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A NOVEL METHOD FOR THE STRUCTURAL AND CONFIGURATIONAL ANALYSIS OF ALKYL 3,4,6-TRI-*O*-ACETYL-2-DEOXY-2-HYDROXYIMINO-α-D-*arabino*- AND -*lyxo*-HEXOPYRANOSIDES, USING E.P.R. SPECTROSCOPY

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ABSTRACT

Alkyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-hydroxyimino-α-D-*arabino*- and -*lyxo*-hexopyranosides were oxidised with lead(IV) acetate in solution, yielding the corresponding *Z*- and *E*-isomeric iminoxy radicals (>C=N–O), which gave very intense and persistent electron paramagnetic resonance (e.p.r.) signals. Applying previous results for cyclohexane iminoxy radicals and the differences between the spectra of the *arabino* and *lyxo* compounds, it has been possible to assign the observed, hydrogen hyperfine structure for both *Z*- and *E*-radicals to the hexopyranoid-ring hydrogen atoms at C-1,3,4, and 5 or 6. From *Z*- and *E*-oximes, the same *Z*/*E*-equilibrium mixture of iminoxy radicals is obtained. Also, conclusions on the conformation of the hexopyranoid ring have been drawn, based on solvent and temperature effects. The specificity and sensitivity of the novel e.p.r. method have been used to characterise α-D-oximes in μg-amounts in t.l.c. The presence of other (mainly β) oximes has also been demonstrated.

INTRODUCTION

Alkyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-hydroxyimino-α-D-*arabino*- (**1**) and -*lyxo*-hexopyranosides (**3**) can be prepared by the reaction of dimeric 3,4,6-tri-*O*-acetyl-2-deoxy-2-nitroso-α-D-gluco- and -galacto-pyranosyl chlorides, respectively, with an alcohol in an appropriate solvent. Pure *Z*-α- and, in a few cases, *Z*-β-compounds have been obtained[1]. The stereoselective formation of *Z*-α-D-hydroxyiminoglycosides may involve anomerisation of initially formed *Z*-β-isomers. Apart from this, the existence of *Z*/*E*-isomerism in the oximes of some ketoglycosides has been demonstrated by Collins[2].

From the oximes **1** and **3**, the corresponding iminoxy radicals **2** and **4** (>C=N–O) have been generated by *in situ* oxidation. The stability of these radicals allows e.p.r. analysis with amounts of material that are several orders of magnitude lower

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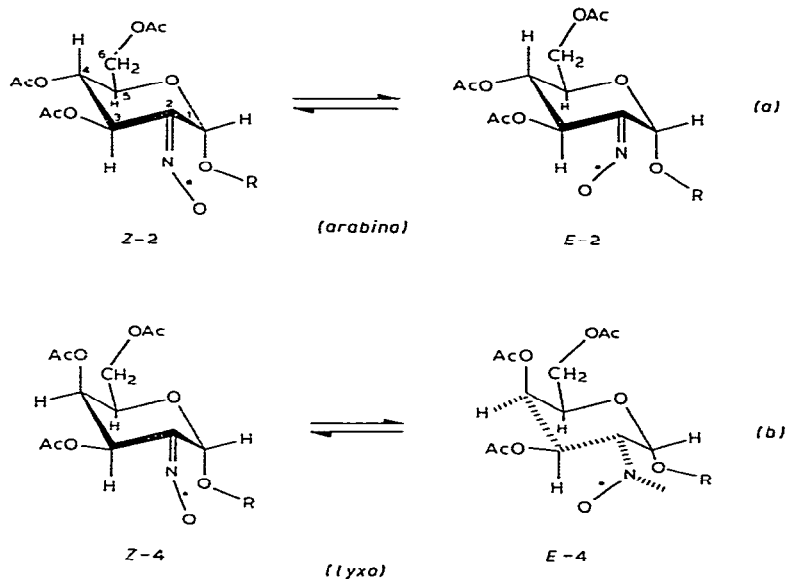
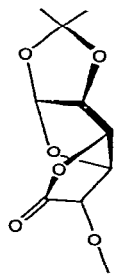


Fig. 1. Iminoxy radicals: a, R = H; b, R = D; c, R = Me, d, R = CD_3; e, R = *t*-Bu;

f, R = 

than those routinely used in n.m.r. spectroscopy. The method has been used for the analysis of complex mixtures of oximes, as shown in the synthesis of 5-*O*-(2-acetamido-2-deoxy-α-D-glucopyranosyl)-D-glucofuranose[3].

In previous work on cyclohexane iminoxy radicals[4], relationships have been established between the structure and conformation of the cyclohexane ring and the various mechanisms for the transmission of unpaired spin-density from the iminoxy function to the ring-hydrogen atoms. The study now reported was set up to test whether these conclusions have a more-general validity for other six-membered ring systems.

RESULTS

When methyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-hydroxyimino-α-D-*arabino*-hexopyranoside (**1c**) was oxidised in various organic solvents with lead(IV) acetate, a persistent e.p.r. signal could be detected, characteristic of a mixture of two iminoxy radicals, with nitrogen hyperfine coupling-constants a_N of ~30 gauss, as shown in Table I and Fig. 2. These signals were observed at, or slighly below, ambient temperature for periods ranging from hours, in most cases, to days.

The iminoxy function has its unpaired electron contained in a σ-type orbital, which is derived from an oxygen p-orbital and the nitrogen non-bonding sp_2-orbital, both of which are in the C=N—O plane[5a]. The spin density in iminoxy radicals is

TABLE I

E.P.R. DATA FOR THE IMINOXY RADICALS FROM 3,4,6-TRI-*O*-ACETYL-2-DEOXY-2-HYDROXYIMINO-α-D-HEXOPYRANOSIDES BY OXIDATION WITH LEAD(IV) ACETATE IN CS_2

Compound	Z-*Radical*[a]						E-*Radical*[a]						*Temperature (degrees)*
	a_N	a_H^1	a_H^3	$a_H^{5(6)}$	a_{OH}^1 *(gauss)*	*g-Value*	a_N	a_H^1	a_H^3	a_H^1	a_{OH}^1 *(gauss)*	*g-Value*	
2a	31.3	1.24	1.88		1.10		30.0	0.51	0.74		0.18		20
2a[b]	31.3	1.24	1.88		1.24	2.0059	30.3	0.47	0.61		0.17	2.0052	−20
2b[b]	31.3	1.24	1.88		—		30.2	~0.515	~0.515		—		−20
2c	31.3	1.29	1.93			2.0057	30.0	0.51	0.88			2.0052	23.5
2c	31.4	1.31	1.99	0.12			30.2	0.47	0.69				−40
2e	31.2	1.40	1.95			2.0058	29.8	0.51	0.76			2.0053	−4
2f	31.5	1.34	1.93			[c]	30.0	0.52	0.86			[c]	0
4c	31.4	1.245	2.06			2.0056	29.7	0.44	0.52	1.87		2.0051	25
4c	—	1.29	2.17	0.15			—	0.43	0.60	1.93			−50
4d	31.8	1.27	2.17	0.15			29.7	0.42	0.58	1.92			−30
4e	31.7	1.36	2.02			2.0059	29.4	0.45	0.45	1.82		2.0053	30

[a] *Z* and *E*: iminoxy oxygen with respect to C-1. Assignments are given in the text. [b] In toluene. [c] $|g(Z-E)| = 0.0005$.

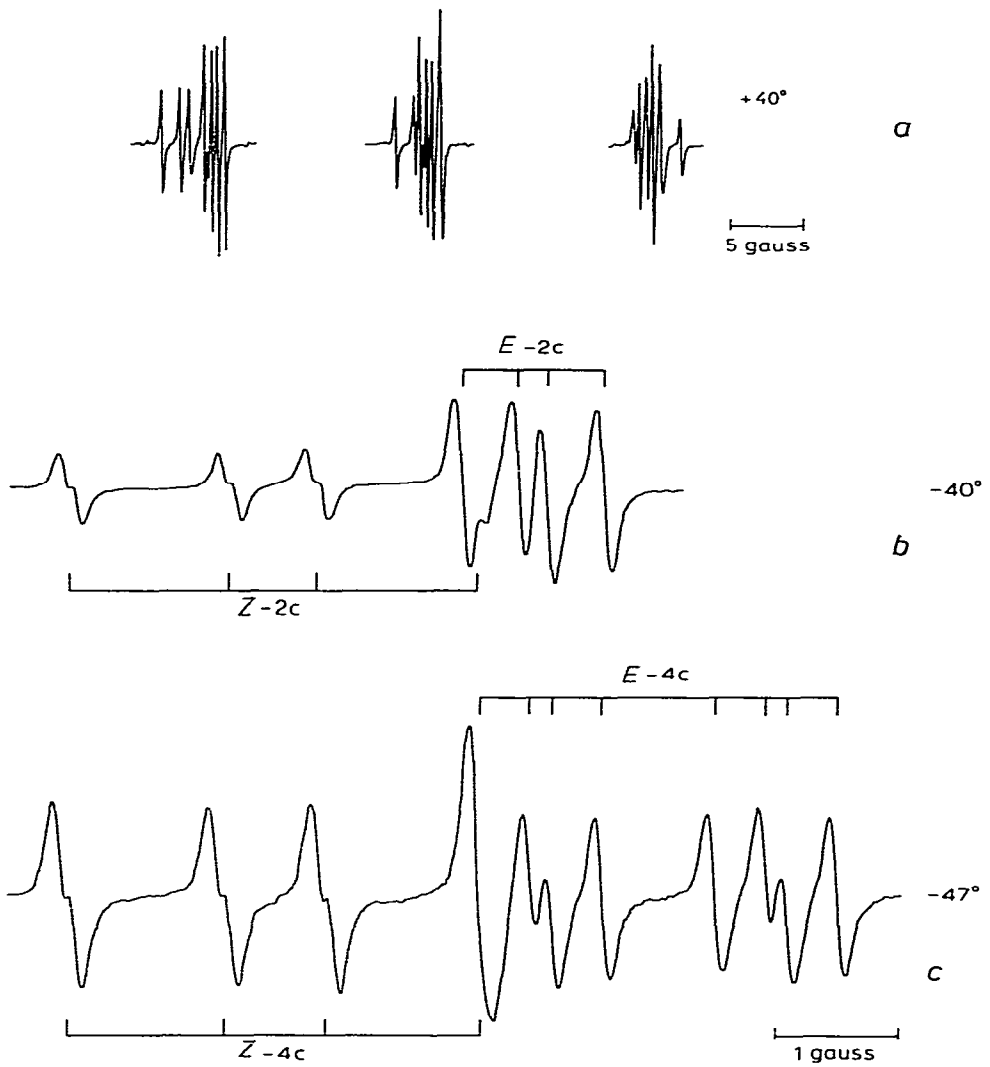


Fig. 2. (*a*) E.p.r. spectrum of iminoxy radicals **2c** at 40°, (*b*) low-field nitrogen groups of *Z*- and *E*-**2c** at −40°, and (*c*) idem for *Z*- and *E*-**4c** at −47°.

almost evenly distributed over nitrogen and oxygen. The C=N—O angle has been calculated to be ~139° and is thus larger than in the parent oxime[5b]. This difference in bond angle supposedly influences the relative stabilities of *Z*- and *E*-isomers, the *Z*/*E*-equilibrium ratio for iminoxy radicals in general being less pronounced than that for the corresponding oximes. The difference in ratios is ascribed to a diminished steric influence of the asymmetric iminoxy function as compared to the oxime (an example is given in ref. 6).

In a number of studies[6,7], it has been established that *Z*/*E*-isomerism in iminoxy radicals generally leads to an equilibrated mixture of two radicals having separate

e.p.r. signals. Also, a mixture of *Z*- and *E*-isomeric radicals **2c** is found upon oxidation of *Z*-**1c**. Each of the three ^{14}N groups of lines contains hydrogen hyperfine structure from two radicals having different a_N, a_H, and g-constant values (Table I). It is most clearly observed in the low-field nitrogen group, *cf.* Fig. 2*b*.

The difference in a_N values between the two radicals is taken as evidence for steric hindrance in the *E*-radical between the iminoxy function and the equatorial AcO-3 group, leading to a somewhat distorted structure as compared to *Z*-**1c**. Rehybridisation will lead to a slightly different distribution of unpaired spin over oxygen and nitrogen and thus to different g-values for the two radicals.

Conclusive evidence for the assignment as given in Table I was obtained by comparison of the e.p.r. signals of the *arabino*-radicals **2c** with those of the *lyxo*-analogues **4c**, *cf.* Figs. 1 and 2. In the *E*-isomer of radicals **4**, a long-range, planar W-type of interaction, as indicated in Fig. 1*b*, exists between the orbital of the unpaired electron on nitrogen and the equatorial H-4. This interaction is highly stereospecific in cyclohexane iminoxy radicals and it takes place exclusively with the indicated H atom[4]. Actually, in cyclohexane iminoxy radicals, this hydrogen coupling-constant a(H-3; syn-eq) is the largest (2.2 G). Apparently, the same situation holds for *E*-**4c**. Inspection shows the e.p.r. spectra of **2c** and **4c** to be similar in all respects but one, *cf.* Fig. 2 and Table I.

One of the isomers of **4c** shows a largest hydrogen-coupling of 1.93 G, which is absent from the corresponding isomer of **2c**. Therefore, these radicals have been assigned the *E*-structure, which leaves the *Z*-structure for the remaining isomers of **2c** and **4c**. This interpretation is consistent with all results for the α-D-*arabino*-(**2a–f**) and -*lyxo*-iminoxy radicals (**4a–f**). Thus, the first conclusion of this study is that, in the α-D series, *arabino* and *lyxo* configurations in the iminoxy radicals (and therefore in the parent oximes) can be distinguished unambiguously.

Assignment of the hydrogen hyperfine structure

Upon replacement of $-OCH_3$ by $-OCD_3$ at C-1, no changes in the hyperfine structure of **2c** are observed. Neither does the introduction of a *tert*-butoxy group, as in **2e**, affect the number of hyperfine lines. Consequently, it is concluded that alkyl substituents attached to O-1 in the α-D series do not give rise to observable hyperfine splittings ($a_H < 0.1$ G). However, when C-1 carries a hydroxyl group, the hydroxyl hydrogen influences the e.p.r. spectra of both isomers of **2a** (*Z*, 1.24 G; *E*, 0.17 G). This coupling is removed by the addition of CD_3OD to the solvent.

The two remaining hydrogen-couplings in all *Z*- and *E*-radicals were assigned by analogy with rigid cyclohexane iminoxy radicals, *viz.* to the two neighbouring ring-hydrogens at C-1 and C-3. For the two *Z*-isomers, these couplings are 1.9–2.0 and 1.3–1.4 G, respectively.

In principle, two assignments are possible: *A*, $a_H^1 = \sim 1.9$ G and $a_H^3 = \sim 1.3$ G; and *B*, $a_H^1 = \sim 1.3$ G and $a_H^3 = \sim 1.9$ G.

In six-membered, chair-type ring systems that contain an exocyclic double-bond, it has been well-established that the interaction between the exocyclic group

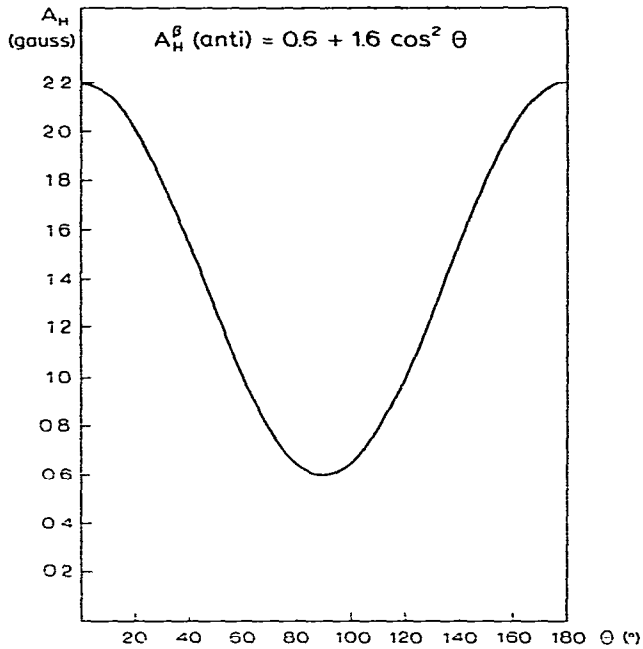


Fig. 3. Dihedral dependence of a_H^β (anti) in cyclohexane-type iminoxy radicals.

and the neighbouring equatorial substituents predominates over 1,3-diaxial interaction, so that the substituent preferably takes an axial position[4]. Hydrogen atoms in equatorial syn-β-position in iminoxy radicals obtain their unpaired spin-density by three mechanisms: (*1*) direct, through-space overlap between the σ-orbital of the unpaired electron on oxygen and the hydrogen orbital: (*2*) a through-bonds interaction with the σ-orbital on nitrogen; and (*3*) a hyperconjugative contribution by interaction with the $2p_z$ orbital on carbon, which becomes observable when the two previous mechanisms are ineffective, *viz.* in the anti-β-hydrogens.

In radicals *Z-2*, H-3ax is in the *anti*-position with respect to the iminoxy function. For this type of hydrogen atom, Căldăraru *et al.*[8] have calculated that the following relation holds in cyclohexane-type iminoxy radicals:

$$a_H^{\beta\text{-anti}} = 0.6 + 1.6\cos^2\theta \quad \text{(G)},$$

where θ is the dihedral angle between the C-H bond and the $2p_z$ orbital on carbon. This relation is depicted graphically in Fig. 3.

The formula is based on the assumption that unpaired spin-density at the anti-β-hydrogen originates exclusively from interaction with the $2p_z$-orbital, which carries part of the unpaired spin-density[4,6]. For assignments *A* and *B*, dihedral angles of $\sim 50°$ and $\sim 25°$, respectively, are now calculated. We prefer assignment *B*, in which the hydrogen atom is closer to the ideal axial position. Then, a_H^1 is 1.3 G, which is a smaller value than that (1.7 G) found for an equatorial hydrogen atom in a cyclo-

TABLE II

TEMPERATURE AND SOLVENT EFFECTS ON THE E.P.R. SPECTRA OF RADICALS **2c** AND **4c**

Compound	*Solvent*	*Temperature (degrees)*	Z-*Radical*				E-*Radical*				⊿g (Z–E)
			a_N	a^1_H	a^3_H	$a^{5(6)}_H$ *(gauss)*	a_N	a^1_H	a^3_H	a^4_H *(gauss)*	
2c	CS_2	23.5	31.3	1.29	1.93		30.0	0.51	0.88		0.0005
2c	CS_2	−40	31.4	1.31	1.99	0.12	30.2	0.47	0.69		
2c	Me_2CO	20	31.2	1.30	1.95		30.4	0.50	0.50		
2c	Me_2CO	−20	31.2	1.27	2.01		30.4	0.49	0.49		
2c	Me_2CO	−60	31.35	1.18	1.98		30.55	0.37	0.37		
2c	Me_2SO	~25	31.1	1.19	1.79		30.5	~0.59	~0.59		0.0005
4c	CS_2	25	31.4	1.245	2.06		29.7	0.44	0.52	1.87	0.0005
4c	CS_2	−50		1.29	2.17	0.15		0.43	0.60	1.93	
4c	Me_2CO	20	31.5	1.23	2.075	0.17	29.8	0.41	0.29	1.94	
4c	Me_2CO	−20	31.5	1.26	2.11	0.18	30.05	0.42	0.21	1.98	
4c	Me_2CO	−60	31.55	1.26	2.10	~0.18	30.2	0.43	<0.15	2.02	
4c	Me_2SO	25	31.3	1.20	2.23	0.17	30.1	0.45	—	1.98	0.0006

TABLE III

^{1}H-N.M.R. SPECTRAL DATA FOR *arabino*-COMPOUNDS *Z*-1 AND *lyxo*-COMPOUNDS *Z*-3 IN $CDCl_3$

Hexopyranose	*Chemical shifts (δ)*								*Coupling constants (Hz)*					*Ref.*
	H-1	*H-3*	*H-4*	*H-5*	*H-6,6'*	*OR*	*OAc*	*OH*	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	$J_{5,6'}$	$J_{6,6'}$	
arabino														
Z-1a; R = H	6.11	5.80	5.16	4.0–4.4		—	2.06, 2.08, 2.10	~9.45	9.5	9.5				
Z-1c; R = Me	5.86	5.76	5.16	4.0–4.4		3.45	2.05, 2.07, 2.08	9.42	9.5	9.5				12
Z-1e; R = *t*-Bu	6.31	5.83	5.14	4.39	4.27, 4.08	1.29	2.05, 2.05, 2.06	9.62	9.5	9.5		4.5	14	12
lyxo														
Z-3c; R = Me	5.91	5.83	5.48	4.38	4.11	3.45	2.05, 2.06, 2.12	9.56	3.5	≤1.0	6.4	6.4		
Z-3e; R = *t*-Bu	6.34	5.88	5.47	4.54	4.07	1.28	2.03, 2.03, 2.11	9.42	3.5	≤1.0	6.7	6.7		

hexane iminoxy radical, in accordance with some deviation from the ideal equatorial position in radicals *Z*-**2** and *Z*-**4**.

For the *E*-radicals, a similar reasoning is applied. Hydrogen couplings of 0.5 G and a more-variable, larger coupling of 0.5–0.9 G are observed. The smaller coupling is comparable to that of H(anti-β; eq) in cyclohexane iminoxy radicals (~0.55 G), and it is therefore assigned to H-1. The larger coupling of H-3 apparently reflects some conformational lability of the radicals *E*-**2** and *E*-**4**, where a considerable local distortion of the hexopyranoid ring at C-2 and C-3 must be assumed in order to accommodate the experimental data, *cf.* Table I. Measurements in various solvents and at temperatures ranging from room temperature to −60° support this conclusion. These results are collected in Table II. The long-range, planar W-type interaction in *E*-**4c** between H-4 and the nitrogen σ-orbital apparently is not disturbed by this local distortion, since a(H-4) even increases slightly at lower temperatures.

In the low-temperature spectra of *Z*-**2c** and *Z*-**4c**, a small, additional coupling-constant (~0.15 G; 1 H) is present, which is assigned to H-5 or, more probably, to that H-6 which fits best in a planar zigzag arrangement. Apparently, an ineffective, long-range through-bond interaction is present, to which no further attention has been given.

g-Factors

The g-factor is of diagnostic value for distinguishing *Z*- and *E*-radicals in this case. However, we cannot explain the observed changes from 2.0056–2.0059 in the *Z*-radicals to 2.0051–2.0053 in the *E*-isomers. These changes do not reflect decreased spin-density on nitrogen and an increased spin-density on oxygen in the *Z*-radicals alone, which would account for a higher g-value, since a_N is larger in the *Z*- than in *E*-radicals. The change is probably related to some distortion of the iminoxy function in the *E*-isomers and a corresponding change in hybridisation.

Temperature and solvent effects

The *E*/*Z* equilibrium ratio in radical **2c** at 20°, determined by planimetry, is 74/26, which is quite different from the preponderance of the *Z*-isomer in the oxime. Also, in **4c**, the *E*-isomer preponderates at 20° by 64/36, increasing to 69/31 at 55° and decreasing to 52/48 at −52° (in CS_2). Thus, it seems that the *E*/*Z* ratios are not determined mainly by steric hindrance between the exocyclic double-bond and the neighbouring, equatorial acetoxy substituent, as known for 2-acetoxycyclohexanone oxime, where, in the *syn*-acetoxy compound, the substituent takes the axial position and the *syn*/*anti* ratio is 0.05 or smaller[9]. However, steric hindrance plays a role with sufficiently bulky groups at C-1, *e.g.*, in **4e** (R = *tert*-butyl), the *E*/*Z* ratio is 38/62 at 20°.

It is therefore concluded that a factor other than steric hindrance contributes to the stability of the *E*-isomers. It is reasonable to propose that some stabilising interaction may be established between the iminoxy function and the neighbouring acetoxyl group, which counteracts the steric hindrance and balances it in a locally

distorted conformation. To test this hypothesis, we have used the electron-donating solvents acetone and dimethyl sulphoxide which should interfere with an intramolecular-bonding effect. With the conformationally labile *E*-molecules, this leads to a new preferred conformation and thus to changes in the e.p.r. spectrum, *cf.* Table II. The largest changes in hydrogen coupling-constants of the *E*-radical are expected to occur in a(H-3). Indeed, the coupling assigned to this H atom was affected by acetone and Me_2SO: a(H-3) can even be made to disappear for solutions in acetone at low temperature or in Me_2SO at ambient temperature ($a_H < 0.15$ G).

For bonding of the iminoxy function to solvent molecules, it seems likely that the polar canonical form in which the unpaired electron resides on nitrogen is more important than the neutral form with the unpaired electron formally on oxygen.

$$\geq C=\overset{\oplus}{\dot{N}}—\overset{\ominus}{\underline{O}}| \leftrightarrow \geq C=\ddot{N}—\underline{\bar{O}}\cdot$$

A slight increase of a_N in the polar solvents used may point in this direction. It is also likely that, for solvent bonding, the iminoxy radical exists in a conformation that is slightly different from that in neutral solvents.

When H-3 becomes less axial, its hyperconjugative interaction with the carbon $2p_z$-orbital decreases and, at the same time, its direct overlap with the oxygen σ-orbital increases[4].

It has been predicted that hyperconjugative spin-density at H-3 has a negative sign and direct overlap gives rise to positive spin-density[10,11]. Therefore, on changing the conformation from an axial to an equatorial H-3, there must be an intermediate position with a zero spin-density. Apparently, for *E*-**4c** in acetone at low temperatures or in Me_2SO, this situation is almost reached.

Scope and sensitivity

In general, we have found this e.p.r. method suitable for detecting small quantities of α-D-oximes, *e.g.*, a 5-μg sample of **1c** gave a fully resolved spectrum of **2c** upon oxidation with lead(IV) acetate without special efforts. We have used e.p.r. successfully to monitor t.l.c. separations of crude reaction products, thereby obtaining evidence that not only the *Z*-isomeric α-D-2-hydroxyimino compounds were formed. For several oxime preparations, there were two spots on the t.l.c. plate which gave identical e.p.r. spectra, and therefore the oximes must have been *Z*- and *E*-isomers, *e.g.*, of **1c**. Also, in all reaction mixtures that we have investigated, there were other oximes present; these were separated by t.l.c. and subsequently extracted from the silica gel with chloroform or methanol. After evaporation of the solvent, the e.p.r. spectra were recorded in carbon disulphide or toluene. In several cases, we have observed the somewhat different spectra of the β-D-2-iminoxy radicals, to which further attention has been given[12].

As reported[3], the α-structure of 1,2-*O*-isopropylidene-5-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-hydroxyimino-α-D-*arabino*-hexopyranosyl)-α-D-glucofuranurono-6,3-lactone (**1f**) was established by e.p.r. spectroscopy, (*cf.* Table I).

In principle, it also seems possible to use the nitrosyl chloride adducts of glucals as precursors of spin-labelled, biologically active molecules, by incorporation, *via* glycosidation of hydroxylic functions, of substrates having biological interest.

EXPERIMENTAL

General methods. — Melting points were determined on a Mettler FP5/FP51 photoelectric apparatus. Specific rotations were determined at ambient temperature with a Perkin–Elmer 141 Polarimeter. ^{1}H-N.m.r. spectra (internal Me_4Si) were recorded with a Varian HA-100 spectrometer and e.p.r. spectra with a Varian E-4 spectrometer, equipped with a variable-temperature accessory. The e.p.r. measurements were performed on solutions in carbon disulphide (Table I), toluene, and other solvents (Table II) which were freed from oxygen by purging (N_2) for 5 min.

T.l.c. was performed on silica gel (Schleicher and Schull, FR-1500) with detection by charring with sulphuric acid. Column chromatography was performed on Kieselgel 60 (Merck, 230–400 mesh) with ether–light petroleum (b.p. 40–60°) 3:1 (*A*) and 4:1 (*B*).

Alkyl 3,4,6-tri-O-acetyl-2-deoxy-2-hydroxyimino-D-arabino- (**1**) *and* -lyxo-*hexopyranosides* (**3**). — A 0.3M solution of dimeric 3,4,6-tri-*O*-acetyl-2-deoxy-2-nitroso-α-D-gluco- (**5**) or -galacto-pyranosyl chloride[1] (**6**) in dry *N,N*-dimethylformamide was flushed with nitrogen. The specified dry alcohol was added, and the reaction mixture was kept in the dark (20 h, 20°) and then concentrated *in vacuo*.

The resulting syrup (1.41 g) from **5** (3 g) and methanol (0.8 g) consisted of four components (t.l.c., solvent *A*) having R_F values of 0.34, 0.42, 0.50, and 0.56, which were partly resolved by column chromatography (solvent *B*). Crystallisation of the major component (R_F 0.42) from methanol afforded *Z*-**1c**, as shown by ^{1}H-n.m.r. spectroscopy[13]; m.p. 144°, $[\alpha]_D$ +50° (*c* 2, chloroform); lit.[13] m.p. 145–146°. The minor components were shown to contain other oximes by t.l.c. (solvent *A*), and ^{1}H-n.m.r. and e.p.r. spectroscopy. The characterisation of these (mainly β) oximes and their iminoxy radicals will be described elsewhere[12].

The syrup obtained from **6** (2 g) and methanol (0.6 g) was subjected to column chromatography (solvent *B*) and gave *Z*-**3c**, m.p. 44°, $[\alpha]_D$ +58° (*c* 2, chloroform), R_F 0.50 (solvent *A*), as established by comparison of the ^{1}H-n.m.r. spectra of *Z*-**1** and the 1- or 2-propyl homologues[13]. The mother liquor consisted of three components having R_F values of 0.50, 0.60, and 0.65.

Likewise, on a smaller scale, the syrup obtained from **6** (0.2 g) and methanol-d_3 (0.2 g) in dry *N,N*-dimethylformamide (0.5 ml) gave **3d** which exhibited the same spots and spot-intensities in t.l.c. (solvent *A*) as did **3c**. The slowest-moving component was shown to be *Z*-**3d** by the complete identity of the e.p.r. spectrum upon oxidation with that of *Z*-**3c**. Since the middle spot (R_F 0.60) was found by e.p.r. spectroscopy to be a mixture of the other isomer of **3d** and an isomer of the fastest-moving β-oxime, these components are identified as *Z*-**3d** (R_F 0.50), *E*-**3d**, one β anomer (R_F 0.60), and the other β isomer[12] (R_F 0.65). These assignments are in accordance with other

three- and four-spot patterns in t.l.c., where β compounds move faster than the α isomers, and *E*-α-oximes have larger R_F values than the *Z*-α-isomers.

tert-*Butyl 3,4,6-tri*-O-*acetyl-2-deoxy-2-hydroxyimino*-α-D-arabino- (**1e**) *and* -lyxo-*hexopyranosides* (**3e**). — The syrups (both 0.27 g) obtained from **5** and **6**, respectively, and *tert*-butyl alcohol (0.12 g) were subjected to column chromatography, to give two separate fractions, as shown by t.l.c. (solvent *B*), which were characterised by ^{1}H-n.m.r. and e.p.r. spectroscopy as α and β anomers, for the faster- and slower-moving (t.l.c., solvent *B*) derivatives, respectively. Compound *Z*-**1e** crystallised from methanol–ether as a vacuum-stable, 1:1 complex with ether; m.p. 46–47°, $[\alpha]_D$ +41° (*c* 2, chloroform) (Found: C, 53.21; H, 7.61; N, 3.21. $C_{16}H_{25}NO_9 \cdot C_4H_{10}O$ calc.: C, 53.44; H, 7.85; N, 3.12%).

Pure *Z*-**3e** had m.p. 115–117° (from ether–hexane), $[\alpha]_D$ +88° (*c* 2, chloroform) (Found: C, 50.92; H, 6.70; N, 3.55. $C_{16}H_{25}NO_9$ calc.: C, 51.20; H, 6.71; N, 3.73%). Both *Z*-**1e** and *Z*-**3e** were characterised by ^{1}H-n.m.r. and e.p.r. spectroscopy.

3,4,6-Tri-O-*acetyl-2-deoxy-2-hydroxyimino*-D-arabino-*hexopyranose* (**1a**). — Condensation of **5** (100 mg) and water (50 μl), as for **1** and **3**, afforded a syrup which consisted of three components, R_F 0.18 (medium), 0.24 (strong), and 0.45 (weak) (t.l.c., solvent *A*). The main component (R_F 0.24) was identified by its ^{1}H-n.m.r. and e.p.r. spectra (Tables I and III), and by deuterium-exchange experiments (HO-1, MeOD). Compound **1a** could be detected in all condensations using **5** when moisture was not rigorously excluded from the reaction mixture.

1,2-O-*Isopropylidene-3*-O-(*3,4,6-tri*-O-*acetyl-2-deoxy-2-hydroxyimino*-α-D-arabino-*hexopyranosyl*)-α-D-*glucofuranurono-6,3-lactone*[3] (**1f**). — Compound **1f** was prepared as described in ref. 3. The structure of the *Z*-α-isomer of **1f** has been assigned by ^{1}H-n.m.r. spectrosocpy and on the basis of the close similarity of the e.p.r. spectrum of **1f** with those of the other radicals derived from **2** (*cf.* Table I and the differences in a_N, a_H, and g-values from those assigned[12] to the β isomers of radicals **2**).

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