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Historical Paper

»Was schön ist, ist auch gut«

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A recollection of how one of the steps in an attempted synthesis of 1,6-dimethyl-cyclodecapentaene became a glassblower's nightmare.

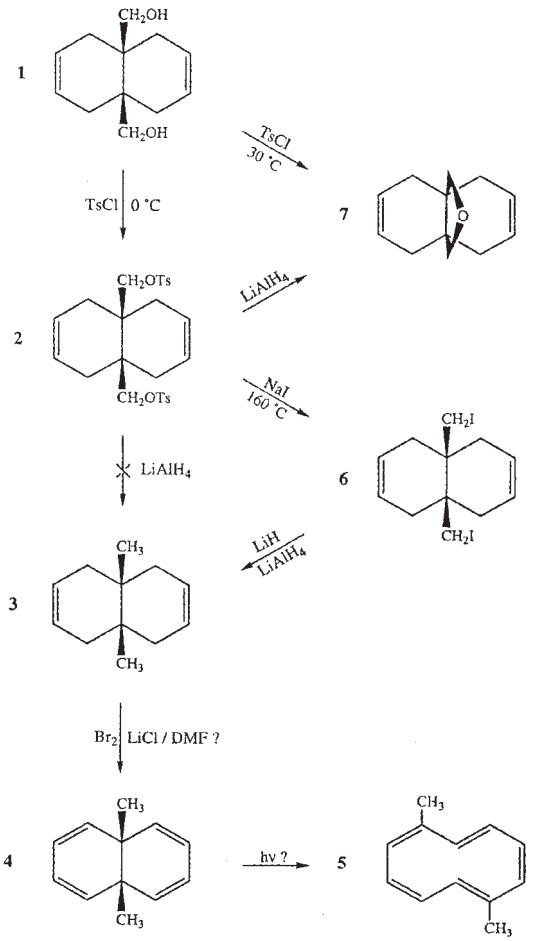
The year 1957 was not only the year when the first Sputnik was launched. For organic chemists the launching of the journal *Tetrahedron* by Sir Robert Robinson was more important. For Vladimir Prelog, who had prepared adamantane in a many-step synthesis when he was still in Zagreb,[1] the discovery by Paul Schleyer of a simple way to prepare adamantante by enthalpy-driven isomerization[2] may have had a stronger impact. Perhaps most important was the arrival at ETH of Jack Dunitz, who together with Prelog should lay the foundation for a deeper understanding of the conformations of medium-sized rings.[3] As for myself, 1957 was the year when I had the great privilege to work with Prelog.

The preceding year Prelog wrote a paper about »Bedeutung der Vielgliedrigen Ringverbindungen« wherein the cyclodecapentaene problem was discussed.[4] The project that was assigned to me was to synthesize 9,10-dimethyl-9,10-dihydronaphthalene, in the hope that irradiation would open the bridge to give some isomer of 1,6-dimethyl-cyclodecapentaene. The last among several attempts is presented in the Scheme by the planned sequence of steps **1**, **2**, **3**, **4** and **5**. The starting material **1** was readily synthesized, but the ditosylate **2** formed the cyclic ether **7** so easily that it could not be reduced to the hydrocarbon **3**. However, after conversion to the diiodide **6**, reduction to the hydrocarbon proceeded smoothly.

It was this trivial conversion of the ditosylate to the diiodide, using sodium iodide in acetone at 160 °C, that required the use of a sealed glass tube and gave us a problem. To seal such tubes we could rely on Prelog's services. Being an expert glass-blower, he seemed to enjoy sealing glass tubes when these were needed, considering it a welcome relaxation from of-

fice work. At the end of the job, while rotating the tube, keeping the hot glass in a »cool« flame, he used to express his satisfaction by saying: »Was schön ist, ist auch gut!«

And indeed our first experiment was a success; the tube survived, and the yield of crystalline diiodide was 56%. It was then decided to scale up the reaction, and more sodium iodide had to be fetched from the stock-room. The sealed glass tube was again declared »schön«, and »gut«, but when I opened the protective steel-tube after reaction, the glass-tube had been smashed to thousand pieces. This had never happened before to Prelog, and we could not find an explanation. The experiment was repeated once, then once more, each time with the same disastrous result.



Scheme

At this point the reader will no doubt ask a most reasonable question. Why did we not check the material from the stock-room? We had in fact a very good excuse for our lack of suspicion: After each experiment I carefully extracted the remains in the steel tube and could in fact isolate small amounts of the desired iodo-compound.

Eventually, I recalled that the sodium iodide that was used in the first experiment dissolved rapidly and completely in acetone, whereas the sample from the stock-room remained as a suspension. On heating, some iodide could well have been formed by reduction if the reagent contained iodine in an oxidized state. The sample was then quickly identified as sodium iodate. I further recalled having noted that Latin names for chemicals were used on the shelves in the stock-room. Clearly, the clerk had assumed that *iodicum* came closest to *iodide*, while in Latin it is in fact *iodatum* that corresponds to *iodide*, and *iodicum* corresponds to *iodate*.

When this became clear, Prelog rushed to the stock-room at such a speed that »die Mantelschösse flatterten im Wind«.[5] Left alone in the laboratory, I reflected the irony that this happened in a country which presents itself on coins and stamps by its Latin name!

About the last steps of the synthetic scheme there is little to report. My time ran out after having obtained the bicyclic diene **3** by hydride reduction. The prospect of dehydrogenation to the tetraene **4** seemed favourable since the byproduct **7** was dehydrogenated successfully to the corresponding tetraene by the procedure given.

Many years later S. Masamune attacked the cyclodecapentaene problem successfully.[6]

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SAŽETAK

»Što je lijepo, također je i dobro«

Johannes Dale

Sjećanje kako je jedan od stupnjeva u studiranoj sintezi 1,6-dimetilciklodekapentaena postao noćna mora staklopuhača.