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Preliminary communication

2-*C*-Diacetoxythalliation of D-galactal triacetate

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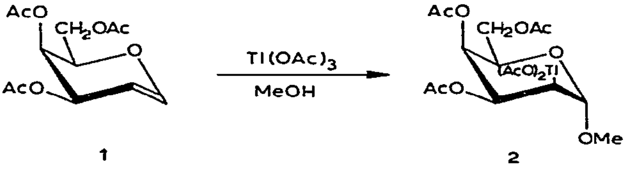
Impressed by the ease with which glycal triacetates participate in the methoxymercuration reaction[1], and by the utility of these mercurated adducts as models in studies[2] of the stereospecific dependencies of ^{199}Hg–^{1}H and metal–^{13}C coupling-constants, we have investigated the analogous diacetoxythalliation reaction of D-galactal triacetate[3] (1).

Reaction of 1 in anhydrous methanol with solid thallium(III) triacetate during 15 min at room temperature afforded a single product (t.l.c.) which, by conventional processing, was isolated as a clear oil in 75% yield, and which subsequently crystallized from methanol–isopropyl ether as colorless crystals in 60% overall yield, m.p. 151° (dec.), $[\alpha]_D$ −12.9° (*c* 5, $CHCl_3$). This compound is stable as the solid, is very soluble in both chloroform and water, is less soluble in acetone or methanol, and is only slightly soluble in hexane or isopropyl ether. Both elemental microanalytical data, and ^{1}H- and ^{13}C-n.m.r.-spectroscopic parameters, are consistent with the formulation of this compound as methyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-(diacetoxythallio)-α-D-talopyranoside (2); interestingly, the configuration of the product isolated from the methoxymercuration reaction of 1 is also α-D-*talo*.



1 2

Without giving details here of the assignment of the n.m.r. spectra of 2, which are decidedly non-trivial[4], we have summarized in Table I the coupling constants measured for 2 in chloroform-*d* solution. In most instances, separate resolution of the couplings from the two thallium isotopes, ^{203}Tl (29.5%, spin 1/2) and ^{205}Tl (70.5%, spin 1/2), proved impossible; hence, the couplings given are averaged values. The most important of these data are the couplings into H-1 and H-3, which differ from one another by a factor of almost seven, and which constitute a further example of the already well established[5] dependence of *vicinal* ^{1}H–C–C–X couplings.

The abundance of large, long-range couplings between thallium and both ^{1}H and ^{13}C nuclei of 2 suggests that it would be most worthwhile to study other, configurationally related *C*-thalliated sugars; and the fact that Tl–^{1}H couplings are so much larger than their

TABLE I

^{1}H-Tl AND ^{13}C-Tl COUPLING-CONSTANTS[a] FOR 2 IN CHLOROFORM-*d* SOLUTION

Proton	*H-1*	*H-2*	*H-3*	*H-4*			*OCH$_3$*
	386	630	2646[b] 2622[c]	52			6
Carbon-13	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*OCH$_3$*
	12	6466[b] 6404[c]	663	182	21	10	110

[a] In Hz; measured at 35° with a Varian XL-100 (15) spectrometer operating at 100 MHz in the continuous-wave mode. [b] From ^{205}Tl. [c] From ^{203}Tl.

^{1}H—^{1}H, or even ^{1}H—^{19}F, counterparts[6] prompts us to suggest that workers attempting to detect conformational changes accompanying enzymic cleavage of glycosides should give serious consideration to studies of *C*-thalliated sugars, especially those substituted at carbon atoms other than C-2.

Although Pande and Winstein[7] reported examples of acetoxythalliation of alkenes the present communication describes the first example of an acetoxythalliation of a glycal, and, should analogy with methoxy- and hydroxy-mercuration reactions[8] be appropriate, it would seem that this reaction will have substantial generality beyond the glycal area.

ACKNOWLEDGMENT

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