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Closing Remarks at the Symposium in Honour of Daniel Belluš

Pharmacenter, University of Basel, February 6, 2009

Camille Ganter*

Dedicated to Prof. Dr. Daniel Belluš on the occasion of his 70th birthday

Abstract: In the Closing Remarks at the Symposium on 'Frontiers in Bioorganic Chemistry' (Friday, February 6, 2009, Pharmacenter, University of Basel) in honour of Daniel Belluš, his arrival in Zürich in fall 1967 and especially his postdoctoral work at the Laboratorium für Organische Chemie at the Eidgenössische Technische Hochschule (ETH) in Zürich throughout the year 1967/68 were mentioned. In his most remarkable paper (published in 1969 in *Helv. Chim. Acta*), the photochemistry of the α,β-unsaturated cyclohexenones O-acetyl-testosterone and 10-methy-$\Delta^{1,9}$-octalon-(2) is described in detail. Change of solvent leads to lowering or increasing of the n,π*- and (π,π*)-triplet energies, resulting in a crossing of the two energy levels. Personal remarks on Daniel Belluš and warmest thanks to him, to Profs. Beat Ernst and Bernd Giese (the organizers of the symposium) and to all the speakers concluded this most special event.

Keywords: Belluš, D. · Ernst, B. · Giehse, B. · Photochemistry · Schaffner, K.

On the occasion of Prof. Dr. Daniel Belluš' 70th birthday, a symposium entitled 'Frontiers in Bioorganic Chemistry' was held in his honour at the University of Basel. More than 200 friends and colleagues of Daniel Belluš came together and enjoyed contributions from Stephan Hanessian, Léon Ghosez, Bernd Giese as well as from several former co-workers of Daniel (Fig. 1).

Actually Prof. Kurt Schaffner of the Max-Planck-Institut für Bioanorganische Chemie in Mühlheim an der Ruhr in Germany should have been the speaker for the Closing Remarks and not myself. Unfortunately, he cannot be with us today. However, he asked me to convey his warmest regards to all of you and added that he is very sorry for not being able to participate today in the symposium. Kurt Schaffner and I know each other since I started my Ph.D. thesis in Professor Oskar Jeger's group at the ETH in Zürich quite a few decades ago. Showing you a photo of Kurt Schaffner would make things absolutely clear and avoid any confusion between Kurt Schaffner and myself. Although he is some years older than Daniel Belluš and me, I have to admit that he looks still very young for his age.

09:00 Welcome	**14:00 Passive and Active Light Management, a Chance for the Chemical Industry** Dr. Andreas Hafner, Head Bio Science, Ciba Inc. Basel/CH
09:10 Structure-based Organic Synthesis: From Natural Products to Drug Prototypes Prof. Dr. Stephen Hanessian, Department of Chemistry, University of Montreal/Ca	**14:30 Exploring Chemical Space of Agronomics** Dr. Gerardo Ramos, Head of Research, Syngenta Crop Protection, Basel
09:50 Natural Products as Leads for Anticancer Drug Discovery Prof. Dr. Karl-Heinz Altmann, Department of Chemistry and Applied Biosciences, ETH Zürich/CH	**15.00 – 15:30 Coffee Break**
10:20 - 10:50 Coffee Break	**15:30 Challenges and Opportunities in Peptide Manufacturing** Dr. Thomas Früh, Chief Operating Officer, Bachem AG, Bubendorf/CH
10:50 Fragment-based Lead Discovery for Lectin Targets Prof. Dr. Beat Ernst, Department of Pharmaceutical Sciences, University of Basel/CH	**16:00 Sugar-derived Nitrones and Their Utilization in Synthesis** Prof. Dr. Lubor Fisera, Institute of Organic Chemistry, Catalysis and Petrochemistry, Slovak University of Technology Bratislava/SK
11:20 Click Chemistry-based Development of New Molecular Imaging Biomarkers Dr. Hartmuth Kolb, Vice President Siemens MI Biomarker Research, Culver City, CA/USA	**16:30 New Chemistry from an Oldtimer** Prof. Dr. Léon Ghosez, University of Bordeaux/F
12:00 Buffet Lunch - offered to all participants by the sponsors	**17:10 Closing Remarks** Prof. Dr. Camille Ganter
13:30 Electron Relay Race in Peptides Prof. Dr. Bernd Giese, Department of Chemistry, University of Basel/CH	**17:30 End of Symposium**

Fig. 1. Programme of the symposium 'Frontiers in Bioorganic Chemistry' in honour of Daniel Belluš, Friday, February 6, 2009, at the Pharmacenter, University of Basel, Klingelbergerstrasse 50, Basel.

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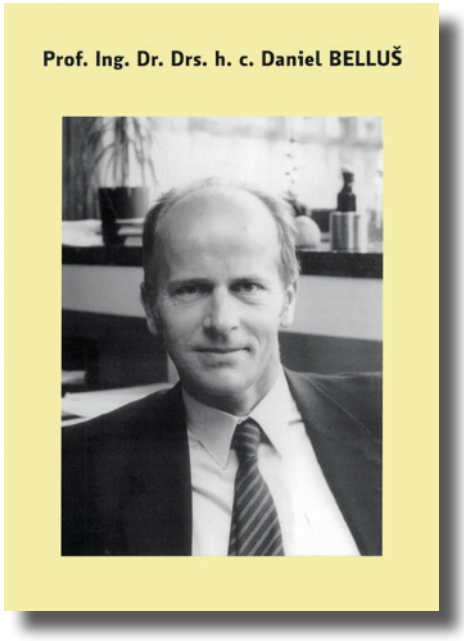


Fig. 2. Front page of the booklet of the Slovak Chemical Society.[1]

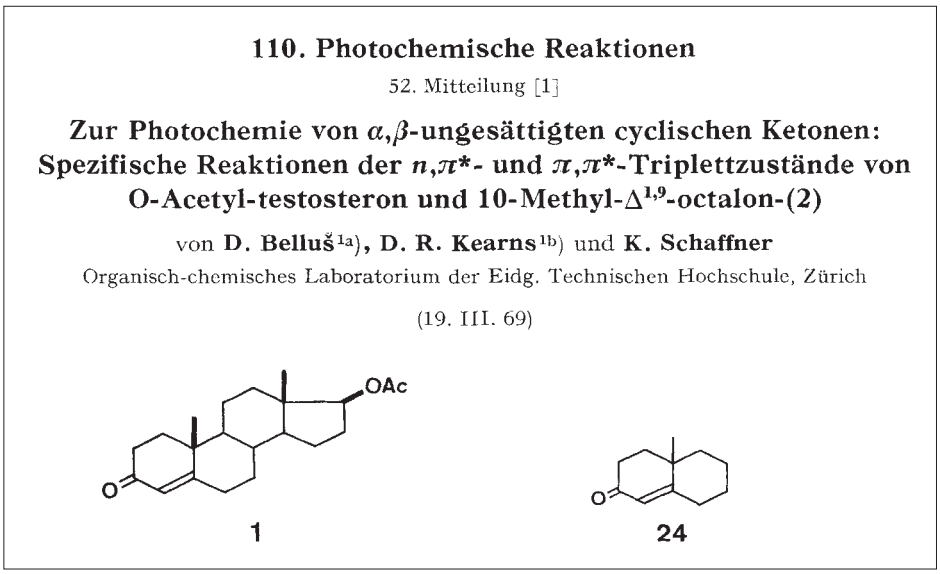
That brings me to a most noteworthy statement of Daniel made recently on some other person. He said: "I had just a photo in my hands of … (thoughtfully the name of the person will not be given here). Wow, today he really looks much older than 20 years ago." Daniel seems not to have such problems. He still looks to be and is indeed full of energy and active in many different fields, as ever. He obviously needs not yet to apply any anti-aging drugs – so far.

Last year the Slovak Chemical Society (SCHS) edited a small booklet in honour of the 70th birthday of Daniel Belluš.[1] If you look at the picture on the front side of the booklet (Fig. 2, I guess the photo was also taken about 20 years ago), Daniel has not changed very much since. One chapter of this booklet contains a collection of letters to and statements on Daniel Belluš, written by several different colleagues and friends. One contribution originates from Kurt Schaffner. Let me present an excerpt of some paragraphs from his personal letter in the mentioned booklet: "Daniel Belluš came to the Eidgenössische Technische Hochschule (ETH) in Zürich in fall 1967 from Bratislava. He was on a one-year leave to do postdoctoral work at the Laboratorium für Organische Chemie. … The granting of such a leave was by no means a trivial routine in those days. ... Professor Oskar Jeger entrusted me with taking care of the newcomer. … I welcomed Daniel who appeared ambitious, and eager to strive and accomplish results. And so he did, although I asked him to change experimentally from what he had been used to in Bratislava: he was to address a photochemical project with steroids rather than photochemistry with polymers. …The collaboration with Daniel throughout the year 1967-8 was thoroughly enjoyable and very fruitful, and it developed into a lasting friendship. I was particularly pleased – and impressed – that Daniel managed in no time to resolve some key questions addressed in our on-going research in mechanistic organic photochemistry, altogether resulting in five publications." So far some comments by Kurt Schaffner.

The most remarkable of these papers was the one published in 1969 in *Helvetica Chimica Acta* on the photochemistry of α,β-unsaturated ketones[2] (Fig. 3). I am quite sure that Kurt Schaffner intended to present some highlights of this paper by Daniel Belluš, if he would have been able to attend the symposium. Thus, I will try to do my best to substitute Kurt Schaffner.

The photochemistry of the conjugated cyclohexenones O-acetyl-testosterone (**1**) and 10-methyl-$\Delta^{1,9}$-octalone-(2) (**24**) has been investigated in detail. On the basis of the parallelism in their behaviour, the following comments will be restricted to the formation of the photoproducts **25**–**29** obtained from **24** (Scheme) which structurally correspond precisely to the ones obtained from **1**. A variety of different reaction types is observed: molecular rearrangements (→**25** and **26**), reduction processes in the presence of partner molecules by hydrogen atom abstraction (→**27**), addition to unsaturated systems, *e.g.* addition of solvent molecules like toluene (→**28**), and double bond shift, *i.e.* α,β to β,γ-photodeconjugation of enones (→**29**).

The different reaction types depend on structural parameters, solvents, and the chromophore of the conjugated enone. The latter can exist in different reactive excitation states. Some of them may even appear simultaneously and differ in electron configuration, spin multiplicity, and conformation, and by consequence in their reactivity. Without going into de-



110. Photochemische Reaktionen

52. Mitteilung [1]

Zur Photochemie von α,β-ungesättigten cyclischen Ketonen: Spezifische Reaktionen der n,π*- und π,π*-Triplettzustände von O-Acetyl-testosteron und 10-Methyl-$\Delta^{1,9}$-octalon-(2)

von **D. Belluš**[1a]), **D. R. Kearns**[1b]) und **K. Schaffner**

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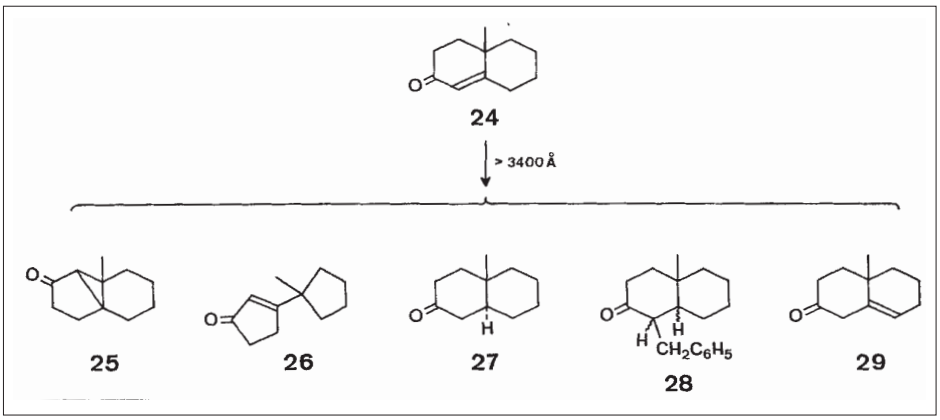
Fig. 3. Title and authors of the paper (ref. [2], p. 971) as well as the formulae **1** and **24** (ref. [2], p. 975 and 978, respectively). © Helvetica Chimica Acta, reproduced with permission.



Scheme. 10-Methyl-$\Delta^{1,9}$-octalone-(2) (**24**): Photoproducts **25**–**29** (from ref. [2], p. 978). © Helvetica Chimica Acta, reproduced with permission.

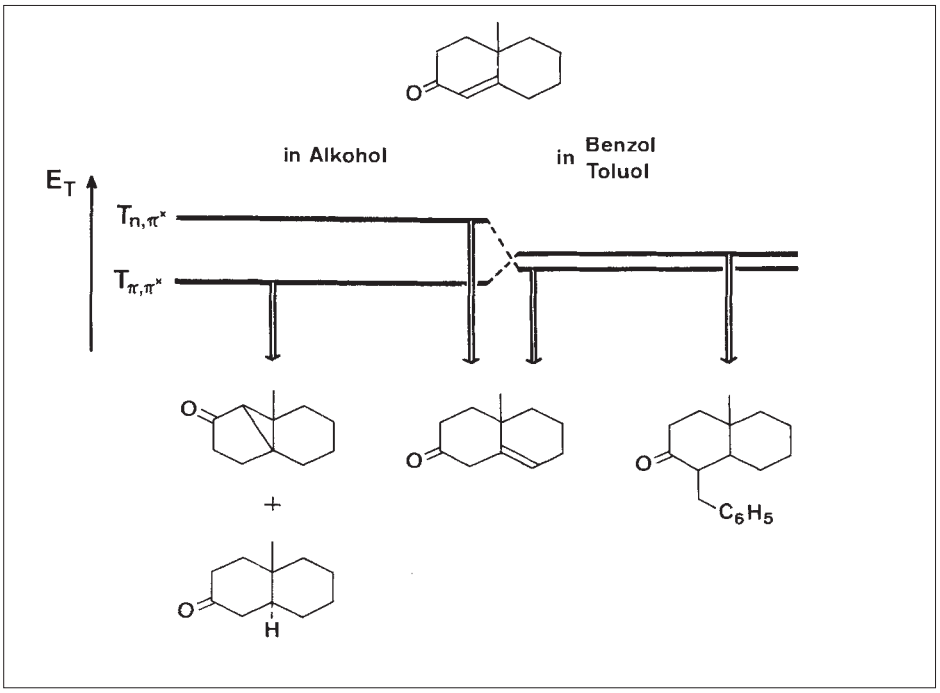


Fig. 4. Solvent specificity of triplet states (ref. [2], p. 999). © Helvetica Chimica Acta, reproduced with permission.

tail, sensitization (by acetophenone) and quenching experiments (with naphthalin and 1,3-pentadiene) established the triplet nature (Fig. 4) of the above reactions of O-acetyl-testosterone (**1**) and 10-methyl-$\Delta^{1,9}$-octalone-(2) (**24**). Rearrangement, double bond reduction, and toluene addition are attributed to one triplet state of the enone (the $^3(\pi,\pi^*)$ state), the double bond shift to another triplet state (the $^3(n,\pi^*)$ state). Change of solvent leads to lowering and increasing, respectively, of the triplet energies, resulting in a crossing of the two energy levels. So much on the start of the scientific activity of Daniel Belluš at the ETH in Zürich.

I have the privilege to know Daniel since the first day he arrived in Switzerland in 1967. We both worked in the group of Professor Jeger. Several months later his wife Mirka arrived with their first daughter Jelka. We became friends and remained friends although they moved from Zurich to Basel, where he started his impressive career in industry.

As Daniel has a very distinct sense of humour he kindly asked me not to present details of his curriculum with the argument: "At the end of a symposium nobody is interested any longer to listen to such boring facts." Furthermore, he asked me not to mention too much about his early time in Slovakia with the brilliant argument: "After all, I became a Swiss citizen already in the last millenium!" No wonder that on a special occasion, *e.g.* a speech in front of friends, he even likes to put a kind of an artificial Edelweiss on his jacket (Fig. 5).

Fig. 5. Daniel Belluš.

Let me close. I'm sure that everybody agrees with the statement: We have had a very special symposium today. A lot of work had to be done already before the symposium. The two organizers, Prof. Beat Ernst and Prof. Bernd Giese, did a most remarkable, marvellous job. One can feel that they did it with pleasure for a highly esteemed friend. Many thanks to both of them. All the speakers presented most interesting aspects of their work and research. In addition one could also feel their great appreciation of Daniel Belluš. Let's also warmly thank them again. Finally, many thanks go to you, Daniel. We all are fortunate and grateful that we could celebrate your birthday by such an impressive symposium. We wish you and your family all the best for the future.

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[1] M. Uher, V. Milata, 'Prof. Ing. Dr. Drs. h. c. Daniel Belluš, Slovenský a švajčiarsk vedec svetového formátu', Slovenská chemická spoločnost' (SCHS), Bratislava, **2008**, ISBN 978-80-227-2876-8.
[2] D. Belluš, D. R. Kearns, K. Schaffner, *Helv. Chim. Acta* **1969**, *52*, 971.