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The Regio- and Stereo-Selective Formation of Allylic Chlorides During the Overman Rearrangement of Trichloroacetimidates Derived from Certain Brominated Conduritols

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Microwave irradiation of imidate **2** at 165°C affords a ~3:1 mixture of the Overman rearrangement product **3** and the allylic chloride **4** (83% combined yield). Under the same conditions the deoxy-conduritol **6** gives a comparable mixture of compounds **7** and **8**. The single-crystal X-ray structure of a derivative of chloride **8** is reported together with a mechanism that accounts for the selective formation of this compound and congener **4**.

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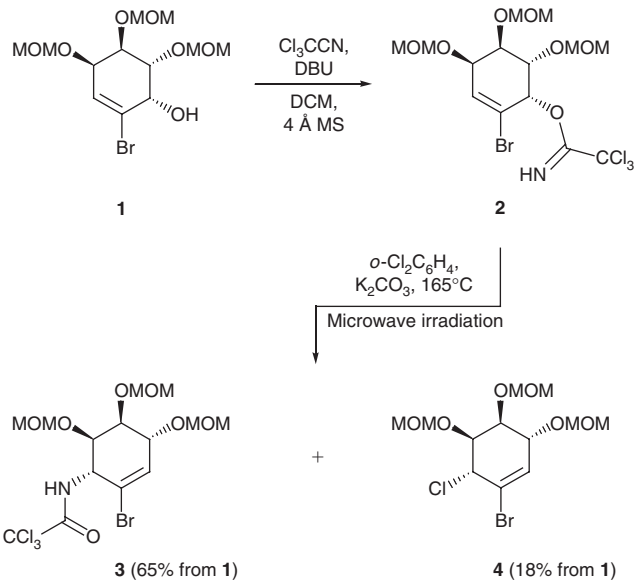
Introduction

The Overman or allylic trihaloacetimidate rearrangement process is a thermally promoted, suprafacial [3,3]-sigmatropic process that allows for the stereoselective, three-step conversion of an allylic alcohol into the corresponding (rearranged) allylic amine.[1] This generally very reliable and robust reaction sequence has found broad application, including in the synthesis of natural products. Catalytic enantioselective variants have been introduced in recent years and promise to further enhance the utility of this important process.[2] By-products are rarely observed during the Overman rearrangement although the allylic trihaloacetamide can sometimes undergo a [1,3]-rearrangement to the corresponding (non-double-bond migrated) trihaloacetamide, or ionize to form an allylic cation that then engages in a range of reactions including proton loss to give a diene.[1a] The ionization process is catalyzed by acid and so it can be suppressed by adding potassium carbonate to the reaction mixture and thus ensuring the Overman rearrangement process prevails. Given this background we are now prompted to describe a hitherto unreported process that, under certain conditions, appears to compete with the trichloroacetimidate variant of the Overman rearrangement. The products of this process are allylic chlorides that possess the same regio- and stereo-chemistry as the rearranged trichloroacetamide. Details are presented in the following section as is a mechanistic rationalization for the formation of these by-products.

Results and Discussion

In connection with the development of the total syntheses of certain *Amaryllidaceae* alkaloids[3] we have prepared various halogenated conduritols and subjected them to an Overman rearrangement reaction. For example, compound **1**[3a] was treated with a mixture of trichloroacetonitrile and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in dichloromethane (DCM) to afford the trichloroacetimidate **2**[3a] (Scheme 1). Subjection of an *o*-dichlorobenzene solution of this material that contained anhydrous potassium carbonate to microwave irradiation at ~165°C resulted in the desired rearrangement taking place and thus produced the acetamide **3**[3a] in 65% yield.* However a by-product, which we now believe to be the allylic chloride



Scheme 1.

*It is worth noting that the conversion **2** → **3** represents a rare example of a microwave-promoted Overman rearrangement[5] and seemingly only the second example of such a process involving a halogenated alkene.[3]

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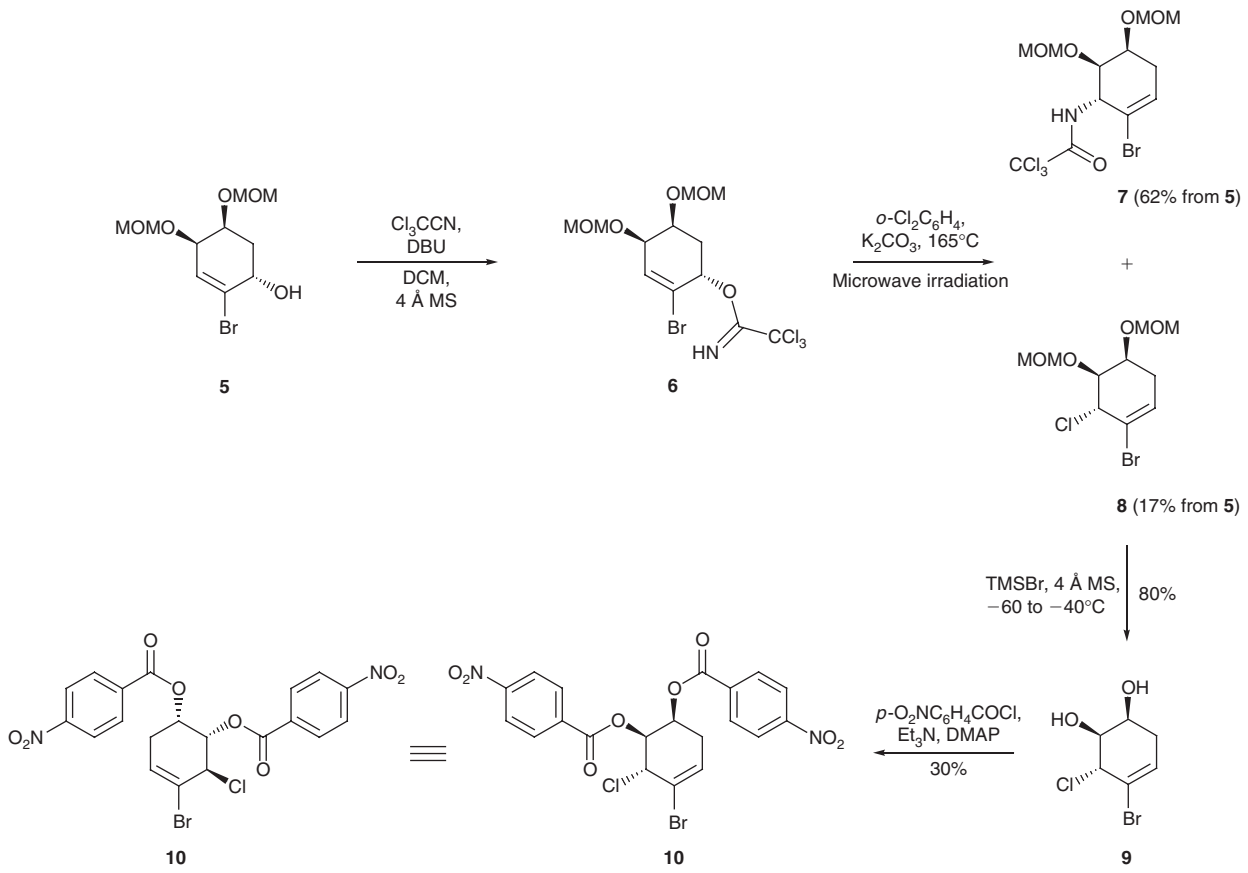


Scheme 2.

4 (18%), was also generated. While the structure of compound **3** follows from the single-crystal X-ray analysis of a derivative,[3a] we had been unable to gain similarly rigorous and direct evidence for the stereo-structure of congener **4**. Now, though, we describe additional experiments that have led us to assign the illustrated structure to compound **4**.

The critical additional experiments are presented in Scheme 2 and involved preparing, using standard conditions, the trichloroacetimidate **6** from the previously reported allylic alcohol **5**.[4] When the former compound was subjected to the same rearrangement conditions as defined earlier,[3] a chromatographically separable mixture of compounds **7** (62% from **5**) and **8** (17% from **5**) was obtained. The spectroscopic data acquired on the Overman rearrangement product **7** were in full accord with the assigned structure and similar to those obtained on related products that have been converted into various congeners of lycoricidine or narciclasine.[3] The analogous data obtained on by-product **8** were consistent with the assigned structure but in order to confirm this the compound was subjected to treatment with trimethylsilyl bromide so as to effect cleavage of the methoxymethyl ether residues and thereby produce diol **9**. Conversion of this last compound into the corresponding bis-*p*-nitrobenzoate **10** was readily achieved under standard conditions.

The crystalline nature of compound **10** allowed an X-ray analysis to be undertaken and thus confirming its structure and that of its precursors, particularly by-product **8**. The *ORTEP* diagram derived from this analysis is shown in Fig. 1.

Clearly compound **8** arises from an allylic rearrangement process in which the stereochemistry of the starting imidate **6** is

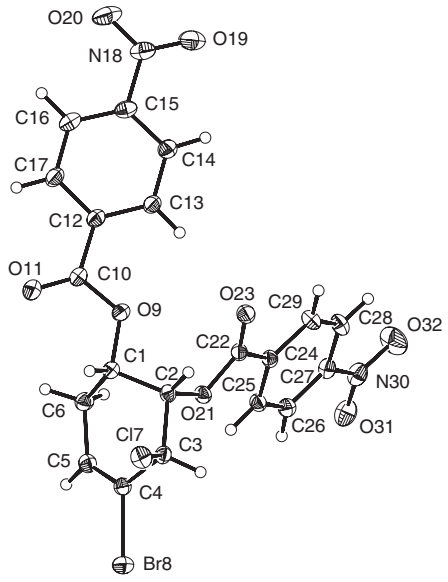
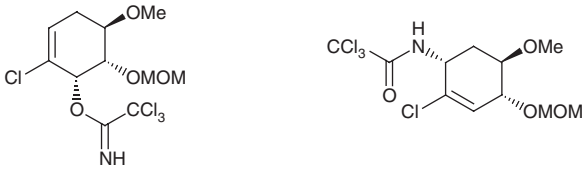


Fig. 1. Molecular structure of compound **10** ($C_{20}H_{14}BrClN_2O_8$) with labelling of selected atoms. Anisotropic displacement ellipsoids show 30% probability levels. Hydrogen atoms are drawn as circles with small radii.

reflected in the product. On this basis, it is believed that the by-product from the Overman rearrangement of compound **2** arises from the same type of process and must, therefore, possess the illustrated structure **4**. Interestingly, the Overman rearrangement of compound **11**[6] (Fig. 2), which incorporates a



11 **12**

Fig. 2. Compounds **11** and **12**.

chloro- rather than a bromo-cyclohexene residue, proceeds smoothly to give the trichloroacetamide **12**[6] in high yield (88% from the alcohol precursor to compound **11**) and without any evidence of the formation of the sort of allylic chloride by-product discussed above.

The precise mode of formation of the allylic chloride by-products **4** and **8** from their trichloroacetimidate precursors **2** and **6**, respectively, remains unclear at the present time. That having been said, given the stereochemical outcomes of the processes that lead to these compounds, internal delivery of chloride seems a distinct possibility and the sort of process illustrated in structure **13** (Fig. 3), or a related but non-concerted variant, would appear plausible. If this pathway were indeed operative then the other primary by-product would be the oxiranimine **14**, although under the reaction conditions involved such a highly strained species would be expected to hydrolyze to give two equivalents of carbonic acid. The origin of the seemingly divergent behaviours of the brominated systems **4** and **8** relative to the chloro-congener **11** remains uncertain but could well be a reflection of steric factors. The optimization of the processes that lead to allylic chlorides such as **4** and **8** as well as their exploitation in synthetic chemistry are the subject of ongoing studies in our laboratories. Details will be presented in due course.

13 **14**

Fig. 3. Compounds **13** and **14**.

Experimental

General Procedures

Unless otherwise specified, proton (^{1}H) and carbon (^{13}C) NMR spectra were recorded at 18°C in base-filtered $CDCl_3$ on a Varian Mercury or Inova 300 spectrometer operating at 300 MHz for proton and 75 MHz for carbon nuclei. In certain cases, a Varian Inova 500 spectrometer operating, at 500 MHz for proton nuclei, or a Bruker 800 MHz machine were used. For ^{1}H NMR spectra, signals arising from residual protio-forms of the solvent were used as the internal standards. ^{1}H NMR data are recorded as follows: chemical shift (δ_H) [multiplicity, coupling constant(s) J (Hz), relative integral] where multiplicity is defined as: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, or combinations of the above. The residual $CHCl_3$ peak (δ_H 7.26) was used as a reference for ^{1}H NMR spectra, and the central peak (δ_C 77.0) of the $CDCl_3$ 'triplet' was used as a reference for proton-decoupled ^{13}C NMR spectra. Infrared spectra (ν_{max}) were recorded on a Perkin–Elmer 1800 Series FTIR spectrometer. Samples were analyzed as KBr disks (for solids) or as thin films on NaCl plates (for oils and low-melting solids). A VG Fisons AutoSpec three-sector (E/B/E) double focusing mass spectrometer was used to obtain both low- and high-resolution electron impact (EI) mass spectra. Low- and high-resolution electrospray (ESI) mass spectra were obtained on a VG Quattro II triple quadrupole MS instrument operating in positive ionization mode.

Optical rotations were measured at 18°C, in spectroscopic grade solvents, with a Perkin–Elmer 241 polarimeter at the sodium-D line (589 nm) and at the concentrations (c) (g per 100 mL) indicated. The measurements were carried out in a cell with a path length (l) of 10 cm. Specific rotations $\{[\alpha]_D\}$ were calculated using the equation $[\alpha]_D = 100 \cdot a/(c \cdot l)$ and are given in 10^{-1} deg cm^2 g^{-1}. Melting points were measured on an Optimelt automated melting point system or a Reichert hot-stage microscope apparatus and are uncorrected.

Analytical TLC was performed on aluminium-backed 0.2 mm thick silica gel 60 F_{254} plates as supplied by Merck. Eluted plates were visualized using a 254 nm UV lamp and/or by treatment with a suitable dip followed by heating. These dips included phosphomolybdic acid:ceric sulfate:sulfuric acid (conc.):water (37.5 g:7.5 g:37.5 g:720 mL) or potassium permanganate:potassium carbonate:5% w/v sodium hydroxide aqueous solution:water (3 g:20 g:5 mL:300 mL). The retardation factor (R_F) was quoted to the nearest 0.1. Flash column chromatography was performed using silica gel 60 (0.040–0.0063 mm) as the stationary phase and the analytical reagent (AR) or HPLC grade solvents indicated.

Starting materials and reagents were generally available from Sigma–Aldrich, Merck, TCI, Strem, or Lancaster Chemical Companies and were used as supplied. Drying agents and other inorganic salts were purchased from AJAX, BDH, or Unilab Chemical Companies. Tetrahydrofuran (THF) and diethyl ether (ether) were distilled from sodium benzophenone ketyl. Methanol was distilled from its magnesium alkoxide salt. Benzene and toluene were distilled from sodium wire. Dichloromethane was distilled from calcium hydride. Triethylamine was distilled from and stored over potassium hydroxide pellets.

Microwave Irradiation Experiments

All microwave irradiation experiments were carried out in a CEM Explorer microwave apparatus operating at a frequency of 2.45 GHz with continuous irradiation power from 0 to 300 W using the standard absorbance level of 300 W to represent maximum power. The reactions were carried out in 80 mL sealed Pyrex vessels (working volume of 50 mL) equipped with a magnetic stirrer. The temperature was measured with a fibre optic temperature sensor immersed in the reaction vessel. After the specified irradiation period, the reaction vessel was cooled rapidly (1–2 min) to ambient temperatures using a nitrogen jet.

Synthetic Studies

*Compound **2***

A magnetically stirred solution of compound **1**[3a] (210 mg, 0.59 mmol) in CH_2Cl_2 (3 mL) containing 4 Å molecular sieves (100 mg) and maintained under an atmosphere of nitrogen was cooled to 0°C and then treated, sequentially, with DBU (132 μL, 0.88 mmol) and trichloroacetonitrile (106 μL, 1.06 mmol). The resulting mixture was warmed to 18°C over ~0.5 h, stirred at this temperature for 1.5 h, and then treated with NH_4Cl (5 mL of

a saturated aqueous solution). The separated aqueous layer was extracted with CH_2Cl_2 (3 × 15 mL) and the combined organic phases were filtered through a pad comprised of a layer of TLC-grade silica (1 cm) covered by a layer of anhydrous $MgSO_4$ (2 cm). The pads were then washed with 1:49 v/v MeOH/CH_2Cl_2 solution (50 mL) and the combined filtrates concentrated under reduced pressure to afford the previously reported compound **2**[3a] (296 mg, ~100%) as a yellow oil, R_F 0.5 (in 1:1 v/v ethyl acetate/hexane). δ_H (300 MHz, $CDCl_3$) 8.51 (br s, NH), 6.37 (d, *J* 4.2, 1H), 6.00 (d, *J* 3.6), 4.82–4.64 (complex m, 6H), 4.53–4.43 (complex m, 2H), 4.20 (dd, *J* 7.8 and 3.6, 1H), 3.43 (s, 3H), 3.40 (s, 3H), 3.39 (s, 3H). ν_{max} (cm^{-1}) 3344, 2931, 2894, 1669, 1290, 1151, 1118, 1099, 1076, 1041, 917, 794. This material was used, without further purification, in the Overman rearrangement reaction.

*Compounds **3** and **4***

A solution of trichloroacetimidate **2**[3a] (296 mg, ~0.59 mmol) in anhydrous *o*-dichlorobenzene (10 mL) that contained K_2CO_3 (20 mg, 0.14 mmol) was stirred at 165°C for 0.25 h in the microwave reactor. The resulting black reaction mixture was cooled and then loaded directly onto a 2.5 cm × 12 cm column of silica gel and eluted with hexane then 1:9 → 15:85 → 1:4 → 2:3 v/v ethyl acetate/hexane. In this manner two fractions, A and B, were obtained.

Concentration of fraction A (R_F 0.4 in 1:1 v/v ethyl acetate/hexane) afforded the title compound **3**[3a] (192 mg, 65%) as a clear, pale-tan oil, $[\alpha]_D$ +9 (*c* 0.4, $CHCl_3$) [Found: $(M + Na)^+$ 523.9447. $C_{14}H_{21}{}^{79}Br^{35}Cl_2{}^{37}ClNO_7$ requires $(M + Na)^+$ 523.9435]. δ_H (300 MHz, $CDCl_3$) 6.73 (br d, *J* 8.1, NH), 6.34 (dd, *J* 3.9 and 1.2, 1H), 4.83–4.68 (complex m, 7H), 4.26 (dd, *J* 5.1 and 4.5, 1H), 4.11 (dd, *J* 6.0 and 2.1, 1H), 3.93 (dd, *J* 5.7 and 2.1, 1H), 3.41 (s, 6H), 3.38 (s, 3H). δ_C (75 MHz, $CDCl_3$) 161.8 (CO), 132.6 (CH), 122.3 (C), 96.8 (CH_2), 96.3 (CH_2), 96.2 (CH_2), 92.2 (CCl_3), 75.0 (CH), 74.4 (CH), 74.1 (CH), 56.7 (CH), 55.9 (CH_3), 55.8 (CH_3), 55.7 (CH_3). ν_{max} (cm^{-1}) 3310, 2930, 2895, 1714, 1642, 1520, 1214, 1151, 1103, 1034, 822. *m/z* (ESI) 529, 528, 527, 526, 525, 524, 523, and 522 $[(M + Na)^+$, 3, 18, 10, 65, 16, 100, 10, and 52%].

Concentration of fraction B (R_F 0.5 in 1:1 v/v ethyl acetate/hexane) afforded the previously reported, but at that time configurationally unassigned, chloride **4**[3a] (39 mg, 18%) as a clear, colourless oil, $[\alpha]_D$ +53 (*c* 1.0, $CHCl_3$) [Found: $(M + Na)^+$ 399.0013. $C_{12}H_{20}{}^{81}Br^{35}ClNO_6$ requires $(M + Na)^+$ 399.0009]. δ_H (300 MHz, $CDCl_3$) 6.23 (d, *J* 3.0, 1H), 4.83–4.70 (complex m, 6H), 4.64 (d, *J* 3.6, 1H), 4.38 (br dd, *J* 7.8 and 3.0, 1H), 4.21 (dd, *J* 3.6 and 2.4, 1H), 4.16 (dd, *J* 7.8 and 2.4, 1H), 3.41 (s, 6H), 3.40 (s, 3H). δ_C (75 MHz, $CDCl_3$) 133.9 (br, CH), 120.8 (br, C), 97.3 (CH_2), 97.1 (CH_2), 96.7 (CH_2), 79.6 (CH), 75.6 (br, CH), 73.8 (CH), 60.8 (br, CH), 55.8 (CH_3), 55.7 (CH_3), 55.7 (CH_3). ν_{max} (cm^{-1}) 2931, 2891, 1640, 1151, 1108, 1036, 917, 810. *m/z* (ESI) 401, 400, 399, 398, and 397 $[(M + Na)^+$, 26, 13, 100, 10, and 76%].

*Compound **6***

A magnetically stirred solution of compound **5**[4] (270 mg, 0.91 mmol) in CH_2Cl_2 (5 mL) that contained 4 Å molecular sieves (100 mg) and was maintained under an atmosphere of nitrogen was cooled to 0°C and then treated with DBU (205 μL, 1.36 mmol) and trichloroacetonitrile (165 μL, 1.63 mmol). The ensuing mixture was warmed to 18°C over ~0.5 h, stirred at this temperature for 1.5 h, and then treated with NH_4Cl (5 mL of a saturated aqueous solution). The separated aqueous layer was extracted with CH_2Cl_2 (3 × 15 mL) and the combined organic phases were filtered through a pad comprised of a layer of TLC-grade silica (1 cm) covered by a layer of anhydrous $MgSO_4$ (2 cm). The pad was washed with MeOH/CH_2Cl_2 (1 × 50 mL of a 1:49 v/v mixture) and the combined filtrates were concentrated under reduced pressure to afford the *title compound **6*** (420 mg, ~100%) as a yellow oil, R_F 0.5 (in 2:3 v/v ethyl acetate/hexane) [Found: $(M + Na)^+$ 461.9253. $C_{12}H_{17}{}^{79}Br^{35}Cl_3NO_5$ requires $(M + Na)^+$ 461.9253]. δ_H (300 MHz, $CDCl_3$) 8.50 (br s, 1H, NH), 6.44 (d, *J* 5.4, 1H), 5.74 (m, 1H), 4.82–4.68 (complex m, 4H), 4.24 (m, 1H), 4.13 (ddd, *J* 10.8, 3.0 and 3.0, 1H), 3.41 (s, 3H), 3.38 (s, 3H), 2.59–2.50 (complex m, 1H), 2.10 (m, 1H). *m/z* (ESI) 468, 467, 466, 465, 464, and 462 $[(M + Na)^+$, 17, 9, 60, 13, 90, and 48%]. This material was used, without further purification, in the Overman rearrangement reaction.

*Compounds **7** and **8***

A solution of trichloroacetimidate **6** (420 mg, ~0.91 mmol) in anhydrous *o*-dichlorobenzene (10 mL) that contained anhydrous K_2CO_3 (20 mg, 0.14 mmol) was stirred at 165°C for 0.25 h in the microwave reactor. The resulting black reaction mixture was cooled and then loaded directly onto a 2.5 cm × 12 cm column of silica gel and eluted with hexane then 1:9 → 15:85 → 1:4 → 2:3 v/v ethyl acetate/hexane. In this manner two fractions, A and B, were obtained.

Concentration of fraction A (R_F 0.3 in 2:3 v/v ethyl acetate/hexane) afforded the *title compound **7*** (247 mg, 62% from **5**) as a clear, colourless oil, $[\alpha]_D$ +61 (*c* 0.4, $CHCl_3$) [Found: $(M + Na)^+$ 461.9249. $C_{12}H_{17}{}^{79}Br^{35}Cl_3NO_5$ requires $(M + Na)^+$ 461.9253]. δ_H (500 MHz, $CDCl_3$) 6.65 (d, *J* 8.1, 1H, NH), 6.25 (tm, *J* 4.5, 1H), 4.83 (d, *J* 6.9, 1H), 4.78 (d, *J* 6.9, 1H), 4.75–4.70 (complex m, partially obscured, 1H), 4.73 (d, *J* 6.9, 1H), 4.67 (d, *J* 6.9, 1H), 4.06 (dd, *J* 5.1 and 2.4, 1H), 3.95 (m, 1H), 3.43 (s, 3H), 3.37 (s, 3H), 2.51 (m, 1H), 2.40 (m, 1H). δ_C (75 MHz, $CDCl_3$) 161.5, 131.5, 117.5, 96.0, 95.2, 92.2, 75.7, 70.1, 57.5, 55.7, 55.4, 30.5. ν_{max} (cm^{-1}) 3319, 2935, 2894, 1702, 1522, 1151, 1105, 1035, 1009, 917, 822. *m/z* (ESI) 468, 467, 466, 465, 464, and 462 $[(M + Na)^+$, 20, 8, 60, 13, 100, and 50%].

Concentration of fraction B (R_F 0.4 in 3:7 v/v ethyl acetate/hexane) afforded the *title compound **8*** (52 mg, 17% from **5**) as a clear, colourless oil, $[\alpha]_D$ +120 (*c* 0.6, $CHCl_3$) [Found: $(M + Na)^+$ 338.9798. $C_{10}H_{16}{}^{81}Br^{35}ClO_4$ requires $(M + Na)^+$ 338.9798]. δ_H (800 MHz, $CDCl_3$) 6.16 (dd, *J* 5.6 and 3.2, 1H), 4.83 (d, *J* 7.2, 1H), 4.76 (d, *J* 7.2, 1H), 4.73 (d, *J* 7.2, 1H), 4.69 (d, *J* 7.2, 1H), 4.63 (d, *J* 3.2, 1H), 4.23 (ddd, *J* 9.6, 6.4 and 2.4, 1H), 4.16 (dd, *J* 3.2 and 2.4, 1H), 3.40 (s, 3H), 3.39 (s, 3H), 2.46 (m, 1H), 2.44 (m, 1H). δ_C (75 MHz, $CDCl_3$) 132.2, 118.6, 97.2, 95.5, 79.0, 68.9, 61.5, 55.7, 55.6, 30.3. ν_{max} (cm^{-1}) 2946, 2893, 1151, 1109, 1052, 1034, 982, 941, 917, 837, 768. *m/z* (ESI) 341, 340, 339, 338, and 337 $[(M + Na)^+$, 25, 11, 100, 9, and 77%].

*Compound **9***

A magnetically stirred solution of compound **8** (22 mg, 0.07 mmol) in CH_2Cl_2 (1 mL) that contained 4 Å molecular sieves (500 mg) and was maintained under a nitrogen atmosphere at −60°C was treated with TMS-Br (71 μL, 0.55 mmol). The reaction was warmed to −40°C over ~0.5 h, stirred at this temperature for 2 h, and then treated with $NaHCO_3$ (3 mL of a saturated aqueous solution). The ensuing mixture was warmed to 18°C, stirred at this temperature for ~0.25 h, and then diluted with ethyl acetate (10 mL). The aqueous layer was separated and extracted with ethyl acetate (4 × 10 mL). The combined organic phases were dried ($MgSO_4$) and filtered before being treated

with silica (500 mg), and then concentrated under reduced pressure. The resulting white powder was loaded onto a silica column that was then eluted with CH_2Cl_2 followed by 1:99 → 1:49 v/v MeOH/CH_2Cl_2. Concentration of the appropriate fractions (R_F 0.2 in 5% v/v MeOH/CH_2Cl_2) under reduced pressure afforded the *title compound* ***9*** (12 mg, 80%) as a clear, colourless oil. δ_H (300 MHz, $CDCl_3$) 6.14 (dd, *J* 4.8 and 3.9, 1H), 4.54 (d, *J* 3.9, 1H), 4.29 (m, 1H), 4.18 (m, 1H), 2.52–2.43 (complex m, 2H), 2.34 (m, 1H), 2.01 (d, *J* 5.4, 1H, OH).

Compound ***10***

Triethylamine (17 μL, 0.12 mmol), 4-(*N*,*N*-dimethylamino) pyridine (DMAP) (2 mg, 0.02 mmol), and then *p*-nitrobenzoyl chloride (25 mg, 0.12 mmol) were added to a magnetically stirred solution of alcohol **9** (7 mg, 0.03 mmol) in CH_2Cl_2 (1 mL) maintained at 0°C under an atmosphere of nitrogen. The reaction was warmed to 18°C and after 16 h $NaHCO_3$ (5 mL of a saturated aqueous solution) was added. The ensuing mixture was extracted with CH_2Cl_2 (3 × 10 mL) and the combined organic phases were then dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The resulting orange residue was loaded onto a silica column that was eluted with hexane and then 1:9 v/v ethyl acetate/hexane. The appropriate fractions (R_F 0.3 in 1:4 v/v ethyl acetate/hexane) were concentrated under reduced pressure to afford the *title compound* ***10*** (5 mg, 30%) as a pale-orange solid, mp 188–194°C, $[\alpha]_D$ +38 (*c* 0.4, $CDCl_3$) [Found: $(M - Cl\bullet)^+$ 490.9899 and 488.9933. $C_{20}H_{14}{}^{81}BrClN_2O_8$ and $C_{20}H_{14}^{79}BrClN_2O_8$ require $(M - Cl\bullet)^+$ 490.9913 and 488.9934, respectively]. δ_H (300 MHz, $CDCl_3$) 8.35–8.08 (complex m, 8H), 6.36 (dd, *J* 5.4 and 3.3, 1H), 5.93–5.80 (complex m, 2H), 4.71 (d, *J* 3.6, 1H), 2.90 (dt, *J* 18.0 and 5.4, 1H), 2.69 (m, 1H). δ_C (75 MHz, $CDCl_3$) 163.7, 163.4, 151.1, 150.8, 134.5, 134.2, 131.0, 130.8, 130.6, 123.9, 123.7, 118.4, 73.9, 66.8, 59.3, 29.3. ν_{max} (cm^{-1}) 2924, 2854, 1731, 1608, 1526, 1347, 1271, 1261, 1097, 1014, 872, 835, 717. *m/z* (EI) 491 and 489 (both 3%, $[M - Cl\bullet]^+$), 192 (36), 150 (100). Recrystallization (ethyl acetate/hexane) of this material afforded pale-orange needles suitable for X-ray crystallographic structure determination.

X-Ray Crystallographic Study on Compound ***10***

Crystal Data

$C_{20}H_{14}BrClN_2O_8$, *M* 525.70, *T* 200(1) K, orthorhombic, space group $P2_12_12_1$, *Z* 4, *a* 6.8298(1), *b* 14.9660(3), *c* 20.3511(3) Å, *V* 2080.18(6) $Å^3$, D_x 1.678 g cm^{-3}, 6060 unique data ($2\theta_{max}$ 60°); *R* 0.026 [for 5043 reflections with $I > 2.0\sigma(I)$], *Rw* 0.030 (all data), *S* 1.11. Absolute configuration determined by refinement of the Flack parameter [final value −0.014(5)].

Structure Determination

Images were measured on a Nonius Kappa CCD diffractometer ($Mo_{K\alpha}$, graphite monochromator, λ 0.71073 Å) and data extracted using the DENZO package.[7] The structure was solved by direct methods (SIR92).[8] The structure of the abovementioned compound was refined using the *CRYSTALS* program package.[9]

Atomic coordinates, bond lengths and angles, and displacement parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC number 704835). These data can be obtained free-of-charge from www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Acknowledgements

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References

[1] (a) L. E. Overman, N. E. Carpenter, *Org. React.* **2005**, *66*, 1.
(b) L. Kürti, B. Czakó, *Strategic Applications of Named Reactions in Organic Synthesis* **2005**, pp. 322–333 (Elsevier Academic Press: Burlington, MA).

[2] (a) C. E. Anderson, L. E. Overman, *J. Am. Chem. Soc.* **2003**, *125*, 12412. doi:10.1021/JA037086R
(b) C. E. Anderson, L. E. Overman, M. P. Watson, *Org. Synth.* **2005**, *82*, 134.

[3] (a) M. Matveenko, O. J. Kokas, M. G. Banwell, A. C. Willis, *Org. Lett.* **2007**, *9*, 3683. doi:10.1021/OL701552R
(b) M. Matveenko, M. G. Banwell, A. C. Willis, *Tetrahedron* **2008**, *64*, 4817. doi:10.1016/J.TET.2008.01.113

[4] M. G. Banwell, O. J. Kokas, A. C. Willis, *Org. Lett.* **2007**, *9*, 3503. doi:10.1021/OL071344Y

[5] For a recent report on the microwave-promoted Overman rearrangement see: J. Gonda, M. Martinková, A. Zadrošová, M. Šoteková, J. Raschmanová, P. Čonka, E. Gajdošíková, C. O. Kappe, *Tetrahedron Lett.* **2007**, *48*, 6912. doi:10.1016/J.TETLET.2007.07.157

[6] M. Matveenko, M. G. Banwell, A. C. Willis, *Org. Lett.* **2008**, *10*, 4693. doi:10.1021/OL801815K

[7] DENZO-SMN Z. Otwinowski W. Minor, Processing of X-Ray Diffraction Data Collected in Oscillation Mode, in *Methods in Enzymology, Volume 276: Macromolecular Crystallography, Part A* (Eds C. W. Carter, Jr, R. M. Sweet) **1997**, pp. 307–326 (Academic Press: New York, NY).

[8] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camalli, *J. Appl. Crystallogr.* **1994**, *27*, 435. doi:10.1107/S002188989400021X

[9] P. W. Betteridge, J. R. Carruthers, R. I. Cooper, K. Prout, D. J. Watkin, *J. Appl. Crystallogr.* **2003**, *36*, 1487. doi:10.1107/S0021889803021800