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ALKYLOXYTRIS(DIMETHYLAMINO)PHOSPHONIUM (ATDP) SALTS XIV*

REACTIONS OF SILVER TOSYLATE AND HEXAFLUOROANTIMONATE WITH THE ATDP CHLORIDE DERIVED FROM 2.3.5.6-DI-O-ISOPROPYLIDENE-α-D-MANNOFURANOSE : A NOVEL ROUTE TO SULFONIC ESTERS AT THE ANOMERIC POSITION

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Recently, we have activated anomeric hydroxyl groups in some special cases (1, 2), by the joint action the tris(dimethylamino)phosphine and carbon tetrachloride (TDAP-CCl_4).

We have reported that in the case of the title compound, one cannot isolate an ATDP salt contrary to the instance of primary and secondary alcohols (3, 4). Nevertheless the alcohols do react on the reaction mixtures obtained from 1 and TDAP-CCl_4 at -40°C in methylene chloride. This reaction performed in the presence, or the absence of silver alkyl - or arylsulfonates yields satisfactorily the corresponding glycosides.

This paper is devoted to the presentation of physico-chemical data showing :

- the existence of a sulfonate in such a case ; such compounds, extremely unstable have been recently reported (5, 6) in related series
- the very special behaviour of tris(dimethylamino)phosphonium leaving group attached to the anomeric position of a furanose bearing no participating group in the C-2 position.

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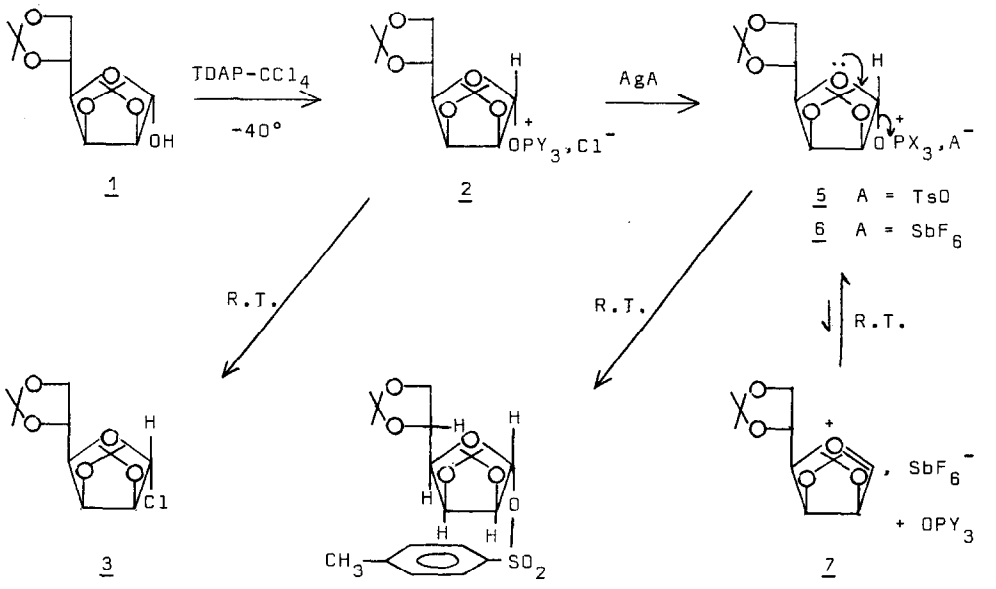

1 2 5 A = TsO 6 A = SbF_6 3 4 7

A solution of 1 in $CDCl_3$ at -40°C is treated with one equivalent of TDAP in the presence of CCl_4. The t.l.c. analysis shows the disappearance of 1 and the emergence of a polar spot, R_F = 0 (7). The ^1H NMR spectrum at -40°C exhibits two doublets (dimethylamino groups, δ = 2.88 ppm, $^3J_{H-P}$ = 10 Hz, 18 H ; H_1, δ = 5.62 ppm, $^3J_{H-P}$ = 5 Hz, $^3J_{H_1-H_2}$ ≃ 0 Hz, 1 H). The $^{31}P\{^1H\}$ NMR spectrum, at the same temperature, shows the only singlet at -34.4 ppm (PO_4D_3 as external reference). These data support the existence in solution of the only compound 2 in the α configuration. These observations can be done until -10°C ; at room temperature the spectra change towards those of the mixture of 3 (1) and HMPA.

The treatment, at -40°C, of the solution of 2 by 1.5 equivalent of silver tosylate induces the precipitation of silver chloride. The ^{31}P NMR spectrum shows that the -34.4 ppm signal remains steady until one reaches -10°C, stating the limit of stability of 5 ; thereafter, it vanishes to the benefit of the -24.5 ppm HMPA signal. The centrifugation of this solution, at room temperature and rigorous exclusion of air moisture (argon line manipulation) allows the recording of the ^1H NMR spectrum ; this spectrum is a good evidence supporting the structure 4 (aromatic two doublets δ = 7.74 ; δ = 7.30 ppm, $^3J_{o-m}$ = 8 Hz, 4 H ; H_1, singlet, δ = 5.88 ppm, 1 H ; H_6, δ = 4.75 ppm, 2 H ; H_2,H_3, H_4, H_5, 3 unassigned multiplets δ = 4.2, 3.82 and

3.27 ppm, 4 H ; CH_3 (arom.), δ = 2,42 ppm, singlet, 3 H ; CH_3 (isopropyl), δ = 1.42 and 1.30 ppm, singlets, 12 H).

An upfield shift is observed for the H_2, H_3 and H_4 signals by comparison to the spectrum of 3 (δ = 4 to 5.33 ppm) ; this can be due to a shielding by the aromatic nucleus in some special configuration. The α configuration of proton H_1 is supported by the singlet structure of the signal.

The treatment, at -40°C, of the solution of 2 by a slight excess of silver hexafluoroantimonate induces too the precipitation of silver chloride. In this case, the ATDP salt 6 is still characterized at room temperature.

Neverless, in spite of its apparent stability, 6 is as reactive as 4 (1, 8). This feature is explained by the existence of an equilibrium 6 ⇌ 7, that we have demonstrated by the observation of ^1H NMR spectrum of 6 after addition of HMPA d_{18} : while the sugar protons part remains unaffected the dimethylamino signal vanishes in one hour and gives rise to the characteristic doublet of HMPA (δ = 2.65 ppm, $^3J_{H-P}$ = 9 Hz).

All these reactions are summarized in the scheme.

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7) This spot contains free mannose coming from the in situ removal of the isopropylidene groups by the acid released during the hydrolysis of 2 on the plate. The normal migration of 1 is indeed observed if one spots one drop of Et_3N before analysis.

8) To be published.