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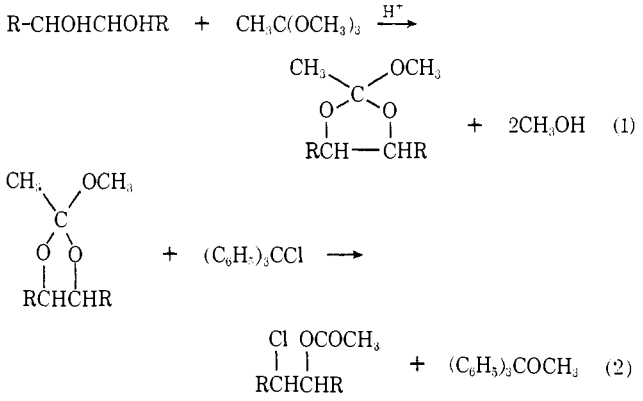
Conversion of Diols *via* Cyclic Orthoacetates to Acetates of Chlorohydrins by Treatment with Trityl Chloride

Sir:

In earlier papers, the conversion of 1,2-, 1,3-, and 1,4-diols to esters of the corresponding halohydrins was accomplished in two steps: (a) the acid-catalyzed reaction of diol with an α-keto acid to yield a ketal acid and (b) the reaction of the ketal acid (or the sodium salt thereof) with phosphorus pentachloride (or thionyl chloride) to yield the ester of the halohydrin.[1,2]

The overall yields from diol to halohydrin ester suffer because a high yielding method for step a was not developed. Furthermore, the use of phosphorus pentachloride (or thionyl chloride) places limitations on the other functionality that may be present. In this communication a new route for conversion of 1,2- and 1,3-glycols to esters of halohydrins is described which overcomes both of the limitations outlined above.

The new route is illustrated by eq 1 and 2.



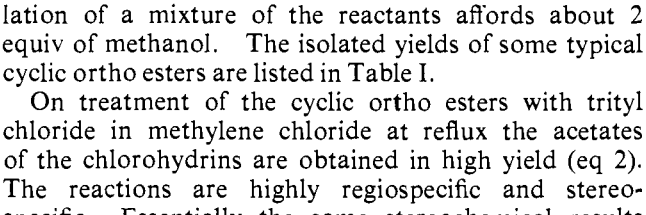
(1)

(2)

As catalysts for ortho ester formation acids as mild as benzoic and chloroacetic acid are satisfactory.[3] Distillation of a mixture of the reactants affords about 2 equiv of methanol. The isolated yields of some typical cyclic ortho esters are listed in Table I.

On treatment of the cyclic ortho esters with trityl chloride in methylene chloride at reflux the acetates of the chlorohydrins are obtained in high yield (eq 2). The reactions are highly regiospecific and stereospecific. Essentially the same stereochemical results are obtained as in the ketal acid reactions described.[1,2] Our results are listed in Table II.

These results suggest a mechanism illustrated with 2-methoxy-2,4-dimethyl-1,3-dioxolane (**1**) which involves attack of the trityl cation on the methoxy group of the ortho ester,[4] followed by reaction of the ambident



cation[5] A thus produced with trityl chloride (or chloride ion). The geometry of the latter reaction is that which would be expected from an SN2 type displacement at the carbon–oxygen bond being broken.

In a typical experiment which illustrates the mild conditions for reaction and the ease of isolation of product, a solution of 2.0 g of D(−)-2-methoxy-2,4,5-trimethyl-1,3-dioxolane (**2**) and 3.8 g (1 equiv) of trityl chloride in 6 ml of CH_2Cl_2 was refluxed for 1–2 hr.[6]

Table I. Synthesis of Cyclic Ortho Esters from Diols

Diol $R_1CHOHCHOHR_2$	Compd, ortho ester[a] $R_1CHO(R_2CHO)C(OCH_3)CH_3$	Bp,[b] °C (P, mm)	Yield, %[c]
$R_1 = CH_3$; $R_2 = H$	**1**[d]	94–95 (14)	85
$R_1 = R_2 = CH_3$[e]	**2**[f]	37.0–37.5 (9.7)	88
$R_1 = C_6H_5$; $R_2 = H$[g]	**3**[d,h]	87.5–89.0 (1.3)	91
2,2-Dimethyl-1,3-propanediol	**4**	51 (10)	80
1,4-Butanediol	**5**	63–64 (20)	62

[a] All cyclic ortho esters were new compounds which gave C and H analyses within ±0.3% of the theoretical. The nmr, ir, and mass spectral data were consistent with the assigned structures. [b] The boiling points listed are those of the cuts isolated by simple distillation. [c] The per cent yield (based on diol) of distilled material. [d] A mixture of diastereoisomeric forms not precisely analyzed. [e] D(−)-2,3-butanediol, $\alpha^{22}D$ −12.9° (neat, 1 dm). [f] $\alpha^{22}D$ −6.26° (neat, 1 dm). [g] $[\alpha]^{19.5}D$ −39.24° (c 0.0304, EtOH), 100% optical purity. [h] $\alpha^{19}D$ −51.8° (neat, 1 dm).

Table II. Reactions of Cyclic Ortho Esters with Trityl Chlorides

Ortho ester[a]	Products[b]	Yield, %[c]
1	**6**, $CH_3C(OCOCH_3)HCH_2Cl$[d]	89
2	**7**, $CH_3C(Cl)HC(OCOCH_3)HCH_3$[e]	90
3	**8**, $C_6H_5CHClCH_2OCOCH_3$[f–h]	93
4	**10**, $ClCH_2C(CH_3)_2CH_2OCOCH_3$	83
5	**11**, $Cl(CH_2)_4OCOCH_3$[i]	38

[a] Ortho esters were used as obtained, Table I. Reactions in CH_2Cl_2 unless otherwise noted. [b] These products had essentially the same properties as described in ref 2. [c] The yield of distilled material. [d] The product was shown by nmr analysis to consist of *ca.* 94% of **6** and 6% of 2-chloropropyl acetate. [e] L(+)-Erythro compound, $\alpha^{23}D$ +12.48° (neat, 1 dm), hence inversion has occurred. D(+)-2,3-Epoxybutane, $[\alpha]^{22}D$ +76.2° (c 0.0613, xylene), was obtained on treatment of **7** with KOH (see ref 2 for details). [f] $[\alpha]^{21}D$ +88.54° (c 0.0324, $CHCl_3$), $\alpha^{19}D$ −67.95° (neat, 1 dm). This compound ((*S*)-**8**) is mixed with about 5% of (*R*)-2-chloro-1-phenylethyl acetate (**9**) (see ref 2 for details of nmr analysis). [g] When run in CH_3CN the product (91% yield) consisted of about 88% of (*S*)-**8** and 12% of (*R*)-**9**. [h] (*R*)-(−)-styrene oxide, $[\alpha]^{22}D$ −21.29° (c 0.0324, $CHCl_3$), was obtained on treatment with KOH. [i] No attempts were made to optimize this yield or to identify the other products formed.

(1) M. S. Newman and C. H. Chen, *J. Amer. Chem. Soc.*, **94**, 2149 (1972).
(2) M. S. Newman and C. H. Chen, paper submitted to *J. Org. Chem.*
(3) R. H. DeWolfe, "Carboxylic Ortho Acid Derivatives," Academic Press, New York, N. Y., 1970.
(4) Compare H. Meerwein, V. Hederich, H. Morschel, and K. Wunderlich, *Justus Liebigs Ann. Chem.*, **635**, 1 (1960).
(5) S. Hünig, *Angew. Chem., Int. Ed. Engl.*, 3, 548 (1964), C. V. Pittman, Jr., S. P. McManus, and J. W. Larsen, *Chem. Rev.*, 72, 357 (1972).
(6) In the case of 3, the reflux period was 10 hr.

Distillation afforded 1.85 g (90%) of **7**,[2] bp 54.5–55.0° (20 mm) $\alpha^{23.5}D$ +12.5° (neat, 1 dm), and 3.48 g (92%) of trityl methyl ether,[7] bp 161–163° (0.8 mm). In most cases the trityl ether was not distilled.

The new cyclic ortho esters prepared are the following: 2-methoxy-2,4-dimethyl-1,3-dioxolane (**1**); D-(−)-2-methoxy-2,4,5-trimethyl-1,3-dioxolane (**2**); (*R*)-(−)-2-methoxy-4-phenyl-1,3-dioxolane (**3**); 2-methoxy-2,5,5-trimethyl-1,3-dioxane (**4**); and 2-methoxy-2-methyl-1,3-dioxepane (**5**). Analyses of these compounds are shown in Table III.

Table III. Analyses of New Compounds

		Analyses[a]			
		C		H	
Compd	Emp formula	Calcd	Found	Calcd	Found
1	$C_6H_{12}O_3$	54.6	54.6	9.1	8.9
2	$C_7H_{14}O_3$	57.5	57.5	9.6	9.7
3	$C_{11}H_{14}O_3$	68.0	67.9	7.2	7.3
4	$C_8H_{16}O_3$	60.0	60.2	10.0	10.2
5	$C_7H_{14}O_3$	57.5	57.7	9.6	9.8

[a] Analyses by M-H-W Laboratories, Garden City, Mich.

Recently, the substitution of trimethylsilyl chloride for trityl chloride has been shown to give similar results. A study of the stereochemical results in these reactions is now being made.[8]

(7) C.-H. Wang, *J. Org. Chem.*, **28**, 2914 (1963).
(8) The use of $(CH_3)_3SiCl$ was demonstrated by Dr. Paul Tornstrom and is being studied by Dr. Dan Olson.
(9) Postdoctoral Fellow supported by Grant No. GP-12445X of the National Science Foundation.

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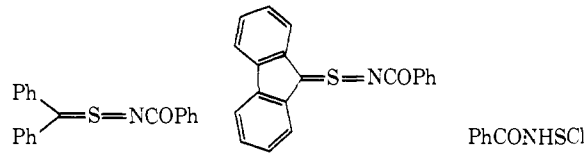
Thione *S*-Imides. Preparation and Cycloaddition Reactions

Sir:

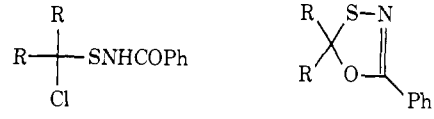
We wish to report the synthesis of the first representative system containing the functional group, $R_2C{=}S{=}NR'$ derived from a thione and to be designated as a thione *S*-imide. Such derivatives should exhibit electrophilic reactivity between thione ylides[1] ($R_2C{=}S{=}CR_2$) and thione *S*-oxides[2] ($R_2C{=}S{=}O$) for similar substitution, and the site (carbon *vs.* sulfur) of such electrophilic reactivity as well as stability would be a function of substituent choice in controlling the degree of contribution of the canonical structures, $C{=}S^+{-}N^- \leftrightarrow C^+{-}S{-}N^- \leftrightarrow {}^-C{-}S^+N$.[3] Consideration of such substitutent effects led to our selection of the thione *S*-imides, **1** and **2**, as an initial target with 1,3-dehydrohalogenation of a precursor α-chlorosulfenamide as the ultimate synthetic step.[4]

(1) M. Takaku, S. Mitamura, and H. Nozaki, *Tetrahedron Lett.*, 3651 (1969); R. M. Kellogg and S. Wassenaar, *ibid.*, 1987 (1970); R. M. Kellogg, S. Wassenaar, and J. Butler, *ibid.*, 4689 (1970).
(2) W. A. Sheppard and J. Diekmann, *J. Amer. Chem. Soc.*, **86**, 1891 (1964); B. Zwannenburg, L. Thijs, and J. Strating, *Tetrahedron Lett.*, 4461 (1969), and references cited therein.
(3) To illustrate this point a stable but apparently unreactive dithioester *S*-tosylimine has been reported: S. Tamagaki and S. Oai, *ibid.*, 1159 (1972).



1 **2** **3**

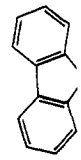
The reaction of *N*-(trimethylsilyl)benzamide[5] with an excess of sulfur dichloride in THF solution at −30° afforded (80–85%) benzamide-*N*-sulfenyl chloride (**3**), mp 105–108° dec, ir ($CHCl_3$) 1670 (C=O) cm^{-1}.[6] Treatment of **3** with an equivalent of diphenyldiazomethane or diazofluorene in THF solution at −78° gave the requisite α-chlorosulfenamides, **4a**, mp 114–117° dec, and **4b**, mp 114–116° dec. Triethylamine reacts rapidly with **4a** in THF solution at −78° without visible formation of a colored intermediate to yield an equivalent of triethylamine hydrochloride and 30% of the oxathiazole, **5a**, mp 118–120°. On the other



4 **5**

a, R = Ph—

b, R,R =



hand, dehydrohalogenation of **4b** under the same conditions provided a deep red (λ_{max} 484 nm) solution of **2**. Upon warming to *ca.* −30° the color of such solutions was discharged and 46% of the electrocylic closure product, 5-phenylspiro(fluorene-9,2′-[1,3,4]oxathiazole) (**5b**), mp 102–103° dec, could be isolated.[7] Both **5a** and **5b** were characterized by their absorption in the ir, ($CHCl_3$) 1605 (C=N), 1575 (C=C) cm^{-1}, and consistent mass spectra. Furthermore, upon standing at room temperature **5b** decomposed to give fluorenone, benzonitrile, and sulfur.

The electrophilic addition of dry HCl to **2** in THF solution at −78° results in the immediate re-formation of **4b**. Although the reactivity at −30° of **2** was not sufficient to compete against internal cyclization for the capture of nucleophiles such as ketene acetals, reaction with enamines or ynamines occurred readily at −78° in THF solution. With *N*-isobutenylpyrrolidine (**6a**) there was obtained (31%) a 1:1 adduct [mp 185–187° dec; ir ($CHCl_3$) 1635 (C=O), 1600 (C=C) cm^{-1}; nmr δ 7.47 (m, 13 H), 5.62 (s, 1 H), 3.23 (m, 4

(4) The potential synthesis of a thione *S*-imide from the addition of a nitrene (or equivalent) to a thione has not been successful. For example, the thermal decomposition of benzenesulfonylazide in the presence of xanthione gives only the corresponding imine of xanthone: A. Schonberg and W. Urban, *J. Chem. Soc.*, 530 (1935). However, the dithio ester derivative reported in ref 3 was a result of the reaction of methanolic chloroamine-*t* with a trithione.
(5) N. Y. Derkach and N. P. Smetankina, *Zh. Obshch. Khim.*, **34**, 3613 (1964).
(6) Satisfactory (±0.3%) elemental analyses (C, H, N, S) have been obtained for all new isolated compounds.
(7) At −78° removal by filtration of the triethylamine hydrochloride and addition of hexane to the filtrate caused red needles of **2** to form. After collection at −78° the solid **2** obtained appeared to be stable at room temperature; however, the slightest amount of mechanical deformation of the crystals resulted in an instantaneous transformation to **5b**.