so highly substituted. The effect of the α-amino group should be essentially the same for most amino acids except perhaps for tryptophane or proline. In any event, the variation in esterification rates for the amino acids will act mainly to demand increased esterification time to reach equilibrium. The importance of the amino acids would seem to warrant some studies along these lines.

It has been our experience that an important difference in behavior between the amino acids is the rates of solution of their hydrochloride salts.[13] The magnitude of this feature has not as yet been investigated in a systematic manner. In any case it is clear from the preceding data that increasing the temperature of the esterification reagent to speed the rate of solution of amino acid hydrochlorides may not be a wise approach. With the thought in mind that a salt with an anion larger than chloride would dissolve more rapidly, we observed the rate of solution of a mixture of amino acid hydrobromides and found no dramatic increase in solubility rate. Sulfate salts do dissolve rapidly[14] but the acid, H_2SO_4, is not volatile and would interfere with steps subsequent to esterification. Gehrke[9] has suggested sonic energy to aid in dissolving the amino acid hydrochlorides.

Clearly, then, esterification of amino acid hydrochlorides at 100° is marginal with respect to reproducible quantitative conversion to esters. If the acids are esterified within less than 5–10 min the water produced at 100° can cause at most a 2–10% decrease in the yield of ester formed depending on esterification equilibrium constant. A rapidly dissolving and esterifying amino acid would be little influenced by the water from the 1-butanol–HCl.

(13) Unpublished work of J. P. Hardy and S. L. Kerrin.
(14) G. E. Pollock, private communication.

Conclusions

It has been shown that, above 100°, 2.7 *M* HCl–1-butanol Fischer esterification reagent produces considerable water in a time comparable to the times required for esterification of the amino acids and probably other carboxylic acids. Thus, to realize good yields or satisfactory quantitative results in esterification reactions with Fischer-type reagents, the reactions should be carried out at temperatures below 100° and for times long enough to ensure complete solution of the amino acid hydrochlorides. To ensure reproducible quantitation of amino acids by gc analysis of their volatile derivatives, such as the *N*-trifluoroacetyl-*O*-butyl esters,[4–8] *N*-trimethylsilyl-*O*-1-butyl esters,[15] and other ester derivatives, the initial esterification step with a Fischer-type reagent should be carried out at temperatures below 100°.

Acknowledgment.—The authors wish to thank Dr. E. A. Cohen for assistance in putting together the Hewlett-Packard 2116 computer program to perform the equilibrium calculations. This paper presents the results of one phase of research carried out at the Jet Propulsion Laboratory, California Institute of Technology, under Contract No. NAS 7-100, sponsored by the National Aeronautics and Space Administration.

Registry No.—1-Butanol–HCl, 42031-19-6; leucine 1-butyl ester hydrochloride, 42031-13-0; 1-chlorobutane, 109-69-3; di-1-butyl ether, 142-96-1; 1-butanol, 71-36-3; leucine HCl, 760-84-9.

(15) J. P. Hardy and S. L. Kerrin, *Anal. Chem.*, **44**, 1497 (1972).

Notes

O-Carbamoyloximes[1]

DAVID R. DALTON* AND H. GRANT FOLEY

Department of Chemistry, Temple University, Philadelphia, Pennsylvania 19122

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Shortly after the turn of the century, a general azoxirane synthesis was reported by Conduché.[2] The method for realizing these compounds (**1**) involved careful treatment of an aqueous suspension of aldehyde with hydroxyurea (presumably generated *in situ* from hydroxylamine hydrochloride and potassium cyanate) or, alternatively, of the hydrogen chloride salt of the oxime of the aldehyde with potassium cyanate.

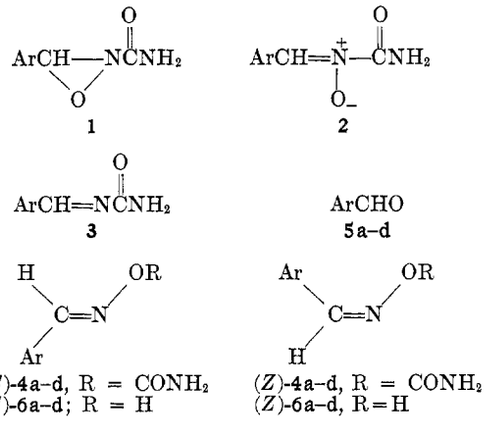
The same products were reportedly obtained by Bellavita and Cagnoli[3] utilizing the first method of Conduché, although the structural class was modified to that of the nitrones (**2**). The new structures were preferred largely because the compounds appeared more stable than would be expected were their structures **1** and, so it was reported, treatment of the compounds **2** with cyanide ion in aqueous solution resulted in formation of the ureides **3**.

The alternative structure **4**, *i.e.*, an *O*-carbamoyloxime, for the original azoxirane was considered possible by Grammaticakis,[4] but clearly this would not satisfy the ureide formation of Bellavita and Cagnoli[3] and he concluded (largely on the basis of ultraviolet spectral comparisons with oximes) that **4** could be rejected.

Finally, however, the elegant interpretation of the available spectral and chemical data by Exner[5] sug-

(1) A communication dealing with a portion of the material contained herein has appeared: D. R. Dalton, H. G. Foley, K. N. Trueblood, and M. R. Murphy, *Tetrahedron Lett.*, 779 (1973).
(2) A. Conduché, *Bull Soc. Chim. Fr.*, [3] **35**, 418 (1906); *Ann. Chim. Phys.*, [8] **12**, 533 (1970); [8] **13**, 5 (1908).
(3) V. Bellavita and N. Cagnoli, *Gazz. Chim. Ital.*, **69**, 583, 602 (1939).
(4) P. Grammaticakis, *Bull. Soc. Chim. Fr.*, **8**, 101 (1941).
(5) O. Exner and M. Horack, *Collect. Czech. Chem. Commun.*, **24**, 2992 (1959), and earlier papers.

gested that the *O*-carbamoyloxime structure (**4**) was correct after all. The formation of the ureides reported by Bellavita and Cagnoli[3] was, however, ignored by Exner and he did confess that his proof was based upon the "proper interpretation of ... the ultraviolet spectra" and examination of the products of reduction with lithium aluminum hydride on the one hand and aluminum amalgam on the other. However, his work has been largely ignored, particularly as regards the nitrones **2**[6] and, indeed, definitive proof was lacking.



4a, 5a, 6a, Ar = *p*-bromophenyl
4b, 5b, 6b, Ar = *p*-chlorophenyl
4c, 5c, 6c, Ar = *m*-nitrophenyl
4d, 5d, 6d, Ar = 3-ethoxy-4-hydroxyphenyl

Our initial interest in this problem stemmed from the reported facile synthesis of ureides through the unprecedented reaction with cyanide ion (*vide supra*).[3] As might be expected, the report is spurious.

Results and Discussion

On treatment of an aqueous solution of hydroxylamine hydrochloride and potassium cyanate with representative aldehydes (**5a–d**) under the original conditions of Conduché[2] a mixture of oximes [(*E*)- and (*Z*)-**6a–d**] and "azoxirane" is obtained. Elemental analyses are in accord with all of the possible formulations presented (**1**, **2**, and **4**) for the "azoxirane."

Mass spectrometric[7] examination of the compound obtained, for example, from *m*-nitrobenzaldehyde (**5c**) is also in concert, potentially, with the formulations **1**, **2**, and **4**. Thus, the molecular ion, *m/e* 209, accords the compound a monomeric nature and the base peak, *m/e* 166, corresponds to that of the *E* oxime [(*E*)-**6c**], as does the remainder of the spectrum. All three formulations, *i.e.*, **1**, **2**, and **4**, could, *a priori*, fragment to generate such a pattern.

The infrared spectra of the compounds prepared by Conduché's method revealed that the 1170–1280-cm^{-1} absorption characteristic of nitrones[8] was absent. Nevertheless, structure **2** could not be eliminated because its unusual nature, *i.e.*, a carbonyl directly attached to the nitrogen of the nitrone, might result in an anomalous shift.

Reduction of the presumed "azoxiranes" with diborane in tetrahydrofuran solution generated the corresponding benzylamines. This result is not in accord with structures **1** and **2**, since nitrogen–oxygen, but not nitrogen–carbon, bond cleavage is expected under these conditions.[9] The same conclusion was reached by Exner[5] concerning lithium aluminum hydride reduction of similar compounds and we therefore concur with his opinion that structure **4** (the *O*-carbamoyloximes) represents the correct formulation for the presumed azoxiranes.

We suggest further that the *O*-carbamoyloximes are formed from isohydroxyurea present in the initial reaction mixture and that the oximes which accompany them are derived from the reaction between aldehyde and hydroxyurea (see Experimental Section). Both hydroxy- and isohydroxyurea are formed on mixture of hydroxylamine hydrochloride and potassium cyanate. The nature of this essentially irreversible reaction (at 0°) to generate two urea derivatives was established unequivocally by Kofod,[10] who also demonstrated that aqueous solutions of the isolable products involved "no decomposition involving formation of ions" on prolonged standing at 0° in water; the structure of isohydroxyurea has been established by X-ray crystal analysis.[11]

As to the ureides of Bellavita and Cagnoli,[3] careful inspection of the experimental data presented by them indicates that the melting points for the reported ureides are, within experimental error, identical with the reported values of the corresponding *E* oximes.[12] The comparison is presented in Table I. We suggest that cyanide ion attacks the carbon of the carbonyl of the *O*-carbamoyloxime (**4**), liberating the oxime. If this is correct, it implies that all of the *O*-carbamoyloximes possess the *E* configuration.

In an effort to determine the configuration unequivocally, oximes (*E*)- and (*Z*)-**6a,b** were treated with chlorosulfonyl isocyanate[13] and the resulting unstable[14] carbamoyl chlorosulfonates were hydrolyzed directly to the corresponding *O*-carbamoyloximes. Regardless of the geometry of the starting oxime (*E* or *Z*) the same *O*-carbamoyloxime was obtained. Attempted examination of the *O*-carbamoyl chlorosulfonates from any pair of oximes was hampered by their rapid decomposition in solution. After only a few minutes at ambient temperatures in acetone-d_6 only the spectrum of the *E* oxime could be observed (regardless of the configuration of the starting oxime). We suggest, therefore, that rapid isomerization of the *O*-carbamoyl chlorosulfonate occurs, concomitant with hydrolysis to the oxime and the

(6) In particular, see (a) J. Hammer and A. Malacuso, *Chem. Rev.*, **46**, 473 (1964), and (b) G. R. Delpierre and M. Lamchen, *Quart. Rev. Chem. Soc.*, **19**, 329 (1965). The latter authors state "If ... a carbonyl group is attached to the nitrogen atom, its −I effect influences the nitrone system to lose oxygen; thus potassium cyanide reacts with the nitrone ... to give the deoxygenated product ... and potassium cyanate."

(7) Mass spectra were obtained on an AEI MS-9 at 70 eV. We gratefully acknowledge the aid of Dr. S. Schrader in obtaining these spectra.

(8) P. A. S. Smith and J. E. Robertson, *J. Amer. Chem. Soc.*, **84**, 1197 (1962).

(9) See, *e.g.*, H. Feuer and D. M. Braunstein, *J. Org. Chem.*, **34**, 1817 (1969).

(10) H. Kofod, *Acta Chem. Scand.*, **7**, 938 (1953).

(11) I. K. Larsen, *Acta Chem., Scand.*, **22**, 843 (1968).

(12) It should be pointed out that the authors were aware that the elemental analyses for the ureides were unacceptable. However, the analyses were reported as being correct, and only later was the problem noted. See V. Bellavita, *Atti X Congr. Int. Chim.*, **3**, 33 (1939); *Chem. Abstr.*, **34**, 10,043 (1940).

(13) R. Graf, *Ber.*, **96**, 56 (1963).

(14) The crystalline materials slowly decompose with evolution of HCl on standing in closed vials at room temperature for several hours. We suspect adventitious moisture responsible but made no effort to keep the carbamoyl chlorosulfonates for extended periods.

TABLE I

Aldehyde RCHO, R	Registry no.	Ureide[a] (presumed) $RCHNCOCH_2$ mp, °C	*E* oxime[b] mp, °C	Registry no.	*Z* oxime[c] mp, °C	Registry no.
C_6H_5	100-52-7	Oil	35	622-31-1		
$C_6H_5CH{=}CH$	104-55-2	75–77	72–73[d]	21737-13-3		
o-$NO_2C_6H_4$	552-89-6	103	102–103[e]	4836-00-4		
m-$NO_2C_6H_4$	99-61-6	123.5	121–123[e]	3717-29-1	121–123	3717-30-4
p-$NO_2C_6H_4$	555-16-8	131	129[e]	3717-19-9	171–172	
p-ClC_6H_4	104-88-1	112	110–111	3717-24-6	157–158	3717-23-5
p-BrC_6H_4	1122-91-4		115–116	40979-16-6	166–167	25062-46-8
p-$CH_3OC_6H_4$	123-11-5	66–67	65[e]	20747-40-4		
3,4-$CH_2O_2C_6H_3$	120-57-0	113.5	110	20747-41-5		
p-$(CH_3)_2CHC_6H_4$	122-03-2	110	112[e,f]	30950-38-0		
p-$(CH_3)_2NC_6H_4$	100-10-7	147	144[e,g]	37961-71-0		

[a] All melting points obtained from ref 3 and subsequent papers. [b] Unless otherwise specified, all melting point data are from R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 5th ed, Wiley, New York, N. Y., 1965 [c] Values are given only for compounds referred to in this paper. [d] B. Unterhalt, *Arch. Pharm. (Weinheim)*, **303**, 661 (1970). [e] These materials are often considered to have the configuration opposite to the one assigned here. However, the assignment is correct as presented here. See R. J. Crawford and C. Woo, *Can. J. Chem.*, **43**, 3178 (1965), and data therein. [f] H. Goldschmidt, *Ber.*, **23**, 2175 (1890). [g] J. C. Duff, *J. Chem. Soc.*, 276 (1945).

O-carbamoyloxime in aqueous solution, and that this too implies that the latter possesses the *E* configuration.

Finally, the *O*-carbamoyloximes (**4a–d**) were identified as indeed possessing the *E* configuration by X-ray crystal analysis of **4a**[15] and correlation of the proton magnetic resonance (pmr) spectra of the analogous **4b–d** with **4a**.[16] In all of these compounds, as with the corresponding oximes, the chemical shift of the benzylic proton is downfield of the aromatic protons (oximes 8.0–8.7 ppm, acetone-d_6, TMS 0.00; *O*-carbamoyloximes 8.0–8.7 ppm, acetone-d_6, TMS 0.00) while in the *Z* oximes, all benzylic proton resonances are upfield (7.3–7.6 ppm, acetone-d_6, TMS 0.00) of the aromatic protons.

We are currently attempting to prepare the (*Z*)-*O*-carbamoyloximes and materials corresponding to the nitrone **2**.

Experimental Section

Aldehydes were obtained from the Aldrich Chemical Co. and used as received. Hydroxylamine hydrochloride and potassium cyanate were Fisher Certified Reagent and used as received. Thin layer chromatography (tlc) was performed on precoated silica gel, GF, 250-μ plates obtained from Analtech, Inc. Infrared spectra were run on a Beckman IR-5A spectrophotometer[17] and proton magnetic resonance (pmr) spectra on a Varian XL-100-15 spectrometer. Analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Melting points were obtained on a Fisher-Thomas melting point apparatus and are uncorrected.

Preparation of *O*-Carbamoyloximes (4a–d).—These compounds were prepared according to the procedure of Conduché.[2] ***p*-Bromobenzaldehyde *O*-carbamoyloxime (4a)**, mp 164–165°, was accompanied by a mixture of the corresponding *E* and *Z* oximes. Tlc (2:1 benzene–ether) showed the presence of all three species, *E* oxime, R_f 0.77, *Z* oxime, R_f 0.56, and *O*-carbamoyloxime, R_f 0.21. Fractional crystallization (CH_2Cl_2) of the solid residue from the above reaction permitted removal of the mixture of oximes ($E/Z > 95/5$):[18] ir (KBr) 1695 cm^{-1} (C=O); pmr (acetone-d_6, TMS 0.00) δ 6.50 (s, 2 H), 7.67 (m, 4 H), 8.41 ppm (s, 1 H). *Anal.* Calcd. for $C_8H_7N_2O_2Br$: C, 39.50; H, 2.88; N, 11.52. Found: C, 39.77; H, 3.10; N, 11.75. This compound forms monoclinic needles, space group $P2_1/c$, with a = 14.39, b = 5.101, c = 12.5 Å, β = 99.51°, and four molecules in the unit cell.[15]

***p*-Chlorobenzaldehyde *O*-carbamoyloxime (4b)** had mp 159–160°; R_f 0.29 (2:1 benzene–ether) (lit.[1] mp 132–135°); ir (Nujol) 1712 cm^{-1} (C=O); pmr (acetone-d_6, TMS 0.00) δ 6.50 (s, 2 H), 7.64 (m, 4 H), 8.42 ppm (s, 1 H). *Anal.* Calcd for $C_8H_7N_2O_2Cl$: C, 48.36; H, 3.52; N, 14.10. Found: C, 48.31; H, 3.65; N, 14.26.

***m*-Nitrobenzaldehyde *O*-carbamoyloxime (4c)** had mp 192° (lit.[1] mp 180°); R_f (2:1 benzene–ether) 0.28; ir (Nujol) 1786 cm^{-1} (C=O); pmr (DMSO-d_6) δ 7.27 (s, 2 H), 8.31 (m, 4 H), 8.73 ppm (s, 1 H). *Anal.* Calcd for $C_8H_7N_3O_4$: C, 45.93; H, 3.35; N, 20.09. Found: C, 45.95; H, 3.63; N, 20.21.

3-Ethoxy-4-hydroxybenzaldehyde *O*-carbamoyloxime (4d) had mp 143–144° (lit.[1] mp 139–140°); R_f (2:1 benzene–ether) 0.14; ir (Nujol) 1724 cm^{-1} (C=O); pmr (acetone-d_6) δ 1.36 (t, 3 H), 2.7 (s, 2 H), 4.1 (q, 4 H), 6.46 (s, 1 H), 7.14 (m, 3 H), 8.27 ppm (s, 1 H). *Anal.* Calcd for $C_{10}H_{12}N_2O_4$: C, 53.57; H, 5.35; N, 12.50. Found: C, 53.37; H, 5.41; N, 12.23.

Attempted Preparation of the Ureides (3).—The compounds obtained above (**4a–c**) were treated with potassium cyanide under the conditions of Bellavita and Cagnoli.[3] The insoluble precipitate which formed was removed by filtration and evaporation of the filtrate yielded, in each case, *E* oxime: *p*-bromobenzaldehyde (*E*)-oxime, mp 115–116° (lit.[19] mp 110–111°), 85%; *p*-chlorobenzaldehyde (*E*)-oxime (**6b**), mp 107–108° (lit.[19] mp 110–111°), 91%; *m*-nitrobenzaldehyde (*E*)-oxime (**6c**), mp 119.5–120° (lit.[19] mp 121–122°); 69%.

Reduction of the *O*-Carbamoyloximes with Diborane.—The procedure of Fauer and Braunstein[9] was followed. *p*-Bromobenzaldehyde *O*-carbamoyloxime (**4a**) yielded *p*-bromobenzylamine (86%); *p*-chlorobenzaldehyde *O*-carbamoyloxime (**4b**) yielded *p*-chlorobenzylamine (100%); *m*-nitrobenzaldehyde *O*-carbamoyloxime (**4c**) yielded *m*-nitrobenzylamine (83%); and 3-ethoxy-4-hydroxybenzaldehyde *O*-carbamoyloxime (**4d**) yielded 3-ethoxy-4-hydroxybenzylamine (80%). The amines were identified by comparison of their spectra with those previously reported where

(15) Compound **4a** forms monoclinic needles, space group $P2_1/c$ with a = 14.39, b = 5.101, c = 12.5 Å, β = 99.51°, and four molecules in the unit cell. The structure was solved by Patterson and Fourier methods and full-matrix least-squares refinement is in progress. The crystal and molecular structure will be the subject of a future communication.

(16) See, *e.g.*, L. M. Jackman and S. Sternhall, "Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, New York, N.Y., 1969, p 226.

(17) The spectrophotometer was purchased from funds provided by a grant (CA 08841) from the National Cancer Institute, National Institutes of Health. We gratefully acknowledge this financial assistance.

(18) While the *Z* oxime could be detected by tlc (comparison with an authentic sample) it proved unreasonable to isolate it. In addition, it could not be detected by pmr spectroscopy of the reaction mixture. Therefore, since we are confident that we could detect 5% of this material were it present by the latter method, we believe its concentration to be far smaller than that indicated.

(19) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 5th ed, Wiley, New York, N. Y., 1965.

available.[20] Alternatively, they were analyzed as their HCl salts.

Preparation of the Oximes (*E*)- and (*Z*)-6a–d.—The *E* oximes were prepared by standard procedures[19] and isomerized to their *Z* counterparts by the method of Crawford and Woo.[21] The melting point data are given in Table I.

Reaction of *E* and *Z* Oximes 4a and 4b with Chlorosulfonyl Isocyanate.—Each of the oximes (0.01 mol) was dissolved in anhydrous benzene and treated with chlorosulfonyl isocyanate (0.01 mol) at room temperature. The precipitate that formed was collected by filtration and washed with hexane. The adducts were permitted to stand in aqueous solution (20 ml) overnight and filtered and the solids obtained were examined by pmr (acetone-d_6) spectroscopy. *E* oxime and *O*-carbamoyloxime (2:1, respectively, by comparison to known mixtures) were found in each case.

Reaction of Aldehydes with Hydroxyurea.—*p*-Bromobenzaldehyde (1.0 g, 5.4 mmol) and *N*-hydroxyurea (814 mg, 10.7 mmol) were mixed, at room temperature, in ethanol–water (2:1) (25 ml), and acid (1.9 ml, 1 *N* HCl) was added. The solution was heated to reflux for 1 hr and poured over ice. The solid so generated (67%) was identified as (*E*)-*p*-bromobenzaldehyde oxime by comparison with a known sample (*vide supra*). In a similar fashion, but without heating, *m*-nitrobenzaldehyde yielded crystalline (*E*)-*m*-nitrobenzaldehyde oxime (83%). It should be pointed out for this latter material that tlc (2:1 benzene–ether) always demonstrates a small amount of *Z* contaminant. The *Z* isomer cannot be detected by pmr.

Acknowledgment.—One of us (H. G. F.) gratefully acknowledges financial assistance from the Fund for Scientific Education, Inc., Philadelphia, Pa.

Registry No.—**4a**, 41514-42-5; **4b**, 41514-43-6; **4c**, 41514-44-7.

(20) "The Sadtler Standard Spectra," Sadtler Research Laboratories, Philadelphia, Pa., 1972.

(21) R. J. Crawford and C. Woo, *Can. J. Chem.*, **43**, 3178 (1965).

Conversion of 1,2-Diols *via* Cyclic Ortho Acetates to Acetates of Chlorohydrins by Treatment with Trimethylsilyl Chloride[1]

MELVIN S. NEWMAN* AND DANIEL R. OLSON[2]

Evans Chemistry Laboratory, The Ohio State University, Columbus, Ohio 43210

Received July 23, 1973

In earlier papers, the conversion of 1,2-diols, **1**, into esters of the corresponding chlorohydrins, **2**, was accomplished by two methods: A, reaction with an α-keto acid to produce a ketal acid, **3**, followed by treatment of the latter with phosphorus pentachloride or thionyl chloride,[3] and B, reaction with trimethyl orthoacetate to form a cyclic ortho ester, **4**, followed by treatment with triphenylmethyl (trityl) chloride.[4] In both cases the reactions were shown to be highly regio- and stereospecific. Since the chlorohydrin esters are readily converted into epoxides by suitable treatment with bases, the synthesis of optically active epoxides is readily accomplished.

A disadvantage of method A is that the yields of **3** based on **1** lie in the 50–70% range. The yields of **4** in method B are excellent but the removal of methyl trityl ether can be troublesome. In this paper we describe method C, in which the disadvantages of methods A and B are overcome. The new method consists of heating the ortho esters, **4**, in methylene chloride with excess trimethylsilyl chloide[5] (much less expensive than trityl chloride). The conversions of **4** to **2** are of the same excellence as the corresponding steps in methods A and B. The removal of excess trimethylsilyl chloride and methyl trimethylsilyl ether is easily accomplished by distillation. The stereochemical results are the same as those reported.[3,4]

(1) This work was supported by Grant CA-07394 from the National Institutes of Health.

(2) Postdoctoral research associate.

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

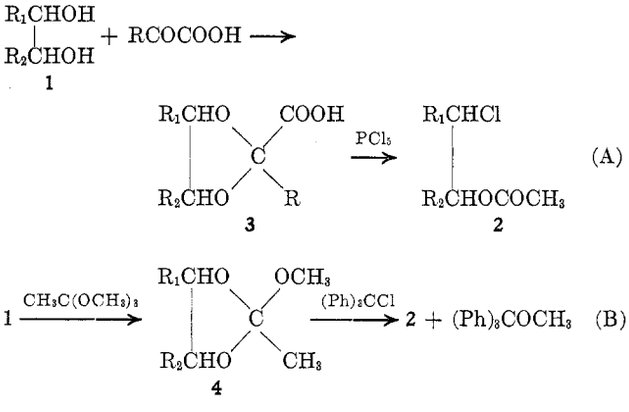
(4) M. S. Newman and C. H. Chen, *J. Amer. Chem. Soc.*, **95**, 278 (1973).

TABLE I

REACTIONS OF CYCLIC ORTHO ESTERS WITH $(CH_3)_3SiCl$

Cyclic ortho ester **4**	Time, hr	Ortho ester, mmol	$(CH_3)_3$-SiCl, mmol	Yield, % **2**
4a, $R_1 = CH_3$; $R_2 = H$	2	20.3	33	86[a]
4b, $R_1 = Ph$; $R_2 = H$	1.5	17.8	28	91[b]
4b, $R_1 = Ph$; $R_2 = H$	2	11.3	12	92[c]
4c, $R_1 = R_2 = CH_3$	1.7	11.8	19	97[d]
4c, $R_1 = R_2 = CH_3$	5	35	37	73[e]
$(CH_3)_2CO$ $>C<$ OCH_3 / H_2CO CH_3	0.5	20.6	26	89[g]

[a] Bp 48–49° (25 mm). This compound was 1-chloro-2-propyl acetate as shown by nmr. However, no europium shift reagent was used as was the case when the same compound was obtained previously and shown to contain about 6% of 2-chloro-1-propyl acetate (see footnote 7 in ref 4). [b] Bp 83–85° (0.2 mm), inactive, mixture of about 95% 2-chloro-2-phenyl acetate and 5% 2-chloro-1-phenyl acetate. [c] $[\alpha]^{25}D$ 86 ± 1° (*c* 3.550, $CHCl_3$). Treatment with sodium hydroxide gave (*R*)-(−)styrene oxide, $\alpha^{25}D$ 34.1° neat, 1 dm, of 97% optical purity [the highest rotation for styrene oxide, 35.2° neat, 1 dm, is reported by C. R. Johnson and C. W. Schroeck, *J. Amer. Chem. Soc.*, **93**, 5303 (1971)], $[\alpha]^{25}D$ −22.5 ± 0.2° (*c* 2.39, $CHCl_3$). [d] Bp 83–84° (52 mm), inactive. [e] The center cut only, bp 75.5–76.0° (34 mm), was taken for measurement of optical activity, $\alpha^{25}D$ 13.32°, neat, 1 dm. Treatment with sodium hydroxide gave D-(+)-2,3-epoxybutane, $\alpha^{25}D$ 45.6°, neat, 1 dm [P. J. Leroux and H. J. Lucas, *J. Amer. Chem. Soc.*, **73**, 41 (1951), report $\alpha^{25}D$ 46.75°]. [f] Bp 82.0–82.5° (85 mm); nmr [CCl_4, $(CH_3)_4Si$] δ 3.75 (s, 2, CH_2), 3.22 (s, 3, OCH_3), 1.45, 1.35 [2 singlets, 6, $(CH_3)_2C$], 1.27 [s, 3, $OC(CH_3)O$]; molecular ion, 146. *Anal.* Calcd for $C_7H_{14}O_3$: C, 57.5; H, 9.7. Found (analysis by Galbraith Laboratories, Knoxville, Tenn.): C, 57.5; H, 9.6. This new compound was prepared by the method described.[4] [g] Bp 63.5–64.5° (23 mm) [A. Bruylants, M. Tits, C. Dieu, and R. Gauthier, *Bull. Soc. Chim. Belg.*, **61**, 366 (1952), give bp 90–91°]. No isomer detected (see footnote 7 in ref 4). Nmr [CCl_4, $(CH_3)_4Si$] δ 4.09 (s, 2, CH_2), 2.40 (s, 3, CH_3CO), 1.77 [s, 6, $(CH_3)_2C$].



(5) The use of $(CH_3)_3SiCl$ was first demonstrated by Dr. Paul Tornstrom in our laboratory.

$$4 + (CH_3)_3SiCl \longrightarrow 2 + (CH_3)_3SiOCH_3 \qquad (C)$$

In a typical reaction a solution of 3.46 g (17.8 mmol) of inactive 2-methoxy-2-methyl-4-phenyl-1,3-dioxolane[4]