The Preparation of Macrocyclic Polyether-Diester Compounds by Transesterification Including The Preparation of Two New Nitrogen Containing Diester-Crown Compounds

Jerald S. Bradshaw*, Brian A. Jones, Ralph B. Nielsen, Neil O. Spencer and Patricia K. Thompson

Department of Chemistry and Contribution No. 303 from the Institute for Thermochemical Studies, Brigham Young University, Provo, UT 84602

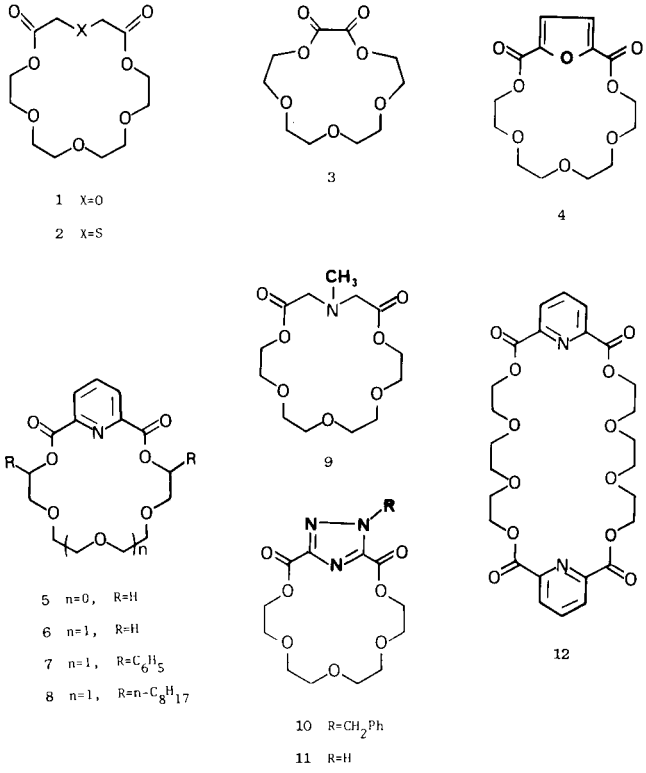
Received December 27, 1982

Macrocyclic polyether-diester compounds have been prepared by reacting oligoethylene glycols with the appropriate dimethyl esters in the presence of catalytic amounts of alkali metal methoxides. The methanol by-product was removed by molecular sieves. Product yields were improved for the preparation of all macrocyclic compounds except a compound containing a furan subcyclic group (**4**). Six new macrocyclic diester compounds (**7-12**) could only be prepared using the base catalyzed transesterification process since the acid chloride synthetic method failed or the acid chloride could not be made. The formation of compounds **5** and **6** from dimethyl 2,6-pyridine dicarboxylate (**17**) and the triethylene and tetraethylene glycols proceded by way of half-transesterified intermediates. These intermediates were also observed for the base catalyzed decomposition of **5** and **6** in methanol to form the glycol and the diester **17**.

J. Heterocyclic Chem., **20**, 957 (1983).

Macrocyclic diester compounds have been prepared from the reaction of diacids, diacid salts and diacid chlorides with various glycols, but there are few examples of the formation of macrocyclic diesters by the transesterification process (1). The macrocyclic polyether-diester compounds (the diester-crown compounds) which exhibit important cation complexation properties (2-5), have been prepared mainly by the reaction of diacid chlorides and glycols (4-8) and to a lesser extent by the reaction of the cesium salts of the diacids with dihalides (9,10).

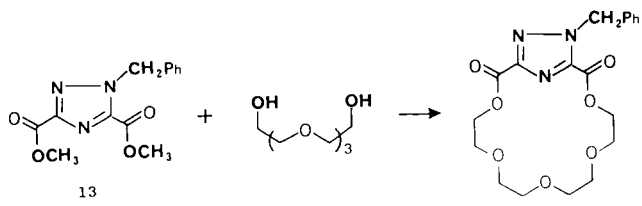
FIGURE 1
COMPOUNDS PREPARED IN THIS STUDY
(7-12 ARE NEW)



The transesterification process to make the macrocyclic polyether-oligoester ligands has been reported in only three instances. Okahara and his coworkers successfully cyclized oligoethylene glycol mono-carboxymethyl ethers to the macrocycle polyether-monoester compounds using various alkali metal carbonates as catalysts (11). Thulin and Vogtle prepared two macrocyclic tetraesters by reacting dimethyl malonate with ethylene and diethylene glycols using alkali metal chlorides as templates with *para*-toluene sulfonic acid as catalyst (12). We have reported the use of the transesterification reaction in the preparation of 4-alkoxypyridino diester-crown ligands (13). This paper reports the transesterification reaction of various dimethyl diesters with the oligoethylene glycols to form the diester-crown compounds. Improved yields for compounds **1-5** (with the exception of **4**) were observed for transesterification over the diacid chloride method. New macrocyclic compounds **7-12**, which could not be prepared from the diacid chlorides, are also reported.

Results and Discussion.

The compounds shown in Figure 1 were prepared by reacting a dimethyl ester with the appropriate oligoethylene glycol in the presence of an alkali metal methoxide catalyst. The methanol by-product was removed by molecular sieves. An acid catalyzed transesterification reaction attempted for compounds **2** and **6** failed to yield the desired macrocyclic products. The preparation of compound **10** is shown as follows:

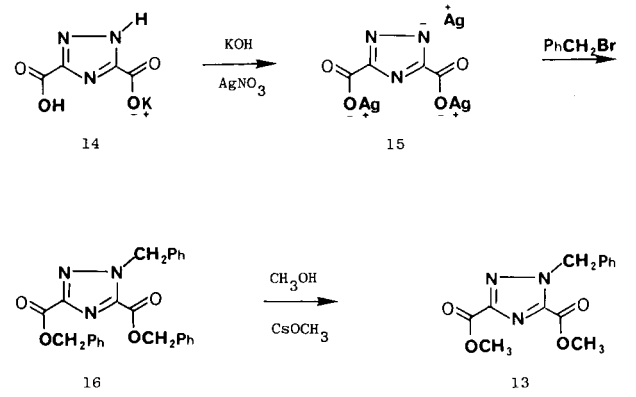


13 10

The starting diesters were prepared from readily available diacids except for dimethyl 1-benzyl-1*H*-1,2,4-triazole-3,5-dicarboxylate (**13**). Compound **13** was prepared by a modification of the prodedure of Vereshchagina and his coworkers (14,15) (see Scheme I). The diphenyl-substituted tetraethylene glycol needed to prepare compound **7** was synthesized from mandelic acid (16) in a manner similiar to the preparation of the dimethyl-substituted tetraethylene glycol (17). The other glycols were used as purchased.

Table I shows the results of several experiments. The yields shown are based on isolated products except for compounds **5, 6,** and **12**. The yields for those products were determined from hplc data (see later). The yields for compound **6** did not vary greatly when the catalyst used was sodium, potassium, rubidium or cesium methoxide. The structures for all compounds are consistent with data obtained from ir, nmr combustion analyses and molecular weight determinations. The wide melting range for compound **7** (124-142°) is due to the presence of both *syn* and *anti* isomers.

SCHEME I



14 15 16 13

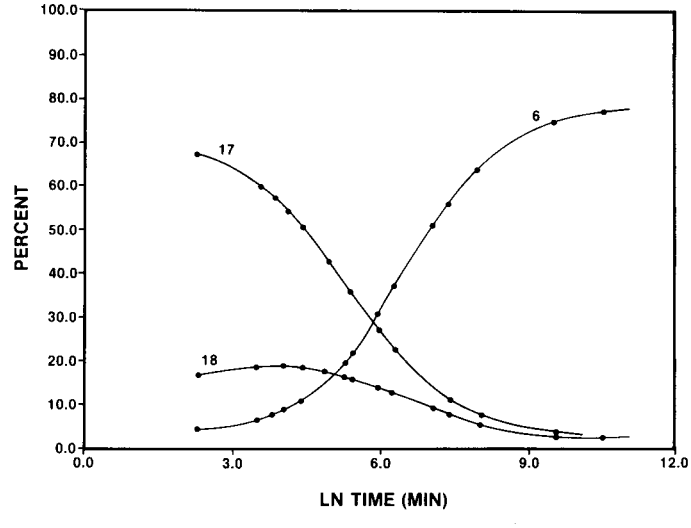
The usefulness of the transesterification procedure is shown by the fact that higher yields were obtained by the new procedure over that for the previous procedure using the diacid chlorides. The preparation of furano compound **4** is an exception probably because the higher electron density imparted by the furan ring makes the attached methyl esters less reactive. The yields for the two separate preparations of compound **6** are the same within experimental error. The higher yields could be due to a template effect. If this is the case, a lower yield could be expected for compound **4** since furano-crown compounds do not complex as well as do the pyridino-crowns (4).

Compounds **7-12** have not been previously reported. We had tried to prepare **8** using the acid chloride method (15). We also tried to prepare **7** from the acid chloride. In both cases, only the starting glycol could be isolated. The acid chloride needed for compounds **9** cannot be prepared. Methyliminodiacetic acid forms the cyclic anhydride when treated with thionyl chloride. The acid and (presumably) the diacid chloride derivatives of compound **13** are likewise not stable. Thus, compound **9** and **10** can only be prepared by transesterification of the stable dimethyl esters of the corresponding diacids.

Compound **12** is the 2:2 adduct of the reaction of dimethyl 2,6-pyridinedicarboxylate (**17**) and triethylene glycol. We also observed a similar 2:2 adduct for the transesterification of 4-pentoxy substituted **17** and triethylene glycol (13). In both cases the 1:1 adducts (**5** and its 4-pentoxy derivative respectively) were also isolated. Only the 1:1 adduct was isolated when 2,6-pyridine dicarbonyl chloride and its 4-substituted derivatives were reacted with triethyl glycol (5,7,13 and 19). We believe that an equilibrium process is involved in the transesterification reaction resulting in the formation of both 1:1 and 2:2 adducts. A study of the mechanism of the reaction seems to verify the above supposition.

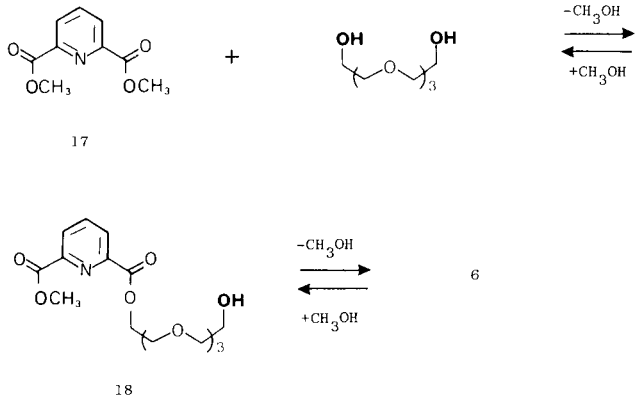
The course of the reaction of diester **17** with tetraethylene and triethylene glycols has been studied using reverse phase high performance liquid chromatography (hplc) to determine the amounts of the reactants and products. Figure 2 shows that when **17** is reacted with tetraethylene glycol in the presence of molecular sieves and potassium

FIGURE 2
A plot of the reaction of 17 with Tetraethylene Glycol in Benzene with Potassium Methoxide Catalyst in the Presence of Molecular Sieves



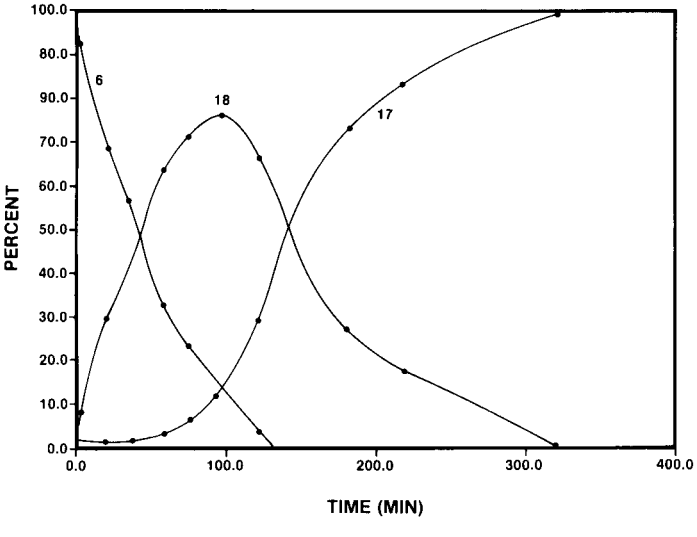
methoxide, an intermediate (**18**) is formed during the reaction (see Scheme II). The same reaction proceeds in a mixture of benzene and molecular sieves without the methoxide catalyst only more slowly (55% yield of **6** after several months). Apparently the sieves alone can play a catalytic role in the reaction. The reverse of the above

SCHEME II



reaction was observed when compound **6** was allowed to stand in methanol in the presence of a catalytic amount of potassium methoxide (Figure 3). Compound **6** is stable in pure methanol. Intermediate **18** could not be isolated.

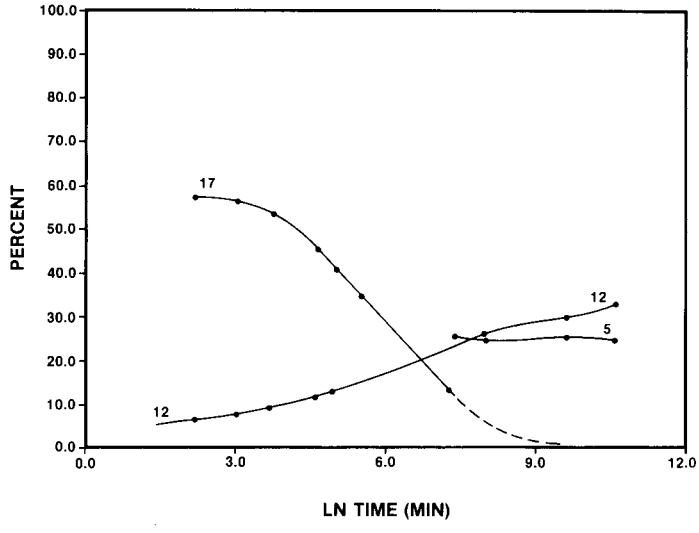
FIGURE 3
A plot of the decomposition of 6 in Methanol with Potassium Methoxide as Catalyst



However, since the intermediate was formed in the macrocycle formation and decomposition processes, we believe compound **18** is the half transesterified product (Scheme II).

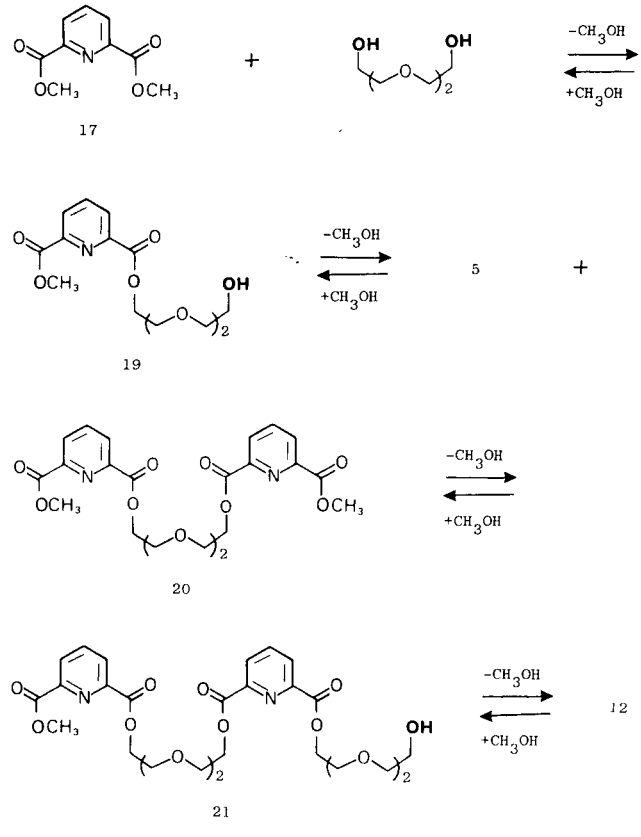
The reaction of diester **17** with triethylene glycol is more complicated. Two products (**5** and **12**) were formed. Compounds **5** and starting **17** could not be effectively separated on the chromatograph resulting in some uncertainty in the data. After the starting **17** was at least 80% reacted, two peaks were observed so that final percentages for the formation of **5** are correct (see Figure 4). Many

FIGURE 4
A plot of the reaction of 17 with Triethylene Glycol in Benzene with Sodium Methoxide as Catalyst and in the Presence of Molecular Sieves



intermediates and by-products were observed in low concentrations during this reaction. The first intermediate observed had a retention time on the chromatograph about the same as compound **18**, which was observed during the reaction of **17** with tetraethylene glycol (see above). We

SCHEME III



believe this new intermediate to be compound **19** (see Scheme III) since this intermediate was also observed when **5** was decomposed in methanol to form **17**. Compound **12** also degraded to **17** in methanol but the reaction was so slow that no intermediates were observed. It is most interesting that when compound **12** was treated with catalytic amounts of sodium methoxide and methanol in benzene at room temperature, a mixture of 28% of compound **5** and 32% of **12** was isolated. This ratio of products is about the same as that found when **5** and **12** were initially prepared from **17**.

The results reported in the preceeding two paragraphs point to the mechanisms shown in Schemes II and III. We believed that all transesterification processes to form macrocyclic diester compounds proceed in an analogous fashion.

EXPERIMENTAL

The ir spectra were obtained on a Beckman Acculab 2 spectrophotometer. The proton and Carbon-13 nmr (^1H and ^{13}C nmr) spectra were obtained on a JEOL FX-90Q spectrometer. Elemental analysis were performed by MHW Laboratories, Phoenix, Arizona. Molecular weights were obtained by osmometry on a Hitachi Perkin-Elmer model 115 molecular weight apparatus. Melting points were determined on a Thomas-Hoover melting point apparatus and are uncorrected. A Bechman model 332 gradient hplc with a Hitachi model 100-40 uv detector, set at 254 nm and an Altex C-RIA recorder and data processor was used for all analytical work. A Waters LC/System 500A was used for preparative chromatographic separations.

Starting Materials.

The starting tri- and tetraethylene glycols were used as purchased from Aldrich. 11,14,17-Trioxaheptacosane-9,19-diol used to prepare compound **8** was previously reported (15). The preparation of 1,11-diphenyl-3,6,9-trioxaundecane-1,11-diol used to prepare compound **7** will be reported at a later date (18). The diester starting materials were all prepared from the commercially available diacids or diacid chlorides except for diester **13** described below.

Dibenzyl 1-Benzyl-1*H*-1,2,4-triazole-3,5-dicarboxylate (**16**) (see Scheme I).

Potassium hydrogen 1*H*-1,2,4-triazole-3,5-dicarboxylate (**14**), prepared as described (16), was converted to the trisilver salt **15** by the procedure of Vereshchagina and coworkers (17). Compound **15** (73.14 g, 0.1531 mole) was placed in 400 ml of dry toluene and 78.6 g (0.46 mole) of benzyl bromide was slowly added. The temperature was raised to reflux during a 3 hour period and the solution was refluxed for 3 additional hours. The solution was filtered and the solid was washed with two portions of 200 ml of toluene. The filtrate and washings were combined and the solvents removed to give an oil which was chromatographed on silica gel using dichloromethane as eluent. The product was recrystallized from dichloromethane/hexane to give white needles, 25.0 g (38%); mp 95-97°; ir: 695, 750, 1110, 1175, 1227, 1275, 1495, 1720, 1740 cm^{-1}; ^1H nmr: δ 5.37 (s, 2H, CO_2CH_2), 5.42 (s, 2H, CO_2CH_2), 5.78 (s, 2H, NCH_2) 7.2-7.5 (m, 15H, ArH).

Anal. Calcd. for $C_{25}H_{21}N_3O_4$: C, 70.25; H, 4.95. Found: C, 70.08; H, 5.05.

Dimethyl 1-Benzyl-1*H*-1,2,4-triazole-3,5-dicarboxylate (**13**).

Compound **16** (17.5 g, 0.041 mole) and 0.01 g of cesium methoxide were refluxed in 300 ml of dry methanol for 1 hour. Acetic acid (0.02 g) was then added and the methanol was removed under reduced pressure. The benzyl alcohol side product was removed under vacuum (0.02 mm). The residue was recrystallized from methanol to give 7.5 g (67%); mp 106.5°; ir: 717, 842, 1109, 1169, 1223, 1276, 1470, 1501, 1723, 1740 cm^{-1}; ^1H nmr: δ 3.99 (s, 3H, CH_3), 4.01 (s, 3H, CH_3), 5.87 (s, 2H, CH_2), 7.35 (m, 5H, ArH).

Anal. Calcd. for $C_{13}H_{13}N_3O_4$: C, 56.73, H, 4.76. Found: C, 56.50; H, 4.80.

Compound **13** was also prepared by reaction of dimethyl 1*H*-1,2,4-triazole-3,5-dicarboxylate (17) with benzyl bromide in methanol solution in the presence of potassium carbonate. The crude product was purified by chromatography on silica gel using dichloromethane as eluent to give a 30% yield. This compound exhibited the same physical properties and spectra as the material derived from compound **16**.

General Procedures for the Synthesis of Macrocyclic Compounds by Transesterification. Method A.

A mixture of 0.02 mole of the diester and 0.02 mole of the glycol in 700 ml of benzene was refluxed for 3 hours through a soxhlet apparatus containing 30 gm of 4A molecular sieves. Three drops of 30% alkali metal methoxide in methanol were added to the solution and the reflux was continued until tlc analysis showed that all the dimethyl ester had reacted. The spent molecular sieves were replaced by fresh molecular sieves after 18 hours. Upon completion of the transesterification reaction, 3 drops of glacial acetic acid were added to neutralize the methoxide catalyst and the macrocyclic compound was isolated by a hot hexane extraction followed by distillation or recrystallization as we have previously reported (5-8).

Method B.

A mixture of 0.02 mole of the diester, 0.02 mole of the glycol and 50 g of 4A molecular sieves was stirred in 700 ml of dry benzene for 1 hour. Three drops of 30% alkali metal methoxide in methanol was added and the mixture was stirred until a tlc analysis showed that all the diester had reacted. Additional methoxide catalyst was added at 24 hour intervals. Upon completion of the reaction, 3 drops of glacial acetic acid was added and the mixture was filtered. The macrocyclic compound was isolated as we have previously described (5-8).

Preparation of Compounds **1-6**.

Compounds **1-6** were prepared by the following methods: **1**, method A; **2** A; **3**, B; **4**, A; **5**, B; and **6**, B. The isolated compounds exhibited the same physical properties as previously reported. The results are shown in Table I.

4,14-Diphenyl-3,6,9,12,15-pentaoxa-21-azabicyclo[15.3.1]heneicosa-1(12),-17,19-triene-2,16-dione (**7**).

Method B was used reacting 2.81 g (0.014 mole) of diester **17**, 5 g (0.014 mole) of 1,11-diphenyl-3,6,9-trioxaundecane-1,11-diol and 18 g of 4A molecular sieves with sodium methoxide as catalyst. The solid product was recrystallized from methanol to yield 1.75 g (26%) of a white solid, mp 124-142°; ir: 1720 cm^{-1}; nmr: δ 3.60-4.10 (m, 12H, OCH_2), 6.20 (m, 2H, OCH), 7.3-7.6 (m, 10H, ArH), 8.2-8.4 (m, 3H, Pyridine H).

Anal. Calcd. for $C_{25}H_{27}NO_7$: C, 67.91; H, 5.70; mol. wt. 477.5. Found: C, 68.02; H, 5.66; mol. wt. 491.3.

When the preparation of compound **7** was attempted using 2,6-pyridinedicarbonyl chloride and the diphenyl glycol, the glycol was recovered and no **7** could be isolated.

4,14-Di-*n*-octyl-3,6,9,12,15-pentoxa-21-azabicyclo[15.3.1]heneicosa-1(12),-17,19-triene-2,16-dione (**8**).

Method A was followed using 1.38 g (0.007 mole) of diester **17** and 2.95 g (0.007 mole) of 11,14,17-trioxaheptacosane-9,19-diol with potassium methoxide as catalyst. The product was purified by chromatography on silica gel using hexane-chloroform (50:50) as eluent, 0.210 g (9%); ir: 1712 cm^{-1}; nmr: δ 0.84 (t, 6H, CH_3), 1.3 (m, 24H, CH_2), 1.8 (m, 4H, $CHCH_2$), 3.5-4.1 (m, 12H, OCH_2), 5.23 (m, 2H, OCH), 7.8-8.3 (m, 3H, ArH).

Anal. Calcd. for $C_{31}H_{51}NO_7$: C, 67.73; H, 9.35; mol. wt. 549.8. Found: C, 67.67; H, 9.38; mol. wt. 574.

4-Methyl-1,7,10,13,16-pentaoxa-4-azacyclooctadecane-2,6-dione (**9**).

Method A was followed using 3.0 g (0.017 mole of dimethyl methyl-

iminodiacetate and 3.33 g (0.017 mole) of tetraethylene glycol with cesium methoxide as catalyst. The product (4.0 g 77%) was a viscous oil that was purified and characterized as the potassium thiocyanate complex.

The potassium thiocyanate complex of compound **9** was prepared by adding 55.7 mg of potassium thiocyanate to 175 mg (0.57 mmole) of **9** in 10 ml of chloroform. The excess potassium thiocyanate was filtered and 10 ml of toluene was added to the filtrate. The solid complex thus formed was filtered and recrystallized from chloroform/toluene to give 100 mg (43%) of white crystals, mp 184-185°; ir: 1730 and 1720 cm^{-1}; ^1H nmr: δ 2.36 (s, 3H, NCH_3), 3.48 (s, 4H, NCH_2), 3.72 (s, 8H, OCH_2), 3.80 (m, 4H, $CO_2CH_2CH_2$), 4.41 (m, 4H, CO_2CH_2); ^{13}C nmr: 43.1, 60.1, 64.1, 68.8, 70.1, 70.4, 169.0.

Anal. Calcd. for $C_{13}H_{23}NO_7 \cdot KSCN$: C, 41.78; H, 5.76; mol. wt. 402.5. Found: C, 41.61; H, 5.89; mol. wt. 376.4.

19-Benzyl-3,6,9,12,15-pentaoxa-18,19,20-triazabicyclo[15.2.1]eicosa-1(20),17-diene-2,16-dione (**10**).

Diester **13** (5.61 g, 0.020 mole) and 3.96 g (0.020 mole) tetraethylene glycol were used in method A with cesium methoxide as catalyst. The product was isolated by hexane extraction and crystallization from methanol to give a white solid, 3 g (36%), mp 120-121° ir: 725, 1110, 1181, 1218, 1280, 1444, 1495, 1730, 1740, 2870 cm^{-1}; ^1H nmr: δ 3.6-3.9 (m, 12H, CH_2), 4.40-4.56 (m, 4H, CO_2CH_2), 5.85 (s, 2H, NCH_2), 7.35 (m, 5H, ArH).

Anal. Calcd. for $C_{19}H_{23}N_3O_7$: C, 56.29; H, 5.72; mol. wt. 405.4. Found: C, 56.28; H, 5.87; mol. wt. 402.

Table I

A Comparison of Yields for Macrocyclic Diester Compounds Prepared from Diacid Chlorides vs the Transesterification Reaction.

Compound	% Yield	A (a)	% Yield	T (a)	mp
1	35	(b)	45.6	(c)	78.5-79.5
2	20	(b)	42.7	(c)	43.5-44.5
3	27.7	(d)	55.9	(c)	45-46
4	60	(e)	37	(c)	117-118
5	9.6	(f)	25.2	(c)	139-140
6	78	(f,g)	76.6	(c)	86.5-87.5
7	0	(c)	25.5	(c)	124-142
8	0	(h)	9	(c)	oil
9	0	(c)	33	(c,i))	184-185 (i)
10	0	(c)	36	(c)	120-121
11	0	(c)	37	(c,j)	134-135
12	0	(f)	35.7	(c)	163-164

(a) A = Diacid chloride procedure; T = Transesterification; isolated yields are reported in all cases except for compounds **5**, **6**, and **12** which were determined from the hplc analyses (b) Ref (5). (c) This work. (d) Ref (6). (e) Ref (4). (f) Ref (7). (g) Ref (18). (h) Ref (19). (i) Isolated as the potassium thiocyanate complex. (j) From the reduction of **10**.

3,6,9,12,15-Pentaoxa-18,19,20-triazabicyclo[15.2.1]eicosa-1(20),17-diene-2,16-dione (**11**).

Compound **10** (284 mg, 0.70 mmole) was placed in a bomb with 20 mg of 10% Pd/C and 100 ml of tetrahydrofuran. The bomb was shaken 40 hours at 15° with hydrogen at a pressure of 450 psi. The solution was filtered and the solvents removed under reduced pressure. The product was crystallized from chloroform/hexane to give 82.1 mg (37%) of white hydroscopic crystals, mp 134-135°; ir: 945; 1095; 1212. 1745, 3470 cm^{-1}; ^1H nmr: δ 3.4 (s (broad), 3H, NH, H_2O), 3.6-3.9 (m, 12H, CH_2), 4.60 (m, 4H, CO_2CH_2).

Anal. Calcd. for $C_{12}H_{17}N_3O_7 \cdot H_2O$: C, 43.24; H, 5.75. Found: C, 43.25; H, 5.86.

Compound **11** could not be prepared by the base catalyzed transesterification of dimethyl 1*H*-1,2,4-triazole-3,5-dicarboxylate.

3,6,9,12,20,23,26,29-Octoxa-35,36-diazatricyclo[28.3.1.1^{14,18}]-hexatriconta-1(35),14(36),15,17,31,33-hexaene-2,13,19,30-tetraone (**12**).

Compound **12** was isolated as a by-product when diester **17** was reacted with triethylene glycol to form macrocycle **5**. Compound **5** was extracted from the reaction mixture with hot hexane. Compound **12** was isolated on a preparatory reverse phase hplc column, 36% yield (based on hplc analyses, mp 163-164°; ir: 1710 cm^{-1}; ^1H nmr: δ 3.5-3.7 (m, 8H, OCH_2), 3.95 (m, 8H, $CO_2CH_2CH_2$), 4.55 (m, 8H, CO_2CH_2), 8.1-8.4 (m, 6H, ArH).

Anal. Calcd. for $C_{26}H_{30}N_2O_{12}$: C, 55.52; H, 5.38; mol. wt. 562.5. Found: C, 55.28; H, 5.46; mol. wt. 563.9.

Determination of Reactants and Products for the Reaction of **17** and Tetraethylene and Triethylene Glycols.

To a solution of 0.50 g of **17** in 25.6 ml of benzene (0.1 *M* in substrate) over 4.8 g of molecular sieves (4A) was added either 0.523 g of tetraethylene glycol and 0.1 ml of saturated potassium methoxide in methanol or 0.404 g of triethylene glycol and 0.1 ml of saturated sodium methoxide in methanol. The course of the reaction was followed by subjecting small amounts (2.0 μl) of the reaction mixture to hplc analysis using a 55:45 (v/v) acetonitrile: phosphate buffer (6.76 x 10^{-3} F sodium dihydrogen-phosphate and 2.91 × 10^{-2} F disodium hydrogen phosphate in water) solution as eluent through an Altex C_{18} 25 cm × 4.6 mm reverse phase column. The hplc peaks were identified from authentic samples of **5**, **6**, **12** and **17**. The results are shown in Figures 2 (tetraethylene glycol reaction) and 4 (triethylene glycol reaction).

Degradation Reactions of Compounds **5**, **6**, and **12**.

A solution of the macrocyclic compound (1 ml of 0.1 *M* substrate in benzene) was placed in 9 ml of pure methanol and catalytic amounts of potassium (for **6**) or sodium (for **5** or **12**) methoxide were added. Analysis was done as reported above for the macrocycle formation reactions. Results for the degradation of compound **6** are shown in Figure 3. The other compounds (**5** and **12**) also gave **17**. When **12** was treated with molecular sieves (4A) and sodium methoxide in benzene, a mixture of 28% of **5**, 32% of **12** and 34% of other unresolved material was observed.

Acknowledgement.

Financial support by the National Science Foundation (CPE-8ll9634) is gratefully acknowledged. RBN received a grant from the Associated Students, BYU.

REFERENCES AND NOTES

(1) See J. S. Bradshaw, G. E. Maas, R. M. Izatt and J. J. Christensen, *Chem. Rev.*, **79**, 37 (1979) for a review of the synthesis of macrocyclic diester compounds.

(2) J. D. Lamb, R. M. Izatt, C. S. Swain, J. S. Bradshaw and J. J. Christensen, *J. Am. Chem. Soc.*, **102**, 479 (1980).

(3) J. D. Lamb, R. M. Izatt, D. G. Garrick, J. S. Bradshaw and J. J. Christensen, *J. Membrane Sci.*, **9**, 83 (1981).

(4) J. S. Bradshaw, S. L. Baxter, J. D. Lamb, R. M. Izatt and J. J. Christensen, *J. Am. Chem. Soc.*, **103**, 1821 (1981).

(5) G. E. Maas, J. S. Bradshaw, R. M. Izatt and J. J. Christensen, *J. Org. Chem.*, **42**, 3937 (1977).

(6) P. E. Fore, J. S. Bradshaw and S. F. Nielsen, *J. Heterocyclic Chem.*, **15**, 269 (1978).

(7) J. S. Bradshaw, A. E. Asay, G. E. Maas, R. M. Izatt and J. J. Christensen, *ibid.*, **15**, 825 (1978).

(8) J. S. Bradshaw, G. E. Maas, J. D. Lamb, R. M. Izatt and J. J. Christensen. *J. Am. Chem. Soc.*, **102**, 467 (1980).

(9) O. Piepers and R. M. Kellogg, *J. Chem. Soc., Chem. Commun.*, 383 (1978).

(10) W. Kruizinga and R. M. Kellogg, *ibid.*, 286 (1979).

(11) T. Nakatsuji, N. Kawamura and M. Okahara, *Synthesis*, 42 (1981).

(12) B. Thulin and F. Vögtle, *J. Chem. Res. (S)*, 256 (1981).

(13) J. S. Bradshaw, N. O. Spencer, G. R. Hansen, R. M. Izatt and J. J. Christensen, *J. Heterocyclic Chem.*, in press.

(14) T. N. Vereshchagina, V. A. Copyrev. M. S. Pevzner and L. M. Kogna, Khim., *Geterotsikl. Soedin.*, 913 (1969); *Chem. Abstr.*, **72**, 111375 (1969).

(15) T. N. Vereshchagina, K. L. Krupin and V. A. Copyrev. *Tr. Sev. Zapadn, Zaochn. Politekh. Inst.*, **6**, 49 (1969); *Ref. Zh. Khim.*, 14Zh429 (1970); *Chem. Abstr.*, **76**, 3766j (1971).

(16) J. S. Bradshaw, P. K. Thompson and R. M. Izatt, unpublished observations.

(17) B. A. Jones, J. S. Bradshaw and R. M. Izatt, *J. Heterocyclic Chem.*, **19**, 551 (1982).

(18) K. Frensch and F. Vögtle, *Tetrahedron Letter*, 2373 (1977).

(19) S. T. Jolley and J. S. Bradshaw, *J. Org. Chem.*, **45**, 3554 (1980).