Dedicated to the memory of
acad. Ecaterina Cioranescu-Nenitzescu

Rearrangement Reaction of *exo*-Benzocyclobutanorbornene Derivative

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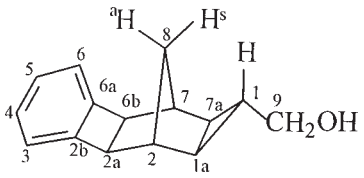
*The reaction of of cyclopropilalcohol **1** with the $SOCl_2$ is presented. The new alkyl chlorides **6** and **7** were characterized by NMR, IR and MS. A ionic mechanism is suggested in order to rationalize the formation of the reaction products.*

Keywords: exo- benzocyclobutanorbornene; benzotetracyclic primary alcohol; alkyl chloride; reaction with thionyl chloride

In the previous papers we described the flow-vacuum pyrolyses of some benzo-annelated polycyclic compounds [1, 2].

We extended our studies for the synthesis of organic compounds through the halogenation reaction. This reaction is an important process because the halogen derivatives have numerous applications and can be valuable for the synthesis of other derivatives. The halogen derivatives of the bicyclo[2.2.1] heptane offer the possibility of several mechanistically interesting investigations [3-4].

In this paper we present our results regarding the reaction the cyclopropylalcohol 1[5] with $SOCl_2$ at low temperature.



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Experimental part

Melting points are uncorrected. The NMR spectra were registered on a Varian Gemini 300 apparatus at 300 MHz for ^1H and 75 MHz for ^{13}C, using TMS as internal standard. The IR spectra were registered on a Bruker Vertex 70 spectrophotometer.

Varian 3400 gas-chromatograph with split/ splitless injector, coupled with a Varian SATURN II mass-spectrometer provided with ion trap. A capillary DB-5 column (30 m length, 0.25 mm internal diameter) was used. The analysis conditions were: injector temperature 250°C, split rate 1: 60, temperature program 60-280°C with 10°C/ min, carrier gas helium (1 mL/ min); temperature of transfer line 250°C; electron ionisation 70 eV.

The methyl ester **5** was obtained as a colourless solid (m.p. 94°C; methanol) from *exo*-benzocyclobutanorbornene [6] according to the literature method [5].

Synthesis of 1a,2,2a,6b,7,7a-hexahydro-1β-(hydroxymethyl)-2,7-methano-cyclopropa[b]biphenylene, (**1**)

The cyclopropylalcohol **1** was obtained by $LiAlH_4$-reduction (90% yield) of the corresponding carboxymethyl derivative **5** as a colourless solid (m.p. 112°C; methanol). The spectral data of **1** confirm the proposed structure [6].

IR spectrum (solid ATR, cm^{-1}): 723 m; 1006 m; 1226 m; 1736 m; 2864 m; 2936 s; 3010 m; 3056 w; 3376 m; 3613 w.

^{1}H-NMR spectrum ($CDCl_3$, δ ppm, J Hz)*:* 0.48 (d; 12.5; 1H; H-8^s); 0.72 (dt; 12.5; 1H; H^{8a}); 0.78 (d; 2.6; 2H; H-1a; H-7a); 1.30 (tt; 2.5; 7.0; 1H; H-1); 2.38 (bs; 2H; H-2; H-7); 3.33 (s; 2H; H-2a H-6b;); 3.40 (d; 7.0; 2H; H-9); 7.05 (m; 2H; H-3; H-6); 7.20 (m; 2H; H-4; H-5).

^{13}C-NMR spectrum ($CDCl_3$, δ ppm): 19.42 (C-1); 20.91 (C-1a; C-7a); 22.16 (C-8); 36.34 (C-2; C-7); 51.56 (C-2a; C-6b); 64.99 (C-9); 121.79 (C-4; C-5); 127.23 (C-3; C-6); 146.07 (C-2b; C-6a).

Mass spectrum (m/z; relative abundance %): 39 (30); 41 (14); 43 (9); 50 (12); 51 (19); 53 (8); 63 (22); 65 (12); 76 (15); 77 (28); 79 (12); 89 (10); 91 (12); 102 (68); 103 (18); 115 (50); 116 (17); 126 (5); 128 (100; PB); 129 (22); 139 (9); 141 (82); 142 (27); 152 (33); 153 (28); 155 (9); 165 (52); 166 (32); 167 (20); 168 (5); 169 (2); 176 (4); 179 (80); 181 (40); 182 (4); 193 (9); 194 (5); 212 (1; M).

Reaction of 1a,2,2a,6b,7,7a-hexahydro-1β-(hydroxymethyl)-2,7-methano-cyclopropa[b]biphenylene, (**1**) *with $SOCl_2$.*

A stirred soln. of alcohol **1** (1.2g, 6.60 mmol) in 20 mL of $CHCl_3$ was cooled to -10°C and treated dropwise with a soln. of $SOCl_2$ (8 mL) in 20 mL of $CHCl_3$ for 30 min. Then the mixture was allowed to warm at room temperature. After stirring for one day, the solvent and excess $SOCl_2$ were removed by evaporation. The residue was submitted to column chromatography on neutral alumina (Merck 90-activity II) using hexane as eluent. There were obtained two fractions. The distribution of products was determined by GC/ MS analyses. In scheme 2 the products are mentioned in the order of their elution from GC column.

3-Chloro-2-ethenyl-1a,2,2a,6b,7,7a-hexahydro-2,7—methanobiphenylene (**6**)

The compound **6** (fraction 1) was obtained as a colourless oil.

^{1}H-NMR spectrum ($CDCl_3$,δ ppm, J, Hz): 0.98 (ddt; 11.3; 2.6; 1.6; 1H; H-9^s); 1.29 (ddt; 11.3;3.0; 1.4; 1H; H-9^a); 2.13 (7.5; 4.4; 1.4 1.2; 1H; H-2); 2.22 (1H; H-4); 2.58(dl; 3.7;

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1H; H-1); 3.35 (dl; 3.8; 1H, H-8b); 3.95 (dl; 3.9; 1H; H-4a); 5.06 (dt; 10.3; 1.2; 1H; H-11cis); 5.14 (dt; 17.2; 1.4; 1H; H-11trans); 5.80 (ddd; 17.2; 10.3; 7.5; 1H; H-10); 7.00 (m; 2H; H-arom.); 7.20 (m; 2H; H-arom.).

^{13}C-NMR spectrum ($CDCl_3$, δ ppm): 29.81 (C-9); 42.81 (C-4); 43.884 (C-4a); 44.18 (C-1); 49.61 (C-8b); 55.27 (C-2); 66.15 (C-3); 114.67 (C-11); 122.04 (C-5; C-8); 127.74 (C-6;C-7); 139.19 (C-10); 145.20 (C-4a; C-8b).

Mass spectrum (m/z; relative abundance %): 67(4); 77(4); 89(5); 102(6); 115(22); 128(14); 129(29); 141(48); 142(100); 143(12); 152(10); 153(9); 165(11); 167(7); 178(7); 179(7); 195(8).

1a,2,2a,6b,7,7a-hexahydro-1β-(Chloromethyl)-2,7-methano-cyclopropa[b]-biphenylene (**7**)

The compound **7** (fraction 2) was obtained as a colourless solid (m.p. 97°C).

IR spectrum (solid ATR, cm^{-1}): 700 w;750 m; 800 w; 910 w; 1190 w; 1450 s; 2950 vs; 3200 w; 3250 w.

^{1}H-NMR spectrum ($CDCl_3$, δ ppm, J, Hz):): 0.45 (dl; 12.1; 1H; H-8^s); 0.70 (dl; 12.1; 1H; H-8^a); 0.89 (d; 2.5; 2H; H-1a; H-7a); 1.45 (tt; 2.5; 7.6; 1H; H-1); 2.41 (bs; 2H; H-2; H-7); 3.33 (bs; 2H; H-2a H-6b;); 3.35 (d; 7.6; 2H; H-9); 6.98 (m; 2H; H-3; H-6); 7.19 (m; 2H; H-4; H-5).

^{13}C-NMR spectrum ($CDCl_3$, δ ppm): 19.36 (C-1); 22.03 (C-8); 23.82 (C-1a; C-7a); 36.40 (C-2; C-7); 48.20 (C-9); 51.15 (C-2a; C-6b); 121.83 (C-4; C-5); 127.27 (C-3; C-6); 145.90 (C-2b; C-6a).

Mass spectrum (m/z; relative abundance %): 39(4); 51(5); 63(4); 65(4); 67(17); 76(7); 77(10); 79(5); 82(4); 89(7); 91(11); 102(32); 103(14); 104(3); 115(28); 116(9); 117(4); 127(4); 128(70); 129(22); 141(100); 142(22); 152(21); 153(22); 154(12); 155(5); 165(43); 167(35); 178(18); 179(22);181(23); 182(4); 189(3); 195(22); 196(2); 230(2).

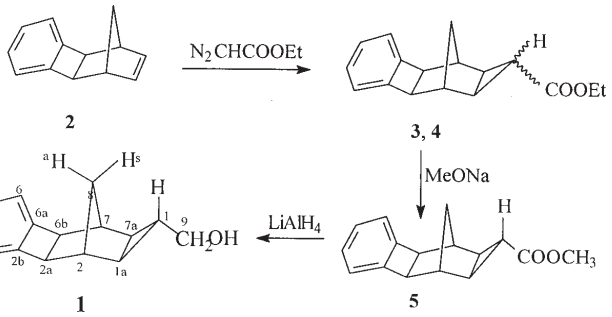
Results and discussions

The synthesis of alcohol **1** (scheme 1) was performed by a method described in literature [5].

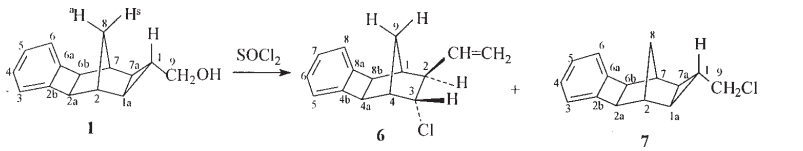
The cyclopropanation of *exo* – benzocyclobutan-orbornene (**2**) was carried out with an excess of ethyl diazoacetate (EDA) in presence of π-allyl palladium chloride complex at 0-5°C according to the literature method. From this reaction was obtained a mixture of two isomeric esters **3** and **4** with the *exo* configuration of the cyclopropane ring. The epimerization of the mixture of the isomeric esters with natrium methoxide in refluxing methanol affords the methyl ester **5** with *anti* configuation of the carbomethoxy group. By the reduction of the ester **5** with $LiAlH_4$ was obtained the cyclopropylalcohol **1** (90% yield) with the same configuration as **5**. The spectral data of compound **1** confirm the proposed structure .

The cyclopropylalcohol **1** reacted with $SOCl_2$ in $CHCl_3$ at low temperature to give two compounds : **6** (6.10 %) and **7** (93.90 %) (scheme 2) . The distribution of products (scheme 2) was determined by GC/ MS analyses.

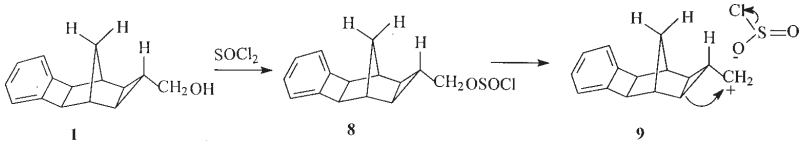
The reaction products were separated by CC on neutral alumina using hexane as eluent and characterized by spectral methods: IR, MS, ^{1}H- and ^{13}C-NMR. The main compund **7** is nonrearranged and could easily be distinguished; it has a symmetrical structure and exhibits an AA'BB' system for the aromatic H-atoms in the ^{1}H-NMR spectrum. Also consistent with structure **7** is the nine lines ^{13}C-NMR spectrum.

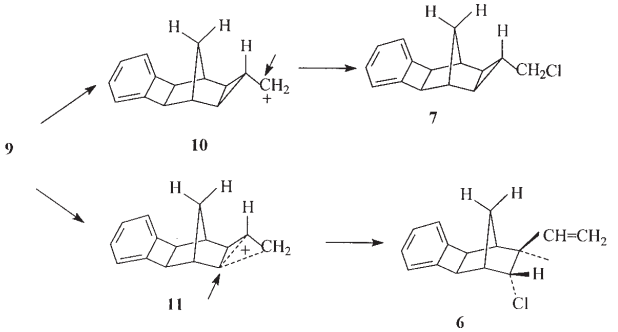


Scheme 1



Scheme 2





Scheme 3

The nonsymmetrical structure of the minor compound **6** results from the opening of the cyclopropane ring . There were no signals due to the cyclopropane ring visible in its spectrum.

Formation of the reaction products **6** and **7** during reaction of alcohol **1** with $SOCl_2$ can be rationalized by the mechanism suggested in scheme 3.

Alkyl chlorosulfite **8**, which is formed in the reactions of alcohol with $SOCl_2$ to give alkyl halides, react in a two-step process [7-9]. The first step is the same as the very first step of the S_Ni mechanism, i.e. dissociation into an intimate ion pair[7-9]. Cl^- transferred from $ClSO_2^-$ can attack the intermediate **10** to give **7** (major product) with retention of configuration and the intermediate **11** to give **6** (minor product) by opening the cyclopropane ring in an initial rearrangement.

Conclusions

In this paper we studied the reaction of alcohol **1** with $SOCl_2$. The reaction products were two new chlorides **6** and **7**. The chloride **7** resulted by opening the cyclopropane ring in an initial rearrangement. An ionic mechanism is suggested for this reaction.

References

1.OLTEANU, E., POPESCU, A., DRĂGHICI, C., BRĂTANESCU, S., BANCIU, M. D., Rev. Chim.(Bucuresti), **58**, nr.11, 2007, p.1057

2.OLTEANU, E., DRĂGHICI, C., CIUCULESCU, D., BANCIU, M. D., Rev. Roum. Chim., **48**, nr. 10, 2003, p.829

3.AVRAM, M., POGANY, I., BADEA, F., NENITZESCU, C. D., Tetrahedron Lett. **44**, 1969, p.3851

4.DASTAN, A., TASKESENLIGIL, Y., TUMER, F., BALCI, M., Tetrahedron **52**, 1996, p. 14005

5.GHEORGHIU M. D., OLTEANU, E., J. Org. Chem., **52**, 1987, p. 5158.

6.SIMMONS, M. E., J. Amer. Chem. Soc., **83**, 1961, p. 1657

7.MARCH, J., Advanced Organic Chemistry, 3th edn., John Wiley & Sons, New York, 1985, p. 287

8.LEE, C. C., FAINLAYSON, A. J., Can. J. Chem. 1961, p. 260

9.MENZEK, A., GOKMEN, M., Helv. Chim. Acta, **86,** 2003, p.324

Manuscript received: 10. 06.2009