current is increased by addition of reducing agents such as hydroquinone.[1-12] This behavior, termed supersensitization, is based on the donation of electrons by the reducing agents to the excited or oxidized dyes. The reducing agents are, therefore, oxidized in the supersensitization process, as has been demonstrated experimentally by the rotating ring-disk electrode technique.[24] The effect of excitation with short wavelength light on the spectrally sensitized currents in the presence of a reducing agent was also investigated. When hydroquinone was added to the dye-containing solution, the spectrally sensitized current increased as expected. However, additional irradiation with the continuous ultraviolet light in the presence of hydroquinone showed no detectable effect (Figure 3c). This suggests that the irradiation with ultraviolet light and the supersensitization by the reducing agent are competitive with respect to increasing the modulated sensitized current at the ZnO electrode. During the dissolution reaction of ZnO, electron donor levels may be formed on the surface (such as surface levels of O^-, O_2^-, or O_2^{2-})[16-18] which may be able to play the same role as the reducing agent, i.e., to supply electrons continuously to the excited or oxidized dye molecule. Note that although the current resulting from this donation of electrons from the electrode to the dye is a cathodic one, it does not contribute to the modulated anodic spectrally sensitized photocurrent. The hydroquinone, which can act as a strong supersensitizer, may compete with the electron transfer to the dye by the surface electron donor levels. Another possible reason for the lack of an effect of the continuous ultraviolet light in the presence of hydroquinone is that the formation of the surface electron donor levels (O^-, O_2^-, or O_2^{2-}) is prevented by the suppression of the anodic dissolution reaction because of a reaction between the holes in the valence band and the hydroquinone.[18]

These experiments suggest that surface states on a ZnO semiconductor electrode are involved in dye spectral sensitization. It is known that the spectral sensitization plays an important role in the silver halide photographic system. By analogy with the photographic process, photoelectrochemical studies can be expected to contribute to the elucidation of spectral sensitization in photography. Similar investigations using silver halide electrodes are now in progress.

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Oxidative Deamination of Primary Amines by Copper Halide Nitrosyls. The Formation of Geminal Dihalides[1]

Sir:

The properties and reactions of copper halide nitrosyls provide a distinct contrast to those of the better known coordinated metal nitrosyls.[2] Passing nitric oxide into a mixture of anhydrous copper(II) bromide or chloride in acetonitrile converts the relatively insoluble copper(II) halide into a deep violet-black soluble nitrosyl complex.[3,4] The nitrosyl stretching frequencies of these nitrosyl complexes (X = Br, ν_{NO} 1865, 1846 cm^{-1}; X = Cl, ν_{NO} 1854, 1837 cm^{-1})[6] are characteristically those of linearly coordinated nitrosyls.[8] When these copper nitrosyl solutions are purged with nitrogen or are opened to an inert atmosphere, however, nitric oxide is evolved and the copper(II) halide is quantitatively recovered. Nitric oxide is, therefore, weakly and reversibly[9] associated with anhydrous copper(II) bromide and chloride in acetonitrile (eq 1).

$$(CuX_2)_n + nNO \rightleftharpoons n/2(CuX_2 \cdot NO)_2 \qquad (1)^{10}$$

The weak association of nitric oxide with copper(II) bromide or chloride and the relatively low nitrosyl stretching frequencies of the copper halide nitrosyls do not reflect the electrophilic behavior of the coordinated nitrosyl group.[11] Reactions of copper halide nitrosyls have been reported to resemble those of the more common nitrosating agents: alcohols form alkyl nitrites,[12a] secondary amines yield nitrosamines,[12b] and anilines are converted in a one-step procedure to aryl chlorides and bromides by copper halide nitrosyls in acetonitrile.[12c] Copper halide nitrosyls also react with sodium azide to form nitrogen, nitrous oxide, and copper(I) halide,[13] and with ammonia to give nitrogen and copper(I) halide. With aliphatic amines, however, reaction products have been observed to be complex and believed to result from reactions typical of the nitrosonium ion.[12c]

We have found that primary amines coordinated with copper(II) halides are rapidly oxidized by copper halide nitrosyls primarily to geminal dihalides. Nitrogen and nitrous oxide are the gaseous products from these reactions; copper(I) halide is the principal reduction product. Oxidative deamination of amines by copper(II) halides is not observed in the absence of copper halide nitrosyl. In a typical procedure, a solution of 40 mmol of copper chloride nitrosyl in 50 ml of anhydrous acetonitrile is added dropwise by syphon addition under a slow flow of nitrogen to a well-stirred solution of 10 mmol of the amine complexed with 12 mmol of anhydrous copper(II) chloride in 50 ml of acetonitrile. After stirring the reaction solution for 16 h at room temperature, a 4 M excess of ethylenediamine is added,[14] the resulting solution is poured into aqueous sodium hydroxide-ether, and the reaction products are isolated in the usual manner. Table I gives the yields of geminal dihalides prepared from representative aliphatic amines by this selective method. When the copper bromide system is employed, chromatographically pure geminal dibromide is conveniently isolated by distillation procedures.

In addition to geminal dihalides, alcohols, alkyl halides, and nitriles are formed in reactions of copper(II) halide coordinated amines with copper halide nitrosyls. 2-Phenylethylamine, for example, yields four identified products (eq 2); no other compounds formed in comparable amounts,

$$C_6H_5CH_2CH_2NH_2{\cdot}CuX_2 + (CuX_2{\cdot}NO)_2 \xrightarrow[25^\circ]{CH_3CN}$$

$$\begin{array}{lcccc}
 & C_6H_5CH_2CHX_2 & + & C_6H_5CH_2CN & + \\
X = Cl & 58 & & 3 & \\
Br & 54 & & 7 & \\
 & C_6H_5CH_2CH_2X & + & C_6H_5CH_2CH_2OH & (2) \\
 & 9 & & 5 & \\
 & 14 & & 9 &
\end{array}$$

including *N*-(2-phenylethyl)acetamide, 1-chloro-1-phenylethane, and 1-phenylethanol, could be detected. The yield of nitrous oxide is approximately equal to that of the nitrile. When the free amine is added directly to an acetonitrile solution of copper halide nitrosyl, nitric oxide is evolved along with nitrogen and nitrous oxide, and the yield of geminal dihalide is significantly reduced (23% $C_6H_5CH_2CHCl_2$ from 2-phenylethylamine) relative to the procedure (eq 2) in which the copper(II) complexed amine is added to $(CuX_2{\cdot}NO)_2$. The comparative yields of alkyl halide and alcohol from the two procedures are not similarly affected.

These results suggest the occurrence of at least three separate reactions of copper halide nitrosyls with amines: displacement of nitric oxide (eq 3), deamination of the free amine (eq 4), and oxidative deamination (eq 5). The sensitivity of copper halide nitrosyls to water[5,7] may, by analogy, be explained by the displacement of nitric oxide from the coordinated nitrosyl complex. Alkyl halide and alcohol formation is believed to be due to nitrosation of the free amine by $(CuX_2{\cdot}NO)_2$, which results in the formation of an alkyldiazonium ion. The nature of the reaction products[15] and the lack of rearrangement in reactions with 2-phenylethylamine suggest, however, that the copper halide is intimately involved in the deamination of the alkyldiazonium ion. The process yielding geminal dihalides may be represented as occurring through a diazoalkane or copper-complexed diazoalkane intermediate. Ethyl diazoacetate and copper(II) chloride are reported to produce ethyl dichloroacetate under reaction conditions similar to those employed in this study.[16] Competitive nitrosation of the diazoalkane intermediate by $(CuX_2{\cdot}NO)_2$ would be expected, by analogy to the fate of aldiminodiazonium ions,[17] to result in the production of nitrile and nitrous oxide.

$$2RCH_2NH_2 + (CuX_2 \cdot NO)_2 \rightarrow 2RCH_2NH_2 \cdot CuX_2 + 2NO \quad (3)$$

$$2RCH_2NH_2 + (CuX_2 \cdot NO)_2 \rightarrow RCH_2X + RCH_2OH + N_2 + CuX + H_2O \quad (4)$$

$$2RCH_2NH_2 + (CuX_2NO)_2 \rightarrow 2RCHX_2 + 4CuX + 2N_2 + 2HCl + 2H_2O \quad (5)$$

α-Branched primary amines did not yield geminal dihalides. 1-Phenylethylamine complexed with copper(II) chloride, for example, gave styrene (17%), 1-chloro-1-phenylethane (25%), and 1-phenylethanol (28%) in reactions with copper chloride nitrosyl. 1-Adamantamine, which could not form a geminal dihalide in the same manner as those amines listed in Table I, yielded only 1-chloroadamantane (31%) and 1-adamantanol (21%) when the same procedure was used. The sensitivity of the oxidative deamination process to α-branching of the amine may be related to the relative rates for deamination by eq 4 rather than to differences in steric or electronic factors on the processes outlined by eq 5.

Table I. Yields of Geminal Dihalides from Oxidative Deamination of Amines by Copper Halide Nitrosyls

RCH_2NH_2, R =	CuX_2, X =	$RCHX_2$	$RCHX_2$ % yield[a]
C_6H_5-	Cl	$C_6H_5CHCl_2$	14[b,c]
	Br	$C_6H_5CHBr_2$	30[b,d]
$C_6H_5CH_2$-	Cl	$C_6H_5CH_2CHCl_2$	58[e]
	Br	$C_6H_5CH_2CHBr_2$	54[f]
$C_6H_5CH_2CH_2$-	Cl	$C_6H_5CH_2CH_2CHCl_2$	34
$C_6H_5(CH_2)_3$-	Cl	$C_6H_5(CH_2)_3CHCl_2$	32
$CH_3(CH_2)_5$-	Cl	$CH_3(CH_2)_5CHCl_2$	34
	Br	$CH_3(CH_2)_5CHBr_2$	39
$CH_3(CH_2)_8$-	Cl	$CH_3(CH_2)_8CHCl_2$	26
	Br	$CH_3(CH_2)_8CHBr_2$	37
$EtO_2C(CH_2)_4$-	Cl	$EtO_2C(CH_2)_4CHCl_2$	30
$HOCH_2(CH_2)_4$-	Cl	$HOCH_2(CH_2)_4CHCl_2$	39[g]
Cyclohexyl-	Cl	$(CH_2)_5CHCHCl_2$	26

[a] Actual yield of geminal dihalide determined from the average of at least two reactions through GLC and ^1H NMR analyses with an internal standard. Variations of ±3% were observed from multiple reactions with these amines. Yields are based on the amount of amine initially employed; unreacted amine could be isolated only with difficulty and was, therefore, not taken into account in the calculation of percent yield of geminal dihalide. [b] Uncomplexed amine was added to copper halide nitrosyl. [c] Benzyl chloride (27%), benzyl alcohol (16%), and benzonitrile (6%) were also formed. [d] Benzyl bromide (33%) and benzyl alcohol (15%) were detected. [e] Average of seven reactions. [f] 1,1-Dibromo-2-phenylethane was isolated in 40% yield by distillation. [g] Nitrite products were not observed.

Investigations are underway to elucidate the mechanisms of these novel reactions and to determine the scope and selectivities of oxidative deaminations by copper and related metal nitrosyls.

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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.

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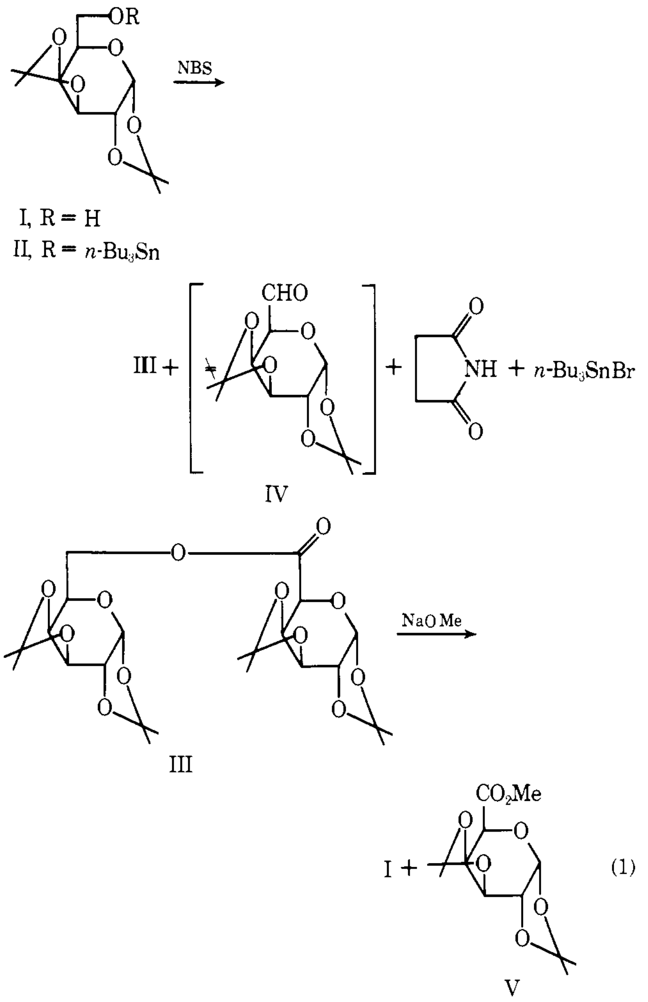
A Novel Oxidative Transformation: Oxidative Esterification

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).



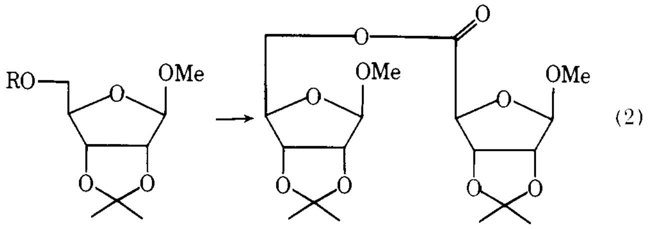
I, R = H
II, R = n-Bu$_3$Sn

IV

III

V

(1)



(2)

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-