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(13) Alkyl azides are unreactive towards $(CuX_2{\cdot}NO)_2$, however, suggesting that reactions of copper halide nitrosyls occur only with substrates that can coordinate with copper and not through a "free" nitrosonium ion.

(14) Ethylenediamine complexes effectively with the copper products and allows the complete separation of organic products in the isolation procedure. The organic products are stable to ethylenediamine in this procedure.

(15) Deamination of these same amines by $NO^+BF_4^-$ in acetonitrile gives acetamides almost exclusively.

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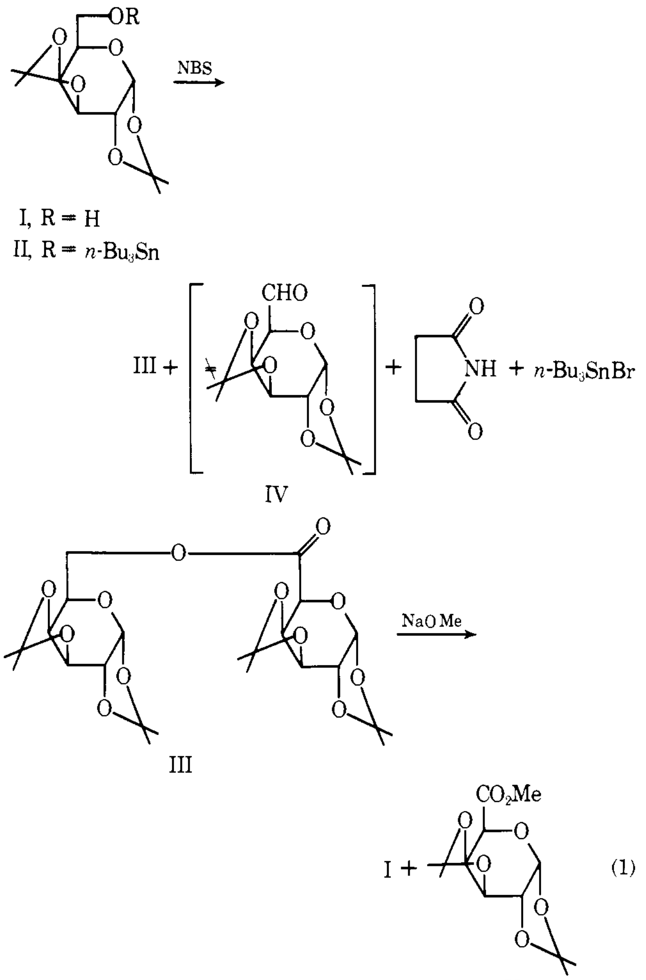
A Novel Oxidative Transformation: Oxidative Esterification

Sir:

In the field of carbohydrate and nucleoside chemistry, silylated organic molecules have been extensively employed to achieve specific chemical transformations through their modification of the reactivity of the original molecules.[1] Recently, reactivity enhancement of alcohols through stannylation has also been developed. Thus sulfamoylation[2] and alkylation[3] of stannylated hydroxy functions were successfully performed under mild conditions by employing nucleosides as substrates. Very recently the oxidation of triethylstannyl alkoxides by bromine was reported to afford the corresponding ketones and aldehydes in good yields.[4]

In this report we describe a mild oxidative transformation based on the reactivity of trialkylstannyl alkoxides toward NBS.[5]

Treatment of 1,2:3,4-di-*O*-isopropylidene-6-*O*-tri-*n*-butylstannyl-α-D-galactopyranoside (II),[6] prepared from the corresponding alcohol (I),[7] by an equivalent amount of NBS in dry carbon tetrachloride at room temperature afforded both a new compound (III) $[\alpha]^{25}\text{D}$ −76.0° (c 1.2, $CHCl_3$) and succimide in high yields. Compound III was different from the expected aldehyde (IV)[8] on TLC. The presence in the ^1H NMR ($CDCl_3$) of two anomeric proton signals at δ 5.53 (1 H, d, $J = 5$ Hz) and 5.67 (1 H, d, $J = 5$ Hz), together with the presence of four signals for isopropylidene groups at δ 1.35 (6 H, s), 1.36 (6 H, s), 1.47 (6 H, s), and 1.54 (6 H, s), which correspond to eight methyl groups by integration, indicates the dimeric nature of the product. The structure was substantiated by the saponification of III by sodium methoxide in methanol, which gave both I and 1,2:3,4-di-*O*-isopropylidene-α-D-galacturonic acid methyl ester (V)[9] in a ratio of 1:1. A similar transformation was achieved in the case of methyl 2,3-*O*-isopropylidene-β-D-ribofuranoside (VI)[10] to afford dimeric ester VIII $[\alpha]^{25}\text{D}$ −69.3° (c 1.5, $CHCl_3$) quantitatively. ^1H NMR revealed two anomeric proton signals at δ 4.99 (1 H, s) and 5.05 (1 H, s), two glycosidic methyl signals at δ 3.42 and 3.34 (both 3 H, s), and two methyl signals of isopropylidene groups at δ 1.34 (6 H, s) and 1.50 (6 H, s).

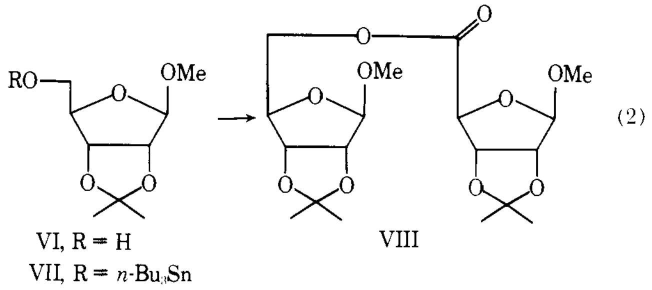


I, R = H
II, R = n-Bu$_3$Sn

IV

III

V



VI, R = H
VII, R = n-Bu$_3$Sn

VIII

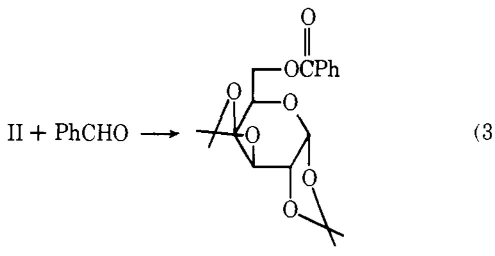
To determine whether aldehydes are formed as reaction intermediates during the oxidative transformation, the reaction of II was repeated in the presence of added benzaldehyde to give benzoate IX in good yield.

Next NBS oxidation of 1,2:5,6-di-*O*-isopropylidene-3-*O*-tri-*n*-butylstannyl-α-D-glucofuranoside (XI) was attempted. Although in the absence of added aldehyde only hydrolyzed starting material (X) was recovered, in the presence of added hexanal XI did afford the expected ester (XII) $[\alpha]^{25}\text{D}$ −30.7° (c 1.8, $CHCl_3$) in excellent yield.

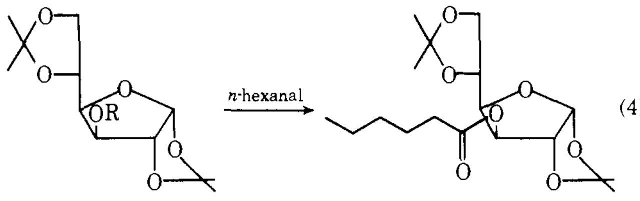
The reaction may proceed through the hypothetical intermediate XIII, which would subsequently be oxidized by NBS to give ester as shown in eq 5.

Although intramolecular oxidative lactonization of diols by silver carbonate on celite has been reported,[11] the oxidative transformation described here, to the best of author's knowledge, is a new type of reaction which can transform alcohols and aldehydes into esters intermolecularly by two simple, successive operations: (i) stannylation of the alcohols, and (ii) NBS treatment of equimolar mixtures of aldehyde and stannylated alcohol.

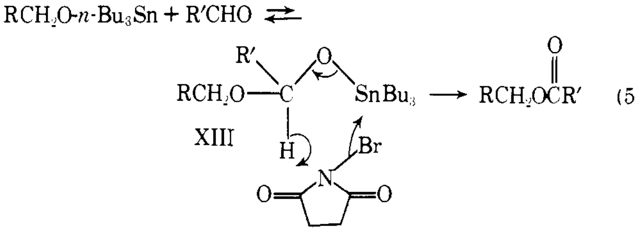
The applicability of this reaction to a group of com-



IX (3)



X, R = H
XI, R = n-Bu$_3$Sn
XII (4)



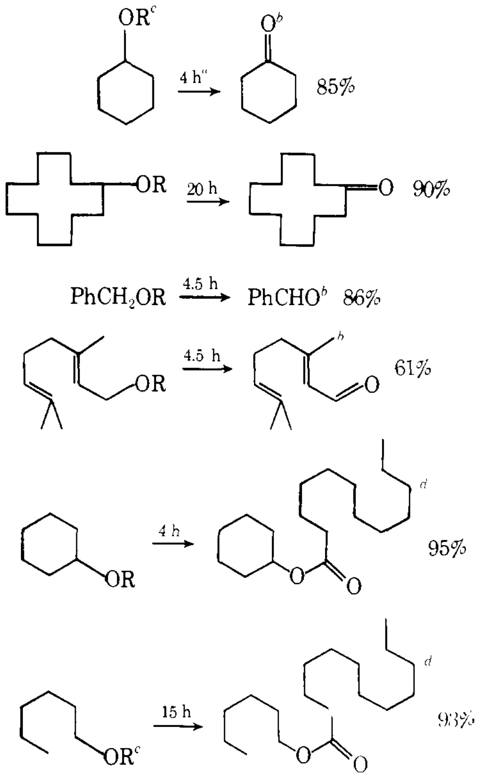
$RCH_2O\text{-}n\text{-}Bu_3Sn + R'CHO \rightleftharpoons$

XIII (5)

pounds other than carbohydrates was examined by using aliphatic alcohols. Preliminary results are shown in Scheme I.

The results described above indicate the following aspects of this reaction: (1) in the absence of added aldehyde, (i) primary alcohols (RCH_2OH) gave dimeric esters (RCH_2OCOR), (ii) primary alcohols of the benzylic or allyic type give aldehydes (RCHO), and (iii) secondary alcohols (R'R''CHOH) give ketones (R'R''CO); and (2) in the presence of added aldehyde (RCHO), (i) primary alcohols ($R'CH_2OH$), excluding benzyl or allyl, give esters ($R'CH_2OCOR$), and (ii) secondary alcohols (R'R''CHOH) give esters (R'R''CHOCOR).

Scheme I



[a] All reactions were performed at room temperature with 1 equiv of NBS in dry CCl_4. [b] Isolated and identified as 2,4-DNP. [c] R should be regarded as $(n\text{-Bu})_3Sn$. [d] The reactions were performed in the presence of added n-dodecanal.

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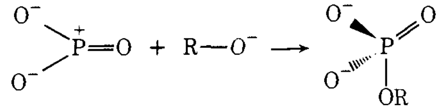
The Reactivity of Monomeric Metaphosphate

Sir:

The postulated intermediacy of the monomeric metaphosphate anion in the hydrolysis of phosphoric acid monoesters[1] and anhydrides[2] and in many biological phosphoryl transfer reactions[3] has evoked a steadily high level of interest in the chemistry of this species. There have been several recent successful demonstrations of a finite liefetime for PO_3^- via chemical trapping experiments,[4] but the isolation of a compound with a stable phosphorus-oxygen (2p-3p) π-bond has not as yet been achieved. This reactivity is manifested as severe electron deficiency at phosphorus:



The instability associated with (2p-3p) π bonding is a general phenomenon[5] but its theoretical source is unclear.[6] It is the purpose of this communication to demonstrate the important contribution of the σ-system to the reactivity of monomeric metaphosphate and to initiate speculation as to the generality of our conclusions for all (2p-3p) π-bonded systems.

Ab initio SCF molecular orbital calculations[7] were performed for PO_3^- and its congener NO_3^-. Bond length optimization led to a value of 1.543 Å for PO_3^- and a total en-