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SYNTHESIS AND SOME REACTIONS OF METHYL 4,6-*O*-BENZYLIDENE-2,3-DIDEOXY-2-PHENYLAZO-β-D-*erythro*-HEX-2-ENOPYRANOSIDE*†

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ABSTRACT

Methyl 4,6-*O*-benzylidene-2,3-dideoxy-2-phenylazo-β-D-*erythro*-hex-2-enopyranoside has been synthesised, and its addition reactions with methoxide, azide, hydride, and deuteride ions have been studied. Comment is made on the stereochemistry of addition reactions of 2- and 3-phenylazo derivatives of methyl 4,6-*O*-benzylidene-2,3-dideoxy-D-hex-2-enopyranosides.

INTRODUCTION

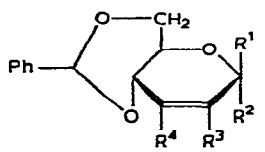
In an earlier paper in this series[2], syntheses of methyl 4,6-*O*-benzylidene-2,3-dideoxy-monophenylazo-D-*erythro*-hex-2-enosides (**1**, **2**, and **3**) were described. The action of nucleophiles on these arylazo-glycenosides was studied, and it was found that the products varied with the configuration at the glycosidic centre and the site of the phenylazo substituent[2]. To complete the investigation of this group of compounds, methyl 4,6-*O*-benzylidene-2,3-dideoxy-2-phenylazo-β-D-*erythro*-hex-2-enoside (**4**) has now been prepared, and its behaviour with some nucleophiles has been examined.

RESULTS AND DISCUSSION

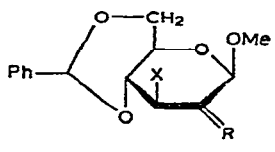
An initital attempt to prepare the 2-phenylazo derivative (**4**) from methyl 3-*O*-benzoyl-4,6-*O*-benzylidene-β-D-*arabino*-hexopyranosid-2-ulose (**5**) by the procedure described previously[2] was unsuccessful. When compound **5** was treated with phenylhydrazine hydrochloride in pyridine, a red, oily, complex mixture was obtained. However, a solid phenylhydrazone of **5** was prepared by using phenylhydrazine in ethanol, and its spectra were consistent with its proposed structure. It exhibited an intense u.v. absorption at 283 nm, close to that observed for phenylhydrazone derivatives of similar ketones[2–4] and similar to that reported for phenylhydrazones of

*Dedicated to the memory of Dr. Hewitt G. Fletcher, Jr.
†Arylazo-glycenosides: Part VI. For Part V, see Ref. 1.

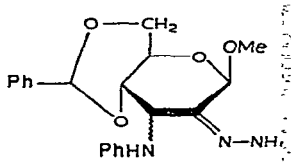
ketones[5,6]. It had strong i.r. absorption at 1610 and 1500 cm^{-1} due to the $\rangle C{=}N{-}\underset{|}{N}{-}Ph$ group[5,6] and, in addition, showed a diagnostic, sharp absorption at 3350 cm^{-1} arising from the $\rangle N{-}H$ group.



1 $R^1 = R^4 = H$, $R^2 = OMe$, $R^3 = N{=}N{-}Ph$
2 $R^1 = R^3 = H$, $R^2 = OMe$, $R^4 = N{=}N{-}Ph$
3 $R^1 = OMe$, $R^2 = R^3 = H$, $R^4 = N{=}N{-}Ph$
4 $R^1 = OMe$, $R^2 = R^4 = H$, $R^3 = N{=}N{-}Ph$



5 X = OBz, R = O
6 X = OTs, R = O
9 X = OMe, R = N—NHPh
11 $X = N_3$, R = N—NHPh
12 X = H, R = N—NHPh
13 X = D, R = N—NHPh



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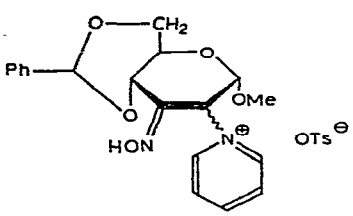

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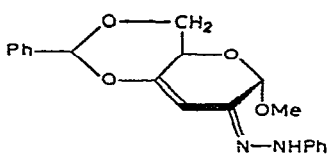

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Attempts to convert this phenylhydrazone into compound **4** by treatment with a variety of bases (*e.g.*, sodium methoxide, potassium *tert*-butoxide, sodium hydroxide, and pyridine) were unsuccessful and led to decomposition.

Subsequently, compound **4** was prepared satisfactorily from methyl 4,6-*O*-benzylidene-3-*O*-tosyl-β-D-glucoside. This 3-*O*-tosyl derivative was obtained from a mixture resulting from tosylation of methyl 4,6-*O*-benzylidene-β-D-glucoside after separation of the 2,3-di-*O*-tosyl and 2-*O*-tosyl derivatives. Selective sulphonylation was more difficult to achieve than was the case for the α-D anomer[7]. The 3-*O*-tosyl derivative could be oxidised best in *N*,*N*-dimethylformamide with a slight excess of methyl sulphoxide in the presence of phosphoric oxide. Methyl 4,6-*O*-benzylidene-3-*O*-tosyl-β-D-*arabino*-hexopyranosid-2-ulose (**6**) was isolated as its geminal diol, which could be dehydrated to the carbonyl form (**6**) by azeotroping with toluene–methanol. Its structure followed from its method of preparation, elemental analysis, and spectral characteristics. Compound **6** was converted into compound **4** by treatment with phenylhydrazine hydrochloride in pyridine at room temperature. The intermediate phenylhydrazone was not isolated, presumably owing to the good leaving-group properties of the tosyloxy residue. However, its presence was indicated by the appearance in the u.v. spectrum of the reaction mixture of an absorption

maximum at 280 nm which slowly decreased while the absorption band at 306 nm (characteristic of phenylazoalkenes) progressively increased. The structure of the 2-phenylazoalkene (**4**) follows from its method of preparation, its elemental analysis, the characteristically intense absorption at 306–307 nm, and its orange–red colour. The absence of absorption bands at 1600–1500 and 3500–3200 cm^{-1} showed the absence of a phenylhydrazone group in the final product. The n.m.r. spectrum supports the structural assignment. The observations reported are consistent with an eliminative loss of toluene-*p*-sulphonic acid from an intermediate tosylated phenylhydrazone derived from compound **6**.

When the reaction of phenylhydrazine hydrochloride with the 3-*O*-tosyl-*β*-hexopyranosid-2-ulose (**6**) in pyridine was carried out at higher temperature (40°), a considerable amount of another product was obtained in addition to the phenylazoalkene (**4**). This new product had typical i.r. and u.v. spectra for a phenylhydrazone. In the mass spectrum, the molecular ion peak was at 445, corresponding to the molecular formula $C_{26}H_{27}N_3O_4$. The elemental analysis conformed to this formula. From the n.m.r. spectrum, it was deduced that the compound contained the anomeric proton, the aglycon methoxyl group, and the 4,6-*O*-benzylidene acetal grouping. In total, there were 15 aromatic protons and 5 additional protons bonded to carbon. One signal at 10.2 p.p.m. and a very broad signal at ~2.5 p.p.m. were attributed to NH protons. A structure which fits this evidence is shown as **7**. If the substance has this structure, then it is of the type of one of the intermediates in osazone formation[8]. At present, it is not clear how this compound is derived from compound **6**. Compound **7** does not undergo a 1,4-elimination reaction on boiling in methanol with sodium methoxide, nor did nucleophilic substitution occur on treatment with sodium azide in *N*,*N*-dimethylformamide at 90°. Szarek *et al.*[9] have found that treatment of methyl 4,6-*O*-benzylidene-2-*O*-tosyl-α-D-*ribo*-hexopyranosid-3-ulose with hydroxylamine hydrochloride in pyridine gives an oximino-pyridinium salt (**8**) which readily undergoes nucleophilic substitution, probably by an overall 1,4-elimination–addition process. It is interesting to speculate whether an analogous phenylhydrazone–pyridinium salt is an intermediate in the formation of compound **7**. The source of the anilino ion in such a process is not explained.

The action of some nucleophiles on compound **4** was investigated. In general, it can be stated that the *β*-D-2- and *β*-D-3-phenylazoalkenes (**4** and **3**, respectively) both showed a higher reactivity towards nucleophiles than the α-D isomers (**1** and **2**).

When compound **4** was treated with sodium methoxide in methanol, it readily yielded methyl 4,6-*O*-benzylidene-3-*O*-methyl-*β*-D-*arabino*-hexopyranosid-2-ulose phenylhydrazone (**9**) in 70% yield. Consequently, the compound behaves with methoxide ion like compounds **2** and **3**, in which 1,4-addition occurs. It is interesting to compare this result with the treatment of the anomeric α-D-2-phenylazoalkene (**1**), in which rearrangement takes place to give compound **10**.

The phenylazoalkene system readily adds the elements of hydrazoic acid[2], and treatment of compound **4** with sodium azide gave methyl 3-azido-4,6-*O*-benzylidene-3-deoxy-*β*-D-*arabino*-hexopyranosid-2-ulose phenylhydrazone (**11**). Reduction of

compound **4** with sodium borohydride in methanol afforded methyl 4,6-*O*-benzylidene-3-deoxy-β-D-*erythro*-hexopyranosid-2-ulose phenylhydrazone (**12**), and treatment with sodium borodeuteride in deuteriomethanol gave the 3-deuterio analogue (**13**).

The structures of the phenylhydrazones **9**, **11**, **12**, and **13** were based on u.v., i.r., and n.m.r. spectral measurements; the configuration at C-3 was deduced from the magnitude of the $J_{3,4}$ coupling (*cf.* Ref. 2).

The direction of addition of nucleophiles to compounds **1**, **2**, and **3** was discussed by Collins *et al.*[2]. It has now been found that the β-2-arylazoglycenoside **4** gives *arabino* (equatorial) addition products, in each case with ease. Attack at C-3 from direction *a* (*trans* to the vicinal C-4 substituent) is sterically favourable and a $B_{2,5}$ conformation in the transition state can be adopted relatively easily[10] (see Fig. 1). In this connexion, it is considered that two factors influence the stereochemistry of the addition: namely, (*i*) the incoming nucleophile should be co-linear with the *p*-orbital of the carbon being attacked, to maintain maximal overlap of these orbitals through the transition state and (*ii*) bulky nucleophiles enter from the sterically less-hindered direction.

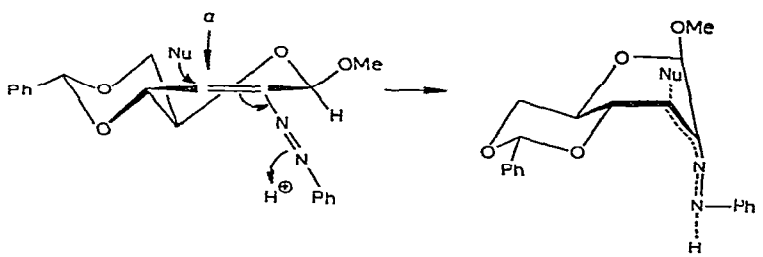

Fig. 1. Addition of a nucleophile to arylazoglycenoside **4**.

EXPERIMENTAL

General methods. — Melting points are uncorrected. Optical rotations were measured either with a Bellingham and Stanley polarimeter or with a Bendix type 147 automatic polarimeter. Chloroformic solutions were used unless stated otherwise.

Thin-layer chromatography was performed on microscope slides coated either with Silicagel GF_{254} (Type 60) (Merck) or Silicagel G (Merck). The plates were developed in benzene–ethyl acetate (9:1); detection was effected under u.v. light, or by spraying with 5% ethanolic sulphuric acid and heating at 150° for a few seconds.

Column chromatography was performed on Silicagel 60 (Merck). Drying of organic solutions was carried out with anhydrous sodium sulphate.

Infrared spectra were measured for solid samples dispersed in potassium bromide with a Perkin–Elmer Infracord model 137, and syrups were smeared on potassium bromide discs. Ultraviolet spectra were obtained for 96% ethanolic

solutions with a Perkin–Elmer model 402 spectrometer. 60-MHz n.m.r. spectra were determined with a Varian A-60D instrument with Me_4Si as internal standard. Mass spectra were measured by courtesy of the Physicochemical Measurements Unit, Harwell.

*Methyl 3-*O*-benzoyl-4,6-*O*-benzylidene-β-*D*-arabino-hexopyranosid-2-ulose phenylhydrazone.* — Methyl 3-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranoside [2 g; prepared according to Collins *et al.*[2]; m.p. 175–177°, $[\alpha]_D$ −109° (*c* 0.5)] was added to a mixture of dicyclohexylcarbodi-imide (2.1 g), anhydrous orthophosphoric acid (0.16 ml), and methyl sulphoxide (20 ml). The reaction mixture was stirred overnight, diluted with dichloromethane (200 ml), and filtered. The filtrate was washed with saturated, aqueous sodium hydrogen carbonate and water, dried, and concentrated to a crude product (1.8 g). This was recrystallised from dichloromethane–light petroleum to give the hexopyranosid-2-ulose (**5**) as fine needles, m.p. 167–168°, $[\alpha]_D$ −125° (*c* 1). Collins *et al.*[2] reported m.p. 166–168°, $[\alpha]_D$ −126°.

This compound (0.4 g) was shaken with phenylhydrazine hydrochloride (0.15 g, added in small portions) in ethanol (5 ml) for 16 h at room temperature. Concentration of the solution under reduced pressure gave a glass which was triturated with warm benzene. From the filtered solution, a buff-coloured solid (0.25 g, 50%) was obtained which was probably a *syn* and *anti* mixture of the title compound with m.p. 106° (dec.); ν_{max} 3350, 1740, 1610, and 1500 cm^{-1}; λ_{max} 283 nm (ε 20,000); δ 5.0–6.1 (complex, H-1,3, and benzylic H), 3.2–4.7 (complex m, H-4,5,6,6'), 3.48 and 3.52 (2 s, OMe), 6.7–8.3 (m, 3 Ph), 9.66 (bs, exchangeable with D_2O, NH).

Anal. Calc. for $C_{27}H_{26}N_2O_6$: C, 68.3; H, 5.5; N, 5.9. Found C, 68.1; H, 5.5; N, 6.0.

*Tosylation of methyl 4,6-*O*-benzylidene-β-*D*-glucoside.* — Methyl 4,6-*O*-benzylidene-β-D-glucoside (14 g) in pyridine (40 ml) was tosylated at room temperature for 20 h with toluene-*p*-sulphonyl chloride (10.5 g) in dry pyridine (40 ml). The mixture was poured into ice–water (500 g), and the oily product was collected and dried. Chromatographic, separation on a column, with gradual elution with benzene–ether, gave successively (*i*) the 2,3-di-*O*-tosyl derivative (1.8 g, 6%), m.p. 188–190°; (*ii*) the 3-*O*-tosyl derivative (7.4 g, 34%), m.p. 160–162°; and (*iii*) the 2-*O*-tosyl derivative (9.4 g, 43%), m.p. 122–124°. These compounds had melting points in good agreement with those given by Stirm[11], who reported m.p. 188–190° for the 2,3-di-*O*-tosyl, m.p. 162–163° for the 3-*O*-tosyl, and m.p. 123–124° for the 2-*O*-tosyl derivatives.

*Methyl 4,6-*O*-benzylidene-3-*O*-tosyl-β-*D*-arabino-hexopyranosid-2-ulose* (**6**). — Phosphoric oxide (1.3 g) was added in small portions to a solution of methyl 4,6-*O*-benzylidene-3-*O*-tosyl-β-D-glucoside (1.2 g) in methyl sulphoxide (1 ml) and *N*,*N*-dimethylformamide (30 ml). The stirred mixture was heated at 70° for 2 h and then poured into ice–water (150 g). The precipitate which formed was collected by filtration, washed with dilute, aqueous sodium hydrogen carbonate and water, and dried. The resulting *gem*-diol of the hexopyranosidulose was dehydrated by azeotropic distillation with toluene–methanol (20:1) to give the title compound (0.8 g, 70%), m.p. 190–191° (from light petroleum–chloroform); ν_{max} 1760 (C=O) and 1600 cm^{-1};

δ [$(CD_3)_2SO$] 5.63 and 5.30 (2 s, H-1 and benzylic H), 3.4–4.5 (m, 6 H), 3.48 (s, OMe), 2.35 (s, C–Me), 7.2–7.9 (Ar).

Anal. Calc. for $C_{21}H_{23}O_8S$: C, 58.0; H, 5.3; S, 7.4. Found: C, 57.8; H, 5.1; S, 7.6.

*Methyl 4,6-O-benzylidene-2,3-dideoxy-2-phenylazo-β-*D-erythro*-hex-2-eno-pyranoside* (**4**). — Methyl 4,6-*O*-benzylidene-3-*O*-tosyl-β-D-*arabino*-hexopyranosid-2-ulose (**6**, 0.8 g) and phenylhydrazine hydrochloride (0.3 g) were dissolved in dry pyridine (20 ml), and the reaction mixture was kept at room temperature for one week, when t.l.c. showed a single product (R_F 0.6) contaminated with a polar material, presumed to be pyridinium toluene-*p*-sulphonate. The reaction mixture was poured into ice–water (150 g) and the product was extracted with benzene (3 × 30 ml). The dried extract was evaporated, and the concentrate was passed through a short column of silica gel with benzene as eluant. The first 50 ml were discarded, and the next 100 ml were concentrated to a red syrup (0.45 g) which crystallised on storage. Compound **4** had m.p. 101–102° (from MeOH), $[\alpha]_D$ −164° (*c* 0.2); ν_{max} 1420 cm^{-1}; λ_{max} 307 nm (ε 22,000); δ (220 MHz) 5.95 (d, H-1, $J_{1,4}$ 2.0 Hz), 7.1 (d, H-3, $J_{3,4}$ 1.5 Hz), 4.68 (sextet, H-4, $J_{4,5}$ 8.5 Hz), 3.75 (octet, H-5, $J_{5,6a}$ 10.5 Hz, $J_{5,6e}$ 5.0 Hz), 3.95 (t, H-6*a*, $J_{6a,6e}$ 10.5 Hz), 4.45 (q, H-6*e*), 5.68 (s, benzylic H), 3.48 (s, OMe), 7.3–7.8 (m, Ar).

Anal. Calc. for $C_{20}H_{20}N_2O_4$: C, 68.1; H, 5.7; N, 8.0. Found: C, 67.8; H, 5.6; N, 8.2.

The reaction of compound **6** *with phenylhydrazine hydrochloride at 40°.* — Methyl 4,6-*O*-benzylidene-3-*O*-tosyl-β-D-*arabino*-hexopyranosid-2-ulose (0.8 g) (**6**) and phenylhydrazine hydrochloride (0.27 g) were dissolved in pyridine (10 ml), and the reaction mixture was kept at 40° for 2 days. The deep-red solution was poured into ice–water (50 g) and extracted with benzene (3 × 30 ml). The combined extracts were dried and concentrated to a glass. On addition of ethanol (5 ml), a white precipitate formed (0.27 g, 30%). This substance had m.p. 187–188°, $[\alpha]_D$ −420° (*c* 0.25); ν_{max} 3300, 1600, and 1500 cm^{-1}; λ_{max} 284 nm (ε 22,000); δ (100 MHz) 5.68 (s, 1 H), 4.48 (d, $J_{3,4}$ 5.0 Hz), 4.4–3.3 (m, 4 H), 5.52 (s, benzylic H), 6.8–7.6 (m, 15 H, Ar), 10.2 (s, N–NHPh), 2.5 (very broad signal, C–NHPh), M^+ 455.

Anal. Calc. for $C_{26}H_{27}N_3O_4$: C, 70.1; H, 6.1; N, 9.4. Found: C, 70.6, 69.5; H, 6.1, 6.1; N, 9.4, 9.4.

When this phenylhydrazone (20 mg) in methanol (1 ml) containing sodium methoxide (50 mg) was heated under reflux for 1 h, t.l.c. indicated no change was occurring and, after addition of water (0.5 ml), unchanged hydrazone (**7**) (20 mg) was isolated.

Likewise, starting material could be isolated when compound **7** (20 mg) was heated in *N*,*N*-dimethylformamide (1 ml) containing sodium azide (0.02 g) for several hours at 90°.

*1,4-Addition reactions with methyl 4,6-O-benzylidene-2,3-dideoxy-2-phenylazo-β-*D-erythro*-hex-2-enopyranoside* (**4**). — (*a*) *Methanol.* Sodium methoxide [generated from sodium hydride (0.02 g) in methanol (2 ml)] was added to a solution of the

2-phenylazo derivative (**4**, 0.2 g) in methanol (5 ml). The reaction mixture was kept at 35°, and within a few minutes a mass of white needles separated. These were collected, washed successively with methanol (1 ml) and water (10 ml), and dried to give methyl 4,6-*O*-benzylidene-3-*O*-methyl-β-D-*arabino*-hexopyranosid-2-ulose phenylhydrazone (**9**; 0.13 g, 70%), m.p. 162–163°; ν_{max} 3350, 1610, and 1500 cm^{-1}; λ_{max} 283 nm (ε 12,000); δ (100 MHz, $CDCl_3$) 5.68 (s, H-1), 4.22 (d, $J_{3,4}$ 7.5 Hz), 3.7–4.7 (m, H-4,5,6'), 4.46 (q, $J_{6,6'}$ 10, $J_{6,5}$ 5 Hz), 5.54 (benzylic H), 3.68 and 3.58 (2 s, OMe).

Anal. Calc. for $C_{21}H_{24}N_2O_5$: C, 65.6; H, 6.3; N, 7.3. Found: C, 65.8; H, 6.5; N, 7.5.

(*b*) *Elements of hydrazoic acid.* Sodium azide (0.2 g) and ammonium chloride (0.04 g) in water (3 ml) were added to a solution of compound **4** (0.2 g) in methanol (15 ml). The mixture was heated gently at 40° until the solution became clear and then was stored at room temperature for 24 h. Water (~0.5 ml) was added, and the cloudy solution was stored at 0° when methyl 3-azido-4,6-*O*-benzylidene-3-deoxy-β-D-*arabino*-hexopyranosid-2-ulose phenylhydrazone (**11**) (0.14 g) separated. It had m.p. 147–149°; ν_{max} 3350, 2080, 1600, and 1500 cm^{-1}; λ_{max} 280 nm (ε 15,000); δ [100 MHz, $(CD_3)_2CO$] 5.73 (s, H-1), 4.48 ($J_{3,4}$ 9.5 Hz), 3.65–4.05 (m, 3 H), 4.25–4.5 (m, 1 H), 5.63 (s, benzylic H), 3.60 (s, OMe), 7.10–7.60 (m, 2 Ph).

Anal. Calc. for $C_{20}H_{20}N_5O_4$: C, 60.9; H, 5.1; N, 17.7. Found: C, 61.0; H, 5.4; N, 17.8.

(*c*) *Sodium borohydride.* Sodium borohydride (45 mg) was added with stirring to a solution of compound **4** (0.27 g) in methanol (8 ml). After 5 min, a white, flocculent precipitate had formed. The reaction mixture was diluted with methanol (2 ml) and stirring was continued for a further 5 min. The reaction mixture was then cooled, and the precipitate which formed was collected. Methyl 4,6-*O*-benzylidene-3-deoxy-β-D-*erythro*-hexopyranosid-2-ulose phenylhydrazone (**12**, 0.25 g) was isolated as a mixture of *syn* and *anti* isomers, m.p. 146–149° (from MeOH); ν_{max} 3350, 1610, and 1500 cm^{-1}; λ_{max} 280 nm (ε 16,000).

Anal. Calc. for $C_{20}H_{22}N_2O_4$: C, 67.7; H, 6.3; N, 7.9. Found: C, 67.1; H, 6.1; N, 7.9.

(*d*) *Sodium borodeuteride.* The previous experiment was repeated on the arylazoglycenoside **4** (0.27 g), using sodium borodeuteride (0.04 g) in deuteriomethanol (6 ml). After reaction for 5 min, the reaction mixture was diluted with deuteriomethanol (2 ml). Methyl 4,6-*O*-benzylidene-3-deoxy-3-deuterio-β-D-*arabino*-hexopyranosid-2-ulose phenylhydrazone (**13**) (0.18 g) was obtained as a white solid, m.p. 154° [from $(CD_3)_2CO$–D_2O]; ν_{max} 3350, 1610, and 1500 cm^{-1}; λ_{max} 281 nm (ε 16,000); δ (C_6D_6) 5.22 and 4.42 (2 s, H-1 and benzylic H), 2.2 (d, $J_{3,4}$ 12 Hz), 4.14 (q, $J_{6,6'}$ 10, $J_{6,5}$ 4.5 Hz), 3.0–3.6 (m, 3 H), 3.03 (s, OMe).

Anal. Calc. for $C_{20}H_{20}D_2N_2O_4$: C, 67.4; H, 6.7; N, 7.9. Found: C, 67.2; H, 6.2; N, 7.9.

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