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# The Syntheses of 6-Methylene-2,4-cyclohexadien-1-imine and Related o-Quinonoids by FVT of 1-Hetero-1,2,3,4-tetrahydronaphthalenes

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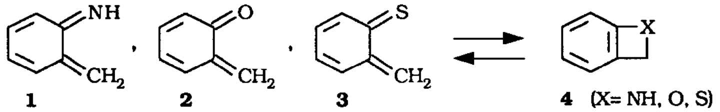
*Key Words:* flash vacuum thermolysis; retro Diels-Alder; o-quinonoids; low temperature IR-UV; MS/MS.

***Abstract:*** *Flash vacuum thermolysis (≈ 1000 °C/$10^{-5}$ hPa) of 1,2,3,4-tetrahydroquinoline, chroman, and thiochroman, led upon loss of ethylene (retro-Diels-Alder reaction) to the o-quinonoids **1-3**. These reactive monomers were identified by IR-UV at -196 °C and/or MS/MS.*

6-Methylene-2,4-cyclohexadien-1-imine **1**, 6-methylene-2,4-cyclohexadien-1-one **2** (o-quinone methide) and 6-methylene-2,4-cyclohexadien-1-thione **3** are important reactive intermediates. According to EHT calculations[1], all the compounds **1-3** should be more stable than their bicyclic isomers **4**. Although no direct experimental evidence of **1** has been hitherto reported, its formation was demonstrated by trapping with phenyl sulfide in the thermolysis of o-aminobenzyl methyl ether[2] and dihydrobenzoxazines[3].



**1** **2** **3** **4** (X= NH, O, S)

The quinone methide **2** is the most stable and best known amongst the compounds **1-3**. Since the papers[4] concerning its formation from o-hydroxybenzyl methyl ether and its oligomerization, direct observations of monomeric **2**, obtained by thermolysis of o-hydroxybenzyl alcohol, were reported by low temperature IR[5], and photoelectron spectroscopy[6]. Trapping by thiones[7] and new methods of obtaining **2**[8] have been since published.

The compound **3** has been generated by photolysis of 3H-1,2-benzodithiole 2,3-dioxide[9], as well as by thermolysis or photolysis of benzothiete (**4**, X = S)[10] and identified by trapping with dienophiles. Recently, the IR and electronic spectra at 12 K of an Ar matrix of benzothiete irradiated at 280 nm showed the presence of monomeric **3**[11].

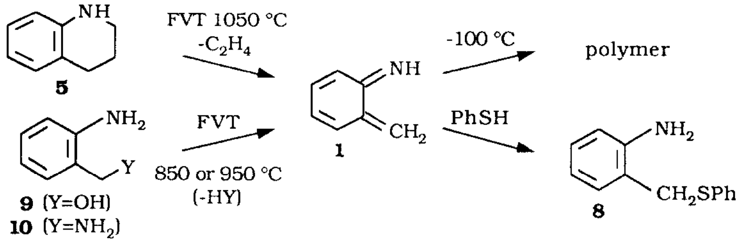
The synthetic usefulness of flash thermolytic retro-Diels-Alder (rDA) reactions[12], and particularly the broad scope of ethylene cycloeliminations leading to o-quinonoid systems[13], prompted us to investigate the flash vacuum thermolysis (FVT) of 1,2,3,4-tetrahydroquinoline **5**, chroman **6**, and thiochroman **7** as sources for compounds **1-3**. These precursors **5-7**, already submitted to static and flow thermolyses, underwent no rDA reaction under the conditions used[14], on the other hand, the FVT of chroman **6** at 800 °C gave, via a rDA reaction, the trimer of **2**[15] [the thermal cleavage of tetralin, a molecule closely related to **5**-**7**, is known to generally proceed unspecifically, most likely via a biradicalar intermediate[16]].

Commercial tetrahydroquinoline **5** (Aldrich) was used, chroman **6** and thiochroman **7** were readily prepared by the Clemmensen-Martin reduction of chroman-4-one and thiochroman-4-one (Aldrich)[17].

In our first FVT's of compound **5**, products were trapped in an optical l'Air Liquide cryostat (-196 °C, NaCl windows and sample carrier) but deceptive results were obtained owing to a too slow heat transfer relative to the reactivity of the expected molecule **1**. Also, we coupled for the following FVT/IR-UV experiments the FVT oven with a home-made Pyrex cryostat* where the NaCl or Suprasil plates are most efficiently cooled by indium sealing into an annular carrier containing liquid nitrogen [oven dimensions: length 10 cm, i.d. 1.2 cm; spectrometers used: Perkin-Elmer 1420 (IR), Jobin-Yvon 201 (UV-visible) and Varian MAT 311 (MS/MS)].

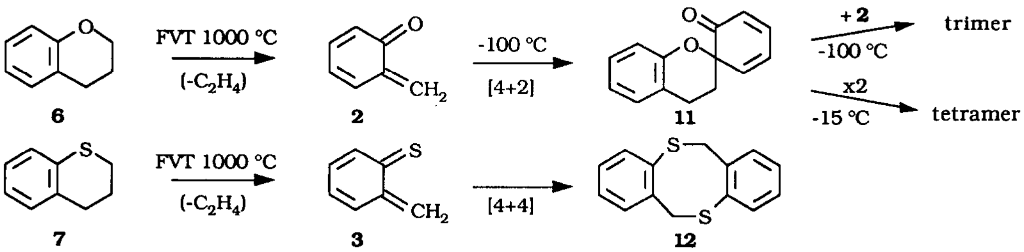
The FVT of tetrahydroquinoline **5** (20 µl) was performed at 1050 °C under $10^{-5}$ hPa. No starting material was recovered at this temperature and a bright yellow product deposited on the plate. IR analysis at -196 °C led us to attribute to the imino-quinone methide **1** the following absorptions: 1629 (s), 1528 (s), 1352 (s), 1335 (s), 1281, 1095 $cm^{-1}$; the characteristic bands of ethylene and of minor by-products (mainly benzonitrile at 2215 $cm^{-1}$) were also present. At *ca* -100 °C, all these absorptions disappeared with bleaching of the plate and a new spectrum, already visible at -196 °C, as weaker absorptions besides **1**, became preponderant. Being unchanged between -80 °C and room temperature, it was attributed to the polymeric white material remaining on the plate (1600, 1492, 1447, 1310, 755 $cm^{-1}$). FVT of **5** in the presence of phenyl sulfide led to the expected adduct **8**[2,3].

The o-aminobenzyl derivatives **9** and **10** (Aldrich), other potential precursors of **1**, were also thermolysed with a view to confirming the above results. No more starting materials were present at FVT temperatures of 850 (**9**) or 950 °C (**10**) and the sets of absorptions reported in the FVT of **5** for monomeric and polymeric **1** were also observed, besides other bands, in both cases.



The thermolysis of chroman **6**, performed under the same conditions, was complete at 1000 °C. The IR spectrum at -196 °C of the yellow product obtained showed, besides that of ethylene, only a set of bands disappearing at -100 °C and attributable to monomeric quinone methide **2**: 1657 (s), 1604 (s), 1560 (s), 1531, 1394 (s), 1350, 1191, 1138 (s), 1063, 859 (s), 798 (s), 714, 690 (s), 658 $cm^{-1}$ (previously reported[5]: 1656, 1565, 1539 $cm^{-1}$). At -100 °C the yellow compound quickly turned white and a new spectrum was obtained: 1672 (s), 1405, 1078 (s), 1008, 813, 682 $cm^{-1}$ (s). These bands, again vanishing at -15 °C, belong most likely to the transient [4 + 2] dimer **11** of **2**[4]. A weaker band at 1683 $cm^{-1}$, remaining until room temperature, can be attributed to the trimer of **2** [band reported at the same value (5.94 μ)[4]]. At -15 °C, the spectrum of **11** was in turn replaced by that of a new compound: 3040, 2940, 1729 (s), 1690 (s), 1580 (s), 1482 (s), 1451 (s), 1228 (s), 1110 $cm^{-1}$ (s); the mass spectrum of which suggests a tetrameric structure ($M^{+\cdot}$ m/z 424).

The dark red monomeric **3**[11] was not observed here when thermolyzing thiochroman **7**, owing to its too great a reactivity. At a FVT temperature of 1000 °C, the cycloreversion was complete and the only products present at -196 °C were ethylene and the compound **12**, [4 + 4] dimer of **3**[10]: 3065, 3010, 2940, 1574 (s), 1440 (s), 1411, 1265, 1189 (s), 1111, 1041 (s), 995, 930, 738 (s), 705 $cm^{-1}$ (s); NMR and mass spectra identical with those described[18].



The UV-visible spectra of compounds **1** and **2** were recorded in the same conditions unless 0.5 μl of precursors **5** and **6** were thermolyzed. The imino-quinone methide **1** showed a first absorption band at 374 nm, disappearing at *ca* -100 °C (no absorption maximum was observed above this temperature). The corresponding band was observed at 395 nm in the case of compound **2**, in agreement with those reported for substituted o-quinone methides[19]. Upon warming up to -100 °C, the band at 395 nm was replaced by absorption maxima at 299, 281 and 274 nm. The first of them (299 nm), disappearing at -15 °C, is attributable to the dimer **11** (this band was found at about the same wavelength for other 2,4-cyclohexadienones[20]). The bands at 281 and 274 nm, remaining until room temperature, correspond to those already described[4] for the trimer of **2**. The electronic spectrum of thio-quinone methide **3**, reported in an Ar matrix[11] [first band at 2.66 eV (466 nm)] was not observed here.

Owing to the lack of trapping monomeric **3** at -196 °C, the FVT of thiochroman **7** was investigated by coupling the oven with a high resolution mass spectrometer, as described previously[21]; all the species produced by FVT of compound **7** at 950 °C have in this way been unambiguously characterized in real time by MS/MS.

The spectrum obtained under these conditions (Fig. 2) is very different to that of the starting material **7** (Fig. 1). The rDA reaction of **7** led both to ethylene (m/z 28) and **3** (m/z 122) which represent the two most significant peaks of the second spectrum (Fig. 2). The minor formation of radicalar cleavage products, benzene (m/z 78) and benzothiophene (m/z 134), is also observable in this spectrum; the same compounds were identified in the already reported thermolysis of **7**[14].

The formation of benzene and benzothiophene can be minimized by lowering the FVT temperature to 850 °C, but with the counterpart of a less complete cycloreversion (relative intensity of m/z 150 ion due to **7** : 4.4 % at 950°C and 10 % at 850°C).

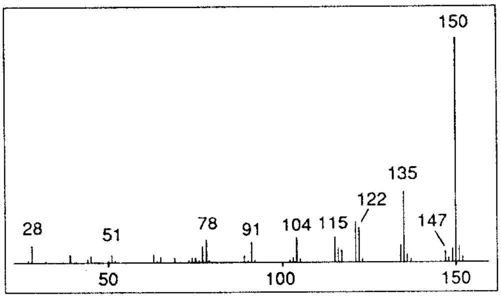


Fig. 1: MS of **7** (150 °C)

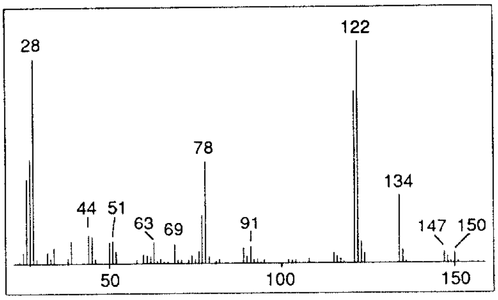


Fig. 2: MS of **3** (FVT of **7** at 950 °C)

The rDA reaction of tetrahydroquinoline **5**, also investigated at 950 °C by FVT-MS/MS coupling, gave a significant peak of ethylene (m/z 28) and another one at m/z 105 (imine **1**), the mass spectrum also being very different to that obtained for the precursor **5**. An important ion at m/z 103, also observed in the FVT of **5**, was identified as benzonitrile by comparison between the MS/MS of m/z 103 and the molecular ion of this compound. Benzonitrile occured most probably by loss of ethylene from the intermediate o-ethylbenzonitrile[14].

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