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Dedicated to the memory of
Professor Ecaterina Ciorănescu-Nenitzescu (1909–2000)

FLOW-VACUUM PYROLYSIS OF POLYCYCLIC COMPOUNDS. 28.[1] PYROLYSIS OF 1a,2,2a,6b,7,7a-HEXAHYDRO-1β-(HYDROXYMETHYL)-2,7-METHANO-CYCLO-PROPA[*b*]BIPHENYLENE

Emilia OLTEANU,[a*] Angela POPESCU,[b] Constantin DRĂGHICI[a] and Crinu CIUCULESCU[a]

[a] "Costin D. Nenitzescu" Institute of Organic Chemistry, Roumanian Academy, 202B Splaiul Independentei, 060023, Bucharest, Roumania
[b] Organic Chemistry Laboratory, Faculty of Applied Chemistry and Materials Science, "Politehnica" University Bucharest, 313, Splaiul Independenței, 060042, Bucharest, Roumania

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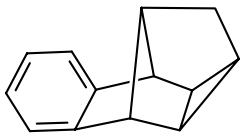
Flow- vacuum pyrolysis of the title benzo-tetracyclic alcohol **7** in quartz tube, inert atmosphere (argon, 4 mL/min), at 1 Torr and 800ºC afforded as main reaction products: 3,3a,10,10a-tetrahydro-3-hydroxymethyl-benzo[*e*]azulene (**12**) and 2a,9,9a,10-tetrahydro-10-hydroxymethyl-benzo[*e*]azulene (**13**). A radicalic reaction mechanism is suggested in order to rationalize the formation of the reaction products.

INTRODUCTION

In the previous papers of this series we described the flow-vacuum pyrolyses of some benzo-annelated polycyclic hydrocarbons e.g. **1**,[2] **2**,[3] **3**[4] as well as of dibenzoannelated cyclic and polycyclic alcohols like **4**,[5] **5** [6] and **6**.[7]



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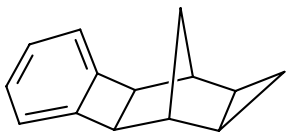

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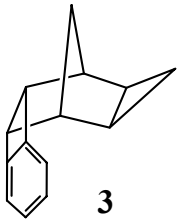

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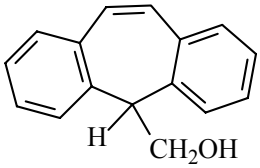

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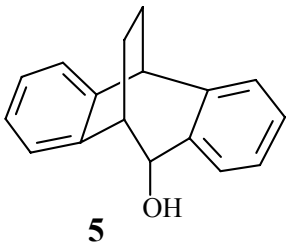

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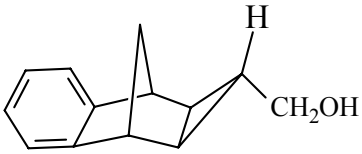

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* Corresponding author: eolteanu@cco.ro

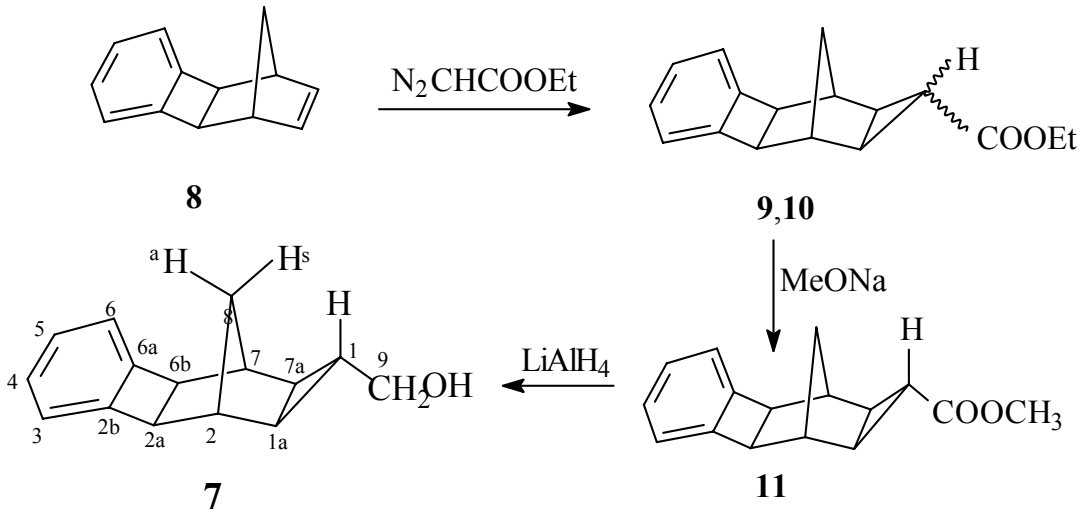
In all cases we evidenced elimination reactions accompanied by rearrangement and aromatization processes.

In this paper we present the results of flow-vacuum pyrolysis of the alcohol **7**, a compound including a hydroxylic group (like **4**–**6**) attached to a benzotetracyclic skeleton (related to **1**-**3**), in order to investigate the influence of both structural moieties on the thermal behaviour in flow-vacuum pyrolysis:

RESULTS AND DISCUSSION

The synthesis of alcohol **7** (Scheme 2) was performed with our method described in literature.[8]

The cyclopropanation of *exo* – benzocyclobutano-norbornene (**8**)[9] was carried out with an excess of ethyl diazoacetate (EDA) in the presence of π-allyl palladium chloride complex at 0-5°C according to the literature method.[10] From this reaction was obtained a mixture of two isomeric esters **9** and **10** 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 **11** with *anti* configuation of the carbomethoxy group. By the reduction of the ester **11** with $LiAlH_4$ was obtained the cyclopropylalcohol **7** (a colourless solid; 90% yield) with a same configuration as **11**. The spectral data of compound **7** confirm the proposed structure.[8]



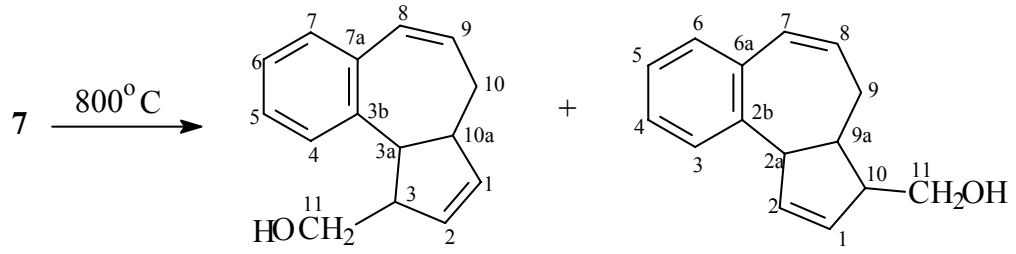
8 **9**,**10** **11** **7**

Scheme 1

The flow-vacuum pyrolyses of the alcohol **7** were performed at 1 Torr, in inert atmosphere (4mL/min argon flow-rate) on a large interval of temperatures (450°C - 800°C) (*see* Experimental).

The alcohol **7** proves a remarkable thermal stability remaining unconverted between 450°C-750°C. At 800°C, the conversion was totally and a mixture of two main compounds **12** and **13** was obtained. The distribution of products (Scheme 2) was determined by GC/ MS analyses.

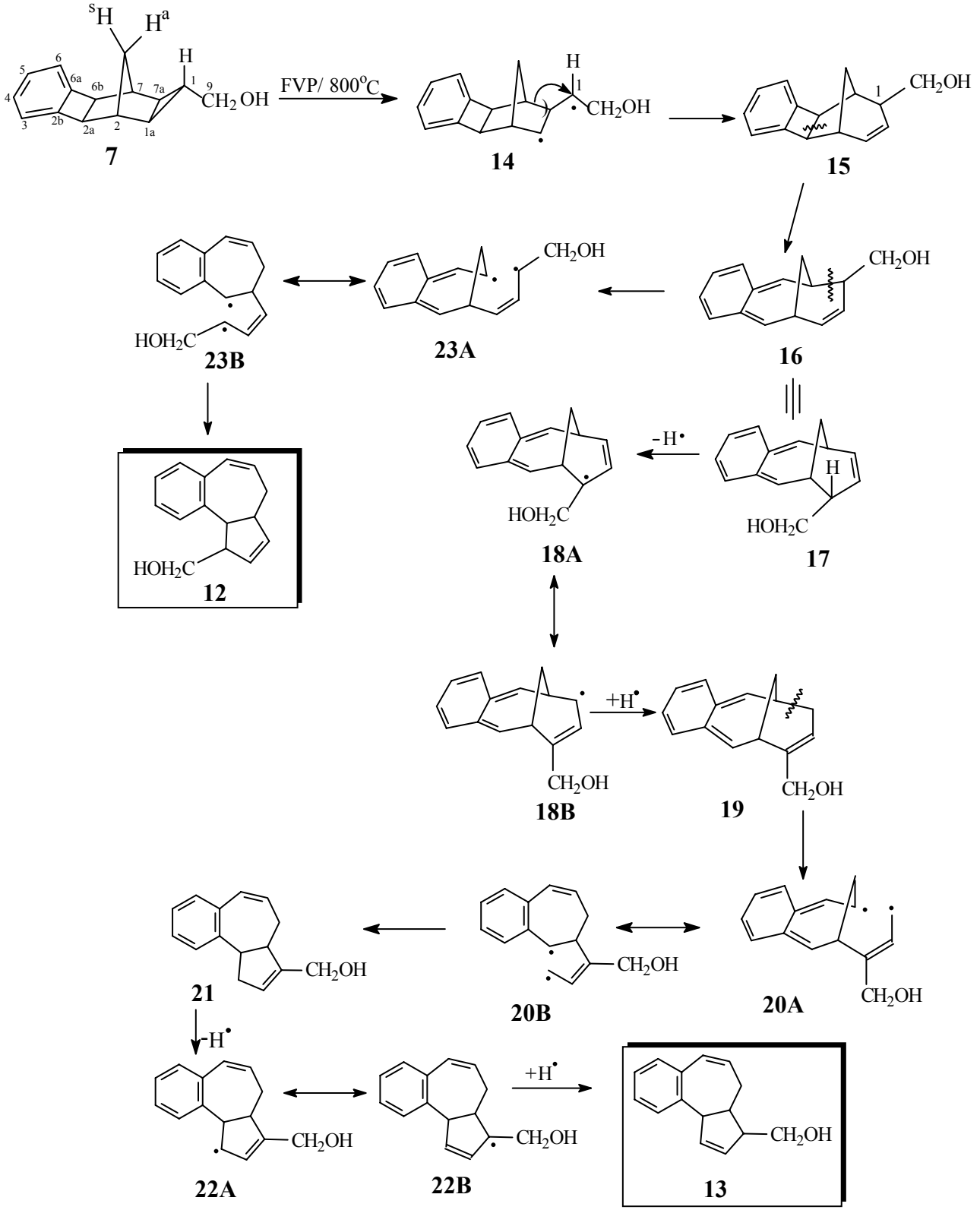
The main reaction products **12** and **13** were separated by TLC on SiO_2 (PF_{254} Merck) using methylene chloride as eluent and characterized by spectral methods: IR, MS, ^{1}H- and ^{13}C-NMR:



12 **13**

Scheme 2

The formation of the reaction products **12** and **13** during the flow-vacuum pyrolysis of compound **7** can be rationalized by the mechanism suggested in Scheme 3.



Scheme 3

The first step of this reaction could be the cyclopropane ring break. According to the literature data,[11] in the simplest case, cyclopropane gives propene when heated to 400-500°C by a diradical intermediate. The diradical **14** formed in the same way is stabilized by bond break of the norbornene system affording the alcohol **15**. The next step of the reaction is a benzocyclobutane→*ortho*-quinodimethane rearrangement: **15→16.** The published data[12] for the parent benzocyclobutane→*ortho*-quinodimethane interconversion indicated ΔH = 10.6-13 kcal.mole^{-1} and E_a = 39.9 Kcal.mole.$^{-1}$ This slight endothermic reaction seems to be very fast (k = 3.7 s^{-1} at 228.1°C) and a transition state is product-like.[13]

However, the geometrical requirements for a thermally allowed process (a conrrotatory one)[14] are not fulfilled in the polycyclic alcohol **7**. The formation of **16** from **15,** can occurs geometrically only in a disrotatory manner. Thus, being thermally forbidden as a concerted reaction,[14] this transformation should occurs in a diradical fashion. It can be assumed that the relatively high reaction temperature (800°C) needed to convert **7** to products is in agreement with a radical mechanism. However, the sequence of the cyclopropane- and cyclobutane ring openings from **7** could occur in the reversed order from that mentioned in Scheme 3. The break of a saturated C-C bond in **16** can produce the stable mesomeric diradical **23** (allylic- and pentadienylic one). Ring closure in **23B** affords the product **12**. By a hydrogen atom elimination from a CH group in **17** is generated relatively stable allylic radical **18A ↔18B** from which the alcohol **19** is formed. The break of a saturated C-C bond in **19** as in **16** can produce the stable diradical **20** (allylic- and pentadienylic one). Ring closure in **20B** affords the product **21**. By a hydrogen atom elimination from a CH_2 group in **21** is generated a relatively stable allylic radical **22A↔ 22B** from which the alcohol **13** is easily obtained. Similar hydrogen eliminations from CH_2 groups of homoannulene — valence isomers were suggested to occur during the thermal reactions (e.g. **1**[2], **2**[3], **3**[4] and **6**[7]).

EXPERIMENTAL

Melting points are uncorrected. The NMR spectra were registered on a Varian Gemini 300 apparatus at 300 MHz for ^{1}H 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. In scheme 2, the pyrolysis products are mentioned in the order of their elution from GC column. The methyl ester **11**[10] was obtained as a colourless solid (m.p. 94°C after recristallization from methanol) from *exo*-benzocyclobutanorbornene[9] according to the literature method.

1a,2,2a,6b,7,7a-hexahydro-1β-(hydroxymethyl)-2,7-methano-cyclopropa[*b*]biphenylene, (**7**)[8]

The cyclopropyl alcohol **7** was obtained as a colourless solid (m.p. 192°C after recristallization from methanol) by $LiAlH_4$-reduction (90% yield) of the corresponding carboxymethyl derivative **11**. The spectral data of **7** confirm the proposed structure.[8]

IR (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 ($CDCl_3$, 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 ($CDCl_3$, 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).

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

The flow-vacuum pyrolyses of compound **7** was performed in a flow system using a previously described apparatus.[2] The pyrolysis quartz tube (40 cm length; 10 mm inner diameter) was filled with quartz chips of 3-5 mm on a 20 cm lengh; this zone was heated with a cylindrical electric oven. The temperature was continuously measured by a thermocouple and the pressure (~1 Torr) with a Varian tc gauge. The compound sample (30 mg for analytical and 100 mg for preparative experiments) was sublimated under argon flow (4mL/ min) into the hot pyrolysis tube. The reaction products were accumulated as an oily liquid at the cooled end of the pyrolysis tube. The products were dissolved in CH_2Cl_2, the solvent was evaporated *in vacuo* and the residue (about 70% yield) was analysed by GC/ MS , ^{1}H- and ^{13}C- NMR.

At 800°C, the totally conversion was observed and a mixture of two main compounds : **12** (53.85%) and **13** (29.85%) was obtained. The reaction products (see Scheme 2) was determined by GC/ MS analyses. The main reaction products were separated by TLC on SiO_2 (PF_{254} Merck) using methylene chloride as eluent and they were characterized by spectral methods: IR, ^{1}H- and ^{13}C-NMR.:

3,3a,10,10a-tetrahydro-3-hydroxymethyl-benzo[e]azulene (**12**)

The compound **12** was obtained as a colourless oil.

IR (solid ATR, cm^{-1}): 3359 s; 3047 m; 3021 m; 2922 s; 2875 s; 1484 w; 1375 w; 1027 m; 747 m.

^{1}H-NMR ($CDCl_3$, δ, ppm, J, Hz): 1.99 (m; 1H; H-10'); 2.23 (m; 1H; H-10); 2.94 (m; 1H; H-3); 3.23 (t; 8.9; 1H, H-3a); 3.37 (dd; 10.6; 5.6; 1H; H-11); 3.59 (dd; 10.6; 4.5; 1H; H-11); 3.78 (m; 1H; H-10a); 5.78-5.82 (m, 2H, H-1; H-2); 6.13 (ddd; 10.5; 8.1; 6.0; 1H; H-9); 6.53 (dd; 10.5; 2.1; 1H; H-8); 7.10-7.30 (m; 4H; H-4; H-7).

^{13}C-NMR ($CDCl_3$, δ, ppm): 148.83 (Cq); 138.20 (Cq); 135.41 (C-1); 133.52 (C-9); 133.11 (C-8); 132.69 (CH); 131.65 (CH); 130.28 (CH); 127.12 (CH); 126.74 (CH); 65.54 (CH_2-O); 63.19 (C-6a); 58.68 (C-3); 51.32 (C-3a); 30.57 (C-10).

Mass spectrum (m/z; relative abundance %): 39 (12); 51 (5); 63 (8); 77 (5); 89 (12); 115 35); 128 (55); 129 (12); 141 (38); 142 (8); 152 (38); 153 (21); 155 (5); 165 (19); 166 (68); 178 (38); 179 (36); 181 (100; BP); 182 (12); 194 (27); 212 (10; M).

2a,9,9a,10-tetrahydro-10-hydroxymethyl-benzo[e]azulene (**13**)

The compound **13** was separated as colourless oil.

IR (solid ATR, cm^{-1}): 3364 s; 3050 m; 3021 m; 2923 vs; 2861 s; 1486 w; 1442 w; 1021 m; 776 m; 748 m; 727 m.

^{1}H-NMR ($CDCl_3$, δ, ppm, J, Hz): 2.14 (m; 1H; H-9'); 2.27 (m; 1H; H-9); 3.19 (m; 1H; H-10); 3.28 (d; 11.0; 1H; H-11); 3.35 (dd; 11.0; 6.0; 1H; H-11); 3.82- 3.94 (m; 2H; H-2a; H-9a); 5.63 (dtl; 6.0; 1.8; 1H; H-1); 5.78 (dtl; 6.0; 1.9; 1H; H-2); 5.93 (ddd; 10.6; 8.1; 6.1; 1H; H-8); 6.53 (dd; 10.6; 2.0; 1H; H-7); 7.10-7.30 (m; 4H; H-3; H-4; H-5; H-6).

^{13}C-NMR ($CDCl_3$, δ, ppm): 140.48 (Cq); 138.83 (Cq); 134.23 (C-2); 133.00 (CH); 132.91 (CH-7); 132.84 (CH-8); 130.80 (CH); 127.29 (CH); 126.95 (CH); 65.57 (CH_2-O); 60.68 (C-2a; C-9a); 55.51 (C-4); 49.77 (C-3a; C-6a); 30.56 (C-9).

Mass spectrum (m/z; relative abundance %): 39 (18); 41 (4); 51 (12); 53 (5); 63 (14); 65 (7); 76 (5); 89 (4); 114 (6); 115 (28); 127 (18); 128 (40); 129 (14); 139 (9); 142 (14); 151 (12); 153 (28); 155 (8); 165 (100; BP); 166 (58); 167 (18); 178 (51); 179 (88); 181 (41); 183 (8); 193 (19); 194 (11); 212 (31; M).

CONCLUSIONS

In this paper we described the synthesis and the thermal behaviour of the benzotetracyclic primary alcohol **7** which presented a remarkable stability in flow-vacuum pyrolysis conditions remaining unconverted between 450°C - 750°C. At 800°C, the conversion was totally and a mixture of two new alcohols (**12** and **13**) with tetrahydrobenzo[*e*] azulene skeleton were obtained. A radicalic reaction mechanism was suggested in order to rationalize the formation of these separated and spectral characterized pyrolysis reaction products.

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