ture was heated under reflux for 3 hr. Most of the methanol was removed (about 200 ml) by distillation and 150 ml of ethyl acetate was added. Potassium chloride was removed (about 15 g) by filtration and was washed several times with ethyl acetate. The combined ethyl acetate solutions were neutralized with saturated $NaHCO_3$ solution and were dried over anhydrous magnesium sulfate. Removal of the solvent at reduced pressure yielded the pale yellow ketoxime. A single recrystallization from ligroin afforded 28.3 g (78%) of 3-oximinocamphor, mp 120–123° (reported[14] 131–133°). The product was used without further purification.

2-*exo*-Hydroxy-3-*exo*-aminobornane.—In a 2-l. three-necked flask, equipped with a condenser, a mechanical stirrer, and a dropping funnel, were placed 400 ml of anhydrous ethyl ether (dried over sodium wire) and 21.4 g (0.56 mol) of $LiAlH_4$. After the mixture had been stirred for 15 min, 33.9 g (0.19 mol) of 3-oximinocamphor in 400 ml of anhydrous ethyl ether was added from a dropping funnel at a rate such as to maintain reflux. After being heated under reflux overnight, the mixture was cooled to room temperature and excess $LiAlH_4$ was then destroyed by addition of wet ether, followed by cold water. A white curdy mass of aluminum hydroxide was removed by filtration and was washed several times with ether. The combined ether solutions were dried over anhydrous magnesium sulfate. When the solvent was removed, the residue was distilled under reduced pressure. The product which distilled at 65.1–65.8° (0.5 mm) solidified and was recrystallized from cold heptane. The yield was 23.6 g (75%), mp 213–214°.

Anal. Calcd for $C_{10}H_{19}NO$: C, 70.96; H, 11.32; N, 8.28. Found: C, 71.12; H, 11.47; N, 8.29.

A benzenesulfonate derivative was prepared, mp 147–149°.

Anal. Calcd for $C_{16}H_{23}NO_3S$: C, 62.13; H, 7.50; N, 10.34. Found: C, 62.33; H, 7.60; N, 10.65.

2-*exo*-Hydroxy-3-*exo*-aminobornane Hydrochloride (I).—Dry hydrogen chloride gas was bubbled through a vigorously stirred solution of 30 g of 2-hydroxy-3-aminobornane in 1 l. of dry ethyl ether. When the ether solution was acidic to litmus paper, addition of hydrogen chloride gas was halted and the white precipitate was collected. The yield was 33 g (90%). Further recrystallization from ether and methanol mixture afforded 27 g (74%) of hydrochloride salt, dec >175°.

Anal. Calcd for $C_{10}H_{20}NOCl$: C, 58.38; H, 9.79; N, 6.80; Cl, 17.23. Found: C, 58.15; H, 9.70; N, 6.93; Cl, 17.42.

When the hydrochloride salt was treated with 20% NaOH, free amine was collected as white crystals, mp 213–214°, which had the same nmr and ir as the amino alcohol from which the salt had been prepared.

2-*exo*-Hydroxy-3-*exo*-aminobornane-2,3-*d*.—The procedure described above for the preparation of the amino alcohol was followed except for the use of $LiAlD_4$. The deuterated hydrochloride salt (3.9 g) was isolated from 4.5 g of 3-oximinocamphor. The nmr spectrum of the deuterated salt in D_2O was identical with the protonated form except for the absence of signals at 3.33 and 3.83 ppm. When subjected to sublimation at 40° (0.5 mm), deuterated amino alcohol with mp 211–213° was obtained. The mass spectrum of the deuterated amino alcohol confirmed two deuterium atoms in the molecule.

Deamination of 2-*exo*-Hydroxy-3-*exo*-aminobornane Hydrochloride (I) in Water.—The hydrochloride salt (4.2 g) in 42 ml of H_2O was stirred and cooled in an ice–water bath. A solution of 3.1 g of $NaNO_2$ in 21 ml of H_2O was added. Eight drops of concentrated H_2SO_4 was added to induce the deamination reaction. The mixture was stirred for 4 hr and was stored overnight in a refrigerator. The mixture was poured into water and then was extracted with ethyl ether. Camphor was isolated by preparative gc using a 10-ft 20% Carbowax 20M column at 150°, mp 177–178° (reported[14] 178.8°). A 2,4-dinitrophenylhydrazone derivative was prepared, mp 167.5–168° (reported[15] 164°).

Deamination of 2-*exo*-Hydroxy-3-*exo*-aminobornane-2,3-d_2 Hydrochloride.—The procedure was the same as that described above. The nmr spectrum of deuterated camphor was identical with protonated camphor except for the signals for 3-exo and 3-endo protons which were absent. The mass spectrum showed two deuterium atoms in the molecule.

Registry No.—I, 25050-53-7; I benzenesulfonate, 30248-03-4; I HCl, 26126-95-4; II, 76-22-2.

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Synthesis of 1-*N*-Glycosyl-1,2,3-triazoles from Glycosyl Azides and Substituted Acetylenes

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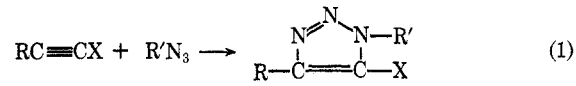
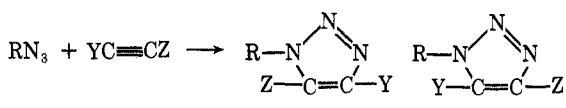
The additions of simple alkyl and aryl azides to various substituted acetylenes are known to produce the corresponding triazoles[1-4] (eq 1). As an extension



(1)

of this work, we investigated the addition of several fully acetylated β-D-glycosyl azides to acetylenes substituted by *N*,*N*-dialkylamino, ethoxy, and ethylthio groups. This study has led to some interesting observations. In particular, the additions of hepta-*O*-acetyl-β-D-maltosyl and hepta-*O*-acetyl-β-D-cellobiosyl azides to ethoxyacetylene were quite significant because each of them yielded both the possible isomeric triazoles. Previously reported additions of azides to ethoxyacetylene afforded only one of the two triazoles.

Addition of Glycosyl Azides 1a–d to Substituted Acetylenes 2a–d. (1) Addition to Ynamines 2a and



1a–d 2a–d 3a–k 4a–c

1a, R = D-glucosyl
b, R = D-galactosyl
c, R = maltosyl
d, R = cellobiosyl

2a, Y = CH_3; Z = $N(Et)_2$
b, Y = Ph; Z = $N(Me)_2$
c, Y = OEt; Z = H
d, Y = SEt; Z = Ph

3a, Y = CH_3; Z = $N(Et)_2$; R = D-glucosyl
b, Y = CH_3; Z = $N(Et)_2$; R = D-galactosyl
c, Y = CH_3; Z = $N(Et)_2$; R = maltosyl
d, Y = CH_3; Z = $N(Et)_2$; R = cellobiosyl
e, Y = Ph; Z = $N(Me)_2$; R = D-glucosyl
f, Y = Ph; Z = $N(Me)_2$; R = D-galactosyl
g, Y = Ph; Z = $N(Me)_2$; R = maltosyl
h, Y = H; Z = OEt; R = D-glucosyl
i, Y = H; Z = OEt; R = D-galactosyl
j, Y = H; Z = OEt; R = cellobiosyl
k, Y = H; Z = OEt; R = maltosyl

4a, Y = H; Z = OEt; R = cellobiosyl
b, Y = H; Z = OEt; R = maltosyl
c, Y = Ph; Z = SEt; R = cellobiosyl

D-glucosyl = 2,3,4,6-tetra-*O*-acetylglucopyranosyl

D-galactosyl = 2,3,4,6-tetra-*O*-acetylgalactopyranosyl

maltosyl = hepta-*O*-acetylmaltosyl

cellobiosyl = hepta-*O*-acetylcellobiosyl

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TABLE I

NMR DATA OF COMPOUNDS 3a–k AND 4a–c

Compd no.	Name	Nmr data, τ
3a	1-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucosyl)-4-methyl-5-*N*,*N*-diethylamino-*v*-triazole	3.9–4.7 (m, 4, ring H), 5.8 (m, 3, OCH_2 and ring H), 6.9 (q, 4, $N(CH_2)_2$), 7.6 (s, 3, CCH_3), 7.9 (s, 3, $OCOCH_3$), 8.0 (s, 3, $OCOCH_3$), 8.2 (s, 3, $OCOCH_3$), 9.0 (t, 6, $N(CH_2CH_3)_2$)
3b	1-(2,3,4,6-Tetra-*O*-acetyl-β-D-galactosyl)-4-methyl-5-*N*,*N*-diethylamino-*v*-triazole	3.74–4.9 (m, 5, ring H), 5.8 (s, 2, OCH_2), 6.9 (q, 4, $N(CH_2)_2$), 7.68 (s, 3, CCH_3), 7.78 (s, 3, $OCOCH_3$), 9.01 (t, 6, $N(CH_2CH_3)_2$)
3c	1-(Hepta-*O*-acetyl-β-D-maltosyl)-4-methyl-5-*N*,*N*-diethylamino-*v*-triazole	4.0–5.2 (m, 8, ring H), 5.7–5.8 (m, 6, OCH_2 and 2 ring H), 6.9 (q, 4, $N(CH_2)_2$), 7.7 (s, 3, CCH_3), 7.9–8.0 (m, 18, $OCOCH_3$), 8.3 (s, 3, $OCOCH_3$), 9.0 (t, 6, $N(CH_2CH_3)_2$)
3d	1-(Hepta-*O*-acetyl-β-D-cellobiosyl)-4-methyl-5-*N*,*N*-diethylamino-*v*-triazole	3.8–6.2 (m, 14, OCH_2 and ring H), 6.9 (q, 4, $N(CH_2)$, 7.7 (s, 3, CCH_3), 7.9–8.0 (m, 18, $OCOCH_3$), 8.2 (s, 3, $OCOCH_3$), 9.0 (t, 6, $N(CH_2CH_3)_2$
3e	1-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucosyl)-4-phenyl-5-*N*,*N*-dimethylamino-*v*-triazole	2.45 (m, 5, Ar H), 3.6–4.9 (m, 4, ring H), 5.7 (m, 3, OCH_2 and 1 ring H), 7.2 (s, 6, $N(CH_3)_2$), 7.9 (s, 9, $OCOCH_3$), 8.1 (s, 3, $OCOCH_3$)
3f	1-(2,3,4,6-Tetra-*O*-acetyl-β-D-galactosyl)-4-phenyl-5-*N*,*N*-dimethylamino-*v*-triazole	2.5 (m, 5, Ar H), 3.9–6.0 (m, 4, ring H), 5.8 (s, 3, OCH_2 and ring H), 7.2 (s, 6, $N(CH_3)_2$), 7.8 (s, 3, $OCOCH_3$), 7.9 (s, 6, $OCOCH_3$), 8.1 (s, 3, $OCOCH_3$)
3g	1-(Hepta-*O*-acetyl-β-D-maltosyl)-4-phenyl-5-*N*,*N*-dimethylamino-*v*-triazole	2.5 (m, 5, Ar H), 3.9–6.0 (m, 14, OCH_2 and ring H), 7.2 (s, 6, $N(CH_3)_2$), 7.9–8.0 (m, 18, $OCOCH_3$), 8.1 (s, 3, $OCOCH_3$)
3h	1-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucosyl)-5-ethoxy-*v*-triazole	3.0 (s, 1, C═CH), 4.0–5.0 (m, 5, ring H), 5.9 (m, 4, OCH_2), 7.9 (s, 6, $OCOCH_3$), 8.0 (s, 3, $OCOCH_3$), 8.2 (s, 3, $OCOCH_3$), 8.5 (t, 3, OCH_2CH_3)
3i	1-(2,3,4,6-Tetra-*O*-acetyl-β-D-galactosyl)-5-ethoxy-*v*-triazole	2.9 (s, 1, C═CH), 4.2–5.0 (m, 5, ring H), 5.7 (m, 4, OCH_2), 7.8–8.1 (m, 12, $OCOCH_3$), 8.6 (t, 3, OCH_2CH_3)
3j	1-(Hepta-*O*-acetyl-β-D-cellobiosyl)-5-ethoxy-*v*-triazole	2.9 (s, 1, C═CH), 4.0–6.1 (m, 16, OCH_2 and ring H), 7.8–8.1 (m, 18, $OCOCH_3$), 8.2 (s, 3, $OCOCH_3$), 8.5 (t, 3, OCH_2CH_3)
3k	1-(Hepta-*O*-acetyl-β-D-maltosyl)-5-ethoxy-*v*-triazole	3.0 (s, 1, C═CH), 4.2–6.1 (m, 16, OCH_2 and ring H), 7.9–8.0 (m, 18, $OCOCH_3$), 8.2 (s, 3, $OCOCH_3$), 8.5 (t, 3, OCH_2CH_3)
4a	1-(Hepta-*O*-acetyl-β-D cellobiosyl)-4-ethoxy-*v*-triazole	2.9 (s, 1, C═CH), 4.2–6.2 (m, 18, $OCOCH_3$), 8.1 (s, 3, $OCOCH_3$), 8.6 (t, 3, OCH_2CH_3)
4b	1-(Hepta-*O*-acetyl-β-D-maltosyl)-4-ethoxy-*v*-triazole	2.9 (s, 1, C═CH), 4.2–6.1 (m, 16, OCH_2 and ring H), 7.9–8.1 (m, 18, $OCOCH_3$), 8.1 (s, 3, $OCOCH_3$)
4c	1-(Hepta-*O*-acetyl-β-D-cellobiosyl-5-phenyl-4-ethylthio-*v*-triazole	2.5 (s, 5, Ar H), 4.2–6.1 (m, 14, OCH_2 and ring H), 7.2 (q, 2, SCH_2), 7.8 (m, 18, $OCOCH_3$), 8.2 (s, 3, $OCOCH_3$), 8.5 (t, 3, OCH_2CH_3)

2b.—The glycosyl azides **1a–d** were found to react readily with *N*,*N*-diethylaminoprop-1-yne (**2a**). The resulting adducts **3a**, **3c**, and **3d** were obtained by simple recrystallization, whereas the adduct **3b** could be isolated only as a colorless gum after column chromatography over silica gel. The addition of azides **1a–d** to *N*,*N*-dimethylaminophenylacetylene (**2b**)[5] required longer periods of refluxing (5–10 hr) and the product isolation involved column chromatography over silica gel. Only one of the adducts, **3e**, could be obtained crystalline, the rest (**3f**, **3g**) were identified as 1-*N*-glycosyl-1,2,3-triazoles by nmr and ir spectroscopy. The nmr data are included in Table I. The nmr spectra of compounds **3a–d** showed the expected signals for pyranose ring hydrogens as well as hydrogens of $OCOCH_3$, CCH_3, and $N(CH_2CH_3)_2$ groups. The nmr data also support the structures assigned to the triazoles **3e–g**, because in each case the phenyl hydrogens

(5) R. E. Harmon, C. V. Zenarosa, and S. K. Gupta, *J. Org. Chem.*, **35**, 1936 (1970).

TABLE II

PROPERTIES OF COMPOUNDS 3a–k AND 4a–c[a]

Compd no.	Mp, °C	Recrystn solvent	Yield, %	$[\alpha]^{25}D$,[b] deg
3a	162–162.5	C_6H_6, petroleum ether	97	−18.5 (*c* 1.5)
3b	Glass		82	−5.6 (*c* 1.5)
3c	138–139.5	C_6H_6, petroleum ether	83	33.2 (*c* 1.0)
3d	196–196.5	>=O, Et_2O	79	−28.4 (*c* 1.0)
3e	124.5–126.5	C_6H_6, petroleum ether	55	−29.3 (*c* 1.1)
3f	Glass		55	−10.6 (*c* 0.9)
3g	Glass		60	30.1 (*c* 1.5)
3h	151–152	>—OH	26	−16.8 (*c* 1.5)
3i	132.5–133.5	>=O, Et_2O, petroleum ether	16	−2.0 (*c* 1.5)
3j	169–170.5	>—OH	22	−22.5 (*c* 1.5)
3k	165.5–166	>=O, Et_2O, petroleum ether	18.5	47.8 (*c* 1.5)
4a	205.5–206.5	$CHCl_3$–Et_2O	11	−23.6 (*c* 1.5)
4b	173–173.5	CH_3OH	16	51.4 (*c* 1.5)
4c	175.5–177	>—OH, $CHCl_3$, Et_2O	18	−26.5 (*c* 1.5)

[a] C, H, and N analyses were within 0.3% of theoretical values. [b] All the rotations were measured using chloroform as solvent.

appeared as a broad multiplet centered around τ 2.50. This is in agreement with the observations of Garcia-Lopez, *et al.*[3] According to them, in the nmr spectrum the phenyl hydrogens of a 1-glycosyl-4-phenyl-*v*-triazole (like **3e–g**) appear as a broad multiplet, whereas in a 1-glycosyl-5-phenyl-*v*-triazole the phenyl hydrogens appear as a singlet.

(2) **Addition to Ethoxyacetylene** (2c).—The addition of glycosyl azides **1a–d** to ethoxyacetylene (**2c**) required much more severe conditions than the corresponding additions to ynamines. The reactions yielded complex mixtures and isolation of the product from them required extensive column chromatography over silica gel using a fraction collector. The resulting triazoles **3h–k** and **4a,b** could only be isolated in low yields (<35%). The addition of azides **1a** and **1b** led to the isolation of only one of the two possible isomeric triazoles in each case (structures **3h** and **3i**). On the other hand, all the possible triazoles (**3j**, **4a**, **3k**, and **4b**) were isolated from the addition of hepta-*O*-acetyl β-D-cellobiosyl azide (**1c**) and hepta-*O*-acetyl-β-D-maltosyl azide (**1d**). The nmr spectra (Table I) of each set of these isomeric triazoles were very similar but consistent with the structures. This is the first time that both the possible isomeric triazoles have been siolated from the addition of azides to ethoxyacetylene. All the previously reported examples[6–8] led to the isolation of only one (1-substituted 5-ethoxy-*v*-triazole) of the two isomeric triazoles.

(3) **Addition to 1-Ethylthio-2-phenylacetylene** (2d).—The reactions of the glycosyl azides **1a–d** with 1-ethylthio-2-phenylacetylene (**2d**) were slow. At temperatures below 110° no reaction seemed to take place except for the slow decomposition of the reactants. A crystalline triazole **4c** was obtained in low (18%) yield when a THF solution of **2d** and hepta-*O*-acetyl-β-D-cellobiosyl azide (**1d**) was heated in a sealed tube at 130–140° for 5 days. Even in this case, the reaction mixture turned black and required column chromatography over silica gel before any product could be isolated. The other additions of **1a–c** to **2d** did not lead to any isolable product. In the nmr spectrum (Table I) of **4c** the phenyl hydrogens appeared as a singlet at τ 2.52, suggesting, thereby, the correct structure of the adduct as depicted. The nmr spectrum of the isomeric triazole structure would have shown a broad multiplet for the phenyl hydrogens.[3] These results are also consistent with the observations of Groen and Arens,[9] who demonstrated that the 1,3-dipolar addition of diazomethane to **1d** takes place in a manner opposite to the 1,3-dipolar additions to ynamines (like **1a**, **1b**) or acetylenic ethers (like **1c**).

Experimental Section

Melting points were taken on a Thomas-Hoover Unimelt apparatus and are uncorrected. The nmr spectra were run using a Varian A-60 spectrometer with tetramethylsilane as internal standard and $CDCl_3$ as solvent. Thin layer chromatography (tlc) was carried out on glass plates coated with silica gel G. Spots on these plates were detected by a sulfuric acid spray followed by baking at 110° for 5–10 min. Dry column chromatography was carried out on glass columns (23 cm × 4.5 cm) packed with silica gel (200–325 mesh). An Instrument Specialist Co. fraction collector Model 272 was used for dry column chromatography.

Preparation of Glycosyl Azides.—The per-*O*-acetyl-β-D-glycosyl azides **1a–d** were prepared by heating the corresponding per-*O*-acetyl-α-D-glycosyl halides with sodium azide in dimethylformamide (DMF) by a procedure similar to that used by Yamamoto, *et al.*,[10] and Carrington, *et al.*[11] The general procedure is described below.

A slurry of per-*O*-acetyl-α-D-glycosyl halide (35.7 mmol) and sodium azide (77 mmol) in dry DMF (100 ml) was heated on a steam bath for 1.5 hr. On pouring the mixture over crushed ice (about 1 l.), the per-*O*-acetyl glycosyl azide precipitated out.

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(7) P. Grunanger, P. Finzi, and E. Fabbri, *Gazz. Chim. Ital.*, **90**, 413 (1969); *Chem. Abstr.*, **55**, 11397 (1961).
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(9) S. H. Groen and J. F. Arens, *Recl. Trav. Chim. Pays-Bas*, **80**, 879 (1961).
(10) A. Yamamoto, C. Miyashita, and H. Tsukamoto, *Chem. Pharm. Bull.*, **13**, 1036 (1965); *Chem. Abstr.*, **64**, 8281*f* (1966).
(11) R. Carrington, G. Shaw, and D. V. Wilson, *J. Chem. Soc.*, 6864 (1965).

Filtration, drying, and crystallization afforded the colorless crystals. A comparison of the observed melting points with the corresponding literature values is given below.

2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl azide (**1a**), mp 125.5–127.5° (lit.[12] mp 129°).

2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl azide (**1b**), mp 95–96° (lit.[13] mp 96°).

Hepta-*O*-acetyl-β-D-maltosyl azide (**1c**), mp 94–96° (lit.[14] mp 91°).

Hepta-*O*-acetyl-β-D-cellobiosyl azide (**1d**), mp 180–181° (lit.[6] mp 182–182.5°).

Preparation of 1-Ethylthio-2-phenylacetylene (**2d**).—The compound **2d** was prepared by treating phenylbromoacetylene[15] with sodium hydride and ethyl mercaptan in dry DMF according to the general procedure of Brandsma, *et al.*[16] The product was characterized: bp 92–96° (1.5 mm); refractive index, $n^{25}D$ 1.6075 (lit.[16] $n^{25}D$ 1.6133); and nmr τ 2.73 (m, 5, Ar H), 7.33 (q, 2, SCH_2), 8.68 (t, 3, SCH_2CH_3).

Addition of Glycosyl Azides 1a–d to Ynamines 2a–b.—A solution of the glycosyl azide (4.6 mmol) and ynamine (7 mmol) in dry THF (10 ml) was heated under reflux. When tlc of the reaction mixture showed the disappearance of the spot due to the azide, the solvent and the excess ynamine were removed by evaporation under reduced pressure. The triazoles **2a**, **3c**, and **3d** were obtained by simple crystallization of the residue. On the other hand, triazoles **3b**, **3f**, and **3g** were obtained by dry column chromatography over silica gel using a fraction collector. A mixture of chloroform and acetone (9:1) was used for elution of the products from the column. The properties are recorded in Table II. The ir spectra were also consistent with the structures proposed.

Addition of 1a–d to Ethoxyacetylene (**2c**).—A solution of the glycosyl azide (4.6 mmol) and ethoxyacetylene (7 mmol) in dry THF (10 ml) was heated in a sealed tube at 60–70° for 12 days. After that the solvent and excess ethoxyacetylene were removed by evaporation *in vacuo*. Dry column chromatography of the resulting black residue, as described above, afforded the corresponding triazole (Table II).

Addition of 1d to 1-Ethylthio-2-phenylacetylene (**2d**).—A solution of **1d** (4.6 mmol) and **2d** (7 mmol) in THF (10 ml) was heated in a sealed tube at 130–140° for 5 days. Column chromatography, as described above, of the resulting black gum afforded the crystalline triazole **4c** in low yield (Table II). The reactions of **2d** with the azides **1a–c** failed to give any isolable products.

Registry No.—**3a**, 29751-37-9; **3b**, 29751-38-0; **3c**, 29751-39-1; **3d**, 29751-40-4; **3e**, 29751-41-5; **3f**, 29751-42-6; **3g**, 29751-43-7; **3h**, 29751-44-8; **3i**, 29751-45-9; **3j**, 29751-46-0; **3k**, 29751-47-1; **4a**, 29751-48-2; **4b**, 29751-49-3; **4c**, 29751-50-6.

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(12) A. Bertho, *Chem. Ber.*, **63**, 836 (1930).
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(16) L. Brandsma, H. E. Wijers, and C. Jonker, *Recl. Trav. Chim. Pays-Bas*, **83**, 208 (1964).

2′,3′-Carbonates of 8-Hydroxypurine Nucleosides

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The synthesis of modified nucleosides has recently attracted a great deal of attention. Much of this effort has been directed toward nucleosides possessing an oxygen,[1–4] a sulfur,[4–6] or a nitrogen[7–8] bridge between the purine or pyrimidine ring and the sugar ring, in addition to the *N*-glycoside bond. Very successful syntheses of pyrimidine 2,2′-*O*-anhydronucleosides, particularly 2,2′-*O*-anhydrouridines[2] have been developed. However, published methods for obtaining purine 8,2′-*O*-anhydronucleosides are much less efficient[4,9,10] involving many steps and very low yields.

It has been shown[11] that uridine 2′,3′-carbonate can be converted in high yield to *O*²,2′-anhydrouridine by heating in dimethylformamide (DMF) in the presence of a base catalyst such as sodium bicarbonate. It occurred to us that the 2′,3′-carbonates of 8-hydroxyadenosine (**1a**) and 8-hydroxyguanosine (**1b**) might closely resemble uridine 2′,3′-carbonate and might therefore be easily converted to the corresponding 8,2′-*O*-anhydronucleosides. This report discusses the synthesis of compounds **1a** and **1b** and attempts to convert them to the anhydronucleosides.

Syntheses of 8-Hydroxypurine Nucleosides.—Syntheses of both 8-hydroxyadenosine and 8-hydroxyguanosine have been reported.[9,12,13] Our approach (Scheme I) to the 8-hydroxynucleosides was similar to that used by Holmes and Robins[12] to obtain 8-hydroxadenosine. The purine nucleoside **2** was first acetylated[14] to **3** and then brominated[15,16] to yield the 8-bromotriacetyl derivative **4**. Treatment with sodium acetate in refluxing acetic anhydride yielded, after work-up, the 8-hydroxytetraacetyl derivative **5**. Hydrolysis of the acetyl groups gave the 8-hydroxy nucleosides **6**.

The scheme worked smoothly for adenosine resulting in an overall yield of 41% for the conversion to 8-hydroxyadenosine. With guanosine the conversion of **4** to **5** was 53%. However, a 28% yield of 8-bromotetraacetylguanosine (**7**) was obtained and this was converted in 55% yield to **5**. Thus a good yield of **5** could be obtained by recycling the recovered 8-bromotetraacetylguanosine.

Conversion of the 8-hydroxypurine nucleosides **6** to their 2′,3′-carbonates was readily accomplished[2] by heating the nucleoside in DMF at 150° for 30 min with diphenyl carbonate in the presence of a catalyst (sodium bicarbonate). For comparison we first subjected guanosine and adenosine to these conditions and obtained guanosine 2′,3′-carbonate (**8**) and the previously reported[2] adenosine 2′,3′-carbonate (**9**) in 77 and 75% yields, respectively. 8-Hydroxyadenosine 2′,3′-carbonate (**1a**) and 8-hydroxyguanosine 2′,3′-car-

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