

*Dedicated to Professor Cristofor SIMIONESCU
on the occasion of his 85-th anniversary*

FLOW-VACUUM PYROLYSIS OF POLYCYCLIC COMPOUNDS. 22¹. PYROLYSIS OF 2,2'-bis(HYDROXYMETHYL)BIPHENYL

Daniela ISTRATI^a, George MARTON^a, Constantin DRĂGHICI^b,
Adriana GRIGORE^a and Mircea D. BANCIU^{a*}

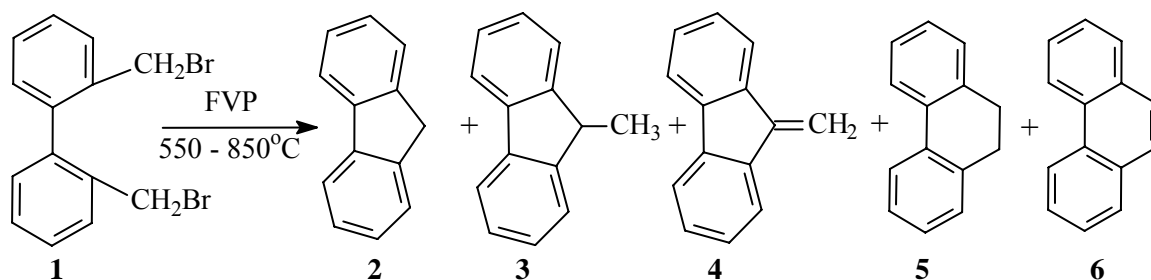
^a Department of Organic Chemistry, "Politehnica" University Bucharest,
Splaiul Independenței 313; 060042, Bucharest, Roumania

^b "C.D. Nenitzescu" - Institute of Organic Chemistry, Roumanian Academy,
Splaiul Independenței 202B; 060023, Bucharest, Roumania

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The flow-vacuum pyrolysis of the title diol, between 600^oC – 800^oC and 1mm Hg in argon atmosphere, was investigated using GC/MS. The main reaction products were: fluorene, 9-methylfluorene, 9-methylenefluorene; 9,10-dihydrophenanthrene; phenanthrene; 9-hydroxy-9,10-dihydroanthracene; 9-fluorenol; 9-fluorenone; 2-methyl-2'-formylbiphenyl (major product; 38% at 850^oC); 2-hydroxymethyl-2'-formylbiphenyl and 2,2'-diphendialdehyde. The amount of products resulted from intramolecular cyclization was 52% at 850^oC and the ratio between products with five-member and six-member central ring was 39:13 at 850^oC. A radical mechanism explaining the formation of the reaction products is suggested and a comparison between pyrolysis of the title diol and of the previously studied 2,2'-bis(bromomethyl)biphenyl is made.

Continuing our investigations in the domain of flow-vacuum pyrolysis of polycyclic compounds we described recently² the thermal behavior of 2,2'-bis(bromomethyl)biphenyl (**1**). The main pyrolysis products of **1** (1mm Hg; 550 – 825^oC) were the hydrocarbons **2 – 6** resulted by intramolecular cyclization (**Scheme 1**).

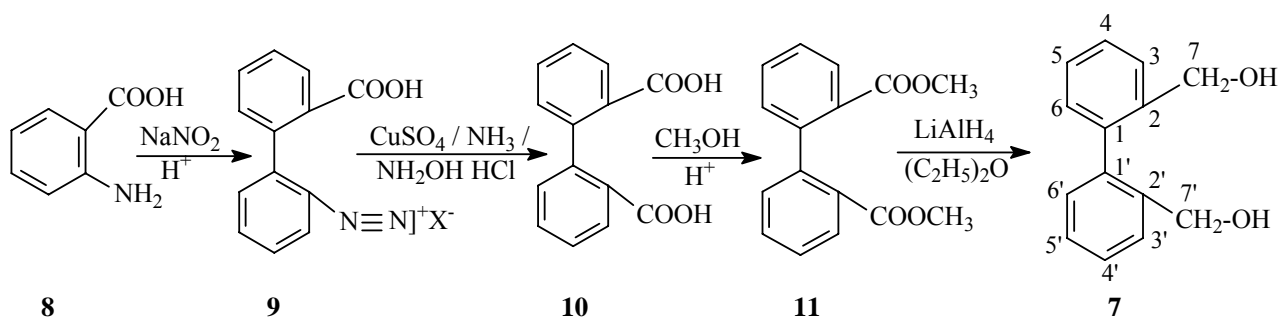


Scheme 1

In order to see if the intramolecular cyclization of the side chains remains dominant on changing the leaving groups (-Br) we investigated in this work the thermal behavior of 2,2'-bis(hydroxymethyl)biphenyl (**7**).

The synthesis of the diol **7** was performed according to literature data³⁻⁵ starting with anthranilic acid (**8**) and following the reaction sequence from **Scheme 2**:

^{a*} Corresponding author: E-mail: dm_banciu@chim.upb.ro



Scheme 2

The diol **7**, m.p. = 112-113⁰C (lit.⁴ m.p. = 111-113⁰C) presents the following spectral data:

I.R. spectrum^(*) (KBr; cm⁻¹): 754 s, 1032 s, 1194 m, 1251 s, 1341 s, 1424 m, 1445 s, 1478 s, 1588 m, 2879 m, 2885 m, 3020 m, 3060 m, 3000-3600 broad.

¹H-NMR spectrum^(**) (CDCl₃; δ, ppm; J, Hz): 3.56 (ls; 2H; OH), 4.23 (d; 11.7; 2H; H^{7a,7a'}), 4.28 (d; 11.7; 2H; H^{7b,7b'} AB system), 7.11 (dd; 7.2; 1.9; 2H; H^{3,3'}), 7.31 (dt; 7.2; 1.7; 2H; H^{4,4'}), 7.35 (td; 7.2; 1.7; 2H; H^{5,5'}), 7.43 (dd; 7.2; 2H; H^{6,6'}).

¹³C-NMR spectrum^(**) (CDCl₃; δ, ppm): 62.56 (C^{7,7'}), 127.54 (C^{5,5'}), 128.00 (C^{3,3'}), 129.51 (C^{4,4'}), 129.54 (C^{6,6'}), 138.57 (C^{2,2'}), 139.92 (C^{1,1'}).

Mass spectrum^(***) (m/e; relative abundance, %): 51(6); 63(5); 89(7); 115(9); 128(7); 139 (5); 152(37); 153(13); 165(51); 166(13); 167(27); 168(6); 178(34); 179(23); 180(6); 181(26); 182(6); 194(13); 195(48); 196(78); 197(100; P.B.); 198(14).

The flow-vacuum pyrolyses of **7** were performed in our previously described apparatus⁶ using a quartz flow-system under argon atmosphere (4 mL/min) at 1 mm Hg (the calculated contacted time being less than 0.2 s). The temperature interval was 600⁰C – 850⁰C. The crude reaction mixtures (yields over 85%) were subjected to GC/MS analysis.^(***)

The main reaction products were identified by MS and GC comparison with authentic samples.

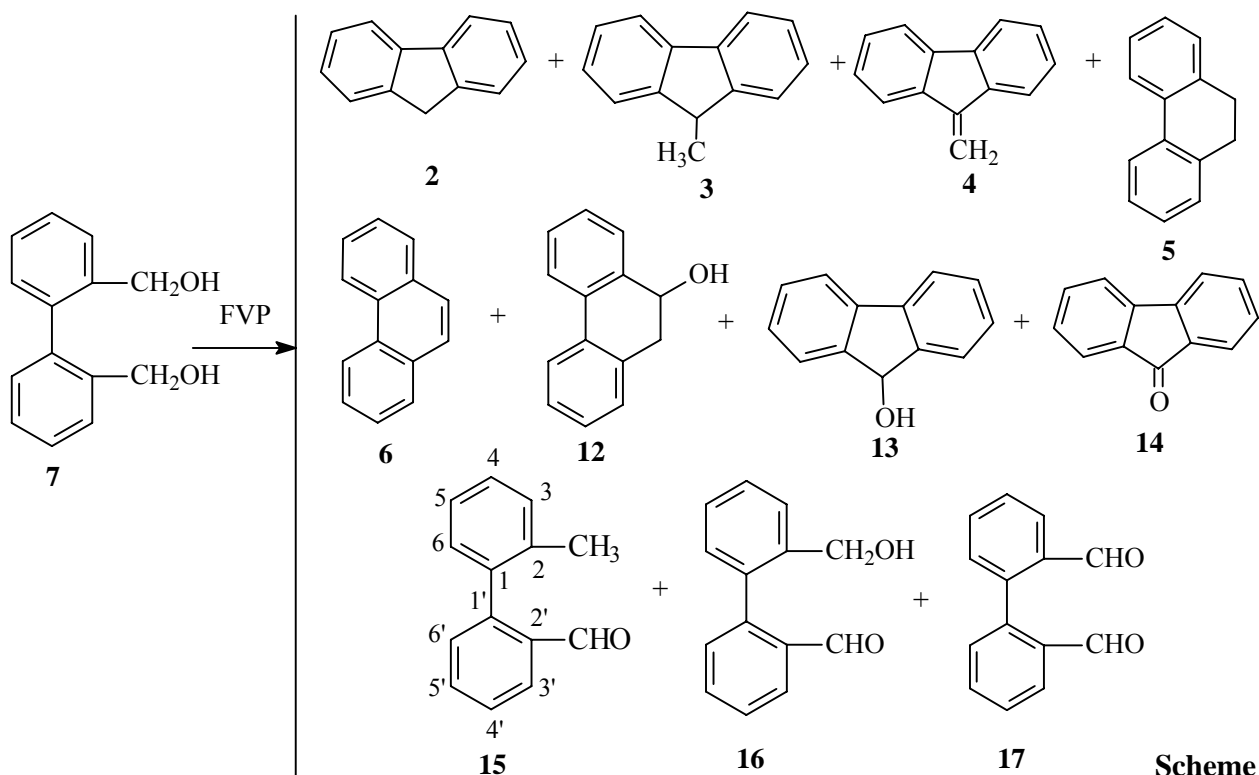
The products of the pyrolysis are presented in **Scheme 3** and their distribution at different temperatures is displayed in **Table 1**.

Table 1
Product distribution in pyrolyses of 7 and 1

Compound	Pyrolysis products of 7 at different temperatures			Pyrolysis products of 1 at 825 ⁰ C ¹
	600 ⁰ C	750 ⁰ C	850 ⁰ C	
2	3.0	7.5	13.0	24.5
3	1.5	2.5	4.0	20.0
4	2.5	4.5	3.0	3.0
5	2.5	1.0	0.5	12.0
6	3.0	1.5	1.0	22.5
12	16.5	19.5	11.5	-
13	0.5	1.5	10.5	-
14	-	4.0	8.5	-
15	12.5	43.0	38.0	-
16	5.0	2.0	1.5	-
17	2.0	3.0	1.5	-
7 (unreacted)	40.5	5.5	2.0	-

(*) IR-Equinox X 55 apparatus

(**) VARIAN GEMINI 300 apparatus working at 300 MHz for ¹H and 75 MHz for ¹³C (TMS as internal standard).



Scheme 3

The mass spectra of the main pyrolysis products (m/e; relative abundance, %) are presented below.

Fluorene (2): 50 (7); 63 (8); 74 (4); 89 (5); 115 (5); 139 (9); 163 (16); 164 (10); 165 (88); 166 (100; P.B.; M); 167 (12; M+1); 168 (1; M+2).

9-Methylfluorene (3): 50 (8); 51 (7); 63 (10); 76 (11); 83 (6); 89 (12); 115 (3); 139 (3); 152 (9); 165 (100; P.B.); 166 (12); 176 (9); 177 (5); 178 (17); 179 (26); 180 (90; M); 181 (12; M+1); 182 (1; M+2).

9-Methylene fluorene (4): 50 (5); 63 (5); 76 (11); 89 (8); 152 (7); 176 (15); 177 (10); 178 (100; P.B.; M); 179 (8; M+1).

9,10-Dihydrophenanthrene (5): 50 (10); 63 (10); 76 (12); 87 (7); 126 (7); 150 (12); 151 (11); 152 (47); 153 (7); 180 (100; P.B.; M); 181 (13; M+1); 182 (2.5; M+2).

Phenanthrene (6): 50 (4); 63 (4); 76 (4); 83 (4); 152 (5); 176 (13); 177 (7); 178 (100; B.P.; M); 179 (13; M+1); 180 (1; M+2).

9-Hydroxy-9,10-dihydrophenanthrene (12): 89 (5); 115 (7); 139 (6); 152 (12); 153 (10); 163 (7); 165 (37); 166 (14); 167 (37); 168 (10); 178 (13); 179 (8); 181 (15); 194 (6); 195 (90); 196 (100; P.B.; M); 197 (26; M+1).

9-Fluorenol (13): 51 (6); 63 (6); 126 (7); 152 (51); 153 (48); 154 (14); 165 (25); 166 (5); 181 (100; P.B.); 182 (58; M); 183 (27; M+1).

9-Fluorenone (14): 126 (5); 150 (10); 152 (50); 153 (7); 180 (100; P.B.; M); 181 (24; M+1); 182 (13; M+2).

2-Methyl-2'-formyl-biphenyl (15): 38 (14); 39 (45); 50 (33); 51 (30); 62 (18); 63 (38); 65 (14); 74 (19); 75 (16); 76 (34); 77 (17); 82 (13); 83 (16); 87 (14); 89 (23); 91 (17); 97 (19); 104 (12); 115 (30); 128 (12); 139 (18); 151 (18); 152 (100; PI); 153 (69); 163 (11); 164 (12); 165 (84); 166 (29); 167 (90); 168 (15); 177 (13); 178 (43); 179 (31); 181 (63); 195 (32); 196 (53; M); 197 (12; M+1); 198 (7; M+2).

(***) VARIAN 3400 gas-chromatograph with split/splitless injector coupled with a VARIAN SATURN II mass-spectrometer provided with ion trap. Column: capillary DB-5 (30 m length, 0.25 mm internal diameter); Analysis conditions: injector temperature: 250°C; temperature program: 100 - 250°C with 5°C/min; carrier gas: helium (flow-rate 2 mL/min); temperature of transfer line, 250°C; temperature of the manifold, 170°C; ionization energy, 70eV.

2-Hydroxymethyl-2'-formyl-biphenyl (16): 106 (8); 167 (12); 168 (10); 180 (12); 182 (25); 183 (5); 194 (13); 196 (8); 210 (9); 211 (100; P.B.); 212 (3; M).

2,2'-Diphendialdehyde (17): 152 (37); 153 (12); 165 (25); 181 (100; P.B.); 182 (12); 210 (14; M).

2,2'-bis(Hydroxymethyl)biphenyl (7): 51 (6); 63 (5); 89 (7); 115 (9); 128 (7); 139 (5); 152 (37); 153 (13); 165 (51); 166 (13); 167 (27); 168 (6); 178 (34); 179 (23); 180 (6); 181 (26); 182 (6); 194 (13); 195 (48); 196 (78); 197 (100; P.B.); 198 (14);

Some of the reaction products were isolated preparatively by column chromatography on silica (Merck 60-230 Mesh); thus fluorene (**2**) and phenanthrene (**6**) were separated on elution with petroleum ether (b.p. = 30-40°C) and 2-methyl-2'-formyl biphenyl (**15**) (thick oil) was separated on elution with a mixture of diethylether: petroleum ether (5 : 95).

IR spectrum of **15** (CHCl₃; cm⁻¹): 1388s, 1450m, 1470s, 1595m, 1693fi, 2747s, 2850s, 2930s.

¹H-NMR spectrum of **15** (CDCl₃; δ, ppm; J, Hz): 2.1 (s; 3H; CH₃), 7.19 (dd; 7.6; 1.6; 1H; H³), 7.24-7.35 (m; 4H; H^{4,5,6,6'}), 7.50 (tt; 7.7; 1.1; 1H; H⁴), 7.64 (td; 7.7; 1.5; 1H; H⁵), 8.01 (dd; 7.7; 1.5; 1H; H^{3'}), 9.74 (s; 1H; CHO).

¹³C-NMR spectrum of **15** (CDCl₃; δ, ppm): 20.3 (CH₃), 125.7 (C³), 127.1 (C^{3'}), 127.8 (C⁴), 128.3 (C⁵), 130.1 (C^{6,4}), 130.8 (C^{6'}), 133.7 (C^{5'}), 136.2 (C^{2'}), 137.5 (C²), 143.8 (C¹), 145.7 (C^{1'}), 192.3 (CHO).

Examination of the data from **Table 1** suggests the following observations:

- the diol **7** indicates a normal thermal stability showing a 60% conversion at 600°C, a 94.5% conversion at 750°C and a 98% conversion at 850°C;
- the main pyrolysis product is 2-methyl-2'-formyl biphenyl (**15**) (43% at 750°C; 38% at 850°C);
- other relative important reaction products are (at 850°C): fluorene (**2**) – 13%; fluoreneol (**13**) – 10.5%; 9-hydroxy-9,10-dihydrophenanthrene (**12**) – 11.5% and 9-fluorenone (**14**) – 8.5%;
- the amount of the products resulted from intramolecular cyclization is 52% at 850°C;
- the ratio of products with five-member central ring to products with six-member central ring is 39 : 13 at 850°C;

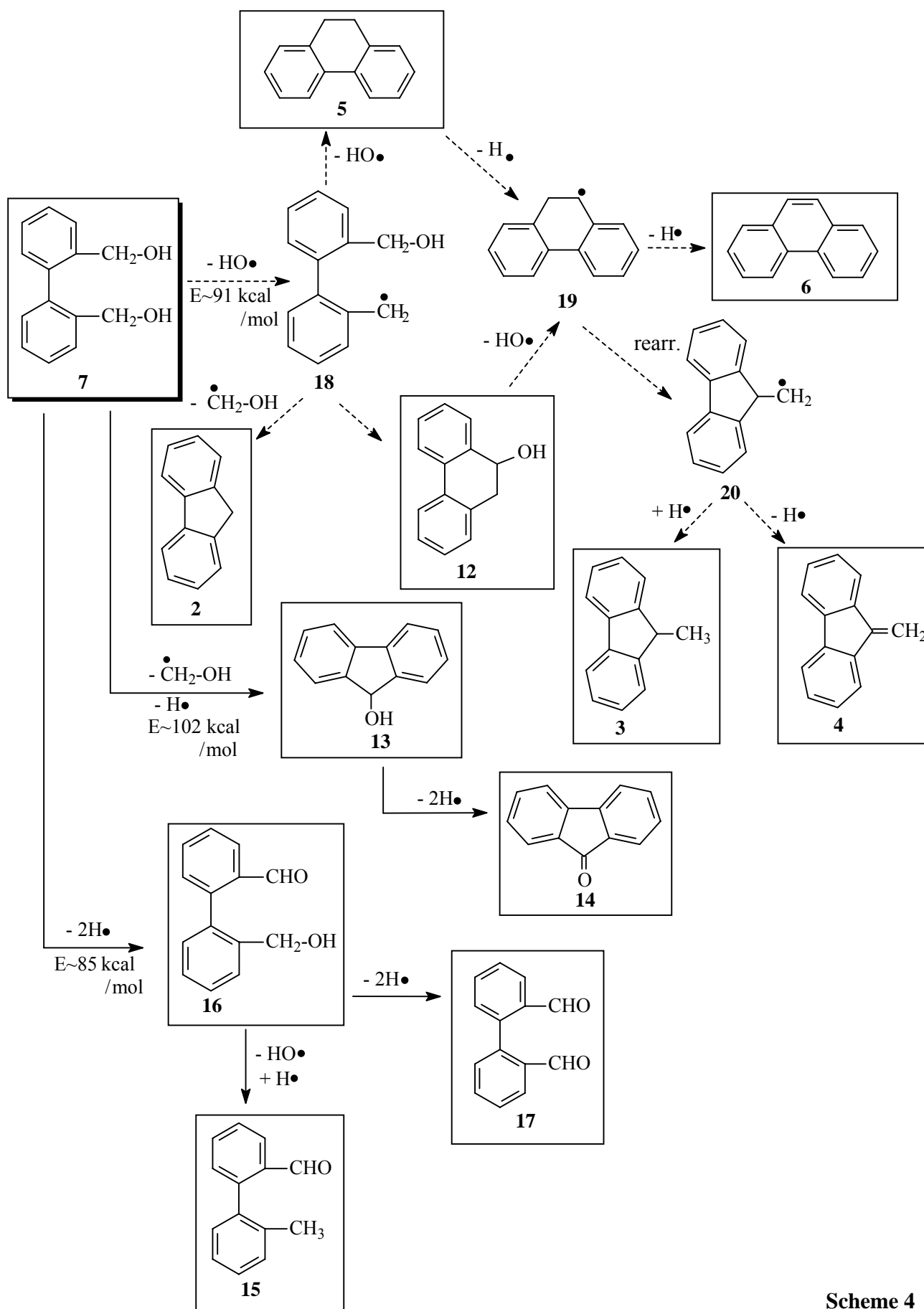
A rationalization of the experimental data is presented in **Scheme 4**.

The reactions marked with dotted lines in **Scheme 4** are similar to those involved in the pyrolysis of dibromide **1**.² Thermal break of a CH₂-OH bond in **7** (needing about 91 Kcal/mol⁷) affords the stable benzylic radical **18**. A hydrogen atom loss in **18** accompanied by cyclization produces the alcohol **12**, which could be dehydrated to **6** (*via* **19**). On the other hand, elimination of the OH group from **18** would produce dihydrophenanthrene (**5**) which is prone to dehydrogenation to phenanthrene (**6**) *via* the same benzylic -type radical **19**. A rearrangement of **19** can afford the ring-contracted radical **20** from which the end-products **3** and **4** can be formed by hydrogen addition, respectively hydrogen elimination. Starting with the above-mentioned radical **18**, fluorene (**2**) can be formed by a •CH₂-OH break accompanied by cyclization.

Along with the reaction routes mentioned above, other thermal processes should be involved in order to rationalize the formation of products **13** – **17** (**Scheme 4**). Thus, elimination of •CH₂-OH and H• from **7** (E ~ 102 kcal/mol), accompanied by cyclization, could conduct to fluoreneol (**13**). A stepwise dehydrogenation of **13** will generate fluorenone (**14**). On the other hand, the products **15-17** preserving the initial biphenyl skeleton could be generated from **7** by stepwise dehydrogenations (E ~ 85 kcal/mol) (**16**, **17**) respectively from **16** by HO• loss and H• addition (**15**).

Comparison of the flow-vacuum pyrolysis of diol **7** with that of the dibromide **1**² allows the following conclusions to be drawn:

- ♦ The biphenyl derivatives **1** and **7** present a comparable thermal stability.
- ♦ The amount of thermal intramolecular cyclization is nearly quantitative at dibromide **1** and only about 52% at diol **7**. The explanation resides in the ability of oxygen atoms to afford thermally stable products containing a single oxygen atom (like **12** – **15**) and stable biphenyl derivatives containing two oxygen atoms (**16**, **17**).
- ♦ The ratio between products with five-member central ring and six-member central ring is 39:13 for diol **7** and 58:15 for dibromide **1** (see **Table 1**). These comparable ratios reflect the known⁸ easier formation of five-member rings during pyrolysis.



Scheme 4

In conclusion this work has shown that the diphenyl-type diol **7** indicates a thermal stability comparable with the related dibromide **1**. The major reaction product, aldehyde **15** (38%) preserves the starting biphenyl skeleton. However, the pyrolysis products of **7** are mainly (52%) formed by intramolecular cyclization, the compounds with five-member central ring prevailing over those with central six-member ring.

REFERENCES

1. Note 21 in this series: M.D. Banciu, A. Popescu, A. Banciu, D. Mihăiescu, C. Draghici, A. Lari and I. Oprean, *Rev. Roum. Chim.*, **2005**, *50*, 000.
2. D. Istrati, D. Ciuculescu, A. Lari and M.D. Banciu, *Rev. Chim. (Bucharest)*, **2004**, *55*, 694-696.
3. E.R. Atkinson and H.J. Lawler, *Org. Synth. Coll., vol.1*, 2-nd Ed., Wiley, New York, 1947, p. 222.
4. H.W. Underwood and E.L. Kochmann, *J. Amer. Chem. Soc.*, **1924**, *46*, 2069.
5. D.M. Hall, M.S. Leslie and E.E. Turner, *J. Chem. Soc.*, **1950**, 711.
6. M.D. Banciu, C. Mangra, A. Petride, A. Banciu and R. Popilian, *Bull. Soc. Chim. Belg.*, **1996**, *105*, 329-334.
7. M.D. Banciu and I. Şaramet, *Hidrocarburi*, Tehnoplast Co, Bucharest, **1997**, p. 20.
8. R.F.C. Brown, *Pyrolytic Methods in Organic Chemistry*, Academic Press, New York, **1980**, p. 250, 306, 307.