Pergamon

Tetrahedron Vol. 50, No. 21, pp. 6433-6440, 1994

0040-4020/94 $7.00+0.00

0040-4020(94)E0268-X

Nucleophilic 1,2 Addition of Bromine to Electron Deficient Double Bonds by Perbromide Reagents

Isidro G. Collado*, Rosario H. Galán, Guillermo M. Massanet and Miguel S. Alonso

Departamento de Química Orgánica. Facultad de Ciencias.
Universidad de Cádiz. Apdo. 40, 11510 Puerto Real, Cádiz, Spain.

Abstract: Perbromide compounds prove to be excellent reagents for achieving nucleophilic 1,2 addition of bromine to the double bond of α,β-unsaturated compounds. This reaction proved to be highly selective in eudesmanolides with an electronegative substituent at C-1. In other subtrates with additional non-conjugated double bonds, competitive electrophilic addition of bromine can be minimized in the presence of alkenes with electron-rich double bonds.

INTRODUCTION

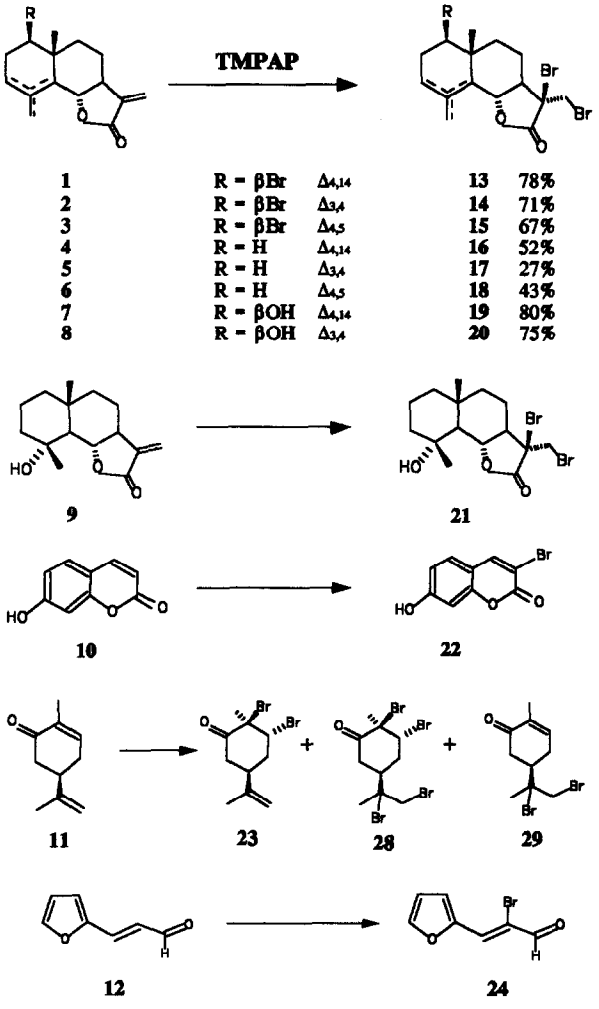
Since 1897 when the first reference about perbromide reagents[1] was published, a wide range of these reagents has been described and used in organic synthesis as a mild and selective brominating agents[2-12]. Particulary, pyridinium perbromide (PPB) and trimethyl(phenyl)ammonium perbromide (TMPAP) are established reagents which have been used for mild bromination, principally in alkenes[13-15] or at the position α to carbonyl groups[16-18]. In these reactions perbromides act as a source of bromine which adds to the double bond by electrophilic addition[19]. During our work directed toward the synthesis of bioactive sesquiterpene lactones functionalized in the lactone ring, we found that reaction of TMPAP with eudesmanolides possessing an α,β-unsaturated γ-lactone group and an additional non conjugated double bond, resulted in a predominant stereospecific addition of bromine to the conjugated double bond. This interesting transformation, which can be rationalized in terms of nucleophilic 1,2 addition of bromine to electron-deficient double bonds, proved to be a very useful tool for the synthesis of sesquiterpenolides functionalized in the lactone ring[20].

Although evidence of nucleophilic bromine addition in some acid catalyzed reactions of bromine with α,β-unsaturated acids[21] has been reported, to our knowledge this is the first time that a selective nucleophilic bromine addition to an α,β-unsaturated carbonyl group is described. This fact has been recently reported by us in a previous communication[22]. In order to provide more insight on the scope of this selective and stereospecific reaction, we undertook a more extensive study whose results we describe in this paper.

RESULTS AND DISCUSSIONS

The starting materials were obtained according to the procedures reported[20,23,24]. The standard procedure can be described as follows: the starting materials **1-12** were dissolved in dioxane, TMPAP was added in

excess (1:1.5) and the reaction mixture was stirred at room temperature until starting material had disappeared. Ether was added to precipitate the excess reagent, the reaction was then filtered, and the solvent evaporated under reduced pressure to furnish the bromo derivatives **13-24** (Scheme 1).

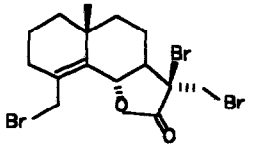


Scheme 1

The bromination of compounds **1-9** has been shown to be stereospecific, giving exclusively 11ß,13-dibromocyclocostunolide derivatives in about 75% yield, except for compounds **16-18** which do not possess substituents at C-1 and were obtained in lower yield. The shift to lower field of the H-6 signals (0.4 ppm) with respect to those for the same proton in the starting compounds indicated a β-orientation for the bromine

atom at C-11. The stereochemistry at carbons C-1, C-11 and C-13 has previously been established by us[20]

From α and ß-cyclocostunolide (**4,5**) were obtained, in addition to the dibromo derivatives derived from the conjugated double bond, the compounds **25-27** which result from bromine addition to the other double bond present in the molecule. The formation of these compounds can be explained by means of an electrophilic addition of bromine, assuming that the Br_3^- species disproportionate to Br_2 and Br^- [25]. Furthermore, it is worth noting that the functionalization on C-1 (R= Br, OH), exerts a protecting effect on double bonds $\Delta^{4,14}$, $\Delta^{3,4}$, $\Delta^{4,5}$, which prevents the double bond of the ring A of the electrophilic addition. The protecting effect on a double bond by the proximity of an electronegative group has been observed by some of us on gibberellic acid and related structures[7].



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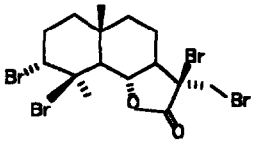

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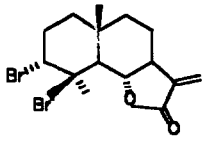

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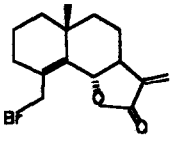

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The absence of this protecting effect would produce a loss of selectivity by increasing the amount of addition compounds arising from the electrophilic attack. With the aim to study this possibility, which would constitute a limitation for the synthetic utility of this reaction, R-(-) carvone (**11**) was selected as substrate. When **11** was treated with TMPAP the compounds **23** (11%),**28** (13%) and **29** (72%) were obtained. Compound **23** was characterized as 2R,3R-dibromo-2,3-dihydro-5S-carvone, thus demonstrating that stereospecificity of the nucleophilic addition is preserved. The orientation of the bromine atoms in the compound **23** was inferred from the small coupling constants for the signal of H-3 (J=2.8 and 3.4 Hz), and the deshielding effect produced on the chemical shift of H-5 (3.10 ppm) and β-H-6 (3.26 ppm).

These results show that the absence of a protecting effect produced by the proximity of an electronegative group increases the amount of addition compounds arising from electrophilic attack. In an attempt to reduce the formation of these undesired compounds, we thought that an alkene added to the reaction medium can act as a trapping agent of the bromine. Thus, when reaction was carried out with carvone:1-hexene (1:2 mmol) in 1,4-dioxane (6 ml), compounds **23**, **28** and **29** were obtained in 26, 52 and 7% respectively. Under these conditions, the amount of the compound **29**, resulting from exclusive electrophilic addition is effectively reduced, but the tetrabromide **28** is obtained in higher ratio. This fact could be explained

if we take into account that the dissociation of perbromide reagents to give free Br_2 is influenced by the aprotic solvent polarity[25]. Thus, small differences in the ratio 1,4-dioxane:1-hexene produce changes in the ratio of the bromo adducts (see experimental).

The above results indicate that the selectivity in the addition to the electron deficient double bond should be increased by controlling the ratio substrate/alkene in each particular case.

In order to know the reactivity of Br_3^- species with electron-deficient double bonds possessing an additional conjugation to an aromatic ring, umbelliferone (**10**) and the furanic derivative **12** were treated with TMPAP following the general procedure. Under these conditions the compounds **22** and **24** were obtained and their formation can be rationalized as bromination reaction followed by dehydrobromination. All attempts to detect the dibromide intermediate were unsuccessful. The fact that the same compounds are also obtained by the addition of Br_2 in CCl_4 indicate that an electrophilic mechanism can not be ruled out.

The competing mechanistic pathways in the bromination reaction with molecular bromine and tribromide complex has extensively been studied by Bellucci et al.[25-26]. These authors showed that, the TMPAP was the only brominating agent[25]. However this reaction is influenced by the solvent polarity and the formation of Br_3^- species in reactions of bromine addition to α,β-unsaturated aldehyde catalyzed by acid has been reported[21].

To exclude the possibility that Br_2 could form Br_3^- in situ and give the same reaction as TMPAP, we carried out reaction of compounds **1-5** (Scheme 2) with Br_2/CCl_4 and Br_2/dioxane. In these instances, with R= Br, no reaction was observed and starting material was recovered. With R= H we obtained compounds **30** and **27**. The formation of **30** can be explained by electrophilic bromination followed by dehydrobromination.

These results indicated that the Br_3^- anion must be responsible of the bromination on an unsaturated carbonyl group under the conditions of this investigation. In order to confirm this aspect, perbromide was generated following the reported method[26]. So, when compounds **1-5** were treated with a solution of equimolar amounts of Br_2 and tetrabutylammonium bromide in 1,2-dichloroetane, compounds (R= Br, **13-15**), (R=H, **16**, **17** and **25,26**), were obtained.

The above results show that reaction of TMPAP with double bonds conjugated with a carbonyl group is an intriguing reaction which involves stereospecific addition of bromine and can be explained as a nucleophilic 1,2 addition of bromine via initial attack of Br_3^- at the β carbon.[25]

Two routes may be proposed to explain the stereospecific bromination reaction. Route "a" implies a cyclic intermediate where Br_3^- is located on the ß face of the lactone ring.

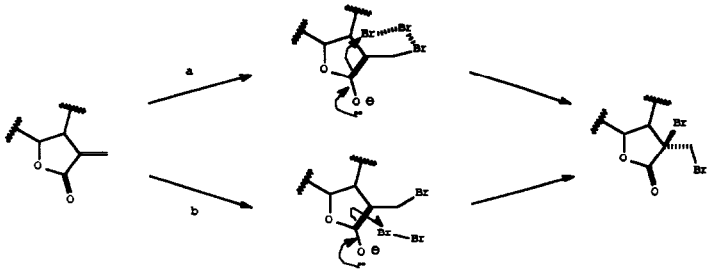
Route "b" involves nucleophilic attack of Br_3^- to the $\Delta^{11,13}$ double bond. The resulting bromoenolate can be captured by bromine to give the corresponding dibromide derivative.

In order to obtain information which would permit us to decide between these possibilities, the mixed perhalide $(IBr_2)^-$ $(NBu_4)^+$ was prepared[27]. If we assume that the trihalide ion XY_2^- has a structure in which the halogen with higher atomic number is the central atom[27], then the reaction of this perhalide with an α-methylene-γ-lactone might decide between the two proposed routes.

When compound **1** was treated with $(IBr_2)^-$ $(NBu_4)^+$ in either 1,4-dioxane or bromoethane compound **13** (60%) together with recovered starting material was obtained. Attempts to obtain derivatives with a substituent other than Br on C-11 were unsuccessful.

The experimental facts mentioned above can be accommodated by the mechanism shown in scheme 2, route"a", which involves a nucleophilic 1,2 addition of bromine, via a cyclic intermediate in which

the chemoselectivity is induced by Br_3^- situated on the ß face of the lactone ring.



Scheme 2

EXPERIMENTAL SECTION

Infrared spectra were determinated with a Perkin-Elmer 881 spectrometer. Proton NMR spectra were made on a Varian Gemini XL-200 or a Varian Unity-400 using $SiMe_4$ as internal reference. Mass spectra were recorded on a VG12.250 spectrometer using 70 eV. Thin layer chromatography was done on MN Alugran SIL G/UV 254 plates, 0.25 mm thick. Merck silica gel was used for column chromatography.

General Procedure for Bromination with TMPAP. The starting material was dissolved in 1,4-dioxane, TMPAP was added in excess (1:1.5) and the reaction mixture was stirred at room temperature until the starting material had disappeared. Diethyl ether was added to precipitate the unreacted TMPAP, the reaction was then filtered and the solvent evaporated under reduced pressure to furnish the dibromo derivative.

1β,11β,13-tribromo-β-cyclocostunolide (13). Compound **1** (0.64 mmol) dissolved in 20 ml of 1,4-dioxane was subjected to bromination with 0.96 mmol of TMPAP as described in the general procedure, yielding 0.50 mmol (78%) of **13**[20].

1ß,11ß,13-tribromo-α-cyclocostunolide (14). According to the procedure above described 0.64 mmol of **2** afforded 0.45 mmol (71%) of **14**[20].

1β,11β,13-tribromoarbusculin B (15). Following the same procedure 0.64 mmol of **3** afforded 0.43 mmol (67%) of **15**: oil; **IR** (cm^{-1}, film) 2965,1786; **^{1}H-NMR** (200 MHz, $CDCl_3$) δ 4.79 (bd, 1H, J=11.5 Hz, H-6), 4.12 (dd, 1H, J=10.5, 4.1 Hz, H-1), 4.08 (d, 1H, J=10.7 Hz, H-13), 3.76 (d, 1H, J=10.7 Hz, H-13'), 1.78 (bs, 3H, H-14), 1.22 (s, 3H, H-15); **EIMS** *m/z* (70 Ev) 393:391:389, 311:309, 231, 216. **Anal.** Cald for $C_{15}H_{19}O_2Br_3$: C, 38.49, H, 4.05; found C, 38.51, H, 4.07.

Bromination of ß-cyclocostunolide (4). Compound **4** (0.5 mmol) was subjected to bromination as described in the general procedure yielding 0.26 mmol (52%) of **16**[20] and 0.08 mmol (16%) of 11β, 13,14-tribromoarbusculin B (**25**)[20].

Bromination of α-cyclocostunolide (5). Compound **5** (0.5 mmol) dissolved in 20 ml of 1,4-dioxane was subjected to bromination as described in the general procedure yielding 0.14 mmol (28%) of 11β,13-dibromo-α-cyclocostunolide (**17**), 0.1 mmol (20%) of 3α,4β,11β,13-tetrabromocyclocostunolide (**26**) and 0.06 mmol (12%) of 3α,4β-dibromocyclocostunolide (**27**). 11ß,13-dibromo-α-cyclocostunolide (**17**): oil; **IR** (cm^{-1},

film) 2930, 1782; **^{1}H-NMR** (200 MHz, $CDCl_3$) ∂ 5.33 (bs, 1H, H-3), 4.16 (t, 1H, J=10.0 Hz, H-6), 4.10 (d, 1H, J=10.7 Hz, H-13), 3.77 (d, 1H, J=10.0 Hz, H-13'), 1.70 (bs, 3H, H-14), 0.86 (s, 3H, H-15); **EIMS** *m/z* (70 Ev) 394:392:390, 377, 311, 232. **Anal.** Calcd for $C_{15}H_{20}O_2Br_2$ C, 45.9; H, 5.10; Found C, 46.1, H, 5.22. 3α,4ß,11ß,13-tetrabromocyclocostunolide (**26**): gum; **IR** (cm^{-1}, film) 1785, 2933, 2861; **^{1}H-NMR** (200 MHz, $CDCl_3$) ∂ 4.70 (bs, 1H, H-3), 4.43 (t, 1H, J=9.4 Hz, H-6), 4.09 (d, 1H, J=10.9 Hz, H-13), 3.75 (d, 1H, J=10.9 Hz, H-13'), 2.00 (s, 3H, H-14), 1.23 (s, 3H, H-15); **EIMS** *m/z* (70 Ev) 475:473:471:469, 393:391:389, 311:309. 231; **Anal.** Cald for $C_{15}H_{20}O_2Br_4$: C, 32.86, H, 3.68; Found C, 32.92; H, 3.72. 3α,4ß-dibromocyclocostunolide (**27**): oil; **IR** (cm^{-1}, film) 2933, 2864, 1760; **^{1}H-NMR** (200 MHz, $CDCl_3$) ∂ 6.01 (d, 1H, J=3.2 Hz, H-13), 5.34 (d, 1H, J=3.2 Hz, H-13'), 4.70 (bs, 1H, H-3), 4.06 (t, 1H, J=10.6 Hz, H-6), 2.61 (m, 2H, H-5 and H-7), 2.09 (s, 3H, H-15), 1.20 (s, 3H, H-14); **EIMS** *m/z* (70Ev) 313:311; 231; **Anal.** Cald for $C_{15}H_{20}O_2Br_2$: C, 45.9, H, 5.10; Found C, 45.81; H, 5.07.

Bromination of arbusculin B (6). Compound **6** (0.18 mmol) was subjected to the treatment described in the general procedure yielding 0.08 mmol of **18** (43%). 11ß,13-Dibromoarbusculin B (**18**): oil; **IR** (cm^{-1}, film) 2932, 2870, 1783; **^{1}H-NMR** (200 MHz, $CDCl_3$) ∂ 4.81 (d, 1H, J=10.3 Hz, H-6), 4.11 (d, 1H, J=11.0 Hz, H-13), 3.77 (d, 1H, J=11.0 Hz, H-13'), 1.78 (s, 3H, H-14), 1.08 (s, 3H, H-15); **EIMS** *m/z* (70 eV) 394:392:290, 313:311, 231. **Anal.** Calcd. for $C_{15}H_{20}O_2Br_2$: C,45.9, H, 5.10; Found C, 46.11 H, 5.20.

Bromination of reinosin (7). Compound **19** (0.08 mmol) was obtained from **7** (0.10 mmol, 80%) following the same procedure. 11β,13-dibromoreinosin (**19**): oil, **IR** (cm^{-1}, film) 3526, 1772; **^{1}H-NMR** (200 MHz, $CDCl_3$) ∂ 5.00 (s, 1H, H-14), 4.83 (s, 1H, H-14'), 4.39 (t, 1H, J=10.4 Hz, H-6), 4.15 (d, 1H, J=10.8 Hz, H-13); 3.83 (d, 1H, J=10.8 Hz, H-13'), 3.52 (dd, 1H, J=11.5, 4.6 Hz, H-1), 0.83 (s, 3H, H-15); **EIMS** *m/z* (70 Ev) 410:408:406, 329:327, 311:309, 247, 231; **Anal.** Calcd for $C_{15}H_{29}O_3Br_2$: C, 44.34, H, 4.96; Found C, 44.11, II, 5.10.

Bromination of santamarin (8). Santamarin (**8**, 0.12 mmol) was subjected to the treatment described in the general procedure yielding 0.09 mmol of **20** (75%). 11ß,13-dibromosantamarin (**20**): oil, **IR** (cm^{-1}, film) 3384, 1769; **^{1}H-NMR** (200 MHz, $CDCl_3$) ∂ 5.40 (bs, 1H, H-3), 4.20 (d, 1H, J=10.7 Hz, H-13), 4.00 (t, 1H, J=9.5 Hz, H-6), 3.85 (d, 1H, J=10.7 Hz, H-13'), 3.48 (dd, 1H, J=11.5, 4.6 Hz, H-1), 1.97 (bs, 3H, H-14), 0.95 (s, 3H, H-15); **EIMS** *m/z* (70 eV) 410:408:406; **Anal.** Calcd for $C_{15}H_{20}O_3Br_2$: C, 44.34, H, 4.96; Found C,44.24; II, 4.87.

Bromination of arbusculin A (9). Arbusculin A (**9**, 0.9 mmol) was subjected to the treatment described in the generall procedure yielding **21** (0.72 mmol, 85%)[20].

Bromination of umbelliferone (10). Umbelliferone (**10**, 1mmol) dissolved in 20 ml of 1,4-dioxane was treated with 1.5 mmol of TMPAP as described in the general procedure yielding **22** (68%)[28].

2R-3R-dibromo-2,3-dihydro-5S-carvone (23). a) The starting material (**11**) dissolved in 10 ml of 1,4-dioxane was subjected to bromination as described in the general procedure. **11** (1 mmol) afforded 0.11 mmol of **23** (11%) together with a mixture of the diasteroisomers **28** and **29**.

b) To 0.33 mmol of **11** and 0.66 mmol of 1-hexene dissolved in 3 ml of 1,4-dioxane, 0.5 mmol of TMPAP were added and the mixture was stirred for 10 min at room temperature. Ether was added to precipitate the unreacted TMPAP, the reaction mixture was filtered and the solvent removed. The crude obtained was purified by HPLC (hexane:EtOAC, 97:3) yielding **23** (28%), **28** (17%), **29** (17%).

c) Compound **11** (0.33 mol) and of 1-hexene (0.66 mmol) dissolved in 6 ml of 1,4-dioxane were subjected

to the procedure described in part b, affording **23** (26%), **28** (52%), **29** (7%) and starting material (15%). 2R-3R-dibromo-2,3-dihydro-5S-carvone (**23**): oil; **IR** (cm^{-1}, KBr) 1722, 1436, 1380, 1107, 896; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 4.85 (bs, 1H, H-9), 4.81 (bs, 1H, H-9'), 4.82 (dd, 1H, $J_{3-4\beta}$=2.8 and $J_{3-4\alpha}$=3.4 Hz, H-3), 3.26 (dd, 1H, $J_{6\beta-5}$=13.3 and $J_{6\beta-6\alpha}$=14.5 Hz, H-6β), 3.10 (dddd, 1H, $J_{5-6\alpha}$=4.3, $J_{5-6\beta}$=13.3, $J_{5-4\alpha}$=3.2 and $J_{5-4\beta}$=12.1 Hz, H-5), 2.84 (ddd, 1H, $J_{4\beta-3}$=2.8, $J_{4\beta-4\alpha}$=14.8, $J_{4\beta-5}$=12.2 Hz, H-4β), 2.47 (ddd, 1H, $J_{6\alpha-6\beta}$=14.5, $J_{6\alpha-5}$=4.3 and $J_{6\alpha-4\alpha}$=2.1 Hz, H-6α), 2.21 (dddd, 1H, $J_{4\alpha-4\beta}$=14.8, $J_{4\alpha-5}$=3.2, $J_{4\alpha-3}$=3.4 and $J_{4\alpha-6\alpha}$=2.1 Hz, H-4α), 1.98 (s, 3H, H-10), 1.77 (s, 3H, H-7); **EIMS** *m/z* (70 Ev) 312:310:308, 231:229, 135:133, 121, 107, 97.

2-Bromo-3-(2-furyl)acrolein (24). **24** was prepared from **12**, the procedure differing slightly from the general above since the starting material descompose quickly, 1 mmol of **12** dissolved in 10 ml of 1,4-dioxane, was stirred at 6°C with 1.5 mmol of TMPAP yielding 0.04 mmol (4%) of **2-bromo-3-(2-furyl)acrolein (24)**: **mp** 78-80° C; **IR** (cm^{-1}, KBr) 2978, 1680, 1604, 1466, 1160, 1023; **^{1}H-NMR** (400 Mz, $CDCl_3$) δ 9.26 (s, 1H, H-1), 7.83 (bs, 1H, H-4'), 7.65 (m, 1H, H-3), 7.62 (d, J=3.7 Hz, H-2'), 6.65 (m, 1H, H-3'); **EIMS** *m/z* (70 Ev) 202:200, 174:172, 145:143, 121, 68, 65.

General procedure for bromination with Br_2/CCl_4. To the starting material dissolved in CCl_4, an equimolar amount of Br_2 in CCl_4 was added and the reaction mixture was stirred for 30 min at room temperature. The reaction was then quenched by addition of a solution of 1 M sodium thiosulfate. The organic layer was washed with brine, dried over anhydrous Na_2SO_4 and the solvent removed by distillation under reduced pressure. When compounds **1**, **2** and **3** were separately subjected to these conditions, no reaction was observed and starting material was recovered.

Bromination of β-cyclocostunolide (4) and α-cyclocostunolide (5) with Br_2/CCl_4. Compounds **30** (0.30 mmol, 47%) and **27** (0.20 mmol, 31%) were obtained from **4** (0.64 mmol) and **5** (0.64 mmol), respectively, as described in the general procedure. 14-Bromoarbusculin B (**30**): oil, **IR** (cm^{-1}, film) 2940, 1759; **^{1}H-NMR** (200 MHz, $CDCl_3$) δ 6.03 (d, 1H, J=3.2 Hz, H-13), 5.38 (d, 1H, J=3.2 Hz, H-13'), 4.90 (d, 1H, J=9.0 Hz, H-6), 4.30 (d, 1H, J=9.5 Hz, H-14). 4.07 (d, 1H, J=9.5 Hz, H-14'), 1.16 (s, 3H, H-15). **EIMS** *m/z* (70 Ev) 312:310, 231.

Treatment of compounds 1-5 with tetrabutylammomiun tribromide. In a standard experiment, to 0.5 mmol of Br_2 in 20 ml of 1,2-dichloroethane, 0.5 mmol of tetrabutylammomiun bromide were added. This solution (9 ml) was dripped into solutions of 0.16 mmol of compounds **1-5** dissolved, separately, in 29 ml of 1,4-dioxane. The reaction mixtures were stirred for 6 h and ethyl ether was added. After removal of the solvent, the crude was purified by column chromatography yielding the results previously obtained with TMPAP (compounds **13**, **14**, **15**, **16**, **17**, **25** and **26**, respectively).

Treatment of 1β-bromo-α-cyclocostunolide (2) with $(IBr_2)^-$ $(NBu_4)^+$. 0.5 mmol of Br_2 in 15 ml of 1,4-dioxane were added to 0.6 mmol of tetrabutylammoniun iodide dissolved in 15 ml of 1,4-dioxane. This solution was slowly added to 0.16 mmol of **2** dissolved in 10 ml of 1,4-dioxane and the reaction mixture was stirred at room temperature for 6 h, then ethyl ether was added. The reaction mixture was filtered and the solvent removed. After purification by columm chromatography 0.10 mmol (60%) of **13** was obtained together with 0.06 mmol of starting material.

ACKNOWLEDGEMENTS

This research was supported by grants fron DGICYT PB 88-0570 and CICYT AGR91-1021 and by fellowship (to MSA) fron Junta Andalucia (Spain).

REFERENCES AND NOTES

1. Trombridge P. F.; Diehl O.C.; *J. Amer. Chem. Soc.* **1897**, *19*, 558.
2. Marquet, A,; Jacques, J.; Tchoubar, B.; *Bull. Soc. Chim. France* **1965**, 511-518.
3. Marquet, A.; Jacques, J.; *Bull. Soc. Chim. France* **1962**, 90-96.
4. Awang, D.V.C.; Wolfe, S.; *Can. J. Chem.* **1969**, *47*, 706-709.
5. Armstrong V.W.; Chishti, N.H.; Ramage R.; *Tetrahedron Lett.* **1975**, 373-376.
6. Frechet, J.M.J.; Farrall, M.J.; Nuyens, L.J.; *J. Macromol. Sci. Chem.* **1977**, *A11*, 507-514.
7. Merkushev, E.B.; Simakhina N.D.; Koveshnikova, G.M.; *Synthesis* **1980**, 486-487.
8. Stanovnik, B.; Tisler, M.; Drnovsek, I.; *Synthesis* **1981**, 987-989.
9. Johar, Y.; Zupan, M.; Sket, B.; *J. Chem. Soc. Perkin Trans. I* **1982**, 2059-2062.
10. Akelah, A.; Hassanein, M.; *Eur. Polym. J.* **1984**, *20*, 221-223.
11. Arrieta, A.; Gamboa, I.; Palomo, C.; *Synth. Commun.* **1984**, *14*, 939-945.
12. Kajigaeshi, S.; Murakawa, K.; Asano, K.; Fujisaki, S.; *J. Chem. Soc. Perkin Trans. I* **1989**, 1702-1703.
13. Marquet, A.; Jacques, J.; *Tetrahedron Lett.* **1959**, 24-26.
14. Marquet, A.; Dvolaitzky, M.; Kagan, H.B.; Mamlok, L.; Ouannes C.; Jacques, J.; *Bull.Soc. Chim. France* **1961**, 1822-1831.
15. Husstedt, U.; Schäfer, H.J.; *Tetrahedron Lett.* **1981**, *22*, 623-624.
16. Devanathan, V.C.; Bhagan, V.U.; Arumugan, N.; *Indian J. Chem.* **1983**, *22B*, 766-770.
17. Omuaru, V.O.T.; Whalley, W. B.; *Indian J. Chem.* **1988**, *27B*, 1041-1042.
18. Dauben, W. G.; Warshawsky, A. M.; *Synth. Commun.*, **1988**, *18*, 1323-1326.
19. Collado, I. G.; Fraga, B. M.; Hanson, J. R.; Hitchcock, P. B.; Tellado, F.G*J.; Chem. Soc. Perkin Trans. I* **1988**, 105-107.
20. Collado, I.G.; Madero, J.G.; Massanet, G.M.; Luis, F.R. *Tetrahedron Lett.* **1990**, *31*, 563-566. I.G. Collado, I.G.; Madero, J.G.; Massanet, G.M.; Luis, F.R. *J. Org. Chem.* **1991**, *56*, 3587-3591.
21. De la Mare , P.B.D.; Robertson, P.W.J. *J. Chem. Soc* **1945**, 888-891.
22. Collado, I.G.; Massanet, G.M.; Alonso, M.S. *Tetrahedron Lett.* **1991**, *32*, 3217-3220.
23. Tikam, C. J.; John E. Mc.; *Tetrahedron Lett.* **1969**, 2917-2919.
24. Pathak, S.P.; Bapat, B.V.; Kulkarni, G.H.; *Indian J. Chem.* **1970**, *8*, 471.
25. Bellucci, G.; Bianchini, R.; Ambrosetti, R.; Ingrosso, G. *J. Org. Chem.* **1985**, *50*, 3313-3318.
26. Bellucci, G.; Bianchini, R.; Chiappe, C.; Ambrosetti, R.; *J. Am. Chem. Soc.* **1989**, *111*, 199-202.
27. Bailar,Jr., J. C.; Emeléus, H. J.; Nyholm, R.; Trotman-Dickenson, A. F. *Comprehensive Inorganic Chemistry*. Ed. Pergamon Press Ltd., **1975**, Vol. 2, p. 1535.
28. Abu-Mustafa, E.A.; Fayez M.B.E. *J. Org. Chem.* **1961**, *26*, 161-166.

(*Received in UK* 11 *February* 1994; *revised* 23 *March* 1994; *accepted* 25 *March* 1994)