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Some Terpenes and Related Derivatives Synthesized in Cold Plasma Systems

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Abstract: The synthesis of bicyclo-[2.2.1]-heptane and bicyclo-[7.2.0]-undec-4-ene derivatives under cold plasma conditions are reported. The reaction systems involve gaseous mixtures at an interface with ice surfaces. The reactions are sensitive to the feed mixture and the ice trapped compounds.

Keywords: Cold plasma synthesis, terpenes, chemical evolution.

Introduction

During the last decade plasmas have been intensively investigated due to the possible application in technology, chemistry, and spectroscopy [1]. The progress of low-temperature plasma applications depends obviously on the development of devices that generate such a plasma, e.g., RF (Radio Frequency) or DC (Direct Current) generators, microwave plasmatrons.

One of the fields in which cold plasma systems have been extensively used concerns chemical evolution simulations. After Miller's successful experiment [2], many more followed in which the synthesis of some significant prebiotic compounds, such as amino acids, nucleic acids bases, sugars, lipids, etc., was reported [3]. The experiments carried out in order to simulate the prebiotic evolution starting from a reduced atmosphere have highlighted the role of formaldehyde [4] and hydrogen cyanide [5] as precursors in the synthesis of the essential biomolecules. Even if the redox character of such an atmosphere [6] is still a matter of debate, it is known that a high level of oxygen results in decomposition of organic compounds.

The study of natural products from contemporary sophisticated superstructures shows the role of lipid compounds (terpenes [7-8] particularly) for living membranes, in reinforcing them against shear stresses. Primitive membranes could initially have been formed by simple terpenoids, and vesicles formed from these membranes may have evolved into progressively more complex units, more and more similar to protocells [9].

Results and Discussion

Our paper reports the cold plasma synthesis of some bicycle terpenoid compounds. The reactants have very simple structures (water, ammonia, and carbon dioxide). The complexity of the raw reaction product is generated by the synthesis pathway [10].

In order to establish the composition and peculiar structures of the organic components of the final reaction products, a chloroform extraction was performed and the

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three resulting fractions (aqueous phase, interface and chloroform phase) were analyzed by GC/MS (Figure 1 - chloroform phase). The formation of lipid-like structures (non-polar hydrocarbon and polar polyacrylamide blocks) have been reported earlier [11].

The chloroform phase shows the presence of bicyclo-[2.2.1]-heptane and bicyclo-[7.2.0]-undec-4-ene derivatives (Table 1, no. 1, 2, 3, 4, and, 5, 6, respectively).

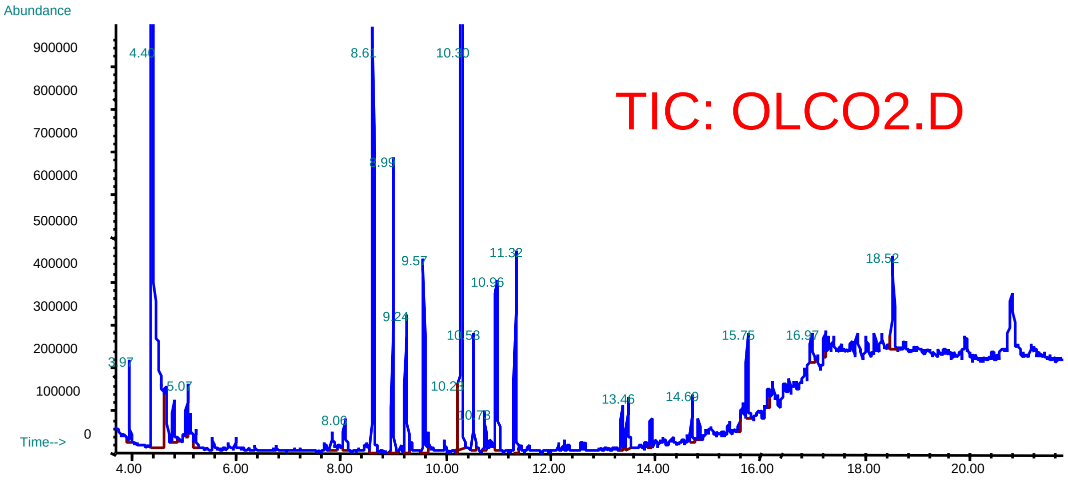
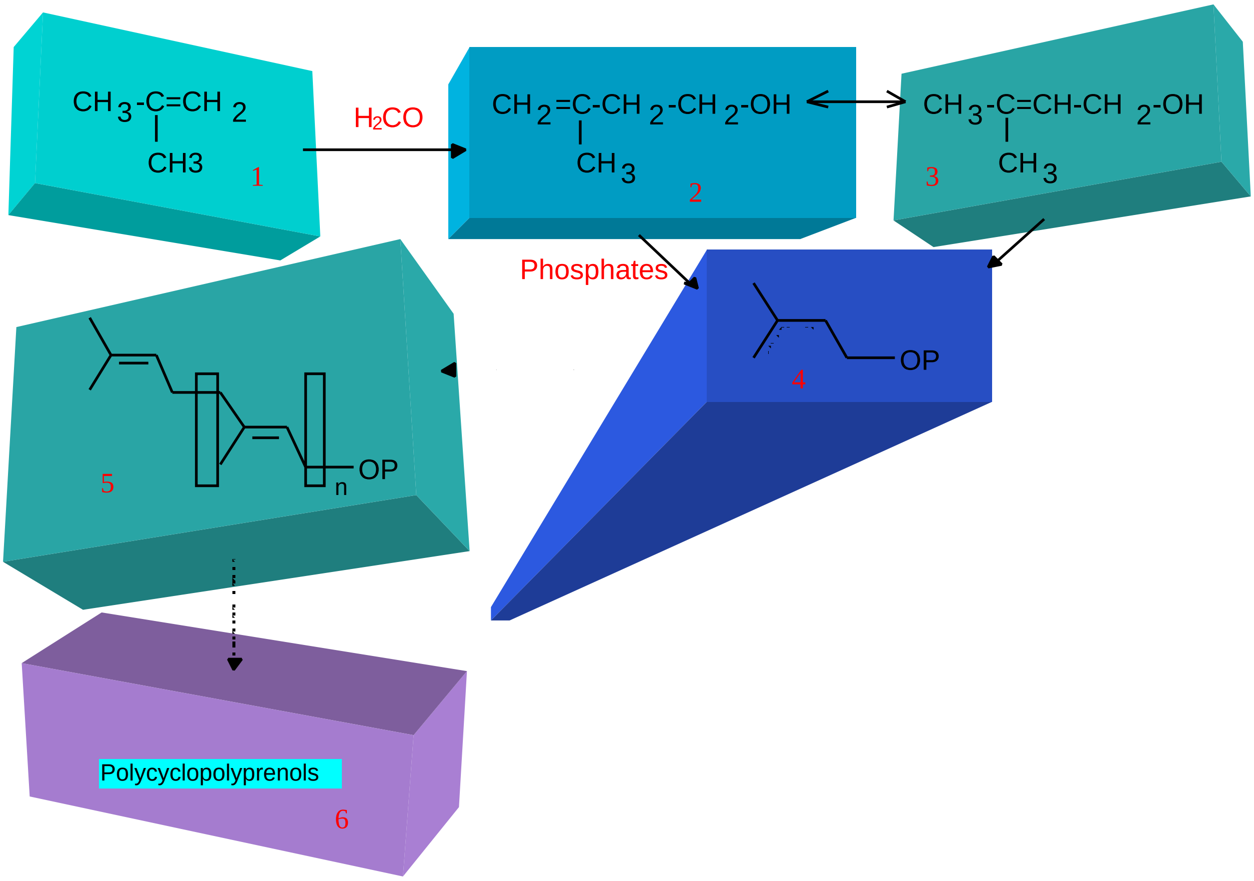
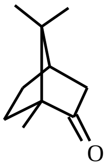
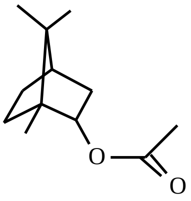
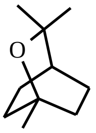
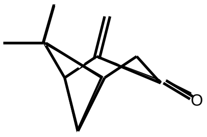
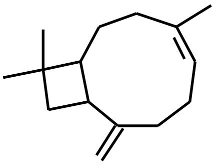
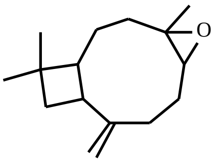
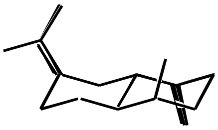
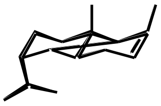
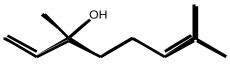


Figure 1. TIC chromatograms (total abundance of ions recorded) of the chloroform extract from raw reaction products plotted versus retention time.



Scheme 1. Scheme of the synthesis of terpenoids from isobutene and formaldehyde.

Table 1. The bicyclic compounds identified in cold plasma synthesis.

No	Quantity (%)	Name	Structure	#NIST	#CAS	Quality Invers	Match PBM
1.	**7.14**	**Bicyclo[2.2.1]heptan-2-one, 1,7,7- trimethyl-**		**66978**	**000076-22-2**	**963**	**97**
2.	**0.06**	**Bicyclo[2.2.1]hept-2-yl acetate, 1,7,7-trimethyl-**		**69502**	**000076-49-3**	**821**	**83**
3.	**4.30**	**Bicyclo[2.2.1]heptane, 1,7,7- trimethyl-1,7-oxo-**		**67089**	**000470-82-6**	**942**	**95**
4.	**1.18**	**Bicyclo[3.1.1]heptan-3-one, 6,6-dimethyl-2-methylene-**		**9819**	**016812-40-1**	**865**	**91**
5.	**0.32**	**Bicyclo[7.2.0]undec-4-ene, 4,11,11-trimethyl-8-methylene-**		**69932**	**000087-44-5**	**890**	**86**
6.	**1.29**	**Bicyclo[7.2.0]undecane, 4,11,11-trimethyl-8-methylene-4,5-oxo-**		**27701**	**001139-30-6**	**908**	**76**
7.	**0.55**	**Naphthalene, decahydro-4a-methyl-1-methylene-7-(1-methylethenyl)-**		**69938**	**017066-67-0**	**765**	**97**
8.	**0.46**	**Tricyclo[4.4.0.02,7]dec-3-ene, 1,3-dimethyl-8-(1-methylethyl)-**		**23969**	**014912-44-8**	**975**	**95**
9.	**2.08**	**1,6-Octadien-3-ol, 3,7-dimethyl-**		**10941**	**000078-70-6**	**818**	**90**

There are many ways in which terpenoid compounds can be obtained [7, 8, 12-13], including Prins reaction of formaldehyde and isobutene with the formation of isopentanol, followed by a sequential elongation to polyprenols.

Eventually these can undergo cyclization which result in the synthesys of polycyclic derivatives [14]. It is worth noting that formaldehyde was identified among the reaction products of many chemical evolution experiments, irrespective of the redox character of the starting gaseous mixture or of the energy source used. However, the complexity of the plasma systems makes it difficult to trace a precise reaction pathways for all of the compounds synthesized. Such systems can favor many side-reaction including cyclization, group transfer, etc., that would justify the presence of decahydro-4a-methyl-1-methylene-7-(1-methylethenyl)-naphthalene (no. 7 in Table 1) as a derivative of a terpenoid.

Conclusion

It can be supposed that one of the most important factors which determined the appearance of an ordered system from a random chemical mixture in the primeval environment was probably the appearance of functional protomembranes [14-16]. The importance of membranes and surfactants (lipid-like compounds, terpenes, etc.) for chemical evolution is unanimously recognized. Further details of these observations are under investigation.

Experimental Section

Synthesis of the compounds

Starting from an open system (CO_2 / NH_3 / H_2O), our simulative experiments were carried out in a plasma installation (Figure 2) joining a spherical RF plasma reactor (10) and a cylindrical cooling part (13) for species recombination in the afterglow zone. Experiments were developed with ice deposited on the inner surface of the cylindrical part (13). The ultracryostat (14) maintains the temperature of the cylindrical flask at -60°C.

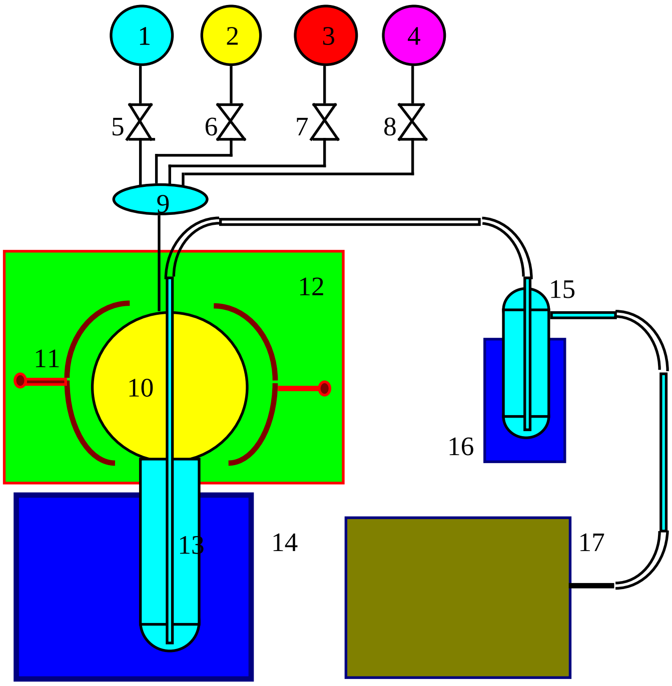


Figure 2. The installation for cold plasma synthesis. 1,2,3,4 - gas cylinders; 5,6,7,8 - valves; 9 - mixing vessel; 10 - plasma reactor; 11 - capacitive electrodes; 12 - RF plasma generator; 13 - cylindrical reactor; 14 - ultracryostat; 15 - liquid N_2 cooled trap; 16 - cryostat; 17 - vacuum pump.

The parameters of the plasma syntheses were: pressure during the synthesis, 460 - 660 Pa; temperature of cooling zone, 113 K; time, 4 hours, and dissipated power, 4.8 kW. Water was introduced in different ways: 500 ml initially (ice from artificial "sea water" on the cylindrical surface of the reactor) and during the synthesis 5 mg/s water vapor in the atmosphere for RF plasma discharge. The feed mixtures were: initial CO_2 partial pressure, 200 Pa; initial NH3 partial pressure, 66 Pa; initial water partial pressure, 66 Pa. Artificial "sea water" was prepared from salts (p.a. purity grade) in order to achieve the main marine ionic composition: NaCl 25.082 g/l, $CaCl_2$ 1.360 g/l,

$MgSO_4 7H_2O$ 7.093 g/l, $Na_2HPO_4 12H_2O$ 1.081 g/l, KCl 1.070 g/l and $MgCl_2$ 2.078 g/l.

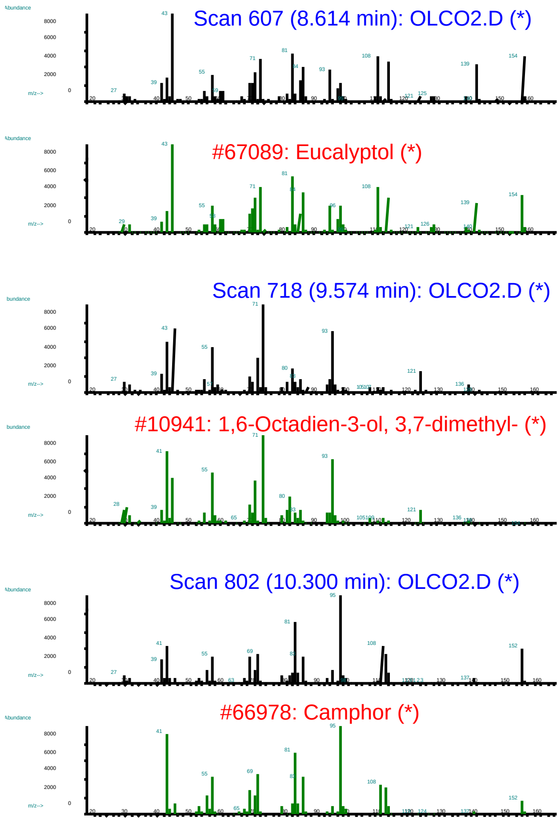
Before the reaction, the installation was cleaned with air (direct valve injection) and H_2 (from cylinder (4) through a needle valve (8)) plasma. Known amounts of carbon dioxide, ammonia and water were introduced into the mixing chamber (9) through needle valves (5-7). The mixture obtained was continuously admitted into the spherical part (10) of the apparatus, where an electric discharge was provided by (12) a high-frequency generator (5 kW and 13.6 MHz) by means of two external silver-plated electrodes (11). The vacuum (460 - 660 Pa) and open system conditions was ensured by a pump (17) protected by a N_2 cooled trap (15). The volatile compounds from a reactive plasma synthesis are captured in trap (15) cooled with the cryostat (16).

The active species formed in the cold plasma were adsorbed on the ice deposited previously (from "sea water" [10]) on the wall and at the bottom of the cylindrical flask (13), cooled to -60ºC with ethanol and recirculated locally through a cooling system (17).

Analysis of the raw reaction products

Chloroform extraction of the raw reaction products was performed and the three resulting fractions (aqueous phase, interface and chloroform phase) were analyzed.

GC / MS analyses were performed on a Hewlett-Packard GC 5890 series II Plus / MSD 5972A instrument with a 30 m 0.25 mm ID 0.33 m film thickness type HP5MS capillary GC column in order to obtain data on small organic molecules from chloroform phase (Figure 1). GC conditions were as following: initial temperature 40ºC at 2 min.; then to 90ºC at 5ºC/min. rate, to 120ºC at 10ºC/min. and to 250ºC at 15ºC/min.; final time 5 min.; carrier gas helium.


Scan 607 (8.614 min): OLCO2.D (*)

#67089: Eucalyptol (*)

Scan 718 (9.574 min): OLCO2.D (*)

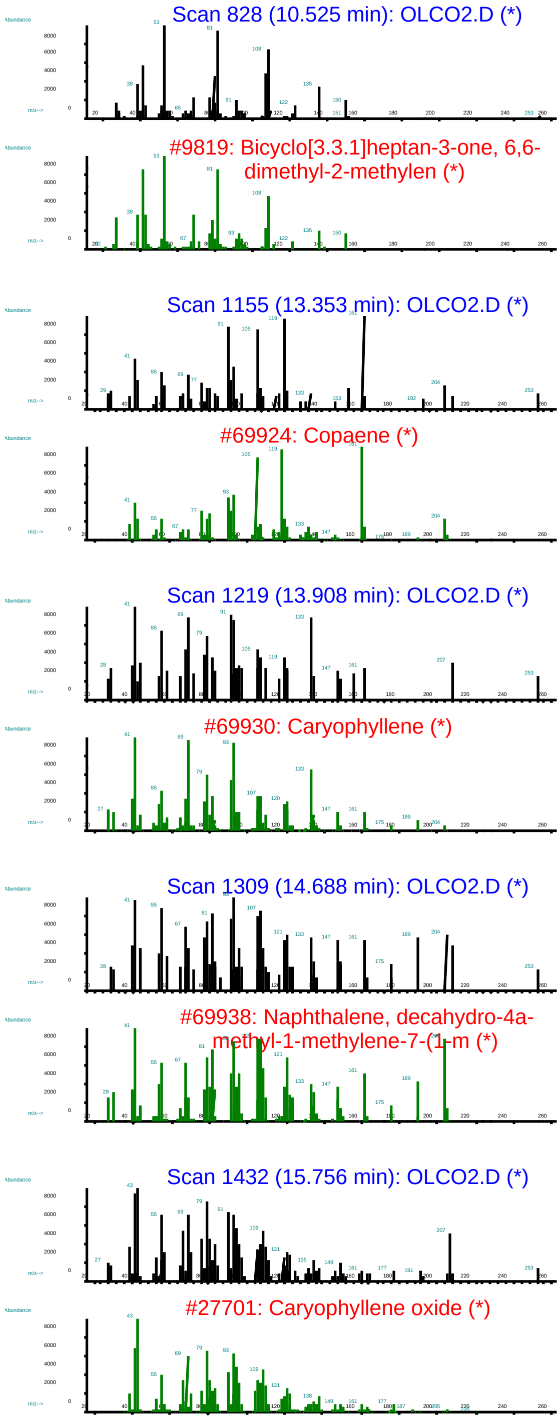
#10941: 1,6-Octadien-3-ol, 3,7-dimethyl- (*)

Scan 802 (10.300 min): OLCO2.D (*)

#66978: Camphor (*)

(To be continued)

Figure 3. The comparison of mass spectra obtained experimentally in a GC/MS analysis (black, side up each frame) and NIST library spectra (green, down). The identification was made using PBM search from HP MSD ChemStation.



Scan 828 (10.525 min): OLCO2.D (*)

#9819: Bicyclo[3.3.1]heptan-3-one, 6,6-dimethyl-2-methylen (*)

Scan 1155 (13.353 min): OLCO2.D (*)

#69924: Copaene (*)

Scan 1219 (13.908 min): OLCO2.D (*)

#69930: Caryophyllene (*)

Scan 1309 (14.688 min): OLCO2.D (*)

#69938: Naphthalene, decahydro-4a-methyl-1-methylene-7-(1-m (*)

Scan 1432 (15.756 min): OLCO2.D (*)

#27701: Caryophyllene oxide (*)

Figure 3. (Continued)

The mass spectra of chromatographic peaks were identified (standard spectra autotune) using NIST / EPA / NIH Mass Spectral Data Base with NIST MS Search Program 1.1a (similarity value presuming an impure searched spectrum [15] - 01000 scale) and HP Chemstation Software (PBM search - 1100% - Figure 3). The graphic comparison is given in Figure 3 and numerical values are presented in Table 1. The compounds 1-3 and 5-6 (Table I) are validated by GC/MS analysis (separate injections) of pure (Merk and Fluka, p.a. grade) supposed derivatives under the same analytical conditions.

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Sample Availability: Available from the authors.