Carbohydrate Research
Elsevier Publishing Company, Amsterdam
Printed in Belgium

Note

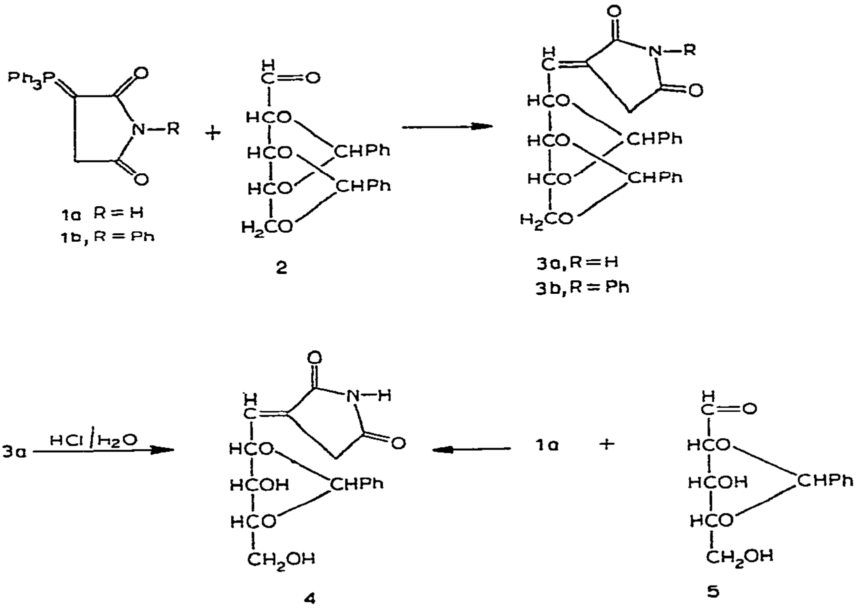
The reaction of ylids of maleimide with derivatives of D-ribose

Robert E Harmon, George Wellman, and S K Gupta
Department of Chemistry, Western Michigan University, Kalamazoo, Michigan 49001 (U S A)

(Received June 12th, 1969)

Because of the importance of long-chain monosaccharides as intermediates in the synthesis of other carbohydrates, we have investigated the reaction of triphenylphosphoranylidenesuccinimide[1] (**1a**) and its *N*-phenyl derivative **1b** with derivatives of D-ribose The reaction of D-ribose with the ylids **1a** and **1b** was studied in order that intermediates for the total synthesis of the antibiotic Showdomycin[2] might be prepared The reaction of resonance-stabilized ylids with several monosaccharides, as well as with acetylated *aldehydo* monosaccharides, has been reported[3]

Attempts to cause unprotected D-ribose and D-glucose to react directly with the ylids **1a** and **1b** were unsuccessful Similarly, the reaction of acetylated *aldehydo*-D-ribose and *aldehydo*-D-glucose with these ylids did not lead to any isolable product In contrast, reaction occurred between 2,4 3,5-di-*O*-benzylidene-*aldehydo*-D-ribose (**2**) (prepared by the procedure of Potgieter and MacDonald[4]) and the ylids **1a** and **1b**, and respectively afforded **3a** and **3b**, each in ~85% yield When **3a** was treated with



aqueous hydrochloric acid, selective hydrolysis of the 3,5-*O*-benzylidene group occurred, yielding 2,4-*O*-benzylidene-1-deoxy-1-(2,5-dioxo-3-pyrrolidinylidene)-D-ribitol (**4**) Compound **4** could also be prepared by the reaction of 2,4-*O*-benzylidene-*aldehydo*-D-ribose[4] (**5**) with the ylid **1a**

In summary, the reaction of ylids **1a** and **1b** derived from maleimide and *N*-phenylmaleimide with benzylidene-protected *aldehydo*-D-ribose (compounds **2** and **5**) gives the corresponding Wittig reaction-products

EXPERIMENTAL

Melting points were determined with a Thomas–Hoover melting-point apparatus and are corrected The elemental analyses were performed by Galbraith Laboratories, Inc , Knoxville, Tennessee 37921. A Beckman IR-8 spectrophotometer was used for recording the i r spectra The ylids **1a** and **1b** were prepared by the procedure of Heyda and Theodoropulos[1] The method of Potgieter and MacDonald[4] was used for preparing the D-ribose derivatives **2** and **5**

*2,4 3,5-Di-O-benzylidene-1-deoxy-1-(2,5-dioxo-3-pyrrolidinylidene)-*D*-ribitol* (**3a**) — To a solution of **2** (1 7 g, 5 mmoles) in ethanol (200 ml) was added the ylid **1a** (1 7 g, 5 mmoles) with stirring. After 1 h, the solution was concentrated under diminished pressure to 75 ml, and cooled to 10° The white precipitate thus obtained was filtered off, dried, and crystallized from absolute ethanol, to yield 1 7 g (86%) of colorless needles, m.p. 194–195°, $[\alpha]_D^{25}$ −94 1° (*c* 0.12, ethanol) ν_{max}^{Nujol} 3180 (NH), 1770, 1730, 1680 cm^{-1} (C = O)

Anal. Calc. for $C_{23}H_{21}NO_6$ C, 67 80, H, 5 16, N, 3 44 Found C, 67 81, H, 5 31, N, 3 40

*2,4 3,5-Di-O-benzylidene-1-deoxy-1-(2,5-dioxo-1-phenyl-3-pyrrolidinylidene)-*D*-ribitol* (**3b**) — Reaction of the ylid **1b** with **2** by the foregoing procedure afforded **3b** in 85% yield, m p. 212–213°, $[\alpha]_D^{25}$ −143 2° (*c* 0 38, ethanol), ν_{max}^{Nujol} 1770, 1710, 1680 cm^{-1} (C=O)

Anal Calc for $C_{29}H_{26}NO_6$ C, 72 04, H, 5 17, N, 2 90 Found C, 72 25, H, 5 32, N, 2 91

*2,4-O-Benzylidene-1-deoxy-1-(2,5-dioxo-3-pyrrolidinylidene)-*D*-ribitol* (**4**) — *Method A* To a solution of **3a** (3 g, 7.3 mmoles) in methanol (300 ml) was added concentrated hydrochloric acid (3 ml) The solution was stirred for 5 h at 30°, and then evaporated under diminished pressure to an oil, this was triturated with cold water, and the resulting precipitate was crystallized from water to yield colorless needles which, after being dried at 110°/0 1 mmHg, afforded 1 6 g (63%) of **4**, m.p. 189–190°, ν_{max}^{Nujol} 3500 (CH), 3380 (NH), 1760, 1720, and 1680 cm^{-1} (C = O).

Anal Calc for $C_{16}H_{17}NO_6$ C, 60 18, H, 5 36, N, 4 38 Found C. 59.93; H, 5 31; N, 4 22

Method B Reaction of **5** with the ylid **1a** by the procedure used for the preparation of **3b** afforded a 51% yield of **4**, m p 189–190° The m p of a mixture of the products from Methods A and B was undepressed, and the i r spectra of the two samples were superposable

ACKNOWLEDGMENT

This work was supported by Grant No CA-06140 from the National Cancer Institute.

REFERENCES

1 E HEYDA AND S THEODOROPULOS, *Tetrahedron*, 24 (1968) 2241

2 Y NAKAGAWA, H KANO, Y TSUKUDA, AND H KAYAMA, *Tetrahedron Lett*, 42 (1967) 4105

3 N K KOCHETKOV AND B A DMITRIEV, *Chem Ind* (London), (1963) 864, *Dokl Akad Nauk SSSR* 151 (1963) 106, YU A ZHDANOV, G N DOROFEENKO, AND L A UZLOVA, *Zh Obshch Khim*, 33 (1963) 3444, 35 (1965) 181, M N MIRZAYANOVA, L P DAVYDOVA, AND G I SAMOKHVALOV, *Dokl Akad Nauk SSSR*, 173 (1967) 367, B A DMITRIEV, N E BAIRAMOVA, L V BOKINOVSKIĬ, AND N K KOCHETKOV, *ibid*, 173 (1967) 350

4 D S POTGIETER AND D L MACDONALD, *J Org Chem*, 26 (1961) 3934