Rearrangements and Cyclization of ω-Alkoxyalkyl- and ω-Phenoxyalkyl-carbamoyl Chlorides

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ω-Alkoxyalkyl- and ω-phenoxyalkyl-carbamoyl chlorides ($R^1O{\cdot}[CH_2]_n{\cdot}NR^2{\cdot}COCl$) (I) rearrange to give, respectively, alkyl or phenyl *N*-(ω-chloroalkyl)carbamates (II). The rearrangement occurs with the greatest facility when n = 2 or 3. When the carbamates (II) (alkyl but not phenyl) are heated, ring closure readily takes place when n = 2 or 3 to give, respectively, 2-oxazolidones (III) or tetrahydro-1,3-oxazin-2-ones (IV). An analogous rearrangement occurs with 2-ethoxyethyl chloroformate, giving 2-chloroethyl ethyl carbonate.

EVEN at ambient temperature the ω-alkoxyalkylcarbamoyl chlorides (I; R^1 = alkyl, R^2 = alkyl, allyl, or phenyl, n = 2 or 3) slowly rearrange to the carbamates (II). The rearrangement is more rapid at higher temperatures and may be virtually complete when R^1 = alkyl if the product is distilled at temperatures above *ca.* 120 °C. Rearrangement has also been observed with the carbamoyl chlorides (I; $R^1 = R^2$ = Et, n = 4 or 5) but it was much slower. Heating even to *ca.* 100 °C in these latter cases caused some decomposition, so that the reaction was not well defined.

The secondary amines in Table 1 were all converted into carbamoyl chlorides (I) by the procedure given in the Experimental section. Only two of these have been reported previously [(I; R^1 = Me, R^2 = Et) and (I; $R^1 = R^2$ = Et)], by Boon.[1] Since he distilled his products, however, they must have been at least partially converted into the corresponding carbamates (II).

Ethyl *N*-(2-chloroethyl)-*N*-propylcarbamate was prepared by the reaction of *N*-(2-chloroethyl)propylamine[2] hydrochloride with ethyl chloroformate, and was identical with the product of rearrangement of *N*-(2-ethoxyethyl)-*N*-propylcarbamoyl chloride.

For characterization, the carbamoyl chlorides (I; R^1 = alkyl, R^2 = alkyl or allyl, n = 2 or 3) were converted into the carbamoyl-1,2,4-triazole derivatives [(V) or (VI)], which have been reported in the patent literature.[3] The solids described therein are the pure 3-substituted 1-carbamoyl-1*H*-1,2,4-triazoles. The liquids contain small amounts of positional isomers and were characterised by their g.l.c. behaviour, n.m.r. spectra, and refractive indices. Satisfactory elemental analyses were obtained in all cases. Because of their instability, the carbamoyl chlorides could not be purified and were used immediately in reactions at ambient temperature with the appropriate triazole, in tetrahydrofuran in the presence of triethylamine as acid acceptor. An excess of the carbamoyl chloride was used to compensate for concurrent rearrangement. The

[1] W. R. Boon, *J. Chem. Soc.*, 1947, 307.
[2] R. H. Hall and G. F. Wright, *J. Amer. Chem. Soc.*, 1951, **73**, 2213.
[3] The Boots Company Ltd., B.P. Appl. 61022–3/1971; Ger. Offen. 2,264,159; Belg. P. 801,701; *etc.*

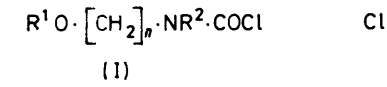
triazoles derived from (I; $R^1 = R^2 = Et$, $n = 4$ or 5) were not included in the patent applications and the triazole derivatives which were prepared from them are described in Table 2.

TABLE 1

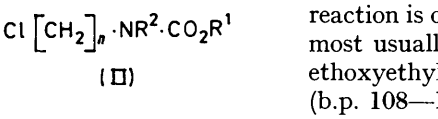
Secondary amines $R^1O\cdot[CH_2]_n\cdot NHR^2$

R^1	R^2	n	Yield (%)	B.p. (°C)	Notes
Me	Et	2	56.4	116	*a*
Me	Pr	2	67.4	137—138	
Me	Bu	2	62.6	158—162	
Me	Allyl	2	35.3	140—142	
Me	Et	3	73.3	141—142	
Et	Et	2	52.7	130—133	*a*
Et	Pr	2	53.6	154—155	
Et	Bu	2	66.7	177—178	*b*
Et	Allyl	2	51.5	155—156	
Et	Et	3	46.4	155—156	*c*
Et	Allyl	3	31.5	178—179	
Et	Et	4	57.0	178—179	
Et	Et	5	61.2	97.5—98 [19 mmHg]	
Pr	Et	2	67.3	154	
Bu	Allyl	2	31.6	85 [20 mmHg]	
Pr^i	Et	2	63.2	144	
$PrO\cdot CH_2\cdot CHMe\cdot NHEt$			57.0	160—161	

[a] Ref. 1 (different method). [b] G. W. Cooper and R. R. Houghton (*Tetrahedron Letters*, 1970, 3915) report b.p. 64—66° at 30 mmHg (different method). [c] R. R. Mod, F. C. Mague, and E. L. Skau, U.S.P., 3 663 582/1972 (*Chem. Abs.*, 1972, **77**, 87 983j); no method given.



(I)



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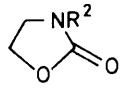

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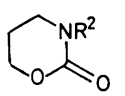

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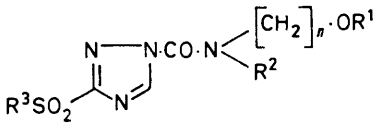
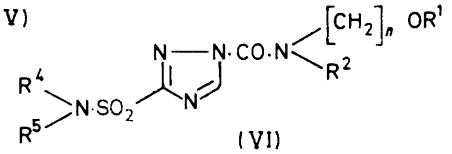


(V)



(VI)

Rearrangement of the carbamoyl chlorides (I) in which R^1 = phenyl occurs much less readily than when R^1 = alkyl, as the following observations show. (i) Compound (I; $n = 2$, R^1 = Ph, R^2 = Pr), distilled twice (127—130° and *ca.* 0.15 mmHg; 125—127° and 0.15 mmHg), contained 6.0 % carbamate. (ii) Compound (I; $n = 2$, R^1 = Ph, $R^2 = Pr^i$), distilled twice (145—148° and 1.5 mmHg; 135—137° and 1.0 mmHg), contained 40.6 % carbamate. (iii) Compound (I; $n = 2$, R^1 = Ph, $R^2 = Bu^s$), distilled once (132—135° and 0.3 mmHg), contained 13.4 % carbamate. The proportions of carbamate were determined by g.l.c., assuming equal detector response. These carbamoyl chlorides have not been reported previously and *N*-s-butyl-2-phenoxyethylamine is also new.

TABLE 2

1,2,4-Triazoles from carbamoyl chlorides

Carbamoyl chloride (I)	1,2,4-Triazole (V)	1,2,4-Triazole (VI)
$R^1 = R^2 = Et$, $n = 4$	$R^1 = R^2 = Et$, $R^3 = Pr$, $n = 4$ Found: S, 9.3% (Calc. 9.25) 1-Isomer (g.l.c.) 99.57% n_D^{22} 1.4989	$R^1 = R^2 = R^4 = R^5 = Et$, $n = 4$ Found: S, 8.7% (Calc. 8.55) 1-Isomer (g.l.c.) 99.63% n_D^{22} 1.4962
$R^1 = R^2 = Et$, $n = 5$	$R^1 = R^2 = Et$, $R^3 = Pr$, $n = 5$ Found: S, 9.2% (Calc. 8.9) M.p. 54.5—55°	$R^1 = R^2 = R^4 = R^5 = Et$, $n = 5$ Found: S, 8.5% (Calc. 8.23) 1-Isomer (g.l.c.) 99.35% n_D^{22} 1.4961

When heated more strongly, the carbamoyl chlorides or the carbamates (I and II; R^1 = alkyl, R^2 = alkyl, allyl, or phenyl, $n = 2$ or 3) cyclize with loss of alkyl chloride, giving 3-substituted 2-oxazolidones (III) ($n = 2$) or 3-substituted tetrahydro-1,3-oxazin-2-ones (IV) ($n = 3$). Small amounts of the cyclized compounds are formed slowly even at ambient temperature, but the reaction is only significant at temperatures above 150 °C, most usually, at *ca.* 180 °C. For instance, when *N*-(2-ethoxyethyl)-*N*-phenylcarbamoyl chloride was distilled (b.p. 108—110° at 0.6 mmHg), it was converted almost completely into the carbamate and *ca.* 5% of 3-phenyl-2-oxazolidone, identified by comparison with an authentic sample,[4,5] was also isolated. When the carbamate was heated at 160—170 °C for 1 h it was completely converted into the oxazolidone. This cyclization does not occur when R^1 = phenyl. No trace of chlorobenzene was detected when the phenoxyethylcarbamoyl chlorides mentioned above were heated for prolonged periods above 200 °C.

In the case of the carbamates (II; $R^1 = R^2 = Et$, $n = 4$ or 5), although there is evidence suggestive of ring closure, *e.g.* the formation of ethyl chloride, it is necessary to heat to 210 °C when $n = 4$ and to 230—240 °C when $n = 5$, and considerable decomposition then takes place even in an atmosphere of nitrogen.

The relative ease of the rearrangement and the cyclization at ambient temperature are indicated by the behaviour of a sample of *NN*-bis-(2-ethoxyethyl)-carbamoyl chloride stored at ambient temperature for 15 weeks. It then had the composition: carbamate 97.67%, carbamoyl chloride 0.08%, oxazolidone 2.24% (by g.l.c., assuming equal detector response).

The carbamoyl chlorides show a CO band in the i.r. at *ca.* 1740 cm^{-1}. The carbamates have a strong CO band at *ca.* 1700 cm^{-1} (film or solution in carbon disulphide or carbon tetrachloride). The oxazolidones, as films, have a very strong CO band at 1740 cm^{-1}. Solutions show the

[4] J. Nemirowski, *J. prakt. Chem.*, 1885, **31**(2), 175.
[5] P. Otto, *J. prakt. Chem.*, 1891, **44**(2), 17.

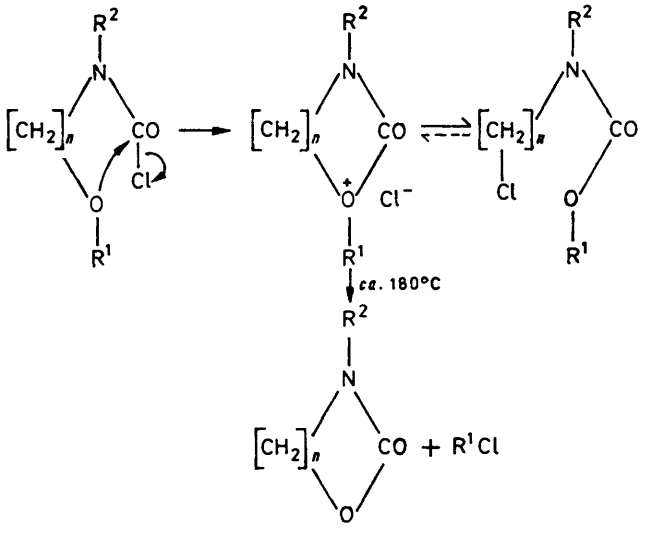
band at 1760 cm^{-1}. Mixtures of carbamate and oxazolidone as films show the oxazolidone CO band closer to 1760 cm^{-1} as the proportion of carbamate is increased. The shift may be due to hydrogen bonding.

N-(3-Ethoxypropyl)-*N*-ethylcarbamoyl chloride showed a CO band at *ca.* 1735 cm^{-1}. After heating at 100 °C overnight, g.l.c. showed 66.75% carbamate and 26.34% oxazine. No carbamoyl chloride remained. The sample then showed a broad band at *ca.* 1690 cm^{-1} and it appears probable that the bands due to carbamate and oxazine overlap or coincide.

G.l.c. retention times are in the order carbamate < carbamoyl chloride < oxazolidone or oxazine. The alkyl chloride evolved in the ring closure was collected in a cold trap and identified by i.r. spectrum in a number of cases.

Mechanism.—The rearrangement of carbamoyl chloride to carbamate takes place readily, particularly when $n = 2$, and at ambient temperature is eventually almost complete, but little cyclization is observed. Cyclization only becomes a major reaction at higher temperatures and can then be taken essentially to completion when $n = 2$, starting from either the carbamoyl chloride or the carbamate. When $n = 3$ the cyclization is less smooth and there is a tendency for decomposition. It appears that the carbamate in this case does not cyclize as readily as the carbamoyl chloride.

The rearrangement may proceed through a cyclic oxonium intermediate (see Scheme). At higher temperatures this intermediate may be assumed to lose alkyl chloride irreversibly, giving the oxazolidone or oxazinone. There is no evidence for the formation of carbamoyl chloride from carbamate, so the rearrangement must proceed from left to right virtually to completion. The carbamate may still exist in equilibrium with a very low concentration of the oxonium intermediate, however. As cyclization of the carbamate proceeds, this equilibrium will move to the left until the whole of the carbamate is converted. The observed difference in behaviour between the carbamates with $n = 2$ and those with $n = 3$ is then explicable in terms of comparative reluctance of the latter to form the oxonium intermediate. When $n > 3$, steric factors are still less favourable for the formation of a cyclic oxonium intermediate, either from the carbamoyl chloride or from the carbamate, and decomposition preponderates.



SCHEME

The rearrangement appears to be a further example of the so-called αω-rearrangement.[6] The nearest analogous rearrangement previously reported[7] is that of 4-alkoxybutyryl chlorides to alkyl 4-chlorobutyrates. A similar rearrangement of chloroformates of cyclic aminoalcohols to cyclic carbamates has also been described.[8]

The generality of the rearrangement is shown by our further observation that 2-ethoxyethyl chloroformate [9] isomerises readily on heating at 100 °C to give 2-chloroethyl ethyl carbonate. After 17 h a sample contained 66.04% chloroformate and 33.53% carbonate (by g.l.c.; relative retention times 1 : 2). The carbonate was identified by comparison with an authentic sample (i.r. and g.l.c.) prepared by the reaction of ethyl chloroformate with 2-chloroethanol. 2-Ethoxyethyl chloroformate has a CO band at 1778 cm^{-1} and 2-chloroethyl ethyl carbonate a CO band at 1747 cm^{-1}.

The rearrangement may therefore be generalized as in

$$RO{\cdot}[CH_2]_n{\cdot}X{\cdot}COCl \longrightarrow Cl[CH_2]_n{\cdot}X{\cdot}CO_2R \quad \text{(i)}$$

where X = NR′, O, or CH_2 and $n = 2$ or 3

equation (i). The cyclization is less general, having been observed when X = NR′ but not when X = O or CH_2.

EXPERIMENTAL

All g.l.c. samples were run on a column of 5% QF1 on Gas Chrom Z (80—100 mesh) with nitrogen flow rate 40 ml min^{-1}.

Secondary ω-Alkoxyalkylamines.—*NN*-Bis-(2-ethoxyethyl)amine was commercially available. The amines listed in Table 1 were prepared by treatment of the appropriate bromoalkoxyalkane with a primary alkylamine (2.5 mol. equiv.) or with allylamine (3.0 mol. equiv.) in the presence of aqueous sodium hydroxide, based on the methods of Tilles [10] and D'Amico.[11]

ω-Alkoxyalkylcarbamoyl Chlorides: General Method.—A solution of phosgene (1.2 mol) in dry ether (400 ml) was stirred with exclusion of moisture and cooled in solid carbon dioxide–acetone. A solution of the secondary ω-alkoxyalkylamine (0.4 mol) in dry ether (120 ml) was added dropwise during 1 h below −20 °C. The cooling bath was removed and the mixture allowed to warm to 0 °C (*ca.* 30 min). The solution was filtered from precipitated amine hydrochloride and evaporated *in vacuo* (water pump) with the flask immersed in water at 25 °C until the vacuum was no longer depressed by ether vapour. Any residual solvent

[6] D. H. R. Barton and S. Prabhakar, *J.C.S. Perkin I*, 1974, 781.
[7] F. F. Blicke, W. B. Wright, jun., and M. F. Zienty, *J. Amer. Chem. Soc.*, 1941, **63**, 2488.
[8] J. Pengman Li and J. H. Biel, *J. Org. Chem.*, 1970, **35**, 4100.
[9] H. G. Ashburn, A. R. Collett, and C. L. Lazell, *J. Amer. Chem. Soc.*, 1938, **60**, 2933.
[10] H. Tilles, *J. Amer. Chem. Soc.*, 1959, **81**, 714.
[11] J. D. D'Amico, U.S.P. 2,943,079/1960 (*Chem. Abs.*, 1960, **54**, 25,943a).

was removed by passage of dry nitrogen through the product for 15 min. The yield was quantitative (*i.e.* 50% based on amine consumed).

If the reaction mixture was allowed to warm up to ambient temperature and stirred for up to 3 h, the amine hydrochloride dissolved more or less completely and the yield of carbamoyl chloride was raised to 80—90% (based on amine consumed). The product contained an appreciable amount of the bis-urea (up to 10%). For some purposes this may be acceptable, but if a pure carbamoyl chloride is required the temperature must not be allowed to rise above 0 °C before filtration, nor must the stirring be unduly prolonged.

Secondary 2-Phenoxyethylamines ($PhO{\cdot}[CH_2]_2{\cdot}NHR^2$).—The amines ($R^2$ = Pr, Pr^i, or Bu^s) were prepared by the method of Chapman and Triggle.[12] The first two are known, but that with R^2 = Bu^s is new (yield 74.5%; b.p. 122—125° at 6.5 mmHg; elemental analysis not determined, but n.m.r. in agreement with assigned structure).

2-Phenoxyethylcarbamoyl Chlorides (I; R^1 = Ph).—These could be prepared in the same way as the ω-alkoxyalkylcarbamoyl chlorides, but since the rearrangement was much slower than for the alkoxy-compounds it was possible to prepare them in an acceptable state of purity for synthetic purposes by treating the amine with phosgene in refluxing ethyl acetate, with the advantage that all the amine was thereby utilized. N.m.r. and i.r. data were compatible with the assigned structures.

R^2	B.p. (°C) [mmHg]	Analysis (%)	
Pr	125—127 [0.15]	Cl, 15.1.	$C_{12}H_{16}ClNO_2$ requires 14.7
Pr^i	135—137 [1.0]	Cl, 14.9.	$C_{12}H_{16}ClNO_2$ requires 14.7
Bu^s	132—135 [0.3]	Cl, 14.25.	$C_{13}H_{18}ClNO_2$ requires 13.9

Phenyl N-Alkyl-N-(2-chloroethyl)carbamates (II; R^1 = Ph).—The corresponding carbamoyl chloride was heated to *ca.* 170 °C for 3 h. N.m.r. and i.r. data were compatible with the assigned structures.

R^2	B.p. (°C) [mmHg]	Analysis (%)		Purity (g.l.c.)
Pr	135—137 [1.0]	Cl, 15.0.	$C_{12}H_{16}ClNO_2$ requires 14.7	99.2%
Pr^i	(M.p. 53—55)	Cl, 15.0.	$C_{12}H_{16}ClNO_2$ requires 14.7	
Bu^s	118—121 [0.25]	Cl, 14.3	$C_{13}H_{18}ClNO_2$ requires 13.9	97.6%

Ethyl N-(2-Chloroethyl)-N-propylcarbamate.—*N*-(2-Chloroethyl)propylamine hydrochloride (0.05 mol) in water (80 ml) and ether (50 ml) was stirred and cooled to near 0 °C. A solution of ethyl chloroformate (0.05 mol) in ether (20 ml) and a solution of sodium hydroxide (0.1 mol) in water (20 ml) were added simultaneously during 30 min at 0—5 °C. After stirring for 15 min the ether layer was separated and the aqueous solution extracted twice more with ether. After drying rapidly (K_2CO_3), the ether was distilled off and the product distilled; b.p. 63° at 0.07 mmHg (Found: Cl, 18.3. Calc. for $C_{12}H_{16}ClNO_2$: Cl, 18.35%), purity 99.32% (g.l.c.). G.l.c. retention time and i.r. spectrum confirmed identity with the product of rearrangement of the corresponding carbamoyl chloride.

3-(2-Ethoxyethyl)-2-oxazolidone.—A sample of *NN*-bis-(2-ethoxyethyl)carbamoyl chloride which had been stored at ambient temperature for 15 weeks was almost completely converted into ethyl *N*-(2-chloroethyl)-*N*-(2-ethoxyethyl)-carbamate. On the assumption of equal detector response, it had the composition 97.67% carbamate, 0.08% carbamoyl chloride, 2.24% oxazolidone (g.l.c.).

This material was heated in an oil-bath. Gas evolution commenced at *ca.* 165 °C. The temperature was maintained at *ca.* 185 °C for 30 min. No further gas evolution was then observed. The evolved gas was condensed in a cold trap and identified as ethyl chloride (i.r.) The product was distilled; b.p. *ca.* 96° at 0.2 mmHg. G.l.c. showed 98.9% of *oxazolidone* and 0.92% of carbamate. I.r. data were compatible with the structure (Found: C, 52.6; H, 8.0; N, 8.8%; M^+, 159.0921. $C_7H_{13}NO_3$ requires C, 52.85; H, 8.12; N, 8.8%; *M*, 159.0896). No molecular ion for the carbamate was observed, but a minor peak corresponding to $C_4H_7ClNO_2$ was present (*m/e* 114.0 527; calc. 114.0511).

3-Propyl-2-oxazolidone.—(*A*) *N*-(2-Ethoxyethyl)-*N*-propylcarbamoyl chloride was heated at *ca.* 180 °C for 30 min. No further gas evolution was then observed. The evolved gas was condensed in a cold trap and identified as ethyl chloride (i.r.) The product was distilled; b.p. 80° at *ca.* 0.1 mmHg. G.l.c. showed 99.36% of *oxazolidone* and 0.57% of carbamate. I.r. data were compatible with the structure (Found: C, 55.7; H, 8.65; N, 10.9. $C_6H_{11}NO_2$ requires C, 55.8; H, 8.55; N 10.85%. Found: Cl 0.17%, equivalent to *ca.* 0.9% carbamate)

(*B*) *N*-(2-Methoxyethyl)-*N*-propylcarbamoyl chloride, which had been kept for 12 months since its preparation and was therefore probably almost completely converted into carbamate, was heated at *ca.* 180 °C for 30 min. The product was distilled; b.p. 83—88.5° at *ca.* 0.05 mmHg. G.l.c. showed 99.9% of oxazolidone (Found: C, 55.9; H, 8.5; N, 10.9%; M^+, 129.0790. Calc. for $C_6H_{11}NO_2$: *M*, 129.0790).

3-Ethyl-2-oxazolidone.—Methyl *N*-(2-chloroethyl)-*N*-ethylcarbamate, obtained by the spontaneous rearrangement of *N*-(2-methoxyethyl)-*N*-ethylcarbamoyl chloride at ambient temperature, was heated at *ca.* 180 °C for 2 h. Evolution of alkyl chloride was more prolonged than in the previous cases. The gas was condensed in a solid carbon dioxide–acetone-cooled trap and identified as methyl chloride (i.r.). The *product* was distilled; b.p. 74—75° at *ca.* 0.1 mmHg (Found: C, 52.0; H, 7.35; N, 12.4%; M^+, 115.0635. $C_6H_{11}NO_2$ requires C, 52.15; H, 7.8; N, 12.15%; *M*, 115.0634); purity 99.6% (g.l.c.).

3-Ethyltetrahydro-1,3-oxazin-2-one.—*N*-(3-Ethoxypropyl)-*N*-ethylcarbamoyl chloride was heated in an oil-bath. Gas evolution started at *ca.* 135 °C and was rapid at 145—150 °C. The temperature was maintained at 155—160 °C for 30 min and gas evolution then appeared to be complete. The gas was collected in a cold trap and identified as ethyl chloride (i.r.). The product was found to be only partly converted (carbamate 50.3%, oxazine 48.29%). A component of much longer retention time was also present (1.08%) (Found: Cl 13.6%, equivalent to *ca.* 74% carbamate). The product was reheated at 180—200 °C for 2 h. Some darkening occurred. G.l.c. (relative retention times in parentheses) showed 0.08% carbamate (7), 94.58% oxazine (33), 4.16% unknown (56) (Found, Cl, 1.55%, equivalent to 8.35% as carbamate, but the unknown may also contain chlorine); M^+ 129.0780 (calc. 129.0790); a peak corresponding to the carbamate was also observed, M^+ 193.0873 (calc. 193.0870).

[12] N. B. Chapman and D. J. Triggle, *J. Chem. Soc.*, 1963, 1390.

A mixture of methyl and ethyl *N*-(3-chloropropyl)-*N*-ethylcarbamate, obtained by spontaneous rearrangement of the corresponding carbamoyl chlorides at ambient temperature was heated at *ca.* 200 °C in an oil-bath in an atmosphere of nitrogen. Gas evolution was slow and heating was discontinued after 2 h when it became evident that marked decomposition was taking place. The product was distilled. Two fractions were collected: (i) b.p. 76—83° at 0.15 mmHg (78.8% pure by g.l.c.); (ii) b.p. 83—86° 0.15 mmHg (90.3% pure by g.l.c.). The impurities were observed as a large number of unidentified g.l.c. peaks. Viscous, undistillable residue (*ca.* 50%) was left in the flask.

1,2,4-*Triazole Derivatives*.—The 3-alkylsulphonyl- or 3-*NN*-dialkylsulphamoyl-1,2,4-triazole (0.03 mol) was dissolved in tetrahydrofuran (40 ml) and triethylamine (6 ml; excess) was added, followed by the *N*-alkoxyalkyl-*N*-alkylcarbamoyl chloride (0.033 mol). The solution was kept at ambient temperature for 2—3 days. Solvent was removed and the product washed with light petroleum. If solid, it was crystallized from ether–light petroleum or benzene–light petroleum. If liquid, it was dissolved in ether; the solution was filtered and evaporated and residual volatile material was removed by heating for 2 h at 100° and 0.1 mmHg.

2-*Chloroethyl Ethyl Carbonate*.—A solution of 2-chloroethanol (0.1 mol) and triethylamine (18 ml) in dry tetrahydrofuran (100 ml) was stirred at ambient temperature and ethyl chloroformate (0.1 mol) was added dropwise during 20 min. The mixture was heated under reflux for 30 min and filtered to remove triethylamine hydrochloride. Solvent was removed and the product distilled *in vacuo*; b.p. 86—94° at 25 mmHg; yield 11.0 g (72%) (lit.,[13] b.p. 92—100° at 40 mmHg) (Found: Cl, 24.0. Calc, for $C_5H_9ClO_2$: Cl, 23.8%). When product was heated to its b.p. (188° at 760 mmHg) there was no sign of decomposition.

G.l.c. examinations were carried out by J. Baylis and n.m.r. spectra obtained by W. Brown. We thank Mrs. P. S. Symonds for technical assistance.

[4/2594 *Received*, 12*th December*, 1974]

[13] A. Takamizawa, K. Hirai, Y. Hamashima, and H. Sato, *Chem. and Pharm. Bull.* (*Japan*), 1963, **11**, 1368.