Carbohydrate Research, 171 (1987) 279–288
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

SYNTHESIS OF (2-DEOXY-α-D-GLYC-2-ENOPYRANOSYL)ARENES BY STEREOSPECIFIC CONJUGATE-ADDITION OF ORGANOCOPPER REAGENTS TO PERACETYLATED HEX-1-ENOPYRAN-3-ULOSES*

VÉRONIQUE BELLOSTA

Laboratoire de Recherches Organiques, E.S.P.C.I., 10, rue Vauquelin, F-75005 Paris (France)

AND STANISLAS CZERNECKI

Laboratoire de Chimie des Glucides, Université P. et M. Curie, T 54–55, 4 Place Jussieu, F-75005 Paris (France)

(Received March 18th, 1986; accepted for publication, May 20th, 1986)

ABSTRACT

The reaction of peracetylated 1,5-anhydro-2-deoxyhex-1-eno-3-uloses with higher-order cyanoorganocuprate in oxolane at low temperature in the presence of acetic anhydride afforded the corresponding glycosylarenes in good yields. A complete stereocontrol could be achieved, leading to the α-D anomer without epimerization at C-4. The configuration of the new products was established by spectroscopic methods and transformation into the crystalline parent oximes, the conformation of which is discussed in terms of stereoelectronic effects.

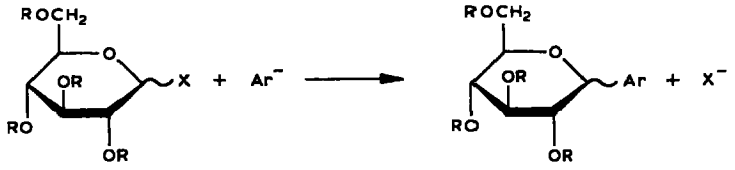
INTRODUCTION

Our laboratory is interested in the synthesis of glycosylarenes with a possible extension to complex aromatic components, including anthraquinone derivatives, and to heterocycles as an entry to *C*-nucleosides, some of which exhibit interesting biological activities[3]. Our efforts are particularly directed toward the study of methods affording new access to 2-deoxyglycosylarenes. Such subunits are often present in natural compounds and, in some cases, OH-6 may be missing and OH-3 be replaced by an amino group[4]. Generally *C*-glycosyl compounds have been prepared by nucleophilic attack on a suitably activated anomeric carbon of protected sugar derivatives (Scheme 1)[5].

These methods could be applied to 2-deoxyglycosyl derivatives, but we thought it would be of interest to explore the conjugate addition of organocopper reagents to protected hex-1-enopyran-3-uloses as an alternative route to this class of compounds, since the stereochemical outcome could be different. The copper-mediated conjugate addition to α,β-enones is well documented[6,7] and plays an in-

*C-Glycosyl compounds IV. Communicated in part, as a poster, at ESOC IV, Aix-en-Provence, Sept. 1985. For preceding papers, see refs. 1 and 2.

0008-6215/87/$ 03.50



Scheme 1.

creasingly important role in C–C bond formation. This reaction was often used to prepare branched-chain sugars[8] but, to the best of our knowledge, only two attempts were made with protected hex-1-enopyran-3-uloses to prepare *C*-glycosyl compounds[9,10]. Unlike these predecessors who used permanent protective groups, we took advantage of the relative inertness of organocopper reagents towards ester groups and hence acetate was used as a temporary protective group.

RESULTS AND DISCUSSION

The recently available[11] 4,6-di-*O*-acetyl-1,5-anhydro-2-deoxy-D-*erythro*- (**1**) and -D-*threo*-hex-1-eno-3-ulose (**2**) were treated under various conditions with different combinations of organocopper reagents in order to examine the influence of several factors (solvent, nature and quantity of reagent, temperature, etc.) (see Table I).

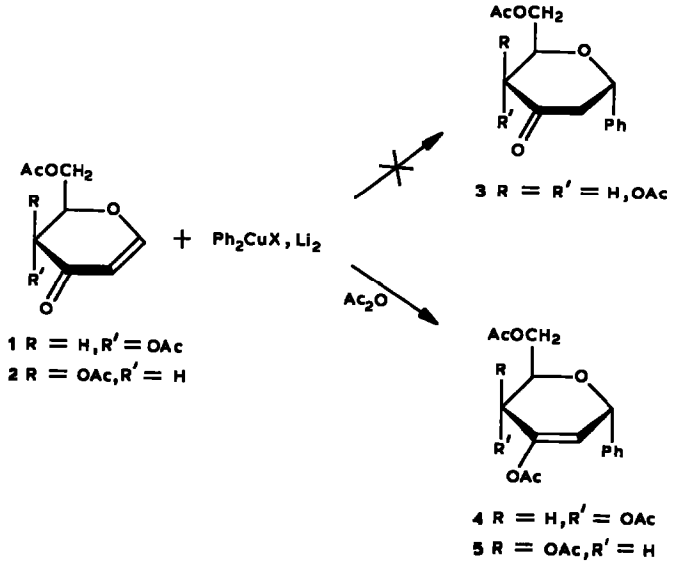
Although Goodwin *et al.*[10] obtained satisfactory yields of 3-keto-*C*-glycosyl compounds when treating alkyl heterocuprates in the presence of ether protective

TABLE I

REACTION OF ORGANOCOPPER REAGENTS WITH ENONES **1** AND **2**

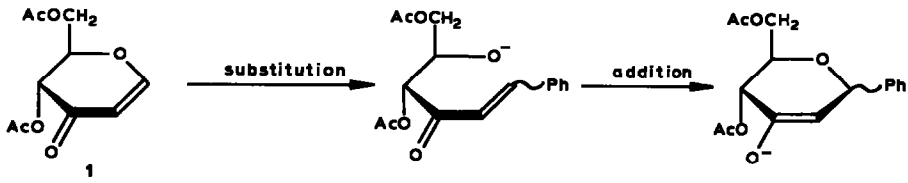
Exp.	*Enone (mmol)*	*Lithium salts (mmol)*	*Ac_2O*[a]	*$Ph_2CuCNLi_2$ (eq.)*	*Conditions*	*Yield of products (%)*[b]	
						4	**5**
1	1 (0.5)	0.026	af.	1.05	−50→0°, 3 h at 0°, and 12 h at 20°	28[c](93)	2(7)
2	1 (0.5)	0.05	af.	2	−50→0° and 2 h at 0°	75[d]	
3	1 (1.5)	present[e]	af.	2	−50→0° and 2 h at 0°	74(96)	3(4)
4	1 (3)	0.30	af.	2	−50→−25°	75(98.7)	1(1.3)
5	1 (3)	0.30	tog.	2	−50→−25°	87(100)	0(0)
6	2 (3)	0.30	tog.	2	−50→−25°	3(3.5)	83(96.5)

[a]Ac_2O (2 eq.) was added after (af.) or together with (tog.) the enone. [b]Yield of isolated product after flash chromatography. The proportions of **4** and **5** were also measured by g.l.c. analysis of the crude mixture. Relative proportions in parentheses. [c]Unreacted **1** (41%) was recovered. [d]Mixture containing 95% of **4** and 5% of **5** (g.l.c. analysis). [e]The percentage of lithium salts was not given in the solution sold by Fluka.



groups, no 3-keto-*C*-glycosylbenzene **3** resulting from a 1,4-addition could be isolated. Whatever the phenylcopper reagent was, t.l.c. showed the disappearance of the starting enone and essentially the presence of polar compounds, likely to be formed by reaction of the intermediate enolate with ester groups. The reactive enolate was quenched with acetic anhydride and the enol ester **4** was obtained in good yield, but an excess of organocopper was necessary to achieve completion of the reaction (Exps. 2 and 3). With a stoichiometric amount of organocopper (Exp. 1), 41% of starting enone was recovered, indicating that some organocopper reagent was consumed by a reaction with the trapping reagent or with the primary acetate group, or both[12].

The course of the reaction of organocopper reagents with 3-alkoxy-enones is not as clear as with simple enones. It has been observed that substitution of the 3-alkoxy group by the organometal could occur with such substrates[13]. In the case of enone **1**, opening of the pyranose ring would result from such a substitution (Scheme 2).

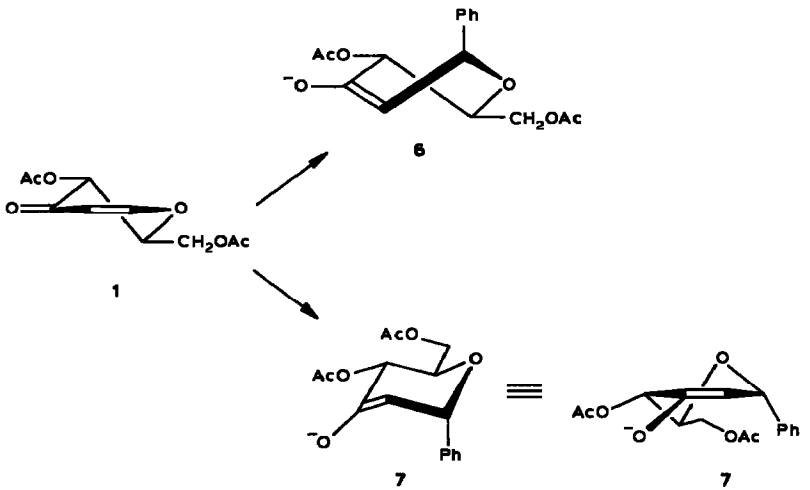


Scheme 2.

It is doubtful whether ring closure by a 1,4-nucleophilic addition could lead to

only one anomer. Moreover, when acetic anhydride was introduced together with the enone, the open structure would have been isolated, at least in small proportion. This substitution–addition sequence could be responsible for the lack of stereoselectivity observed by Yunker *et al.*[9] when treating 1,5-anhydro-4,6-*O*-benzylidene-2-deoxy-D-*erythro*-hex-1-en-3-ulose with dimethylcopperlithium, and by Paulsen and Bünsch[14] when treating the same enone with 2-lithio-1,3-dithiolane-2-carboxylate. The inertia of this rigid bicyclic enone and of the parent alcohols towards addition was also observed in our laboratory[15].

Under the conditions described herein, the reaction was stereospecific (no extra peak attribuable to the β anomer* could be detected by g.l.c. of the crude material), indicating that the flexibility of enone **1** allowed the direct addition of the organocopper compound in the usual manner. Considering the preferred conformation of enone **1**, as deduced from ^{1}H-n.m.r. data[11], it is suggested that an axial attack by the nucleophile with stereocontrol on the β face would lead to an enolate **6** having a boat-like conformation whereas that on the α face would give the enolate **7** having a chair-like conformation. The second process would, therefore, be favored as suggested by Toromanoff[16], affording exclusively the *C*-α-D-glycosyl compound.



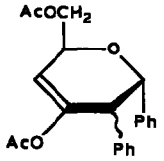
In several cases (Exps. 1, 2, 3, and 4), a small proportion of another product that had the same chromatographic behavior as **5** (already available in our laboratory[1]) was detected (g.l.c. and t.l.c.) in the reaction mixture. This compound was isolated by flash chromatography and was characterized by spectroscopy as **5** resulting from epimerization at C-4**. This epimerization was not mentionned by Goodwin *et al.*[10], but has been observed by Paulsen and Bünsch[14]. It is assumed that epimerization

*The nomenclature used to describe the configuration of *C*-glycosyl compounds is the same as that of glycosides.

**The carbohydrate numbering is used in this paper.

occurred at the enolate step resulting from a 1,4 addition, because the starting enone was recovered unchanged when not completely transformed (Exp. 1), and the degree of epimerization was not increased when the work-up was delayed. In the experiment with the higher-order, mixed cuprate ($Ph_2CuCNLi_2$), the degree of epimerization was significantly lower (3–5%) than in the experiment with the homocuprate (Ph_2CuLi) where the proportion of isomerization could reach 20% in some cases. In the presence of a strong field ligand (CN^-) it may be assumed that the intermediate enolate **7** is more ionic and, therefore, the rate of acylation is greater than that of proton transfer. The preservation of enolate regiospecificity resulted in a low percentage of C-4 epimerization (Exps. 2, 3, and 4). Finally, the epimerization was completely suppressed and the yield of overall isolated product was increased to 87% (Exp. 5) by introducing the trapping reagent together with the enone.

Although lithium salts were shown to influence the coupling of organocopper reagents with organic halides[17], no such effect was observed in our study (Exps. 2, 3, and 4). From enone **1** the best yield was obtained when the reaction was taken to completion at low temperature (−50→ −25°; Exp. 5) in order to avoid any substitution at C-4 of the allylic acetate **4** by the organocopper reagent*. This reaction is well documented[19] and was applied to carbohydrate derivatives, but proceeds rather slower than 1,4-additions[12]. Indeed, in some cases in which the temperature was allowed to raise to 0°, a low-polar compound was isolated in small proportion (≃ 10%) and shown to be **8** by spectroscopy.



8

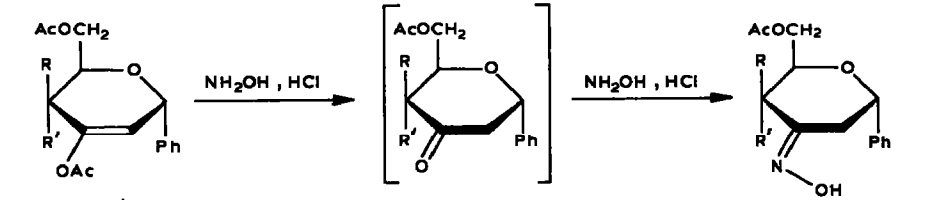
Concerning the organometallic reagent, the best results (yield and stereocontrol) were obtained with a higher-order, mixed organocuprate reagent prepared from commercially available solutions of phenyllithium and copper cyanide[20]. Although good results were obtained with a homocuprate (Ph_2CuLi), the reproducibility was low with this reagent and, sometimes, a low yield, or low stereoselectivity, or both were obtained without predictability.

4,6-Di-*O*-acetyl-1,5-anhydro-2-deoxy-D-*threo*-hex-1-en-3-ulose (**2**) was next investigated. Under the best conditions the rate of phenylation was slightly lower but the yield of isolated *C*-α-D-glycosides **5** was about the same (Exp. 6). In this case, the epimerization at C-4 was not completely avoided, and **4** was isolated (yield 3%)

*Another advantage of a low temperature is that the possible reaction of the organocopper reagent with an enol ester[18] is slowed down, thus keeping the reaction simple and giving a high yield.

from the reaction mixture and characterized. This epimerization may be due to the quasi-axial position of $OCOCH_3$-4 in the intermediate.

The α-D configuration of the *C*-glycosylarenes was unambiguously proved by X-ray crystallography[2] for **5**, but, for the sirupy derivative **4**, additional proofs were needed, as examination of the coupling constants for vicinal sp^3-sp^2 carbon atoms may not be suficient[2]. Accordingly, **4** and **5** were transformed into the corresponding oximes **10** and **11** by action of an excess of hydroxylamine hydrochloride[21] *via* the nonisolated intermediate **9**. This high-yielding transformation being carried out under very mild conditions is a valuable tool for structure elucidation because the intermediate ketone is immediately quenched by an excess of reagent. The ^{1}H-n.m.r. data were easier to interpret as C-1 and C-2 are now sp^3, and spectral assignments were deduced from standard chemical-shifts and coupling-constant data and from extensive spin-decoupling experiments.



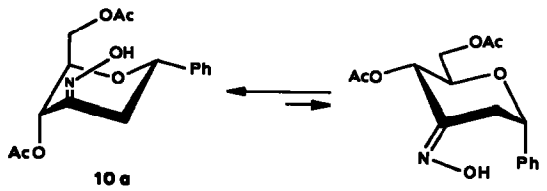
4 R = H, R′ = OAc
5 R = OAc, R′ = H

9

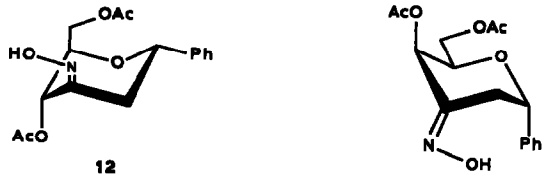
10 R = H, R′ = OAc
11 R = OAc, R′ = H

The crude oximes (**10** and **12**) prepared from **4** were shown to be a mixture of *Z,E* isomers (15 and 85%, respectively) by ^{1}H-n.m.r. [di($^2H_3$)methylsulfoxide]. According to previous work[22,23], the *E* configuration was attributed to the major isomer **10**, which was obtained in crystalline form. From **5**, a single *E* isomer **11** was obtained. In the ^{1}H-n.m.r. spectrum of oxime **11**, the H-1 signal is a doublet of doublet and the $J_{1,2}$ 3 and $J_{1,2}$ 6 Hz were too small for an axial–axial relationship between H-1 and H-2′, indicating that H-1 is not in an axial position. The value of 6 Hz, which may seem to be too large for an equatorial–axial coupling, has already been observed for other *C*-glycosyl compounds[24]. Therefore, only the $^4C_1$(D) conformation is in reasonable agreement with these data. Such conformation was confirmed by $J_{4,5}$ 2 Hz, which is in the range of expected value for the coupling between H-5*a* and H-4*e* of an hexopyranose derivative bearing an axial substituent at O-4 and a terminal CH_2OAc group[24]. Thus, the axial position of the phenyl group provided confirmation of the α-D configuration.

In the case of the oximes obtained from **4**, the H-1 signal of the major *E* isomer **10** was a doublet of doublet [($^2H_3$)Me_2SO] with $J_{1,2}$ 4.5 and $J_{1,2'}$ 8 Hz, suggesting an axial position for H-1 in a $^1C_4$(D) conformation (**10a**). The value $J_{4,5}$ 4.8 Hz was too small for an axial–axial relationship between these two protons, which is usually observed in the *gluco* series; this exclude the $^4C_1$(D) conformation.



10a 10b



12 11

It was also too large for a coupling constant between the equatorial protons in the $^1C_4$(D) conformation. These data favor a conformational equilibrium of compound **10** (**10a** and **10b**) in which the $^1C_4$(D) conformation preponderates. The occurrence of this unusual conformation is supported by the ^{1}H-n.m.r. data for the minor *Z* isomer **12** (examined in the presence of the *E* isomer **10**). In this case, the values $J_{1,2}$ 3.5, $J_{1,2'}$ 11, and $J_{4,5}$ 2 Hz were in agreement with a highly preponderating $^1C_4$(D) conformation having the phenyl group in equatorial position, thus confirming the α-D configuration at C-1. Since C-3 is sp^2, this conformation does not afford strong destabilizing 1,3-diaxial interactions. Similar stereochemical properties of *C*-glycosyl compounds were already observed for solutions in a polar solvent[24]. Furthermore, it can be noted that, in each conformation of **10** or **12**, one bulky group out of two (CH_2OAc or Ph) is in axial, whereas the other one is in equatorial position (Ph or CH_2OAc, respectively).

In compounds in which there is no anomeric effect to strongly influence the conformation, an important factor of stabilization may be the axial position of the acetoxy group in α-position to the sp^2 carbon atom of the oxime group. In this situation, a stabilizing overlap could occur between the σ^* orbital of C-4–O and the π orbital of C=N, the axes of which are parallel. This effect resembles the anomeric effect in which the stabilizing effect occurs between the σ^* orbital of C-1–O and a nonbinding doublet of the ring oxygen atom[25]. A similar effect was observed by Dupuis *et al.*[26] in the stabilization of radicals. This explanation would apply to α-substituted, sp^2 carbon atoms, such as α-halogenated ketone rather than the electrostatic repulsion of dipoles previously proposed[27].

The reaction of organocuprate with hex-1-enopyran-3-uloses in the presence of acetoxy groups provides an excellent method for the preparation of *C*-2-deoxy-α-D-glycosyl compounds, which are more difficult to prepare than β-D-glycosyl com-

pounds[5]. This reaction has several advantages, such as high yields, stereospecificity, and possibility of manipulations of the enol ester function present in the molecule.

EXPERIMENTAL

General methods. — Melting points were determined with a Thomas–Hoover apparatus and are uncorrected. Optical rotations were measured with a Perkin–Elmer polarimeter. I.r. spectra (film or KBr disk) were recorded with a Unicam SP3-300 spectrophotometer, and ^{1}H-n.m.r. spectra with a Brucker WH-250 spectrometer (tetramethylsilane as internal standard). Gas chromatography (g.l.c.) was carried out with a Girdel 75 FD instrument fitted with a column (1 m) of 3% (w/w) *N*-phenyldiethanolamine succinate (PDEAS) on Chromosorb WAW DMCS. Analytical t.l.c. was performed on Merck aluminium precoated plates of Silica gel 60 F-245 with detection by u.v., and by spraying with 3M H_2SO_4 and heating. The following solvent systems were used; solvent *A* (2:1 diethyl ether–ligroin) and solvent *B* (1:1 diethyl ether–chloroform). Merck silica gel 60 (230–400 mesh) was used for flash chromatography. Oxolane was distilled from benzophenone–sodium immediately before use. Phenyllithium solutions were purchased from Aldrich and Fluka and standardized[28] before use. Copper(I) salts from Prolabo were used without purification. Elemental analyses were performed by the Service de Microanalyse of the Université P. et M. Curie.

Typical conjugate addition procedure exemplified by reaction of enone **1** *with higher-order cuprate. Preparation of (3,4,6-tri-*O*-acetyl-2-deoxy-*α*-*D*-erythro-hex-2-enopyranosyl)benzene* (**4**). — To a suspension of copper(I) cyanide (600 mg, 6.6 mmol), in anhydrous oxolane (6 mL) under Ar, was added a 2M solution of phenyllithium (6 mL, 12 mmol) at −50°. After 10 min of being stirred, the solution gave a negative Gilman test[29]. Under vigorous stirring, anhydrous oxolane solution (6 mL) containing enone **1** (684 mg, 3 mmol) and acetic anhydride (570 μL, 6 mmol) was added slowly *via* a syringe needle at such a rate that the temperature was maintained at −50°. Immediately, the dark-brown mixture became an orange homogenous solution. The temperature was allowed to rise up to (≃ 1 h), and maintained at −25°. After completion of the reaction was indicated by t.l.c. (solvent *A*), saturated NH_4Cl solution (2 mL) was added and the product extracted with diethyl ether (3 × 30 mL). The combined ether solutions were washed with saturated NH_4Cl solution (2 × 20 mL) and water (1 × 15 mL), dried ($MgSO_4$), and evaporated. The crude residue was analyzed by g.l.c. Flash chromatography of the residue with mixtures of diethyl ether–ligroin of increasing polarity afforded pure **4** (908 mg, 87%), colorless oil, $[\alpha]_D^{20}$ +69° (*c* 1.7, chloroform); lit.[1] $[\alpha]_D$ +69° (*c* 1.7, chloroform); R_F 0.50 (solvent *A*); r.t. 18.3 min at 140°; i.r. and ^{1}H-n.m.r. spectra were identical to those previously recorded[1].

Anal. Calc. for $C_{18}H_{20}O_7$ (348.34): C, 62.06; H, 5.79. Found: C, 61.82; H, 5.62.

*(3,4,6-Tri-*O*-acetyl-2-deoxy-*α*-*D*-*threo*-hex-2-enopyranosyl)benzene* (**5**). —

The same procedure used for the preparation of **4** was applied to enone **2** to afford **5** (865 mg, 83%), m.p. 126–126.5°, $[\alpha]_D^{20}$ −195° (*c* 1.63, chloroform); lit.[1] m.p. 126–126.5°, $[\alpha]_D^{20}$ −195° (*c* 1.63, chloroform); R_F 0.56 (solvent *A*); r.t. 16.2 min at 140°; i.r. and ^{1}H-n.m.r. spectra identical to those previously recorded[1].

Anal. Calc. for $C_{18}H_{20}O_7$ (348.34): C, 62.06; H, 5.79. Found: C, 62.08; H, 5.74.

Further elution gave 30 mg (3%) of **4**.

Typical procedure for the preparation of oximes. — The reaction was performed at room temperature. The *C*-glycosyl compound (1 mmol) and hydroxylamine hydrochloride (4 mmol) were dissolved in anhydrous pyridine (2.5 mL). After t.l.c. (solvent *B*) indicated completion of the reaction (≃ 15 h), water (5 mL) was added and the product extracted with chloroform (3 × 20 mL). The combined extracts were washed with M HCl (1 × 10 mL), 5% $NaHCO_3$ (1 × 10 mL), and water to neutral pH. After being dried ($MgSO_4$), the solution was evaporated under reduced pressure. The crude product was purified by crystallization or flash chromatography (1:1 diethyl ether–chloroform).

*(4,6-Di-*O*-acetyl-2-deoxy-α-*D*-erythro-hexopyranosyl-3-ulose oxime)benzene* (**10**). Yield 285 mg (89%), m.p. 89–90° (diethyl ether), $[\alpha]_D^{20}$ +112° (*c* 1.3, chloroform); R_F 0.51 (solvent *B*); ν_{max}^{KBr} 3380 (OH), 1740 (ester), and 1650 cm^{-1} (weak, C=N); ^{1}H-n.m.r. [($^2H_3$)Me_2SO]: δ 11.34 (s, 1 H, NOH), 7.24–7.46 (m, 5 H, arom.), 4.99 (dd, 1 H, $J_{1,2}$ 4.5, $J_{1,2'}$ 8 Hz, H-1), 3.0 (dd, 1 H, H-2*e*), 2.82 (dd, 1 H, $J_{2e,2a}$ 14 Hz, H-2*a*), 5.22 (d, 1 H, $J_{4,5}$ 4.8 Hz, H-4), 3.97–4.07 (m, 1 H, $J_{5,6a}$ 6.5 Hz, $J_{5,6b}$ 4 Hz, H-5), 4.35 (dd, 1 H, $J_{6a,6b}$ 12 Hz, H-6*a*), 4.12 (dd, 1 H, H-6*b*), and 2.02–2.06 (2 s, 2 $OCOCH_3$).

Anal. Calc. for $C_{16}H_{19}NO_6$ (321.33): C, 59.81; H, 5.96; N, 4.36. Found: C, 60.05; H, 6.13; N, 4.51.

*(4,6-Di-*O*-acetyl-2-deoxy-α-*D*-threo-hexopyranosyl-3-ulose oxime)benzene* (**11**). Yield 301 mg (94%), m.p. 112–112.5° (diethyl ether–hexane), $[\alpha]_D^{20}$ +175° (*c* 1.13, chloroform); R_F 0.51 (solvent *B*); ν_{max}^{KBr} 3350 (OH), 1750 (ester), and 1665 cm^{-1} (weak, C=N); ^{1}H-n.m.r. [($^2H_3$)Me_2SO]: δ 11.42 (s, 1 H, NOH), 7.29–7.41 (m, 5 H, arom.), 5.28 (dd, 1 H, $J_{1,2}$ 3 $J_{1,2'}$ 6 Hz, H-1), 3.44 (dd, 1 H, $J_{2e,2a}$ 15 Hz, H-2*e*), 2.7 (dd, 1 H, H-2*a*), 5.33 (d, 1 H, $J_{4,5}$ 2 Hz, H-4), 3.71–3.78 (m, 1 H, H-5), 4–4.15 (m, 2 H, H-6*a*,6*b*), and 1.99–2.10 (2 s, 2 $OCOCH_3$).

Anal. Calc. for $C_{16}H_{19}NO_6$ (321.33): C, 59.81; H, 5.96; N, 4.36. Found: C, 59.68; H, 5.98; N, 4.58.

ACKNOWLEDGMENT

The Centre National de la Recherche Scientifique is acknowledged for financial support.

REFERENCES

1 S. Czernecki and V. Dechavanne, *Can. J. Chem.*, 61 (1983) 533–540.
2 H. Gillier-Pandraud, R. Brahmi, V. Bellosta-Dechavanne, and S. Czernecki, *Can. J. Chem.*, 63 (1985) 491–494.
3 J. G. Buchanan, *Progr. Chem. Org. Natur. Prod.* 44, (1983) 243–290.
4 L. J. Haynes, *Adv. Carbohydr. Chem. Biochem.*, 18 (1963) 227–258; 20 (1965) 357–369; S. Hanessian and A. G. Pernet, *ibid.*, 33 (1976) 111–188; M. Zehnder, U. Sequin, and H. Nadig, *Helv. Chim. Acta.*, 62 (1979) 2525–2533.
5 C. D. Hurd and W. A. Bonner, *J. Am. Chem. Soc.*, 67 (1945) 1972–1977; R. R. Schmidt and M. Hoffmann, *Tetrahedron Lett.*, 23 (1982) 409–412; R. M. Williams and A. O. Stewart, *ibid.*, 24 (1983) 2715–2718; G. Grynkiewicz and J. N. BeMiller, *Carbohydr. Res.*, 131 (1984) 273–276; G. H. Posner and S. R. Haines, *Tetrahedron Lett.*, 26 (1985) 1823–1826.
6 G. H. Posner, *Org. React.*, 19 (1972) 1–113.
7 G. H. Posner, *An Introduction to Synthesis Using Organocopper Reagents*, Wiley, New York, 1980.
8 N. L. Holder, *Chem. Rev.*, 82 (1982) 287–332.
9 M. B. Yunker, D. E. Plaumann, and B. Fraser-Reid, *Can. J. Chem.*, 55 (1977) 4002–4009.
10 T. A. Goodwin, C. M. Crowder, R. B. White, J. S. Swanson, F. E. Evans, and W. L. Meyer, *J. Org. Chem.*, 48 (1983) 376–380.
11 S. Czernecki, K. Vijayakumaran, and G. Ville, *J. Org. Chem.*, 51, (1986) 5472–5475.
12 Y. Chapleur and Y. Grapsas, *Carbohydr. Res.*, 141 (1985) 153–158.
13 T. Takahashi, K. Hori, and J. Tsuji, *Chem. Lett.*, (1981) 1189–1192. V. F. Shner, K. F. Turchin, Y. N. Sheinker, and N. N. Suvorov, *J. Org. Chem. USSR (Engl. Transl.)*, 16 (1980) 37–41.
14 H. Paulsen and H. Bünsch, *Chem. Ber.*, 111 (1978) 3484–3496.
15 S. Czernecki, unpublished results.
16 E. Toromanoff, *Bull. Soc. Chim. Fr.*, (1962) 708–712.
17 G. M. Whitesides, W. F. Fischer, Jr., J. San Filippo, Jr., R. W. Bashe, and H. O. House, *J. Am. Chem. Soc.*, 91 (1969) 4871–4882, and references therein.
18 S. Hanessian, P. C. Tyler, and Y. Chapleur, *Tetrahedron Lett.*, 22 (1981) 4583–4586.
19 G. H. Posner, *Org. React.*, 22 (1975) 253–400.
20 B. H. Lipshutz and R. S. Wilhelm, *J. Am. Chem. Soc.*, 103 (1981) 7672–7674; B. H. Lipshutz, R. S. Wilhelm, and J. Kozlowski, *Tetrahedron Lett.*, 23 (1982) 3755–3758.
21 F. W. Lichtenthaler and P. Jarglis, *Tetrahedron Lett.*, 21 (1980) 1425–1428.
22 O. Convert, J. Pinson, and J. Armand, *C. R. Acad. Sci., Ser. C*, 274 (1972) 296–299.
23 G. J. Karabatsos and R. A. Taller, *Tetrahedron*, 24 (1968) 3347–3360.
24 M. Chmielewski, J. N. Bemiller, and D. P. Ceretti, *J. Org. Chem.*, 46 (1981) 3903–3908.
25 P. Deslongchamps, *Stereoelectronic Effects in Organic Chemistry*, Pergamon, Oxford, 1983.
26 J. Dupuis, B. Giese, D. Ruegger, H. Fischer, H.-G. Korth, and R. Sustman, *Angew. Chem., Int. Ed. Engl.*, 23 (1984) 896–898.
27 E. J. Corey, *J. Am. Chem. Soc.*, 75 (1953) 2301–2307.
28 S. C. Watson and J. F. Eastham, *J. Organomet. Chem.*, 9 (1967) 165–168.
29 H. Gilman and F. Schulze, *J. Am. Chem. Soc.*, 47 (1925) 2002–2005.