530. *The Reaction of Carbonyl Chloride with* 1 : 2-*Epoxides.*

By J. IDRIS JONES.

Carbonyl chloride (1 mole) adds readily to an epoxide (1 mole) with formation of the corresponding 2-chloro-substituted chloroformate. With 2 moles of epoxide and 1 mole of carbonyl chloride the product is the corresponding bis-2-chloroalkyl carbonate. The direction of ring opening in some unsymmetrical epoxides has been established: opening appears to be unidirectional. Series of 2-chloro-substituted carbamates and *N*-substituted carbamates have been prepared from the chloroformates, and a convenient synthesis of *N*-substituted oxazolid-2-ones has been evolved based on the removal of hydrogen chloride from the mono-*N*-substituted chloroalkyl carbamates. The chlorine atom in 2-chloro-1-phenylethyl carbamate is readily hydrolysed and elimination of ammonia follows, to give phenylethylene carbonate (2-oxo-4-phenyl-1 : 3-dioxolan). The reaction of thiocarbonyl chloride with epoxyethane has also been examined.

1 : 2-EPOXIDES are highly reactive and many of their reactions have been studied in detail.[1] When this work was undertaken[2] the reaction with carbonyl chloride had not been examined. With equimolar proportions it was found that ring opening occurs readily, with formation of 2-chloro-substituted chloroformates, but with 2 mol. of epoxide further

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[1] Elderfield, " Heterocyclic Compounds," Wiley, 1950, Vol. I, pp. 1—57.

[2] " Chemistry Research," 1953, Department of Scientific and Industrial Research, p. 38.

reaction ensues giving the corresponding bis-2-chloroalkyl carbonates in excellent yield. The latter reaction had been described by Pechukas.[3] Depending on the proportions of reactants and the experimental conditions it is possible to obtain high yields of either chloroformate or carbonate. In most cases the reaction is vigorous and exothermic, and cooling, or the use of an inert diluent, is necessary particularly if a catalyst, *e.g.*, pyridine, is added. Malinowski and Medjanzewa[4] recently reported that in ethyl bromide at 0° without a catalyst reaction proceeds only to the chloroformate stage and with only moderate yields.

When excess of carbonyl chloride was passed into liquid epoxyethane (ethylene oxide) containing a trace of pyridine at —10° to —20°, with cooling, and the temperature then allowed to rise slowly to room temperature, 2-chloroethyl chloroformate was obtained almost exclusively. (Pyridine and other tertiary bases are known to catalyse the decomposition of chloroformates[5] and, for this reason, it is advisable to use only minute amounts as catalyst if the end-product is to be the chloroformate.) When 2 mols. of the epoxide were similarly treated with 1 mol. of carbonyl chloride a quantitative yield of bis-2-chloroethyl carbonate resulted. The carbonate was also obtained in quantitative yield by treating 2-chloroethyl chloroformate with epoxyethane in the presence of a trace of pyridine. Vinyl chloroformate has been prepared by pyrolysis of glycol chloroformate[6] and the possibility that 2-chloroethyl chloroformate serves as an intermediate in this decomposition prompted a study of the pyrolysis of the chloroformate. Decomposition, however, proceeded almost exclusively to give ethylene dichloride. Attempts to prepare divinyl carbonate by removing hydrogen chloride from bis-2-chloroethyl carbonate with triethylamine and by pyrolysis at 450° were also unsuccessful.

1 : 2-Epoxy*cyclo*hexane reacted readily with carbonyl chloride, giving 2-chloro*cyclo*hexyl chloroformate and bis-2-chloro*cyclo*hexyl carbonate. If the usual Walden inversion occurs on ring opening, the chloroformate should have the *trans*-structure. This was confirmed by conversion of *trans*-2-chloro*cyclo*hexanol into the chloroformate by treatment with carbonyl chloride; the two products were identical. Two crystalline modifications of the carbonate, m. p.s 111° and 65—66° severally, were obtained. These correspond to the *meso*- and racemic forms of the *trans-trans*-carbonate, inversion occurring at each opening of the oxide ring.

1 : 2-Epoxypropane, being unsymmetrical, could give rise to two chloroformic esters according to the direction of ring opening. Thus, with hydrogen chloride, both 1-chloropropan-2-ol and 2-chloropropan-1-ol are formed.[7] However, under the conditions of our reaction the sole product was 2-chloro-1-methylethyl chloroformate. Its identity was established by comparison of its physical constants (including infrared absorption spectrum) with those of synthetic material prepared by an unequivocal method, *viz.*, by treating 1-chloropropan-2-ol (derived from allyl chloride by Bancroft's method[8]) with carbonyl chloride. Further, hydrolysis of the chloroformate obtained from the epoxide gave 1-chloropropan-2-ol, identical with the synthetic material. 1 : 2-Epoxypropane (2 mol.) and carbonyl chloride (1 mol.) gave di-(2-chloro-1-methylethyl) carbonate in excellent yield. There are two possible stereoisomeric forms of the carbonate, *meso* and racemic. On long storage one crystalline form (m. p. 50°) was obtained from the mixture. When 2-chloro-1-methylethyl chloroformate was condensed with 1-chloropropan-2-ol in equimolar proportions the mixed stereoisomeric carbonates obtained were the same as those derived from 1 : 2-epoxypropane.

In most reactions of 3-chloro-1 : 2-epoxypropane the oxide ring, although unsymmetrical, opens exclusively in one direction, and in the reaction with carbonyl chloride

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[3] Pechukas, U.S.P. 2,518,058.

[4] Malinowski and Medjanzewa, *J. Gen. Chem.* (*U.S.S.R.*), 1953, **23**, 221.

[5] Nakanishi, Myers, and Jensen, *J. Amer. Chem. Soc.*, 1955, **77**, 5033.

[6] Küng, U.S.P. 2,377,085.

[7] Forsberg and Smith, *Acta Chem. Scand.*, 1947, **1**, 577.

[8] Bancroft, *J. Amer. Chem. Soc.*, 1919, **41**, 426.

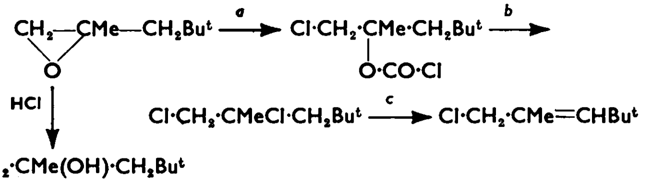
the only products were 2-chloro-1-chloromethylethyl chloroformate and di-(2-chloro-1-chloromethylethyl) carbonate. Attempts to prepare the chloroformate by treating 1 : 3-dichloropropan-2-ol with carbonyl chloride in an open system were unsuccessful, but the same carbonate, m. p. and mixed m. p. 47°, was obtained by heating 1 : 2-dichloropropan-2-ol with the chloroformate derived from the epoxide.

2-Chloroethyl 2-chloro-1-chloromethylethyl carbonate was prepared from 2-chloro-1-chloromethylethyl chloroformate and epoxyethane. This example serves to illustrate the preparation of mixed carbonates from chloroformic esters and epoxides.

2 : 3-Epoxybutane exists in *cis*- and *trans*-forms. The *trans*-form on treatment with carbonyl chloride gave the (±)-*erythro*-2-chloro-1-methylpropyl chloroformate. This structure was confirmed by the identity of the physical constants and infrared spectrum with those of material made from carbonyl chloride and (±)-*erythro*-2-chlorobutan-2-ol (prepared[9] by adding concentrated hydrochloric acid to *trans*-2 : 3-epoxybutane). The corresponding carbonate was also obtained, presumably, as a mixture of stereoisomers.

The chloroformate derived from styrene oxide proved to be exclusively (±)-2-chloro-1-phenylethyl chloroformate. The related carbonate was obtained as a mixture of two stereoisomeric forms, one of which was crystalline.

Attempts to prepare the chloroformate from 1 : 2-epoxy-2 : 4 : 4-trimethylpentane were unsuccessful. Decomposition intervened and the only products characterised were 1-chloro-2 : 4 : 4-trimethylpentan-2-ol, identical with the isomer described by Graham, Millidge, and Young,[10] and a chlorotrimethylpentene, presumably 1-chloro-2 : 4 : 4-trimethylpent-2-ene which appears to be identical with that described by Umnowa[11] as resulting from the reaction of chlorine or hypochlorous acid with di*iso*butene and by Graham *et al.*[10] as a product of dehydration of the chlorohydrin. The reaction with carbonyl chloride is believed to take the following course:



The hydrogen chloride liberated in reaction (*c*) reacts with the epoxide, giving the chlorohydrin.

The infrared absorption spectra of the chloroformates and carbonates prepared have already been reported.[12] The chloroformates have been used for synthesising a series of chlorocarbamates and *N*-substituted chlorocarbamates for screening as selective weed-killers (see Table 1).

In 1885 Nemirowsky[13] prepared 2-chloroethyl *N*-phenylcarbamate from 2-chloroethyl chloroformate (derived from carbonyl chloride and 2-chloroethanol) and found it to cyclise readily in alkaline solution to give 3-phenyloxazolid-2-one. Other 2-chloroethyl carbamates and oxazolidones have been prepared in the same way by others.[14] Delaby *et al.*[15] prepared 2-chloroethyl carbamates by the reaction of thionyl chloride on the corresponding 2-hydroxyethyl carbamates, and Chabrier *et al.*[16] extended this reaction.

[9] Lucas and Gould, *J. Amer. Chem. Soc.*, 1941, **63**, 2547.

[10] Graham, Millidge, and Young, *J.*, 1954, 2180.

[11] Umnowa, *J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1536.

[12] Hales, Jones, and Kynaston, *J.*, 1957, 618.

[13] Nemirowsky, *J. prakt. Chem.*, 1885, **31**, 173.

[14] (*a*) Otto, *ibid.*, 1891, **44**, 15; (*b*) Johnson and Langley, *Amer. Chem. J.*, 1910, **44**, 352; (*c*) Adams and Segur, *J. Amer. Chem. Soc.*, 1923, **45**, 785; (*d*) Pierce, *ibid.*, 1928, **50**, 241; (*e*) Sprinson, *ibid.*, 1941, **63**, 2249; (*f*) McKay and Braun, *J. Org. Chem.*, 1951, **16**, 1829.

[15] Delaby, Sekera, Chabrier, and Piganiol, *Bull. Soc. chim. France*, 1951, 392.

[16] Chabrier, Najer, and Giudicelli, *Compt. rend.*, 1954, **238**, 1593.

TABLE 1.

X	Yield (%)	M. p.	B. p. (°/mm.)	Found (%)				Required (%)				Refs.
				C	H	N	Cl	C	H	N	Cl	
2-*Chloroethyl carbamates*, $Cl\cdot CH_2\cdot CH_2\cdot O\cdot CO\cdot X$												
NH_2	97	77°	—	29·5	4·9	11·3	28·5	29·2	4·9	11·3	28·7	15
NHMe	90	19	111°/13	35·1	5·9	10·3	25·3	34·9	5·8	10·2	25·8	14*e*, 15
NHEt	88	23	115—118°/19	39·4	6·8	8·5	23·3	39·6	6·6	9·2	23·4	14*e*, 15
$NHBu^n$	80	—	142—145°/16	46·8	7·8	7·8	19·6	46·8	7·8	7·8	19·7	14*e*
$NH\cdot C_5H_{11}$-*n*	76	—	87—88°/0·25	49·2	8·4	7·5	18·5	49·6	8·3	7·2	18·3	
$NH\cdot C_6H_{13}$-*n*	77	21·5	102—103°/0·25	52·2	8·8	7·4	17·0	52·0	8·7	6·7	17·1	
$NH\cdot C_7H_{15}$-*n*	70	19	120°/0·35	54·5	9·4	6·6	16·1	54·2	9·1	6·3	16·0	
$NH\cdot C_8H_{17}$-*n*	52	27·5	135—136°/0·15	55·9	9·3	5·8	15·0	56·1	9·4	5·9	15·0	
NHPh	91	52	148—150°/1	54·0	5·0	6·9	17·7	54·1	5·0	7·0	17·8	13, 14*e*
$NH\cdot C_6H_4Me$-*p*	88	62	168—170°/1	56·3	5·8	6·5	16·4	56·2	5·7	6·6	16·6	14*c*
$NH\cdot C_6H_4Me$-*o*	73	49	—	56·6	5·8	6·4	16·6	56·2	5·7	6·6	16·6	14*c*, *f*
$NH\cdot C_6H_4Cl$-*o*	92	58·5	—	46·6	4·0	6·3	29·6	46·0	4·3	6·0	30·2	14*c*, *f*
$NH\cdot C_6H_4Cl$-*m*	83	50	—	46·2	3·9	5·9	30·0	46·0	4·3	6·0	30·2	14*f*
$NH\cdot C_6H_4Cl$-*p*	95	72	—	46·2	3·9	6·1	29·9	46·0	4·3	6·0	30·2	14*c*, *f*
$NH\cdot C_{10}H_7$-α	77	105	—	62·4	4·8	5·9	14·2	62·5	4·8	5·6	14·2	14*a*, *f*
$NH\cdot C_{10}H_7$-β	77	103·5	—	62·6	4·9	5·4	14·8	62·5	4·8	5·6	14·2	14*a*
NEt_2	87	—	109—110°/15	46·8	7·8	7·7	19·5	46·8	7·8	7·8	19·7	14*e*, *f*
NPh_2	75	77	—	65·5	5·1	4·8	12·7	65·3	5·1	5·1	12·9	
NPhMe	82	—	112—115°/0·1	55·8	5·6	7·0	16·5	56·2	5·6	6·6	16·6	
$N<[CH_2]_5$	84	—	101—102°/0·1	49·2	7·1	7·0	19·2	50·1	7·3	7·3	18·5	14*e*
2-*Chloro*-1-*methylethyl carbamates*, $Cl\cdot CH_2\cdot CHMe\cdot O\cdot CO\cdot X$												
NH_2	95	63	—	34·7	5·7	10·1	26·0	34·9	5·8	10·2	25·8	16
NHMe	92	—	116°/15	39·3	6·7	9·0	22·9	39·6	6·6	9·2	23·4	16
$NHBu^n$	83	—	145°/15	49·8	8·5	7·1	18·3	49·6	8·3	7·2	18·3	
$NH\cdot C_5H_{11}$-*n*	72	—	97—99°/0·15	52·0	8·7	7·1	18·1	52·0	8·7	6·7	17·1	
$NN\cdot C_6H_{13}$-*n*	85	1	112—114°/0·2	54·6	9·2	6·9	16·0	54·2	9·1	6·3	16·0	
$NH\cdot C_7H_{15}$-*n*	50	5	130—135°/0·3	55·8	9·5	5·8	15·6	56·1	9·4	5·9	15·0	
$NH\cdot C_8H_{17}$-*n*	64	9	120—121°/0·15	57·5	9·8	5·7	14·9	57·7	9·7	5·6	14·2	
NHPh	95	37	145°/0·1	56·6	5·7	7·1	16·0	56·2	5·7	6·6	16·6	
$NH\cdot C_6H_4Me$-*o*	81	53	—	58·0	6·3	6·7	15·7	58·0	6·2	6·2	15·6	
$NH\cdot C_6H_4Me$-*p*	97	55	—	58·0	6·4	6·6	15·5	58·0	6·2	6·2	15·6	
$NH\cdot C_6H_4Cl$-*o*	92	—	122°/0·25	48·9	4·8	6·0	28·2	48·4	4·5	5·7	28·6	
$NH\cdot C_6H_4Cl$-*m*	83	—	150—155°/0·1	48·2	4·2	5·8	29·1	48·4	4·5	5·7	28·6	
$NH\cdot C_6H_4Cl$-*p*	93	65·5	—	48·4	4·5	6·4	28·6	48·4	4·5	5·7	28·6	
$NH\cdot C_{10}H_7$-α	72	71	—	64·5	5·4	5·1	13·5	63·8	5·4	5·3	13·5	
$NH\cdot C_{10}H_7$-β	89	102·5	—	63·8	5·4	5·8	13·4	63·8	5·4	5·3	13·5	
NEt_2	73	—	110—111°/16	49·6	8·15	7·2	18·4	49·6	8·3	7·2	18·3	
2-*Chloro*-1-*chloromethylethyl carbamates*, $(Cl\cdot CH_2)_2CH\cdot O\cdot CO\cdot X$												
NH_2	80	84	—	28·0	4·0	8·3	41·2	27·9	4·1	8·1	41·2	14*a*
NHMe	89	20	105—107°/0·2	32·4	4·6	7·3	38·4	32·3	4·9	7·5	38·1	
NHPh	89	78	—	48·4	4·5	5·6	28·7	48·4	4·5	5·7	28·6	14*a*
$NH\cdot C_6H_4Me$-*o*	87	72	—	50·7	4·9	5·9	26·9	50·4	5·0	5·3	27·0	
$NH\cdot C_6H_4Cl$-*o*	86	63	—	42·9	3·6	5·3	37·4	42·5	3·6	5·0	37·7	
$NH\cdot C_6H_4Cl$-*m*	92	72·5	—	43·0	3·7	5·2	37·4	42·5	3·6	5·0	37·7	
$NH\cdot C_6H_4Cl$-*p*	77	111	—	42·8	3·6	5·2	35·0	42·5	3·6	5·0	37·7	
$NH\cdot C_{10}H_7$-α	91	121	—	56·2	4·2	5·0	24·0	56·4	4·4	4·7	23·8	14*a*
$NH\cdot C_{10}H_7$-β	90	104·5	—	56·3	4·2	4·7	23·4	56·4	4·4	4·7	23·8	14*a*
NMe_2	97	—	102—104°/0·15	35·9	5·6	6·7	35·4	36·0	5·5	7·0	35·5	
NEt_2	63	—	112—115°/0·15	42·1	6·5	6·1	31·4	42·1	6·6	6·1	31·1	
2-*Chloro*-1-*phenylethyl carbamates*, $Cl\cdot CH_2\cdot CHPh\cdot O\cdot CO\cdot X$												
NH_2	98	71	—	54·15	4·8	7·0	17·8	54·15	5·0	7·0	17·8	
NHMe	84	53	—	56·3	5·7	6·5	16·8	56·2	5·7	6·6	16·6	
NHEt	80	—	141—142°/0·15	60·3	6·4	5·5	16·2	58·0	6·2	6·2	15·6	
NHPh	99	94·5	—	65·1	5·1	5·3	13·1	65·3	5·1	5·1	12·9	
$NH\cdot C_6H_4Cl$-*p*	96	96	—	58·0	4·2	4·3	22·3	58·1	4·2	4·5	22·9	
NMe_2	90	—	138—139°/0·15	58·4	6·4	5·7	15·5	58·0	6·2	6·2	15·6	
(±)-erythro-2-*Chloro*-1-*methylpropyl carbamates*, $CHClMe\cdot CHMe\cdot O\cdot CO\cdot X$												
NH_2	96	67·5	—	39·7	6·4	9·0	23·6	39·4	6·6	9·2	23·3	
NHMe	65	—	120°/16	43·7	7·2	8·5	21·3	43·5	7·3	8·5	21·4	
NHPh	77	66	—	58·1	5·8	5·8	15·9	58·0	6·15	6·15	15·6	
trans-2-*Chloro*cyclo*hexyl carbamates*, $C_6H_{10}Cl\cdot O\cdot CO\cdot X$												
NH_2	92	150	—	47·5	6·8	7·9	19·9	47·3	6·8	7·9	20·0	
NHMe	92	56	161°/16	50·3	7·4	7·4	18·5	50·1	7·4	7·3	18·5	

TABLE 2. 3-R^1-5-R^2-*Oxazolid*-2-*ones.*

		Yield		Found (%)				Required (%)			
R^1	R^2	(%)	M. p.	C	H	N	Cl	C	H	N	Cl.
Ph	Ph	97	129°	75·0	5·4	5·9	—	75·3	5·4	5·9	—
Ph	CH_2Cl	95	108	56·5	4·8	6·4	16·6	56·7	4·7	6·6	16·8
β-$C_{10}H_7$	Me	95	134	73·8	5·7	6·2	—	74·0	5·7	6·2	—
p-C_6H_4Me	Me	93	67·5	68·9	6·7	7·3	—	69·1	6·8	7·3	—
p-C_6H_4Cl	CH_2Cl	93	126·5	48·8	3·6	6·2	28·5	48·8	3·7	5·7	28·8
p-C_6H_4Cl	Ph	96	131	65·8	4·5	5·1	13·0	65·8	4·4	5·1	12·9
p-C_6H_4Cl	Me	94	114	56·6	4·7	6·7	16·4	56·7	4·7	6·6	16·8
p-C_6H_4Cl	H	92	122·5	54·9	4·1	7·1	17·7	54·7	4·1	7·1	18·0
m-C_6H_4Cl	H	95	55	54·5	4·1	7·0	18·0	54·7	4·1	7·1	18·0

An attempt by Boberg and Schultze [17] to condense epoxides with carbamoyl chloride gave only the chlorohydrins. While the 2-chloroalkyl *N*-monosubstituted carbamates are readily converted into *N*-substituted oxazolidones it was not possible to synthesise the parent oxazolidones from the unsubstituted carbamates. When 2-chloroethyl carbamate was treated with 1 mol. of alcoholic alkali breakdown occurred with formation of alkali cyanide and chloride and some epoxide. A similar observation has been reported by Delaby *et al.*[15]

Hexahydrobenzoxazolid-2-one and its *N*-methyl derivative, the *cis*- and the *trans*-form of which have been reported by Mousseron *et al.*,[18] could not be prepared by treatment of *trans*-2-chloro*cyclo*hexyl carbamate and its *N*-methyl derivative with alcoholic alkali. The *N*-substituted oxazolid-2-ones we prepared from the *N*-substituted chlorocarbamates are listed in Table 2. The availability of the 2-chloro-substituted chloroformates from the epoxide–carbonyl chloride reaction makes this approach to the synthesis of *C*- and *N*-substituted oxazolidones attractive.

Crystallisation of 2-chloro-1-phenylethyl carbamate from methanol gave phenylethylene carbonate (2-oxo-4-phenyl-1 : 3-dioxolan) and ammonium chloride. An attempt to prepare the carbamate with concentrated aqueous ammonia also led to the formation of phenylethylene carbonate. The reaction in methanol was found to be due to its water content. The chlorine atom of the carbamate is hydrolysed readily in water and cyclisation of the 2-hydroxy-1-phenylethyl carbamate follows with loss of ammonia. 2-Hydroxyethyl carbamate, which is readily prepared from ethylene carbonate and concentrated aqueous ammonia, is stable even at the boiling point.

The reaction of thiocarbonyl chloride with epoxyethane was also examined. Even in the presence of pyridine the reaction does not proceed very readily at room temperature and the 2-chloroethyl chlorothioformate which is initially formed decomposes on distillation to give ethylene dichloride and carbonyl sulphide. Some bis-2-chloroethyl thiocarbonate was also formed in the reaction, and the infrared absorption spectrum indicates that this is present as a mixture of bis-2-chloroethyl thiol- and thion-carbonates.

EXPERIMENTAL

Reaction of Carbonyl Chloride with Epoxyethane.—Over a period of 1¼ hr. carbonyl chloride (65·9 g.) was passed into epoxyethane (35·5 g.) containing 3 drops of pyridine, held at $< -10°$ by an acetone–carbon dioxide bath. The temperature was allowed to rise to room temperature overnight, and dry air was blown through the product until the weight was constant (98 g.). On fractional distillation the mixture afforded 2-chloroethyl chloroformate (83 g.), b. p. 153°/760 mm., 50°/15 mm., n_D^{20} 1·4460, and bis-2-chloroethyl carbonate (11 g.), m. p. 11°, b. p. 241°/760 mm., 125°/12 mm., n_D^{20} 1·4600.

When epoxyethane (195 g.) containing 3 drops of pyridine was treated with carbonyl chloride (335 g.) during 3 hr. at $-30°$, treatment as above gave a final weight increase of 329 g. and then 2-chloroethyl chloroformate (440 g.), n_D^{20} 1·4460, and 33 g. of the carbonate.

[17] Boberg and Schultze, *Chem. Ber.*, 1955, **88**, 275.

[18] Mousseron, Winternitz and Mousseron-Canet, *Bull. Soc. chim. France*, 1953, 737.

Bis-2-chloroethyl carbonate (188 g.), b. p. 131°/15 mm., was obtained as sole product when epoxyethane (100 g.) containing 2 drops of pyridine was treated at $-15°$ to $-20°$ with carbonyl chloride (101 g.) and left without further cooling for 24 hr., after which a slight excess of the epoxide was removed in a stream of air. A quantitative yield of bis-2-chloroethyl carbonate was also obtained by passing epoxyethane into 2-chloroethyl chloroformate (containing a trace of pyridine) at $<0°$ until the required gain in weight had been attained.

Pyrolysis of 2-Chloroethyl Chloroformate and Bis-2-chloroethyl Carbonate.—During 2 hr. 2-chloroethyl chloroformate (25 g.) was swept with a stream of carbon dioxide through a glass tube packed with broken porous pot and kept at 450°, then through a water-condenser and a cold trap at $-80°$. The total condensate (9·8 g.), b. p. 81—83°, m. p. $-39°$ to $-41°$, n_D^{20} 1·4428, proved to be substantially ethylene dichloride. When bis-2-chloroethyl carbonate (25 g.) was pyrolysed at 450° (3¾ hr.), 16·4 g. of liquid condensate were mostly unchanged material (15 g.), b. p. 130°/14 mm., n_D^{20} 1·4595. Attempts to prepare divinyl carbonate by treating bis-2-chloroethyl carbonate (18·7 g.) in dry ether (50 ml.) with triethylamine (10·5 g.) were unsuccessful: no reaction was observed even on prolonged refluxing or in the absence of the solvent. Treatment with alcoholic potassium hydroxide caused hydrolysis of the carbonate as well as some elimination of hydrogen chloride.

Reaction of Carbonyl Chloride with 1 : 2-*Epoxy*cyclo*hexane.*—At $\sim -10°$ 1 : 2-epoxy*cyclo*hexane[19] (21 g. + 2 drops of pyridine) was treated with carbonyl chloride (16 g.). After being kept overnight, without further cooling, the liquid product was fractionated. It yielded 2-*chloro*cyclo*hexyl chloroformate* (27 g.), b. p. 110—111°/13 mm., n_D^{25} 1·4775 (Found: C, 42·7; H, 5·0; Cl, 35·8. $C_7H_{10}O_2Cl_2$ requires C, 42·6; H, 5·1; Cl, 36·8%), and a viscous carbonate fraction (9·6 g.), b. p. 177—183°/0·7 mm., which solidified and on fractional crystallisation from ethanol and then from light petroleum (b. p. 60—80°) yielded two *isomers* of *bis-2-chloro*cyclo*hexyl carbonate*, m. p. 111° (Found: C, 52·9; H, 6·8; Cl, 23·9. $C_{13}H_{20}O_3Cl_2$ requires C, 52·9; H, 6·8; Cl, 24·0%) and 65—66° (Found: C, 53·0; H, 6·9; Cl, 23·6%). Infrared examination of the two compounds showed only very minor differences, that could well be expected of stereoisomers.

1 : 2-Epoxy*cyclo*hexane and excess of carbonyl chloride at $-20°$ with no catalyst gave exclusively the chloroformate, b. p. 114—114·5°/16 mm.

trans-2-Chloro*cyclo*hexanol was prepared by addition of hypochlorous acid to *cyclo*hexene.[20] The chlorohydrin, n_D^{20} 1·4891, crystallised (m. p. 25°, not hitherto recorded). Carbonyl chloride was passed into the chlorohydrin (20 g.) at 100° until the gain in weight after removal of dissolved carbonyl chloride was 7 g. Distillation afforded unchanged chlorohydrin and some chloroformate (10·5 g.). The recovered chlorohydrin was again treated with carbonyl chloride (3 hr.) and furnished more chloroformate (7·1 g.). Further treatment of the unchanged material gave still more chloroformate (3·2 g.). Redistillation of the combined chloroformate fractions (20·8 g.) gave trans-*2-chloro*cyclo*hexyl chloroformate* (18 g.), n_D^{25} 1·4778, b. p. 114—115°/16 mm., whose infrared absorption was identical with that of the above chloroformate derived from 1 : 2-epoxy*cyclo*hexane.

There was no reaction when *trans*-2-chloro*cyclo*hexyl chloroformate (3·3 g.) and *trans*-2-chloro*cyclo*hexanol (2·3 g.) were heated for 4½ hr. at 100°. At 150° decomposition intervened.

Reaction of Carbonyl Chloride with 1 : 2-*Epoxypropane.*—Carbonyl chloride (211 g.) was passed into 1 : 2-epoxypropane (116 g.) containing 3 drops of pyridine at $<-20°$ (carbon dioxide–acetone). Treatment as above gave 2-chloro-1-methylethyl chloroformate (305 g.), b. p. 59—60°/16 mm., n_D^{20} 1·4420 (Found: C, 30·8; H, 4·0; Cl, 44·8. Calc. for $C_4H_6O_2Cl_2$: C, 30·5; H, 3·85; Cl, 45·1%) (Malinowski and Medjanzewa[4] give b. p. 68—70°/70 mm., n_D^{18} 1·4462).

1-Chloropropan-2-ol,[8] b. p. 126—127°, n_D^{20} 1·4370, on treatment with carbonyl chloride gave the same chloroformate, b. p. 58—59°/15 mm., n_D^{20} 1·4419. The infrared spectra were identical. Further, the chloroformate derived from the epoxide furnished on hydrolysis 1-chloropropan-2-ol, b. p. 125—128°, n_D^{20} 1·4374.

1 : 2-Epoxypropane (40 g.) containing 2 drops of pyridine, when treated with carbonyl chloride (54 g.) at $-10°$ to $-20°$ and kept for 48 hr., furnished a 97·5% yield of *di-*(*2-chloro-*1-*methylethyl*) *carbonate*, b. p. 133°/16 mm., n_D^{20} 1·4522 (Found: C, 39·2; H, 5·6; Cl, 33·0. $C_7H_{12}O_3Cl_2$ requires C, 39·1; H, 5·6; Cl, 33·0%). After several months about half the material crystallised [m. p. 50° after crystallisation three times from light petroleum (b. p. 60—80°)].

[19] *Org. Synth.*, Coll. Vol. I, Wiley, 1947, p. 185.

[20] See ref. 19, p. 158.

The same carbonate, b. p. 133°/15 mm., n_D^{20} 1·4518, presumably as a mixture of stereoisomers, was obtained by heating equimolar proportions of 2-chloro-1-methylethyl chloroformate and 1-chloropropan-2-ol.

Reaction of Carbonyl Chloride with 3-*Chloro*-1 : 2-*epoxypropane*.—3-Chloro-1 : 2-epoxypropane (20·7 g.) with 2 drops of pyridine was treated with a slow stream of carbonyl chloride at room temperature for 1 hr. at $\ngtr$40°. After removal of dissolved carbonyl chloride the gain in weight was 21·8 g. Fractional distillation gave 2-chloro-1-chloromethylethyl chloroformate (10 g.), b. p. 93°/20 mm., n_D^{20} 1·4740 (Found : C, 25·3; H, 2·7; Cl, 55·3. Calc. for $C_4H_5O_2Cl_3$: C, 25·1; H, 2·6; Cl, 55·6%), and *di*-(2-*chloro*-1-*chloromethylethyl*) *carbonate* (25 g.), m. p. 47·5°, b. p. 185°/22 mm. (Found : C, 29·6; H, 3·6; Cl, 50·0. $C_7H_{10}O_3Cl_4$ requires C, 29·6; H, 3·5; Cl, 49·9%). Otto [14] described the preparation of the chloroformate from 1 : 3-dichloropropan-2-ol and carbonyl chloride at 170° in 24 hr. When the dichlorohydrin (20 g.) was treated with a two-fold excess of liquid carbonyl chloride at −10° and the temperature allowed to rise slowly to room temperature no appreciable reaction was observed. Nor was chloroformate obtained by passing carbonyl chloride for 3 hr. into a refluxing solution of the dichlorohydrin (25 g.) in carbon tetrachloride (50 g.). Di-(2-chloro-1-chloromethylethyl) carbonate (24 g.), m. p. 47·5°, was obtained by refluxing the chloroformate (19 g.) with the dichlorohydrin (13 g.) for 2 hr., followed by distillation *in vacuo*. There was no depression in m. p. on admixture with the carbonate obtained from *epi*chlorohydrin and carbonyl chloride.

2-*Chloroethyl* 2-*Chloro*-1-*chloromethylethyl Carbonate*.—Epoxyethane was passed into 2-chloro-1-chloromethylethyl chloroformate (50 g.) containing 2 drops of pyridine until the gain in weight due to combined epoxide was 10·8 g. Some cooling (ice-water) was necessary in the early stages of the reaction. On fractional distillation 2-*chloroethyl* 2-*chloro*-1-*chloromethylethyl carbonate* (53·5 g., 87%), b. p. 152°/13 mm., n_D^{20} 1·4798 (Found : C, 30·8; H, 3·85; Cl, 45·1. $C_6H_9O_3Cl_3$ requires C, 30·6; H, 3·85; Cl, 45·2%), was obtained.

Reaction of Carbonyl Chloride with trans-2 : 3-*Epoxybutane*.—(±)-*trans*-2 : 3-Epoxybutane, b. p. 53·5°, n_D^{20} 1·3729 (36 g. + 3 drops of pyridine), was cooled to −20° and carbonyl chloride (62 g.) passed in during 1½ hr. Next morning working up gave a final increase in weight of 34 g. Two other batches of epoxide, each weighing 36 g., with catalyst were similarly treated. The final weight increases were 30 g. and 24 g. The three liquid products were combined and fractionated through a column (60 × 1 cm.) packed with glass helices, with a reflux ratio of 25 : 1. Material (19·6 g.) of b. p. >64·4°/16 mm. was redistilled twice and gave *di*-(2-*chloro*-1-*methylpropyl*) *carbonate* (17·6 g.), b. p. 134—135°/16 mm. (Found : C, 44·9; H, 6·6; Cl, 28·8. $C_9H_{16}O_3Cl_2$ requires C, 44·5; H, 6·6; Cl, 29·2%), presumably as a mixture of its stereoisomers. Material (53·3 g.), b. p. 61·6—64·4°/16 mm., was refractionated, giving fractions (1) b. p. 61·6—62·4°/16 mm., n_D^{20} 1·4412, (2) b. p. 62·4—63·2°/16 mm., n_D^{20} 1·4417, (3) b. p. 63·2—63·4°/16 mm., n_D^{20} 1·4422, (4) b. p. 63·4—64·0°/16 mm., n_D^{20} 1·4421.

Fraction (3) (17·2 g.) was pure (±)-erythro-2-*chloro*-1-*methylpropyl chloroformate* (cf. below) (Found: C, 35·4; H, 4·7; Cl, 41·2. $C_5H_8O_2Cl_2$ requires C, 35·1; H, 4·7; Cl, 41·5%). The stereochemical configuration was established by converting (±)-*erythro*-3-chlorobutan-2-ol [9] (24 g.) by carbonyl chloride (2 hr.) into the same chloroformate (25·4 g.), b. p. 62·5—63·5°/15 mm., n_D^{25} 1·4400, with an identical infrared spectrum.

trans-2 : 3-Epoxybutane (36 g. + 2 drops of pyridine) when treated at −10° absorbed 25 g. of carbonyl chloride (final gain 23 g.). Distillation gave main fractions (1) b. p. 46°/15 mm. (17 g.), n_D^{20} 1·4460, (2) chloroformate (19 g.), b. p. 63°/15 mm., n_D^{20} 1·4410, and (3) carbonate (12 g.), b. p. 134—135°/16 mm., n_D^{20} 1·4500.

Reaction of Carbonyl Chloride with Epoxyphenylethane (*Styrene Oxide*).—To obtain a high yield of the chloroformate it was necessary to add epoxyphenylethane (24 g.) to excess of carbonyl chloride (60 g.) containing 3 drops of pyridine at −20° and then to allow the temperature to rise slowly. After removal of excess carbonyl chloride 43 g. of liquid remained. Decomposition set in at ~140° during the distillation of the product under water-pump pressure but, at a lower pressure, distillation furnished (±)-2-*chloro*-1-*phenylethyl chloroformate* (35·2 g.), b. p. 109°/0·15 mm. (Found : C, 49·4; H, 3·7; Cl, 32·2. $C_9H_8O_2Cl_2$ requires C, 49·35; H, 3·7; Cl, 32·4%). On hydrolysis the chloroformate gave (±)-2-chloro-1-phenylethanol, b. p. 128°/16 mm., n_D^{20} 1·5400.

Addition of 1 drop of pyridine to a mixture of 2-chloro-1-phenylethyl chloroformate (4·38 g.) and epoxyphenylethane (2·4 g.) caused an immediate rise in temperature. Reaction was completed in 2 hr. on the steam-bath. The product partly crystallised and the solid fraction after several crystallisations from light petroleum (b. p. 60—80°)–chloroform furnished one of the two stereoisomeric forms of *di-(2-chloro-1-phenylethyl) carbonate*, m. p. 51° (Found : C, 60·0; H, 4·75; Cl, 20·8. $C_{17}H_{16}O_3Cl_2$ requires C, 60·2; H, 4·75; Cl, 20·9%). The same mixture (16·9 g.) was obtained by treating epoxyphenylethane (12 g.), containing 3 drops of pyridine, at $-20°$ with carbonyl chloride (6 g.). Seeding induced separation of the isomer, m. p. and mixed m. p. 51°.

Reaction of Carbonyl Chloride with 1 : 2-*Epoxy*-2 : 4 : 4-*trimethylpentane*.—Carbonyl chloride (116 g.) was added during ½ hr. at $-10°$ to the epoxide (128 g.) containing 4 drops of pyridine. After 12 hr., during which room temperature was attained, and removal of dissolved carbonyl chloride, only 26 g. remained combined. More was passed in at room temperature until the weight increase was 80 g. On distillation of the product it was difficult to maintain the vacuum owing to decomposition. The distillate (136 g.) obtained at 16—18 mm. had a wide boiling range and was refractionated; it gave eight fractions. One (37·1 g.), b. p. 78—81°/16 mm., $n_{\rm D}^{20}$ 1·4511 (Found : C, 58·8; H, 10·3; Cl, 21·7. Calc. for $C_8H_{17}OCl$: C, 58·4; H, 10·3; Cl, 21·6%), was probably 1-chloro-2 : 4 : 4-trimethylpentan-2-ol (cf. Graham *et al.*[10]). Another (11·8 g.), b. p. 50—52°/16 mm., $n_{\rm D}^{20}$ 1·4468, was probably slightly impure 1-chloro-2 : 4 : 4-trimethylpent-2-ene (Found : C, 66·2; H, 10·7; Cl, 23·1. Calc. for $C_8H_{15}Cl$: C, 65·5; H, 10·3; Cl, 24·2%) (cf. refs. 10 and 11). No fraction corresponded to a chloroformate.

Preparation of Carbamates from Chloroformates.—The series of 58 carbamates detailed in Table 1 were prepared in the prescribed manner from the appropriate chloroformate (1 mol.) with ammonia or primary or secondary amine (2 mol.), usually in benzene. The hydrochlorides were removed by filtration and the carbamates were isolated from the benzene and distilled or crystallised from light petroleum (b. p. 60—80°)–chloroform.

Hydrolysis of 2-*Chloro*-1-*phenylethyl Carbamate. Preparation of Phenylethylene Carbonate* (2-*Oxo*-4-*phenyl*-1 : 3-*dioxolan*).—Gaseous ammonia was passed into a solution of 2-chloro-1-phenylethyl chloroformate (5 g.) in dry benzene (50 ml.). The solution became warm and ammonium chloride (1·15 g.) when completely precipitated was removed and washed with benzene. The product recovered from the benzene solution was *2-chloro-1-phenylethyl carbamate* (4·6 g.), m. p. 71° [from light petroleum (b. p. 60—80°)–chloroform] (for analysis see Table). Treatment with boiling water gave an oil which solidified. Crystallisation of the latter from aqueous ethanol gave *phenylethylene carbonate*, m. p. 54—56° (Found : C, 65·75; H, 4·9. $C_9H_8O_3$ requires C, 65·85; H, 4·9%). Its structure was confirmed by comparison of its infrared absorption spectrum with those of epoxyphenylethane and ethylene carbonate.[12] Crystallisation of 2-chloro-1-phenylethyl carbamate from methanol also gave phenylethylene carbonate and ammonium chloride. Treatment of the chloroformate with concentrated aqueous ammonia gave phenylethylene carbonate directly.

Synthesis of Oxazolid-2-ones from N-*Substituted Carbamates*.—Treatment of the unsubstituted carbamates (1 mol.) with alcoholic potassium hydroxide (1 mol.) caused formation of some potassium cyanate, potassium chloride, and epoxide. This was true, *e.g.*, of 2-chloroethyl carbamate, *trans*-2-chloro*cyclo*hexyl carbamate and *trans*-2-chloro*cyclo*hexyl *N*-methyl carbamate. Thus, an attempt to prepare hexahydro-3-methylbenzoxazolid-2-one from it was unsuccessful. With these exceptions elimination of hydrogen chloride from *N*-monosubstituted carbamates occurred readily with formation of 3-substituted oxazolid-2-ones. The general procedure adopted for the preparation of the oxazolidones listed in Table 2 was to add the appropriate amount of an $\sim$10% ethanolic solution of potassium hydroxide to the requisite amount of carbamate in 10% ethanol solution. Precipitation of potassium chloride was almost immediate but the reaction was completed by heating for a few minutes at 100°. Because of the somewhat low solubility of some of the oxazolidones the potassium chloride was removed by filtering the hot solution and was washed with alcohol.

Reaction of Epoxyethane with Thiocarbonyl Chloride.—Epoxyethane (13·3 g.) was passed into thiocarbonyl chloride (23 g.) containing 2 drops of pyridine at 0°. After 24 hr. at room temperature the mixture was distilled. Some unchanged epoxyethane was recovered together with some thiocarbonyl chloride. When the temperature had reached 70° an exothermic reaction set in causing violent ebullition. When this stopped the liquid residue was distilled under reduced pressure and gave a pale yellow liquid (4·8 g.). This was redistilled and gave a constant-boiling fraction (4·2 g.), b. p. 127°/13 mm., $n_{\rm D}^{20}$ 1·5031 (Found : C, 30·0; H, 3·9; S, 11·7; Cl, 37·9. Calc. for $C_5H_8O_2SCl_2$: C, 29·6; H, 3·9; S, 15·8; Cl, 34·9%). The infrared absorption spectrum had many features in common with that of bis-2-chloroethyl carbonate;

however, two additional strong bands appeared at ~1150 and ~705 cm.$^{-1}$ which are tentatively assigned to C=S and C–S respectively. A C=O band appeared at 1732 cm.$^{-1}$ with a strong shoulder at 1741 cm.$^{-1}$ and a C–O band at 1270—1245 cm.$^{-1}$. In bis-2-chloroethyl carbonate these appeared at ~1755 cm.$^{-1}$ and 1280—1250 cm.$^{-1}$. Despite the poor agreement in the analytical data (several analyses were performed) this fraction appears to be substantially a mixture of the isomeric bis-2-chloroethyl thion- and thiol-carbonates.

Redistillation of the distillate that surged over during the initial distillation afforded ethylene dichloride, b. p. 83—83·5°, n_D^{20} 1·4444, and this must have originated from the decomposition of 2-chloroethyl chlorothioformate, initially formed.

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