33267-39-9; o-vinylaniline, 3867-18-3; 3-vinylpyridine picrate, 66018-22-2; p-vinylbenzaldehyde, 1791-26-0; o-divinylbenzene, 91-14-5; m-vinylbenzoic acid, 28447-20-3.

Supplementary Material Available: Properties of the products prepared bp or mp NMR data, and molecular weights (Table II) (3 pages). Ordering information is on any current masthead page.

References and Notes

(1) R. F. Heck, *J. Am. Chem. Soc.*, **90**, 5518 (1968).
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Synthesis of Macrocyclic Polyether–Diester Compounds with an Aromatic Subcyclic Unit[1]

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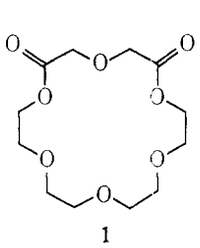
Received November 28, 1977

New series of macrocyclic polyether–diester ligands have been prepared by reacting isophthaloyl chloride and 5-nitroisophthaloyl chloride with tri-, tetra-, penta-, and hexaethylene glycols and one sulfur-substituted analogue (compounds **4–13**), terephthaloyl chloride with tetra-, penta-, and hexaethylene glycols (**14–16**), phthaloyl chloride with penta- and hexaethylene glycol (**17–18**), and 1,8-naphthaloyl chloride with pentaethylene glycol (**19**). All macrocyclic diesters were found to be 1:1 adducts except for the terephthalate prepared from tetraethylene glycol, which was found to be a 2:2 adduct.

The synthesis and unique cation complexing properties of the macrocyclic polyethers, first reported by Pedersen,[2] have been the object of intensive research.[3–7] The majority of work has concerned macrocyclic polyethers, the so-called crown compounds, although many aza[8] and thia crown compounds have been studied.[6,9–13]

We have recently reported the synthesis and cation complexing properties of macrocyclic polyether–diester compounds.[14,15] These compounds have proved to be of interest because stabilities for the ligand–metal complexes are somewhat different than those of the typical crown ethers. Thus, the diketo–crown compounds **1** and **2** gave stability orders of $K^+ \approx Ba^{2+}$ and $K^+ > Ba^{2+}$, respectively, while 18-crown-6 has $Ba^{2+} > K^+$.[14] The inclusion of a pyridine moiety in the macrocyclic compound (**3**) greatly increases the cation complexing ability in methanol.[15]



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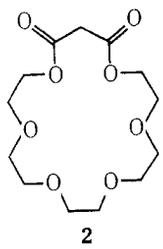

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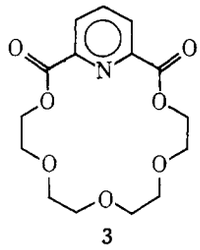

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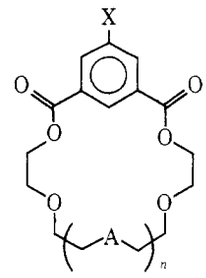
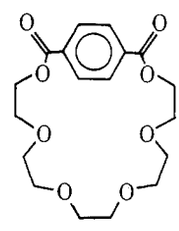
We have previously reported the synthesis of a wide variety of macrocyclic polyether–diester compounds including ether–esters,[14,16–21] thioether–esters,[15,17,19,21] ether–thiol esters,[17,21] amine–esters,[18] ether–ester–amides,[18] ester–amides,[18] and an ether–ester compound with a pyridine subcyclic unit.[15] In this paper we are reporting the synthesis of macrocyclic polyether–diester compounds containing benzene and, in one case, naphthalene subcyclic units (compounds **4–19**, Chart I).

Some macrocyclic diester compounds prepared from aromatic dicarboxylic acid moieties have been reported. Drewes and co-workers have prepared a number of different phthalate and bisphthalate compounds by treating the dipotassium phthalates with various alkyl dihalides.[22–26] None of their phthalate compounds contains the repeating ethylene oxide moiety, although they have reported the preparation of two

Chart I



4 X = H; n = 0
5 X = H; A = O; n = 1
6 X = H; A = S; n = 1
7 X = H; A = O; n = 2
8 X = H; A = O; n = 3
9 X = NO_2; n = O
10 X = NO_2; A = O; n = 1
11 X = NO_2; A = S; n = 1
12 X = NO_2; A = O; n = 2
13 X = NO_2; A = O; n = 3



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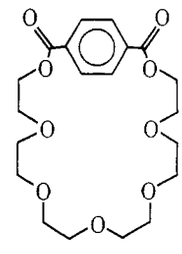

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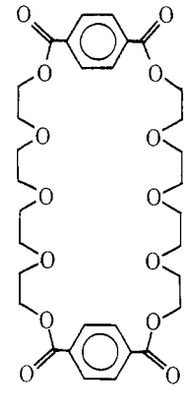

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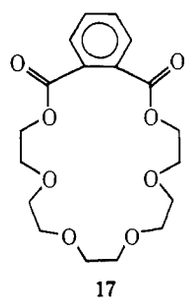

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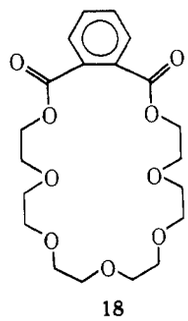
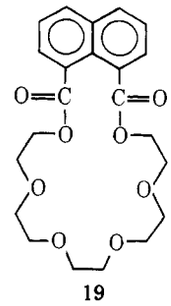


18



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polyether diesters from 2,2′-dithiodibenzoyl chloride.[27] Ehrhart has reported the synthesis of macrocyclic polyether–diester compounds by reacting phthaloyl chloride with di- and triethylene glycols.[28] These compounds are smaller versions of compounds **17** and **18**.

Only two macrocyclic compounds incorporating the isophthalate moiety have been reported. Berr reported the isolation of a bisisophthalate during the polymerization of ethylene isophthalate.[29] Frensch and Vogtle more recently have reported the synthesis of compound **5** by the same reaction reported in this paper.[30]

The preparation of macrocyclic diester compounds containing the terephthalic acid moiety is also rare. Zahn and co-workers have prepared various terephthalates and bisterephthalates by reacting terephthalic acid and various glycols.[31,32] Frensch and Vogtle also reported a terephthalate in their recent paper.[30] Compounds similar to the terephthalates but containing a methylene group between the benzene ring and each carboxyl group have been prepared by Sakamoto and Oki in their studies of hetera-*p*-carbophane systems.[33] Their synthesis also utilized the diacid chloride and various glycols.

Results and Discussion

Compounds **4–19** were prepared by reacting the diacid chloride and the appropriate glycol in benzene. The products were isolated by a hot hexane extraction followed in most cases by recrystallizing the solid product from hexane. Some solid products were sublimed. The liquid products were repeatedly separated from hot hexane until a good molecular weight was obtained.

The assigned structures are consistent with the IR and NMR spectra and the molecular weights. Isophthalates **4–8** exhibited the expected carbonyl bands in the IR at 1715 ± 5 cm^{-1}, the nitroisophthalates **9–13** at 1725 ± 5 cm^{-1}, the terephthalates **14–16** at 1720 ± 5 cm^{-1}, and the phthalates **17** and **18** at 1720 ± 5 cm^{-1}.[34] The NMR spectra of the aromatic portion of compounds **4–8** exhibited the typical isophthalate peaks[35] at δ 7.57 ± 0.02 (H_5), a doublet at δ 8.25 ± 0.05 (H_4 and H_6) and δ 8.76 ± 0.06 (H_2). The latter NMR peak for compound **4** appeared at δ 9.26 probably because of the influence of the ring ether oxygens. The typical 5-nitroisophthalate aromatic NMR peak[35] at δ 9.07 ± 0.04 was observed for compounds **9–13** except that compound **9** has an additional NMR peak at δ 9.45 probably because of the influence of the ring ether oxygens on the hydrogen on benzene carbon number 2. The typical terephthalate and phthalate aromatic NMR peaks[35] appeared at δ 8.16 ± 0.06 and 7.65 ± 0.20 for compounds **14–16** and **17** and **18**, respectively. The typical polyether–diester NMR peaks appear at δ 4.55 ± 0.10 ($COOCH_2$), 3.85 ± 0.05 ($COOCH_2CH_2$), and 3.75 ± 0.10 (OCH_2) for all compounds. For some unknown reason, the ether methylene hydrogens for compounds prepared from penta- and hexaethylene glycols (**7, 8, 12, 13, 17,** and **18**) exhibited two NMR singlets.

The NMR spectra for the terephthalates (**14–16**) are most instructive. A singlet corresponding to four hydrogens was observed to have an upfield shift from δ 3.70 to 3.46 in the NMR spectrum of compound **14**. Sakamoto and Oki also saw an upfield NMR shift in the spectra of their hetero-*p*-carbophane compounds.[33] A molecular model of compound **14** (Figure 1) shows the center ethylene moiety of the polyether chain to be directly under the benzene ring. Indeed, upfield shifts for the center hydrogens of hydrocarbon chains of the *p*-cyclophanes is common.[36] The NMR spectrum for compound **15** exhibited a triplet peak which had an upfield shift to δ 3.59. The molecular model for this compound (Figure 1) shows that the methylene hydrogens next to the center oxygen of the polyether chain are directly under the benzene ring.

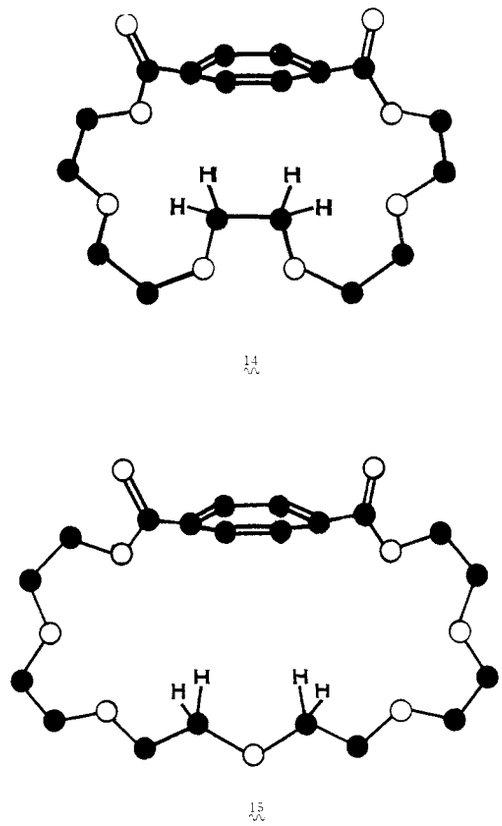
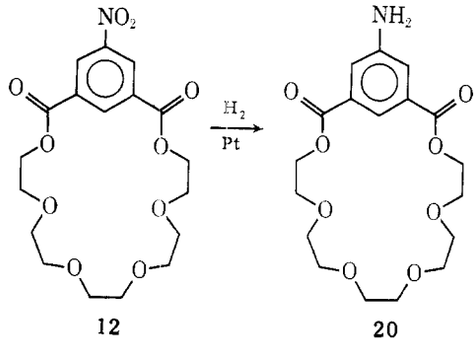


Figure 1.

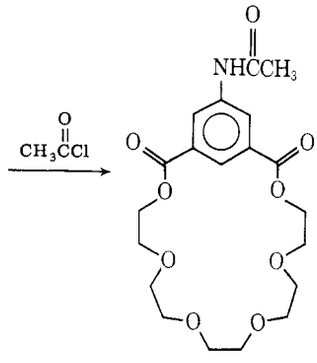
These hydrogens are not as close as those in compound **14** and the upfield shift is not as great. Compounds **14** and **15** were prepared from penta- and hexaethylene glycol, respectively. We expected to see a more pronounced upfield shift for the methylene hydrogens when we prepared a terephthalate from tetraethylene glycol. The NMR peaks corresponding to the polyether chain of the resulting compound (**16**) were essentially the same as those for the isophthalates (compounds **4–13**). This result and the fact that the molecular weight was a little more than twice that of a 1:1 adduct prove that compound **16** is a 2:2 cyclic adduct. Frensch and Vogtle have reported a 1:1 terephthalate adduct from tetraethylene glycol with essentially the same melting point as our compound **16**.[30] They gave no other physical properties. Our data as explained above conclusively demonstrates that the terephthalate prepared from tetraethylene glycol is a 2:2 adduct, not 1:1 as reported by Frensch and Vogtle.

Amino (**20**) and acetamido (**21**) derivatives of compound **12** were prepared. The preparation of these compounds demonstrates the feasibility of modifying the macrocyclic diester compounds.

A satisfactory elemental analysis could not be obtained for five of the compounds (**6, 11, 17–19**). The sulfur-containing compounds appeared to decompose as noted by the development of a distinct yellow color on standing. We have previously reported the difficulty in obtaining combustion analyses for certain sulfur-containing macrocyclic diesters.[17] The mass spectrum of compound **6** did not give a parent peak. Compound **11** exhibited a strong parent peak (385.3) in the MS probably because the ring nitro group stabilizes the two esters. We have noted the difficulty in purifying the phthalates for analysis purposes.[20] Drewes and Coleman have observed difficulty in purifying macrocyclic phthalate esters from octa-, deca-, and dodecamethylene glycols.[25] These latter compounds have a slightly smaller ring size than compounds **17** and **18**. The 1,8-naphthalene dicarboxylate (**19**) was found to be unstable to heat, forming the anhydride. This may have



12 20



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contributed to the unsatisfactory analysis. In every case, the carbon percentage was low. This may indicate that the samples were hydrates. Some of our previous compounds were observed to have satisfactory analyses when water of hydration was postulated.[18,20]

One of the reported compounds (**5**) was found to be unreactive in the complexation of various metals as measured by the lack of heat of reaction in methanol. This is in contrast to compound **3**, which is very reactive toward K^+, Na^+, Ba^{2+}, and Ag^+.[15]

Experimental Section

All infrared (IR) spectra were obtained on a Perkin-Elmer Model 457 spectrophotometer. The nuclear magnetic resonance (NMR) spectra were obtained on a Varian EM-390 spectrometer in deuteriochloroform using tetramethylsilane as an internal standard. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. The molecular weights were determined by osmometry using a Hitachi Perkin-Elmer 115 molecular weight apparatus. Melting points were determined on a Thomas-Hoover capillary type melting point apparatus and are uncorrected.

Starting Materials. *o*-Phthaloyl dichloride (Aldrich), isophthaloyl dichloride (Aldrich), and terephthaloyl dichloride (Aldrich) were used as purchased. 5-Nitroisophthaloyl dichloride was prepared from 5-nitroisophthalic acid (Aldrich) using the method employed by Bennett and Wain.[37] 1,8-Naphthaloyl dichloride was prepared from 1,8-naphthalic anhydride (Aldrich) using the method of Arient and Marhan.[38]

Triethylene glycol (Baker) and tetraethylene glycol (Aldrich) were used as purchased. 1,4,10,13-Tetraoxa-7-thiatridecane was prepared from 2-(2-chloroethoxy)ethanol (Parish) using the method of Maas and co-workers.[19] Pentaethylene glycol was either purchased (Columbia) or prepared by a modification of the method of Hibbert and co-workers.[39] Sodium (73.6 g, 3.2 mol) was dissolved in 500 mL of redistilled ethylene glycol (Mallinckrodt). This solution was then warmed to 100 °C. Slowly 1,2-bis(2-chloroethoxy)ethane (301.1 g, 1.61 mol, Parish) was added. The reaction was allowed to stir at approximately 100 °C until a neutral pH was obtained (5 days). The resulting mixture was filtered on a glass frit. Distillation of the dark solution gave a colorless oil (85.4 g, 17%), bp 172–182 °C (0.7 mm). Hexaethylene glycol was prepared by the same method using redistilled diethylene glycol (Aldrich) and redistilled bis(2-chloroethyl) ether (Eastman).

General Synthesis. The appropriate glycol and acid chloride, each dissolved in 300 mL of benzene, were simultaneously dripped into 500 mL of rapidly stirring benzene at 45 °C. If diacid was present, it was filtered from the acid chloride–benzene solution before addition. The mixture was allowed to stir at 45 °C for at least 2 days, during which time HCl gas was evolved. After the reaction was complete, the benzene was removed under reduced pressure. The crude product was partially purified by continuous extraction with hot hexane.[40] The compound was further purified by recrystallizations with either hexane or a chloroform–hexane mixture, or by sublimation. Specific details are given for each compound.

3,6,9,12-Tetraoxabicyclo[12.3.1]octadeca-1(18),14,16-triene-2,13-dione (4). Isophthaloyl dichloride (12.00 g, 0.059 mol) and triethylene glycol (8.85 g, 0.059 mol) were used. After extraction, the product (0.33 g, 2%) was purified by sublimation at 170 °C (0.5 mm) to give a white powder: mp 138–140 °C; IR 1720 cm^{-1}; NMR δ 3.84 (m, 8 H, CH_2OCH_2), 4.47 (m, 4 H, $COOCH_2$), 7.59 (m, 1 H), 8.19 (d, 2 H), 9.26 (s, 1 H).

Anal. Calcd for $C_{14}H_{16}O_6$: C, 59.99; H, 5.76; mol wt, 280. Found: C, 60.17; H, 5.77; mol wt, 281.

3,6,9,12,15-Pentaoxabicyclo[15.3.1]heneicosa-1(21),17,19-triene-2,16-dione (5). Isophthaloyl dichloride (20.3 g, 0.10 mol) and tetraethylene glycol (19.4 g, 0.10 mol) were used. Purification was by repeated recrystallizations from hexane to yield the product (10.63 g, 33%), a fluffy, white, crystalline solid: mp 95.5–96.0 °C; IR 1710 cm^{-1}; NMR δ 3.72 (s, 8 H, CH_2OCH_2), 3.80 (t, 4 H, $COOCH_2CH_2$), 4.52 (t, 4 H, $COOCH_2$), 7.58 (t, 1 H), 8.27 (d, 2 H), 8.80 (m, 1 H).

Anal. Calcd for $C_{16}H_{20}O_7$: C, 59.25; H, 6.22; mol wt, 324. Found: C, 59.41; H, 6.40; mol wt, 339.

3,6,12,15-Tetraoxa-9-thiabicyclo[15.3.1]heneicosa-1(21),17,19-triene-2,16-dione (6). Isophthaloyl dichloride (5.8 g, 0.029 mol) and 1,4,10,13-tetraoxa-7-thiatridecane (6.0 g, 0.029 mol) were used. Purification was by repeatedly dissolving the product in hot hexane and letting some oil out to finally yield the product (2.06 g, 21%). An analytical sample was prepared by a microdistillation [pot 170 °C (1.0 mm)] to yield a colorless oil: IR 1720 cm^{-1}; NMR δ 2.83 (m, 4 H, SCH_2), 3.64 (t, 4 H, OCH_2), 3.82 (t, 4 H, OCH_2), 4.54 (t, 4 H, $COOCH_2$), 7.57 (t, 1 H), 8.29 (d, 2 H), 8.83 (s, 1 H).

Anal. Calcd for $C_{16}H_{20}O_6S$: mol wt, 340. Found: mol wt, 366.

3,6,9,12,15,18-Hexaoxabicyclo[18.3.1]tetracosa-1(24),20,22-triene-2,19-dione (7). Isophthaloyl dichloride (15.23 g, 0.075 mol) and pentaethylene glycol (17.9 g, 0.075 mol) were used. Purification was by repeated recrystallizations with hexane to yield the product (7.82 g, 28%), a fluffy, white, crystalline solid: mp 103.5–104.5 °C; IR 1714 cm^{-1}; NMR δ 3.64 and 3.72 (both s, 12 H, OCH_2CH_2O), 3.86 (m, 4 H, $COOCH_2CH_2$), 4.54 (t, 4 H, $COOCH_2$), 7.56 (t, 1 H), 8.30 (d, 2 H), 8.71 (m, 1 H).

Anal. Calcd for $C_{18}H_{24}O_8$: C, 58.69; H, 6.57; mol wt, 368. Found: C, 58.83; H, 6.80; mol wt, 386.

3,6,9,12,15,18,21-Heptaoxabicyclo[21.3.1]heptacosa-1(27),23,25-triene-2,22-dione (8). Isophthaloyl dichloride (10.14 g, 0.050 mol) and hexaethylene glycol (14.10 g, 0.050 mol) were used. Purification was by repeated recrystallizations with hexane to yield the product (6.40 g, 31%), a fluffy, white, crystalline solid: mp 106.5–108.5 °C; IR 1710 cm^{-1}; NMR δ 3.57 and 3.69 (both s, 16 H, OCH_2CH_2O), 3.86 (m, 4 H, $COOCH_2CH_2$), 4.54 (m, 4 H, $COOCH_2$), 7.54 (t, 1 H), 8.27 (d, 2 H), 8.70 (m, 1 H).

Anal. Calcd for $C_{20}H_{28}O_9$: C, 58.24; H, 6.83; mol wt, 412. Found: C, 58.50; H, 6.97; mol wt, 421.

16-Nitro-3,6,9,12-tetraoxabicyclo[12.3.1]octadeca-1(18),14,16-triene-2,13-dione (9). 5-Nitroisophthaloyl dichloride (5.5 g, 0.024 mol) and triethylene glycol (3.55 g, 0.024 mol) were used. The product was purified by sublimation at 150 °C (0.7 mm) to yield 0.2 g (2.6%) of light yellow solid: mp 161–163 °C; IR 1540, 1735 cm^{-1}; NMR δ 3.83 (s, 8 H, CH_2OCH_2), 4.47 (m, 4 H, $COOCH_2$), 8.95 (m, 2 H), and 9.45 (m, 1 H).

Anal. Calcd for $C_{14}H_{15}NO_8$: C, 51.69; H, 4.65; mol wt, 325. Found: C, 51.70; H, 4.79; mol wt, 326.

19-Nitro-3,6,9,12,15-pentaoxabicyclo[15.3.1]heneicosa-1(21),17,19-triene-2,16-dione (10). 5-Nitroisophthaloyl dichloride (10.15 g, 0.050 mol) and tetraethylene glycol (14.10 g, 0.050 mol) were used. The product (3.08 g, 17%) was a pale yellow, crystalline solid. An analytical sample was prepared by sublimation at 175 °C (0.5 mm): mp 157–158 °C; IR 1530, 1720 cm^{-1}; NMR δ 3.74 (s, 8 H, OCH_2CH_2O), 3.83 (m, 4 H, $COOCH_2CH_2$), 4.59 (m, 4 H, $COOCH_2$), 9.04 (s, 3 H).

Anal. Calcd for $C_{16}H_{19}NO_9$: C, 52.03; H, 5.18; mol wt, 369. Found: C, 51.89; H, 5.33; mol wt, 368.

19-Nitro-3,6,12,15-tetraoxa-9-thiabicyclo[15.3.1]heneicosa-1(21),17,19-triene-2,16-dione (11). 5-Nitroisophthaloyl dichloride (9.0 g, 0.034 mol) and 1,4,10,13-tetraoxa-7-thiatridecane (7.95 g, 0.038 mol) were used. The solid was purified by recrystallization from hexane to yield a white solid which became yellow on standing (0.22

g, 1.5%): IR 1530, 1730 cm^{-1}; NMR δ 2.88 (m, 4 H, SCH_2), 3.80 (m, 8 H, OCH_2), 4.57 (m, 4 H, $COOCH_2$), 9.10 (m, 3 H).

Anal. Calcd for $C_{16}H_{19}NO_8S$: mol wt, 385. Found: mol wt, 402. MS (*m/e*): 385.3 (17.7), 193.0 (54.5), 238.1 (87.1), 342.2 (98.7), 282.1 (100).

22-Nitro-3,6,9,12,15,18-hexaoxabicyclo118.3.1]tetracosa-1(24),20,22-triene-2,19-dione (12). 5-Nitroisophthaloyl dichloride (11.43 g, 0.050 mol) and pentaethylene glycol (11.87 g, 0.050 mol) were used. Purification was by repeated recrystallizations from hexane to yield the product (6.27 g, 30%), a fluffy, white, crystalline solid: mp 104–105 °C; IR 1530, 1720 cm^{-1}; NMR δ 3.66 and 3.72 (both s, 12 H, OCH_2CH_2O), 3.88 (m, 4 H, $COOCH_2CH_2$), 4.60 (m, 4 H, $COOCH_2$), 9.11 (s, 3 H).

Anal. Calcd for $C_{18}H_{23}NO_{10}$: C, 52.30; H, 5.61; mol wt, 413. Found: C, 52.22; H, 5.73; mol wt, 389.

Amino Derivative (20). Compound **12** (1.73 g, 0.0042 mol) was reduced with hydrogen using PtO_2 as the catalyst. The product (0.89 g, 55%) was purified by recrystallization from a chloroform/hexane mixture to yield an off-white solid: mp 128–129 °C; IR 1710, 3270, 3350 cm^{-1}; NMR δ 3.72 (d, 12 H, OCH_2CH_2), 3.85 (t, 4 H, $COOCH_2CH_2$), 4.50 (t, 4 H, $COOCH_2$), 6.5 (br s, 2 H, NH_2), 7.72 (s, 2 H), 8.14 (s, 1 H).

Amide Derivative (21). The amino compound (**20**) (0.280, 0.00075 mol) was dissolved in 10 mL of tetrahydrofuran and 0.1 g of pyridine. Acetyl chloride (0.20 g) was added. The product (0.040 g, 16%) was purified by crystallization in dilute hydrochloric acid to give pale white crystals: mp 148.5–150.5 °C; IR 1710 cm^{-1}; NMR δ 2.32 (s, 3 H, CH_3), 2.94 (br s, 1 H, NH), 3.65 (d, 12 H, OCH_2CH_2O), 3.80 (m, 4 H, $COOCH_2CH_2$), 4.44 (m, 4 H, $COOCH_2$), 8.15 (s, 1 H), 8.38 (s, 2 H).

Anal. Calcd for $C_{20}H_{27}NO_9 \cdot 3H_2O$: C, 50.10; H, 6.94. Found: C, 50.34; H, 6.62.

25-Nitro-3,6,9,12,15,18,21-heptaoxabicyclo[21.3.1]hepta-cosa-1(27),23,25-triene-2,22-dione (13). 5-Nitroisophthaloyl dichloride (22.52 g, 0.098 mol) and 27.60 g (0.098 mol) of hexaethylene glycol were used. Purification was by repeated crystallization from hexane to yield 2.8 g (6%) of white solid: mp 90–92 °C; IR 1530, 1720 cm^{-1}; NMR δ 3.60 and 3.66 (both s, 16 H, OCH_2CH_2O), 3.87 (m, 4 H, $COOCH_2CH_2$), 4.55 (m, 4 H, $COOCH_2$), 9.08 (m, 3 H).

Anal. Calcd for $C_{20}H_{27}NO_{11}$: C, 52.51; H, 5.95; mol wt, 457. Found: C, 52.41; H, 6.10; mol wt, 439.

3,6,9,12,15,18-Hexaoxabicyclo[18.2.2]tetracosa-20,22,23-triene-2,19-dione (14). Terephthaloyl chloride (10.15 g, 0.050 mol) and pentaethylene glycol (11.90 g, 0.050 mol) were used. Purification was by repeated recrystallization from a chloroform/hexane mixture to yield white needles (0.10 g, <1%): mp 108–109.5 °C; IR 1725 cm^{-1}; NMR δ 3.46 (s, 4 H, OCH_2CH_2O), 3.71 (m, 12 H, CH_2OCH_2), 4.51 (m, 4 H, $COOCH_2$), 8.21 (s, 4 H).

Anal. Calcd for $C_{18}H_{24}O_8$: C, 58.69; H, 6.57; mol wt, 368; Found: C, 58.68; H, 6.63; mol wt, 388.

3,6,9,12,15,18,21-Heptaoxabicyclo[21.2.2]heptacosa-23,25,26-triene-2,22-dione (15). Terephthaloyl chloride (10.15 g, 0.050 mol) and hexaethylene glycol (14.10 g, 0.050 mol) were used. Purification was by repeated recrystallizations from a chloroform/hexane mixture to yield white plates (0.44 g, 2%): mp 69–70 °C; IR 1720 cm^{-1}; NMR δ 3.59 (t, ~4 H, OCH_2CH_2O), 3.70 (s, ~12 H, OCH_2CH_2O) (total for 3.59 and 3.70 is 16 H), 3.83 (m, 4 H, $COOCH_2CH_2$), 4.52 (m, 4 H, $COOCH_2$), 8.19 (s, 4 H).

Anal. Calcd for $C_{20}H_{28}O_9$: C, 58.24; H, 6.84; mol wt, 412. Found: C, 58.31; H, 6.90; mol wt, 431.

3,6,9,12,15,22,25,28,31,34-Decaoxatricyclo[34.2.2.$2^{17,20}$]dotetraconta-17,19,36,38,39,41-hexaene-2,16,21,35-tetraone (16). Terephthaloyl chloride (10.15 g, 0.050 mol) and tetraethylene glycol (9.71 g, 0.050 mol) were used. Purification was by repeated recrystallizations from a chloroform/hexane mixture to yield a white solid (0.080 g, 1%): m.p. 93.5–95.0 °C; IR 1714, 1730 cm^{-1}; NMR δ 3.69 (s, 16 H, OCH_2CH_2O), 3.83 (t, 8 H, $COOCH_2CH_2$), 4.49 t, 8 H, $COOCH_2$), 8.10 (s, 8 H).

Anal. Calcd. for $C_{32}H_{40}O_{14}$: C, 59.25; H, 6.22; mol wt, 649. Found: C, 59.11; H, 6.40; mol wt, 707.

Benzo[*r*]-1,4,7,10,13,16-hexaoxacycloeicosane-17,20-dione (17). *o*-Phthaloyl chloride (10.14 g, 0.050 mol) and pentaethylene glycol (11.90 g, 0.050 mol) were used. Purification was by repeatedly dissolving the product in hot hexane and decanting the cold hexane to yield the product (0.07 g, <1%), a colorless oil: IR 1725 cm^{-1}; NMR δ 3.68 and 3.72 (both s, 12 H, OCH_2CH_2O), 3.85 (t, 4 H, $COOCH_2CH_2$), 4.50 (t, 4 H, $COOCH_2$), 7.45–7.80 (m, 4 H, aromatic H).

Anal. Calcd for $C_{18}H_{24}O_8$: mol wt, 368. Found: mol wt, 390.

Benzo[*u*]-1,4,7,10,13,16,19-heptaoxacyclotricosane-20,23-dione (18). *o*-Phthaloyl chloride (10.2 g, 0.05 mol) and hexaethylene glycol (14.1 g, 0.05 mol) were used. Purification was by repeatedly dissolving the product in hot hexane and decanting cold hexane to yield 0.08 g (0.4%) of a viscous liquid: IR 1720 cm^{-1}; NMR δ 3.62 and 3.67 (both s, 16 H, OCH_2CH_2O), 3.77 (m, 4 H, $COOCH_2CH_2$), 4.47 (m, 4 H, $COOCH_2$), 7.45–7.80 (m, 4 H).

Anal. Calcd for $C_{20}H_{28}O_9$: mol wt, 412. Found: mol wt, 402.

3,4,6,7,9,10,12,13,15,16-Decahydro-1*H*,18*H*-naphtho[1,8-*rs*]-1,4,7,10,13,16-hexaoxacycloheneicosin-1,18-dione (19). 1,8-Naphthaloyl dichloride[41] (11.51 g, 0.0455 mol) and pentaethylene glycol (10.82 g, 0.455 mol) were used. Purification was by repeated recrystallizations from hexane and then from a chloroform/hexane mixture to yield white spheres (0.070 g, <1%): mp 122–125 °C; IR 1700, 1725 cm^{-1}; NMR δ 3.68 and 3.72 (both s, 12 H, OCH_2CH_2O), 3.90 (t, 4 H, $COOCH_2CH_2$), 4.47 (t, 4 H, $COOCH_2$), 7.57 (t, 2 H), 8.07 (m, 4 H). Sublimation of the product gave only the 1,8-naphthoic anhydride.

Anal. Calcd for $C_{22}H_{26}O_8$: mol wt, 418. Found: mol wt, 465.

Acknowledgment. The authors wish to thank Mr. G. E. Maas, Professor E. G. Paul, and Professor R. M. Izatt for their many helpful discussions. This work was supported in part by the National Science Foundation (Grant CHE76-10991) and U.S. Public Health Service (Grant GM-18811-05).

Registry No.—**4,** 65930-69-0; **5,** 65745-83-7; **6,** 65930-70-3; **7,** 65930-71-4; **8,** 65930-72-5; **9,** 65930-73-6; **10,** 65930-74-7; **11,** 65930-75-8; **12,** 65930-76-9; **13,** 65930-77-0; **14,** 65930-79-2; **15,** 65930-80-5; **16,** 65930-81-6; **17,** 65930-82-7; **18,** 65930-83-8; **19,** 65930-84-9; **20,** 65930-78-1; **21,** 65930-85-0; pentaethylene glycol, 4792-15-8; 1,2-bis(2-chloroethoxy)ethane, 112-26-5; isophthaloyl dichloride, 99-63-8; triethylene glycol, 112-27-6; tetraethylene glycol, 112-60-7; 1,4,10,13-tetraoxa-7-thiatridecane, 64036-00-6; hexaethylene glycol, 2615-15-8; 5-nitroisophthaloyl chloride, 24564-72-5; terephthaloyl chloride, 100-20-9; *o*-phthaloyl chloride, 88-95-9; 1,8-naphthaloyl dichloride, 6423-29-6.

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(41) 1,8-Naphthaloyl dichloride was not very stable in a humid room.

New Synthetic Routes to *gem*-Dinitroalkanes and Derivatives[1a]

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Received November 28, 1977

gem-Dinitroalkanes (**3**) have been prepared by reaction of nitro olefins with organolithium reagents, followed by treatment with tetranitromethane. 2-Alkoxy-*gem*-dinitroalkanes (**2**) are obtained similarly by employing alkoxides as the basic addend. The preparation of 1-bromo derivatives of **2** and their reaction with bases are described. The ^1H and ^{13}C NMR spectra of **2** and **3** are presented and discussed.

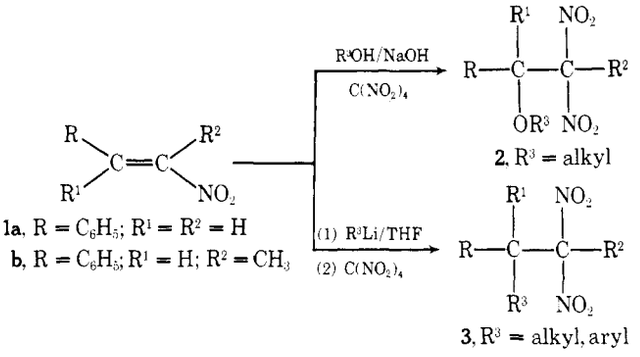
As part of a study of new synthetic routes to polynitro compounds we report a new method of preparing *gem*-dinitro compounds from nitro olefins and precursors. The principal known methods of preparation of these materials are the Kaplan–Shechter reaction (oxidative nitration of mononitroalkanes with silver nitrate),[2] the Ponzio reaction (nitration of an oxime to the pseudonitrole followed by oxidation),[3] the ter Meer synthesis (halogenation of mononitroalkanes and displacement of the halide by nitrite),[4] and alkylation of alkali metal salts of aliphatic polynitro compounds.[5] Each of these synthetic approaches has one or more shortcomings, such as low yield and/or limited scope. Terminal *gem*-dinitro compounds (1,1-dinitroalkanes) undergo reactions such as Michael condensations or Mannich reactions leading to other dinitro and polynitro materials.[6]

Recent synthesis programs in this laboratory have resulted in the facile preparation of several β-alkoxy-α,α-dinitroalkanes (*gem*-dinitro ethers) and *gem*-dinitroalkanes. Treatment of a nitro olefin (**1**) with tetranitromethane (TNM) in the presence of either an alkoxide or alkyllithium yields the corresponding *gem*-dinitro ether (**2**) or *gem*-dinitroalkane (**3**), respectively, Scheme I. The effects of alkyl substitution on the nitro olefin and various alcoholic media have been studied. A special feature of this synthesis is the introduction of two functional units in a one-pot reaction, allowing for the preparation of numerous *gem*-dinitro compounds, not easily accessible by known preparation routes.

The synthetic approach rests on well established experimental observations. Nitro olefins are excellent Michael acceptors and add numerous functional groups in a 1,2 fashion. Also, treatment of a nitronate anion with tetranitromethane, reacting as a nitronium ion source, results in the formation of dinitro and trinitro compounds.[7]

To establish the scope and limitations of this reaction with respect to addends several additions were conducted with ω-nitrostyrene (**1a**) and 2-nitro-1-phenyl-1-propene (**1b**).[8] In the preparation of dinitro ethers (**2**) alkoxides were generated

Scheme I



1a, R = C_6H_5; $R^1 = R^2 = H$
b, R = C_6H_5; $R^1 = H$; $R^2 = CH_3$

from an excess of the required alcohol by reaction with sodium metal or concentrated aqueous sodium hydroxide (2 mol equiv of base). A solution containing the nitro olefin (1 mol), tetranitromethane (1 mol), and the alcohol as solvent was then added slowly (0–10 °C). The dinitroalkanes (**3**) were prepared similarly in ether–tetrahydrofuran solvent at −40 °C by addition of alkyllithium reagents to the nitro olefin, followed by addition of tetranitromethane. The products were obtained as oils or low melting solids (70–90% yields of crude products). Yields of pure samples obtained by column chromatography were 20–60%. Results are summarized in Table I and indicate the versatility of the method.

The reaction is believed to proceed through anion **4**. Tetranitromethane reacts as the nitrating agent eliminating trinitromethide ion. Those 1,1-dinitroalkanes bearing an α hydrogen (**2a–d, 3a,b**) are present as their salts in the reaction mixture which must be acidified prior to workup to secure products.

Products were characterized and identified by examination of their ^1H and ^{13}C NMR spectra and infrared spectra (Tables II and III; see paragraph at end of paper about supplementary