Hz, H-4), 5.94 (1 H, t, $J = 0.7$ Hz, H-4), 6.74 (1 H, dd, $J = 0.7, 15.2$ Hz, H-2), 6.97 (1 H, d, $J = 15.2$ Hz, H-1), $7.76\text{--}7.04$ (5 H, m, H-arom).

¹³C NMR (50 MHz): $\delta = 119.0, 126.9, 127.7, 128.3, 128.9, 129.9, 130.3, 136.1$.

MS (ED): m/z (%) = 208–210 (M^+ , 10), 129 (100), 102 (9).

(Z)-4-Bromohept-3-ene (40a) and (E)-4-bromohept-3-ene (40b)⁸



4-Heptanone **8** (741 mg, 6.4 mmol) was added to a freshly prepared solution of TPPBr₂ in anhydrous dichloromethane at -24 °C. The mixture was stirred for 18 h, allowing the cold bath to reach rt. The mixture was then refluxed for 2 h. GC analysis showed complete conversion and 85% yield of **40a** and **40b** in a 55:45 ratio (calculated with GC analysis using **13** as the internal standard). For analytical purposes the crude residue was purified by column chromatography to afford an inseparable mixture of **40a** and **40b** as a colorless oil. For the assignment of *E/Z* configuration, a NOESY experiment was used.

¹H NMR (400 MHz): δ = 0.93 (3 H, t, J = 7.4 Hz, **40a** H-7), 0.95 (3 H, t, J = 7.4 Hz, **40b** H-7), 1.01–1.06 (m, 3 H, **40a** H-1 and 3 H, **40b** H-1), 1.57–1.67 (m, 2 H, **40a** H-6 and 2 H, **40b** H-6), 2.09 (2 H, quintet, J = 7.5 Hz, **40b** H-2), 2.21 (2 H, quintet, J = 7.4 Hz, **40a** H-2), 2.34–2.46 (m, 2 H, **40a** H-5 and 2 H, **40b** H-5), 5.66 (1 H, t, J = 6.8 Hz, **40a** H-3), 5.91 (1 H, t, J = 7.6 Hz, **40b** H-3).

¹³C NMR (100 MHz): δ = 12.9, 13.1, 13.3, 13.9, 21.2, 21.3, 23.0, 24.8, 37.2, 43.4, 125.3, 127.6, 130.1, 134.1.

MS (EI): **40a** m/z (%) = 176–178 (M⁺, 10), 97 (25), 55 (100).

40b m/z (%) = 176–178 (M⁺, 12), 97 (21), 55 (100).

Elemental analysis (as a mixture of **40a** and **40b**): Anal. Calcd. for C₇H₁₃Br: C, 47.48; H, 7.40.

Found: C, 47.40; H, 7.29.

When the reaction was performed in the absence of triethylamine, analysis of the crude reaction mixture after 4 hrs by ¹H and ¹³C NMR spectroscopy revealed the presence of a conspicuous amount of an additional compound, along with the expected reaction product 4-bromohept-3-ene (as a mixture of *E/Z* stereoisomers). By means of HSQC and HMBC experiments, δ_H and δ_C values

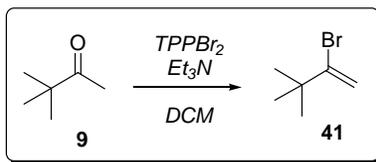
for the additional product were assigned unambiguously and found to match perfectly with those of 4,4-dibromoheptane reported in the literature.²²

¹H NMR (400 MHz): δ = 1.03–1.07 (6 H, m, H-1 and H-7), 1.72–1.81 (4 H, m, H-2 and H-6), 2.34–2.38 (4 H, m, H-3 and H-5).

¹³C NMR (100 MHz): δ = 13.0, 21.0, 52.9, 77.2 (C-4).

²² Dostovalova, V. I.; Velichko, F. K.; Vasil'eva, T. T.; Kruglova, N. V.; Freidlina, R. Kh. *Org. Magn. Reson.* **1981**, *16*, 251.

2-Bromo-3,3-dimethylbutene (**41**)²¹



Pinacolone **9** (645 mg, 6.4 mmol) was reacted with a solution of TPPBr₂ in anhyd dichloromethane at $-55\text{ }^{\circ}\text{C}$. The mixture was stirred for 18 h, allowing to reach rt. The mixture was then refluxed for 2 h, until GC showed complete conversion and 91% yield (using ketone **7** was used as the internal standard). For analytical purposes, the reaction mixture was gently concentrated (760 mmHg) and the residue purified by column chromatography affording **41** as a lightly-yellow oil.

¹H NMR (200 MHz): $\delta = 0.94$ (9 H, s, *tert*-Bu), 5.12 (1 H, d, $J = 2.2$ Hz, H-1), 5.34 (1 H, d, $J = 2.2$ Hz, H-1).

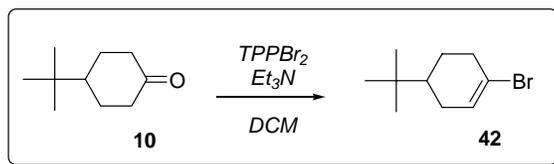
¹³C NMR (50 MHz): $\delta = 28.9, 46.2, 114.0, 150.0$.

MS (EI): m/z (%) = 162–164 (M^+ , 16), 147–149 (13), 83 (100).

Anal. Calcd. for: C, 44.20 ; H, 6.80.

Found: C, 44.40; H, 6.98.

4-*tert*-Butyl-1-bromocyclohexene (**42**)²¹



4-*tert*-Butylcyclohexanone **10** (989 mg, 6.4 mmol) was added to a freshly prepared solution of TPPBr₂ in anhyd dichloromethane at -58 °C. The mixture was stirred for 18 h, allowing to reach rt, and finally refluxed for 2 h. Column chromatography of crude residue afforded **42** as a mint-scented waxy yellowish crystals (1.19 g, 86%).

¹H NMR (200 MHz): δ = 0.87 (9 H, s, *tert*-Bu), 1.43–1.29 (2 H, m, H-5), 1.93–1.79 (2 H, m, H-3), 2.17–2.03 (1 H, m, H-4), 2.50–2.42 (2 H, m, H-6), 6.02 (1 H, m, H-2).

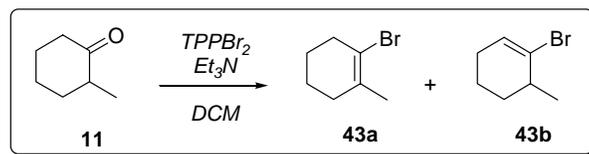
¹³C NMR (50 MHz): δ = 25.9, 27.2, 29.0, 36.4, 42.8, 49.8, 121.9, 128.9.

MS (EI): m/z (%) = 216–218 (M⁺, 16), 160–162 (9), 137 (25), 57 (100).

Anal. Calcd. for C₁₀H₁₇Br: C, 55.31; H, 7.89.

Found: C, 55.35; H, 8.02.

1-Bromo-2-methyl-cyclohexene (**43a**) and 1-bromo-6-methyl-cyclohexene (**43b**)¹⁴



2-Methyl-cyclohexanone **11** (720 mg, 6.4 mmol) was added to a solution of TPPBr₂ in anhydrous dichloromethane at -55 °C. The mixture was stirred for 18 h, allowing to reach rt, and then refluxed over 2 h. Gentle evaporation of the solvent and column chromatography of the crude residue afforded an inseparable mixture of **43a** and **43b** in a 66:34 ratio (determined by GC analysis), as a colorless sticky oil (681 mg, 67%).

¹H NMR (200 MHz): δ = 1.16 (3 H, d, J = 7.0 Hz, **43b** Me-6), 1.75–1.44 (6 H, m, **43b** H-3, H-4, H-5), 1.79 (3 H, m, **43a** Me-2). 2.15–2.00 (m, 4 H, **43a** H-4, H-5 and 1 H, **43b** H-6), 2.52–2.42 (4 H, m, **43a** H-3, H-6), 6.03 (1 H, dt, J = 1.4, 4.1 Hz, **43b** H-2).

¹³C NMR (50 MHz): δ = 18.8, 20.4, 22.7, 23.3, 24.9, 27.8, 31.9, 32.7, 36.4, 37.6, 118.6, 129.1, 129.5, 132.1.

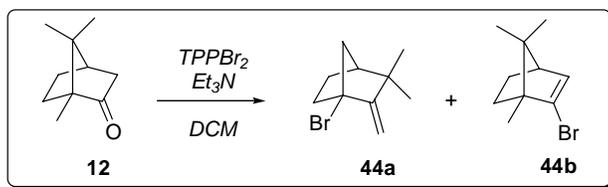
MS (ED): **43a** m/z (%) = 174–176 (M⁺, 19), 95 (100), 67 (35);

43b m/z (%) = 174–176 (M⁺, 6), 95 (100), 67 (35).

Elemental analysis (as a mixture of **43a** and **43b**): Anal. Calcd. for C₇H₁₁Br: C, 48.02; H, 6.33.

Found: C, 48.19; H, 6.41.

1-Bromo-3,3-dimethyl-2-methylene-bicyclo[2.2.1]heptane (44a) and **2-bromo-1,7,7-trimethyl-bicyclo[2.2.1]hept-2-ene (44b)**²³



(+)-Camphor **12** (970 mg, 6.4 mmol) was added to a freshly prepared solution of TPPBr₂ in anhydrous dichloromethane at -50 °C. The mixture was stirred for 18 h, allowing to reach rt, and then refluxed for 2 h. The crude residue was purified by column chromatography to yield an inseparable mixture of **44a** and **44b** in a 81:19 ratio (determined by GC analysis) as a pale-yellow sticky oil (688 mg, 50%).

¹H NMR (200 MHz): δ = 0.82 (3 H, s, **44b** Me-7), 0.88 (3 H, s, **44b** Me-7), 1.02 (3 H, s, **44b** Me-1), 1.11 (3 H, s, **44a** Me-3), 1.13 (3 H, s, **44a** Me-3), 2.21–1.64 (m, 7 H, **44a** H-4, H-5, H-6, H-7 and 4 H, **44b** H-5 and H-6), 2.39 (1 H, t, J = 3.5 Hz, **44b** H-4), 4.80 (1 H, s, **44a** =CH₂), 5.18 (1 H, d, J = 0.8 Hz, **44a** =CH₂), 6.05 (1 H, d, J = 3.5 Hz, **44b** H-3).

¹³C NMR (50 MHz): δ = 12.5, 19.4, 25.5, 26.2, 26.3, 29.9, 30.9, 39.5, 42.6, 45.3, 47.2, 53.0, 55.9, 57.1, 66.5, 68.8, 103.0, 123.2, 133.6, 163.3.

MS (ED): **44a** m/z (%) = 214–216 (M⁺, 17), 171–173 (100);

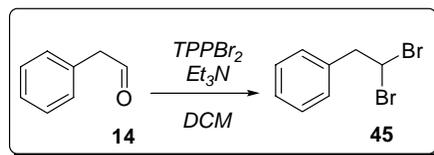
44b m/z (%) = 214–216 (M⁺, 20), 171–173 (70), 135 (70), 91 (100).

Elemental analysis (as a mixture of **44a** and **44b**): Anal. Calcd. for C₁₀H₁₅Br: C, 55.83; H, 7.03.

Found: C, 55.70; H, 6.94.

²³ Fabris, F.; De Martin, A.; De Lucchi, O. *Tetrahedron Lett.* **1999**, *40*, 9121.

(2,2-Dibromoethyl)-benzene (45)¹⁷



Freshly distilled phenyl acetaldehyde **14** (774 mg, 6.4 mmol) was added to a freshly prepared solution of TPPBr₂ in anhyd dichloromethane at $-60\text{ }^{\circ}\text{C}$. The mixture was stirred for 18 h, allowing to reach rt, and finally refluxed for 2 h. Column chromatography of the crude residue yielded **45** as a yellowish stinky oil (1.18 g, 70%).

¹H NMR (200 MHz): δ = 3.75 (2 H, d, J = 6.7 Hz, H-1), 5.80 (1 H, t, J = 6.7 Hz, H-2), 7.37–7.09 (5 H, m, H-arom).

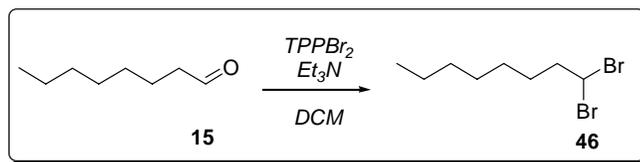
¹³C NMR (50 MHz): δ = 45.2, 51.5, 128.3, 128.7, 129.5, 136.8.

MS (EI): m/z (%) = 262–264–266 (M^+ , 18), 183–185 (23), 104 (22), 91 (100).

Anal. Calcd. for C₈H₈Br₂ : C, 36.40; H, 3.05.

Found: C, 36.51; H, 3.19.

1,1-Dibromooctane (**46**)¹⁸



Octanal **15** (823 mg, 6.4 mmol) was added to a freshly prepared solution of TPPBr₂ in anhydrous dichloromethane at $-60\text{ }^{\circ}\text{C}$. The mixture was stirred for 18 h, allowing to reach rt, and finally refluxed for 2 h. Purification of the crude residue by column chromatography gave **46** as a colorless oil (1.01 g, 60%).

¹H NMR (200 MHz): $\delta = 0.90$ (3 H, t, $J = 6.6$ Hz, H-8), 1.61–1.30 (10 H, m, H-4, -5, -6 and -7), 2.40 (2 H, m, H-2), 5.71 (1 H, t, $J = 6.2$ Hz, H-1).

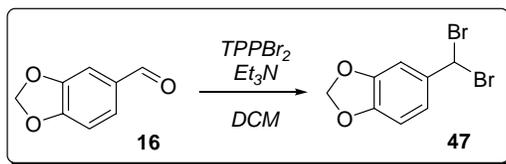
¹³C NMR (50 MHz): $\delta = 14.0, 22.6, 28.1, 28.2, 29.0, 31.6, 45.5, 46.3$.

MS (ED): m/z (%) = 270–272–274 (M^+ , 12), 191–193 (100).

Anal. Calcd. for C₈H₁₆Br₂: C, 35.32; H, 5.93.

Found: C, 35.28; H, 5.90.

Piperonyl dibromide (**47**)²⁴



Piperonal **16** (1.07 g, 6.7 mmol) was added to a freshly prepared solution of TPPBr₂ in anhydrous dichloromethane at $-58\text{ }^{\circ}\text{C}$. The mixture was stirred for 18 h, allowing to reach rt, and then refluxed over 2 h. After removal of the solvent, the residue was purified by distillation under reduced pressure to yield **47** (1.28 g, 65%) as a yellowish almond-smelling waxy solid ($120\text{--}123\text{ }^{\circ}\text{C}$, 0.7 mmHg) that quickly darkened upon storage.

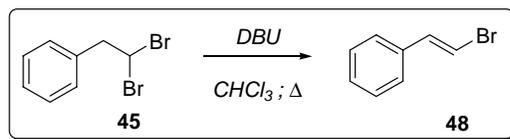
¹H NMR (200 MHz): δ = 6.01 (2 H, s, OCH₂O), 6.61 (1 H, s, Br₂CH), 6.71 (1 H, d, J = 8.0 Hz, H-5), 6.95 (1 H, dd, J = 8.0, 1.9 Hz, H-6), 7.18 (1 H, d, J = 1.9 Hz, H-2).

¹³C NMR (50 MHz): δ = 49.2, 99.9, 106.7, 109.7, 122.7, 132.6, 147.9, 148.3.

MS (EI): m/z (%) = 292–294–296 (M^+ , 12), 213–215 (100).

²⁴ Minai, M. U.S. Patent 4,335,263, 1982.

***trans*-2-Bromovinylbenzene (48)²⁵**



(2,2-Dibromo-ethyl)-benzene **45** (200 mg, 0.76 mmol) was treated with DBU (127 mg, 0.83 mmol) in anhyd CHCl₃ (10 mL) at reflux for 20 h. The mixture was evaporated under reduced pressure and the crude material was purified by column chromatography to afford **48** as a colorless oil (139 mg, 99%).

¹H NMR (200 MHz): δ = 6.78 (1 H, d, J = 14.0 Hz, H-1), 7.13 (1 H, d, J = 14.0 Hz, H-2), 7.40–7.28 (5 H, m, H-arom).

¹³C NMR (50 MHz): δ = 106.5, 126.1, 128.3, 128.8, 129.0, 136.0, 137.2.

MS (EI): m/z (%) = 182–184 (M^+ , 39), 103 (100).

Anal. Calcd. for C₈H₇Br : C, 52.49; H, 3.85.

Found: C, 52.60; H, 3.99.

²⁵ Miller, R. B.; McGarvey, G. J. *Org. Chem.* **1978**, *43*, 4424.