Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Collisional relaxation of apocarotenals: Identifying the S* state with vibrationally excited molecules in the ground electronic state S_0*

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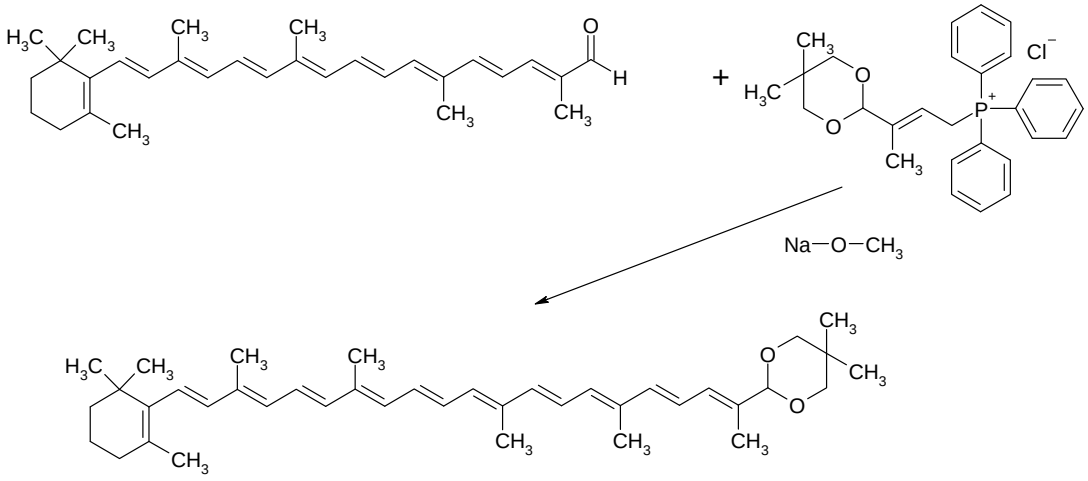
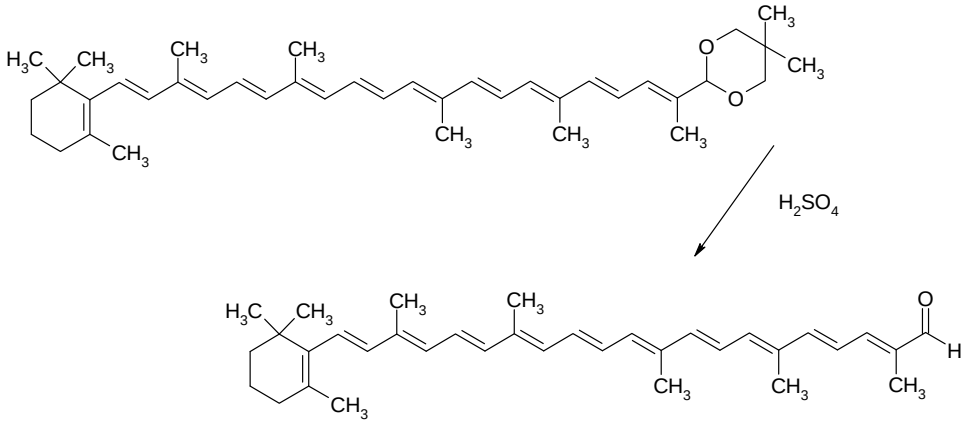
Synthesis

A) 5,5-Dimethyl-2-[(1*E*,3*E*,5*E*,7*E*,9*E*,11*E*,13*E*,15*E*,17*E*,19*E*)-1,5,9,14,18-pentamethyl-20-(2,6,6-trimethyl-cyclohex-1-enyl)-icosa-1,3,5,7,9,11,13,15,17,19-decaenyl]-[1,3]dioxane



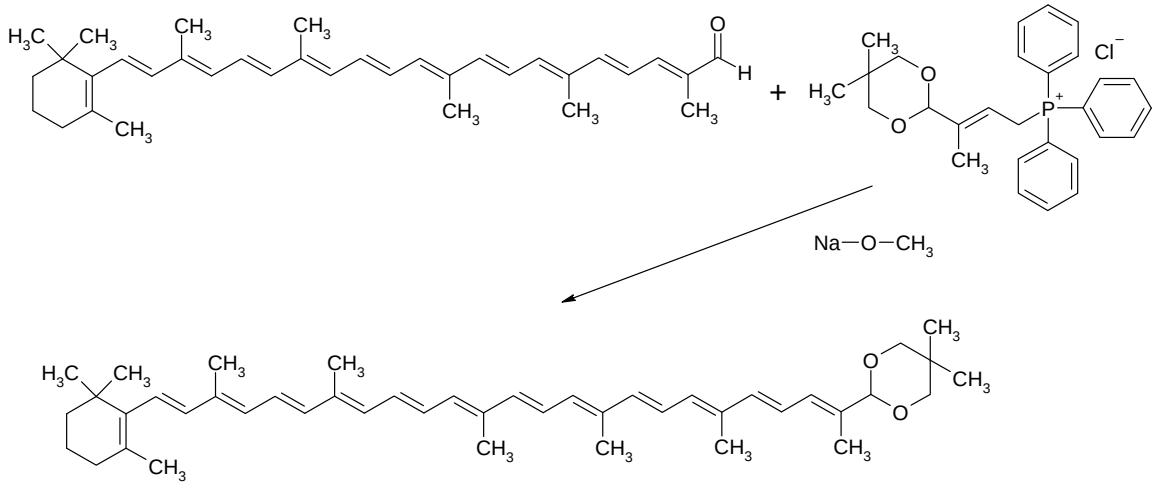
To a solution of sodium methoxide under N_2 atmosphere, prepared from 0.90 g (39.1 mmol) sodium and 90 mL absolute methanol, 13.44 g (28.8 mmol) [(*E*)-3-(5,5-Dimethyl-[1,3]dioxan-2-yl)-but-2-enyl]-triphenylphosphoniumchloride were added stepwise for 10 min under bubbling with N_2 at ambient temperature. After stirring the solution for additional 5 min, a N_2-saturated solution of 12.51 g (30.0 mmol) dried all-*trans*-β-apo-8‘-carotenal dissolved in 30 mL absolute dichloromethane was added dropwise for 10 min. After further stirring for 4 h under reflux, the solvent was removed under reduced pressure.[1] The crude product was dissolved in dichloromethane and washed with water. The combined dichloromethane phases were dried over anhydrous Na_2SO_4, filtrated and concentrated under reduced pressure. The crude product (28.40 g) was purified by repeated silica gel column chromatography to give the ketal (5.94 g, 10.4 mmol) in 36 % yield.

B) (2*E*,4*E*,6*E*,8*E*,10*E*,12*E*,14*E*,16*E*,18*E*,20*E*)-2,6,10,15,19-Pentamethyl-21-(2,6,6-trimethyl-cyclohex-1-enyl)-henicosa-2,4,6,8,10,12,14,16,18,20-decaenal (all-*trans*-β-apo-4'-carotenal)



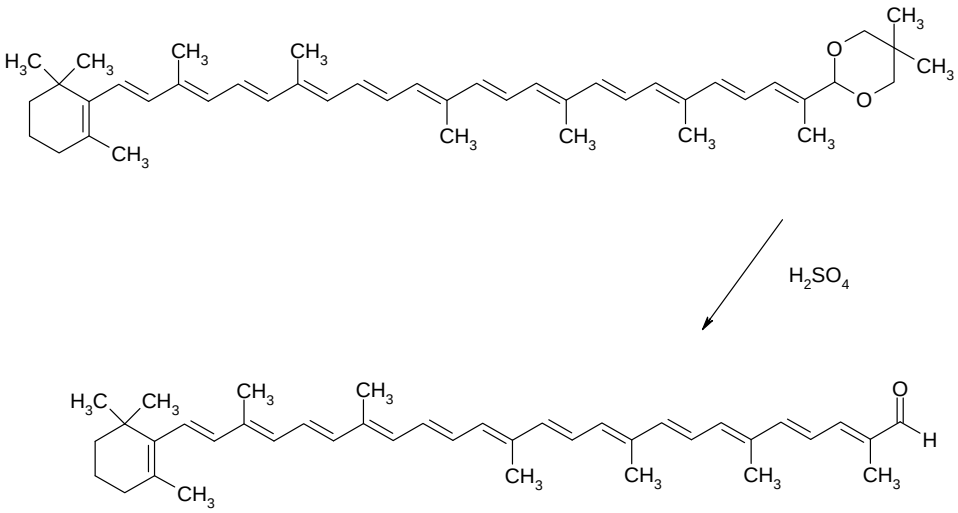
A solution of 5.94 g (10.4 mmol) 5,5-Dimethyl-2-[(1*E*,3*E*,5*E*,7*E*,9*E*,11*E*,13*E*,15*E*,17*E*,19*E*)-1,5,9,14,18-pentamethyl-20-(2,6,6-trimethyl-cyclohex-1-enyl)-icosa-1,3,5,7,9,11,13,15,17,19-decaenyl]-[1,3]dioxane in *ca.* 130 mL diethyl ether was mixed with 100 mL 2n H_2SO_4 and 7 mL methanol (to avoid phase separation). The solution was stirred for 4.5 h under bubbling with N_2 at ambient temperature. Then, 25 mL 2n H_2SO_4 were added and the solution further stirred for 18.5 h. Afterwards, 25 mL 2n H_2SO_4 were added and stirring was performed for additional 2 h. Afterwards, the solution was diluted with water, and the ether phase was separated. The water phase was washed two times with 150 mL diethyl ether. The combined ether phases were dried over anhydrous Na_2SO_4, filtrated and concentrated under reduced pressure. The resulting crude product (5.33 g) contained predominantly the carotenal and still also ketal, as identified by mass spectrometry. It was then purified by silica gel column chromatography to give **all-*trans*-β-apo-4'-carotenal**.

C) 2-[(1*E*,3*E*,5*E*,7*E*,9*E*,11*E*,13*E*,15*E*,17*E*,19*E*,21*E*,23*E*)-1,5,9,13,18,22-Hexamethyl-24-(2,6,6-trimethyl-cyclohex-1-enyl)-tetracosa-1,3,5,7,9,11,13,15,17,19,21,23-dodecaenyl]-5,5-dimethyl-[1,3]dioxane



To a solution of sodium methoxide under N_2 atmosphere, prepared from 0.144 g (4.95 mmol) sodium and 11.5 mL absolute methanol, 1.7 g (3.65 mmol) [(*E*)-3-(5,5-Dimethyl-[1,3]dioxan-2-yl)-but-2-enyl]-triphenylphosphoniumchloride were added stepwise for 10 min under bubbling with N_2 at ambient temperature. After stirring the solution for additional 5 min, a N_2-saturated solution of 1.84 g (3.80 mmol) dried all-*trans*-β-apo-4‘-carotenal (step B) dissolved in 3.8 mL absolute dichloromethane was added dropwise for 10 min. After further stirring for 4 h under reflux, the solvent was removed under reduced pressure.[1] The crude product was dissolved in dichloromethane and washed with water. The combined dichloromethane phases were dried over anhydrous Na_2SO_4, filtrated and concentrated under reduced pressure. The crude product (3.28 g) was purified by silica gel column chromatography to give the ketal (0.18 g, 0.284 mmol) in 7.5 % yield.

D) (2*E*,4*E*,6*E*,8*E*,10*E*,12*E*,14*E*,16*E*,18*E*,20*E*,22*E*,24*E*)-2,6,10,14,19,23-Hexamethyl-25-(2,6,6-trimethyl-cyclohex-1-enyl)-pentacosa-2,4,6,8,10,12,14,16,18,20,22,24-dodecaenal (all-*trans*-3',4'-didehydro-β,ψ-caroten-16'-al, torularhodinaldehyde)



A solution of 0.18 g (0.284 mmol) 2-[(1*E*,3*E*,5*E*,7*E*,9*E*,11*E*,13*E*,15*E*,17*E*,19*E*,21*E*,23*E*)-1,5,9,13,18,22-Hexamethyl-24-(2,6,6-trimethyl-cyclohex-1-enyl)-tetracosa-1,3,5,7,9,11,13,15,17,19,21,23-dodecaenyl]-5,5-dimethyl-[1,3]dioxane in *ca.* 3.5 mL diethyl ether was mixed with 2.8 mL 2n H_2SO_4. Methanol (2 mL) was added to avoid phase separation. The solution was then stirred for 16 h under bubbling with N_2 at ambient temperature. The solution was further stirred for 3.5 h at 40 °C. Then additional methanol (2 mL) and 2 n H_2SO_4 (2 mL) were added and the solution was stirred at 65 °C for additional 2 h. Afterwards, the solution was diluted with water, and the ether phase was separated. The water phase was washed two times with 25 mL diethyl ether. The combined ether phases were dried over anhydrous Na_2SO_4, filtrated and concentrated under reduced pressure. It was then purified by silica gel column chromatography to give **all-*trans*-3',4'-didehydro-β,ψ-caroten-16'-al (torularhodinaldehyde)**.

Comparison of S* signals

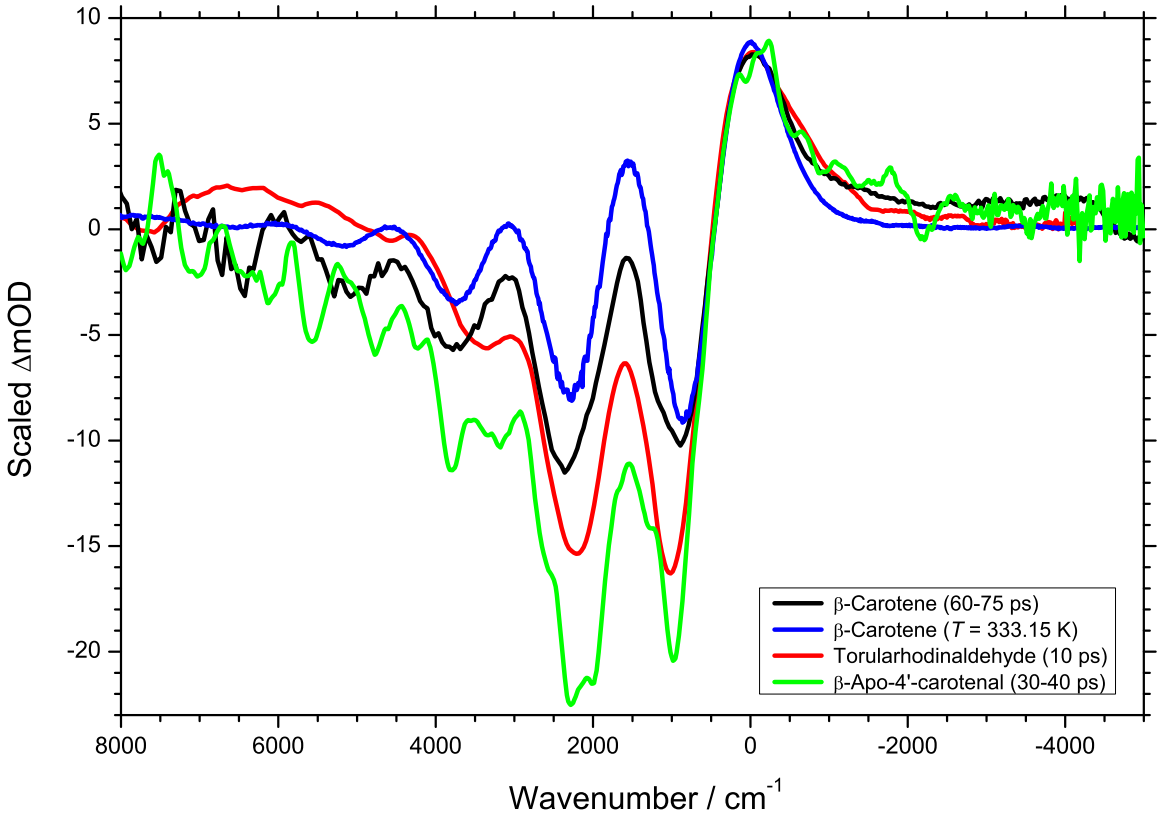


Fig. S1. Comparison of S* signals (difference absorption spectra) in *n*-hexane. All spectra were shifted on the wavenumber axis so that the hot band absorption feature is located at 0 cm^{-1} and scaled to the same amplitude. Black line: PSCP signal of β-carotene averaged over the time range 60-75 ps (ref. 2). Blue line: Steady-state difference absorption signal of β-carotene at T = 333.15 K (ref. 2). Red line: PSCP signal of torularhodinaldehyde at 10 ps (this work). Green line: PSCP signal of β-apo-4'-carotenal averaged over the time range 30-40 ps (this work).

1) adapted from: *Reaktionen und Synthesen im organisch-chemischen Praktikum und Forschungslaboratorium*, L.F. Tietze and T. Eicher, 2. rev. ed., Thieme Verlag, Stuttgart / New York, 1991; K-18.

2) T. Lenzer, F. Ehlers, M. Scholz, R. Oswald and K. Oum, *Phys. Chem. Chem. Phys.*, 2010, **12**, 8832.