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Cationic Rearrangements of an *endo*-Cyclopropyl Methanol System Incorporated in a Benzonorbornadiene System

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Chloride **18** (47%) and alcohol **21** (44%) were isolated from the reaction of alcohol **20** with $SOCl_2$. Cyclopropylcarbinyl – cyclopropylcarbinyl rearrangement leads to chloride **22,** which hydrolyses on separation to give alcohol **21**. Chloride **18** results from cyclopropyl – allylcarbinyl rearrangement, followed by a 1,2 – aryl shift (sequential rearrangement). Syntheses of compounds **23** and **24** support the structures. The behaviour of **20** differs from that of *exo* isomer **14**, probably due to the nature of the intermediates in these reactions.

Key Words: Alcohols, Benzohomonorbornadiene, Halogenation, Rearrangement, Thionyl chloride.

Introduction

Benzonorbornadiene and its derivatives afford the possibility of several mechanistically interesting investigations. These compounds are intriguing for di-π-methane rearrangement[1−3], solvolytic reactivity[4−6] and versatile transformations[7−11]. Depending on the reaction conditions, strained systems such as cyclopropane, benzonorbornadiene, benzobarrelene, benzohomonorbornadiene and benzohomobarralene systems are most likely to undergo rearrangements[12−16].

The transformation of cyclopropyl methanols such as **11** (Scheme 1) into homoallylic halides[17−20] is a useful reaction, and has received considerable attention. The interesting feature of this system is that the formed cyclopropyl cation can rearrange to another cyclopropyl cation. Labelling experiments have demonstrated such rearrangements. As shown in Scheme 1, the transformation of intermediates **1**, **3** and **5** into intermediates **2**, **4** and **6** takes place in their reactions [21−25]. However, the stereochemistry of the cyclopropyl cations such as **3** is important. The *endo*-isomer is rearranged to a secondary cyclopropyl cation, whereas the *exo*-isomer is not (Scheme 1)[23].

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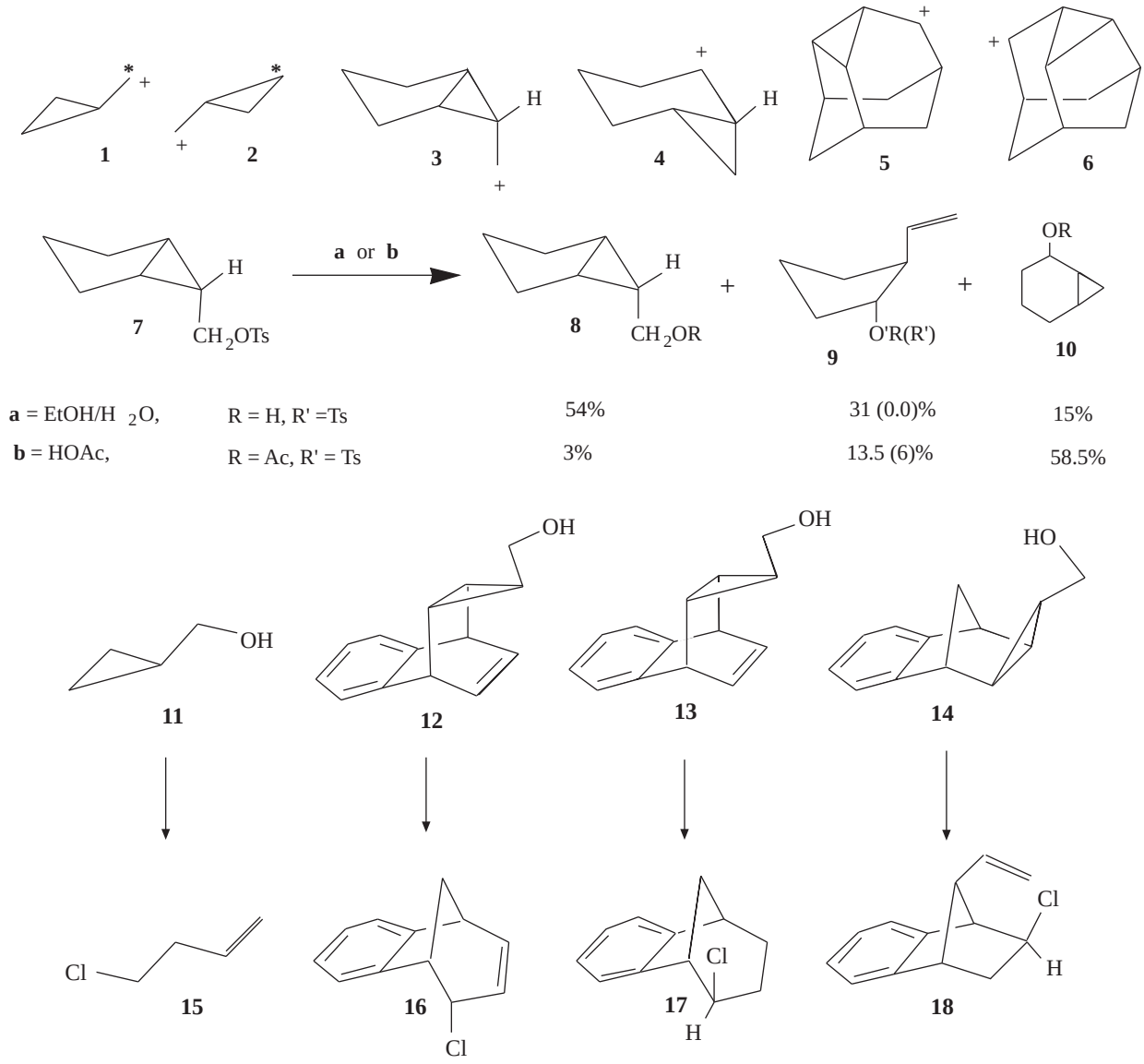


Scheme 1

Recently we investigated the reactivity and the tendency for the rearrangement of some cyclopropyl methanol functional groups incorporated into the benzobarrelene and benzonorbornadiene skeletons. For example, reactions **12, 13** and **14** with thionyl chloride gave chlorides **16**, **17** and **18,** respectively, as major products (Scheme 1)[12−14]. The formation of chlorides **16**, **17** and **18** occurred by sequential rearrangements[12−14]. The sequential rearrangements start by the opening of the cyclopropane ring followed by a rearrangement of the benzobarrelene skeleton. The reaction of **14** with thionyl chloride gave the isomerised product **18**.

This paper concerns the synthesis of alcohol **20**, that is the endo-isomer of **14,** and its reaction with thionyl chloride. We describe the synthesis of **20** and its chemical transformations.

Experimental

General Method: All chemicals and solvents are commercially available and were used after distillation or treatment with drying agents. Melting points were determined on a Thomas-Hoover capillary melting apparatus. IR spectra were obtained from solutions in 0.1 mm cells with a Perkin-Elmer spectrophotometer. The ^{1}H- and ^{13}C- NMR spectra were recorded on a 200 (50)-MHz Varian spectrometer; δ in ppm, Me_4Si as the internal standard. Mass spectra were determined by VG ZabSpec, range 1000 EI, 10,000 for HRMS. Elemental analyses were performed on a Carlo Erba 1106 apparatus. All column chromatography was performed on silica gel (60-mesh, Merck). PLC is preparative thick-layer chromatography: 1 mm of silica gel 60 PF (Merck) on glass plates.

Reduction of 19 with $LiAlH_4$

To a stirred solution of **19**[26,27] (0.8 g, 3.51 mmol) in dry tetrahydrofuran (THF) (40 mL) was added $LiAlH_4$ (0.3 g, 9.98 mmol) in portions over a period of 45 min at 0 °C. After stirring at the same temperature for 1 h, the cold bath was removed and the mixture was stirred at room temperature for 20 h. The grey mixture was returned to 0 °C, and hydrolysed by the addition of methanol and water (1:1). The mixture was filtered (inorganic salts) and the solvent evaporated. The residue was cooled to 0 °C and $CHCl_3$ added (50 mL). The solution was washed with a solution of NH_4Cl (5%, 20 mL) and water (20 mL), dried over Na_2SO_4 and the solvent evaporated to leave alcohol **20** (555 mg, 85%) as a colourless viscous liquid.

1R(S),8S(R),9S(R),11R(S),Endo-10-hydroxymethyltetracyclo[6.3.1.0^{2,7}.0^{9,11}]dodeca-2,4,6-triene (**20**): IR ($CHCl_3$): $\overline{\nu}$ = 3284, 2996, 1706, 1446, 1290, 1246, 1164, 1088, 1020, 960, 933, 881, 761, 725, 677, 645, 537 cm^{-1}. ^{1}H-NMR (200 MHz-$CDCl_3$): δ = 7.25-7.21 (2 H arom., AA′ part of AA′BB′ system), 7.05-7.01 (2 H arom., BB′ part of AA′BB′ system), 4.10 (d, J = 5.98 Hz, 2 H, CH_2OH), 3.45 (bs, 2 H, 1-H, 8-H), 2.75 (m, 1 H, OH), 1.76 (tt, J = 5.98, $J_{9,10} = J_{10,11}$ = 7.69 Hz, 1 H, 10-H), 1.40 (bs, 2 H, 12-H), 1.23 (d,$J_{9,10} = J_{10,11}$ = 7.69 Hz, 2 H, 9-H, 11-H). ^{13}C-NMR (50 MHz, $CDCl_3$): δ = 154.0, 126.7, 122.7, 62.9, 45.6, 43.2, 40.0, 29.7. Anal. Calc. For $C_{13}H_{14}O$: C 83.83, H 7.58; found: C 83.79, H 7.60.

Reaction of alcohol 20 with $SOCl_2$

A stirred solution of alcohol **20** (0.67 g 9, 3.56 mmol) in 10 mL of $CHCl_3$ was cooled to - 10 ± 5 °C and treated dropwise with a solution of $SOCl_2$ (5 mL) in 20 mL of $CHCl_3$ for 30 min. Gas evolution was observed. After the addition was completed, the reaction mixture was allowed to warm to room temperature. After stirring for 1 day, the solvent and excess $SOCl_2$ were removed by evaporation. The residue was submitted to PLC with ethyl acetate/hexane (5/95). Chloride **18**[14] (345 mg, 47%) and alcohol **21** (325 mg, 44%) were isolated in pure form.

1S(R),8S(R),9R(S),11R(S),12R(S)-12-Hydroxytetracyclo[6.4.1.0^{2,7}.0^{9,11}]trideca-2,4,6-triene (**21**): Colourless crystal from $CHCl_3$/hexane. IR ($CHCl_3$): $\overline{\nu}$ = 3948, 3846, 3693, 3412, 3106, 3004, 2927, 2391, 1448, 1293, 1217, 1114, 1038, 910, 757 cm^{-1}. ^{1}H-NMR (200 MHz-$CDCl_3$): δ = 7.32-7.13 (m, 4 H arom.), 4.14 (bd, $J_{11,12}$ = 7.20 Hz, 1 H, 12-H), 3.25 (dd, J = 3.94, J = 3.59 Hz, 1 H, 8-H), 3.00 (dd, $J_{1,13syn}$ = 4.66, J = 2.30 Hz, 1 H, 1-H), 1.90 (d, $J_{13anti,13syn}$ = 11.72 Hz, 1 H, 13-H$_{anti}$, A part of AB system), 1.86 (s, 1 H, OH), 1.81 (dt, $J_{13anti,13syn}$ = 11.72, $J_{1,13syn}$ = 4.66 Hz, 13-H$_{syn}$, B part of AB

system), 1.32-1.20 (m, 1 H, 9-H), 1.09-0.93 (m, 2 H), 0.64-0.51 (m, 1 H). ^{13}C-NMR (50 MHz, $CDCl_3$): δ = 153.0, 145.6, 128.9, 128.4, 126.1, 123.9, 68.4, 44.5, 41.0, 32.1, 22.1, 15.4, 9.0. HRMS: found 186.104469, calc. for $C_{13}H_{14}O$ 186.104465.

Reduction of chloride 18

Chloride **18** (393 mg, 1.92 mmol) and $HOBu^t$ (1.0 g, 13.6 mmol) were dissolved in dry ether (25 mL). Excess metallic Na (850 mg, 37 mmol), in small pieces, was added over a period of 10 min. After stirring at room temperature for 1 day, unreacted Na and solid $KOBu^t$ were removed by filtration and washed with ether (2 x 30 mL). The solution was poured into water (100 mL) and the mixture formed was shaken. The organic layer was separated, and the water layer was extracted with ether (2 x 30 mL). The combined organic layer was washed with water (20 mL), dried over $CaCl_2$ and then the solvent was evaporated. The product **23** was obtained as a colourless liquid (264 mg, 75%).

1R(S),8S(R)-anti-11-vinyltricyclo[6.2.1.0^{2,7}]unadeca-2,4,6-triene (**23**): IR ($CHCl_3$): $\bar{\nu}$ = 3080, 2978, 2902, 1931, 1906, 1855, 1804, 1651, 1472, 1421, 1293, 1191, 1165, 1114, 1038, 987, 936, 859, 757 cm^{-1}. ^{1}H-NMR (200 MHz-$CDCl_3$): δ = 7.22-7.10 (m, 4 H, arom.), 5.87 (ddd, J_{trans} = 17.28, J_{cis} = 10.32, J = 6.98 Hz, 1 H, H-C=CH_2), 5.22 (dd, J_{trans} = 17.28, J_{gem} = 1.08 Hz, 1 H, (E)-H of CH=CH_2), 5.14 (dd, J_{cis} = 10.32, J_{gem} = 1.08 Hz, 1 H, (Z)-H of CH=CH_2), 3.27 (bd, J = 1.83 Hz, 2 H, H-1, H-8), 2.65 (bd, J = 6.98 Hz, bridge, 1 H, H-11), 2.07 (m, 2 H, H-9, H-10), 1.30-1.22 (m, 2 H, H-9, H-10). ^{13}C-NMR (50 MHz, $CDCl_3$): δ = 150.3, 139.3, 127.5, 122.5, 118.3, 64.7, 49.6, 26.5. Anal. Calc. For $C_{13}H_{14}$: C 91.71, H 8.29; found: C 91.74, H 8.27.

Reduction of the mixture of chloride 18 and 22

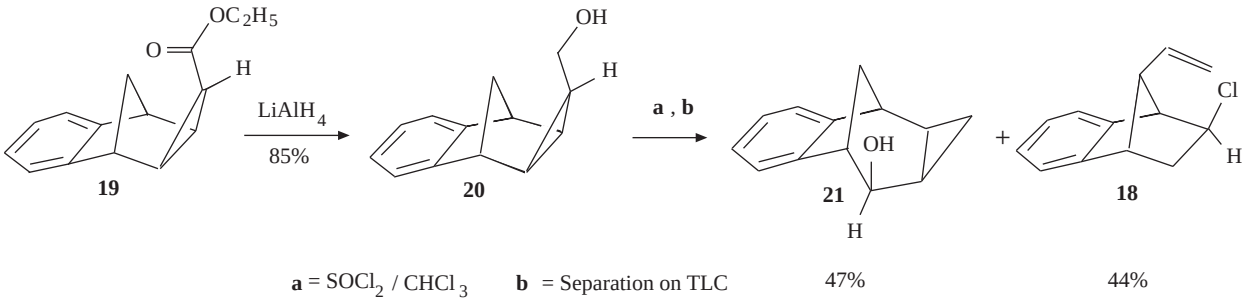
A mixture (308 mg, 1.51 mmol) of chloride **18** and **22** (393 mg, 1.92 mmol) was dissolved in dry ether (30 mL). After adding $HOBu^t$ (1.0 g, 13.6 mmol), excess metallic Na (80 mg, 35 mmol), in small pieces, was added over a period of 15 min. The mixture was stirred at room temperature for 27 h. The other parts of the reaction were studied in the same manner as that of chloride **18**. Compounds **23** and **24** could not be isolated from the corresponding mixture. The mixture of compounds **23** and **24** was obtained as liquid (175 mg, 73%). It was observed that compounds **23** and **24** are present in their NMR spectra, and their ratio is approximately 1:1. The peaks of compound **23** were eliminated from the spectra of the mixture (**23** and **24**), and peaks of the compound **24** were determined in it.

1R(S),8R(S),9R(S),11R(S)-Tetracyclo[6.4.1.0^{2,7}.0^{9,11}]trideca-2,4,6-triene (**24**): ^{1}H-NMR (200 MHz-$CDCl_3$): δ = 7.33-7.08 (m, 4 H, arom.), 3.31-3.01 (m, 1 H, H-1, or H-8), 3.00-2.95 (m, 1 H, H-1, or H-8), 2.02-1.92 (m, 3 H), 1.73 (d, $J_{13anti,13syn}$ = 12.00 Hz, 1 H, 13-H$_{anti}$, A part of AB system), 1.14-1.08 (m, 1 H), 0.68-0.56 (m, 3 H). ^{13}C-NMR (50 MHz, $CDCl_3$): δ = 152.4, 149.0, 128.4, 127.6, 125.2, 123.4, 41.4, 41.2, 37.2, 30.1, 19.9, 13.5, 7.2.

Results and Discussion

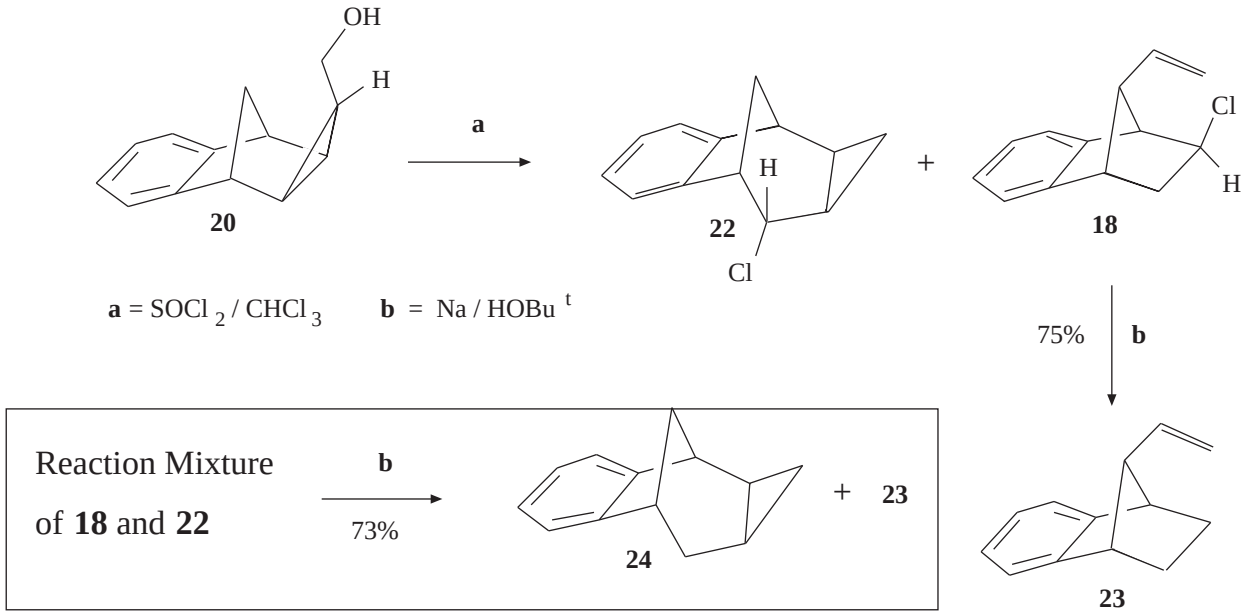
Benzohomobarrelene derivative **19** was synthesised as described in the literature[26,27], and then reduced with $LiAlH_4$ to give dihydrobenzohomobarrelene derivative **20**. To a solution of compound **20** in $CHCl_3$ was added $SOCl_2$ (in $CHCl_3$) at -10 ± 5 °C, followed by stirring at room temperature for 1 day. By thin layer

chromatography (TLC), compounds **18** and **21** were isolated in yields of 47% and 44%, respectively (Scheme 2). Compound **18** was also produced as the major product in the reaction of **14** with $SOCl_2$[14]. The NMR spectra of **21** indicated that this compound was different from **15**, **16**, **17** and **18**. There were no peaks due to the vinyl group in either of its spectra, but cyclopropane was seen. Compound **21** was an alcohol rather than a chloride because its mass (HRMS) was 186.104469. We assume that this alcohol **21** is formed during TLC by the solvolysis of the initially formed chloride **22**.



Scheme 2

In order to support the formation of **21**, the reaction mixture obtained by the reaction of **20** with thionyl chloride was submitted to reduction with $Na/HOBu^t$. Compound **23,** which was also obtained by the reduction of pure **18,** was easily characterized in the reaction mixture by its symmetrical NMR spectrum. The second hydrocarbon was characterised as compound **24**.

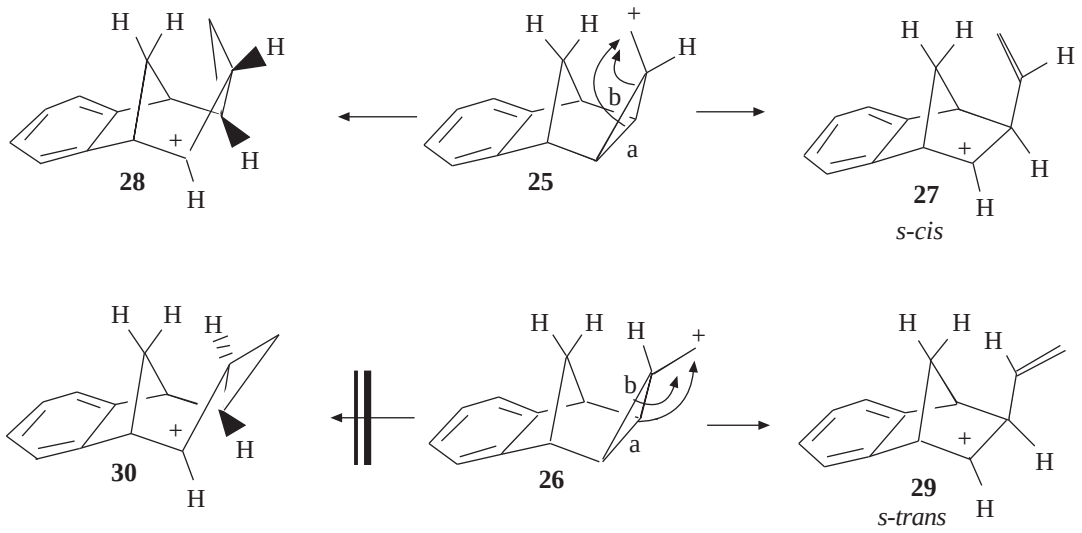


Scheme 3

Compounds **16**, **17** and **18** are produced from **12**, **13** and **14** respectively by sequential rearrangements [12–14,17–25]. There are 2 types of rearrangements whose ratios are approximately 1:1 in the reaction of compound **20** with $SOCl_2$. One of them is sequential rearrangement and the other is cyclopropylcarbinyl–cyclopropylcarbinyl rearrangement. The latter involves different rearrangements in these systems. Compound **20** is an isomer of compound **14**, and the group $–CH_2OH$ occurs in them in different directions, *exo*

and *endo*. It was observed that 2 types of rearrangements are present in the reaction of compound **20**, while only 1, sequential rearrangement, is present in that of compound **14** in a major ratio [14]. Different rearrangements in the reactions of both **14** and **20** can be explained by the stabilities of intermediates **25-30** formed in their reaction. These intermediates **(25-30)** were shown as classical carbocations. Intermediate **25** is less stable than **26** due to the steric effects associated with the cyclopropylmethyl cation and bridge proton. These steric effects can be compared with those of alcohols **14** and **20**. Methylene protons resonate at 3.33 and 4.10 ppm in **14**[27] and **20**, respectively. A shift to low field arises due to steric compression between cyclopropylmethyl and bridge protons in compound **20**.

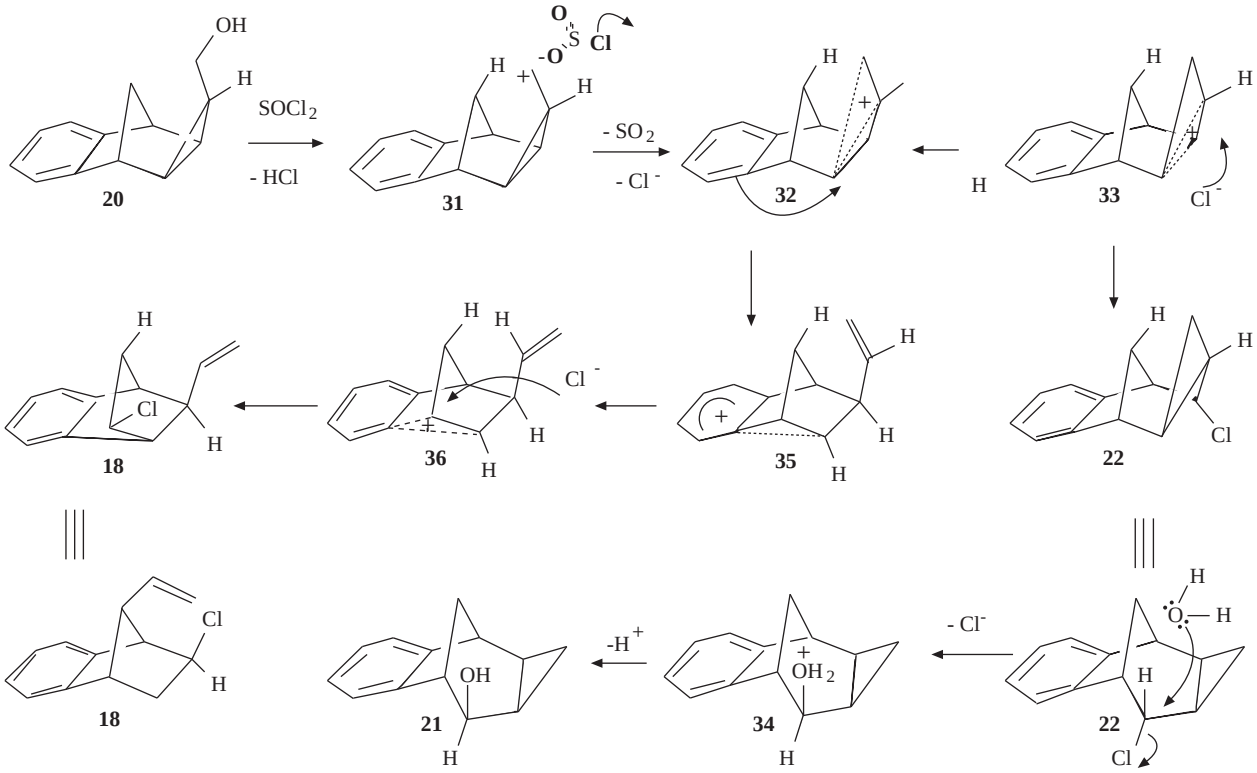
In intermediate **25**, rearrangements can occur via **27** and **28**, which are formed by attacks of $-CH_2+$ on both the **a** and **b** bonds of the cyclopropane ring. In the case of intermediate **26**, rearrangements can only occur via **29**, which is formed by attacks of $-CH_2+$ on the **b** bonds of the cyclopropane ring because unstable intermediate **30** would be produced due to transfused protons of cyclopropanes. The structure of compound **20** is *endo* as in compound **7**[23]. Therefore, the stereochemistry of **25** is important in the transformation of the cyclopropane ring. Probably the factor with the greatest effect on this transformation is the stereochemistry of **25**. As a result, only sequential rearrangements may be observed in the reaction of **14** because **30** does not occur (Scheme 4).



Scheme 4

The following reaction mechanism is proposed in order to rationalise the formation of products **18**, **21** and **22** (Scheme 5). Intermediates **31**, **32, 33, 35** and **36** are formed successively from the reaction of compound **20** with thionyl chloride. Intermediates **32, 33, 35** and **36** are nonclassical carbocations, and a nucleophile (Nu^-) attacks these intermediates selectively. Alkyl chlorosulphites, which are formed in the reactions of alcohols with thionyl chloride to give alkyl halides, react in a 2-step process. The first step is the same as the very first step of the S_N1 mechanism – dissociation into an intimate ion pair [28,29]. Cl^- transferred from $ClSO_2^-$ can attack intermediate **33** to give **22**, and intermediate **36** to give **18**. The nucleophilic substitution of water occurs at CHCl of compound **22** while the reaction products separate on TLC. The formation of alcohol **21** may occur in different ways such as by S_N2 or S_N1. Probably it occurred during separation by the S_N2 mechanism because the reactions usually take place via nonclassical cations in these systems[4–6]. As shown in Scheme 5, there are 2 different rearrangements. One of them is a

sequential rearrangement in the formation of compound **18** by opening the cyclopropane ring in an initial rearrangement, followed by a rearrangement of the benzhomobenzoobarrelene skeleton – an aryl shift – as the second rearrangement. An aryl shift is favoured over an alkyl shift in this type of system[12–16]. The other is cyclopropylcarbinyl–cyclopropylcarbinyl rearrangement in the formation of compound **22** from compound **20**.



Scheme 5

Conclusion

In summary, we obtained chloride **18** and alcohol **21** from the reaction of alcohol **20** with thionyl chloride. The structures of products **18** and **21** were supported by spectral data and chemical reactions. These products are obtained by 2 different rearrangements: sequential rearrangements and the cyclopropylcarbinyl–cyclopropylcarbinyl rearrangement in this system. The transformation of the cyclopropane ring was explained by the nature of the intermediates in these reactions.

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