Preparation of Methyl 2,3-Anhydro-4,6-*O*-benzylidene-3-deoxy-3-nitro-β-D-allopyranoside and Some C^2-Branched-Chain Derivatives of Methyl 4,6-*O*-Benzylidene-2,3-dideoxy-3-nitro-β-D-glucopyranoside

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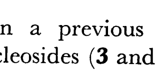
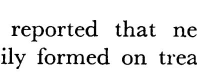
In a previous paper[1] we reported that new nucleosides (**3** and **4**) were easily formed on treatment of 3-nitroglucoside **1** with theophylline or 2,6-dichloropurine in the presence of sodium bicarbonate via a two-step mechanism, *i.e.* (i) elimination of acetic acid from 1 to yield α-nitroolefin **2** and (ii) nucleophilic addition of the purine bases to **2**. Recently Newman and Angier[2] described α-nitroepoxides, a new class of compounds, generated from α-nitroolefins with alkaline hydrogen peroxide.

We have found that on treatment with sodium hypochlorite in THF **2** also gives nitroepoxide **5** as the first member in the field of sugar chemistry. When the solvent was changed from THF to acetone, an unexpected addition of acetone, a very weak nucleophile(K_a[3] 10^{-20}), to **2** predominantly occurred[4] and a branched-chain compound **6** was obtained.

In THF (20 m*l*) **2**[5] (293 mg) was stirred with sodium hypochlorite (*ca.* 20% aq., 1.8 m*l*) for 2 hr at room temperature. It was then diluted with water (40 m*l*), condensed *in vacuo* to a half volume, extracted with chloroform, and on evaporation the remaining material was recrystallized from ethanol/water to give in 74% yield epoxide **5**, $C_{14}H_{15}NO_7$,[6] mp 184—185°C, $[\alpha]_D^{20}$ −96.2° (*c* 1, MeOH).



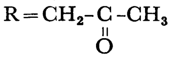


2

1 R=OAc

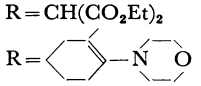
3 R=7-theophyllinyl

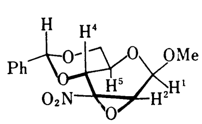
4 R=2,6-dichloro-9-purinyl

6 
$R=CH_2\text{-}\underset{\underset{\displaystyle O}{\|}}{C}\text{-}CH_3$

7 $R=CH(CN)_2$

8 $R=CH(CO_2Et)_2$

9 R= 



5

When stirred in acetone instead of THF overnight at room temperature, **2** gave in 91% yield adduct **6**, $C_{17}H_{21}NO_7$,[6] mp 176—177°C (from EtOH), $[\alpha]_D^{20}$ −66.9° (*c* 1, MeOH), IR(KBr) 1715 cm^{-1} (C=O), NMR($CDCl_3$) 7.89τ (3H-*s*, Ac).

Similarly, addition of malononitrile (K_a[3] 6.5×10^{-12}) and ethyl malonate (K_a[3] 5×10^{-14}) to **2** afforded the following, in an over 88% yield, respectively: *2-C-Dicyanomethyl derivative* **7**, $C_{17}H_{17}N_3O_6$,[6] mp 177—178°C (from EtOH), $[\alpha]_D^{20}$ −40.2° (*c* 1, MeOH); *2-C-(Diethoxycarbonyl)methyl derivative* **8**, $C_{21}H_{27}NO_{10}$,[6] mp 109—110°C (from EtOH), $[\alpha]_D^{20}$ −61.2°C (*c* 1, MeOH).

Under similar conditions cyclohexanone was shown to be inactive as a nucleophile, but its morpholino enamine was made to react with **2** without a catalyzer to afford adduct **9** in 76% yield, $C_{24}H_{32}N_2O_7$,[6] mp 145.5—146°C (from EtOH), $[\alpha]_D^{20}$ −135° (*c* 0.5, $CHCl_3$).

Structures of the products obtained were deduced from NMR-data: The fact that $J_{1,2}=0$(dihedral angle of H^1,H^2=100°) and $J_{4,5}=9.5$ Hz(diaxial of H^4,H^5) in **5** permits only a distorted *β-allo* structure, as shown in the figure. Large values of coupling constants (≳8 Hz) of H^1 - H^5 in **6**—**9** indicate their *β-gluco* configurations.

TABLE 1. 100 MHz NMR SPECTRA IN $CDCl_3$ (TMS as an internal standard)

Compound	Chemical shifts in τ					Coupling constants			
	H^1	H^2	H^3	H^4	$\text{-CH}\langle^{O}_{O}$	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$
5	5.21	6.25	—	4.98	4.30	0	—	—	9.5
6	5.30	?	5.00	5.87	4.47	8	10.5	9.5	9.5
7	5.41	7.16	5.12	5.79	4.44	8	10.5	9.5	9.5
8	4.87	7.10	4.97	?	4.46	8	11.5	10	?
9	5.51	?	5.01	5.87	4.48	8	10.5	10.5	9.5

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

2) H. Newman and R. B. Angier, *Chem. Commun.*, **1969**, 369.

3) Value in water at 25°C [R. G. Pearson and R. L. Dillon, *J. Amer. Chem. Soc.*, **75**, 2439 (1953)].

4) In this case sodium hypochlorite is likely to behave as a basic catalyzer. The reaction proceeds also in the presence of a trace of sodium hydroxide instead of sodium hypochlorite, to give **6** in 86% yield.

5) H. H. Baer and T. Neilson, *Can. J. Chem.*, **43**, 840 (1965).

6) All the new compounds give satisfactory results in elementary analyses.