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ON THE MECHANISM AND STEREOCHEMISTRY OF HYDROGEN TRANSFER INVOLVING PHOTODEOXYGENATION OF SUGAR ESTERS IN HEXAMETHYLPHOSPHORIC TRIAMIDE/WATER

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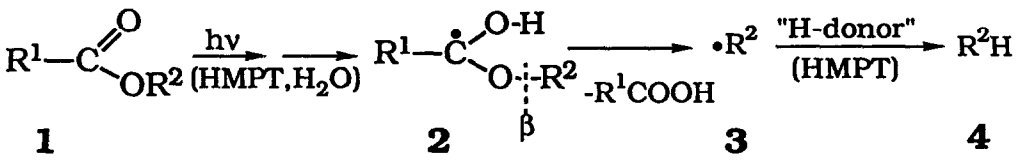
Abstract - The photodeoxygenation of sugar esters of aliphatic acids in hexamethylphosphoric triamide (HMPT) and mixtures thereof with water, is initiated by photoionization of HMPT. The solvated electron thus formed, reduces the ester to its radical anion, which is an intermediate for both the formation of the deoxy sugar and the reproduction of the corresponding alcohol. A separation of the carboxylate anion leads to a radical of the deoxy sugar which reacts further via hydrogen transfer from HMPT, the acid residue, or from other sugar molecules. The incorporation of the hydrogen atom occurs, in all cases, preferentially at the sterically less hindered side.

1. Introduction

The photochemical reduction of esters of aliphatic alcohols **1** to the corresponding deoxy compounds **4** in mixtures of HMPT and water, initially reported by Deshayes at al [1], is of interest as a synthetic method[2a-j] for the preparative carbohydrate chemistry and also as a general method of photoreduction[2k-o]. According to previous mechanistic investigations of this reaction[3,4] either the ester **1** or HMPT is excited by UV light (e.g 254 nm). The subsequent steps are formation of an exciplex which decays into the radical ion pairs: $HMPT^{+\bullet}$ and $R^1COR^{2+\bullet}$.

The latter species leads (via proton transfer) to the ketyl radical **2** which reacts (via homolytic β-cleavage) to the alkyl radical **3** which finally forms (via hydrogen abstraction) the alkane **4**. The role of hydrogen transferring agent is ascribed to HMPT[2n]. In a still unclarified side reaction, which, however, may attain a considerable yield in certain cases[2d], the alcohol (the sugar molecule) R^2-OH is reconstituted and is present in addition to the deoxy sugar



Scheme 1: R^2 = sugar residue

The reduction of carbohydrate with alkalimetals in HMPT or amines[5] is not successful for esters of simple carbohydrates[4,6]. The isolated products in the reaction of **14** and methyl-2,3-O-isopropyliden-4,6-di-O-pivaloyl-α-D-mannopyranoside with metals, either in HMPT or in amines, were the corresponding alcohols Only for the latter compound traces of deoxygenated product could be detected. None of the hitherto formulated reaction steps (scheme 1) in the photochemical reduction of esters have actually been proven on an experimental basis. In order to obtain insight in the course of the photochemical deoxygenation in HMPT and mixtures thereof with water, as well as in the side reactions, and thus create better preparative conditions, we studied a series of sugar esters, compounds **10**, **14**, **15**, **17**, **25**, **31** and **33** (formula 2).

2. Primary photochemical steps

Two transients, a short-lived and a longer-lived, were observed by laser flash photolysis (λ_{exc} = 248 nm) of pure HMPT and in mixtures thereof with water (fig. 1). The short-lived transient is assigned to the solvated electron (e^-_{sol}) since it absorbs in the red spectral range and its decay can be quenched (almost diffusion controlled) by O_2 and N_2O. The decay follows first-order kinetics and the lifetime (τ_{e^-}) depends on the water content; in the absence of water and oxygen the lifetime is approximately 100 ns under our conditions and is prolonged by addition of water, reaching a value of τ_{e^-} = 800 ns in HMPT/H_2O (50 : 50). In the latter case the transient absorption spectrum is very similar, in shape and λ_{max} (fig. 1b), to the well established spectrum[7] of e^-_{sol}. In pure HMPT, however, λ_{max} is obviously red-shifted (fig 1a) which is in agreement with the value of 2200 nm, reported elsewhere[8]. Since the transient absorbance (e.g. at 600 nm) was found to depend linearly on the incident laser intensity we conclude that the photoionization occurs via a monophotonic excitation step (rather than a consecutive or simultaneous biphotonic step) (scheme 2).

$$HMPT \xrightarrow{h\nu} HMPT^{+\bullet} + e^-_{sol}$$

Scheme 2

The remaining second transient is assigned to the radical cation of HMPT due to the following Its absorption spectrum (λ_{max} < 280 nm) lies in the UV, as often found for radical cations[9]. Secondly, it decays mainly by second-order kinetics with a minor contribution of a first-order component; the half-life under our conditions is in the 10-20 μs range. Thirdly, the half-life and the transient absorbance are not discernibly influenced by O_2 and N_2O. Fourthly, the possibility that the longer-lived transient may be assigned to a radical which is formed by a reaction with water is unlikely since the spectral (compare fig 1a and 1b) and kinetic properties are essentially independent of the water content.

The free enthalpy change for the formation of the charged species $HMPT^{+\bullet}$ and e^-_{sol} ($\triangleq HMPT^{-\bullet}$)[10] can be estimated by using scheme[11] 3 and the oxidation[10] (+1V) and reduction[12] (-3V) potential of HMPT (scheme 3).

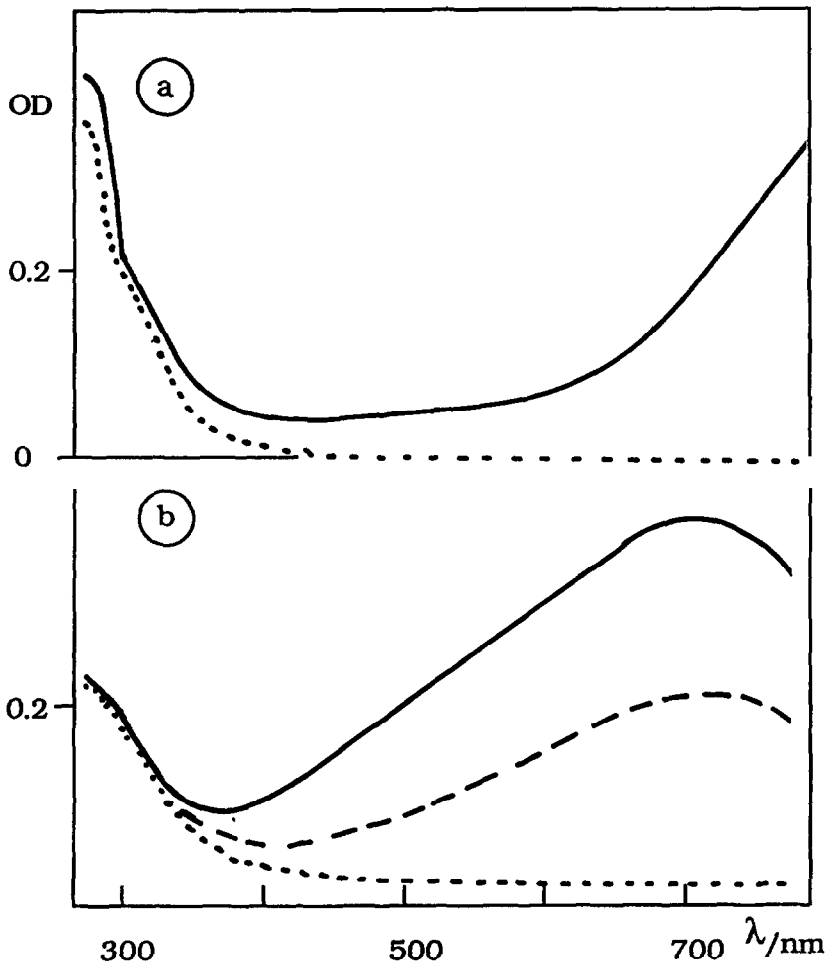


Fig. 1: Transient absorption spectrum in argon-saturated solutions of (a) pure HMPT and (b) HMPT/H_2O (50:50) at the end of the laser pulse after 20 ns (——), 500 ns (– –) and 2μs(-----)

$$\Delta G = 96.5 \bullet (E^{ox}_{1/2}/V - E^{red}_{1/2}/V) \text{ kJ/mol}$$
$$= 386 \text{ kJ/mol}$$

Scheme 3

The reaction is thus endothermic and energetically possible with light of a wavelength shorter than 310 nm The transient absorption spectrum (fig 1) is not discernibly changed by the addition of ester **14**. Notably, formation of the radical anion of the ester could not be observed This is not surprising since pulse radiolysis of **14** in argon-saturated methanol/water mixtures (1 : 99 - 10 · 90) revealed only a weak transient (λ_{max} < 230 nm, half-life >100 μs) which may be assigned to **14**$^{-\bullet}$. On the other hand, a reaction of e^-_{sol} with the ester was clearly detectable, as judged from the reduction of its lifetime in the presence of **14** Since the reciprocal lifetime of the solvated electron depends linearly on the ester concentration (fig. 2), reaction cf. scheme 4 is suggested

Equation cf scheme 2 and 4 are supported by the fact that the ester does not absorb light of λ > 240 nm The presence of

$$e^-_{sol} + \text{ester} \xrightarrow{k_4} \text{ester}^{-\bullet}$$

Scheme 4

water enhances the probability for quenching since τ_{e^-} increases with increasing water content A further effect of water is the possibility to dissolve coatings originating from photoproducts on the surface[2g]

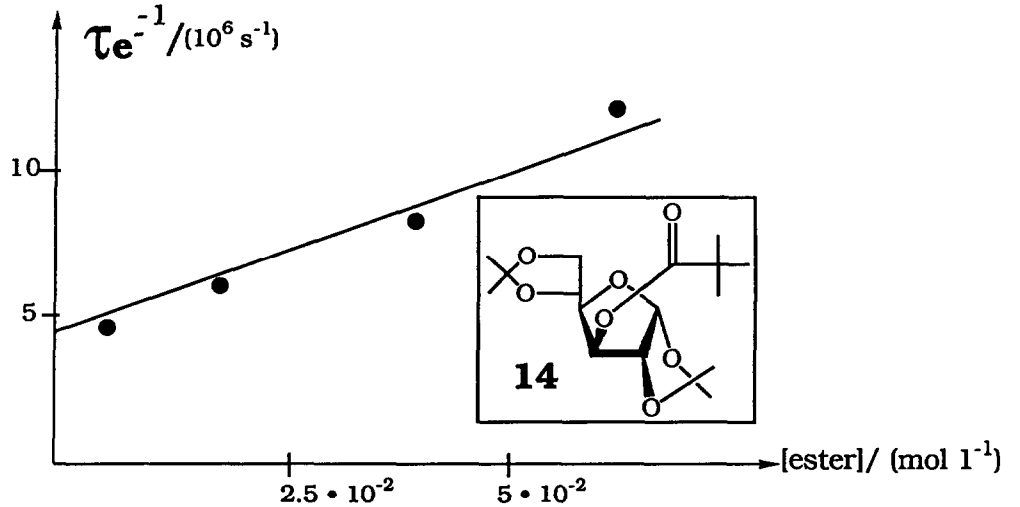


Fig. 2: Stern-Volmer plot for quenching of the solvated electron by **14** in argon saturated HMPT/H_2O (95/5)

$$1/\tau_{e^-} = \frac{1}{\tau^\circ_{e^-}} + k_4[\text{ester}]$$

The rate constant for quenching cf. fig. 2 is $k_4 = (2\pm1)\cdot10^8$ and $(2.5\pm1)\cdot10^8$ l mol^{-1}s^{-1} in HMPT/H_2O mixtures of 95 5 and 50 : 50 respectively. It lies in the range reported for comparable reactions[13] and is thus markedly below the diffusion-controlled limit. This limit is estimated to be approximately $2.5\cdot10^9$ l mol^{-1}s^{-1} in pure HPMT (using a viscosity[14] of 3.5 cP for HMPT[14] and the Debye equation[15]) and should be larger in the presence of water due to its smaller viscosity (1.0 cP). The formation of hydrogen[2n] is quenched by the applied esters, too. Stern-Volmer analysis with **14** in HMPT/H_2O . 95/5 results in $kq = (5\pm2)10^8$ l mol^{-1}s^{-1} which corresponds to k_4 of fig 2 Assuming that the quenching reaction leads solely to the radical anion of the ester, k_4 equals the rate constant for formation of the radical anion of the ester.

In order to test whether quenching of the solvated electron by the ester (scheme 4) initiates its deoxygenation, the reaction was carried out in the presence of the electron quenchers[16,17] N_2O or SF_6 ($kq = 8\ 7\cdot10^9$ or $1\ 6\cdot10^{10}$ l mol^{-1}s^{-1} resp.) with the same result . complete suppression of the formation of deoxy compound R^2H and alcohol R^2OH, as demonstrated by fig. 3 for the system **14** /N_2O In addition the formation of hydrogen[2n] is quenched

After removal of N_2O or SF_6 by flushing with N_2 the reactions continue undisturbed

From fig 3 it can also be seen that as the ester concentration rises, the absolute yield of the deoxygenated product is reduced, while that of the alcohol is increased. However, the formation of both products is quenched by N_2O

Consequently, the photodeoxygenation of esters **1** in HMPT is initiated by photoionization of the HMPT and subsequent reduction of the ester by the solvated electron

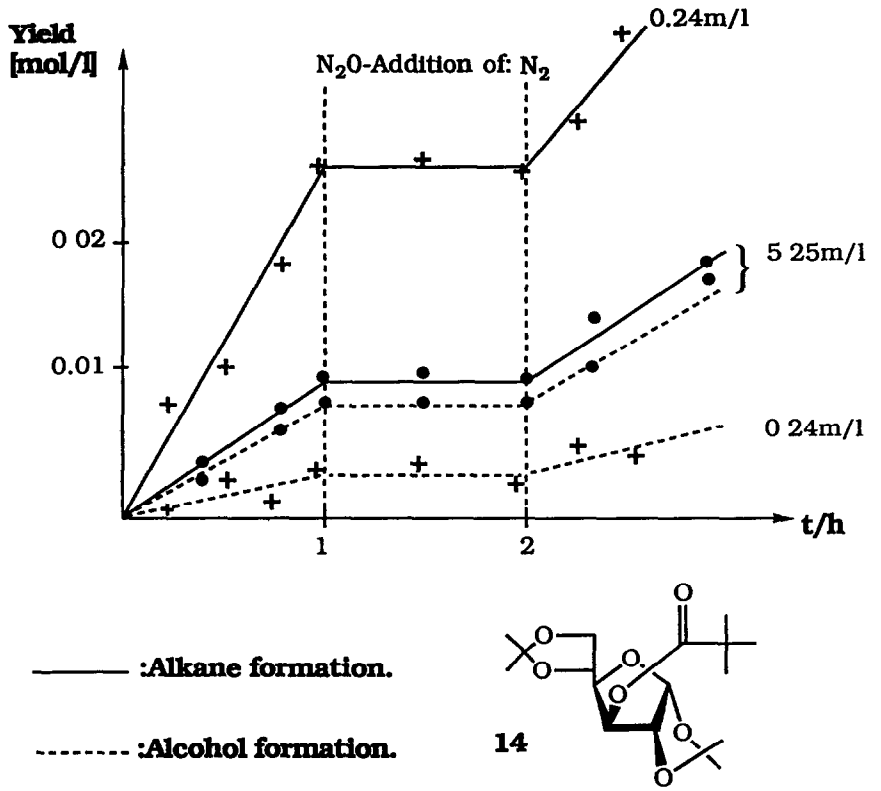


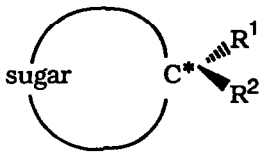
Fig. 3: Quenching of photo-deoxygenation of **14** by N_2O; 2.5ml solution of **14** in HMPT in a 1cm cuvette thermostated 18±1°C.

3. Mechanism and stereochemistry of hydrogen transfer

We prepared specifically isotopic-labelled deoxy sugars (form. 1), to examine stereochemistry and mechanism of hydrogen transfer to the intermediate-formed C-radical **3** (scheme 1).

Our finding confirmed[3] that the use of D_2O instead of H_2O (5% or 10% addition to the HMPT used) does not lead to any deuterated reduction products, not even in trace amounts, and in addition the substitution of D_2O by isopropanol-$2d_1$ to enhance deuterium transfer did not induce any detectable incorporation of deuterium ,Deoxygenation of secondary hydroxyl functions of carbohydrate derivatives (form. 1) leads to the compounds **5** which reveal no further chirality centre at the reduced position. However, the photo-reduction of type **6** esters in HMPT-d_{18} or type **7** in HMPT should result in the formation of diastereomeric deoxy sugars **8** and **9** respectively. We examined both cases

For this purpose suitable starting materials were synthesized (form 2) which were deoxygenated under uniform conditions. The reaction products were isolated and their degree of deuteration was determined, as well as their stereochemical composition. Use was made of the following test substances: ester of 1,2-5,6-di-*O*-isopropylidene-α-D-glucofuranose **10**, 1,2-5,6-di-*O*-isopropylidene-α-D-allofuranose **15** as well as its specifically deuterated derivative **17**, 1,6-anhydro-2,3-*O*-isopropylidene-β-D-mannopyranose **25** and 1,6-anhydro-2,3-*O*-isopropylidene-β-D-talo-



Formula 1

5 $R^1=R^2=H$

6 $R^1=OOCalkyl, R^2=H$

7 $R^1=OOCalkyl, R^2=D$

8 $R^1=H, R^2=D$

9 $R^1=D, R^2=H$

pyranose **31** as well as its specifically deuterated derivative **33**

The photo-reactions resulted in product mixtures which, apart from the easily separable starting sugars (**10**, **15**, **17**, **25**, **31** and **33** respectively), contained type **5**, **8** and **9** compounds in various ratios The degree of deuteration of the reaction products was determined by NMR and mass spectroscopy. GC/MS-analysis enabled determination of the total deuterium content in the molecule ion or a suitable fragment revealing largest possible mass (e g $M^+ - CH_3$) The ^1H- and ^{13}C-NMR spectra supply the degree of deuteration in the deoxygenated position C* (see form 1) as well as the ratio of the formed stereoisomers **8** and **9** The data obtained by these methods are presented in table 1

Examination of the stereochemical course of the reaction by NMR revealed that the addition of hydrogen proceeds, in all cases, from the more accessible *exo* side of the molecule Accordingly, intermediate free radicals are formed, the saturation of which is controlled by the chiral centres remaining in the molecule

Corresponding to the highly reactive character of the radical intermediates **3** (scheme 1), the diastereo selectivities observable here are not as great as in the case of nucleophilic additions to comparable prochiral carbonyl compounds

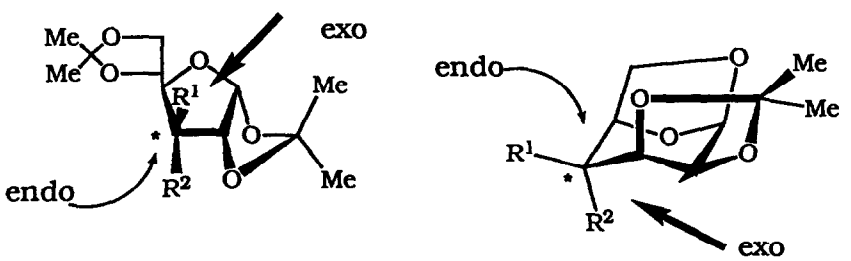
In the case of deoxygenation of derivatives, **11-14**, **16** and **18-21**, analysis of the deuterated reaction products resulted in 8 · 1 preference of the *exo* hydrogen transfer, as compared with *endo* transfer; as far as photoreduction of derivatives **26-29**, **32** and **34** as well as **35** was concerned, the ratio observed was 2 : 1 in favour of the *exo* transfer.

In these reactions neither the kind of ester employed nor the configuration of the ester group was significant as regards the chirality centre to be reduced. Similar to the reduction of xanthates with tri-n-butyltin hydride[18], likewise proceeding radically, no S_R2 mechanism is observed.

Table 1 contains the results of the deuteration experiments with respect to the degree of deuteration of the isolated products. Here it is remarkable that, when employing HMPT-d_{18}/D_2O larger proportions of the non-deuterated deoxy sugar were formed (refer to N°1-4, 9, 10-13 and 19). This suggests that hydrogen transfer does not take place only through HMPT as has previously been assumed[2m], but that other hydrogen donors play a part in the process In order to verify this assumption a check was carried out to exclude an unusually high isotopic effect responsible for this result For this purpose, deoxygenation in HMPT-d_{18} (99% deuterium content cf. experiment 12) /D_2O was carried out with an addition of non-deuterated HMPT (experiment 15, table 1). It was revealed that, although a significant reduction of the deuterated product was observed as compared with experiment 12, the expected HH-proportion (approx 100% by six-fold hydrogen content) was not attained

Experiments 1-4 and 10-13 reveal that there is evidently some relation between the acid group of the starting material used and the observed quantity of non-deuterated product. As branching increases in the α-position, the proportion of non-deuterated reaction product tends to increase, attaining a maximum in the case of isobutyrates **13** and **28** and re-

N°	R^1	R^2	N°	R^1	R^2
10	OH	H	**25**	H	OH
11	OCOMe	H	**26**	H	OCOMe
12	OCOEt	H	**27**	H	OCOEt
13	$OCOCHMe_2$	H	**28**	H	$OCOCHMe_2$
14	$OCOCMe_3$	H	**29**	H	$OCOCMe_3$
15	H	OH	**30**	H	$OCOCD_3$
16	H	$OCOCMe_3$	**31**	OH	H
17	D	OH	**32**	OCOMe	H
18	D	OCOMe	**33**	OH	D
19	D	OCOEt	**34**	OCOMe	D
20	D	$OCOCHMe_2$	**35**	$OCOCMe_3$	D
21	D	$OCOCMe_3$	**36**	H	H
22	H	H	**37**	D	H
23	D	H	**38**	H	D
24	H	D			



Formula 2. Compounds used for the deuterium labeling experiments,
1,2-5,6-di-O-isopropylidene- α-D-glucofuranose **10** and derivatives **11-14**,
1,2-5,6-di-*O*-isopropylidene-α-D-allofuranose **15** and derivatives **16-21**,
3-deoxy-1,2-5,6-di-*O*-isopropylidene- α-D-allofuranose **15** and derivatives **23-24**,
1,6-anhydro-2,3-*O*-isopropylidene- β-D-mannopyranose **25** and derivatives **26-30**,
1,6-anhydro-2,3-*O*-isopropylidene- β-D-talopyranose **31** and derivatives **32-35**,
1,6-anhydro-4-deoxy-2,3-*O*-isopropylidene- β-D-lyxo-hexopyranose **36** and derivatives **37-38**.

turning to a lower value for the pivaloyl esters **14**, **16**, **29** and **35**. The only explanation for these findings is, that the carboxylic acid portion of the ester group partly contributes to saturation of the radical intermediate **3** with hydrogen For clarification, 4-*O*-acetyl-d_3-1,6-anhydro-2,3-*O*-isopropylidene-D-mannopyranose **30** was deoxygenated in HMPT/H_2O (Table 1, experiment 14) and HMPT-d_{18}/D_2O (experiment 16). In the former case no incorporated deuterium could be detected in the reaction product; surprisingly, in the latter instance too, a high percentage (23.4%) of non-deuterated deoxy sugar was discovered to have been formed. From this it may be concluded that, on the one hand, the acetate group is not capable of transferring hydrogen at all or only to a subordinate extent. On the other hand, a third source of hydrogen enters into discussion.

Table 1: Results of deuteration experiments of 3-deoxy-1,2-5,6-di-*O*-isopropylidene-D-ribo-hexofuranose **22-24** as a function of starting esters **11-14, 16** and **20-21** and solvent, as well as of 1,6-anhydro-4-deoxy-2,3-*O*-isopropylidene- β-D-lyxo-hexopyranose **36-38**, starting with the esters **26-30, 32** and **34-35.**

N°	Starting Material	Solvent[b]	MS [%]			NMR[a] [%]	
			HH	HD	DD	HH	HD
1	**11**	A	25.2	74.4	0.4	25	75
2	**12**	A	27 5	72.1	0 4	24	76
3	**13**	A	32.5	67.3	0 2	33	67
4	**14**	A	28.4	71.3	0.3	27	73
5	**18**	B	2.7	97.3	--	2	98
6	**19**	B	2.9	97.1	--	2	98
7	**20**	B	3.0	97.0	--	2	98
8	**21**	B	2.9	97.1	--	2	98
9	**16**	A	c	c	c	27	73
10	**26**	A	27.6	69.3	3.1	c	c
11	**27**	A	35.9	62.4	1 7	39	61
12	**28**	A	41.2	56.9	1.9	45	55
13	**29**	A	31.6	66.1	2.3	37	63
14	**30**	B	100.0	--	--	100	--
15	**28**	C	51.7	45.6	2.7	57	43
16	**30**	A	23.4	70.1	6.5	22	78
17	**34**	B	2.4	97.6	--	2	98
18	**35**	B	2.3	97.7	--	2	98
19	**32**	A		c		37	63

[a] neglection of DD-fraction

[b] A· HMPT-d_{18}/D_2O (95 : 5)

B HMPT/H_2O (95 : 5)

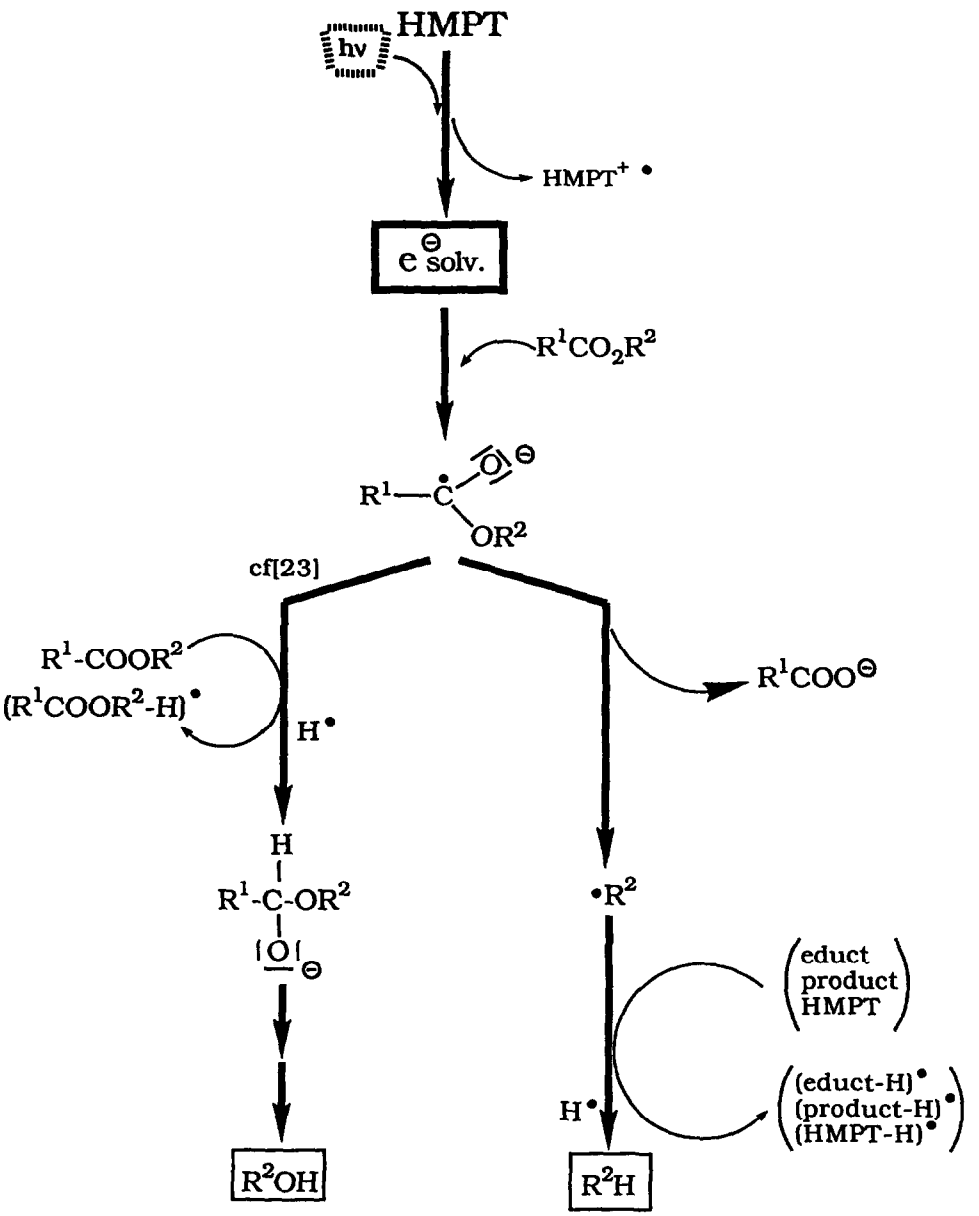
C: HMPT-d_{18}/HMPT/D_2O (90 : 5 : 5)

[c] not measured

A radical chain reaction is active, in which case product molecules are capable once more of releasing a proton or deuteron, and is responsible for a deuterium loss of 2.3% in experiments 5-8 and 17-18 as well as for the presence of 2-3% of dideuterated product in experiments 10-13.

4. Discussion of mechanism

The results so far obtained can be summarized in scheme 5. Primary step is the ester reduction to the radical anion induced by solvated electrons. This is also confirmed by observation of the same products via comparable electrochemical reactions in DMF[19] vs ^{2p}. Formation of hydrogen is a competing reaction, most probably involving HMPT, water, starting material and products[20], particulary since HD . H_2 : D_2 (86 : 13 : 1) is observed after replacing H_2O by D_2O,



Scheme: 5 R^2 = sugar residue

HMPT/D_2O (95 : 5). Alkali metals can retard the action of solvated electrons by association[21].

To examine whether the formation of the alcohol is also induced by light absorption and subsequent α-cleavage of the ester, which was observed only with formiates[22], **12** and **14** were irradiated with 254 nm in n-hexane, diethyl ether, and

acetonitrile. In this case, no deoxygenated product 4 but only the alcohol was observed. Also, quenching by N_2O or SF_6 cf. fig. 3 was not possible. Consequently, in HMPT the formation of the alcohol 5 is undoubtedly induced by ester radical anion formation, as well.The formation of the carboxylate ion was proved by observation (^{1}H-NMR) of the carboxylic acid R^1COOH after irradation in HMPT-d_{18} The fragment (HMPT-H)$^\bullet$ was verified by detection of corresponding byproducts[2g].

The inverse concentration dependence of the observed yield of alkane and alcohol (cf. fig. 3) indicates, that the primarily formed radical anion 2 can be reduced by hydrogen capture from the ester 1 to form the alcohol in a two step mechanism. A similar effect was observed by Barton[23] for the reaction of O-alkyl thioesters with tributylstannane

The results of experiments presented clearly show that hydrogen transfer proceeds on a more complex path than has hitherto been assumed[2m,n,3]. HMPT is only one of the possible H-donors saturating the intermediately formed alkyl radical. Moreover, the acid residue is capable of providing hydrogen as a function of branching degree in α-position. Consequently, this effect is least marked in the case of acetate, while being most intensely pronounced with isobutyrate. Added to this is the H-transfer from product or educt molecules proceeding via radical chain reactions

These results limit the utilization of the HMPT-d_{18}/D_2O system for the photochemical synthesis of isotopic-labelled deoxy sugars.

Experimental

The laser flash photolysis set-up was the same as described elsewhere[24,25]. Briefly, for excitation an excimer laser (Lambda Physik, type EMG 200) was used; pulse width 20 ns, energy 20-500mJ, reduced by appropriate quartz plates or wire mesh filters. The analysing beam passed through the 1 cm quartz sample cell and was detected by a photomultiplier (Hamamatsu R 955) behind a monochromator. Data aquisition and analysis was carried out with a transient digitizer (Tektronix, R 7912) and a computer (PDP 11/04). Melting points were measured by a Büchi Model 510 apparatus and are not corrected. Optical rotation values were determined by a polarimeter Model 241, Perkin Elmer, (d = 10 cm). Gas chromatography was carried out by Fractovap 2101 (Carlo Erba) with capillary column SE 52 Permabend (20m/0.3 mm) and T = 93°C (column, isothermal) and 240° C (injector). Chromatographic columns for preparative separations were filled with silica gel (Woelm 100-200) and eluted with benzene/acetic ester (5 : 2 to 10 : 1). MS spectra were measured by Finegan MAT 212 (70eV, .5mA, 200°C) under MS/GC-coupling with Varian GC 3900. NMR spectra were measured by Varian T 60, 60 MHz (^{1}H); Varian EM 390, 90 MHz (^{1}H); Bruker WH 270, 270 MHz (^{1}H); Varian CFT 20, 20 MHz (^{13}C). TMS was used as internal standard Formation of hydrogen (H_2,HD,D_2) was proven by gas chromatography cf.[26]: F + M Dual 720; T = 50°C; column = 3 m molecular sieve 5 Å; thermal conductivity detector; carrier gas. helium. Quenching of hydrogen formation was determined volumetrically via a burette assuming a constant fraction of H_2 in the gas formed. Hexamethylphosphoric triamide (HMPT), Ega H 1, 160-2, was dried[27] via CaH_2, distilled (CaH_2/.01 mmHg), and kept dry by 4Å molecular sieve. (bp 230^2-32°C/740 mmHg).

General acylation procedure for 10, 15, 17, lit.[28], 25, 31 and 33, lit.[29]. - 12.5 mol of the acylation agent is added dropwise to a stirred solution of 5.0 mmol of the educt and 0.06 g of 4-dimethylaminopyridine in 17.5 ml pyridine. The reaction mixture is warmed up to 60°C and cooled down after complete conversion. The major part of pyridine is re-

moved under reduced pressure (1 mm Hg); the residue is solvated in 30 ml dichloromethane. After a washing of sequence (10% H_2SO_4/water/saturated solution of bicarbonate/water) the sample is dried over dehydrated sodium sulfate. The solvent is distilled off and the residue is purified by recrystallization or by column chromatography.

3-O-Acetyl-1,2-5,6-di-O-isopropylidene-α-D-glucofuranose **(11)**. - Yield: 81%, m.p 64°C. - ^{1}H-NMR ($CDCl_3$). δ 1.30 (s, 6H, CH_3), 1.43 (s, 3H, CH_3), 1.56 (s, 3H, CH_3), 5.90 (d, 1H, H-1), 4 53 (d, 1H, H-2), 5 30 (s, 1H, H-3), 4 0 - 4 3 (m, 4H, H-4, -7), 2.10 (s, 3H, CH_3-acetyl) - ^{13}C-NMR ($CDCl_3$): δ 105.07 (C-1), 72.50, 76.07, 79 72, 83.37 (C-2, -5), 67 09 (C-6), 109.10, 112.10 (O-C-O), 25.26, 26.18, 26.72, 26 80 (4 x CH_3), 25 23 (CH_3-acetyl), 169.33 (CO_2) - calcd for $C_{14}H_{22}O_7$ (302 32): C, 55.62; H, 7.34 Found: C, 55 52; H, 7.31 %.

1,2-5,6-di-O-isopropylidene-3-O-propionyl-α-D-glucofuranose **(12)** - Yield: 75%, m p. 50°C - ^{1}H-NMR ($CDCl_3$) δ 1.33 (s, 6H, CH_3), 1.43 (s, 3H, CH_3), 1.56 (s, 3H, CH_3), 5 90 (d, 1H, H- 1), 4.50 (d, 1H, H-2), 5.30 (s, 1H, H-3), 3.9 - 4.4 (m, 4H, H-4, -7), 1.20 (t, 3H, CH_3), 2.40 (q, 2H, CH_2). - ^{13}C-NMR ($CDCl_3$)· δ 105.15 (C-1), 72.55, 75.93, 79 92, 83 48 (C-2, -5), 67.28 (C-6), 109.26, 112.19 (O-C-O), 25.29, 26.23, 26.78, 26.84 (4 x CH_3), 9.02 (CH_3), 27.52 (CH_2), 172.84 (CO_2). - calcd for $C_{15}H_{24}O_7$ (316.10): C, 56.94; H, 7.65. Found: C, 56.98; H, 7.49 %.

1,2-5,6-di-O-isopropylidene-3-O-(2-methyl-propionyl)-D-glucofuranose **(13)**. - Yield: 83%, m.p. 48°C -. ^{1}H-NMR ($CDCl_3$). δ 1.26 (s, 6H, CH_3), 1.36 (s, 3H, CH_3), 1.50 (s, 3H, CH_3), 5,86 (d, 1H, H- 1), 4.43 (d, 1H, H-2), 5 26 (s, 1H, H-3), 3 9 - 4.4 (m, 4H, H-4, -7), 1.15 (d, 6H, CH_3), 2.50 (m, 1H, CH). - ^{13}C-NMR ($CDCl_3$): δ 105.21 (C-1), 72 50, 75 77, 80.19, 83.53 (C-2, -5), 67.51 (C-6), 109.21, 112.14 (O-C-O), 25.27, 26.25, 26.80 (2x) (4 x CH_3), 18.74, 18.93 (CH_3), 34.02 (CH), 175.28 (CO_2) - calcd for $C_{16}H_{26}O_7$ (330.17): C, 58.17; H, 7.94. Found· C, 58.17; H, 7 93 %.

1,2-5,6-di-O-isopropylidene-3-O-pivaloyl-α-D-glucofuranose **(14)**. - Yield: 77%, m.p. 43°C. - ^{1}H-NMR ($CDCl_3$). δ 1.36 (s, 6H, CH_3), 1.43 (s, 3H, CH_3), 1.53 (s, 3H, CH_3), 5,90(d, 1H, H- 1), 4.43 (d, 1H, H-2), 5.30 (s, 1H, H-3), 3.9 - 4 3 (m, 4H, H-4, -7), 1.25 (s, 9H, CH_3). - ^{13}C-NMR ($CDCl_3$): δ 105.21 (C-1), 72.49, 75.85, 80.35, 83.49 (C-2, -5), 67.71 (C-6), 109.21, 112.19 (O-C-O), 25.24, 26.24, 26.78, 26.83 (4 x CH_3), 27.03 (CH_3), 38 95 (C), 176.64 (CO_2)

1,2-5,6-di-O-isopropylidene-3-O-pivaloyl-α-D- allofuranose **(16)**. - Yield: 93%, m.p. 44 - 45°C, $[\alpha]_D^{24.5}$ + 113 1° (c = 1, chloroform). ^{1}H-NMR ($CDCl_3$): δ 1.23 (s, 9H, tBu, pivaloyl), 1.32 (s, 3H, CH_3, isopropylidene), 1.35 (s, 3H, CH_3, isopropylidene), 1.42 (s, 3H, CH_3, isopropylidene), 1.52 (s, 3H, CH_3, isopropylidene), 3.89 (dd, 1H, H-6), 4.09 (dd, 1H, H-6), 4.14 (dd, 1H, H-4), 4.74 (dd, 1H, H-3), 4 86 (dd, 1H, H-2), 5.83 (d, 1H, H-1), $J_{1,2}$ = 4.0 Hz, $J_{2,3}$ = 5.2 Hz, $J_{3,4}$ = 8 2 Hz, $J_{4,5}$ = 4 0 Hz, $J_{5,6}$ = 6.6 Hz, $J_{5,6'}$ = 6.0 Hz, $J_{6',6'}$ = -8 0 Hz. - calcd for $C_{17}H_{26}O_7$ (344.4). C, 59 28, H, 8 20 Found. C, 59.07; H, 8.14 %.

3-O-Acetyl-1,2-5,6-di-O-isopropylidene-α-D-[3-D_1]-allofuranose **(18)**. - Yield: 95%, m.p. 74 5 - 75.5°C - calcd for $C_{14}H_{21}DO_7$ (303.3)· C, 55.43; H/D, 6.96. Found: C, 55.17; H/D, 6.84 %.

1,2-5,6-di-O-isopropylidene-3-O-propionyl-α-D-[3-D_1]-allofuranose **(19)**. - Yield· 97%, m.p. 65 - 65.5°C. - calcd for $C_{15}H_{23}DO_7$ (317.3). C, 56 77; H/D, 7.31. Found: C, 56.57; H/D, 7.47 %

1,2-5,6-di-O-isopropylidene-3-O-(2-methyl-propionyl)-α-D-[3-D_1]-allofuranose **(20)**. - Yield: 98%, m.p. 37°C. -

calcd for $C_{16}H_{25}DO_7$ (331.4): C, 57.99; H/D, 7.60. Found: C, 58.12; H/D, 7.79 %.

1,2-5,6-di-O-isopropylidene-3-O-pivaloyl-α-D-[3-D_1]-allofuranose **(21).** - Yield: 93%, m.p. 44 - 45°C. - calcd for $C_{17}H_{27}DO_7$ (345.4): C, 59.11; H/D, 8.46. Found: C, 59.33; H/D, 8 26 %

4-O-Acetyl-1,6-anhydro-2,3-O-isopropylidene-β-D-mannopyranose **(26)** - Yield: 91%, lit.[30], **30** (lit[31]).

1,6-Anhydro-2,3-O-isopropylidene-4-O-propionyl-β-D-mannopyranose **(27).** - Yield· 88%, m.p. 100.5 - 101.5°C, $[\alpha]_D^{22.5}$ - 72.5° (c = 1, $CHCl_3$). - ^{1}H-NMR ($CDCl_3$): δ 1.2 (t, 3H, CH_3, propionyl), 1.35 + 1 60 (2s, 6H, $2CH_3$, isopropylidene), 2.4 (q, 2H, CH_2, propionyl), 4.1 - 3.6 (m, 4H, H-2, -3, -6, -6'), 4.6 (ddd, 1H, H-5), 5.05 (m, 1H, H-4), 5.4 (m, 1H, H-1). - calcd for $C_{12}H_{18}O_6$ (258.3): C, 55.81; H, 7.02 Found. C, 55.91; H, 7.28 %.

1,6-Anhydro-2,3-O-isopropylidene-4-O-(2-methyl-propionyl)-β-D-mannopyranose **(28).** - Yield: 71%, m.p 107.0 - 107.5°C, $[\alpha]_D^{25}$ - 72.5° (c = 1, $CHCl_3$). - ^{1}H-NMR ($CDCl_3$): δ 1.23 (d, 6H, $2CH_3$, i-butyryl), 1.35 + 1.60 (2s, 6H, $2CH_3$, isopropylidene), 2.4 - 2.9 (hp, 1H, CH, i-butyryl), 3.6 - 4.2 (m, 4H, H-2, -3, -6, -6'), 4.4 - 4.6 (m, 1H, H-5), 5.0 (m, 1H, H-4), 5.4 (m, 1H, H-1). - calcd for $C_{13}H_{20}O_6$ (272 3): C, 57.34; H, 7.40. Found: C, 57.56; H, 7 55 %.

1,6-Anhydro-2,3-O-isopropylidene-4-O-pivaloyl-β-D-mannopyranose **(29).** - Yield· 85%, m.p. 106 - 106 5°C, $[\alpha]_D^{26}$ - 69.0° (c = 1, $CHCl_3$). - ^{1}H-NMR ($CDCl_3$): δ 1.16 (s, 9H,But, pivaloyl), 1.19 + 1.59 (2s, 6H, $2CH_3$, isopropylidene), 3.37 (dd, 1H, 6 *exo*-H), 3.79 (dd, 1H, 6 *endo*-H), 3.91 (dd, 1H, H-2) 4.10 (dm, 1H, H-3), 4.20 (dm, 1H, H-5), 5.02 (m, 1H, H-4), 5.36 (m, 1H, H-1), $J_{1,2}$=3.0 Hz, $J_{1,3}$=1.2 Hz, $J_{1,4}$=0.5 Hz, $J_{2,3}$=6 2 Hz, $J_{3,4}$=0 8 Hz, $J_{4,5}$ = 1 3 Hz, $J_{5\,6endo}$ = 1.2 Hz, $J_{5\,6exo}$ = 6.3 Hz, $J_{6endo,6exo}$ = 7.3 Hz. - calcd for $C_{14}H_{22}O_6$ (286.3) : C, 58.73, H, 7.75. Found· C, 58.79; H, 7.95 %.

1,6-Anhydro-2,3-O-isopropylidene-4-O-pivaloyl-β-D-talopyranose **(32).** - Yield: 86%, m.p. 92-93°C, $[\alpha]_D^{26}$ - 85 4° (c=1, $CHCl_3$). - ^{1}H-NMR ($CDCl_3$): δ 1.23 (s, 9H,But, pivaloyl); 1.28+1 56 (2s, 6H, $2CH_3$, isopropylidene), 3.70 (dd, 1H, 6 *exo*-H), 4.05 (dd, 1H, H-2), 4.35 (dd, 1H, 6 *endo*-H) 4.41 (t, 1H, H-5), 4.65 (t, 1H, H-3), 5 04 (t, 1H, H-4), 5 30 (dm, 1H, H-1), $J_{1,2}$=3.0 Hz, $J_{1,3}$=1.0 Hz, $J_{2,3}$=5.8 Hz, $J_{3,4}$=5.4 Hz, $J_{4,5}$=5.4 Hz, $J_{5\,6endo}$=1.0 Hz, $J_{5\,6exo}$=5.4 Hz, $J_{6endo,6exo}$ = - 6.9Hz. - calcd for $C_{14}H_{22}O_6$ (286.3): C, 58.73; H, 7.75. Found: C, 58.79; H, 7.92 %.

4-0-Acetyl-1,6-anhydro-2.3-O-isopropylidene-β-D-[4-D_1]-talopyranose **(35).** - Yield: 96%, m.p. 118 - 119°C, $[\alpha]_D^{25}$ -86.0°(c=1, $CHCl_3$). - calcd for $C_{11}H_{15}DO_6$ (295.3)· C, 53.87; H/D, 6.99. Found: C, 53 77; H/D, 6 84 %, lit.[32]

Deoxy sugars

In all cases 0.23 mmol of the corresponding starting material was solvated in HMPT/H_2O (95 : 5, v/v) or in HMPT-d_{18}/D_2O (95: 5, v/v) ad 1.0 ml. In the case of experiment 15, 5% HMPT was added to HMPT-d_{18}. The solutions were filled into quartz tubes, degassed by N_2, and irradiated in a Gräntzel reactor[33]. After 36 h the reaction was stopped, and the products were separated by a chromatographic column (silica gel, acetic ester/n-hexane 1 : 1 v/v). The obtained fractions were directly analyzed by GC/MS and/or ^{1}H- and ^{13}C-NMR.

3-Deoxy-1.2-5,6-di-O-isopropylidene-D-ribo-hexofuranose **(22)** - sirup. - $[\alpha]_D^{22}$ - 2 5° (c = 1.2, $CHCl_3$), lit [28] - 2 75 ($CHCl_3$). - ^{1}H-NMR ($CDCl_3$): δ 1.28, 1.31, 1 38, 1.46 (4s, 12H, $4CH_3$, 2 isopropylidene), 1 74 (ddd, 1H, H-3a), 2 21

(ddd, 1H, 1H, H-3b), 3.81 (m, 1H, H-5), 3.9 - 4.3 (m, 3H, H-4, -6, -6'), 4.70 (m, 1H, H-2), 5.77 (d, 1H, H-1), $J_{1,2}$ = 3 8 Hz, $J_{2,3a}$ = 4.8 Hz, $J_{2,3b}$ = 0.5 Hz, $J_{3a,3b}$ = - 14.0 Hz, $J_{3a,4}$ = 9.8 Hz, $J_{3b,4}$ = 3.9 Hz. - ^{13}C-NMR ($CDCl_3$): δ 25.23, 26.19, 26 25, 26.83 ($4CH_3$, isopropylidene), 35.44 (C-3), 67.28 (C-6), 77.00, 78 75, 80.51 (C-2, -4, -5), 105.70 (C-1), 109 66 + 111.36 (2-O-C-O, isopropylidene) - calcd for $C_{12}H_{20}O_5$ (244 3): C, 59.00; H, 8.25. Found· C, 59.12; H, 8 15 %

1,6-Anhydro-4-deoxy-2,3-O-isopropylidene-β-D-lyxo-hexopyranose **(36).** - m.p. 127 -128°C, lit.[34], 126°C, $[\alpha]_D^{26}$ - 20 2° (c = 1, $CHCl_3$), lit.[34] -22 ± 2° ($CHCl_3$). - ^{1}H-NMR ($CDCl_3$): δ 1 32 + 1.55 (2s, 6H, $2CH_3$, isopropylidene), 2 06 (dm, 1H, H- 4eq), 2 28 (ddd, 1H, H-4_{ax}), 3.71 (t, 1H, H- 6 *exo*) 3.94 (dd, 1H, H-2), 4.04 (dd, 1H, H-6*endo*), 4 34 (tm, 1H, H-3), 4.47 (tm, 1H, H-5), 5.31 (dm, 1H, H-1), $J_{1,2}$ = 2 8 Hz, $J_{1,3}$ = 1.0 Hz, $J_{1,6exo}$ = 0.5 Hz, $J_{2,3}$ = 5 9 Hz, $J_{3,4ax}$ = 5 3 Hz, $J_{3,4eq}$ = 2.0 Hz, $J_{4ax,4eq}$ = - 15 1 Hz, $J_{4ax,5}$ = 4.8 Hz, $J_{5\ 6endo}$ = 1.3 Hz, $J_{6endo,6exo}$ = - 6 5Hz - ^{13}C-NMR ($CDCl_3$) δ 25 91 + 26.02 ($2CH_3$, isopropylidene), 31.98 (C-4), 67.48 (C-6), 70.29, 70 54, 73.87 (C-2, -3, -5), 99.53 (C-1), 109 75 (O-C-O, isopropylidene). - calcd for $C_9H_{14}O_4$ (186 2). C, 58.05; H, 7.58 Found· C, 58.02, H, 7 54 %.

The primary fragmentation in the mass spectra of the acetonides **22-24** and **36-38** (table 1) is clearly the loss of a methyl group while forming a highly stabilized oxonium ion. Provided that spectrometer and data system are adjusted for reproducing accurate peak intensities, the deuterium content can be determined from the intensities of these oxonium ions mass peaks. The photodeoxygenated products were purified and examined by GC-MS, monitoring about 5 to 10 mass spectra across the product GC peak. The intensities of the relevant mass peaks are integrated across the GC peak and corrected for the ^{13}C-content. Scrambling could be excluded as followed from blind experiments.

From the ^{13}C-NMR spectra of the acetonide **22-24** and **36-38** (table 1), the deuterium content can be determined in two ways, provided that peak heights and integrals can be determined accurately. Therefore the digital resolution of the spectra was increased using threefold zero filling Both methods, however, only reveal the ratio of CHD/CHH. For one thing one observes for the monodeuterated carbon atom a triplet that is clearly separated from the singulet of the CH_2 group because of the deuterium isotope shift and the carbon deuterium coupling $^1J_{CD}$. The deuterium content can be calculated from the ratio of the intensities of the former CH_2-signal and a second CH_2-signal which appears equally intensive in the spectrum of the fully protonated species, and which does not reveal any carbon deuterium long range coupling. For another one observes, due to the β deuterium isotope shift, separate signals for the carbon atom signal next to the deuterated carbon atom and for the signal of this carbon atom in the protonated molecule. An integration of both signals yields the ratio CHD/CHH

The ^{1}H-NMR spectra offer likewise two different methods to determine the ratio of **23-24** on the one hand and of **37/38** on the other. For compound **22** one observes in an proton H-1 decoupled ^{1}H-NMR spectrum for proton H-2 a doublet of doublets. The partially deuterated molecule yields, under these conditions, a more complicated spectrum With a spin simulation program it is possible to determine the relative amounts of the three sub spectra of **22-24** and thus of the relative amounts of **22-24**. The ^{1}H-NMR spectrum of **36** reveals an ABXY pattern, AB bring protons H_4 and H_4' (R1, R_2 in formula 2) and XY being H_3 and H_5, from which the chemical shifts of proton R_1 are proton R_2 can be determined Again the ^{1}H-NMR spectrum of the mixture of **36-38** reveals the sum of the three spectra in which the signals of proton R2 in **37** and R1 in **38** are shifted due to the deuterium isotope shift. Accurate integration of these spectra delivers the relative amounts of **36, 37** and **38.**

References

1. H. Deshayes, J.P. Pete, C. Portella, D. Scholler, *J. Chem.. Soc. Chem. Comm* **1975**, 439.
2. a) P.M. Collins, V.R. Munasinghe, *J. Chem. Soc. Chem. Comm.* **1977**, 927.
   b) J.P. Pete, C. Portella, C. Monneret, J.C. Florent, Q. Khuong-Huu, *Synthesis* **1977**, 774.
   c) T. Tsuchiya, F. Nakamura, S. Umezawa, *Tetrahedron Lett* **1979**, 2805.
   d) R. Bonjouklian, B. Ganem, *Carbohydr. Res* **1979**, *76*, 245.
   e) T. Kishi, T. Tsuchiya, S. Umezawa, *Bull. Chem Soc. Jpn* **1979**, 3015.
   f) J. Thiem, B. Meyer, *Chem. Ber* **1980**, *113*, 3058.
   g) A. Klausener, J. Runsink, E. Müller, H.-D. Scharf, *Carbohydr Res.* **1983**, *116*, 295
   h) A. Klausener, J. Runsink, H.-D. Scharf, *Liebigs Ann. Chem.* **1984**, 793
   i) R.W. Binkley, *Adv Carbohydr Chem. and Biochem.* **1982**, *38*, 105.
   j) W. Hartwig, *Tetrahedron* **1983**, *39*, 2609 and cited literature.
   k) C. Portella, *Ann Chim.* Fr. **1984**, *9*, 689.
   l) C Portella, J.P. Pete, *Tetrahedron Lett.* **1985**, *26*, 211.
   m) J.P Pete, C. Portella, *Xth IUPAC Symposium on Photochemistry p* 269, Press Pol. Romandes **1984**.
   n) C. Portella, H. Deshayes, J.P. Pete, D. Scholler, *Tetrahedron* **1984**, *40*, 3635.
   o) J.P. Pete, C. Portella, *Bull. Soc. Chim Fr* **1985**, *2*, 195.
   p) D. Belotti, J. Cossy, J.P. Pete, C. Portella, *J. Org Chem* **1986**, *51*, 4196
   q) J. Cossy, D. Belotti, J.P. Pete, *Tetrahedron Lett* **1987**, *28*, 5547
3. H. Deshayes, J.P. Pete, C. Portella, *Tetrahedron Lett* **1976**, 2019.
4. Y.A. Dembele, H. Deshayes, J.P. Pete, *Tetrahedron Lett.* **1982**, 3489.
5. a) H. Deshayes, J.P. Pete, *J Chem , Soc Chem. Comm.* **1978**, 567.
   b) A.G.M. Barrett, P.A. Prokopiou, D.H.R. Barton, *J. Chem., Soc Chem. Comm* **1979**, *1173 and 1175*.
   c) R.B. Boar, L. Joukhadar, J.F. McGhie, S.C. Misra, A.G.M. Barrett, D.H.R. Barton, P.A. Prokopiou, *J. Chem , Soc Chem. Comm* **1978**, 68.
6. K. Kobayashi, H. Sumitomo, *Carbohydr. Res.* **1983**, *115*, 243.
7. J.P. Keene, *Radiat. Res.* **1964**, *1*, 22.
8. E A. Shaede, L.M. Dorfman, G.J. Flynn, D.C. Walker, *Can. J. Chem.* **1973**, *51*, 3905.
9. A.M. Koulkes-Pujo, L. Gilles, B. Lesigne, J. Sutton, J.Y. Gal, *J. Chem., Soc Chem. Comm* **1971**, 71
10. L. Eberson, N. Nyberg, *Adv. Phys. Org. Chem.* **1976**, *12*, 12.
11. D. Rehm, A. Weller, *Isr. J. Chem* **1970**, *8*, 259.
12. S.E. Zabusove, M.G. Fomicheva, L.I. Krishtalik, *Elektrokhimiya* **1985**, *11*, 1888
13. a) M. Anbar. E.J. Hart, *J. Phys Chem.* **1967**, *71*, 3700.
    b) G. Köhler, S. Solar, N. Getoff, A.R. Holzwarth, K. Schaffner, *J Photochem* **1985**, *28*, 383.
    c) A.N. Asaad, P. Krebs, *Chem. Phys Lett* **1987**, *137*, 553.
14. S.L. Murov, *Handbook of Photochemistry*, Dekker, New-York, **1973**.
15. N.J. Turro, *Modern Molecular Photochemistry*, The Benjamin/Cummings Publishing Co., Inc., **1978**.
16. A.M. Koulkes-Pujo, B.D. Michael, E.J. Hart, *Int J Radiat Phys. Chem* **1971**, *3*, 333
17. M Crawford, R. Rumfeldt, *Can. J Chem* **1971**, *49*, 3336.
18. a) J.J Patroni, R.V. Stick, *J. Chem , Soc. Chem. Comm* **1978**, 449.
    b) J.J. Patroni, R.V. Stick, *Aust. J. Chem* **1979**, *32*, 411.
    c) T.S Fuller, R.V. Stick, *Aust. J. Chem* **1980**, *33*, 2509.
19. J.E. Swartz, T.J. Mahachi, E. Kariv-Miller, *J. Am. Chem. Soc.* **1988**, *110*, 3622.
20. K Eiben, *Angew Chem.* **1970**, *82*, 65; *Angew Chem Int. Ed Engl.* **1970**, 9 .
21. N M Alpatova, L I Krishtalik, Y.V. Pleskov, *Top Curr Chem.* **1987**, *138*, 149.
22. J.D. Coyle, *Chem. Rev* **1978**, *78*, 97, and cited literature.
23. D.H.R. Barton, St.W. McCombie, *J.C.S Perkin I* **1975**, 1574.
24. H Görner, *J. Phys. Chem.* **1982**, *86*, 2028, *Photochem* **1980**, *13*, 269.
25. H. Görner, *J. Phys Chem* **1985**, *89*, 4112.
26. H. Russel, G. Tölg, *Top Curr. Chem.* **1972**, *33*, 1.
27. D.R. Burfield, R.H. Smithers, *J. Org Chem.* **1978**, *43*, 3966.
28. C.R. Haylock, L.D. Melton, K.N. Slessor, A.S. Tracey, *Carbohydr Res* **1971**, *16*, 375.
29. a) D. Horton, J.S. Jewell, *Cabohydr Res* **3**, 255 (1965); *Cabohydr. Res.* **1971**, *16*, 375
    b) D. Horton, J.S. Jewell, E.K. Just, J.D. Wander, *Cabohydr. Res.* **1971**, *18*, 49.
30. Physical constants and analytic data cf A.E. Knauf, R H Hunn, C.S. Hudson, *J. Am Chem Soc* **1941**, *63*, 1447.
31. Trideuterioacetate **30** was synthetisized analogically **26** by use of hexadeuterioacetic anhydride. Yield 88%.
32. The 4-D1 labelled compound **35** was synthetisized cf.[31]. Yield 86%.
33. H.-D. Scharf, J. Fleischhauer, J. Aretz, Houben-Weyl, *"Methoden der organischen Chemie"* Bd IV/5a Teil B
34. D Horton, H.S. Prihar, *Carbohydr Res* **1967** *4*, 115.