

Molecule of the Month

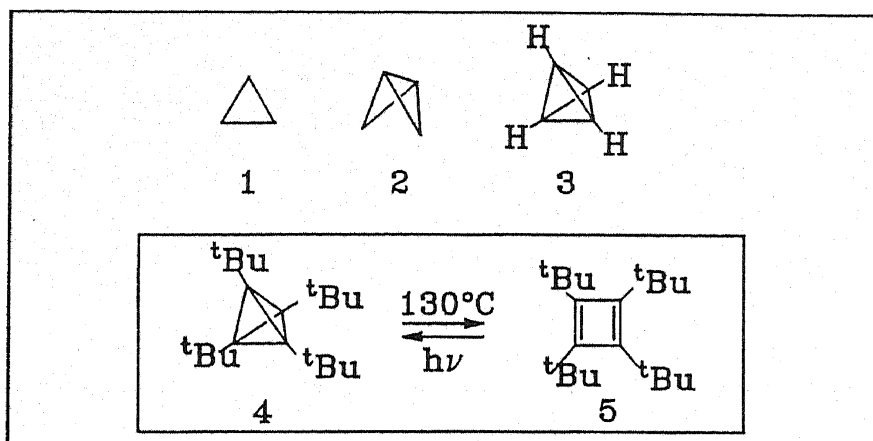
A Tetrahedrane Derivative

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Studies on a highly strained hydrocarbon are discussed.

Atoms in a molecule generally prefer, particularly among the neighbouring ones, certain optimum geometrical relationships. These are manifested in specific ranges of bond lengths, bond angles, torsion angles etc. As it always happens, chemists are interested in making molecules where these 'standard relationships' are violated! Such molecules, by virtue of their altered bond lengths, bond angles, or torsion angles, store a lot of strain within the molecule. For example, whereas propane ($\text{CH}_3\text{CH}_2\text{CH}_3$) is virtually strain-free, cyclopropane (**1**) is highly strained, because of the deviation of the bond angles ($\angle\text{CCC}$) from the normal value of 109.5° . If you put two cyclopropane rings together, as in compound **2** (known as bicyclo [1.1.0] butane), the strain energy more than doubles. One molecule that has interested chemists for many decades is **3** which can be derived from **2** (remove two hydrogens, and make an additional carbon-carbon bond). This (hypothetical) molecule has been named *tetrahedrane*, and is the smallest molecule with the general formula $(\text{CH})_n$ without a double bond. It has four carbons arranged at the vertices of a regular tetrahedron, with each carbon being bonded to the other three, and to one hydrogen. This small but beautiful molecule has been the synthetic target of many chemists, but all attempts to generate it failed. Why? The answer is rather simple! If we compute the strain energy of **3**, and compare it with **2** we can easily see that tetrahedrane is about as strained as two molecules of **2**! This much strain leads to thermodynamical instability. Thus, such high energy molecules will always decompose to produce more stable molecules, in that process

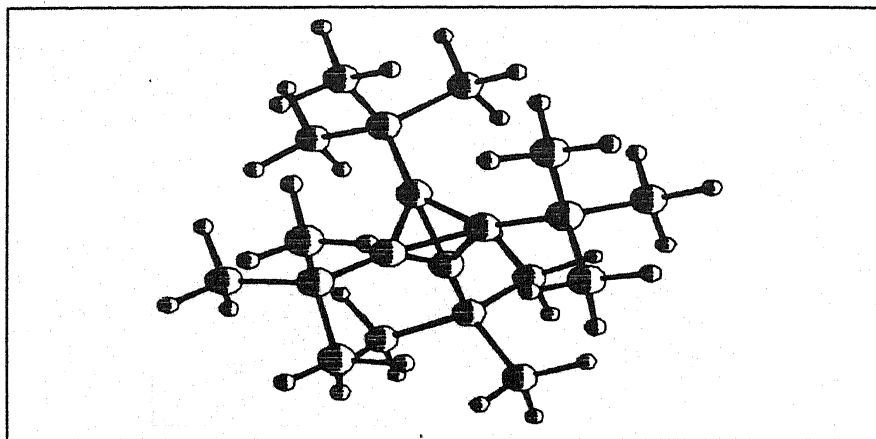


releasing the strain energy (just like releasing a compressed spring). Thus, compound 3 can in principle decompose to other $(\text{CH})_n$ molecules (such as a molecule of cyclobutadiene which would in turn dimerize to form cyclooctatetraene, or fragment to two molecules of acetylene) which do not have as much strain.

Going by these theories, it seems that the construction of a molecule such as 3 would be an impossible task! However, there is usually a way out of the thermodynamic instability. Even when a process is highly favourable thermodynamically, it may be kinetically slow. Once again, we can find an analogy with a compressed spring, kept in a container too small to let it expand. The highly thermodynamically favourable, but kinetically slow, reaction $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$ is an example closer to this. How does this idea help chemists design a stable tetrahedrane analog? The approach taken by Günther Maier and coworkers is simple in principle. They decided to substitute the four hydrogens of 3 with bulky tertiary butyl groups. In compound 4, these groups are as far apart from each other as possible compared to any other C_4 framework. Thus, any attempt by compound 4 to become a cyclobutadiene unit will be resisted because that process will bring the big t-butyl groups too close to each other causing van der Waals' repulsion. Thus, compound 4 seems to be the right choice to make the tetrahedrane skeleton. Chemists generally employ another trick to make high energy molecules. It is usually easier to put in the extra energy (which appears as the strain energy) in the form of

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Figure 1 Ball and stick representation of tetrahedrane derivative 4



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light. In other words, photochemical processes are ideally suited for constructing high-energy molecules. That is indeed how compound 4 was successfully synthesized in about 35% yield by a photochemical route (see Figure 1 for a ball and stick representation of compound 4). This molecule was found to be a colourless solid melting at 135°C! It was also found that heating compound 4 at 130°C slowly converted it to the yellow-orange cyclobutadiene derivative 5. But 5, upon photochemical irradiation, may be converted back to 4. This interconversion clearly points out the kinetic stability of 4. A space filling model (not shown) of 4 clearly shows the tetrahedron skeleton well-covered by four t-butyl groups.

In 1984, Maier was successful in obtaining the crystal structure of tetrahedrane 4. Interestingly, it was found that the C-C bond distance within the tetrahedron skeleton was shorter (1.485 Å) than a normal C-C bond (1.54 Å).

These studies therefore show that even seemingly unstable molecules can be stabilized by making their path to destruction (reaction) inaccessible! Readers may be interested to learn that a similar tetra t-butyl substituted ethylene has not been made so far.

If any of our readers is interested in learning how compound 4 was synthesized, (s)he is welcome to write to me for the details.

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