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OXIDATIVE DEPROTECTION OF ALLYL GLYCOSIDES

Ralf Krähmer[a], Lothar Hennig[a], Matthias Findeisen[a], Dietrich Müller[b], Peter Welzel[a*]

[a] Fakultät für Chemie und Mineralogie der Universität Leipzig, Talstr. 35, D-04103 Leipzig (Germany)

[b] Fakultät für Chemie der Ruhr-Universität, D-44780 Bochum (Germany)

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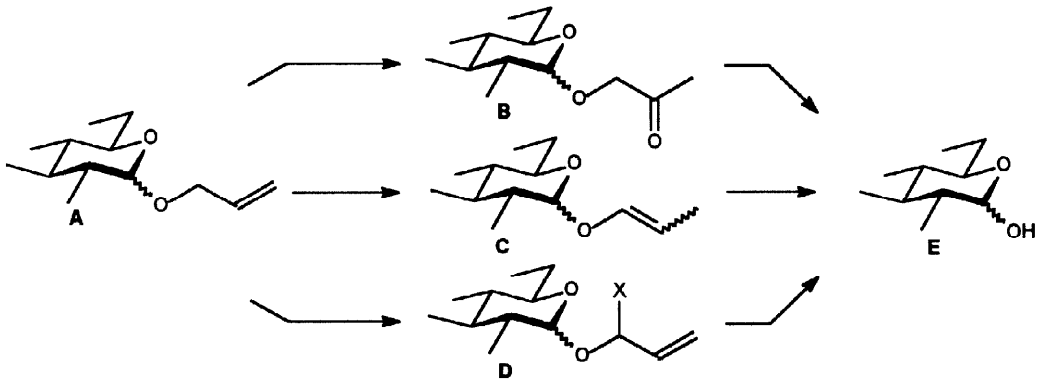
Abstract - Allyl glycosides can be deprotected under the condition of the *Kharasch-Sosnovsky* reaction and by photoinduced reaction with di-^{t}butylperoxide in the presence of bromotrichloromethane.

Key words: carbohydrates, protecting groups, oxidation, radicals

Introduction

Allyl protection of the anomeric position is common in carbohydrate chemistry[1,2] and much of our moenomycin synthetic work is based on this protecting strategy. Deprotection is often achieved by a three - step process consisting of (i) allyl propenyl rearrangement (A→C), (ii) addition of HOX to the double bond of C and (iii) formation of the free sugar from the intermediate hemiacetal. It has been shown that in the case of polar carbohydrates the rearrangement may fail.[3] For these cases we developed a new deprotection method consisting of (i) Wacker oxidation (A→B) and (ii) cleavage of the C-O bond α to the carbonyl group by electron transfer in the photoexcited state (B→E).[3]



Another quite general method seems to be *Nakayama's* Pd(0)-mediated cleavage of the allyl glycoside bond in acetic acid solution.[4] But even with this very useful procedure we have sometimes encountered problems due to the difficulties associated with removal of the catalyst.[5] Recently a new method was reported in which the allyl group is removed reductively in a 1,3-bis(diphenylphosphino)propane nickel (II) chloride-mediated reaction with DIBAL-H in aprotic solvents.[6] It can be foreseen that this method will have its shortcomings in situations with highly polar or easily reducible functional groups. Thus, the method for deprotection in each case has to be carefully selected with respect to the functional groups present in the substrate. In order to overcome problems associated with highly polar compounds we have recently introduced C_9 alkynyl and alkenyl protecting groups for the anomeric position which can be removed by an elimination process via a β-alkoxy ketone.[7]

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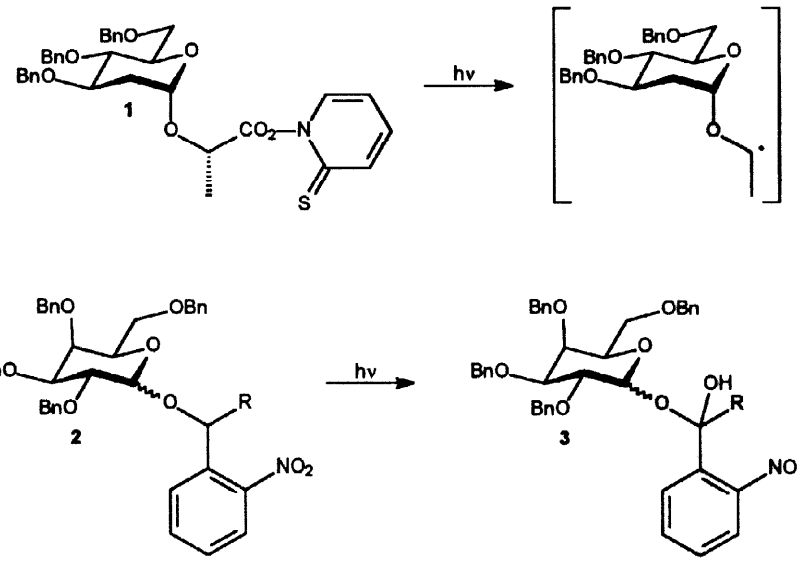
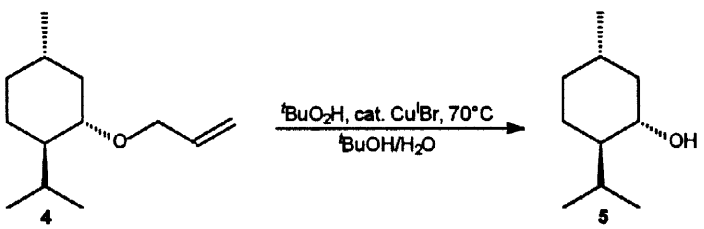


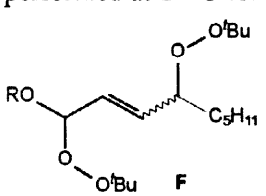
Here we wish to report on an attempt to deprotect allyl glycosides oxidatively. There is some precedent. *Diaz et al.* described the allylic bromination of allyl glycosides with NBS to give an intermediate of type D (X = Br) which is hydrolysed via D (X=OH) to give the free sugar E.[8] The allylic bromination is, of course, limited to unpolar solvents. Intermediate D (X=OH) is also assumed to be formed by SeO_2 oxidation of A.[9] We anticipated to arrive at D by radical oxidation of A to be conducted in a polar solvent. Radicals in the α-position of glycosides have been prepared by photolysis of **1**,[10] and *Fraser-Reid* has deprotected o-nitrobenzyl ethers **2** by photo-induced cleavage via **3**.[11]

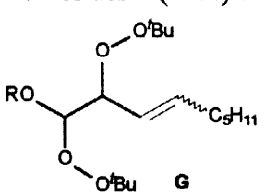
Cleavage of model allyl ethers and glycosides using the *Kharasch-Sosnovsky* reaction

We planned to convert allyl glycosides of type **6** to give peroxyacetals **9**, which on reduction would furnish the deprotected compound **8**. In model experiments we submitted the allyl ether of *rac*-menthol (*rac*-**4**) to different *Kharasch-Sosnovsky*-type reaction conditions[12] using ^{t}butyl peresters and ^{t}butyl hydroperoxide as



oxidants and (in most cases) Cu(I) as catalyst. The substrate *rac*-**4** was chosen in order to be able to determine the yield of the deprotected product (*rac*-**5**) by GC using n-dodecane as internal standard. Reaction conditions and yields are summarised in Table 1. The best yields were observed using the system ^{t}butyl hydroperoxide - Cu^IBr in ^{t}butanol-water solution. The reaction was performed at 70°C. Under these conditions (reaction time: 24 h) **6** reacted to provide **8** in 60% yield (at 90% conversion) alongside with about 10% of the stereoisomeric alkoxyacrylates **7a** and **7b**. Interesting results were obtained when the reaction was performed at 20°C for 224 h. Besides **8** (35%) and the alkoxyacrylates **7a** and **7b** (30%) the diastereoisomeric peracetals **9a** and **9b** (11%) could be isolated. The result seems to indicate that the conversion of peracetal intermediates to the free sugar is preferred at higher temperatures. The structures of **9a** and **9b** were assigned mainly on the basis of NMR spectra: δ = 102.4 and 105.3 for C-1^{allyl} and 81.5 and 81.8 for Me_3-C-O- and they are in

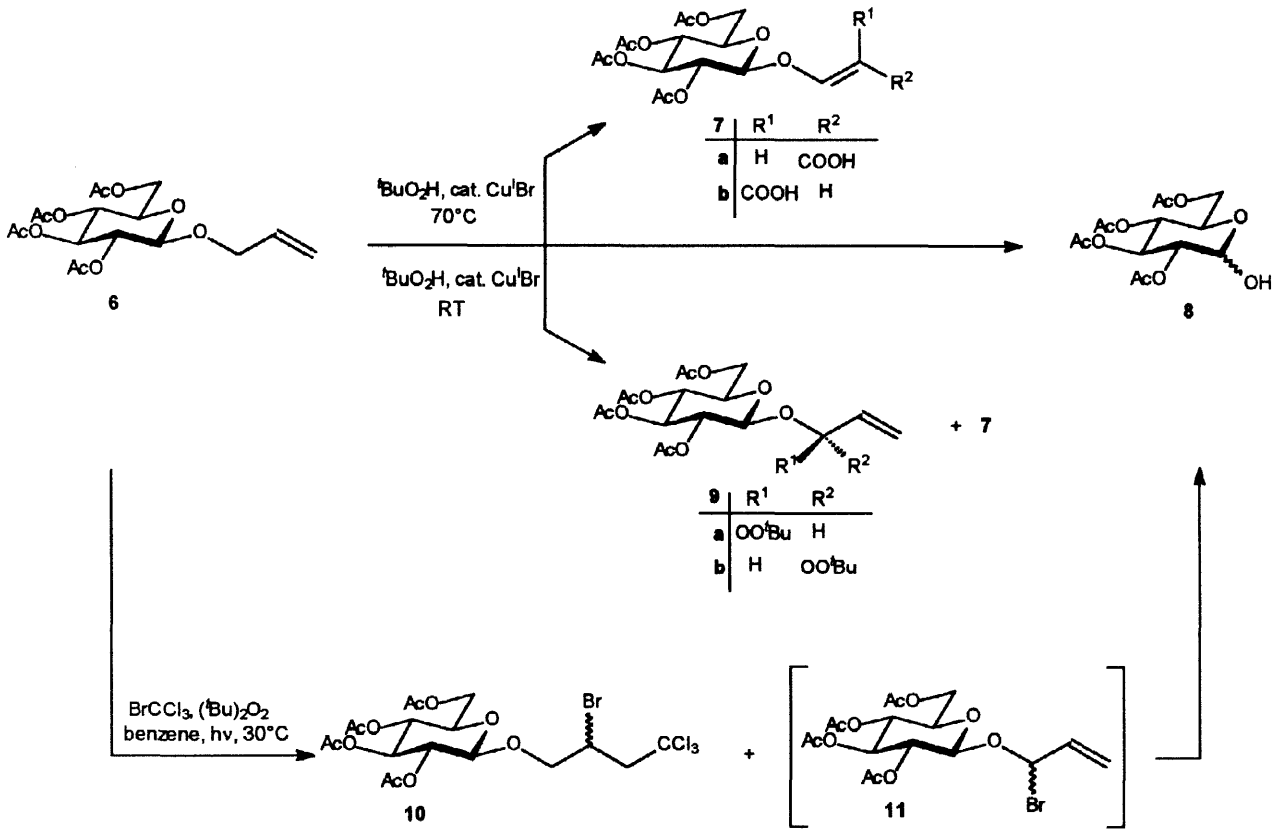




agreement with FAB MS results.-We like to add at this point, that long-chain allylic glycosides cannot be deprotected under these conditions with useful yields. Thus, when **12** was treated with ^{t}butyl hydroperoxide - Cu^{I}Br in ^{t}butanol-water at 20°C a complex mixture of products resulted from which the free sugar **8** was isolated in 30% yield alongside with the isomeric ene-diones **14a** (5%) and **14b** (1%) and the formate **13** (2%). The 70°C reaction mixture was so complicated that isolation of pure reaction products was hopeless. We assume that the ene-diones and the formate are formed from intermediates of type F and G, respectively.

Attempted cleavage of allyl glycosides with ^{t}butoxy radicals in the presence of trapping reagents

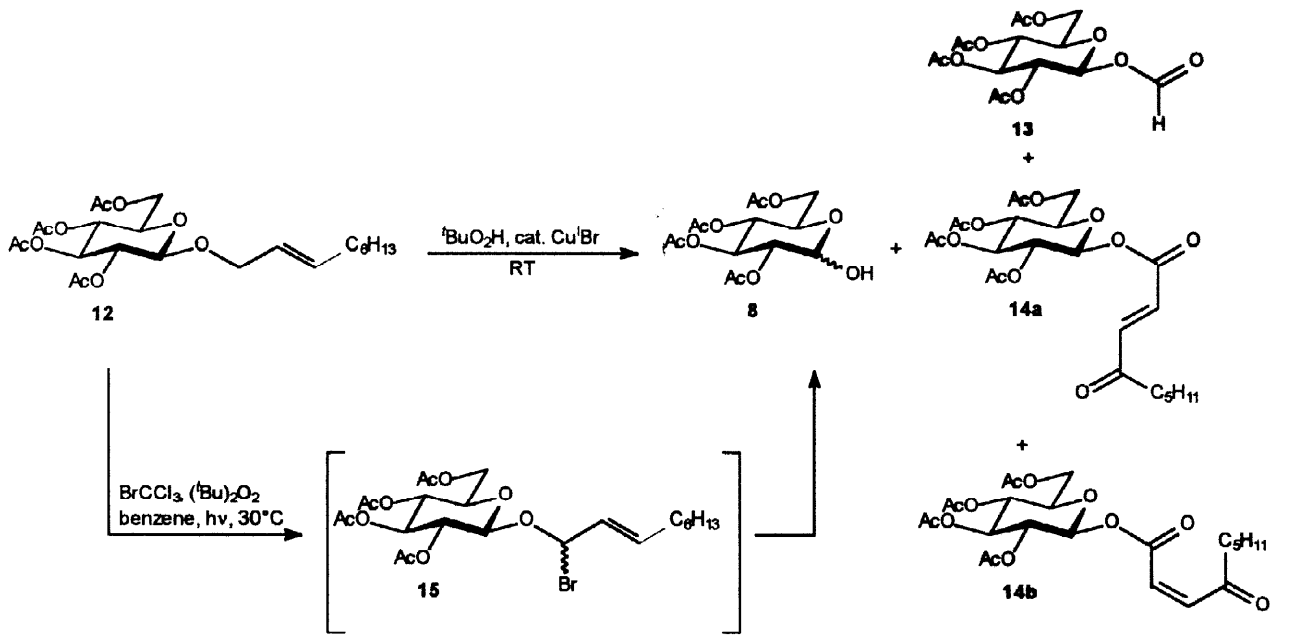
There are a number of suitable alkoxy radical precursors known in the literature. Some of the most convenient precursors seem to be thiohydroxamic acid esters as described by *Beckwith*[13] and recently by *Hartung*.[14] Unfortunately, the ^{t}butyl esters are until now not conveniently available. We turned, therefore, our attention to *Pasto's* ^{t}butyl p-nitrobenzenesulfenate[15] which is easily prepared. However, all attempts to perform allyl glycoside cleavage by irradiation (at 300 nm) of a benzene solution of **6** containing the ^{t}butyl sulfenate and $BrCCl_3$ failed. **6** was consumed very slowly and the yield of **8** was less than 10% after 2.5 h. In these experiments the solutions turned quickly turbid, and we believe that this is one reason for the failure.[16] Finally, **6** was photolysed in benzene solution at 300 nm in the presence of di-^{t}butyl peroxide and $BrCCl_3$. Two



compounds were isolated. One was the free sugar **8** (48%), probably formed via an intermediate of type D. The other compound was the *Kharasch* addition product **10** (about 50%). The latter product can probably be converted to **8** under suitable reduction conditions as recently has been shown by *Yu et al.* in their very elegant allyl glycoside deprotection reaction consisting of (i) radical addition of a perfluoroalkyl iodide to the double bond in acetonitrile-water solution and (ii) Zn-mediated reductive ß-elimination.[17]

When compound **12** was irradiated with di-^{t}butyl peroxide and $BrCCl_3$ in benzene solution the desired cleavage occurred and the free sugar **8** was obtained in 69% yield.

In conclusion: Oxidative cleavage of allyl glycosides under radical conditions is possible and the method may be useful in appropriate cases.



Experimental

Instrumentation and methods: NMR: Gemini 200 (Varian, ^{1}H NMR 200 MHz, ^{13}C NMR 50.3 MHz), Gemini 2000 (Varian, ^{1}H NMR 200 MHz, ^{13}C NMR 50.3 MHz), Gemini 300 (Varian, ^{1}H NMR 300 MHz, ^{13}C NMR 75.5 MHz), Unity 400 (Varian, ^{1}H NMR 400 MHz, ^{13}C NMR 100.6 MHz). Chemical shifts are given in δ values. IR: FT IR spectrometer (ATI Mattson, Genesis Series). FAB MS: Fisons VG. Matrices were lactic acid and 3-nitrobenzyl alcohol, respectively. Two molecular masses are always communicated, the first was calculated using the International Atomic Masses, the second refers to ^{12}C, ^{1}H, ^{16}O. Analytical TLC: Merck precoated silica gel 60 F_{254} plates (0.2 mm), spots were identified under a UV lamp (λ=254 nm and λ=366 nm) and with a 2.22 mol·l^{-1} H_2SO_4 solution which contained $Ce(SO_4)_2 \cdot 4H_2O$ (10 g·l^{-1}) and $H_3[PO_4(Mo_3O_9)_4] \cdot H_2O$ (25 g·l^{-1}) and heating at 140°C[18] FC (flash chromatography) was performed as described by Still[19] (ICN Biomedicals Silica 32-63 µm and 63-100 µm, respectively).- Solvents were dried using standard procedures, molecular sieves were dried at 320°C for 18 h at 10 Pa. If necessary, solvents were degassed by sonication (Bandelin, Sonorex Super RK 106).- All O_2 - or moisture-sensitive reactions were performed in oven-dried glassware under a positive pressure of argon. Liquids and solutions were transferred by syringe. Small-scale reactions were performed in Wheaton serum bottles sealed with aluminum caps with open top and Teflon®-faced septum (Aldrich). Organic solvent evaporations were performed in vacuo at 40°C using a rotatory evaporator.

(1*SR*, 2*SR*, 4*SR*)-2-Allyloxy-1-isopropyl-4-methyl-cyclohexane (*rac*-4)

Rac-4 was prepared from *rac*-menthol and allyl bromide under *Williamson* conditions.

Bp.$_{0.8}$: 63°C.- ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.79 (d, $J_{8,7}$ = 7.0 Hz, 3 H, CH_3-8), 0.91 (d, $J_{9,7}$ = 7.0 Hz, 3 H, CH_3-9), 0.92 (d, $J_{10,4}$ = 6.5 Hz, 3 H, CH_3-10), 0.85-0.93 (m, 3 H, 3-H, 5-H, 6-H), 1.21-1.30 (m, 1 H, 1-H), 1.31-1.41 (m, 1 H, 4-H), 1.60-1.68 (m, 2 H, 5-H', 6-H'), 2.06-2.14 (m, 1 H, 3-H'), 2.18-2.31 (m, 1 H, 7-H), 3.09 (ddd, $^3J_{1,2}$ = $J_{3',2}$ 10.4 Hz, $J_{3,2}$ = 4.1 Hz, 1 H, 2-H), 3.90 (ddt, $^2J_{1,1'}$ = 12.4 Hz, $J_{1,2}$ = 5,8 Hz, $J_{1',2}$ = 5.5 Hz, ^{4}J = 1.4 Hz, 1 H, allyl 1-H), 4.14 (ddt, 1 H, allyl 1-H'), 5.12-5.18 (m, $^2J_{3cis,3trans}$ = 3.3 Hz, $J_{2,3trans}$ = 10.4 Hz, 1 H, allyl 3-H_{trans}), 5.23-5.32 (m, $J_{2,3cis}$ = 17.3 Hz, 1-H, allyl 3-H_{cis}), 5.89-5.60 (m, 1 H, allyl 2-H).- ^{13}C NMR (100.6 MHz, C,H COSY, APT, $CDCl_3$): δ = 15.84 (C-8), 20.54 (C-9), 21.91 (C-10), 23.01 (C-6), 25.18 (C-7), 31.15 (C-4), 34.16 (C-5), 40.12 (C-3), 47.89 (C-1), 69.12 (allyl C-1), 78.35 (C-2), 115.86 (allyl C-3), 135.39 (allyl C-2).- $C_{13}H_{24}O$ (196.23, 196.18).- EI MS: m/z (%) 196 [M]$^+$ (4), 181 [M-CH_3]$^+$ (13), 153 (11), 139 (38), 138 (25) 124 (13), 111 (52), 110 (20), 95 (41), 82 (90), 72 (100).

General procedure for the *Kharasch-Sosnovsky* cleavage of *rac*-4
To a mixture of *rac*-4 (50 mg, 255 μmol), the catalyst (0.1 eq.), and solvent (3 mL) 10 eq. of the oxidant and n-dodecane as an internal standard were added. The best yields were obtained when the oxidant was added gradually. The reaction mixture was stirred at 70°C for the time indicated. Triphenylphosphine (1 eq.) and sat. aq. Na_2CO_3 were added and the mixture was stirred at 20°C for 30 min and was then extracted with either dichloromethane or diethyl ether. The yields were determined by quantitative GC (25 m x 0.2 mm glass capillary column, methylsilicone, 120°C, carrier gas: H_2, FID), response factors: f_m = 1.164 (*rac*-4), 1.199 (*rac*-5, Merck), 1.246 (*rac*-menthone, Fluka), standard: n-dodecane. The results are collected in Table 1.

***Kharasch-Sosnovsky* cleavage of 6 at 70°C**
To a mixture of **6** (250 mg, 644 μmol) and Cu^IBr (0.1 eq.) in 1:1 ^{t}butanol-water (1 mL) ^{t}butyl hydroperoxide (80% solution, 1 mL, 8.4 mmol) was added. The resulting suspension was stirred at 70°C for 26 h. The reaction mixture was diluted with methanol (2 mL), triphenylphosphine (1 eq.) was added and the mixture was stirred at 20°C for 30 min. After solvent evaporation FC (hexanes - ethyl acetate1:1 and then $CHCl_3$ - methanol- ethyl acetate 19:1:0.2) provided a 4:1 mixture of the E,Z-isomers **7a/7b** (28 mg, 10%) and **8**[20] (134 mg, 60%). 25 mg of 6 were recovered (90% conversion).

3-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-(*E*^{a} and *Z*^{b})-propenoic acid (7a/7b)
^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.02, 2.04, 2.06, 2.10 (4 × s, 24 H, $COCH_3^a$, $COCH_3^b$), 3.60-3.78 (m, 1 H, 5-H^b), 3.83 (ddd, $J_{5a,4a}$ = 9.9 Hz, $J_{5a,6'a}$ = 4.9 Hz, $J_{5a,6a}$ = 2.2 Hz, 1 H, 5-H^a), 4.07-4.35 (m, $^2J_{6a,6'a}$ = 12.4 Hz, 4 H, CH_2-6^a, CH_2-6^b), 4.94 (d, $J_{1a,2a}$ = 7.7 Hz, 1 H, 1-H^a), 5.00-5.35 (m, 8 H, 2-H^a, 3-H^a, 4-H^a, 2-H^b, 3-H^b, 4-H^b, 1-H^b, propenoic acid 2-H^b), 5.47 (d, 1 H, propenoic acid 2-H^a), 6.79 (d, $J_{3b,2b}$ = 7.1 Hz, 1 H, propenoic acid 3-H^b), 7.57 (d, $J_{3a,2a}$ = 12.4 Hz, 1 H, propenoic acid 3-H^a).- ^{13}C NMR (75.5 MHz, C,H COSY, APT, $CDCl_3$): δ = 20.56, 20.68, 20.85, 20.92 ($CO\underline{C}H_3^a$, $CO\underline{C}H_3^b$), 61.58 (C-6^a, C-6^b), 67.80, 70.49, 70.65, 71.92, 72.38, 72.75, 72.86 (C-5^a, C-4^a, C-3^a, C-2^a, C-5^b, C-4^b, C-3^b, C-2^b), 99.99 (C-1^a), 100.50 (C-1^b), 101.30 (propenoic acid C-2^a), 103.4 (propenoic acid C-2^b), 153.58 (propenoic acid C-3^b), 160.22 (propenoic acid C-3^a), 166.98 (propenoic acid C-1^a), 168.20 (propenoic acid C-1^b), 169.12, 169.33, 170.16, 170.63, 171.23 ($\underline{C}OCH_3^a$, $\underline{C}OCH_3^b$).]$^+$.- IR ($CHCl_3$): 3024, 3022, 3019, 1756, 1700, 1696, 1226, 1223, 1206, 1073, 1039 cm^{-1}.- $C_{17}H_{22}O_{12}$ (418.35, 418.11).- FAB MS: m/z 441.3 $[M+Na]^+$, 419.3 $[M+H]^+$, 331.3 $[f]^+$.

Table 1: *Kharasch-Sosnovsky* reaction of rac-4

catalyst	solvent	oxidant	reaction temperature [°C]	reaction time [h]	yield rac-5 [%]	conversion [%]
CuCl	chlorobenzene	t-BuOOAc	60	144	25	
$Co(Oac)_2$	chlorobenzene	t-BuOOAc	60	166	43	
$Mn(Oac)_2$	chlorobenzene	t-BuOOAc	60	166	13	
CuBr	chlorobenzene	t-BuOOAc	70	122	33	43
CuBr[1]	chlorobenzene	t-BuOOH	70	108	52	95
CuBr	methanol	t-BuOOAc	70	122	11	11
CuBr	methanol	t-BuOOH	70	108	17	22
CuBr	1:1 ^{t}BuOH - H_2O	t-BuOOAc	70	140	42	55
CuBr	^{t}BuOH	t-BuOOH	70	116	35	90
CuBr	1:1 ^{t}BuOH - H_2O	t-BuOOH	70	116	72	90
CuBr	pyridine	t-BuOOH	70	116	17	50
CuBr	1:1 pyridine - H_2O	t-BuOOH	70	116	25	25
CuBr	CH_3CN	t-BuOOH	70	116	36	80
CuBr	1:1 CH_3CN - H_2O	t-BuOOH	70	116	50	65
CuBr	AcOH	t-BuOOH	70	116	32	75
CuBr	1:1 AcOH - H_2O	t-BuOOH	70	116	52	58

[1] In this experiment *rac*-menthone (16%) was detected

***Kharasch-Sosnovsky* cleavage of 6 at 20°C**

To a mixture of **6** (250 mg, 644 μmol) and $Cu^{I}Br$ (0.1 eq.) in 1:1 ^{t}butanol-water (1 mL) ^{t}butyl hydroperoxide (1 mL, 8.4 mmol, 80% solution) was added in two portions within 1 h. The suspension was stirred at 20°C for 224 h. After dilution with methanol (2 mL), reduction with triphenylphosphine (1 eq.), and solvent evaporation the residue was separated by FC (hexanes - ethyl acetate 1:1, $CHCl_3$ - methanol - ethyl acetate 19:1:0.2) to give the E,Z-isomers **7a/7b** (80 mg, 30%) as a colorless oil, a (2^a:3^b)[2] mixture of **9a/9b** (33 mg, 11%) as a white solid, and the deallylated product **8** (77 mg, 35%).

{(1Ξ)-*tert*-Butylperoxy-propen-1-yl}-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (9a/9b)

^{1}H NMR (200 MHz, COSY, $CDCl_3$): δ = 1.24 (s, 18 H, $OOC(CH_3)_3^a$, $OOC(CH_3)_3^b$), 1.99-2.10 (24 H, $COCH_3$ signals), 3.70 (ddd, $J_{5a,6a}$ = $J_{5b,6b}$ = 2.5 Hz, $J_{5a,6'a}$ = $J_{5b,6'b}$ = 4.4 Hz, 2 H, 5-H^a, 5-H^b), 4.11 (dd, $^2J_{6a,6a'}$ = $^2J_{6b,6'b}$ = 12.1 Hz, 2 H, 6-H^a, 6-H^b), 4.18-4.32 (m, 2 H, 6-H'^a, 6-H'^b), 4.86 (d, $J_{1a,2a}$ = 8.1 Hz, 1 H, 1-H^a), 4.90-5.38 (m, 9 H, 4-H^a, 3-H^a, 2-H^a, 4-H^b, 3-H^b, 2-H^b, =CH_2-3^b, 1-H^b), 5.41 (dd, $J_{1a,2a}$ = 4.4 Hz, ^4J = 1.0 Hz, 1 H, allyl 1-H^a), 5.46-5.56 (m, 2 H, allyl 1-H^b, allyl 3-H^a), 5.62-5.88 (m, 2 H, allyl 2-H^a, allyl 2-H^b, allyl 3-H'^a).- ^{13}C NMR (50.3 MHz, C,H COSY, $CDCl_3$): δ = 21.07, 21.21 ($COCH_3^a$ signals, $COCH_3^b$ signals), 26.82, 26.91 [$OOC(CH_3)_3^a$, $OOC(CH_3)_3^b$], 62.52, 62.67 (C-6^a, C-6^b), 68.96, 69.12, 71.69, 71.88, 73.42 (C-4^a, C-3^a, C-2^a, C-4^b, C-3^b, C-2^b), 72.33, 72.54 (C-5^a, C-5^b), 81.51, 81.76 [$OOC(CH_3)_3^a$, $OOC(CH_3)_3^b$], 97.84 (C-1^a), 98.17 (C-1^b), 102.42 (allyl C-1^b), 105.32 (allyl C-1^a), 120.46, 120.51 (allyl C-3^a, allyl C-3^b), 131.71 (allyl C-2^a, allyl C-2^b), 169.89, 170.78, 170.81, 171.11 ($COCH_3^a$ signals, $COCH_3^b$ signals).- IR ($CHCl_3$): 3022, 3017, 1756, 1226, 1220, 1207, 1054, 1040 cm^{-1}.- $C_{21}H_{32}O_{12}$ (476.48, 476.19).- FAB MS: m/z 515.3 $[M+K]^+$, 499.3 $[M+Na]^+$, 477.4 $[M+H]^+$, 331.2 $[f]^+$.

***Kharasch-Sosnovsky* cleavage of 12**

a) To a suspension of **12** (700 mg, 1.5 mmol) and $Cu^{I}Br$ (21 mg, 150 μmol) in acetonitrile (5 mL) ^{t}butyl hydroperoxide (920 μL, 7.5 mmol, 80%) was added. The solution was stirred at 20°C. After 24 h another portion of ^{t}butyl hydroperoxide (920 μL, 7.5 mmol, 80%) was added and the mixture was stirred for another 234 h.

b) A practically identical experiment **12** was performed in ^{t}butanol - water (2mL) instead of acetonitrile. TLC (hexanes - ethyl acetate 1:1) indicated that the same reaction products were formed. The two reaction mixtures were therefore combined. Solvent evaporation and repeated FC (hexanes - ethyl acetate 3:2) furnished **8** (303 mg, 29%) as a white solid. The other fractions were separated by HPLC (10 μm silical gel, hexanes - ethyl acetate 2:1) and provided **13** (19 mg, 2%, colourless oil), **14a** (75 mg, 5%, white solid), **14b** (17 mg, 1%, white solid).

2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl formate (13)

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.02, 2.04, 2.06, 2.09 (4 × s, 12 H, $COCH_3$), 3.87 (ddd, $J_{5,4}$ = 9.7 Hz, $J_{5,6'}$ = 4.5 Hz, $J_{5,6}$ = 2.2 Hz, 1 H, 5-H), 4.12 (dd, $^2J_{6,6'}$ = 12.4 Hz 1 H, 6-H), 4.29 (dd, 1 H, 6-H'), 5.00-5.34 (m, 3 H, 4-H, 3-H, 2-H), 5.82 (d, $J_{1,2}$ = 7.8 Hz, 1 H, 1-H), 8.06 (s, 1 H, formyl-H).- ^{13}C NMR (50.3 MHz, APT, $CDCl_3$): δ = 21.02, 21.16 ($COCH_3$), 61.84 (C-6), 68.10, 70.52, 73.11, 73.37 (C-5, C-4, C-3, C-2), 91.65 (C-1), 159.03 (formyl-C), 169.67, 169.83, 170.56, 171.10 ($COCH_3$ signals).- IR ($CHCl_3$): 3029, 3025, 2962, 1755, 1368, 1231, 1220, 1074, 1040 cm^{-1}.- $C_{15}H_{20}O_{11}$ (376.32, 376.10).- FAB MS: m/z 331.3 $[f]^+$.[21]

(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl) (*E*)-4-oxo-non-2-enoate (14a)

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.85 (t, $J_{9,8}$ = 6.6 Hz, 3 H, CH_3-9^{N3}), 1.04-1.36 (m, 4 H, CH_2-8^N, CH_2-7^N), 1.50-1.68 (m, 2 H, CH_2-6^N), 1.98, 1.99, 2.04 (3 × s, 12 H, $COCH_3$), 2.59 (t, $J_{5,6}$ = 7.3 Hz, 2 H, CH_2-5^N), 3.85 (ddd, $J_{5,4}$ = 9.5 Hz, $J_{5,6'}$ = 4.6 Hz, $J_{5,6}$ = 2.0 Hz, 1 H, 5-H), 4.07 (dd, $J_{6,6'}$ = 12.6 Hz, 1 H, 6-H), 4.26 (dd, 1 H, 6-H'), 5.02-5.32 (m, 3 H, 4-H, 3-H, 2-H), 5.76 (d, $J_{1,2}$ = 7.7 Hz, 1 H, 1-H), 6.59 (d), 7.07 (d) ($J_{2,3}$ = 16 Hz 2 H, 2-H^N, 3-H^N).- ^{13}C NMR (50.3 MHz, APT, $CDCl_3$): δ = 14.21 (C-9^N), 20.89, 21.02 ($COCH_3$ signals), 22.74, 23.59 (C-8^N, C-7^N), 31.57 (C-6^N), 42.14 (C-5^N), 61.77 (C-6), 68.08, 70.51, 73.00, 73.24 (C-5, C-4, C-3, C-2), 92.77 (C-1), 129.03, 141.81 (C-2^N; C-3^N), 164.04 (C-1^N), 169.73, 169.91, 170.58, 171.10 ($COCH_3$

[2] a and b refer to the two diasteroisomers

[3] N refers to the C_9 unit

signals), 199.89 (C-4^N).- IR ($CHCl_3$): 3028, 2960, 2934, 1757, 1704, 1368, 1233, 1203, 1076, 1038 cm^{-1}.- $C_{23}H_{32}O_{12}$ (500.50, 500.19).- FAB MS: m/z 523.3 $[M+Na]^+$, 501.3 $[M+H]^+$, 331.2 $[f]^+$.

2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl) (*Z*)-4-oxo-non-2-enoate (14b)
^1H NMR (200 MHz, $CDCl_3$): δ = 0.80-1.05 (m, 3 H, CH_3-9^N), 1.10-1.42 (m, 4 H, CH_2-8^N, CH_2-7^N), 1.52-1.80 (m, 2 H, CH_2-6^N), 2.01, 2.03, 2.06, 2.09 (4 × s, 12 H, $COCH_3$), 2.57 (dt, $J_{5,6}$ = 7.3 Hz and 1.8 Hz, 2 H, CH_2-5^N), 3.80-3.87 (m, 1 H, 5-H), 4.10 (dd, $J_{5,6}$ = 2.5 Hz, $J_{6,6'}$ = 12.5 Hz, 1 H, 6-H), 4.30 (dd, $J_{5,6'}$ = 4.5 Hz, 1 H, 6-H'), 5.08-5.36 (m, 3 H, 4-H, 3-H, 2-H), 5.78 (d, $J_{1,2}$ = 8.0 Hz, 1 H, 1-H), 6.01 (d), 6.56 (d) ($J_{2,3}$ = 12 Hz, 2 H, 2-H^N, 3-H^N).- ^{13}C NMR (50.3 MHz, APT, $CDCl_3$): δ = 14.36 (C-9^N), 21.03, 21.16 ($\underline{C}OCH_3$ signals), 22.90, 23.41 (C-8^N, C-7^N), 31.71 (C-6^N), 42.99 (C-5^N), 61.89 (C-6), 68.18, 70.46, 73.31 (C-5, C-4, C-3, C-2), 92.59 (C-1), 123.94, 143.52 (C-2^N,C-3^N), 163.90 (C-1^N), 169.88, 170.53, 171.06 ($\underline{C}OCH_3$ signals), 203.18 (C-4^N).- IR ($CHCl_3$): 3027, 2960, 2934, 1756, 1705, 1368, 1232, 1215, 1074, 1037 cm^{-1}.- $C_{23}H_{32}O_{12}$ (500.50, 500.19).- FAB MS: m/z 523.0 $[M+Na]^+$, 331.0 $[f]^+$.

Photochemically induced oxidative cleavage of 6 and of 12
a) A Rayonet Photochemical Chamber Reactor Model RPR-100 equipped with 300 nm lamps was used to irradiate the reaction solution. In a quartz tube containing a solution of **6** (100 mg, 258 μmol) in freshly distilled benzene (15 mL) di-^{t}butyl peroxide (470μl, 2.6 mmol) and bromotrichloromethane (254 μl, 2.6 mmol) were added. Then the reaction solution was irradiated under argon. The temperature of the solution was about 30°C. Progress of the reaction was followed by TLC (hexanes - ethyl acetate 1:1). After 45 min the solvent was removed under reduced pressure and the resulting residue (yellow oil) was separated by FC (hexanes - ethyl acetate 1:1) to give **8**(43 mg, 48%) and a fraction (128 mg) containing **10** (yield ~ 50%) and a small amount (as indicated by TLC) of **6**.
b) **12** was submitted to exactly the same conditions and yielded **8** in 69% yield.

{(2Ξ)-Bromo-3-trichloromethyl-prop-1-yl} 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (10) (2:3 mixture of two diastereoisomers, a and b)
^1H NMR (200 MHz, COSY, $CDCl_3$): δ = 2.01-2.11 (m, 24 H, $COCH_3$ signals), 3.15-3.52 (m, 4 H, propyl CH_2-3^a, propyl CH_2-3^b), 3.65-3.95 (m, 4 H, 5-H^a, 5-H^b, propyl 1-H^a, propyl 1-H^b), 4.10-4.47 (m, 8 H, 6-H^a, 6-H^b, 6-H'^{a}, 6-H'^{b}, propyl 1-H'^{a}, propyl 1-H'^{b}, propyl 2-H^a, propyl 2-H^b), 4.62 (d, $J_{1a,2a}$ = 8.1 Hz, 1 H, 1-H^a), 4.61 (d, $J_{1b,2b}$ = 7.9 Hz, 1 H, 1-H^b), 5.01-5.31 (m, 6 H, 4-H^a, 3-H^a, 2-H^a, 4-H^b, 3-H^b, 2-H^b). The assignment of propyl CH_2-1 and propyl CH_2-3 is not proven since we did not find appropriate crosspeaks in the C,H COSY spectrum.- ^{13}C NMR (50.3 MHz, C,H COSY, APT, $CDCl_3$): δ = 20.99, 21.12 ($CO\underline{C}H_3{}^a$ signals, $CO\underline{C}H_3{}^b$ signals), 44.35 (propyl C-2^a), 44.59 (propyl C-2^b), 58.95 (propyl C-3^a, propyl C-3^b), 62.21 (C-6^a, C-6^b), 68.70, 71.44, 72.44, 72.60, 72.95 (C-5^a, C-4^a, C-3^a, C-2^a, C-5^b C-4^b, C-3^b, C-2^b), 73.68 (propyl C-1^a, propyl C-1^b), 97.34 ($CCl_3{}^a$, $CCl_3{}^b$), 100.88 (C-1^a), 101.73 (C-1^b), 169.94, 170.82, 171.20 ($\underline{C}OCH_3{}^a$ signals, $\underline{C}OCH_3{}^b$ signals).- $C_{18}H_{24}BrCl_3O_{10}$ (583.96, 586.65).- FAB MS: m/z 607.0 $[M+Na]^+$, 585.0 $[M+H]^+$, 331.0 $[f]^+$.- The isotope pattern was in agreement with the molecular formula.

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REFERENCES AND NOTES

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