B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **1998**.

[11] The global B_4H_4 minimum was described as a B_3 ring with a bridging BH group: P. Mach, I. Hubač, A. Mavridis, *Chem. Phys. Lett.* **1994**, *226*, 469–474.

[12] Compound $\mathbf{1u}^{2-}$ is a transition state in D_{4h} symmetry, **1u** and $\mathbf{1u}^{2+}$ (each D_{2h}) are stationary points of the third order. The electronic structure corresponds with the schematic representation.

[13] Calculations were carried out for B_nH_n as well as $B_n(NH_2)_n$ ($n = 3-6$): M. L. McKee, *Inorg. Chem.* **1999**, *38*, 321–330.

[14] We thank one of the referees for suggesting that we propose a mechanism of formation. Owing to the low yield of **1**, which formed instead of the expected *cyclo*-triborane, we had originally not provided a mechanism.

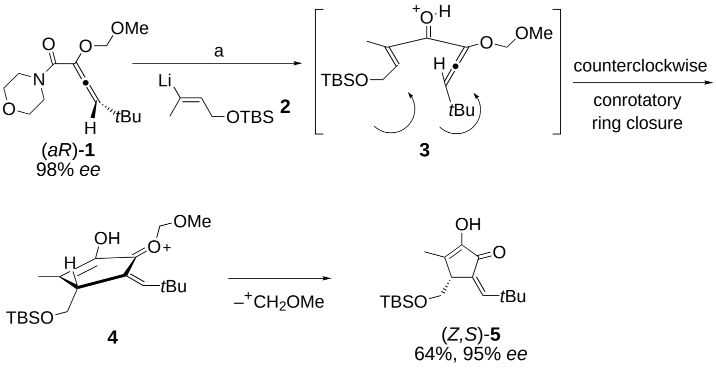
[15] K. H. Hermannsdörfer, E. Matejčikova, H. Nöth, *Chem. Ber.* **1970**, *103*, 516–527.

Synthesis of Enantioenriched 5-Alkylidene-2-cyclopentenones from Chiral Allenyl Carbamates: Generation of a Chiral Lithium Allenolate and Allylic Activation for a Conrotatory 4π-Electrocyclization**

Carsten Schultz-Fademrecht, Marc A. Tius,*
Stefan Grimme,* B. Wibbeling, and Dieter Hoppe*

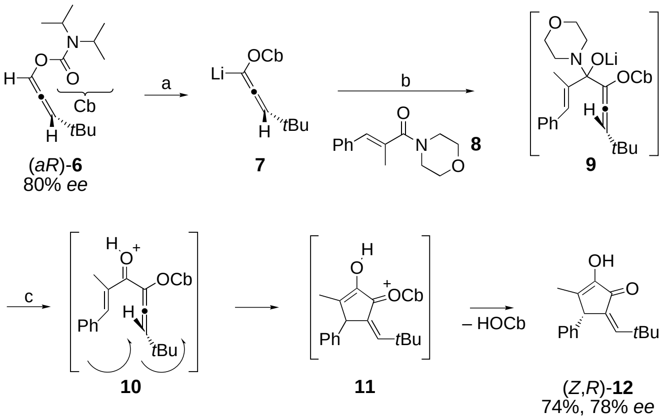
Dedicated to Professor Lutz F. Tietze
on the occasion of his 60th birthday

Chiral allenes have assumed an increasing importance in organic synthesis.[1, 2] A surprising application was reported by Tius et al.:[3] Allenyl alkenyl ketone (*aR*)-**3** cyclized under proton catalysis to form optically active 5-((*Z*)-alkylidene)-2-hydroxy-2-cyclopentenone **5** (Scheme 1). The chirality of the axial unit was transferred to the tetrahedral carbon atom of the cyclopentenone by means of a conrotatory electrocyclization of the 4π-system **3**, in a process that is similar to the Nazarov reaction.[4] The cyclization occurs through a counterclockwise conrotation because of steric demands.[5]



Scheme 1. Cyclization of (*aR*)-**1**. a) 1) **2**, THF, −78 °C, 30 min; 2) saturated aqueous KH_2PO_4. TBS = *tert*-butyldimethylsilyl.

Hoppe and co-workers had developed a simple method for the synthesis of enantiomerically enriched allenyl carbamate **6** (Scheme 2),[6] which initiated a collaboration to utilize **6** in this modified Nazarov reaction. Herein we describe a new stereospecific ring closure, which can be seen as a hybrid of an intramolecular vinylic cycloalkylation of a lithium allenolate and a modified Nazarov cyclization. The lithiation of allene (*aR*)-**6** (80% *ee*)[6] and subsequent acylation with (*E*)-alkenoylmorpholinide **8**, followed by transfer of the reaction mixture into hydrochloric acid in ethanol (5%), occurred as expected for the modified Nazarov cyclization to give hydroxycyclopentenone (*Z*,*R*)-**12**[7] (Scheme 2, 74%, 78% *ee*). The chirality transfer amounted to 98%.



Scheme 2. Cyclization of (*aR*)-**6**. a) *n*BuLi, TMEDA, toluene, −78 °C, 30 min; b) **8**, −78 °C, 2.5 h; c) rapid transfer of the mixture through a cannula into a solution of HCl in ethanol (5%). TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine.

When the reaction mixture was warmed to room temperature after the addition of amide **8** to the lithiated allenyl carbamate **7**, diastereomers of 2-morpholine-2-cyclopentenone (*Z*,*R*)-**14** and (*E*,*S*)-**15** were isolated in 74% yield, with >98% chirality transfer (Scheme 3). We assume that a rearrangement of intermediate **9**, which involves a migration of the *N*,*N*-diisopropylcarbamoyl group (Cb), leads to the formation of a lithium 1,2-dienolate (an “allenolate”).[8, 9] The

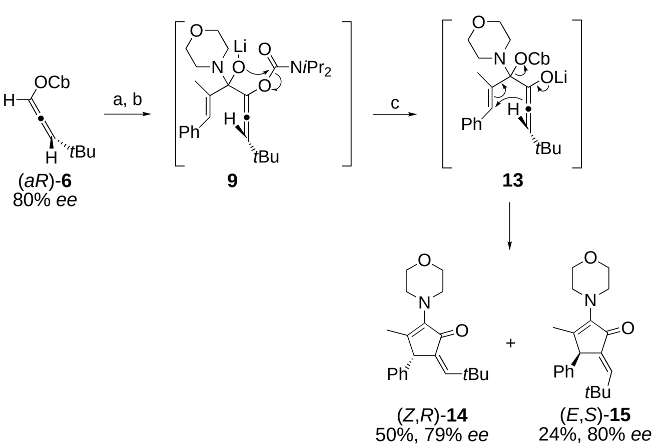
---

[*] Prof. Dr. S. Grimme, Prof. Dr. D. Hoppe, Dr. C. Schultz-Fademrecht, B. Wibbeling
Organisch-chemisches Institut
Westfälische Wilhelms-Universität Münster
Corrensstrasse 40, 48149 Münster (Germany)
Fax: (+49) 251-83-36531
E-mail: grimmes@uni-muenster.de
dhoppe@uni-muenster.de

Prof. Dr. M. A. Tius
Department of Chemistry, University of Hawaii at Manoa
2545 The Mall, Honolulu, HI 96822-2275 (USA)
Fax: (+1) 808-956-5908
E-mail: tius@gold.chem.hawaii.edu

[**] This work was supported by the Deutsche Forschungsgemeinschaft (SFB 424), the Fonds der Chemischen Industrie and the Alexander von Humboldt Foundation. M.A.T thanks the National Institutes of Health (GM57873) for generous support. We thank K. Gottschalk for her skillful technical assistance.

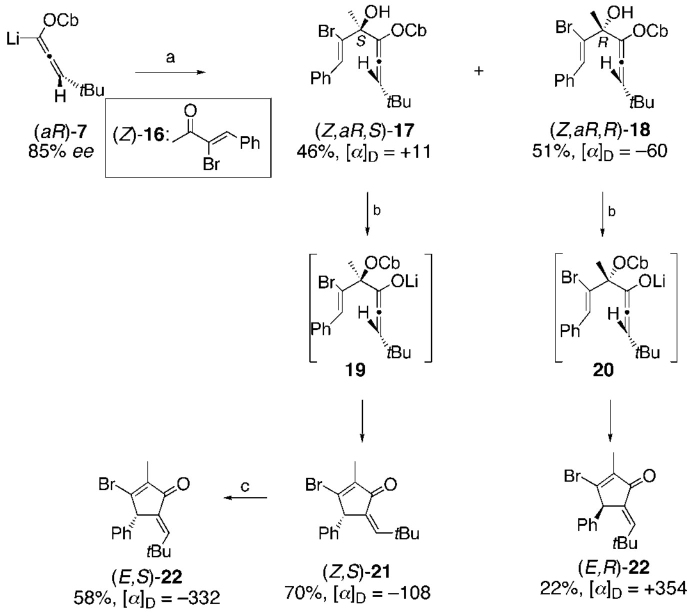
Supporting information for this article is available on the WWW under http://www.angewandte.com or from the author.



Scheme 3. Cyclization to **14** and **15**. a) *n*BuLi, toluene, −78 °C, 30 min; b) **8**, 1 h; −78 °C; c) 1) 1 h, room temperature; 2) HCl (2 N). Cb = CO-N*i*Pr$_2$.

bisallylic tertiary carbamoyloxy group acts as a leaving group during the cycloalkylation; which leads to (*Z*,*R*)-**14** and (*E*,*S*)-**15**.

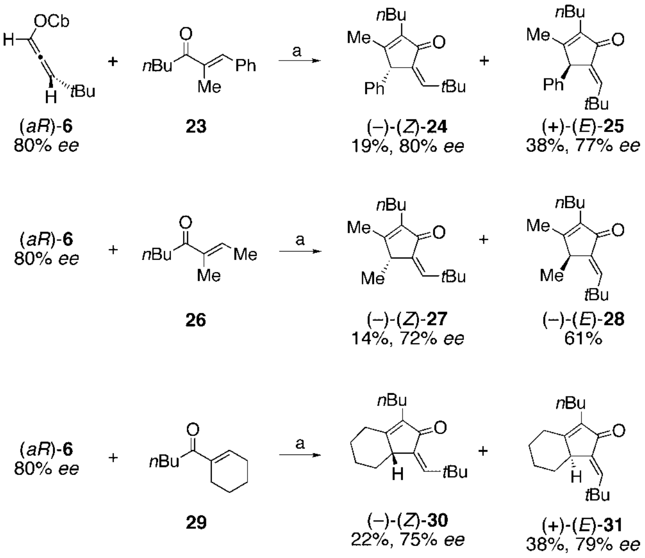
The different geometries of the exocyclic double bonds in diastereomers **14** and **15** and the very high chirality transfer suggests a conrotatory mechanism for the modified Nazarov cyclization, but also raises a question: is the direction of the conrotation controlled by the steric requirement of the allene, or does the new stereocenter at C4 in **13** determine the stereochemistry? We were able to determine the absolute configuration of the intermediates and the products of the reaction of (*aR*)-**7** and (Z)-α-bromoenone **16**[10] (Scheme 4). The epimeric adducts (*Z*,*aR*,*S*)-**17** and (*Z*,*aR*,*R*)-**18** were synthesized by hydrolyzing the intermediate lithium alkoxides at low temperature and separating by flash column chromatography. Because crystalline derivatives of these sensitive tertiary alcohols could not be prepared, we determined the absolute configuration of epimer **17** by time-dependent density functional response theory (TDDFT).[11]



Scheme 4. Independent cyclization of **17** and **18**. a) 1) *n*BuLi, toluene, −78 °C, 30 min; 2) **16**, 10 min, −78 °C; 3) saturated aqueous NH$_4$Cl; b) 1) *n*BuLi, TMEDA, toluene, 1 h, −78 °C, 1 h, room temperature; 2) HCl (2 N); c) benzene, room temperature, 48 h.

Both alcohols (*Z*,*aR*,*S*)-**17** and (*Z*,*aR*,*R*)-**18** were deprotonated separately with *n*BuLi/TMEDA in toluene. Subsequent warming of the reaction mixture to room temperature led to the isolation of cyclopentenones (*Z*,*S*)-**21** (70%, $[\alpha]_D^{20} = -108$) and (*E*,*R*)-**22** (22%, $[\alpha]_D^{20} = +354$), respectively, with no traces of the other isomer. The absolute configuration of (*E*,*R*)-**22** was elucidated by X-ray crystallographic analysis.[12a] Exposure of (*Z*,*S*)-**21** ($[\alpha]_D^{20} = -108$) to daylight led to (*E*,*S*)-**22** ($[\alpha]_D^{20} = -332$), the enantiomer of the (*E*,*R*)-**22**.

The topology of the ring closure is determined by the stereochemistry of the carbon that bears the leaving group. In the cycloalkylation (as in the modified Nazarov cyclization) a conrotatory ring closure takes place in a manner that is an allowed *anti* S_E' substitution in the allylic system. Apparently the cleavage of the C–OCb bond in the transition state has progressed to the stage that the developing partial positive charge is sufficient to follow the stereoelectronic requirements of 4π cyclizations.[13] Further examples of this reaction in which the intermediate epimeric alcohols were not isolated are shown in Scheme 5.[7]



Scheme 5. Cyclization reactions with different enones. a) 1) *n*BuLi, toluene, −78 °C, 30 min; 2) enone **23**, **26**, or **29**, 1 h, −78 °C, then 1 h, room temperature; 3) HCl (2 N).

In conclusion, we have reported an unusual method for the conversion of chiral allenyl carbamates into highly substituted 5-alkylidene-2-cyclopentenones. The process is characterized by:

- a stereoretentive α-lithiation and subsequent carbonyl addition of an allenyl carbamate;
- a simultaneous activation of nucleophilic and electrophilic characteristics of the open-chain intermediate by the migration of the carbamoyl group; and
- a stereospecific conrotatory ring closure of the 4π-electron system.

Experimental Section

Reactions were performed under an argon atmosphere in flame-dried glassware. *n*BuLi (1.3 equiv, 1.6 M in hexane) was added to a solution of (*aR*)-**6** (1.5 equiv) and TMEDA (1.5 equiv) in absolute toluene (6 mL mmol^{-1}) at $-78\,^\circ$C. After 30 min, a solution of an enone or an unsaturated amide (1.0 equiv) in absolute toluene (2 mL mmol^{-1}) at $-78\,^\circ$C was added through a cannula. The reaction mixture was stirred for 1 h at $-78\,^\circ$C and for 1 h at room temperature. The mixture was then quenched by the rapid addition of HCl (1 N, 10–20 mL mmol^{-1}) and diethyl ether (10–20 mL mmol^{-1}) and stirred for 3 min. After the aqueous layer was extracted three times with diethyl ether, the combined organic layers were neutralized with $NaHCO_3$, dried over Na_2SO_4, and concentrated under vacuum. Purification by flash column chromatography gave the desired cyclopentenone. (Spectroscopic data can be found in the Supporting Information.)

Received: November 19, 2001 [Z18243]

---

[1] For recent examples of the preparation of chiral allenes, see: a) Y. Nishibayashi, J. D. Singh, S.-i. Fukuzawa, S. Uemura, *J. Org. Chem.* **1995**, *60*, 4114–4420; b) A. G. Myers, B. Zheng, *J. Am. Chem. Soc.* **1996**, *118*, 4492–4493; c) P. H. Dixneuf, T. Guyut, M. D. Ness, S. M. Roberts, *Chem. Commun.* **1997**, 2083–2084; d) J. A. Marshall, M. A. Wolf, E. M. Wallace, *J. Org. Chem.* **1997**, *62*, 367–371; e) K. Mikami, A. Yoshida, *Angew. Chem.* **1997**, *109*, 892–894; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 858–860; f) Y. Naruse, H. Watanabe, Y. Ishiyama, T. Yoshida, *J. Org. Chem.* **1997**, *62*, 3862–3866; g) M. Franck-Neumann, D. Martina, D. Neff, *Tetrahedron: Asymmetry* **1998**, *9*, 697–708; h) Y. Noguchi, H. Takiyama, T. Katsuki, *Synlett* **1998**, 543–545; i) H. Ohno, A. Toda, Y. Miwa, T. Taga, N. Fujii, T. Ibuka, *Tetrahedron Lett.* **1999**, *40*, 349–352; j) T. Satoh, Y. Kuramochi, Y. Inoue, *Tetrahedron Lett.* **1999**, *40*, 8815–8818; k) Z. K. Sweeney, J. L. Salsman, R. A. Andersen, R. G. Bergman, *Angew. Chem.* **2000**, *112*, 2429–2433; *Angew. Chem. Int. Ed.* **2000**, *39*, 2339–2343.

[2] For reviews, see: a) S. Patai, *The Chemistry of Ketenes, Allenes, and Related Compounds*, Wiley, Chichester, **1980**; b) S. R. Landor, *The Chemistry of the Allenes*, Academic Press, New York, **1982**; c) H. F. Schuster, G. M. Coppola, *Allenes in Organic Synthesis*, Wiley, New York, **1984**.

[3] a) M. A. Tius, J. Busch-Petersen, M. Yamashita, *Tetrahedron Lett.* **1998**, *39*, 4219–4222; b) H. Hu, D. Smith, R. E. Cramer, M. A. Tius, *J. Am. Chem. Soc.* **1999**, *121*, 9895–9896; b) P. E. Harrington, M. A. Tius, *Org. Lett.* **2000**, *2*, 2447–2450.

[4] For reviews, see: a) C. Santelli-Rouvier, M. Santelli, *Synthesis* **1983**, 429–442; b) S. D. Denmark in *Comprehensive Organic Synthesis, Vol. 5* (Eds.: B. M. Trost, I. Fleming, L. A. Paquette), Pergamon, Oxford, **1991**, pp. 751–781; c) K. L. Habermas, S. Denmark, T. K. Jones in *Organic Reactions, Vol. 45* (Ed.: L. A. Paquette), Wiley, New York, **1994**, pp. 1–158.

[5] The clockwise conrotation leads to the *E* alkylidene derivative with the opposite absolute configuration at the stereogenic center; this occurs to a small extent, depending on the nature of the substituents.[3]

[6] C. Schultz-Fademrecht, B. Wibbeling, R. Fröhlich, D. Hoppe, *Org. Lett.* **2001**, *3*, 1221–1224.

[7] The absolute configuration was deduced from the reaction mechanism and not determined experimentally.

[8] We had observed this carbamoyl group rearrangement earlier: U. Behrens, PhD thesis, Universität Kiel, **1990**.

[9] For a similiar carbamoyl group rearrangement of vinyl carbamates, see: S. Sengupta, V. Snieckus, *J. Org. Chem.* **1990**, *55*, 5680–5683.

[10] E. S. Krijnen, H. Zuilhof, G. Lodder, *J. Org. Chem.* **1994**, *59*, 8139–8150.

[11] All density functional calculations (DFT) were performed with the TURBOMOLE program.[11b] First, the geometry of **17** and **18** were optimized with the BP86 functional,[11c] in which an AO-basis of valence-double-zeta quality with polarization functions (SV(P))[11d] and the RI approximation were employed. These structures were used for the calculation of the frequency-dependent optical-rotatory dispersion at the sodium D wavelength. The calculations were performed within the framework of time-dependent density functional theory (TDDFT),[11f] as is described in ref. [11g]. In these calculations, diffuse functions (C, O, N, Br: [1s1p1d], H: [1s1p]) were added to the SV(P) basis and the B3LYP hybrid functional[11h] was employed. We calculated an optical rotation of $[\alpha]_D = +64$ for (*Z,aR,S*)-**17** and $[\alpha]_D = -50$ for (*Z,aR,R*)-**18**, which allows a definite assignment of the absolute configuration. The almost opposite $[\alpha]_D$ values of these diastereomers shows that the bromostyrene chromophore has the greatest influence on the optical rotation. To prove these results, we calculated (at the same level of theory) the $[\alpha]_D$ values of two conformations (nonplanar bromostyrene substituent) of the *E* isomer (*E,aR,R*)-*N,N*-diisopropylcarbamidic acid 1-(2-bromo-1-hydroxy-1-methyl-3-phenylpropenyl)-4,4-dimethyl-1,2-butadienyl ester (**32**), for which the absolute configuration was determined by X-ray crystal-structure analysis under anomalous X-ray dispersion conditions.[12b] The results of these calculations are in perfect agreement with the experimental data. b) TURBOMOLE (Vers. 5.3): R. Ahlrichs, M. Bär, H.-P. Baron, R. Bauernschmitt, S. Böcker, M. Ehrig, K. Eichkorn, S. Elliott, F. Furche, F. Haase, M. Häser, H. Horn, C. Huber, U. Huniar, M. Kattannek, C. Kölmel, M. Kollwitz, K. May, C. Ochsenfeld, H. Öhm, A. Schäfer, U. Schneider, O. Treutler, M. von Arnim, F. Weigend, P. Weis, H. Weiss, Universität Karlsruhe, **2000**; c) A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098–3100; J. P. Perdew, *Phys. Rev. B* **1986**, *33*, 8822–8824; d) A. Schäfer, H. Horn, R. Ahlrichs, *J. Chem. Phys.* **1992**, *97*, 2571–2577; e) K. Eichkorn, O. Treutler, H. Öhm, M. Häser, R. Ahlrichs, *Chem. Phys. Lett.* **1995**, *240*, 283–290; f) R. Bauernschmitt, R. Ahlrichs, *Chem. Phys. Lett.* **1996**, *256*, 454–464; g) S. Grimme, *Chem. Phys. Lett.* **2001**, *339*, 380–388; P. J. Stephens, F. J. Devlin, J. R. Cheeseman, M. J. Frisch, *J. Phys. Chem. A* **2001**, *105*, 5356–5371; h) P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, *J. Phys. Chem.* **1994**, *98*, 11623–11627.

[12] a) X-ray crystal-structure analysis of **22**: $C_{17}H_{19}OBr$, $M_r = 319.23$, orthorhombic, space group $P2_12_12_1$ (no. 19), $a = 6.469(1)$, $b = 13.857(1)$, $c = 17.202(4)$ Å, $V = 1542.0(3)$ Å^3, $\rho_{calcd} = 1.375$ g cm^{-3}, colorless crystal, $0.25 \times 0.20 \times 0.15$ mm, $\mu = 35.39$ cm^{-1}, empirical absorption correction by means of ψ scan data ($0.472 \leq T \leq 0.619$), $Z = 4$, $\lambda = 1.54178$ Å, $T = 223$ K, $\omega/2\theta$ scans, 1818 reflections collected ($+h$, $+k$, $+l$), $[(\sin\theta)/\lambda] = 0.62$ Å^{-1}, 1818 independent and 1734 observed reflections with $[I \geq 2\sigma(I)]$, 177 refined parameters, $R = 0.028$, $wR^2 = 0.081$, max. residual electron density $= 0.27$ (-0.25) e Å^{-3}, Flack parameter 0.04(3), hydrogen atoms calculated and refined as riding atoms; b) X-ray crystal structure analysis of **32**: $C_{24}H_{34}NO_3Br$, $M_r = 464.43$, monoclinic, space group $P2_1/n$ (No. 14), $a = 9.668(1)$, $b = 12.688(1)$, $c = 20.590(1)$ Å, $\beta = 97.90(1)^\circ$, $V = 2501.8(3)$ Å^3, $\rho_{calcd} = 1.233$ g cm^{-3}, colorless crystal, $0.35 \times 0.20 \times 0.20$ mm, $\mu = 16.65$ cm^{-1}, empirical absorption correction by means of SORTAV ($0.593 \leq T \leq 0.732$), $Z = 4$, $\lambda = 0.71073$ Å, $T = 198$ K, ω and ϕ scans, 16314 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.65$ Å^{-1}, 5948 independent ($R_{int} = 0.040$) and 3996 observed reflections $[I \geq 2\sigma(I)]$, 271 refined parameters, $R = 0.039$, $wR^2 = 0.078$, max. residual electron density $= 0.22$ (-0.42) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms. The data sets were collected with an Enraf–Nonius CAD4 and a Nonius Kappa CCD diffractometer, the later equipped with a rotating anode generator Nonius FR591. Programs used: data collection: EXPRESS (Nonius B.V., **1994**) and COLLECT (Nonius B.V., **1998**), data reduction MolEN (K. Fair, Enraf–Nonius B.V., **1990**) and Denzo-SMN (Z. Otwinowski, W. Minor, *Methods Enzymol.* **1997**, *276*, 307–326), absorption correction for CCD data SORTAV (R. H. Blessing, *Acta Crystallogr. Sect. A* **1995**, *51*, 33–37; R. H. Blessing, *J. Appl. Crystallogr.* **1997**, *30*, 421–426), structure solution SHELXS-97 (G. M. Sheldrick, *Acta Crystallogr. Sect. A* **1990**, *46*, 467–473), structure refinement SHELXL-97 (G. M. Sheldrick, Universität Göttingen, **1997**), graphics SCHAKAL (E. Keller, Universität Freiburg, **1997**). CCDC-173069 and -173919 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

[13] A related reaction mechanism is the electrocyclic ring opening of cyclopropyl tosylates; the direction of the ring opening depends on the stereochemistry of the carbon atom that bears the leaving group:

a) J. D. Roberts, V. C. Chambers, *J. Am. Chem. Soc.* **1951**, *73*, 5034–5040; b) R. B. Woodward, R. Hoffmann, *J. Am. Chem. Soc.* **1965**, *87*, 395–397; c) H. C. Longuet-Higgins, W. H. Abrahamson, *J. Am. Chem. Soc.* **1965**, *87*, 2045–2048; d) W. Kutzelnigg, *Tetrahedron Lett.* **1967**, 4965–4971; e) U. Schöllkopf, *Angew. Chem.* **1968**, *80*, 603–613; *Angew. Chem. Int. Ed. Engl.* **1968**, *7*, 588–598; f) P. v. R. Schleyer, W. F. Sliwinski, G. W. Van Dine, U. Schöllkopf, J. Paust, K. Fellenberger, *J. Am. Chem. Soc.* **1972**, *94*, 125–133.

Near-UV Photoionization of $[Ru(bpy)_3]^{2+}$: A Catalytic Cycle with an Excited Species as Catalyst**

Martin Goez,* Martin Schiewek, and
Mohammad H. O. Musa

Photoionization of the tris-2,2′-bipyridyl ruthenium(II) ion $[Ru(bpy)_3]^{2+}$ is the archetype of a class of reactions that might effect photochemical water splitting:[1] the ejected electron $e^{\bullet -}_{aq}$ reacts with H^+, ultimately yielding hydrogen,[2] and the remaining oxidized complex $[Ru(bpy)_3]^{3+}$ is thermodynamically capable of oxidizing OH^- to oxygen,[1] although in practice this has only been realized with additional cocatalysts[3] or in microheterogeneous environments.[4] Herein, we identify the excited metal-to-ligand charge-transfer (MLCT) complex $*[Ru(bpy)_3]^{2+}$ as a catalytic intermediate of this photoionization. Near-UV light (308 or 355 nm) drives both the ionization of this species and the reduction of $[Ru(bpy)_3]^{3+}$, which then regenerates the ruthenium(II) complex in its excited state.

Despite its model character, the mechanism of photoionization in this system has received very little attention. On the basis of flash-lamp experiments with polychromatic light (300–360 nm, 17 µs flash duration) and indirect detection of $e^{\bullet -}_{aq}$, a sequential reaction (Scheme 1) with a very low quantum yield of the ionization proper (0.0015) was proposed.[5a] Later studies using nanosecond laser flash photolysis, with optical detection of $e^{\bullet -}_{aq}$, gave somewhat contradictory results for the dependence of the electron yield on the excitation intensity,[5b, c] and focused mainly or exclusively[5d] on the effect of surface-active molecules on the electron yield.

$$[Ru(bpy)_3]^{2+} \xrightarrow[(\kappa_1)]{h\nu} *[Ru(bpy)_3]^{2+} \xrightarrow[(\kappa_2)]{h\nu} [Ru(bpy)_3]^{3+} + e^{\bullet -}_{aq}$$

Scheme 1. Linear reaction sequence for photoionization of $[Ru(bpy)_3]^{2+}$.

To elucidate the mechanism and determine the relevant photokinetic parameters, we decided to investigate the intensity dependence of the yield not only for the final product $e^{\bullet -}_{aq}$ but also for the presumed intermediate $*[Ru(bpy)_3]^{2+}$. Such an approach obviously provides much more information about a reaction that is expected to have multiple steps. Laser flash photolysis with different excitation wavelengths and detection of luminescence or optical absorbance was performed (see Experimental Section).

Figure 1 a shows the dependence of the concentrations of $*[Ru(bpy)_3]^{2+}$ and $e^{\bullet -}_{aq}$, relative to the starting concentration c_0 of $[Ru(bpy)_3]^{2+}$, on the excitation intensity at 308 nm. A high turnover can be achieved; at our highest laser intensity the electron concentration approaches 50 % of c_0.

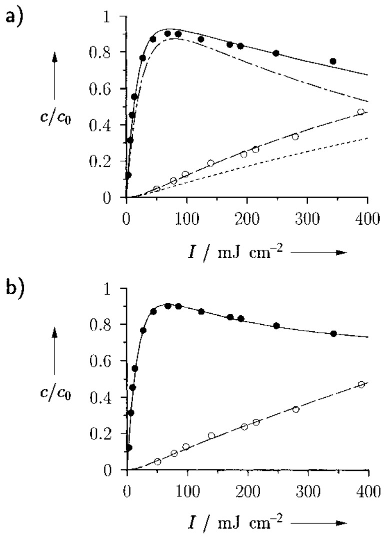


Figure 1. Photoionization of 3×10^{-5} M $[Ru(bpy)_3]^{2+}$ with light of wavelength 308 nm. The concentrations c, relative to the substrate concentration c_0, of $*[Ru(bpy)_3]^{2+}$ (●) and $e^{\bullet -}_{aq}$ (○) are shown as functions of the laser intensity I. a) The fit curves refer to the mechanism of Scheme 1: —— shows a fit of Equation (1) to the experimental data for $*[Ru(bpy)_3]^{2+}$, which yields the best-fit parameters $\kappa_1' = 5.68\times10^{-2}\,cm^2mJ^{-1}$, $\kappa_2' = 1.03\times10^{-3}\,cm^2mJ^{-1}$, ---- the curve calculated with κ_1' and κ_2' for $e^{\bullet -}_{aq}$ [Eq. (2)]. --- is the best fit of Equation (2) to the experimental data for $e^{\bullet -}_{aq}$, yielding $\kappa_1'' = 4.21\times10^{-2}\,cm^2mJ^{-1}$, and $\kappa_2'' = 1.69\times10^{-3}\,cm^2mJ^{-1}$, and -•- is the calculated result with κ_1'' and κ_2'' for $*[Ru(bpy)_3]^{2+}$ [Eq. (1)]. b) The curves refer to the mechanism of Scheme 2, and are simultaneous fits of Equation (3) to the experimental data for $*[Ru(bpy)_3]^{2+}$ (——) and of Equation (4) to those for $e^{\bullet -}_{aq}$ (----). Best-fit parameters are $\kappa_1 = 5.73\times10^{-2}\,cm^2mJ^{-1}$, $\kappa_2 = 1.52\times10^{-3}\,cm^2mJ^{-1}$, and $\kappa_3 = 3.19\times10^{-3}\,cm^2mJ^{-1}$.

Because the concentrations of $*[Ru(bpy)_3]^{2+}$ and $e^{\bullet -}_{aq}$ are measured immediately after the end of the 308 nm pulse, the whole reaction sequence leading to photoionization must be completed within about 25 ns. On that time scale, bimolecular steps involving two ruthenium-based species, or one such species and $e^{\bullet -}_{aq}$, are negligible at the low concentrations used. As our solutions were optically thin, all the absorption steps can be described as first-order processes.[6] For a simple two-step photoreaction according to Scheme 1, that is, for the mechanism proposed in the literature, the intensity dependences of the observed species would be given by Equations (1) and (2). These expressions are valid for random shapes of the laser pulse, and depend only on its total intensity I

---

[*] Prof. Dr. M. Goez, M. Schiewek, M. H. O. Musa
Fachbereich Chemie
Martin-Luther-Universität Halle-Wittenberg
Kurt-Mothes-Strasse 2, 06120 Halle/Saale (Germany)
Fax: (+49) 345-55-27657
E-mail: goez@chemie.uni-halle.de

[**] This work was supported by the Volkswagen Foundation. We are grateful to a referee for suggesting the scavenging experiment with benzoic acid; bpy = 2,2′-bipyridine.