Anal. Calcd for $C_{10}H_9ClN_2O_2$: C, 53.46; H, 4.00; Cl, 15.81; N, 12.47. Found: C, 53.36; H, 4.08; Cl, 15.95; N, 12.60.

With acetic anhydride the *N*-oxide (IIb) rearranged to 6-chloro-7-ethoxy-2-hydroxyquinoxaline (VIIb) as light brown needles from ethanol, mp 255° dec.

Anal. Calcd for $C_{10}H_9ClN_2O_2$: C, 53.46; H, 4.00; N, 12.47. Found: C, 53.37; H, 4.04; N, 12.33.

Both IIb and VIIb with $POCl_3$ were converted to the same compound, 2,6-dichloro-7-ethoxyquinoxaline (Vb), as greyish-white needles from light petroleum, mp 133°.

Anal. Calcd for $C_{10}H_8Cl_2N_2O$: C, 49.39; H, 3.29; Cl, 29.22; N, 11.52. Found: C, 49.16; H, 3.33; Cl, 29.04; N, 11.55.

(2) The residue, obtained from the filtrate after removal of acetyl chloride, gave on crystallization from ethanol pink microneedles of 3-chloro-7-ethoxyquinoxaline 1-oxide (IIIb), mp 143–145°, yield 37%.

Anal. Calcd for $C_{10}H_9ClN_2O_2$: C, 53.46; H, 4.00; Cl, 15.81; N, 12.47. Found: C, 53.30; H, 4.10; Cl, 15.71; N, 12.56.

With $POCl_3$ IIIb gave a compound, mp 137–138° (pinkish white flakes from light petroleum), identical with 2,3-dichloro-7-ethoxyquinoxaline (VIb) prepared by the reaction of 2,3-dihydroxy-7-ethoxyquinoxaline[19] with $POCl_3$.

Procedure B.—A dark brown, clear solution was obtained after 16 hr of heating. The dark red, sticky residue left after removal of acetyl chloride was chromatographed on alumina and eluted with light petroleum. The first fraction (about 800 ml) of the eluent yielded colorless needles of 2,6-dichloro-7-ethoxyquinoxaline (Vb), mp 135° (yield 12%). The subsequent fraction (1 l.) gave light pink needles of 2,3-dichloro-7-ethoxyquinoxaline (VIb), mp 137–138° (yield 15%). Further elution with various solvent failed to give any more identifiable products.

(19) W. Autenrieth and O. Hinsberg, *Ber.*, **25**, 492 (1892).

Registry No.—Ia, 2423-66-7; Ib, 39266-91-6; Ic, 39266-92-7; Id, 33368-89-7; IIa, 39266-93-8; IIb, 39266-94-9; IIc, 39266-95-0; IId, 39266-96-1; IIIa, 5227-59-8; IIIb, 39266-98-3; IIIc, 39266-99-4; IIId, 39267-00-0; Vb, 39267-01-1; Vc, 39267-02-2; Vd, 39267-03-3; VIc, 39267-04-4; VId, 39267-05-5; VIIa, 39267-06-6; VIIb, 39267-07-7; VIIc, 39267-08-8; VIId, 39267-09-9; VIIIa, 35676-70-1; acetyl, 75-36-5; 6,7-dichloroquinoxaline, 19853-64-6; 7-chloroquinoxaline 1-oxide, 39267-11-3.

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The Reaction of Phenyl 2-*O*-Acetyl-4,6-*O*-benzylidene-3-deoxy-3-nitro-β-D-glucopyranoside with Alkali Azide

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The title compound **3** reacts with sodium azide or lithium azide in various media to yield predominantly one of the following products by selecting appropriate conditions: nitro azide **5**, triazole **6**, and **7**. The key factor in determining product was found to be the basicity of the medium. Similar results were obtained when nitro olefin **4**, derived from the title compound, or nitro azide **5** was used as a starting material. Structures **6** and **7** were deduced from their nmr, mass, and ir spectra, and the mechanisms involved in the formation of **5**, **6**, and **7** are discussed.

In previous papers[2,3] we have dealt with the synthesis of a new type of nucleosides, in which the purine or pyrimidine moiety is linked to the C-2 position of a 3-nitroglucopyranoside. In this reaction α-nitro olefin **2**, formed from methyl 2-*O*-acetyl-4,6-*O*-benzylidene-3-deoxy-3-nitro-β-D-glucopyranoside (**1**) by the elimination of acetic acid, was assumed to be an intermediate.[4]

Recently the following similar substitution reaction was observed. The thermodynamically unstable *all-cis*- (1*r*,2*c*,3*c*) and *cis,trans*- (DL-1*r*,2*c*,3*t*) dianilino derivatives were isolated in 30 and 20% yields, respectively, on treatment of 1*r*,3*c*-diacetoxy-2*t*-nitrocyclohexane with aniline, but only a trace of thermodynamically more stable *all-trans* (1*r*,2*t*,3*c*) isomer was detectable by tlc.[5] The fact that the thermodynamically stable isomer was not formed in quantity in this reaction can be explained by assuming that subsequent epimerization of the two products is slow. If the reaction proceeds *via* a nitro olefin intermediate, the products may be formed by kinetic control; on the other hand, they may conceivably be formed by an SN2 reaction with starting material. We have therefore studied further the reaction of **3** with alkali azide, which is generally accepted as a typical SN2-type nucleophile, in a variety of media and we have found that this reaction affords the corresponding nitro azide **5** and/or the triazole derivatives (**6**, **7**) in excellent yield (Scheme I) and that one of the three products can be obtained exclusively by selecting appropriate reaction conditions. The details are described herewith.

Results and Discussions

Structural Assignment of the Products.—Phenyl 2-azido-4,6-*O*-benzylidene-2,3-dideoxy-3-nitro-β-D-glucopyranoside (**5**), phenyl 4,6-*O*-benzylidene-2,3-dideoxy-β-D-*erythro*-hexopyranosido[2,3-*d*]triazole (**6**), and phenyl 4,6-*O*-benzylidene-2,3-dideoxy-3-nitro-2-(phenyl 4′,6′-*O*-benzylidene-2′,3′-dideoxy-β-D-*erythro*-hexopyranosido[2′,3′-*d*]triazolyl)-β-D-glycopyranoside (**7**) were obtained as exclusive products by the reaction

(1) Department of Chemistry, Yokohama City University, Mutuura-cho, Kanazawa-ku, Yokohama 236, Japan.

(2) T. Nakagawa, T. Sakakibara, and S. Kumazawa, *Tetrahedron Lett.*, 1645 (1970).

(3) T. Sakakibara, S. Kumazawa, R. Sudoh, and T. Nakagawa, *Carbohyd. Res.*, in press.

(4) The chemistry of nitro sugars was reviewed by H. H. Baer: H. H. Baer, *Advan. Carbohyd. Chem.*, **24**, 69 (1969).

(5) T. Nakagawa, T. Sakakibara, and F. W. Lichtenthaler, *Bull. Chem. Soc. Jap.*, **43**, 3861 (1970).

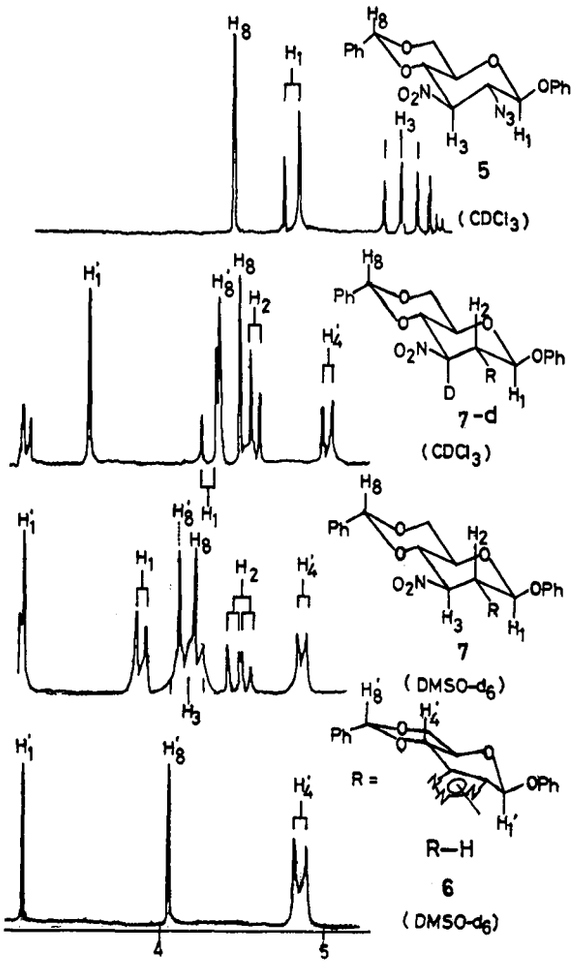


Figure 1.—Partial nmr spectra of **5**, **6**, and **7** at 100 MHz.

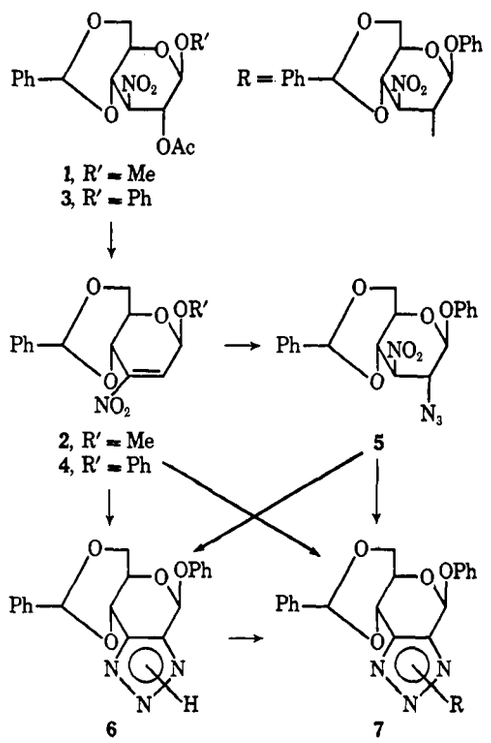
of **3** with alkali azide when reaction conditions which will be described later are employed. Structural assignment of **5**, **6**, and **7** was based on the following data.

5.—Its ir spectrum (KBr) shows the presence of an azide group (2100 cm^{-1}) and of a nonconjugated nitro group (1560 cm^{-1}). The large value of the coupling constants of the nmr signals of the ring protons, *i.e.*, $J_{1,2} = 7.5$, $J_{2,3} = J_{3,4} = 10$ Hz, indicates the β-gluco configuration.

6.—No ir absorption bands corresponding to nitro and azide group were observed. The elemental analysis of this product is in full accordance with the formula $C_{19}H_{17}H_3O_4$ which was, in addition, supported by the observation of a mass spectral peak at *m/e* 351. The sugar moiety contains only five protons as shown by the nmr spectrum (Figure 1). A sharp 1 H singlet at τ 3.16 and a 1 H doublet at 4.86 with a spacing of 7.5 Hz are assigned to H-1 and H-4, respectively, suggesting the absence of protons on the C-2 and C-3 atoms. From these data, and in the view of the results reported by Zefirov, *et al.*,[6] on the similar reaction of nitrostyrenes with sodium azide in DMSO giving triazoles, compound **6** is deduced to have a triazole skeleton, but the location of the hydrogen on the ring has not yet been determined.

7.—The ir spectrum (KBr) of this product showed

SCHEME I



no absorption of an azide group but a nitro group (1560 cm^{-1}). Its elemental analysis corresponded to $C_{38}H_{34}N_4O_{10}$, which is further confirmed by the appearance of the molecular ion peak at *m/e* 706. Catalytic reduction of **7** with Raney nickel in dioxane containing a trace amount of triethylamine afforded colorless crystalline phenyl 3-amino-4,6-*O*-benzylidene-2,3-dideoxy-2-(phenyl 4′,6′-*O*-benzylidene-2′,3′-dideoxy-β-D-*erythro*-hexopyranosido[2′,3′-*d*]triazolyl)-β-D-glucopyranoside (**8**), which was characterized as its *N*-acetyl derivative **9** after acetylation as usual. In the nmr spectrum of **7** (Figure 1) 1 H signals at τ 3.13 (s), 4.07 (s), and 4.85 (d) could be assigned to H-1′, H-8′ (benzylidene methine proton), and H-4′, respectively, by comparison with those of **6**; hence the other signals at τ 3.83 (d), 4.19 (s), 4.15 (t), and 4.45 (q) corresponded to H-1, H-8 (benzylidene methine proton), H-3, and H-2, respectively. These assignments were further confirmed by comparison with the spectrum of the C-3-deuterated derivative of **7** (Figure 1). **7** was deduced to have the β-gluco configuration for its nitro sugar moiety on the basis of the coupling constants $J_{1,2} = 7.5$, $J_{2,3} = J_{3,4} = 10$ Hz. The presence of the triazole nucleus[7] was indirectly confirmed by determining the uv spectrum of methyl 4,6-*O*-bromoethylidene-2,3-dideoxy-2-(methyl 4′,6′-*O*-bromoethylidene-2′,3′-dideoxy-β-D-hexopyranosido[2′,3′-*d*]triazolyl)-3-nitro-β-D-hexopyranoside (**10**) at 228.5 nm, (ε 1.1 × 10^4), which was prepared from methyl 2-*O*-acetyl-4,6-*O*-bromoethylidene-3-deoxy-3-nitro-β-D-glucopyranoside (**14**) and sodium azide by treatment under the same condition as had been employed in the reaction of **3**. This fact is, moreover, in good agreement with the proposed mechanism for the formation of **7** which will be

(6) N. S. Zefirov, N. K. Chapovakaya, and V. V. Kolesnikov, *Chem. Commun.*, 1001 (1971). 8-Azapurines and *v*-triazole[4,5-*b*]pyridines were obtained on the treatment of 5-nitropyrimidines and 5-nitropyridines with sodium azide, respectively: H. Ulrich, I. Wempen, and J. J. Fox, *J. Org. Chem.*, **35**, 1131 (1970).

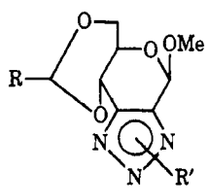
(7) These compounds involving such a nucleus generally show an uv absorption band in the vicinity of 225 nm with molar extinction coefficient of ~4 × 10^4. *E.g.*, L. W. Hartzel and F. R. Benson, *J. Amer. Chem. Soc.*, **76**, 667 (1954); G. B. Barlin, *J. Chem. Soc., B*, 641 (1967).

TABLE I

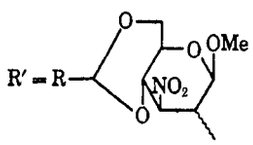
REACTIONS WITH SODIUM AZIDE AND HYDRAZOIC ACID

Expt	Starting material (S)	Reagents (R)	Mole ratios of R to S	Solvent systems[a]	Yields, %, of products[b] 5 (5-*d*)	6	7 (7-*d*)
1	3	NaN_3	1	A	93	t	t
2	3	NaN_3	1	B or C		t	85
3	3	NaN_3, NaOH	1, 1	A		t	q
11	4	NaN_3	1	A		t	83
12	4	NaN_3	2	A		t	q
13	4	NaN_3	1	B or C		t	q
14	4	HN_3, AcONa	excess, 1	D			
	4	NaN_3, AcOH	1, 1	A	q		
15	4	NaN_3, AcOH	1, 1	B		t	q
16	4	HN_3	1	A	q		
17	4	HN_3	1	A-*d*	50 (50)		
18	4	NaN_3, HN_3	1, excess	A	q	t	
19	4	NaN_3, HN_3	1, excess	A-*d*	(q)	t	
20	4	NaN_3	1	E			q
21	5	NaN_3	1	A-*d*	(q)		
22	5	NaN_3	1	B-*d*		t	(q)
23	5	NaOAc	1	A	q		
24	5	NaOAc	1	B		t	q
25	5	NaN_3	1	DMF or DMSO	t	q	t
26	5	NaN_3	1	THF-D_2O	(q)	t	t

[a] A, CH_3CN-H_2O (8:1, v/v); A-*d*, CH_3CN-D_2O (8:1, v/v); B, DMF-H_2O (8:1, v/v); B-*d*, DMF-D_2O (8:1, v/v); C, DMSO-H_2O (8:1, v/v); D, $CHCl_3$-H_2O (8:1, v/v); E, Carbitol. [b] t, trace; q, quantitative or almost so; blank indicates that product could not be detected by tlc.



10, R = CH_2Br
11, R = Ph



discussed later, but final determination of the bonding position of the nitro sugar moiety on the triazole skeleton has not yet been accomplished, although it likely linked to N-2 of the triazole nucleus on steric grounds.

Incidentally, the mass spectra of **6** and **7** were examined in detail. Although carbohydrates[8] and aliphatic and alicyclic nitro compounds[9] are generally said to exhibit no molecular ion peaks, weak peaks corresponding to the molecular ion were observed in the case of **6** and **7** at *m/e* 351 and 706, respectively. Comparatively strong peaks appear in mass spectra of **7** at *m/e* 613.1972, 583.1854, 507.1538, and 477.1453, which are in accord with M − C_6H_5O (613.1934), M − $C_7H_7O_2$ (583.1828), M − $C_{13}H_{11}O_2$ (507.1515), and M − $C_{14}H_{13}O_3$ (477.1410), respectively. Analogous peaks were observed in **6** at *m/e* 258, 228, 152, and 122. These results may be explained as follows. The phenoxy radical is split off from the molecular ions Ia,b to give cations IIa,b, which were presumably subjected to a successive elimination of formaldehyde and benzaldehyde affording oxetane ions IIIa,b, IVa,b, and pyran ions Va,b, respectively (Scheme II).

Correlation of Products and Reaction Conditions.— As previously described, the structure of the product varies depending on the reaction conditions. The details are discussed in this section.

The reaction of nitro acetate **3** with an equivalent of sodium azide in acetonitrile–water (8:1 v/v) at room temperature gave nitro azide **5** in 93% yield, along with trace amounts of the triazole derivatives **6** and **7** (expt 1, Table I). Under similar conditions, on the other hand, nitro olefin **4** afforded a different product, *i.e.*, **7**, in 83% yield. A trace of **6** was also detected by tlc (expt 11), but no **5**. On the basis of these results **4** can not be assumed to be the intermediate for the reaction leading from **3** to **5**, but this assumption ignores the potential participation of acetic acid, which may equilibrate with sodium azide as shown in eq 1 and is thus

$$NaN_3 + CH_3COOH \rightleftharpoons HN_3 + CH_3COONa \quad (1)$$

released in the course of the reaction. Therefore, the reaction of **4** with hydrazoic acid in aqueous chloroform with sodium azide in aqueous acetonitrile was studied in the presence of sodium acetate and acetic acid, respectively. Both reaction conditions afforded **5** exclusively and no **7** (expt 14). If sufficient amounts of a base were present to neutralize the acetic acid produced, the reaction of **3** with sodium azide could be expected to proceed similarly to that of **4**. In fact, treatment of **3** with sodium azide in the presence of an equivalent of sodium hydroxide yielded only **7** (expt 3). Consequently, the assumption that **4** is not the reaction intermediate can be said to be erroneous.

A striking solvent effect was observed in the reaction of **3** with sodium azide. When either aqueous DMF or aqueous DMSO was used as the solvent, **7**, but no **5**, was isolated in 85% yield (expt 2). In most instances, the amount of **6** produced was too small to isolate and it was only detected by tlc. However, the reaction of **5** with sodium azide in freshly distilled DMF afforded **6** as the major product, which was isolated by silica gel column chromatography (expt 25). The application of lithium

(8) N. K. Kochetkov and O. S. Chizhvov, *Advan. Carbohyd. Chem.*, **21**, 39 (1966).

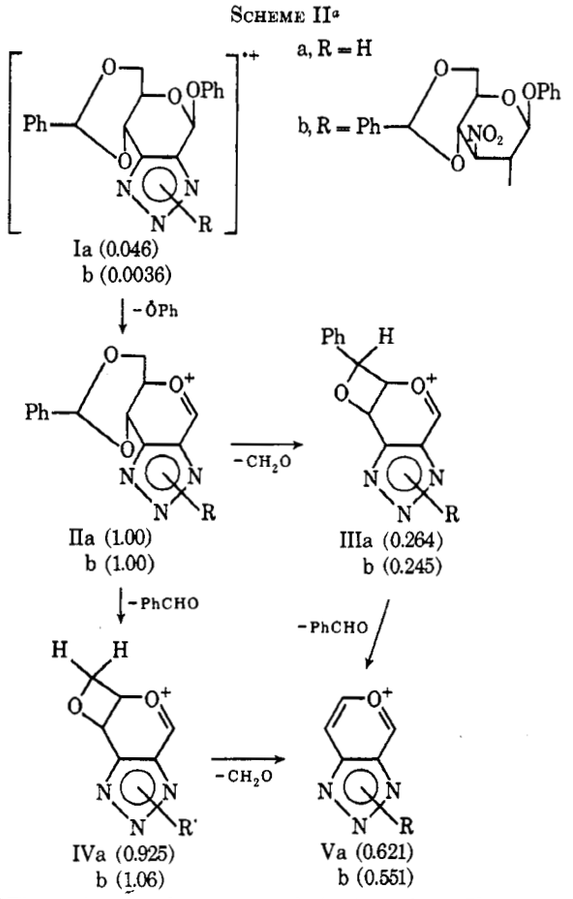
(9) R. T. Aplin, M. Fischer, D. Becher, H. Budzikiewicz, and C. Djerassi, *J. Amer. Chem. Soc.*, **87**, 4888 (1965).

TABLE II
REACTIONS WITH LITHIUM AZIDE

Expt	Starting materials (S)[a]	Reagents (R)[a]	Solvent	Yields of products 5	6	7
31	3	LiN_3	EtOH	q		t
32	3	LiN_3	THF	q		
33	3	LiN_3	CH_3CN	q		
34	3	LiN_3	DMF		q	
35	3	LiN_3	DMSO		q	
41	4	LiN_3	EtOH	t	t	q
42	4	LiN_3	THF	t	t	q
43	4	LiN_3	CH_3CN			q
44	4	LiN_3	DMF		q	t
45	4	LiN_3	DMSO		q	t
46	4	6	CH_3CN			q
51	5	LiN_3	CH_3CN	q	t	t
52	5	LiN_3	THF	q	t	t
53	5	LiN_3	DMF		q	t
54	5	LiOAc	CH_3CN	q	t	
55	5	LiOAc	DMF		q	t

[a] Mole ratio of reagent to starting material is 1:1.

SCHEME II[a]



[a] Figures in parentheses mean relative intensity to II.

azide as a nucleophile in these aprotic solvents made the exclusive formation of **6** possible (expt 34, 35, 44, 45, and 53, Table II).

The reaction of **4** with hydrazoic acid was studied by use of deuterium oxide in order to shed light on the possibilities that the reaction may proceed through 1,4 addition[10] to afford an *aci*-nitro form which isomerizes to the corresponding nitro form by an intermolecular proton exchange, that reversal of the Michael-type addition[11] could occur with great ease, and that the rate of deuterium exchange between deuterium oxide and hydrazoic acid may be much more rapid than that of the addition. If this were the case, deuteration at the 3 position should go to completion. Treatment of **4** with hydrazoic acid in acetonitrile–deuterium oxide (8:1, v/v), however, gave **5** containing the deuterated derivative in only 50% yield, which was determined from the nmr spectrum (expt 17). This suggests that the reaction of hydrazoic acid with **4** may involve, at least partly, irreversible 1,2 addition of hydrazoic acid to the C_2–C_3 double bond of **4**, and that the rate of reaction 2 is comparable with that of the addition reaction.

$$HN_3 + D_2O \rightleftharpoons DN_3 + HOD \qquad (2)$$

To our knowledge, no example is known of a one-step cyclization involving the powerfully nucleophilic azide ion. It has been accepted that the reaction of nitriles with lithium azide to give tetrazoles proceeds by a two-step mechanism involving initial nucleophilic attack of the azide ion on the carbon atom of the cyano group followed by cyclization of the adduct to the tetrazole.[12] On this basis, the reaction of **4** with sodium azide giving triazole **6** seems to proceed by a two-step mechanism, a conclusion which may be supported by the fact that nitro azide **5** also afforded triazole **6** or **7** depending on the reaction condition. In this case, nitrite ion must be eliminated from nitro azide **5** or its nitronate **5′**. Two routes may be considered for this process: (i) one *via* a vinyl azide or a carbene,[6] (ii) the other *via* a sodium nitronate. Of these the former may be discounted since the Michael-type addition is, in general, considered as one involving a reversible process,[11] and elimination of hydrazoic acid would occur more easily than that of nitrous acid. In fact, treatment of **5** with sodium methoxide in methanol gave phenyl 4,6-*O*-benzylidene-3-deoxy-2-*O*-methyl-3-nitro-β-D-glucopyranoside (**12**) by a reaction involving only exchange of the azide group for the methoxy group. Thus the reaction should proceed by the second route: sodium 2-azido-3-nitronate **5′**, which was formed directly by the attack of sodium

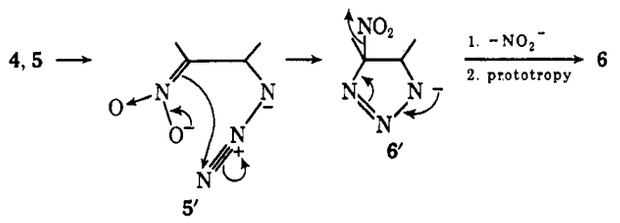
(10) The Michael-type addition is generally accepted to proceed through 1,4 addition. *E.g.*, J. March, "Advanced Organic Chemistry. Reactions, Mechanisms, and Structure," McGraw-Hill, London, 1968, pp 567–568.

(11) S. Patai and Z. Rappoport in "The Chemistry of Alkenes," S. Patai, Ed., Interscience, London, 1964, Chapter 8.

(12) A. I. Meyers and J. C. Sircar in "The Chemistry of the Cyano Group," Z. Rappoport, Ed., Interscience, London, 1970, Chapter 8.

azide on **4** (1,4 addition) or indirectly from **5**, cyclizes irreversibly to an unstable intermediate triazoline **6'**, which leads to the more stable triazole **6** by rapid elimination of a nitrite ion[13] and subsequent prototropy (Scheme III).

SCHEME III



With regard to the formation of **7** from **3** or **4**, it is deduced to be formed not by 1,3 cycloaddition of **5** to **4**, but by Michael-type addition of intermediate **6** to **4** on the basis of the following facts: (i) treatment of **6** with **4** affords **7** exclusively and with great ease even in the absence of ctalysts (expt 46), similar to the reaction of heterocyclic compounds such as theophylline, 2,6-dichloropurine, and uracil with nitro acetate **1** or nitro olefin **2**;[2,3] (ii) nitro azide **5** does not react with methyl 2-eno-3-nitropyranoside **2** without catalyst and both compounds were recovered quantitatively [in the presence of an equivalent of sodium azide in aqueous acetonitrile, on the other hand, **2** was converted into **11** (the methyl glycoside analog of **7**) in 62% yield, whereas most of **5** was recovered]; (iii) nitro olefin **4** does not react at room temperature in the absence of catalyst with picryl azide,[14] which is known as a typical reagent for 1,3 cycloaddition.

Tables I and II show the following trends: (i) **3**, **4**, and **5** in anhydrous DMF or DMSO gave **6** exclusively (expt 25, 34, 35, 44, 45, and 53); (ii) **3**, **4**, and **5** gave **7** exclusively in aqueous DMF or DMSO (expt 2, 13, and 22); (iii) treatment of **3** and **5** in anhydrous or aqueous ethanol, THF, chloroform, or acetonitrile afforded no product other than **5** (expt 1, 21, 26, 31, 32, 33, 51, and 52); (iv) treatment of **4** under the same conditions as described in iii afforded only **7** (expt 11, 12, 41, 42, and 43).

Experimental Section

Melting points were determined in capillaries and are uncorrected. Specific rotations were measured with a Carl Zeiss photoelectric polarimeter. Nmr spectra were recorded at 100 MHz with a spectrometer JNM-4H-100 (JEOL), using tetramethylsilane as an internal standard. Column chromatography was carried out on silica gel (100 mesh powder, Mallinckrodt, St. Louis) and developed with benzene. Tlc were performed on silica gel (Wakogel B-5, Japan) with a solvent system of xylene–acetonitrile (10:1, v/v). Mass spectra were taken on a spectrometer JMS-01SG (JEOL).

Solvents.—Anhydrous acetonitrile was prepared by treatment with anhydrous potassium carbonate, followed by several distillations from phosphorus pentoxide. Ethanol was purified by adding ~5% benzene as azeotroping agent followed by fractional distillation. Tetrahydrofuran was purified by treatment with potassium hydroxide and distilled from sodium. Dimethylformamide, dimethyl sulfoxide, and Carbitol were purified by distilling under reduced pressure followed by treatment with molecular sieves 3A (1/16).

Materials.—Hydrazoic acid was prepared according to Wolff.[15] Commercial sodium azide was used without further purification. Lithium azide prepared from lithium sulfate and sodium azide was recrystallized twice from water and dried [90°, (20 mm), 3 hr] before use. Typical procedures for the reaction of nitro acetate **3** and nitro olefin **4** with sodium azide and lithium azide are described. These procedures are almost exact prototypes for the experiments summarized in Tables I and II.

Phenyl 2-*O*-Acetyl-4,6-*O*-benzylidene-3-deoxy-3-nitro-β-D-glucopyranoside (3).—Phenyl 3-deoxy-3-nitro-β-D-glucopyranoside (30 g),[16] zinc chloride (50 g), and benzaldehyde (125 g) were stirred together at room temperature for 30 hr. Water (500 ml) was added to this mixture. A semicrystalline mass, separated upon addition of petroleum ether (600 ml, bp 30–60°), was collected and washed twice with 200 ml of petroleum ether. Without further purification, to a solution of pyridine (200 ml) dissolved in the benzylidene derivative was added acetic anhydride (65 ml) under cooling with ice water. The reaction mixture was left overnight at room temperature and then poured into 800 ml of ice water. The separated crude acetate was washed thoroughly with water to remove all traces of pyridine and dried. Crystallization from benzene furnished the acetate **3** (35 g): mp 204–205°; $[\alpha]^{20}D$ −109° (*c* 1, $CHCl_3$).

Anal. Calcd for $C_{21}H_{21}NO_8$: C, 60.72; H, 5.10; N, 3.37. Found: C, 60.67; H, 5.23; N, 3.22.

Phenyl 4,6-*O*-Benzylidene-2,3-dideoxy-3-nitro-β-D-*erythro*-hex-2-enopyranoside (4).—**3** (80 g) and dry sodium bicarbonate (120 g) in distilled benzene (600 ml) were refluxed, with stirring, for 60 hr. The reaction mixture was allowed to cool and filtered, and the filtrate was evaporated to give a nearly colorless crystalline residue of **4**. Recrystallization from benzene afforded compound **4** (80%): mp 144–145°; $[\alpha]^{20}D$ −142° (*c* 1, $CHCl_3$).

Anal. Calcd for $C_{19}H_{17}NO_6$: C, 64.22; H, 4.82; N, 3.94. Found: C, 64.38; H, 4.98; N, 3.72.

Methyl 4,6-*O*-Bromoethylidene-3-deoxy-3-nitro-β-D-glucopyranoside (13).—Methyl 3-deoxy-3-nitro-β-D-glucopyranoside (1.9 g), bromo acetal (4 ml), and concentrated sulfuric acid (0.1 ml) in diethyl ether (15 ml) were stirred for 3 days at room temperature. The mixture was neutralized of 1 *N* sodium hydroxide and poured into 10 ml of water. A semicrystalline material, precipitated upon addition of petroleum ether (80 ml), was collected and washed twice with 10 ml of petroleum ether. Recrystallization from ethanol afforded **13** (75%): mp 215–216° dec; $[\alpha]^{20}D$ −78.5° (*c* 1, acetone).

Anal. Calcd for $C_9H_{14}NO_7Br$: C, 32.93; H, 4.27; N, 4.27. Found: C, 32.75; H, 4.21; N, 4.29.

Methyl 2-*O*-Acetyl-4,6-*O*-bromoethylidene-3-deoxy-3-nitro-β-D-glucopyranoside (14).—To a solution of 3.2 g of **13** in pyridine (20 ml) was added 12 ml of acetic anhydride under cooling with ice water. The reaction mixture was allowed to stand overnight at room temperature and then poured into 150 ml of ice water. The precipitated crude acetate was washed thoroughly with water. Crystallization from aqueous ethanol furnished the acetate **14** (95%): mp 177.0–177.5°; $[\alpha]^{20}D$ −46.8° (*c* 1, $CHCl_3$).

Anal. Calcd for $C_{11}H_{16}NO_8Br$: C, 35.68; H, 4.32; N, 3.78. Found: C, 35.67; H, 4.06; N, 3.85.

Reaction of Phenyl 2-*O*-Acetyl-4,6-*O*-benzylidene-3-deoxy-3-nitro-β-D-glucopyranoside (3) with Sodium Azide. i. Using Acetonitrile as the Solvent.—To a solution of **3** (830 mg, 2.0 mmol) in acetonitrile (24 ml) containing water (3 ml) was added sodium azide (143 mg, 2.2 mmol). The mixture was gently agitated for 10 hr at room temperature by means of a magnetic stirrer and then evaporated *in vacuo* at 40°. The remaining material was washed with water and crystallized from ethanol to give 740 mg (93%) of **5** as needles of mp 180° dec, R_f 0.78, and $[\alpha]^{20}D$ −43.1° (*c* 1, $CHCl_3$).

Anal. Calcd for $C_{19}H_{18}N_4O_6$: C, 57.28; H, 4.55; N, 14.07. Found: C, 57.47; H, 4.68; N, 14.10.

ii. **Using Dimethylformamide as the Solvent.**—To a solution of **3** (830 mg, 2.0 mmol) in DMF (12 ml) and water (1.5 ml) was added sodium azide (143 mg, 2.2 mmol). The mixture was stirred for 10 hr at room temperature and then poured into 100 ml of water. A separated semicrystalline mass was collected. Recrystallization from acetone–ethanol afforded **7** (600 mg, 85%): mp 238–239° dec; R_f 0.69; $[\alpha]^{20}D$ −36.7° (*c* 1, $CHCl_3$).

(13) If the nitro group is situated at the β position of carbonyl or ester group, nitrous acid can be eliminated easily. *E.g.*, M. C. Kloetzel, *J. Amer. Chem. Soc.*, **70**, 3571 (1948); H. H. Baer and W. Rank, *Can. J. Chem.*, **47**, 2811 (1969).

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Anal. Calcd for $C_{38}H_{34}N_4O_{10}$: C, 64.58; H, 4.85; N, 7.93. Found: C, 64.77; H, 4.98; N, 8.15.

Reaction of Phenyl 4,6-*O*-Benzylidene-2,3-dideoxy-3-nitro-β-D-*erythro*-hex-2-enopyranoside (4) with Hydrazoic Acid.—To **4** (355 mg, 1 mmol) in acetonitrile (8 ml) was added a chloroform solution containing excess hydrazoic acid. The mixture was stirred for 10 hr at room temperature and then evaporated *in vacuo* to give a crystalline residue. Recrystallization from ethanol afforded an almost quantitative yield of **5** which was found to be identical with the product obtained above by tlc, ir, and nmr comparison.

Reaction of Phenyl 2-Azido-4,6-*O*-benzylidene-2,3-dideoxy-3-nitro-β-D-glucopyranoside (5) with Sodium Azide.—Nitro azide **5** (398 mg, 1 mmol) and sodium azide (65 mg, 1 mmol) were stirred in distilled DMF (10 ml) for 10 hr at room temperature. The mixture was evaporated *in vacuo* to afford a white material which was washed with water. Recrystallization from ethanol to give **6** with contamination of a trace of **7**. Column chromatography on silica gel with benzene removed the trace of **7** completely to afford pure **6**: mp 188.5–189.0°; R_f 0.08; $[\alpha]^{20}D$ −108° (*c* 1, acetone).

Anal. Calcd for $C_{19}H_{17}N_3O_4$: C, 64.95; H, 4.88; N, 11.96. Found: C, 65.13; H, 4.80; N, 12.27.

Hydrogenation of 7.—**7** (706 mg, 1 mmol) was stirred under hydrogen with prereduced Raney nickel in dioxane containing a catalytic amount of triethylamine for 2 days. After the reaction mixture was filtered, evaporation of the filtrate afforded white powder. Recrystallization from ethanol afforded crystalline **8** (85%): mp 215° dec; $[\alpha]^{20}D$ −93.9° (*c* 0.25, DMSO); ir (KBr) 3350 cm^{-1} (NH).

Anal. Calcd for $C_{38}H_{36}N_4O_8$: C, 67.44; H, 5.36; N, 8.28. Found: C, 67.17; H, 5.65; N, 8.25.

To a solution of **8** (338 mg, 0.5 mmol) in methanol (40 ml) was added acetic anhydride (5 ml). The solution was allowed to stand for 2 hr and then evaporated *in vacuo*. The remaining material was washed with water and recrystallized from DMF–water to give a white powder phenyl 3-acetamido-4,6-*O*-benzylidene-2,3-dideoxy-2-(phenyl 4′,6′-*O*-benzylidene-2′,3′-dideoxy-β-D-*erythro*-hexopyranosido[2′,3′-*d*]triazolyl)-β-D-glucopyranoside (**9**) in 87% yield: mp 222–224° dec; $[\alpha]^{20}D$ −17.0° (*c* 0.5, DMSO); ir (KBr) 3270 (NH) and 1660 cm^{-1} (NHAc).

Anal. Calcd for $C_{40}H_{38}N_4O_9$: C, 66.84; H, 5.33; N, 7.80. Found: C, 66.40; H, 5.47; N, 7.85.

Reaction of 4 with 6.—**4** (355 mg, 1 mmol) and triazole **6** (351 mg, 1 mmol) were stirred in acetonitrile (24 ml) for 10 hr at room temperature, and the mixture was then evaporated *in vacuo* to afford a white crystalline material. Recrystallization from ethanol–acetone gave **7** (88%).

Phenyl 4,6-*O*-Benzylidene-3-deoxy-2-*O*-methyl-3-nitro-β-D-glycopyranoside (12).—To a solution of **5** (398 mg, 1 mmol) in absolute methanol (30 ml) was added a catalytic amount of sodium methoxide. The mixture was stirred for 8 hr at room temperature and evaporated *in vacuo*. The remaining material was washed with water and crystallized from ethanol to give **12** (290 mg, 75%): mp 170.0–170.5°; $[\alpha]^{20}D$ −64.6° (*c* 1, $CHCl_3$); ir (KBr) 1560 cm^{-1} (NO_2); nmr ($CDCl_3$) τ 4.92 (d, 1, J = 7 Hz, H-1), 5.22 (t, 1, J = 10 Hz, H-3), 6.40 (s, 3, OMe).

Anal. Calcd for $C_{20}H_{21}NO_7$: C, 62.01; H, 5.46; N, 3.62. Found: C, 61.72; H, 5.42; N, 3.65.

Reaction of Methyl 4,6-*O*-Benzylidene-2,3-dideoxy-3-nitro-β-D-*erythro*-hex-2-enopyranoside (2) with Sodium Azide in the Presence of 5.—To solution of **5** (398 mg, 1 mmol) and **2**[17] (293 mg, 1 mmol) in acetonitrile (16 ml) and water (2 ml) was added sodium azide (65 mg, 1 mmol). After stirring for 3 hr at room temperature, the reaction mixture was evaporated *in vacuo*. The remaining material was washed with water and chromatographed on a column (3 × 14 cm) of silica gel using benzene as an eluent. The azide **5**, which was eluted as the first portion, was recovered in 70% yield and a trace amount of several products were fractionally isolated, although their structures have not yet been determined. Methyl 4,6-*O*-benzylidene-2,3-dideoxy-2-(methyl 4′,6′-*O*-benzylidene-2′,3′-dideoxy-β-D-*erythro*-hexopyranosido-[2′,3′-*d*]triazolyl)-3-nitro-β-D-hexopyranoside (**11**), corresponding to **7**, but its configuration at C-2 of the nitro sugar moiety has not been determined, was eluted as the last portion and obtained in 62% yield: mp 222° dec; $[\alpha]^{20}D$ −62.5° (*c* 1, $CHCl_3$); ir (KBr) 1560 cm^{-1} (NO_2); nmr ($CDCl_3$) τ 4.18 (s, 1, H-1′), 6.49 (s, 3, OMe), 6.64 (s, 3, OMe).

Anal. Calcd for $C_{28}H_{30}N_4O_{10}$: C, 57.73; H, 5.19; N, 9.62. Found: C, 57.79; H, 5.32; N, 9.80.

Reaction of Nitro Olefin 4 with Picryl Azide.—To a solution of nitro olefin **4** (355 mg, 1 mmol) and picryl azide (254 mg, 1 mmol) in distilled dioxane (20 ml) was added 1 *N* sodium hydroxide (0.4 ml). The reaction mixture was allowed to stand at room temperature for 12 hr and then evaporated *in vacuo*. Diethyl ether (70 ml) was added to the residue, and the resultant solid was filtered. The precipitate was recrystallized from ethanol–benzene to give 240 mg (68%) of **7**.

Reaction of Methyl 2-*O*-Acetyl-4,6-*O*-bromoethylidene-3-deoxy-3-nitro-β-D-glucopyranoside (14) with Sodium Azide.—To a solution of **14** (740 mg, 2 mmol) in DMF (16 ml) and water (2 ml) was added sodium azide (130 mg, 2 mmol). The mixture was stirred for 10 hr at room temperature and poured into water (100 ml). Separated semicrystalline material was collected. Recrystallization from ethanol afforded **10** (72%): mp 170.0–170.5°; $[\alpha]^{20}D$ −40.7° (*c* 1, CH_2Cl_2); ir (KBr) 1560 cm^{-1} (NO_2); nmr ($CDCl_3$) τ 4.13 (s, 1, H-1′), 6.42 (s, 3, OMe), 6.58 (s, 3, OMe).

Anal. Calcd for $C_{18}H_{24}N_4O_{10}Br_2$: C, 35.07; H, 3.90; N, 9.09. Found: C, 35.47; H, 4.05; N, 9.35.

Registry No.—**2**, 25541-58-6; **3**, 39727-45-2; **4**, 39727-46-3; **5**, 39727-47-4; **6**, 39710-80-0; **7**, 37342-70-4; **8**, 37342-71-5; **9**, 37342-72-6; **10**, 37342-68-0; **11**, 37342-69-1; **12**, 39727-48-5; **13**, 39727-49-6; **14**, 39727-50-9; phenyl 3-deoxy-3-nitro-β-D-glucopyranoside, 39727-51-0; methyl 3-deoxy-3-nitro-β-D-glucopyranoside, 39727-52-1; sodium azide, 26628-22-8.

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