Highlights

Trityloxy Radical

The Rearrangement of the Trityloxy Radical: Sherlock Holmes' Most Recent Case

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analytical methods · radicals · rearrangements · time-resolved spectroscopy

N owadays when the police attempt to solve a criminal case, they make use of modern analytical and physical techniques such as DNA analysis and the calculation of a projectile's trajectory. But until only a few decades ago, the methods of investigation police had at their disposal were limited to comparing fingerprints, questioning suspects, and applying detective's intuition. This is reflected in detective novels— Sherlock Holmes had a working style very different from that of modern-day police inspector on television.

The "criminal case" to be considered here has been on record for a very long time, to be accurate, since 1911. Back then, Heinrich Wieland described the rearrangement of triphenylmethoxyl (or trityloxy, 1) into phenoxydiphenylmethyl (2).^[1] Thermolysis of ditritylperoxide (3) in xylene yielded diphenoxytetraphenylethane (4) as the main product (65–75% yield). As side products, benzophenone, phenol, and an unspecified amount of triphenylmethanol (5) were formed (Scheme 1).



Scheme 1. Heinrich Wieland's experiment.

Wieland's experiment is easily interpreted in terms of a rapid rearrangement of 1 into the more stable carboncentered radical 2, which then dimerizes. Hydrogen abstraction from the solvent, yielding the stable alcohol 5, competes with the rearrangement of 1. To return to our detective analogy: Wieland proved the rearrangement of the suspect 1 by questioning the witnesses 4 and 5. However, has the course of events been sufficiently elucidated? The motive is obvious (thermodynamics), and the weapon used is well known (an oxygen-centered radical). But many details are not so clear. How fast was the rearrangement? Had there been accomplices (oxygen...), intermediates? The fact that this reaction

[*] Dr. G. Bucher University of Glasgow, Joseph-Black-Building University Avenue, Glasgow G12 8QQ (UK) E-mail: goebu@chem.gla.ac.uk was re-investigated many years after 1911, when new experimental methods like laser flash photolysis (LFP) and modern quantum chemistry could give new insights into the mechanism, does not come as a surprise.^[2-5] In the context of our analogy, laser flash photolysis can be compared to a closed-circuit video recording of the crime scene. Ideally, one obtains a direct spectroscopic (UV/Vis, IR, or ESR) portrait of the suspect. A disadvantage of LFP lies in the fact that reactive intermediates are generated photochemically in an LFP experiment. While the photochemical fragmentation of labile compounds frequently involves the same intermediates as the thermal reaction, this cannot be assumed. A study aimed at elucidating the photochemistry of 3 by LFP with picosecond resolution was published in 1990.^[6] In contrast to Wieland's report, the authors found practically no triphenylmethanol in the product mixture, and the formation of 2 was observed to occur during the laser pulse. Based on these findings, they determined the lower limit for the rate constant of the rearrangement of **1** to be $k_1 > 5 \times 10^{10} \text{ s}^{-1}$.

The discrepancy between the results of the LFP study^[6] and Wieland's preparative work is obvious. Along the lines of our metaphor, we have a video recording of the crime scene and we have witness testimony, but they contradict each other. Did the video camera and the witnesses observe the same crime? A group of researchers from Canada, Poland, and the Netherlands has now searched for a different precursor for **1**; they have studied the thermal decomposition of hyponitrite **6** in great detail by means of classical product analysis.^[7] In other words: away from video recordings and back to the painstaking interrogation of witnesses and deduction, back to the method of Sherlock Holmes. However, the new study does utilize some more recent techniques like HPLC which had not been available to Heinrich Wieland in 1911.

Hyponitrite **6** is a thermally highly labile compound that quantitatively decomposes in CH₂Cl₂ within a couple of hours, even at ambient temperature. In the presence of air, ether **4**, phenol, benzophenone, a little phenyl benzoate, and ditrityl-peroxide **3** (10% yield) are formed. In the absence of air, but with the addition of 80% 1,4-cyclohexadiene as a hydrogen donor, **5** is formed as main product, while ether **7** is only a side product along with peroxide **3** in 2.6% yield (Scheme 2). The rate constant for the abstraction of a hydrogen atom from 1,4-cyclohexadiene by **1** can be estimated quite accurately as $k_2 = 4 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, as there are published values for a range of

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Scheme 2. Thermal decomposition of hyponitrite **6** in 1,4-cyclohexadiene/ CH_2Cl_2 at ambient temperature. Yields of the major products after 7 h. Note: The pyrolysis of **6** yields two equivalents of the trityloxy radical; the yields therefore add up to more than 100%.

similar reactions. Based on this rate constant and the product ratio, the rate constant of the rearrangement is determined to be $k_1 = 1.4 \times 10^8 \text{ s}^{-1}$, corresponding to a lifetime of **1** at ambient temperature of approximately 7 ns. This may be very short, yet it is a lot longer than the lifetime of < 20 ps from the LFP measurements.^[6]

In the new study Wieland's original experiment is also revisited using contemporary analytic methods. Pyrolysis of 3 in refluxing xylene at 138°C showed that 98.66% of 1 isomerizes at this temperature, and only 1.34% abstracts hydrogen from the solvent. The rate constant for hydrogen abstraction can be reliably estimated using published Arrhenius parameters for similar reactions of the tert-butoxy radical and by extrapolating to the boiling point of xylene: $k \approx 4 \times$ $10^{6} \text{ m}^{-1} \text{ s}^{-1}$. The rate constant for the rearrangement of **1** at 138 °C follows as $k_1 = 2.1 \times 10^9 \text{ s}^{-1}$. The two values of k_1 yield a (relatively inaccurate) Arrhenius plot, which gives $E_a =$ 5.6 kcalmol⁻¹ and $lg(As^{-1}) = 12.3$ for the rearrangement of 1. Are these figures in the ballpark? Just as a modern police department is inconceivable without computers and databanks, quantum chemistry plays a crucial role in modern physical organic chemistry. The use of DFT calculations led to an estimate of $E_a = 6.2 \text{ kcal mol}^{-1}$ and $\lg(A \operatorname{s}^{-1}) = 12.9$. Considering the error margins for both experiment and theory, there is satisfactory agreement between the two!

If both Heinrich Wieland's study and—one hundred years later—the renewed analysis of the chemistry of the trityloxy

radical (1) present convincing evidence that 1 can be intercepted by hydrogen atom donors, why wasn't it possible to trap 1, when it had been generated photochemically?^[6] Very likely, UV photolysis of 3 does not yield radical 1 in its ground state, but rather in its excited doublet state. In other words: the video recording proves to be a recording of another crime scene and of another suspect...

Why is this study^[7] worthy of a Highlight? It is a good example of how the combination of accurate product analysis and well-founded kinetics estimates can yield convincing kinetic data—and that this method may sometimes be superior to time-resolved spectroscopy.

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