extracted twice with $CHCl_3$. The organic layer was dried, filtered, and concentrated to yield 0.82 g (98%) of **6**; an analytical sample was prepared by crystallization from CH_2Cl_2–C_6H_{14}: mp 106–8 °C; ^1H NMR ($CDCl_3$) δ 3.35 (3 **H**, s), 7.50 (1 H, dd, J = 4 and 6 Hz), 8.47 (1 H, dd, J = 2 and 6 Hz), and 8.63 (1 H, dd, J = 2 and 4 Hz); IR (Nujol) 1300 and 1160 cm^{-1}.

Anal. Calcd for $C_6H_6ClNO_2S$: C, 37.60; H, 3.16; N, 7.31. Found: C, 37.88; H, 3.10; N, 7.36.

2-Chloro-3-thiocyanopyridine (7). To a solution of **2** (25.7 g, 0.2 mol) in concentrated HCl (350 mL) was added dropwise at −10 to 0 °C a solution of $NaNO_2$ (17 g, 0.2 mol) in H_2O (65 mL). After complete addition, the mixture was stirred an additional 0.5 h and then added with stirring to a solution of KCu $(SCN)_2$ (24.4 g, 0.11 mol) and KSCN (120 g) in H_2O (2.5 L). After the evolution of N_2 ceased, the dark-colored solution was filtered through super cel, and the pad was washed well with Et_2O. After separating the Et_2O layer, the aqueous layer was extracted twice with Et_2O. The combined Et_2O extracts were washed with H_2O, saturated NaCl, and saturated Na_2CO_3, dried, filtered, and concentrated. The residue was sublimed at 80 °C (0.2 mm) to yield 25.6 g (75%) of **7**: mp 79–80 °C; ^1H NMR ($CDCl_3$) δ 7.43 (1 H, dd, J = 4 and 8 Hz), 8.07 (1 H, dd, J = 5 and 8 Hz), and 8.43 (1 H, dd, J = 2 and 4 Hz); IR (Nujol) 2175 cm^{-1}.

Anal. Calcd for $C_6H_3ClN_2S$: C, 42.24; H, 1.77; N, 16.42. Found: C, 42.35; H, 1.80; N, 16.30.

2-Chloro-3-(trichloromethylthio)pyridine (8). To a solution of **7** (3.42 g, 0.02 mol) and TEBA (0.5 g) in $CHCl_3$ (76 g, 0.6 mol) was added dropwise a solution of 50% aqueous NaOH (40 mL). After complete addition, the black solution was stirred for 1 h at 25 °C and then filtered through super cel. The layers were separated, and the aqueous layer was further extracted twice with $CHCl_3$. The organic phases were dried, filtered, and concentrated. The residue was placed on a column of dry silica gel and eluted with $CHCl_3$ to yield, after evaporation of the solvent, 5.3 g (59%) of **8**: bp 93–5 °C (0.15 mm); ^1H NMR ($CDCl_3$) δ 7.37 (1 H, dd, J = 4 and 8 Hz), 8.3 (1 H, dd, J = 2 and 8 Hz), and 8.53 (1 H, dd, J = 2 and 4 Hz).

Anal. Calcd for $C_6H_3Cl_4NS$: C, 27.40; H, 1.15; N, 5.33. Found: C, 27.69; H, 1.30; N, 5.35.

2-Chloro-3-(trichloromethylsulfinyl)pyridine (10). To a solution of **8** (10.6 g, 0.04 mol) in AcOH (50 mL) was added aqueous H_2O_2 (30%, 12 mL). After the solution was stirred for 48 h at 25 °C, additional H_2O_2 (30%, 1 mL) was added, and the mixture was stirred at 25 °C for 24 h. The mixture was then concentrated at 40 °C. The residual orange oil was partitioned between H_2O–$CHCl_3$ and separated, and the aqueous layer was further extracted with $CHCl_3$ (2×). The organic phases were dried, filtered, and concentrated to yield 9.7 g (82%) of **10**. An analytical sample was crystallized from C_6H_{14}: mp 86–87 °C; ^1H NMR ($CDCl_3$) δ 7.50 (1 H, dd, J = 5 and 8 Hz), 8.41 (1 H, dd, J = 2 and 8 Hz), and 8.64 (1 H, dd, J = 2 and 5 Hz); IR ($CHCl_3$) 1095 cm^{-1}.

Anal. Calcd for $C_6H_3Cl_4NOS$: C, 25.83; H, 1.08; N, 5.02; Cl, 50.84. Found: C, 26.24; H, 0.99; N, 5.41; Cl, 50.52.

2-Chloro-3-(trichloromethylsulfinyl)pyridine 1-Oxide (11). 3,5-Dinitroperbenzoic acid was prepared according to the procedure of Rastetter[11] from 3,5-dinitrobenzoic acid (16.4 g, 0.078 mol) and 90% H_2O_2 (10 mL) in methanesulfonic acid (42 g). The mixture was stirred for 3 h at 53 °C after an initial exotherm. The workup as described[11] yielded 14 g of a light yellow solid, mp 182–90 °C dec (lit.[11] mp 113–15 °C then 195–200 °C). Iodometric titration indicated 106.2% of theoretical active oxygen.

A slurry of **10** (0.7 g, 0.0025 mol) and the above peracid (0.57 g, 0.0025 mol) in $CHCl_3$ (10 mL) was stirred for 2 days at 25 °C and then refluxed for 2 h. The mixture was cooled, diluted with four volumes of $CHCl_3$, and extracted with aqueous $NaHCO_3$. The $CHCl_3$ extract was chromatographed on a dry column of silica gel, and the product was eluted with $CHCl_3$ to yield 0.35 g (47%) of **11**: mp 150–151 °C (n-C_4H_9Cl); IR ($CHCl_3$) 1410, 1265, 1103 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.44 (1 H_5, m), 7.85 (1 H_4, bd, J = 8 Hz), and 8.47 (1 H_6, bd J = 6 Hz); MS m/e 292.8643 ($C_6H_3Cl_4NO_2S$), 175.9574 (M − CCl_3), 159.9627 (M − $OCCl_3$), and 116.9068 (CCl_3).

2-Bromo-3-(trifluoromethyl)pyridine (9b). A solution of Ac_2O (52 mL), 1,1,3,3,tetramethoxypropane (26.4 g, 0.16 mL), **15** (14.5 g, 0.1 mol), and $ZnCl_2$ (1 g) was heated at reflux. After 18 h, the mixture was distilled up to 110 °C at atmospheric pressure. The residue was then cooled to 25 °C and filtered. The clear solution was distilled to yield 3.5 g of **16** (bp 65–93 °C (18 mm)) and 5.3 g of **17** (bp 83–105 °C (0.5 mm)). This material was combined and used in the next step without further purification.

A solution of 30% HBr·AcOH (70 mL) was added dropwise with stirring at 40 °C to a solution of **16** and **17** (8.8 g) in AcOH (40 mL). After the addition, the solution was heated at 55 °C for 2 h, poured onto ice, and neutralized with solid Na_2CO_3. The solution was extracted with CH_2Cl_2 (3×), and the CH_2Cl_2 extracts were dried, filtered, and concentrated to dryness. The residual oil was distilled at 68–71 °C (0.3 mm) to yield 4.2 g (16%) of **9b**: ^1H NMR ($CDCl_3$) δ 7.35 (1 H, dd, J = 4 and 8 Hz), 8.05 (1 H, dd, J = 2 and 8 Hz), 8.45 (1 H, dd, J = 2 and 4 Hz); ^{19}F NMR ($CDCl_3$) +40.7 (s).

The exact mass was 256.9130 (calcd for $C_6H_3NBr^{79}SF_3$, 256.9122) and 258.9106 (calcd for $C_6H_3NBr^{81}SF_3$, 258.9102).

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Registry No. **2**, 6298-19-7; **3**, 70682-07-4; **4**, 65753-48-2; **5**, 70682-08-5; **6**, 70682-09-6; **7**, 2769-31-5; **8**, 70682-10-9; **9b**, 70682-11-0; **10**, 70682-12-1; **11**, 70682-13-2; **15**, 34033-79-9; **16**, 70682-14-3; **17**, 70682-15-4; 1,1,3,3-tetramethoxypropane, 102-52-3.

Phosphoric Acid Systems.[1] 9. Trimethyl Phosphate (TMP) Mediated Halogenative Cleavage of Cyclic Acetals

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Both mechanistic and stereochemical aspects involved in the conversion of cyclic acetals **1** to haloesters **2** with various halogenating agents have been intensively examined issues in recent years.[2-8] Traditionally, this synthetically useful transformation[3,5,8,9] has been effected with *N*-bromosuccinimide.[2-5,7,10-14] Reaction conditions

(1) Part of this work in preliminary form was presented at the 30th South Eastern American Chemical Society Regional Meeting held at Savannah, GA, Nov. 8–10, 1978. For part 8, see ref 18.

(2) J. D. Prugh and W. C. McCarthy, *Tetrahedron Lett.*, 1351 (1966).

(3) T. L. Huller and S. B. Siskin, *J. Org. Chem.*, **35**, 225 (1970).

(4) J. Gelas and S. Michaud, *Bull. Soc. Chim. Fr.*, 2445 (1972).

(5) D. A. Seeley and J. McElwee, *J. Org. Chem.*, **38**, 1691 (1973).

(6) Y. Kamiya and S. Takemura, *Chem. Pharm. Bull.*, **22**, 201 (1974).

(7) H. H. Lee and S. F. Chen, *J. Chem. Soc., Perkin Trans. 1*, 270 (1978).

(8) (a) M. S. Newman and C. H. Chen, *J. Am. Chem. Soc.*, **94**, 2149 (1972); (b) M. S. Newman and C. H. Chen, *J. Org. Chem.*, **38**, 1173 (1973).

(9) For a few examples, see: (a) D. H. R. Barton, L. Bould, D. L. C. Clive, P. D. Magnus, and T. Hase, *J. Chem. Soc. C*, 2204 (1971); (b) F. S. Legagneur and M. Le Gall, *Bull. Soc. Chim. Fr.*, 553 (1966); (c) M. M. Ponpipom and S. Hanessian, *Can. J. Chem.*, **50**, 253 (1972).

(10) L. C. Anderson and H. W. Pinnick, *J. Org. Chem.*, **43**, 3417 (1978).

(11) (a) A. Reiche, E. Schmitz, and E. Beyer, *Chem. Ber.*, **91**, 1935 (1958); (b) A. Reiche, E. Schmitz, W. Schade, and E. Beyer, *ibid.*, **94**, 2926 (1961).

(12) M. M. Movsumzade, A. L. Shabanov, N. V. Petrova. Sh. S. Muradova, and F. Kh. Agaev, *J. Org. Chem. USSR (Engl. Transl.)*, **10**, 2483 (1974).

(13) The conversion of **1** → **2** with NBS has been reported (a) in the presence of a radical initiation (ref 2-4, 7, 10, and 11), (b) by irradiation with UV light (ref 11 and 12), (c) in the presence of an acid acceptor (ref 3 and 4), (d) with a trace of acid (ref 5), and (e) in the presence of Cu^+ ions and a radical source (ref 7).

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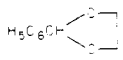
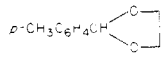
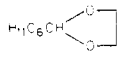
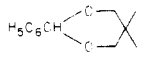
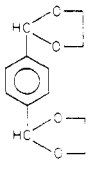
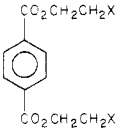
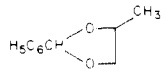
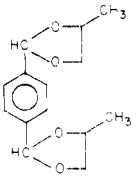
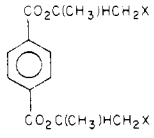
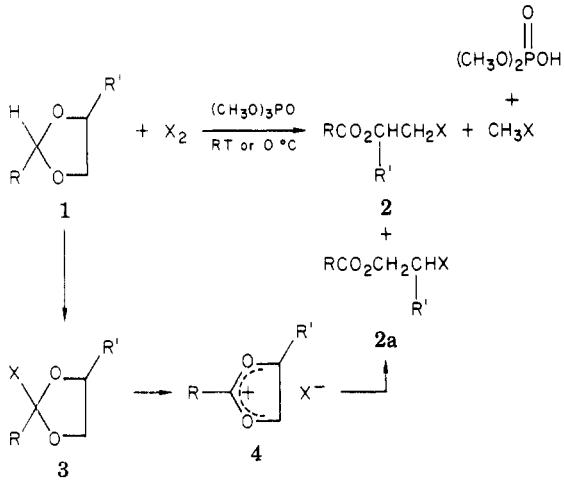
Table I

no.	cyclic acetal	mp, °C, or bp, °C (mm)	reaction conditions	halo ester	X	mp, °C, or bp, °C (mm)	yield, %[a]
1		65-68 (0.5)	RT/1 h	$C_6H_5CO_2CH_2CH_2X$	Br	100 (0.7)	87
2		80 (0.2)	RT/1 h	p-$CH_3C_6H_4CO_2CH_2CH_2X$	Br	95 (0.2)	81
3		103-5 (19)	0 °C/1 h RT/3 h	$H_{11}C_6CO_2CH_2CH_2X$	Br	110 (5)	88
4		[88-94 (0.5)] 32-33	RT/24 h	$H_5C_6CO_2CH_2C(CH_3)_2CH_2X$	Br	106-7 (0.4)	80[b]
5		89-90	RT/2 h		Br Cl	96-97 90-92	81[c] 83[c]
6		70 (0.25)[d]	0 °C/1 h RT/1 h	$H_5C_6CO_2C(CH_3)HCH_2X$	Br Cl	104 (0.8) 135 (1.1)	93[e] 88[e]
7		[137-8 (0.2)][b,d] 58-60[f]	RT/2 h		Br Cl	48-50 62-64	72[b,c] 81[b,c]

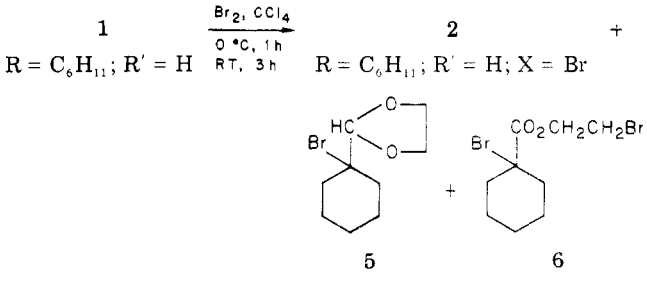
[a] Isolated yield of product after purification which was homogeneous by ^1H NMR. [b] Satisfactory elemental analyses were obtained. [c] Recrystallized from methanol-water. [d] A mixture of cis and trans isomers (3:2).[20] [e] Contaminated with less than 5% of the regioisomer. [f] Crystallized from an ether-hexane mixture.

Scheme I



X = Br, Cl

Scheme II



are key factors in the control of regioselectivity of this process.[15] For instance, reaction of acetal **1** (R = C_6H_5; R′ = CH_3) with NBS catalyzed by a radical source[2] gives isomeric esters **2** and **2a** (R = C_6H_5; R′ = CH_3; X = Br) in the ratio 5:1, whereas in the acid-catalyzed reaction **2** and **2a** are formed in a 10:1 ratio.[5,16] We have elsewhere[17,18] demonstrated the utility of trimethyl phosphate (TMP) in the halogenation reaction both as an excellent aprotic dipolar solvent and as a scavenger for hydrogen halide coproduced. Continuing our work in this area, we have found exceptional ease of cleavage of cyclic acetals **1** by halogens (Br_2, Cl_2) leading to halo esters **2** under mild conditions with high regioselectivity.

2-Phenyl-1,3-dioxolane (**1**, R = C_6H_5; R′ = H) reacted readily with bromine in TMP to give 2-bromoethyl benzoate (**2**, R = C_6H_5; R′ = H; X = Br) in 87% yield. Examples of systems investigated are listed in Table I. In all cases, cleavage with bromine or chlorine occurred readily to give the corresponding haloester in excellent yield. An interesting case is the bromination of 2-cyclohexyl-1,3-dioxolane in TMP which afforded only 2-bromoethyl cyclohexanecarboxylate (entry 3). The same reaction in CCl_4 produced, in addition to the bromoester (**2**, R = C_6H_{11}; R′ = H; X = Br), two other products, **5** and **6**, resulting from an acid-catalyzed bromination of the 1,3-dioxolane group (Scheme II). This example is il-

(14) Several halogenating agents have been employed in this reaction. See: (a) D. L. Rakhmankulov, S. S. Zlotskii, V. N. Uzikova, and Ya. M. Paushkin, *Dokl. Akad. Nauk. SSSR*, **218**, 156 (1974) [*Chem. Abstr.*, **82**, 42634h (1975)]; (b) D. L. Rakhmankulov, S. S. Zlotskii, and V. N. Uzikova, *Zh. Prikl. Khim. (Leningrad)*, **48**, 919 (1975) [*Chem. Abstr.*, **83**, 43249u (1975)]; (c) D. L. Rakhmankulov, P. S. Belov, N. E. Maksimova, and A. Yu Adzhiev, *Tr. Ufim. Neft. Nauchno-Issled. Inst.*, **16**, 276 (1974) [*Chem. Abstr.*, **83**, 164095z (1975)]; (d) see also ref 6.

(15) S. Hunig, *Angew. Chem., Inter. Ed. Engl.*, **3**, 548 (1964).

(16) *N*-Dibromobenzenesulfonamide without added catalysts also gave a similar regiochemical result. See ref 6.

(17) D. E. Pearson, M. G. Frazer, V. S. Frazer, and L. C. Washburn, *Synthesis*, 621 (1976).

(18) D. E. Pearson, S. D. Venkataramu, and W. E. Childers, Jr., *Synth. Commun.*, **9**, 5 (1979).

lustrative of the utility of TMP in suppressing acid-catalyzed side reactions. 2-Phenyl-5,5-dimethyl-1,3-dioxane was also smoothly cleaved (entry 4).

The bis(ethylene acetal) of terephthalaldehyde with bromine and chlorine showed the same behavior to provide the halo esters in good yield (entry 5). Several methods for the preparation of these esters, which are highly sought for intermediates in polymer chemistry, have been described in patented procedures.[19] Most of them suffer from lengthy reaction conditions, high temperatures, difficult manipulations, and moderate yields only.[19] The present procedure has the advantages of both high yield and procedural simplicity.

With respect to the regioselectivity involved in the conversion 1 → 2, treatment of a mixture (3:2)[20] of *cis*- and *trans*-4-methyl-2-phenyl-1,3-dioxolane (1, R = C_6H_5; R′ = CH_3) with bromine in TMP at 0 °C afforded 1-methyl-2-bromoethyl benzoate and 2-methyl-2-bromoethyl benzoate (2 and 2a, R = C_6H_5; R′ = CH_3; X = Br) in the ratio 24:1, respectively (entry 6).[21] The same isomer distribution was found in the chlorination reaction. The bis(propylene acetal) of terephthalaldehyde with bromine and chlorine showed a similar trend (entry 7). This aspect coupled with the fact halogenative cleavage takes place without a radical source implies an ionic pathway indicated in Scheme I.[2-7,15] Halide attack on the ambident cation 4 from the least hindered side accounts for the major isomer formed. High regioselectivity observed in TMP may be due to solvation of the cation in the ion pair 4 resulting in reduced reactivity of the counterion.

In summary, TMP mediated halogenative cleavage is convenient and proceeds rapidly without added catalysts to give pure halo esters in high yields. In most cases, the reaction can be run in a homogeneous medium. Both neutral and mild reaction conditions should permit easily cleavable functional groups to remain intact. The present procedure is also significantly superior with respect to the regioselectivity than with the reported methods.[2-6]

Experimental Section

General Data. Melting points were determined with a Thomas–Hoover capillary melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin–Elmer 727 infrared spectrophotometer. ^1H NMR spectra were obtained on a Jeol MH-100 nuclear magnetic resonance spectrometer. Elemental analyses were carried out by Galbraith Laboratories, Knoxville, Tenn. Trimethyl phosphate (TMP) was distilled over P_2O_5 (bp 52–54 °C (0.5 mm)) and stored in amber-colored bottles.

Starting Materials. The starting acetals were prepared by boiling a mixture of the aldehyde (0.5 mol), glycol (0.55 mol), anhydrous benzene (100 mL), and a catalytic amount of *p*-toluenesulfonic acid with the removal of water (Dean–Stark). After evaporation of the solvent, the residue was distilled under vacuum. Physical data are given in Table I.

General Procedure for the Preparation of Halohydrin Esters. The reactions were run at the temperatures indicated in Table I. To a magnetically stirred solution or suspension of the acetal (0.1 mol) in 50 mL of TMP, protected from moisture, bromine (17.6 g, 0.11 mol in 50 mL of TMP)[22] or chlorine (the gas was bubbled at 0 °C into 50 mL of TMP until 0.11 mol was absorbed) was added dropwise during 1 h. An exothermic reaction ensued in all the cases, and the temperature was not permitted to rise above 10 °C. During the addition, a gas (CH_3Br or CH_3Cl) was evolved. After being stirred for an additional period of time (Table I), about 300 mL of water was added with ice cooling. If an oil separated, it was extracted with hexane (3 × 50 mL), and the combined organic extract was washed with cold water (3 × 50 mL). After being stirred with anhydrous $MgSO_4$ in a hood to expel excess bromine or chlorine, the solvent was removed in a rotoevaporator, and the residue was distilled under vacuum.

If a solid was formed on dilution with water, it was filtered, washed with cold water, and recrystallized from an appropriate solvent.

Physical data and yields are given in Table I.

Bromination of 2-Cyclohexyl-1,3-dioxolane in CCl_4. To a stirred solution of the acetal (15.62 g, 0.1 mol) in 50 mL of CCl_4 cooled to 0 °C was added bromine (17.6 g, 0.11 mol) dissolved in 50 mL of CCl_4 during 1 h ($CaCl_2$ tube). The temperature of the reaction was not allowed to rise above 8 °C by controlled addition. After the solution was stirred at room temperature for 3 h, the usual workup afforded a colorless oil (24.0 g). ^1H NMR analysis of the reaction product showed it to be a mixture of 2 (R = C_6H_{11}; R′ = H; X = Br), 5, and 6. Only bromoester 2 was obtained when the above reaction was run in TMP.

Registry No. 2 (R = C_6H_5, R^1 = H, X = Br), 939-54-8; 2 (R = *p*-$CH_3C_6H_4$, R^1 = H, X = Br), 7143-95-5; 2 (R = C_6H_{11}, R^1 = H, X = Br), 36262-27-8; 2 (R = $Br(CH_2)_2$-O-CO-*p*-C_6H_4, R^1 = H, X = Br), 32676-75-8; 2 (R = $Cl(CH_2)_2$-O-CO-*p*-C_6H_4, R^1 = H, X = Cl), 1026-93-3; 2 (R = C_6H_5, R^1 = CH_3, X = Br), 6065-70-9; 2 (R = C_6H_5, R^1 = CH_3, X = Cl), 36220-92-5; 2 (R = $BrCH_2CH(CH_3)$-O-CO-*p*-C_6H_4, R^1 = CH_3, X = Br), 70659-69-7; 2 (R = $ClCH_2CH(CH_3)$-O-CO-*p*-C_6H_4, R^1 = CH_3, X = Cl), 70659-70-0; 5, 70659-71-1; 6, 70659-72-2; 2-phenyl-1,3-dioxolane, 936-51-6; 2-*p*-tolyl-1,3-dioxolane, 2403-51-2; 2-cyclohexyl-1,3-dioxolane, 4362-48-5; 5,5-dimethyl-2-phenyl-1,3-dioxane, 776-88-5; 2,2′-(1,4-phenylene)bis[1,3-dioxolane], 5660-56-0; *cis*-4-methyl-2-phenyl-1,3-dioxolane, 5932-73-0; *trans*-4-methyl-2-phenyl-1,3-dioxolane, 51591-49-2; 2,2′-(1,4-phenylene)bis[4-methyl-1,3-dioxolane], 70659-73-3; 3-bromo-2,2-dimethylpropyl benzoate, 70659-74-4; benzaldehyde, 100-52-7; *p*-methylbenzaldehyde, 104-87-0; cyclohexanecarboxaldehyde, 2043-61-0; terephthalaldehyde, 623-27-8; ethylene glycol, 107-21-1; 2,2-dimethylpropylene glycol, 126-30-7; 1,2-propylene glycol, 57-55-6.

(19) (a) Netherlands Patent 108 150 [*Chem. Abstr.*, **62**, 7696f (1965)]; (b) Japanese Patent 7503 295 [*Chem. Abstr.*, **83**, 27603z (1975)]; (c) U.S. Patent 3 280 173 [*Chem. Abstr.*, **66**, P 10767h (1967)].

(20) T. D. Inch and N. Williams, *J. Chem. Soc. C*, 263 (1970).

(21) ^1H NMR analysis was performed on the crude reaction product. At room temperature, the ratio of 2:2a is 18:1.

(22) Bromine or chlorine do not react with TMP in the dark. See ref 17.

2β-(Hydroxymethyl)penicillin

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Recent interest in 2β-(hydroxymethyl)penicillins as possible precursors in the biosynthetic conversion of penicillins to cephalosporins[1] prompts us to report a successful synthesis of the title compound.

The first attempt to implicate the 2-(hydroxymethyl)penicillin as a possible intermediate in the biosynthesis of penicillin and cephalosporin antibiotics was reported in 1972 by Cooper.[2] He obtained the 2β-(hydroxymethyl)penicillin 1β-oxide 1 and the corresponding lactone 2 by the oxidation of the thiazolidine azetidinone 3 (Scheme I).

Thus the corresponding 2-(hydroxymethyl)penicillin sulfides were not isolated and the yield of 1 and 2 was less than 5%.[3]

Morin et al.[4] first reported the derivatization of the β-methyl group in penicillin by obtaining 2β-(acetoxymethyl)penicillins from the Pummerer rearrangement on the penicillin sulfoxide with acetic anhydride. Since then

(1) J. E. Baldwin, S. R. Herchen, J. C. Clardy, K. Hirotsu, and T. S. Chou, *J. Org. Chem.*, **43**, 1342 (1978).

(2) R. D. G. Cooper, *J. Am. Chem. Soc.*, **94**, 1018 (1972).

(3) Personal communication with R. D. G. Cooper.

(4) R. B. Morin, B. G. Jackson, R. A. Mueller, E. R. Lavagnino, W. B. Scanlon, and S. L. Andrews, *J. Am. Chem. Soc.*, **91**, 1401 (1969).

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