427 nm; *m/e* 282 (M, 100 %). *trans-8* had λ_{max} (acetone) 431 nm; δ ($CDCl_3$) 1.83 s (6 H) *gem.* dimethyl, 1.98 s (6 H) CH_3-20,20′, 1.90 s (3 H) CH_3-19, 5.99–6.88 (10 H) olefinic and 9.45 (1H) aldehyde; *m/e* 282 (M, 100 %).

(b) To *6* (27 mg) in $CHCl_3$ (40 ml) was added 0.022 N HBr in $CHCl_3$ (1 ml). After 15 h separation by TLC afforded *cis-8* (0.54 mg), *trans-8* (1.84 mg), *9* (1.38 mg) and *5* (0.86 mg). The ethoxyaldehyde *9* had λ_{max} (acetone) 427 nm; δ ($CDCl_3$) *ca.* 1.25 CH_3CH_2-, 1.84 s (3 H) CH_3-19′, 1.99 s (6 H) CH_3-20,20′, 1.91 (3 H) CH_3-19, 3.95 s (2 H) CH_2-8, 3.46 q, (2 H) $-OCH_2CH_3$, 6.18–6.9 (10 H) olefinic and 9.45 (1 H) aldehyde; *m/e* 326 (M, 100 %), 281 (M – 45, 4.4 %).

Further experimental details are given elsewhere.[3]

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Formation of 2-Oxazolidinones from *N*-Benzyloxycarbonyl-2,2′-dichlorodiethylamine; Demonstration of Chloride Catalysis

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As part of our studies of nitrogen analogs of crown ethers, we have tried to prepare the derivative *1* of 1,4,7,10-tetraazacyclododecane which after hydrogenolytic removal of the benzyloxycarbonyl group would permit selective alkylation reactions of one amine function. For this synthesis urethane-protected 2,2′-dichlorodiethylamine *2a* was allowed to react with the disodium salt of *N*,*N*′,*N*″-tris-*p*-toluenesulfonyl diethylenetriamine *3* in DMF.[1] However, besides unreacted starting material *3* (7 %), the only isolated products were the 2-oxazolidinone derivative *4* (9 %), which is actually an isomer of the desired product *1*, and the monobenzylated trisulfonamide *5* (12 %).

Similarily, in an attempt to prepare the urethane derivative *6* of 1,4,7-trioxa-10-aza-cyclododecane from protected 2,2′-dichlorodiethylamine *2a* and diethylene glycol with potassium *tert*-butoxide as a base, the benzyloxycarbonyl group proved to be unstable. The isolated products were 3-ethenyl-2-oxazolidinone *7* (25 %), benzyl chloride (29 %) and the monobenzyl ether of diethylene glycol (17 %).

The formation of 2-oxazolidinones and the various benzylated products can be rationalized by either of the two reaction paths shown in Scheme *1*. According to Path I, an S_N2 substitution in the benzylic position of *2a* gives a new benzylic compound $PhCH_2X$ and a carbamate anion.[2] This anion does not decarboxylate under the reaction conditions, but cyclizes to yield 3-(2-chloroethyl)-2-oxazolidinone *8*,[3] which is further transformed to *4* and *7*. A pyrolytic mechanism, as proposed by Katchalsky *et al.*[4] for the related formation of 2-oxazolidinone from *N*-carbalkoxy-2-haloalkylamines, seems unlikely here because of the low reaction temperatures (80–100 °C).

In an experiment designed to exclude the less plausible alternative Path II,[5] both urethanes *2* were allowed to react in DMSO at 170 °C with one equivalent of NaCl and thereafter with Na_2CO_3. The benzyl derivative *2a* furnished 40 % of the cyclized product *7* besides benzyl chloride and other unidentified products, whereas the ethyl derivative *2b* failed to yield any 2-oxazolidinones under the same conditions. These results render Path II very improbable, since both compounds *2* should show the same tendency to undergo the initial substitution of chloride by the carbonyl oxygen.

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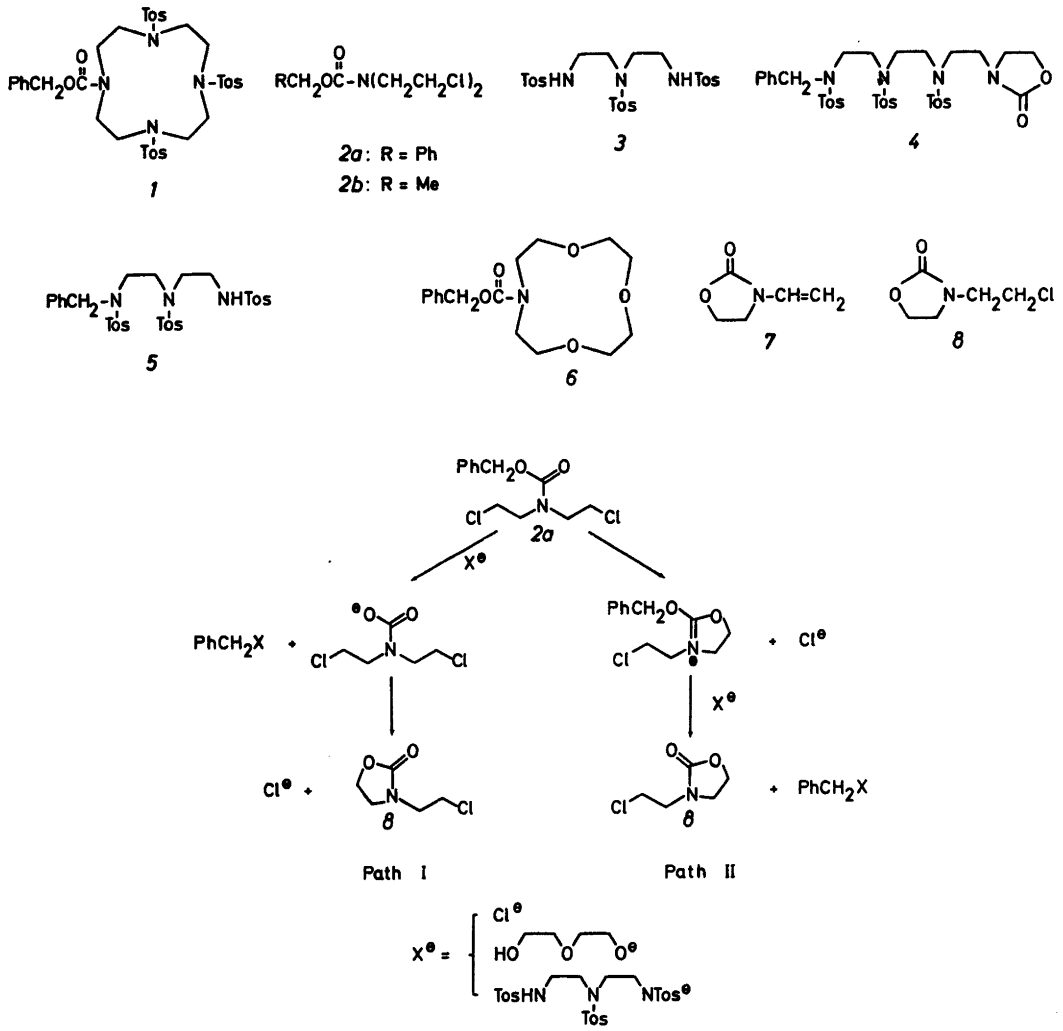

The same two urethanes were then treated in refluxing benzene with catalytic amounts of chloride ion in the form of the 18-crown-6 complex of KCl. While the ethyl derivative *2b* did not react at all, the benzyl derivative *2a* gave the 2-oxazolidinone *8* in 66 % yield. Since only Path I (X = Cl) of Scheme *1* constitutes a complete catalytic cycle, we conclude that all these reactions proceed by this same mechanism and at a temperature about 90 °C lower than the pyrolytic process.[6]

Experimental. The melting and boiling points are uncorrected. Gas liquid chromatography (GLC) analyses were performed on a Hewlett Packard 5 700 A Gas Chromatograph. IR spectra were recorded on a Jasco IRA-1 spectrophotometer and NMR spectra on a Varian A 60A or a Jeol JNM-FX60 Fourier Transform NMR spectrometer. MS data were collected with an A.E.I. MS 902 spectrometer. For the molecular weight determination a Knauer vapour pressure osmometer (Knauer Dampfdruck-osmometer) was used. The elemental analysis was carried out at Mikroanalytisches Laboratorium Ilse Beetz, 8 640 Kronach, West Germany.

Starting materials. *N*-Ethyloxycarbonyl-2,2′-dichlorodiethylamine *2b*,[7] *N*,*N*′,*N*″-tris-*p*-toluenesulfonyl diethylenetriamine *3*,[8] 3-ethenyl-2-oxazolidinone 7 [9] and 3-(2-chloroethyl)-2-oxazolidinone *8* [9] were prepared according to standard methods and had physical and spectroscopic properties in agreement with the literature.

N-Benzyloxycarbonyl-2,2′-dichlorodiethylamine 2a. 2,2′-Dichlorodiethylamine hydrochloride [10]

(26.6 g, 0.15 mol) in dry $CHCl_3$ (200 ml), freshly distilled benzyl chloroformate (25.4 g, 0.15 mol) in $CHCl_3$ (100 ml) and triethylamine (30.2 g, 0.30 mol) in $CHCl_3$ (120 ml) were mixed at 0 °C. The solution was stirred at room temperature overnight, warmed to 50 °C during 1 h and poured into a mixture of ice (200 g) and concentrated HCl (70 ml). Work-up with ether and distillation furnished the urethane *2a* in 75 % yield, b.p. 122–136 °C/0.01–0.06 mmHg. MS, *m/e* (% rel. int.) 279 (0.1, M+4), 277 (0.9, M+2), 275 (1.4, M), 91 (100.0, C_7H_7). IR (film): 1690(s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.66(8 H, s), 5.16 (2H,s), 7.34(5H,s). ^{13}C NMR (15 MHz,$CDCl_3$): δ 155.6(C=O), 137.4, 136.2, 128.6 and 127.7 (aromatic carbons), 67.4(CH_2O), 50.9, 50.4-(CH_2N), 41.9(CH_2Cl).

*Attempted synthesis of 1-benzyloxycarbonyl-4,7,10-tris-*p*-toluenesulfonyl-1,4,7,10-tetraazacyclododecane* 1. *N*-Benzyloxycarbonyl-2,2′-dichlorodiethylamine *2a* (13.7 g, 0.05 mol) and the disodium salt of *3* [1] (30.5 g, 0.05 mol) were dissolved in dry DMF (500 ml) and stirred at 100 °C during 3 h. After cooling and filtering, the solution was concentrated until the volume was 250 ml, then diluted with water (1 500 ml). The precipitate was extracted with ether–methanol (1:1) and benzene–hexane (9:2), the combined extracts washed with 5 % NaOH (6 × 50 ml), dried ($MgSO_4$) and the solvents evaporated. Recrystallization from methanol–ether (1:1) yielded 3.6 g (9 %) of the 2-oxazolidinone *4*, m.p. 179–181 °C. Anal. $C_{37}H_{44}N_4O_8S_3$: C, H, N. Ms, *m/e* (% rel.int.) 613(9.7, M-Tos), 155 (9.4, Tos), 91(100.0, C_7H_7). IR (KBr): 1 740(s) cm^{-1}. ^1H NMR ($CDCl_3$–TFA): 2.44(9H,CH_3), 3.4(16H, complex, CH_2O and CH_2N), 4.27 (2H,s, benzylic protons), 7.31 and 7.5(17H,s and AA′BB′-system, aromatic protons). The NaOH washing solution contained 1.9 g (7 %) of the unreacted diethylenetriamine derivative *3*, m.p. 174–176 °C. To achieve selective fission of any benzyloxycarbonyl groups present,[11] the remaining solid after extration was dissolved in acetic acid containing 45 % HBr and left at room temp. for several days. On cooling 3.9 g (12 %) of the benzylic compound *5* crystallized, m.p. (ethanol) 144–151 °C. Mol. wt., calc. 655, found 655 ± 10. MS, *m/e* (% rel.int.) 500 (1.1,M – Tos), 155(3.8, Tos) 91(100.0,C_7H_5). IR(KBr): 3250(s) cm^{-1}. ^1H NMR($CDCl_3$): δ 2.40 and 2.45(9H, 2 s, CH_3), 3.0(8H, complex, CH_2N), 4.22(2H, s, benzylic protons), 7.36 and 7.6(17H, s and AA′BB′-system, aromatic protons). No basic products were isolated.

Attempted synthesis of 10-benzyloxycarbonyl-1,4,7,-trioxa-10-azacyclododecane 6. A solution of potassium *tert*-butoxide (20 ml, 1.05 M) was diluted with benzene (20 ml) and heated to boiling. The benzyl urethane *2a* (2.7 g, 0.01 mol) and diethylene glycol (1.06 g, 0.01 mol) in benzene (200 ml) were added with vigorous stirring during 45 min. After 10 h the mixture was cooled, filtered and the solvents were evaporated. Chromatography of the remaining oil on silica gel using light petroleum–ethyl acetate (2:1) furnished the known products, 3-ethenyl-2-oxazolidinone *7* [9] (25 %), benzyl chloride (29 %) and the monobenzyl ether of diethylene glycol [12] (17 %), which were identified by IR–^1H NMR–GLC analysis.

2-Oxazolidinone formation in DMSO in the presence of sodium chloride. The benzyl urethane *2a* (2.76 g, 10 mol) and NaCl (0.59 g, 10 mmol) were dissolved in dry DMSO (50 ml) and stirred at 170 °C during 5 h. Na_2CO_3 (0.8 g, 7.5 mmol) was added and after additional 2 h the solution was cooled and diluted with water (100 ml). Work-up with ether gave 3-ethenyl-2-oxazolidinone *7* [9] in 90 % purity (GLC), yield 0.5 g (40 %).

2-Oxazolidinone formation in benzene in the presence of potassium chloride. The benzyl urethane *2a* (0.5 g, 1.8 mmol), KCl (28 mg, 0.38 mmol) and 18-crown-6 (0.11 g, 0.42 mmol) were stirred in boiling benzene during 20 h. After evaporation of the solvent *in vacuo* it was shown by ^1H NMR-GLC analysis that the remaining mixture consisted of the 2-oxazolidinone *8* [9] (47 %) and benzyl chloride (29 %), besides unreacted starting material *2a* (24 %). This corresponds to a formation of the 2-oxazolidinone *8* in 66 % yield.

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