Syntheses and Reactions of Glycosylcobaloximes

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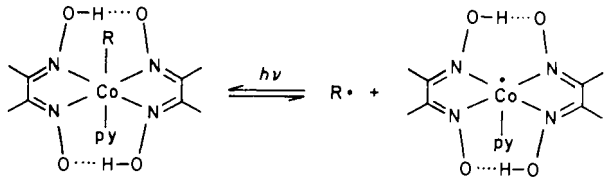
Glycosylcobaloximes 6a, b are synthesized by reactions of glycosyl bromides 4a, b with the cobalt(II) complex 5 under reducing conditions. Under irradiation, α-glycosylcobaloximes 6a, b isomerize to give the β isomers 9 and 15, respectively. These isomerization reactions occur via radicals that can be trapped by nitroso alkane 12, nitrogen monoxide, and alkenes. Reactions with alkenes 17 yield addition products 18 and/or substitution products 19. The product ratio 18:19 depends on the electron-withdrawing ability of the substituents of the alkenes.

Synthese und Reaktionen von Glycosylcobaloximen

Die Synthese von Glycosylcobaloximen 6a, b gelingt durch Umsetzung von Glycosylbromiden 4a, b mit dem Cobalt(II)-Komplex 5 unter reduzierenden Bedingungen. Bei Bestrahlung gehen die α-Glycosylcobaloxime 6a, b in die β-Isomeren 9 bzw. 15 über. Diese Isomerisierung verläuft über Radikale, die vom Nitrosoalkan 12, von Stickstoffmonoxid und Alkenen abgefangen werden können. Die Reaktionen mit Alkenen 17 liefern Additionsprodukte 18 und/oder Substitutionsprodukte 19. Das Produktverhältnis 18:19 hängt vom Elektronenzug der Alken-Substituenten ab.

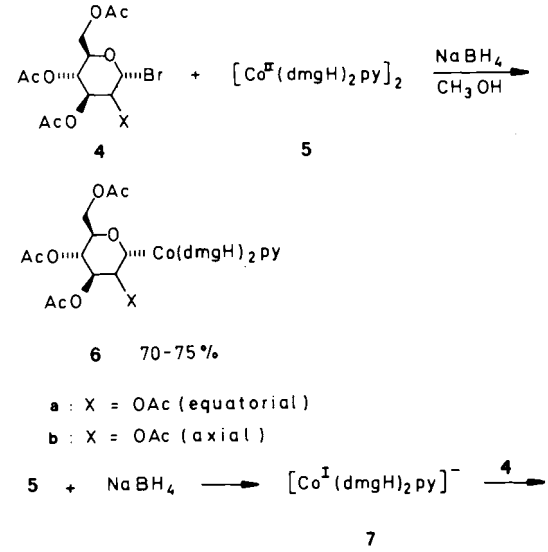
Alkylcobaloxime complexes **1** can act as radical precursors, because irradiation cleaves the Co–C bond homolytically[1]. In the absence of radical traps, the so formed alkyl radicals **2** recombine with the Co(II) complexes **3** and lead back to starting alkylcobaloximes **1**. Dimerization and disproportionation reactions between the alkyl radicals occur only to a small extent[2]. This surprising feature of alkylcobaloximes **1** can be explained by two effects: (1) Alkyl radicals **2** and Co(II) complexes **3** form radical pairs in a solvent cage[1], and (2) different dimerization rates between the alkyl radicals **2** on the one side, and between the Co(II) complexes **3** on the other side, lead predominantly to cross coupling products[3].



1 = R Co(dmgH)$_2$py 2 3

Therefore, alkylcobaloximes **1** have advantages compared with radical initiators like peresters or azo compounds, that yield product mixtures of combination and disproportionation reactions unless the alkyl radicals are trapped by suitable reagents. Nature uses this benefit of alkylcobalt complexes in vitamin B_{12} catalyzed isomerization reactions[4]. We have now synthesized glycosylcobaloximes **6a, b** by reaction of glycosyl bromides **4a, b** and the dimeric Co(II) complex **5** under reducing conditions in methanol/water mixtures[5].

The Co(II) complex is first reduced to the Co(I) complex **7**[6], which reacts with glycosyl halides **4a, b** and yields α-glycosyl complexes **6a, b** as substitution products. The stereochemistry of the reaction excludes an S_N2 mechanism, and



the absence of methyl glycosides makes the S_N1 mechanism unlikely. Presumably, the glycosylcobaloximes **6a, b** are formed via glycosyl radicals that could be generated by electron transfer from Co(I) complex **7** to glycosyl halides **4**. Reactions of glycosyl radicals with the Co complexes then yield products **6** by an $S_{RN}1$ mechanism[7]. The stereochemistry of the reaction is in accord with this radical hypothesis because the formation of α-products is typical for reactions between glycosyl radicals and non-radicals[8]. The coupling constants of the ^{1}H-NMR spectrum show that the α-glucosylcobaloxime **6a** adopts a $B_{2,5}$ boat conformation, in which the bulky Co complex substituent is equatorial. Irradiation of **6a** leads to the β-glucosylcobaloxime **9** and to glucal **10**, the product of elimination.

Intermediate of the α,β-isomerization reaction is the glucosyl radical **8**[9], which can be trapped by NO radicals yielding oxime **11** or by the spin trap 1,1-dimethyl-1-nitrosoethane (**12**) yielding nitroxyl radical **13**. At 25°C, nitroxyl

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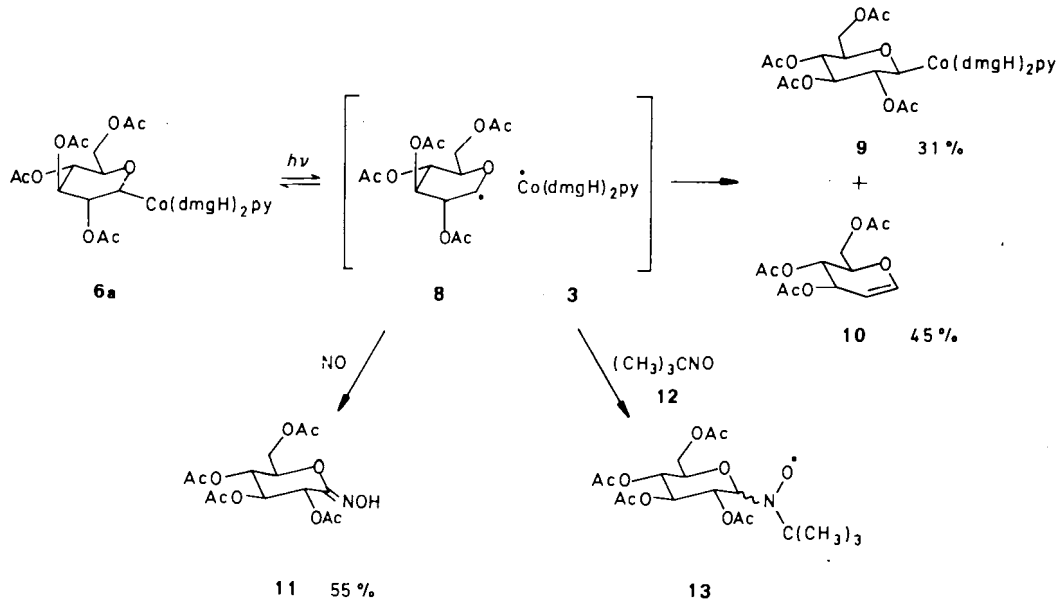


radical **13** exhibits a triplet with $a(N) = 12.93$ G, in which each line is split into two doublets by 1-H and 2-H of the glucose ring [$a(H) = 0.76$ G, 1.46 G].

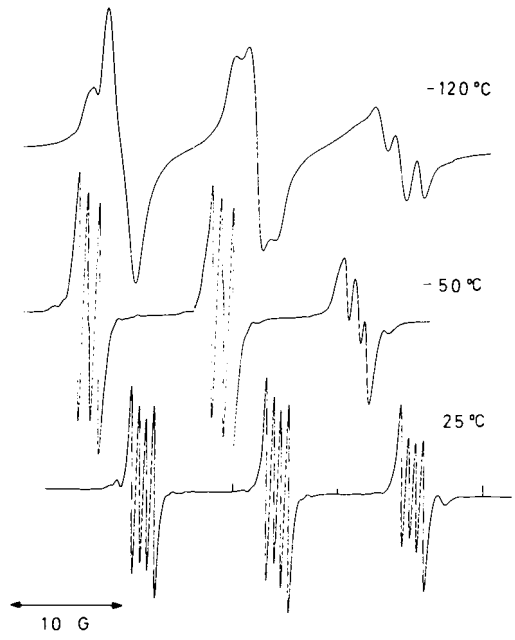
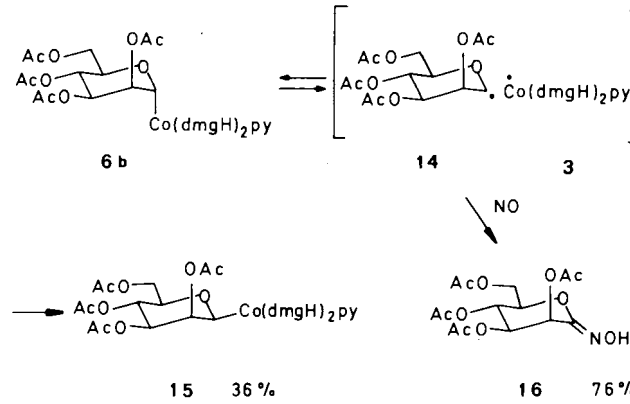


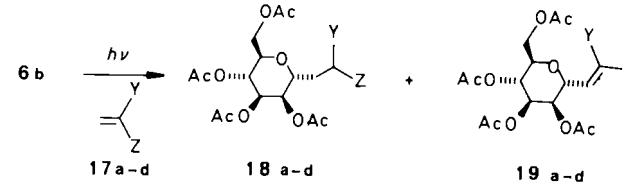
Fig. ESR spectra recorded during the photolysis of glucosylcobaloxime **6a** in the presence of nitrosoalkane **12**

The α-mannosylcobaloxime **6b** adopts a $^4C_1$ conformation that isomerizes to the β-mannosylcobaloxime **15** under irradiation. Trapping of the intermediate mannosyl radical **14** yield oxime **16**.

These experiments demonstrate that under irradiation the glycosylcobaloximes **6a, b** generate glycosyl radicals, which can be trapped by suitable reagents. Of synthetic interest are trapping experiments with alkenes, which could lead to *C*-glycosides[8]. We have, therefore, irradiated mannosylcobaloxime **6b** in benzene or ethanol at 15°C and/or at 80°C with an excess of alkenes **17a–d** for several hours. This leads to addition products **18** and/or substitution products **19** in 40–75% yield.



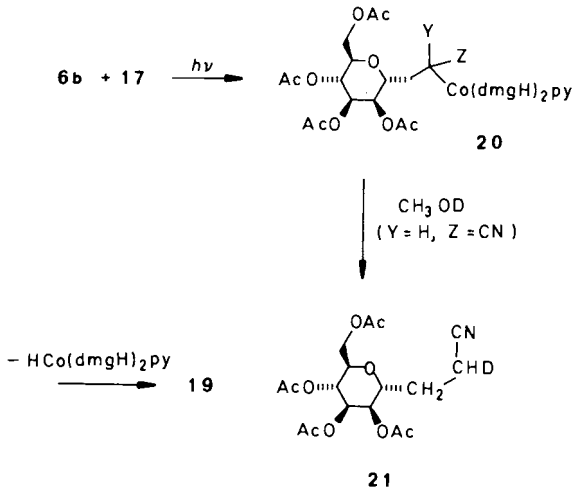
The formation of addition products like **18** in reactions between alkylcobalt complexes and alkenes has been observed before only in vitamin B_{12} catalyzed reactions under



	Alkene Y	Alkene Z	Product Ratio 18 : 19	Yield (%) 15°C	Yield (%) 80°C
a	H	CN	> 98 : 2	51	75
b	H	CO_2CH_3	15 : 85	27	40
c	H	C_6H_5	< 2 : 98	65	47
d	OC_2H_5	CN	< 2 : 98	60(68)[a]	

a) in ethanol

reducing conditions[10], whereas up to now intermolecular reactions with alkylcobaloximes gave only substitution products[5b,11]. Intermediates in reactions of alkylcobalt complexes with alkenes are presumably the insertion products **20**, which are formed after addition of the mannosyl radical **14** to alkene **17** and subsequent combination with the Co(II) complex **3**[5b,11]. If Y or Z are strong electron-withdrawing substituents like cyano, then the Co–C bond in **20** can be cleaved via a carbanion and a Co(III) complex. We have proved this by experiments in the presence of CH_3OD, which yielded the monodeuterated product **21**. With less electron-withdrawing substituents Y and Z like ester or phenyl groups, however, the reductive elimination is faster than the protonation.



An interesting alkene is 2-ethoxyacrylonitrile (**17d**), which yields only substitution product **19d**. We are now investigating, whether this alkene can be used as an in vitro substitute of phosphoenol pyruvate, which reacts with carbohydrates in enzymatic aldol reactions[12].

We like to thank *P. Krusic* for carrying out the ESR measurements, and the *Volkswagen-Stiftung*, the *Deutsche Forschungsgemeinschaft*, and the *Fonds der Chemischen Industrie* for their financial support.

Experimental

NMR: Bruker WM 300 (TMS as internal standard). – MS: Finnigan MAT 311 A. – Optical rotation: Perkin-Elmer polarimeter 141. – ESR: Bruker ER 420. – Flash chromatography: Macherey-Nagel silica gel 60 (0.040–0.063 mm).

General Synthesis of Glycosylcobaloximes **6**: A suspension of 695 mg (2.5 mmol) of hexaquocobalt(II) chloride and 580 mg (5.0 mmol) of dimethylglyoxime in 15 ml of methanol was treated for 15 min at room temp. with argon to remove molecular oxygen, combined with 0.2 ml (2.5 mmol) of pyridine and 0.25 ml (5.0 mmol) of a 50% aqueous solution of sodium hydroxide, and cooled to –10°C. This temperature was maintained during the reaction. After stirring for 15 min, a solution of 598 mg (4.0 mmol) of triethanolamine and 18 mg (0.1 mmol) of triethanolamine hydrochloride, dissolved in 5 ml of methanol/water (4:1), and 820 mg (2.0 mmol) of **4**[13] in 2 ml of dichloromethane was added. A total amount of 2.5–3.0 mmol of sodium borohydride was added in portions of 20 mg (0.5 mmol), each dissolved in 0.5 ml of ice/water. The addition was stopped, when the color of the reaction mixture turned to orange and a yellow precipitate appeared. The mixture was then warmed up to room temp., the solvent removed in vacuo, and the residue treated with 20 ml of water containing 1% of pyridine. An orange-red product crystallized, which was dissolved in dichloromethane and subjected to flash chromatography on silica gel.

Bis(dimethylglyoximato)(pyridine)(2,3,4,6-tetra-O-acetyl-α-D-glucopyranosyl)cobalt (**6a**): The synthesis following the general procedure yielded 1.05 g (75%) of the orange-red product, m.p. 158–160°C (from methanol containing 5% of pyridine). – ^{1}H-NMR ($CDCl_3$): δ = 2.01, 2.05, 2.07, 2.21 (4 s, 12H, 4 OAc), 2.06, 2.14 (2 s, 12H, 4 CH_3), 3.80 (ddd, *J* = 3.4, 3.5, 8.8 Hz, 1H, 5-H), 3.91 (dd, *J* = 3.4, 12.0 Hz, 1H, 6-H'), 4.06 (dd, *J* = 3.6, 12.0 Hz, 1H, 6-H), 4.43 (dd, *J* = 2.2, 3.8 Hz, 1H, 2-H), 4.69 (dd, *J* = 3.8, 4.4 Hz, 1H, 3-H), 4.97 (dd, *J* = 4.4, 8.8 Hz, 1H, 4-H), 5.17 (d, *J* = 2.2 Hz, 1H, 1-H), 7.28, 7.70, 8.52 (3 m, 5H, pyridine), 18.25 (s, 2H, OH). – MS (FD): *m/z* = 621 ($M^+ - C_6H_5N$).

$C_{27}H_{38}CoN_5O_{13}$ (699.6) Calcd. C 46.36 H 5.47 N 10.01
Found C 45.95 H 5.58 N 9.77

Bis(dimethylglyoximato)(pyridine)(2,3,4,6-tetra-O-acetyl-α-D-mannopyranosyl)cobalt (**6b**): The synthesis following the general procedure yielded 1.17 g (84%) of the orange-red product, m.p. 170–172°C (from methanol containing 5% of pyridine). – ^{1}H-NMR ($CDCl_3$): δ = 1.90, 2.04, 2.05, 2.08 (4 s, 12H, 4 OAc), 2.12, 2.20 (2 s, 12H, 4 CH_3), 3.58 (ddd, *J* = 1.5, 4.0, 10.0 Hz, 1H, 5-H), 3.75 (dd, *J* = 1.5, 12.0 Hz, 1H, 6-H'), 4.18 (dd, *J* = 4.0, 12.0 Hz, 1H, 6-H), 4.93 (dd, *J* = 0.5, 3.3 Hz, 1H, 2-H), 5.09 (dd, *J* = 3.3, 10.0 Hz, 1H, 3-H), 5.31 (t, *J* = 10.0 Hz, 1H, 3-H), 5.36 (d, *J* = 0.5 Hz, 1H, 1-H), 7.34, 7.74, 8.53 (3 m, 5H, pyridine), 18.40 (s, 2H, OH). – MS (FD): *m/z* = 621 ($M^+ - C_6H_5N$).

$C_{27}H_{38}CoN_5O_{13}$ (699.6) Calcd. C 46.36 H 5.47 N 10.01
Found C 46.28 H 5.49 N 9.99

Isomerization of α-Glycopyranosylcobaloximes **6a,b** *into β-Glycopyranosylcobaloximes* **9** *and* **15**: A solution of 700 mg (1.00 mmol) of **6a** or **6b** in 100 ml of benzene was treated for 15 min with argon to remove molecular oxygen and irradiated for 20 h with a 300-W sun-lamp at 15°C. The solvent was distilled off in vacuo, and the residue subjected to flash chromatography [silica gel, dichloromethane/ether/acetone (2:1:1)].

Bis(dimethylglyoximato)(pyridine)(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)cobalt (**9**): Isomerization of **6a** following the general procedure gave 215 mg (31%) of **9**, m.p. 165–168°C (from methanol containing 5% of pyridine) and 124 mg (45%) of **10**. – ^{1}H-NMR ($CDCl_3$): δ = 1.92, 1.95, 2.04, 2.12 (4 s, 12H, OAc), 2.09, 2.16 (2 s, 12H, CH_3), 3.25 (ddd, *J* = 2.0, 5.0, 8.5 Hz, 1H, 5-H), 3.34 (d, *J* = 10.0 Hz, 1H, 1-H), 4.03–4.06 (m, 2H, 6-H, 6-H'), 4.37 (dd, *J* = 8.0, 10.0 Hz, 1H, 2-H), 4.85 (dd, *J* = 8.5, 9.0 Hz, 1H, 4-H), 4.97 (dd, *J* = 8.0, 9.0 Hz, 1H, 3-H), 7.26, 7.67, 8.54 (3 m, 5H, pyridine). – MS (FD): *m/z* = 621 ($M^+ - C_6H_5N$).

$C_{27}H_{38}CoN_5O_{13}$ (699.6) Calcd. C 46.36 H 5.47 N 10.01
Found C 46.15 H 5.48 N 9.89

Bis(dimethylglyoximato)(pyridine)(2,3,4,6-tetra-O-acetyl-β-D-mannopyranosyl)cobalt (**15**): Isomerization of **6b** following the general procedure gave 253 mg (36%) of **15**, m.p. 183–185°C (from methanol containing 5% of pyridine) and 65 mg (24%) of **10**. – ^{1}H-NMR ($CDCl_3$): δ = 1.90, 2.00, 2.07, 2.21 (4 s, 12H, OAc), 2.05, 2.15 (2 s, 12H, CH_3), 3.35 (ddd, *J* = 2.1, 5.6, 9.9 Hz, 1H, 5-H), 3.84 (dd, *J* = 5.6, 12.1 Hz, 1H, 6-H), 4.10 (dd, *J* = 2.1, 12.1 Hz, 1H, 6-H'), 4.40 (s, 1H, 1-H), 4.67 (d, *J* = 3.2 Hz, 1H, 2-H), 4.85 (dd,

J = 3.2, 9.9 Hz, 1H, 3-H), 5.10 (t, J = 9.9 Hz, 1H, 4-H), 7.31, 7.73, 8.57 (3 m, 5H, pyridine). – MS (FD): m/z = 699 (M^+).

$C_{27}H_{38}CoN_5O_{13}$ (699.6) Calcd. C 46.36 H 5.47 N 10.01
Found C 46.35 H 5.66 N 10.04

General Procedure for the Synthesis of Oximes **11** *and* **16**: A solution of 700 mg (1.0 mmol) of **6** in 20 ml of DMF was treated for 30 min with argon to remove molecular oxygen; 1.0 ml of triethylamine was added, and the argon replaced by nitrogen monoxide. The reaction mixture was irradiated at 15°C with a 300-W sunlamp. After 6 h, when no more nitrogen monoxide was consumed, the solvent was distilled off in vacuo, and the residue dissolved in dichloromethane and subjected to flash chromatography (silica gel, ether).

2,3,4,6-Tetra-O-acetyl-D-glucono-1,5-lactone Oxime (**11**): The synthesis following the general procedure gave 199 mg (55%) of a colorless sirup. – $[\alpha]_D^{20}$ = +82.4 (c = 1.03 in chloroform) ⟨ref.[14] $[\alpha]_D^{25}$ = +84.1 (c = 1.06 in chloroform)⟩.

2,3,4,6-Tetra-O-acetyl-D-manno-1,5-lactone Oxime (**16**): The synthesis following the general procedure gave 273 mg (76%) of a colorless sirup. – $[\alpha]_D^{20}$ = –9.2 (c = 1.01 in chloroform). – IR (KBr): ν = 3450 cm^{-1} (NOH), 1750 (C=O), 1665 (C=NOH). – ^{1}H-NMR ($CDCl_3$): δ = 2.05, 2.10, 2.13, 2.15 (4 s, 12H, 4OAc), 4.27 (dd, J = 3.7, 8.5 Hz, 1H, 5-H), 4.36 (m, 2H, 6-H, 6-H'), 5.25 (dd, J = 3.4, 8.4 Hz, 1H, 3-H), 5.45 (t, J = 8.4 Hz, 1H, 4-H), 5.86 (d, J = 3.4 Hz, 1H, 2-H), 8.50 (s, 1H, OH). – MS (FD): m/z = 361 (M^+).

$C_{14}H_{19}NO_{10}$ (361.1) Calcd. C 46.54 H 5.30 N 3.88
Found C 46.04 H 5.31 N 3.85

Typical Procedure for Reactions of Glycosylcobaloximes **6** *with Alkenes* **17**: A solution of 700 mg (1.0 mmol) of **6b** in 30 ml of benzene was treated for 30 min with argon to remove molecular oxygen; 10–20 mmol of alkene **17** were added, and the solution was irradiated with a 300-W sun-lamp at 15°C (method A) or under reflux (method B). After 24 h the solvent was distilled off in vacuo and the residue chromatographed.

1-C-(2'-Cyanoethyl)-2,3,4,6-tetra-O-acetyl-1-deoxy-α-D-mannopyranoside (**18a**): The reaction of 700 mg (1.00 mmol) of **6b** with 531 mg (10.0 mmol) of **17a** in 30 ml of benzene yielded after flash chromatography [silica gel, ether/ethyl acetate (2:1)] according to method A 200 mg (51%) and according to method B 294 mg (75%) of a colorless oil. – $[\alpha]_D^{20}$ = +20.3 (c = 0.995 in chloroform) ⟨ref.[15] $[\alpha]_D^{20}$ = +20.3 (c = 4.3 in chloroform)⟩.

1-C-(2'-Cyano-2'-deuterioethyl)-2,3,4,6-tetra-O-acetyl-1-deoxy-α-D-mannopyranoside (**21**): The reaction of 700 mg (1.00 mmol) of **6b** with 531 mg (10.0 mmol) of **17a** in 25 ml of benzene and 4 ml of CH_3OD gave after flash chromatography [silica gel, ether/ethyl acetate (2:1)] following method A 218 mg (56%) of a colorless oil. – ^{1}H-NMR ($CDCl_3$): δ = 1.96 (m, 2H, 1'-H', 1'-H), 2.09, 2.11, 2.12 (3 s, 12H, OAc), 2.47 (m, 1H, 2'-H), 3.97 (ddd, J = 3.6, 4.9, 7.8 Hz, 1H, 5-H), 4.04 (m, 1H, 1-H), 4.10 (dd, J = 3.6, 12.2 Hz, 1H, 6-H'), 4.58 (dd, J = 7.8, 12.2 Hz, 1H, 6-H), 5.06 (dd, J = 3.5, 5.9 Hz, 1H, 2-H), 5.06 (dd, J = 4.9, 6.6 Hz, 1H, 4-H), 5.25 (dd, J = 3.5, 6.6 Hz, 1H, 3-H). The integral of the signal at δ = 2.47 is equivalent to one hydrogen, so that one deuterium is introduced into the molecule.

1-C-(2'-Methoxycarbonylethyl)-2,3,4,6-tetra-O-acetyl-1-deoxy-α-D-mannopyranoside (**18b**) *and 1-C-[(1'E)-2'-Methoxycarbonylvinyl]-2,3,4,6-tetra-O-acetyl-1-deoxy-α-D-mannopyranoside* (**19b**): The reaction of 2.10 g (3.00 mmol) of **6b** with 3.87 g (45.0 mmol) of **17b** in 90 ml of benzene gave after flash chromatography [silica gel, ether/pentane (3:1)] according to method A 43 mg (4%) of **18b** and 290 mg (23%) of **19b** and according to method B 85 mg (7%) of **18b** and 414 mg (33%) of **19b** as colorless oils. A 15:85 ratio of **18b**:**19b** was determined by gas chromatography of a sample of the reaction mixture.

18b: $[\alpha]_D^{20}$ = +9.7 (c = 0.960 in chloroform). – ^{1}H-NMR ($CDCl_3$): δ = 2.00 (m, 2H, 1'-H, 1'-H'), 2.04, 2.07, 2.10, 2.13 (4 s, 12H, OAc), 2.44 (m, 2H, 2'-H, 2'-H'), 3.69 (s, 3H, OCH_3), 3.89 (ddd, J = 3.0, 6.3, 8.0 Hz, 1H, 5-H), 3.99 (m, 1H, 1-H), 4.06 (dd, J = 3.0, 12.1 Hz, 1H, 6-H'), 4.38 (dd, J = 6.3, 12.1 Hz, 6-H), 5.15 (t, J = 3.4 Hz, 1H, 2-H), 5.18 (t, J = 8.0 Hz, 1H, 4-H), 5.25 (dd, J = 3.4, 8.0 Hz, 1H, 3-H). – MS (FD): m/z = 418 (M^+).

$C_{18}H_{26}O_{11}$ (418.4) Calcd. C 51.67 H 6.22
Found C 51.22 H 6.39

19b: $[\alpha]_D^{20}$ = +37.4 (c = 1.074 in chloroform). – ^{1}H-NMR ($CDCl_3$): δ = 2.04, 2.06, 2.12, 2.16 (4 s, 12H, OAc), 3.79 (s, 3H, OCH_3), 3.94 (ddd, J = 2.7, 6.2, 8.9 Hz, 1H, 5-H), 4.12 (dd, J = 2.7, 12.3 Hz, 1H, 6-H'), 4.35 (dd, J = 6.2, 12.3 Hz, 1H, 6-H), 4.71 (dd, J = 2.2, 3.7 Hz, 1H, 1-H), 5.10 (dd, J = 3.2, 8.9 Hz, 1H, H-3), 5.26 (t, J = 8.9 Hz, 1H, 4-H), 5.39 (d, J = 3.2 Hz, 1H, 2-H), 6.20 (dd, J = 2.2, 16.1 Hz, 1H, 2'-H), 6.93 (dd, J = 3.7, 16.1 Hz, 1H, 1'-H). – MS (FD): m/z = 416 (M^+).

$C_{18}H_{24}O_{11}$ (416.4) Calcd. C 51.92 H 5.81
Found C 51.86 H 5.89

1-C-[(1'E)-2'-Phenylvinyl]-2,3,4,6-tetra-O-acetyl-1-deoxy-α-D-mannopyranoside (**19c**): The reaction of 700 mg (1.00 mmol) of **6b** with 521 mg (5.00 mmol) of **17c** in 30 ml of benzene gave after flash chromatography [silica gel, ether/pentane (2:1)] according to method A 282 mg (65%) and according to method B 204 mg (47%) of colorless crystals with m.p. 109°C. – $[\alpha]_D^{20}$ = +79.6 (c = 1.087 in chloroform). – ^{1}H-NMR ($CDCl_3$): δ = 2.06, 2.12, 2.20 (3 s, 12H, OAc), 4.02 (ddd, J = 2.6, 5.7, 9.2 Hz, 1H, 5-H), 4.15 (dd, J = 2.6, 12.2 Hz, 1H, 6-H'), 4.35 (dd, J = 5.7, 12.2 Hz, 1H, 6-H), 4.73 (ddd, J = 1.9, 2.8, 4.6 Hz, 1H, 1-H), 5.25 (dd, J = 2.8, 9.2 Hz, 1H, 3-H), 5.33 (t, J = 9.2 Hz, 1H, 4-H), 5.54 (t, J = 2.8 Hz, 1H, 2-H), 6.21 (dd, J = 4.6, 16.4 Hz, 1H, 1'-H), 6.80 (dd, J = 1.9, 16.4 Hz, 1H, 2'-H), 7.50–7.25 (m, 5H, C_6H_5). – MS (FD): m/z = 434 (M^+).

$C_{22}H_{26}O_9$ (434.4) Calcd. C 60.81 H 6.03
Found C 60.54 H 5.96

1-C-(2'-Cyano-2'-ethoxyvinyl)-2,3,4,6-tetra-O-acetyl-1-deoxy-α-D-mannopyranoside (**19d**): A mixture of 700 mg (1.0 mmol) of **6b** and 1.94 g (20 mmol) of **17d** in 50 ml of benzene was irradiated for 46 h at 15°C and gave after flash chromatography [silica gel, ether/pentane (3:1)] 168 mg (39%) of **19d** (isomer **A**) and 87 mg (20%) of **19b** (isomer **B**). The reaction in 50 ml of ethanol and with an irradiation time of 24 h at 15°C yielded 187 mg (44%) of **19d** (isomer **A**) and 104 mg (24%) of **19d** (isomer **B**). **A** and **B** are *E,Z* isomers.

19d, *Isomer* **A**: Colorless crystals, m.p. 99°C. – $[\alpha]_D^{20}$ = +48.4 (c = 1.013 in chloroform). – ^{1}H-NMR ($CDCl_3$): δ = 1.36 (t, J = 7.0 Hz, 3H, OCH_2CH_3), 2.02, 2.06, 2.11, 2.16 (4 s, 12H, OAc), 3.87 (ddd, J = 2.5, 5.5, 9.5 Hz, 1H, 5-H), 4.12 (dd, J = 2.5, 12.3 Hz, 1H, 6-H'), 4.15 (q, J = 7.0 Hz, 2H, OCH_2CH_3), 4.29 (dd, J = 12.3, 5.5 Hz, 1H, 6-H), 4.90 (dd, J = 2.7, 6.5 Hz, 1H, 1-H), 5.12 (dd, J = 3.1, 9.5 Hz, 1H, 3-H), 5.27 (t, J = 9.5 Hz, 1H, 4-H), 5.46 (dd, J = 2.7, 3.1 Hz, 1H, 2-H), 5.59 (d, J = 6.5 Hz, 1H, 1'-H). – MS (FD): m/z = 427 (M^+).

$C_{19}H_{25}NO_{10}$ (427.4) Calcd. C 53.39 H 5.89 N 3.28
Found C 53.30 H 5.75 N 3.18

19d, *Isomer* **B**: Colorless oil. – $[\alpha]_D^{20}$ = +24.4 (c = 1.04 in chloroform). – ^{1}H-NMR ($CDCl_3$): δ = 1.37 (t, J = 7.0 Hz, 3H, OCH_2CH_3), 2.10, 2.11, 2.12 (3 s, 12H, OAc), 3.91 (q, J = 7.0 Hz,

2H, OCH_2CH_3), 3.98 (m, 1H, 5-H), 4.19 (dd, J = 3.6, 12.2 Hz, 1H, 6-H'), 4.45 (dd, J = 6.8, 12.2 Hz, 1H, 6-H), 4.77 (dd, J = 5.3, 8.6 Hz, 1H, 1-H), 5.19–5.13 (m, 2H, 2-H, 4-H), 5.26 (dd, J = 3.0, 7.2 Hz, 1H, 3-H), 5.52 (d, J = 8.6 Hz, 1'-H). – MS (FD): m/z = 477 (M^+).

$C_{19}H_{25}NO_{10}$ (427.4) Calcd. C 53.39 H 5.89 N 3.28
Found C 53.42 H 5.82 N 3.18

ESR Measurements: Under argon and in the dark, 140 mg (0.2 mmol) of **6a** and 87 mg (1.0 mmol) of **12** were dissolved in 100 ml of tetrahydrofuran/dichloromethane (9:1, v/v). A portion of this mixture was UV-irradiated for 60 s at −120°C using a Kasha filter[16] to absorb visible and infrared irradiation. The ESR spectra were recorded at −120°C, −50°C, and 25°C (Fig. 1). The ESR data at 25°C are: a(N) = 12.93 G, a(H) = 0.76, 1.46 G, g = 2.0063.

CAS Registry Numbers

4a: 572-09-8 / **4b**: 13242-53-0 / **6a**: 114820-58-5 / **6b**: 114883-98-6 / **9**: 114883-99-7 / **10**: 2873-29-2 / **11**: 114924-06-0 / **15**: 114884-00-3 / **16**: 114924-07-1 / **17a**: 107-13-1 / **17b**: 96-33-3 / **17c**: 100-42-5 / **17d**: 19479-65-3 / **18a**: 86563-29-3 / **18b**: 114837-33-1 / **19b**: 114837-34-2 / **19c**: 114837-35-3 / **19d**, isomer **A**: 114837-36-4 / **19d**, isomer **B**: 114837-37-5 / **21**: 114837-32-0 / hexaquocobalt(II) chloride: 13185-10-6 / cobalt(II) chloride, hexaquo: 7791-13-1 / dimethylglyoxime: 95-45-4

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