



## PROBLEM 26

### [SUPPL Problem 26 # 1]

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Arabic compound numbers in TAPSOC,  
Roman numerals in Supplementary material

#### In Perspective

Heating monoterpenes at very high temperature may seem to some a waste of time because compounds simply rip apart to a dearth of much less complex materials, uninteresting ones like isoprene, and without much preparative interest.

As it turns out, this procedure has been used for a long time for the preparation of substituted benzenes and aromatic hydrocarbons up to C<sub>10</sub>, polyoxygenated compounds and several others of interest to the pharmaceutical industry.

Over the years, mechanistic organic chemistry has learned a great deal about molecular behavior using these vapor phase thermolysis. Compounds have nothing but themselves and energy from molecular collisions under quantum constraints to create new element arrangements, frequently with unexpected results.

With the advent of supercritical fluid technology, the gas phase pyrolysis methodology has evolved into thermolysis in supercritical water or low molecular weight alcohols at high pressure with microwave radiation heating (e.g. 270 °C). Radical based as well as protonation of functional groups residing in the terpene scaffold drive the thermal decompositions in a more controlled fashion [e.g. 1, 2].

The reactions opening this TAPSOC problem, which were thoroughly investigated by professor Georg Rüedi and his group at the University of Zurich, using a flow reactor under vacuum (thus securing short reaction times), led to the discovery of an unprecedented reaction sequence based, anyhow, on well known sigmatropic rearrangements. But there is a mechanistic novelty here. If this last feature makes

mechanism design more difficult (no one to imitate), you will agree that this additional challenge makes it far more interesting.

**One more comment on the biological side**, which you may skip if you still think that organic chemistry begins at a lab bench and ends in an industrial product or a scientific paper only.

This topic has to do with wildfires.

**For a more thorough description, and a couple of fascinating stories, see THE CHEMISTRY OF BURNING FORESTS, in the Green Chemistry Section of this Website.**

Forest fires are a disgrace. Millions of hectares are burned by man each year to expand the agricultural frontier, for ranching, urbanism, land management, on purpose, by accident, or felony. Recurrent bush and forest fires, however, are hardly new. Fire sparked by natural forces (lightning, fermentation of organic heaps, lava flows) has been and continues to be a major force modeling entire ecosystems, extant and extinct.

Chemically speaking, the burning of plant material is a complex combination of high temperature heating, that is, thermolysis, and oxidative pyrolysis depending on the proximity of open flames and heat transport across wood. Myriads of burned products are created from a vast array of biological compounds: charred material, smokes and vapor or gas result. Infamous PAB, benzo[b]pyrenes, and polyaromatic amines are among the less volatile. Products from isoprene derivatives, including terpenoids as classical members, lignin and cellulose-derived substances constitute an important fraction of the volatiles and smoke particles [3]. This subject has been of central interest to the tobacco industry for years.

Laboratory thermolysis/pyrolysis experiments and highly developed mass spectroscopy analysis are fundamental tools to understand this complex chemistry and its impact on ecosystem functioning and people's health. Smokes from forest fires travel long distances to large cities affecting the public health condition to a still undetermined

extent. Thus, the chemistry of terpene thermolysis cannot be disregarded lightly as a waste of time; of course not.

## REFERENCES

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- [1] Anikeev AI. *Flav. Frag. J.* 2004;25:443-455.
- [2] Szuppa T, Stolle A, Ondruschka B. *Org. Biomol. Chem.* 2010;8:1560-1567.
- [3] For example, see: Maleknia SD, Bell TL, Adams MA. *Eucalypt smoke and wildfires: Temperature dependent emissions of biogenetic volatile organic compounds.* *Int. J. Mass Spec.* 2009;279:126-133.