Catalytic hydrogenation[5] of the hydroperoxide in ethyl acetate, using PtO_2 catalyst, produced a crude alcohol n_D^{20} 1.4612, which was similar to that obtained by sodium sulfide reduction. The hydroperoxide absorbed 1.01 moles of hydrogen per mole.

A portion of the alcohol mixture remaining after crystallization of *cis*-terpin was distilled at a pressure of 0.9 mm. of mercury. The first fraction (about 5%) had b.p. 48–54°, n_D^{20} 1.4561. This was primarily ketonic material and was discarded. The main fraction (about 72%) had b.p. 54–57°/0.9 mm. 207–209°/approximately 760 mm., n_D^{20} 1.4610. Infrared spectral data[16] (Fig. 2) indicated that this product was a mixture of *p*-menthanols with a trace of ketone (5.8 micron band). Attempts to obtain solid derivatives from it were unsuccessful.

Reduction of p-menthane hydroperoxide from cis-p-menthane. Preparation and reduction were carried out as described for the *trans* isomer. The crude reduction product was steam distilled to give a product having n_D^{20} 1.462, d_4^{20} 0.910 and an infrared spectrum quite similar to that of the product from *trans-p*-menthane. A small amount of non-steam volatile matter was recovered by ether extraction. After removal of the ether and addition of pentane, crystals melting at 115–130° were obtained. Recrystallization reduced the melting range to 122–124°. The amount was too small for further purification and identification.

Acidic oxidation products Acidification of the sodium carbonate extracts obtained during preparation of the hydroperoxide and extraction with chloroform yielded a liquid product, neut. equiv. 208. Partition chromatographic analysis[17] of this material indicated the presence of both mono- and dicarboxylic acids. On the basis of a quantitative hypoiodite oxidation, only 60% of the monocarboxylic acid fraction was the methyl keto acid which would be expected as a decomposition product of *p*-menthane-1-hydroperoxide.

Thermal decomposition of p-menthane hydroperoxide. Thermal decomposition was carried out in the same manner as previously described for pinane hydroperoxide.[5] In the present case 0.3 g. samples of a *p*-menthane oxidate containing 25% of hydroperoxide by weight were used.

OLUSTEE, FLA.

(16) All spectra were obtained on the neat liquids using a Perkin-Elmer 21 spectrophotometer with NaCl optics and an 0.025 mm. cell.

(17) D. E. Baldwin, V. M. Loeblich, and R. V. Lawrence, *Anal. Chem.*, **26**, 760 (1954).

[CONTRIBUTION FROM RESEARCH LABORATORIES OF S. B. PENICK AND COMPANY]

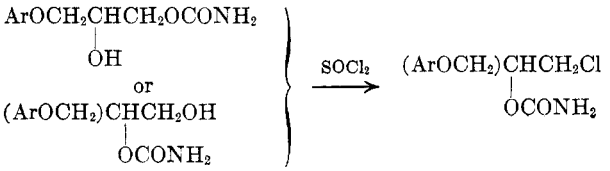
Rearrangement of Substituted 1,2-Glycol Monocarbamates and Related Reactions

JOHN R. CLARK AND MICHAEL PUGLIESE

Received January 29, 1959

The influence of substituents on the rearrangement of β-hydroxyethylcarbamates in the presence of thionyl chloride is discussed. Analogous reactions of epoxides in strongly acid media are related.

It was recently shown that structurally isomeric β-hydroxyethylcarbamates react with $SOCl_2$ to give the same β-chloroethylcarbmate through rearrangement of one of the isomers.[1] This rearrangement has now been confirmed by several more examples. (Table I)

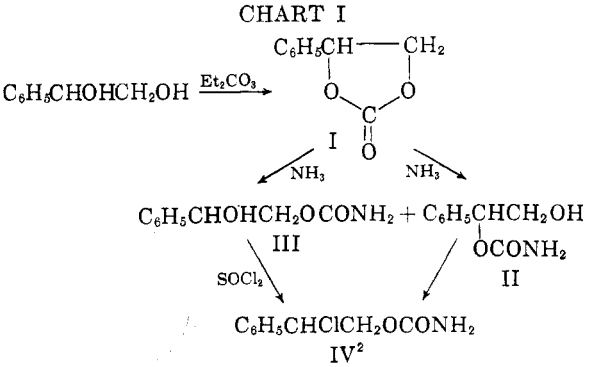


Further investigation of the generality of this process, however, revealed that the nature of the substituent in β-hydroxyethylcarbamates determined the position of the chloro group formed by reaction with thionyl chloride. When the substituent was phenyl, the rearrangement occurred to give the chlorocarbamate in which the chlorine was attached to a secondary carbon atom.

The synthetic method was the same as was previously described.[1]

(1) M. M. Baizer, J. R. Clark and J. Swidinsky, *J. Org. Chem.*, **22**, 1595 (1957).

CHART I



The importance of the substituent in β-hydroxyethylcarbamates, as shown in Chart I, was emphasized by contrast with our previous experience.[1] In that case, rearrangement of the primary carbamate occurred and was assumed to result from addition of the chloride ion to the primary carbon atom of a carbonium ion intermediate, but in both instances a chlorosulfite intermediate is presumably decomposed to give the carbonium ion.[1]

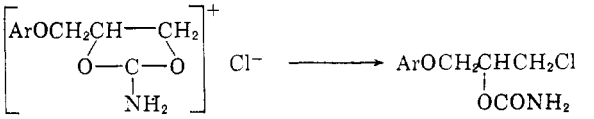
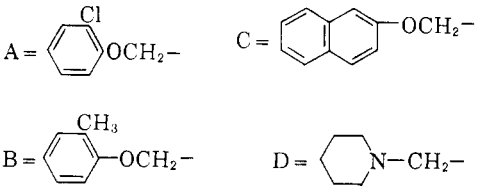
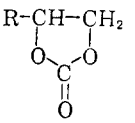


TABLE I



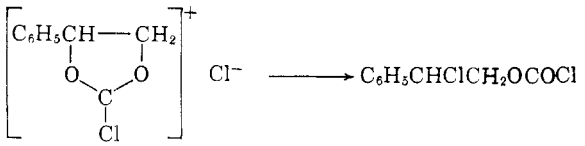
Section I



R	Formula	M.P., °C.	Analyses							
			Calcd.				Found			
			C	H	N	Cl	C	H	N	Cl
IA	$C_{10}H_9ClO_4$	109.0–109.3	52.52	3.93			53.15	3.96		
IB[a]		95.4–96.0								
IC	$C_{14}H_{12}O_4$	127.0–127.5	68.84	4.95			69.23	5.09		
ID[b]	$C_9H_{15}NO_3$		58.35	8.16	7.56		60.17	8.51	8.14	
		Section II								
		$RCH(OCONH_2)CH_2OH$								
IIA	$C_{10}H_{12}ClNO_4$	123.2–123.5	48.87	4.92	5.70		49.49	5.01	6.07	
IIB	$C_{11}H_{15}NO_4$	115.0–115.6	58.65	6.71	6.22		58.82	6.69	6.58	
IIC	$C_{14}H_{15}NO_4$	150.8–151.0	64.36	5.79	5.36		64.38	5.70	5.68	
IID[c]	$C_9H_{19}ClN_2O_3$	170.0–171.0	45.70	8.02	11.32		45.34	8.16	11.47	
		Section III								
		$RCHOHCH_2OCONH_2$								
IIIA	$C_{10}H_{12}ClNO_4$	98.4–98.8	48.87	4.92	5.70		48.99	5.16	5.74	
IIIB[d]		92.0–93.0								
IIIC	$C_{14}H_{15}NO_4$	144.5–145.0	64.36	5.79	5.36		64.40	5.86	5.88	
IIID	$C_9H_{18}N_2O_3$	121.5–122.0	53.39	8.97	13.85		52.99	8.79	13.71	
		Section IV								
		$RCH(OCONH_2)CH_2Cl$								
IVA	$C_{10}H_{11}Cl_2NO_3$	81.2–82.0	45.45	4.17	5.30		45.72	4.35	5.48	
IVB	$C_{11}H_{14}ClNO_3$	87.2–88.0	54.21	5.79	5.75	14.55	54.36	6.04	5.68	14.30
IVC	$C_{14}H_{14}ClNO_3$	125.5–126.0	60.11	5.05	5.01	12.67	60.05	5.01	4.45	12.05
IVD[e]	$C_9H_{17}ClN_2O_2 \cdot H_2O$	142–143	45.69	8.02	11.73	14.85	45.56	7.84	11.57	15.20

[a] Described by B. J. Ludwig and E. C. Piech, *J. Am. Chem. Soc.*, **73**, 5894 (1951). [b] A redistilled oil, b.p. 130–132° (0.5 mm.), n_D^{20} 1.4798; picrate, m.p. 145°, with neut. equiv. calcd. 414 and found by non-aqueous titration, 420. [c] An oil, isolated as the hydrochloride salt, for which the m.p. and analysis are given. [d] Described by H. L. Yale, E. J. Pribyl, W. Braker, F. H. Bergeim, and W. A. Lott, *J. Am. Chem. Soc.*, **72**, 3715 (1950). [e] Isolated as the monohydrate, for which the m.p. and analysis are given.

A related reaction was found to occur when styrene oxide was treated with phosgene.[2] In this case the secondary carbon atom, influenced by the electron-repelling phenyl group, is attacked. In both reactions addition of the chloride ion to the carbonium ion occurs where the electron cloud is least dense.



The apparent analogy between the reaction of phosgene with epoxides[2,3] and the reaction of thionyl chloride with β-hydroxyethylcarbamates bears a striking resemblance to earlier work with hydrohalides and epoxides. Tiffeneau first described the "reverse" addition of hydriodic acid to styrene

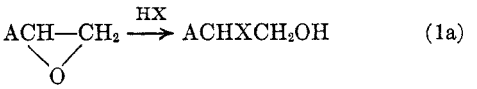
(2) J. I. Jones, *J. Chem. Soc.*, 2735 (1957). The chlorocarbamate (IV) was incorrectly described by Jones as 1-phenyl-1-carbamoxy-2-chloroethane, m.p. 71°C. It was derived from the reaction of styrene oxide with phosgene and subsequent treatment of the chloroformate ester with ammonia.

(3) L. K. Frevel and L. J. Kressley, U. S. Patents **2,820,809** and **2,820,810**, Jan. 21, 1958, *Chem. Abstr.*, **52**, 11897c.

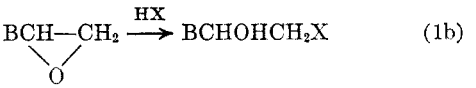
oxide[4] and similar additions to styrene oxide were studied by Golumbic and Cottle.[5]

Our findings appear to be in accord with the excellent discussion published by Kadesch[6] on his work with 3,4-epoxy-1-butene. Other related reactions of epoxides are described in the review by Winstein and Henderson.[7]

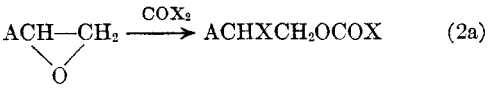
The effect of the substituent may best be illustrated by general equations. Where A is an electron -repelling group, B is an electron -attracting group and X is a halogen, these three sets of equations summarize the expected reactions:



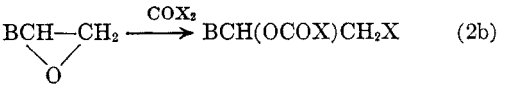
(1a)



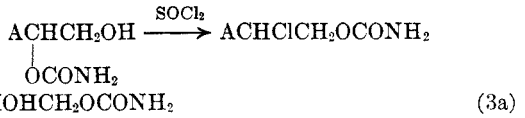
(1b)



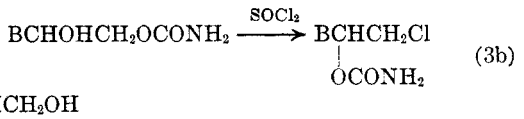
(2a)



(2b)

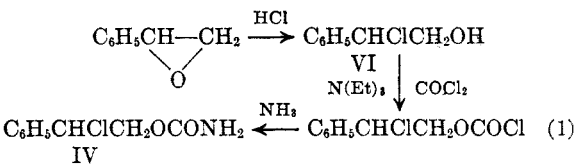


(3a)



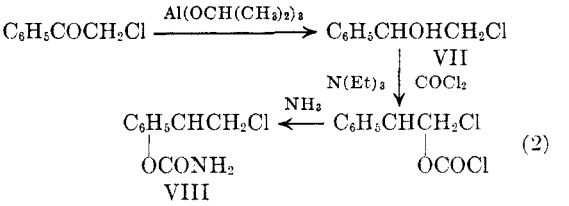
(3b)

Structural Investigation. IV was also prepared by addition of HCl to styrene oxide and successive treatment with phosgene and ammonia. That this



(1)

is an "abnormal" addition to an epoxide was confirmed by the following independent synthesis of the structurally isomeric chlorocarbamate. 1-Phenyl-1-hydroxy-2-chloroethane (VII) was prepared by the reduction of phenacyl chloride.[8] VII was identified by its known *p*-nitrobenzoate[9] and converted to the carbamate (VIII) by stepwise treatment with phosgene and ammonia.



(2)

The structure of IV was further confirmed by cyclization to 4-phenyl-2-oxazolidinone,[10] by a procedure which we soon hope to describe. By the same method, 1-(2-chlorophenoxy)-2-carbamoxy-3-chloropropane and 1-(2-methylphenoxy)-2-carbamoxy-3-chloropropane, respectively, were cyclized to known 5-substituted oxazolidinones.[11]

EXPERIMENTAL[12]

4-Phenyl-2-dioxolone (I). Styrene glycol (138 g., 1 mole) was stirred mechanically and heated in a 2-liter flask with 236 g. (2 moles) of diethyl carbonate and 2.8 g. of sodium methylate for approximately 2 hr. while distilling the alcohol which was formed through a short helices-packed column. When the still temperature had reached 124° the distillation had virtually ceased and the residue was treated with 6 g. of ammonium chloride. The excess ethyl carbonate was distilled *in vacuo* (10 mm.) with the final temperature of the still at 124°. A sample of the residue (I) was recrystallized twice from ethanol; m.p. 55.7–56.7°.

Anal.[13,14] Calcd. for $C_9H_8O_3$: C, 65.85; H, 4.91. Found: C, 65.11; H, 4.83.

1-Phenyl-1-carbamoxy-2-hydroxyethane (II) *and 1-phenyl-1-hydroxy-2-carbamoxy ethane* (III). The crude I, without isolation, was stirred overnight with 1000 ml. of isopropyl alcohol containing 40 g. of ammonia in a tightly stoppered flask. The nearly clear solution was heated to reflux to remove the excess ammonia and filtered hot after stirring with charcoal. The solvent was removed *in vacuo* on a steam bath to recover 190 g. of crude oily hydroxycarbamates. A 5 g. sample of the mixture was dissolved in 50 ml. of isopropyl acetate and chromatographed through a 15-inch column of active alumina. Two fractions, which crystallized on evaporation of the solvent, were recrystallized from isopropyl alcohol to obtain isomeric carbamates; m.p. 100° and 111°, respectively. The mixture melting point of these isomers was from 80–90°.

Using these crystals as seeds it was possible to fractionally crystallize the mixture from isopropyl alcohol to obtain sufficient material for further work.

Anal. Calcd. for $C_9H_{11}NO_3$: C, 59.65; H, 6.12; N, 7.73. Found II, m.p. 100.2–101.4°: C, 60.07; H, 5.94; N, 7.63. III, m.p. 111.6–112.6°: C, 60.34; H, 6.13; N, 7.97.

1-Phenyl-1-chloro-2-carbamoxyethane (IV). A. The crude mixture of hydroxycarbamates (18.1 g., 0.10 mole) was sus-

(4) M. Tiffeneau, *Ann. chim. phys.* [8] **10**, 322 (1907), *Chem. Abstr.*, **2**, 265.

(5) C. Golumbic and D. L. Cottle, *J. Am. Chem. Soc.*, **61**, 996 (1939).

(6) R. G. Kadesch, *J. Am. Chem. Soc.*, **68**, 41 (1946).

(7) S. Winstein and R. B. Henderson in *Heterocyclic Compounds*, R. C. Elderfield, editor, John Wiley and Sons, Inc., New York, 1950, Vol. I, pp. 1–60.

(8) T. Bergkvist, *Svensk Kem. Tid.*, **59**, 24 (1947), *Chem. Abstr.*, **41**, 5119h.

(9) W. E. Hanby and H. N. Rydon, *J. Chem. Soc.*, 114 (1946).

(10) M. S. Newman and W. M. Edwards, *J. Am. Chem. Soc.*, **76**, 1840 (1954).

(11) Y. M. Beasley, V. Petrow, O. Stephenson, and A. J. Thomas, *J. Pharm. and Pharmacol.*, **9**, 13 (1957).

(12) Melting points are corrected unless otherwise stated, boiling points are not.

(13) Microanalyses by Schwarzkopf Microanalytical Laboratory, Woodside, L. I., N. Y.

(14) Reported[2] 54–56°.

pended by stirring in 80 ml. of dry toluene and 13 g. (0.11 mole) of thionyl chloride was added at 30°. The evolution of hydrogen chloride was rapid at about 35°, and the mixture was slowly heated to 85°. It was then heated rapidly to 110°, and at reflux temperature for 2 hr. while passing in a slow stream of nitrogen to remove sulfur dioxide. The hot solution was then treated with charcoal and filtered. After concentrating to about 40 ml. and cooling, the crystallization was rapid. The total crude yield was 14.43 g., m.p. 67–71° (uncorrected). A sample of this was recrystallized twice from toluene-cyclohexane to obtain pure IV; m.p. 67.5–68.5°.

Anal. Calcd. for $C_9H_{10}ClNO_2$: C, 54.65; H, 5.01; N, 7.02; Cl, 17.76. Found: C, 54.36; H, 5.35; N, 7.01; Cl, 17.57.

B. A sample of IV was also prepared from 5 g. of styrene oxide according to the procedure of J. I. Jones[2] without purification of the intermediate chloroformate. On recrystallization of the crude product from toluene-cyclohexane, a yield of 4.29 g. (52.3%) of IV was obtained; m.p. 66.5–68°. This gave no depression in a mixture melting point with crystals from A.

C. Commercial styrene oxide (28 ml.) was added with cooling at 30–35° to 150 ml. of concentrated hydrochloric acid. The oil which separated was extracted with benzene, washed with water, dilute sodium carbonate, and finally with water. The solution was dried over sodium sulfate and, after removal of the solvent, was distilled at 110–114°/8 mm.; n_D^{29} = 1.5532. Only 11 g. of the crude chlorohydrin (VI) was obtained by this procedure, while the major portion remained as a polymer in the still.

The chlorohydrin (VI) (7.85 g., 0.05 mole) was added with 5.05 g. (0.05 mole) of triethylamine in 50 ml. of dry toluene to 5.45 g. (0.055 mole) of phosgene in 50 ml. of toluene while stirring at 5–7°. The mixture was then washed with ice water to remove triethylamine hydrochloride and added below 15° to 100 ml. of concentrated ammonium hydroxide with rapid stirring. After standing overnight at room temperature the toluene solution was evaporated *in vacuo* and the residue was recrystallized to obtain 2.5 g. of IV; m.p. 66–68°. A mixture melting point with material prepared by method A showed no depression. The low yield in this experiment may be accounted for by the relative ease with which IV is hydrolyzed.[2]

D. Samples of both II and III yielded IV on treatment with thionyl chloride as described in method A.

1-Phenyl-1-carbamoxy-2-chloroethane (VIII). Phenacyl chloride (15.5 g., 0.109 mole) was reduced in 100 ml. of isopropanol with aluminum powder (1.8 g.) and 0.1 g. mercuric chloride according to the procedure described by Bergkvist.[8] The yield of 1-phenyl-1-hydroxy-2-chloroethane (VII) was 11.5 g. (73%), b.p. 82–85°/0.5 mm., n_D^{20} 1.5480. This formed a *p*-nitrobenzoate,[9] m.p. 80–81°.

A sample of VII (7.84 g., 0.05 mole) with triethylamine (5.05 g., 0.05 mole) in 30 ml. of dry toluene was added at 3–7° with good stirring to phosgene (5.45 g., 0.055 mole) in 50 ml. of toluene. The amine salt was removed by washing with ice water and the toluene solution was added to 50 ml. of 28% ammonium hydroxide at 10–15°.

After stirring 1 hr. longer, the toluene was separated and washed with water. The solvent was distilled *in vacuo* and the residue was recrystallized from cyclohexane to recover 5.5 g. of crude VIII; m.p. 83.5–84.5°. A sample recrystallized twice from cyclohexane-toluene yielded pure VIII; m.p. 84.2–84.8°.

Anal. Calcd. for $C_9H_{10}ClNO_2$: C, 54.65; H, 5.01; N, 7.02; Cl, 17.76. Found: C, 54.95; H, 5.09; N, 7.05; Cl, 17.56.

A mixture melting point of VIII with IV was 48.0–50.0°.

1-(2-Methoxyphenoxy)-2-carbamoxy-3-chloropropane. Although no yield data is given in Table I for the compounds described, the high yields which can be obtained are illustrated by the following three step synthesis.

The crude mixture of hydroxycarbamates, obtained from the stepwise treatment of 1-(2-methoxyphenoxy)-2,3-propanediol (99 g., 0.5 mole) with diethyl carbonate and ammonia,[1] was stirred in 400 ml. of toluene and 65 g. (0.55 mole) of thionyl chloride was added at room temperature. The mixture was heated slowly to 85° while passing in a slow stream of nitrogen and stirred 3 hr. longer at this temperature.

The mixture was cooled slowly, finally in an ice bath, and filtered. After washing with 50 ml. of benzene the 1-(2-methoxyphenoxy)-2-carbamoxy-2-chloropropane was dried to obtain 110 g. (85%) of virtually pure product, m.p. 105.0–106.0°.

1-(1-Piperidyl)-2-carbamoxy-3-chloropropane (IVD). IVD was prepared by a procedure analogous to that used in the three step synthesis of the 1-aryloxy-2-carbamoxy-3-chloropropanes already described. In the chlorination-rearrangement step excess thionyl chloride, however, was used as solvent for the reaction rather than toluene. The product was isolated by distillation of the excess thionyl chloride and treatment of the residue with aqueous sodium carbonate. The chlorocarbamate was extracted with chloroform, and the residual oil from evaporation of the solvent was recrystallized from isopropanol.

Acknowledgment. We are grateful to Dr. W. G. Bywater, S. B. Penick and Co., for reviewing this paper.

NUTLEY, N. J.