Carbohydrate Research, 40 (1975) C1–C2

Preliminary communication

Carbohydrate triflates: synthesis, and conversion into pyridinium salts*

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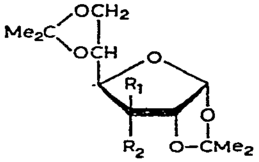
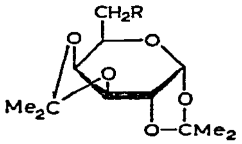
(Received January 11th, 1975; accepted for publication, January 28th, 1975)

As part of a continuing program on the synthetic utility of fluorinated reagents in carbohydrate chemistry[1], we have now extended investigation of the formation[2] and reactions[2] of trifluoromethanesulfonates (triflates)[3] to some carbohydrates.

Reaction of 1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose (**1**) with trifluoromethanesulfonic (triflic) anhydride in pyridine for 3.5 h at ~−15° (ice–salt bath) afforded, after conventional processing, 1,2:5,6-di-*O*-isopropylidene-3-*O*-triflyl-α-D-allofuranose (**2**) in 80% yield; m.p. 40.0° (from light petroleum), $[\alpha]_D$ +63.6° (*c* 2.14, acetone). In a similar way, reaction of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**3**) with triflic anhydride afforded the corresponding 3-triflate (**4**) in 90% yield; m.p. 70.0° (from light petroleum), $[\alpha]_D$ −35.1° (*c* 1.00, acetone); in this instance, the reactants were mixed at −10°, and the stirred solution was allowed to warm to room temperature during 24 h. Both of these esters (**2** and **4**) are stable for several months if kept at 0°, and may be manipulated in the laboratory without difficulty.



1, R_1 = H, R_2 = OH
2, R_1 = H, R_2 = OTf
3, R_1 = OH, R_2 = H
4, R_1 = OTf, R_2 = H
9, R_1 = $C_5H_5N^+OTf^-$, R_2 = H
10, R_1 = $C_5H_5N^+I^-$, R_2 = H
($Tf = F_3CSO_2-$)



5, R = OH
6, R = OTf
7, R = $C_5H_5N^+OTf^-$
8, R = $C_5H_5N^+I^-$
11, R = $(NH_2CO)C_5H_4N^+OTf^-$

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*All compounds reported here had elemental microanalyses and nuclear magnetic resonance spectra in complete accord with the structures assigned.

Reaction of 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (5) with triflic anhydride in pyridine at ~−15° was complete after ~30 min. Processing, followed by recrystallization of the product from 95% ethanol, gave, instead of the anticipated triflate (6), the corresponding pyridinium salt (7), yield 90%; m.p. 217–218° (dec.) (from aqueous ethanol), $[\alpha]_D$ −35.1° (*c* 2.53, acetone). Compound 7 was quantitatively converted into the corresponding iodide (8), m.p. 253° (dec.) (from aqueous ethanol) by boiling under reflux with sodium iodide in acetone.

Similar formation of a pyridinium salt at a suitably reactive, secondary carbon atom may be achieved either directly from the alcohol or with prior isolation of the triflate. For example, reaction of **1** with triflic anhydride in boiling pyridine under reflux for 25 h afforded, in 70% yield, 1,2:5,6-di-*O*-isopropylidene-α-D-glucopyranose-3-*C*-(pyridinium triflate) (**9**); this compound is extremely hygroscopic, and was characterized as the corresponding iodide (**10**), m.p. 193.0° (from aqueous ethanol), $[\alpha]_D$ −2.8° (*c* 0.39, acetone). It should be noted that other nitrogen nucleophiles react with triflic esters; for example, we have prepared the nicotinamide salt (**11**) from **5**.

The enhanced susceptibility of triflates to nucleophilic attack compared with that of the conventionally used sulfonates is demonstrated by the fact that the 6-*O*-tosyl derivative of **5** is readily isolated from pyridine solution, and that heating it under reflux with pyridine results in the formation of the pyridinium tosylate (salt) in only ~30% yield. A similar difference is found for the two sulfonates of **1**; the 3-*O*-tosyl derivative is recovered unchanged after heating in pyridine under reflux for 24 h. This reactivity of triflic esters augurs well for many model syntheses in the carbohydrate area; interestingly, this kind of enhancement of reactivity was anticipated by Tipson more than 20 years ago[4].

ACKNOWLEDGMENT

It is a pleasure to thank the National Research Council of Canada for their financial support of this work.

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