of the reaction mixture was continued even after the disappearance of the starting material. Evaporation of the solvent after 5 h of irradiation of the reaction mixture afforded a dark pink residue which upon preparative TLC in $CHCl_3$ gave 24 mg (10%) of oxazine **10** from the fastest band and 129 mg (46%) of alkoxy lactam **11** from a slower moving band (R_f 0.17): NMR ($CDCl_3$) δ 3.30 (3 H, s), 3.83 (3 H, s), 3.94 (3 H, s), 4.62 and 5.08 (2 H, AB quartet, J_{AB} = 15 Hz), 6.31 (1 H, d, J = 6.0 Hz), 6.58 (1 H, d, J = 2.5 Hz), 6.72 (1 H, d, J = 2.5 Hz), 7.02 (1 H, d, J = 6.0 Hz): IR ($CHCl_3$) 1704 cm^{-1}; mass spectrum m/e (rel intensity) 277 (5), 262 (100).

3a-Methoxy-5H-pyrrolo[1,2-*a*][3,1]benzoxazin-1(3a*H*)-one (14). A solution of alcohol **12** (173 mg, 1 mmol) in 100 mL of methanol with added Rose Bengal (10 mg) was irradiated under the conditions described for the formation of **10**. After the consumption of the starting material which took 6 h, no oxazine **13** could be isolated by preparative TLC in $CHCl_3$, but an alkoxy lactam **14** was obtained from a slow moving band (R_f 0.12) as a yellow solid: (56 mg, 20%) NMR ($CDCl_3$) δ 3.34 (3 H, s), 4.92 and 5.37 (2 H, AB quartet, J_{AB} = 15 Hz), 6.44 (1 H, d, J = 6.0 Hz), 7.17 (1 H, d, J = 6.0 Hz), 7–7.3 (3 H, m), 8.12 (1 H, dd, J = 8.0, 2.5 Hz).

1-[α-(*tert*-Butyldimethylsiloxy)-4,6-dimethoxy-*o*-tolyl]pyrrole (15). To a solution of pyrrole alcohol **9** (466 mg, 2 mmol) in 2 mL of DMF were added dimethyl-*tert*-butylsilyl chloride (450 mg, 3 mmol) and imidazole (204 mg, 3 mmol) at 0 °C under nitrogen. The solution was stirred at this temperature for 10 min and at room temperature for 1 h. Workup involved diluting the reaction mixture with ether. The ethereal layer was washed with H_2O and dried over Na_2SO_4 and the solvent was removed in vacuo. Silica gel chromatography of the crude reaction mixture on three 20 × 20 cm preparative TLC plates ($CHCl_3$) yielded 556 mg (80%) of silyl ether **15** as a colorless gum. An analytical sample was prepared by sublimation of **15** at 100 °C (0.03 Torr): NMR ($CDCl_3$) δ 0.05 (6 H, s), 0.90 (9 H, s), 3.72 (3 H, s), 3.85 (3 H, s), 4.42 (2 H, s), 6.31 (2 H, t, J = 2.1 Hz), 6.48 (1 H, d, J = 2.5 Hz), 6.62 (2 H, t, J = 2.1 Hz), 6.83 (1 H, d, J = 2.5 Hz).

Anal. Calcd for $C_{19}H_{29}NO_3Si$: C, 65.70; H, 8.35; N, 4.02. Found: C, 65.80; H, 8.33; N, 4.08.

1-[α-(*tert*-Butyldimethylsiloxy)-4,6-dimethoxy-*o*-tolyl]-5-methoxy-3-pyrrolin-2-one (16). A 250-mL Pyrex graduated cylinder inside of which was placed a filter (soft glass) was charged with alcohol **15** (150 mg, 0.43 mmol), Rose Bengal (15 mg), and 150 mL of methanol. The solution, with a slow stream of oxygen passed through, was irradiated with a Sylvania tungsten Halogen quartz lamp No. Q/Cl (80 V) which was in a water-cooled immersion apparatus. The reaction was carried out at 0 °C in an ice bath and was monitored by TLC (3% MeOH/$CHCl_3$). After 40 min the reaction was complete. The solvent was removed on a rotary evaporator below 45 °C, and the dark residue was roughly separated by column chromatography on silica gel (8 in. × 1 in.) eluting successively with $CHCl_3$ and 3% MeOH/$CHCl_3$. The combined fractions were purified by preparative thin-layer chromatography to give one major product (R_f 0.46 in 3% MeOH/$CHCl_3$) (68 mg, 45%): IR ($CHCl_3$) 1710 cm^{-1} (C=O); NMR ($CDCl_3$) δ 0.6 (6 H, s), 0.98 (9 H, s), 3.28 (3 H, s), 3.76 (3 H, s), 3.83 (3 H, s), 4.78 (2 H, s), 5.65 (1 H, m), 6.25 (1 H, dd, J = 6.0, 1.0 Hz), 6.43 (1 H, d, J = 2.5 Hz), 6.88 (1 H, d, J = 2.5 Hz), 7.03 (1 H, dd, J = 6.0, 1.5 Hz).

Desilylation of 16. A solution of silyl lactam **16** (40 mg, 0.11 mmol) in 5.5 mL of an acetic acid–H_2O–THF mixture (3:1:1.5) was stirred overnight at 50 °C. The reaction mixture was diluted with EtOAc and washed with 5% $NaHCO_3$, water, and brine and then dried with Na_2SO_4. Removal of solvent afforded 30 mg of crude alcohol **17:** NMR ($CDCl_3$) δ 3.32 (3 H, s), 3.80 (3 H, s), 3.88 (3 H, s), 4.52 (2 H, s), 5.72 (1 H, m), 6.38 (1 H, dd, J = 6.0, 1.0 Hz), 6.52 (1 H, d, J = 2.5 Hz), 6.72 (1 H, d, J = 2.5 Hz), 7.2 (1 H, dd, J = 6.0, 1.0 Hz); IR ($CHCl_3$) 1710 cm^{-1}.

Registry No.—9, 66769-50-4; **10,** 66769-51-5; **11,** 66769-52-6; **12,** 61034-86-4; **14,** 66769-53-7; **15,** 66769-54-8; **16,** 66787-42-6; **17,** 66769-55-9; 1-(2,4-dimethoxy-6-methoxycarbonylphenyl)pyrrole, 66769-56-0; 1-(2-carboxyphenyl)pyrrole, 10333-68-3; dimethyl-*tert*-butylsilyl chloride, 18162-48-6.

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Preparation of Carboxylic Acids from Protected Aldehydes

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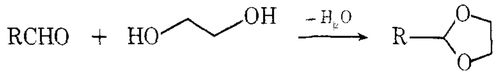
Received February 1, 1978

The acetal is the most common protecting group for aldehydes and 1,3-dioxolanes are the most commonly encountered type of acetal, usually prepared by reaction of the aldehyde with ethylene glycol with azeotropic removal of water (eq 1).[1] Regeneration of the carbonyl is normally carried out with aqueous acid.[2]

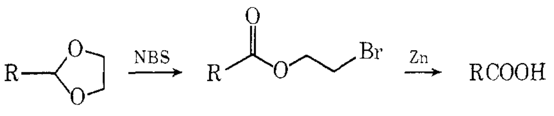


(1)

We have been concerned with the general problem of converting dioxolanes into carboxylic acids without employing acid to first remove the protecting group (eq 2). The nonacidic alternative to eq 2 would allow the introduction of acid groups into a molecule containing various acid-sensitive functionalities.[3]

(2)

Our solution to this problem is outlined in eq 3. Prugh and McCarthy in 1966[4] showed that cyclic acetals are converted into bromo esters when treated with *N*-bromosuccinimide (NBS).[5,6] Indeed, a variety of dioxolanes give good yields of the corresponding 2-bromoethyl esters when refluxed with NBS in CCl_4 (see Table I). For example, 2-phenyl-1,3-dioxolane gives a 98% yield of 2-bromoethyl benzoate (88% after distillation).



(3)

The transformation of eq 3 is completed by a zinc-induced 1,2 elimination which yields the acid upon workup (see Table I). Despite the precedent for this second step,[7,8] a variety of reaction conditions failed to give any acid from 2-bromoethyl benzoate. Zinc in refluxing THF gave no reaction. Even zinc which had been activated with copper sulfate was ineffective and ultraactive zinc from the potassium metal[9a] or sodium naphthalenide[9b] reduction of zinc chloride also failed to promote elimination. Zinc in refluxing methanol or ethanol gives 42–46% benzoic acid plus 47–52% of transesterification product. Ester interchange can be avoided by using zinc in refluxing aqueous THF to give a 44% yield of benzoic acid and a 41% recovery of starting material. Addition of catalytic sodium iodide improves the yield of benzoic acid from this reaction to 86% with only 13% of starting material recovered.

Because of the general catalytic effect of zinc halides,[10,11] we tried a mixture of zinc and zinc chloride. Indeed, this combination of reagents in refluxing THF for 24 h converts

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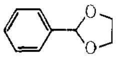
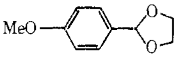
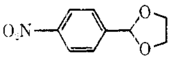
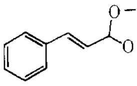
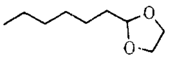
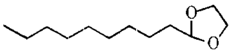
Table I. Conversion of Dioxolanes into Carboxylic Acids

acetal	registry no.	% yield of 2-bromoethyl ester (*a*)	registry no.	% acid[b,c]	registry no.
	936-51-6	98 (88)	939-54-8	99[d]	65-85-0
	2403-50-1	68 (59)	19263-28-6	96[d]	100-09-4
	2403-53-4	60 (51)	23574-40-5	58[e]	62-23-7
	5660-60-6	91 (75)	39257-72-2	91[e]	621-82-9
	1708-34-5	87 (70)	5454-31-9	91[e]	111-14-8
	4353-06-4	67 (55)	52001-54-4	76[e]	334-48-5

[a] % yield of purified material. [b] Pure by NMR and mp. [c] Based on recovered starting material. [d] Using zinc (5 equiv) and catalytic sodium iodide (2–5 mol %) in refluxing 50% aqueous THF. [e] Using zinc (5 equiv) and zinc chloride (1 equiv) in refluxing dimethyl sulfoxide (Me_2SO).

2-bromoethyl benzoate into benzoic acid (61%) with a 30% recovery of starting material. Cleavage of other 2-bromoethyl esters may require Me_2SO as a solvent in order to maintain synthetically useful yields.

Two recent literature methods for the conversion of 2-haloethyl esters to acids offer excellent alternatives for the second step of eq 3. Ho[12] has shown that thiocarbonate ion gives 75–86% yields of acids and Ugi[13] used cobalt(I)-phthalocyanine to cleave bromoethyl and chloroethyl esters to acids.[14]

Experimental Section

^1H NMR spectra were obtained on a Varian T-60 nuclear magnetic resonance spectrometer. Melting points were determined with a Thomas-Hoover capillary melting point apparatus and are corrected.

The typical experimental procedure for benzaldehyde follows.

2-Bromoethyl Benzoate. 2-Phenyl-1,3-dioxolane (17.8 g, 0.12 mol; prepared from benzaldehyde and 1.2 equiv of ethylene glycol at reflux in benzene containing catalytic *p*-TsOH with water removal (Dean-Stark trap) for 6 h) was dissolved in 150 mL of CCl_4. NBS (21.4 g, 0.12 mol) was added along with a catalytic amount of benzoyl peroxide and the mixture was refluxed overnight. The succinimide was filtered off and the filtrate was washed with aqueous $Na_2S_2O_3$ and then water. The CCl_4 solution was dried ($MgSO_4$) and concentrated to give 26.8 g (98%) of an orange liquid which was distilled to yield 24.1 g (88%) of a colorless liquid: bp 90–92 °C (0.5 mm); NMR (CCl_4) δ 3.7 (t, J = 6 Hz, 2 H), 4.7 (t, J = 6 Hz, 2 H), 7.6 (m, 3 H), 8.2 (m, 2 H).

Benzoic Acid. The ester above (1.00 g, 4.36 mmol) was dissolved in 20 mL each of THF and water. Zinc powder[15] (1.43 g, 21.8 g-atom) and sodium iodide (20 mg) were added. The mixture was refluxed for 24 h, cooled, and filtered. Acidification of the filtrate and extraction with ether gave a solution which was further extracted with aqueous $NaHCO_3$. The remaining ether was dried and concentrated to give 0.13 g (13%) of starting material (as determined by NMR). The bicarbonate layer was acidified and extracted with ether to yield 0.46 g (86%) of white solid (benzoic acid), mp 119–121 °C. Thus, the yield of benzoic acid is 99% based on recovered starting material.

Registry No.—Benzaldehyde, 100-52-7; *p*-anisaldehyde, 123-11-5; *p*-nitrobenzaldehyde, 555-16-8; cinnamaldehyde, 104-55-2; heptanal, 111-71-7; decanal, 112-31-2; ethylene glycol, 107-21-1.

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(14) This paper is dedicated to the memory of Lawrence C., Anderson, deceased February 17, 1978.
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(3-Methyl-3-methoxy-1-butynyl)copper, a Useful Reagent for the Generation of Mixed Cuprates

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Received March 30, 1978

The use of mixed cuprate (Gilman) reagents derived from terminal alkynes, $RC{\equiv}CCuR_T$, for the selective transfer of alkyl or alkenyl groups (R_T) was introduced several years ago[1] for the purpose of conserving valuable R_T groups in synthetic processes such as cross coupling or enone conjugate addition. These cuprates are generally formed by reaction of a cuprous