Remarkably Selective Formation of Macrocyclic Aromatic Carbonates: Versatile New Intermediates for the Synthesis of Aromatic Polycarbonates

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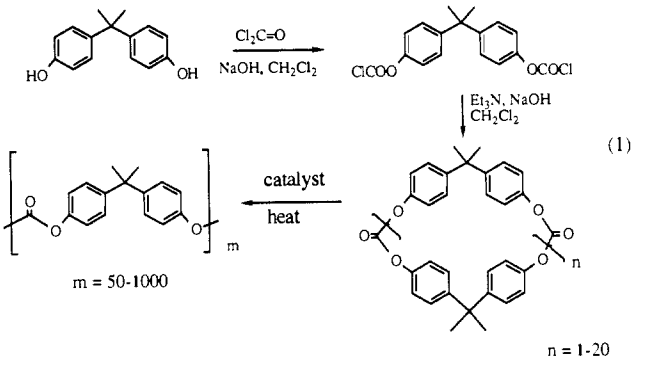
Abstract: A convenient and efficient route for preparation of macrocyclic aromatic carbonates, which provides a mixture of cyclic oligomers (from dimer to docosamer) which is almost totally devoid of linear oligomeric materials is described. Cyclic carbonate formation is achieved in a pseudo-high dilution, triethylamine-catalyzed hydrolysis/condensation reaction of bisphenol A bis(chloroformate) using CH_2Cl_2 and NaOH. The reaction is unusual in that long reaction times and dilute concentrations are not necessary. The role of the amine catalyst in discriminating between formation of cyclic vs linear oligomers is discussed. Cyclic oligomeric carbonates based on bisphenol A are solids, melting at 200–220 °C, anionic, ring-opening polymerization of which provides polymer with molecular weights significantly higher than possible with conventional techniques. The cyclization reaction is broad in scope, and many varied cyclic materials have been prepared.

Methodology for the construction of macrocycles continues to generate considerable interest in synthetic organic and polymer chemistry.[1] It occurred to us that the use of *cyclic* oligomers as intermediates in the preparation of aromatic polycarbonates could offer significant advantages over known procedures[2] for preparation of this important class of engineering thermoplastics. Ring-opening polymerization reactions are commercially important in the preparation of polyamides, aliphatic polyesters, silicones, and epoxide thermosets.[3] However, use of cyclic oligomers of aromatic polyesters or polycarbonates has been limited not only by low-yielding procedures for their preparation but also by the high melting points of the products.[4] By conventional thinking, the required ring size would seem to preclude high-yielding cyclizations. Thus, even the cyclic dimer, the smallest cyclic oligomer possible from bisphenol A (4,4′-isopropylidene diphenol) and phosgene has a ring size of 24 atoms; each oligomeric unit adds 12 atoms to the ring. High-dilution techniques are known for the preparation of discrete cyclic carbonate oligomers (trimer and tetramer) of bisphenol A,[5] but only in special cases (e.g., from O,O′-bisphenols[6]) have useable yields of cyclic carbonates been obtained.

Surprisingly, we have found that macrocyclic aromatic carbonates can be prepared in high yields, via an amine-catalyzed hydrolysis/condensation of aromatic bis(chloroformates). Our procedure affords a mixture (mp ca. 200–210 °C) of macrocyclic aromatic carbonates, with a range of oligomerization from cyclic dimer to about docosamer, with almost total exclusion of linear oligomeric materials. *Typical levels of linear oligomers (MW < 5000) in the crude reaction products are 0.01 to 0.05%, even though many of the macrocycles have over 200 atoms in the ring!* This hydrolysis/condensation reaction is an excellent example of pseudo-high dilution reactions,[7] in that final product concentrations of >0.5 M can be obtained with 30-min reaction times, even on very large scales (12 L), where the rate of addition of a 1.0 M bis(chloroformate) solution is extremely high (150 mL/min).

In our procedure, bisphenol A bis(chloroformate) in CH_2Cl_2 was added to a rapidly stirred mixture of triethylamine, CH_2Cl_2, and aqueous base over 30 min, concurrently adding triethylamine and 25–50% aqueous NaOH during the reaction to maintain a constant amine/CH_2Cl_2 concentration and constant pH (eq 1).



(1)

Because the macrocyclic products are essentially inert to the reaction conditions,[8] only the reactive intermediates need be dispersed. The isolated crude reaction products generally comprise 85–90% macrocyclic carbonates and 10–15% high molecular weight polymer[9] (Figure 1). Extraction of the crude product into acetone affords the mixture of cyclic oligomers; the polymer is insoluble. Macrocyclic products were identified by separation and comparison of several cyclic oligomers (trimer, tetramer, pentamer,

(1) For example, see: (a) Hocker, H. Organic Cyclic Oligomers and Polymers. In *Cyclic Polymers*; Semlyen, J. A., Ed.; Elsevier Applied Science: New York, 1986; Chapter 6. (b) Schill, G. *Catenanes, Rotaxanes, and Knots*; Academic Press: New York, 1971. (c) Gokol, G. W.; Korzeniowski, S. H. *Macrocyclic Polyether Synthesis*; Springer-Verlag: New York, 1982. (d) Paterson, I.; Mansuri, M. M. *Tetrahedron* **1985**, *41*, 3569. (e) Masamune, S.; McCarthy, P. A. *Macrolides* Omura, S., Ed.; Academic Press: New York, 1984; Chapter 4.

(2) (a) Schnell, H. *Chemistry and Physics of Polycarbonates*; Interscience: New York, 1964. (b) Freitag, D.; Grigo, U.; Muller, P. R.; Nouvertne, W. *Encyclopedia of Polymer Science and Engineering*; Kroschwitz, J. I., Ed.; John Wiley and Sons: New York, 1988; Vol. 11, pp 648–718.

(3) For recent reviews on ring-opening polymerizations, see: (a) McGrath, J. E., Ed. *Ring-opening Polymerization: Kinetics, Mechanisms, and Synthesis*; American Chemical Society: Washington, DC, 1985. (b) Ivin, K. J., Saegusa, T., Eds. *Ring-opening Polymerization*; Elsevier Applied Science: London, 1984; Vols. 1–3.

(4) Bisphenol A cyclic trimer mp = 350 °C, ref 5d; cyclic tetramer mp = 375 °C, ref 5c.

(5) Cyclic tetramer: (a) Schnell, H.; Bottenbruch, L. Ger. Pat. 1,229,101, 1966. (b) *Ibid.* Belg. Pat., 620,620, 1962. (c) *Ibid. Makromol. Chem.* **1962**, *57*, 1. Cyclic trimer: (d) Prochaska, R. J. U.S. Pat. 3,274,214, 1966. (e) Moody, L. S. U.S. Pat. 3,155,683, 1964.

(6) Prochaska, R. J. U.S. Pats. 3,422,119, 1969, 3,220,980, 1965, 3,221,025, 1965, and 3,274,214, 1966.

(7) In our *pseudo*-high dilution reaction, reactants and products are very concentrated; only the *reactive intermediates* need be dilute to prevent intermolecular reactions. For a discussion of the dilution principle, see: Rossa, L.; Vogtle, F. Synthesis of Medio- and Macrocyclic Compounds By High Dilution Principle Techniques. In *Topics in Current Chemistry*; Boschke, F. L., Managing Ed., Springer-Verlag: New York, 1983; No. 113, Chapter 1.

(8) At reaction times of over 2 h, amine-catalyzed hydrolysis of the cyclic aromatic carbonates can occur in the basic media if the pH is >12.

(9) It has not yet been determined whether the high molecular weight polymer is macrocyclic or linear. The ratio of high molecular weight polymer (MW ca. 60000) does not increase during the reaction; samples taken at 2–5 min and at the end of reaction have the same ratio of cyclics to polymer.

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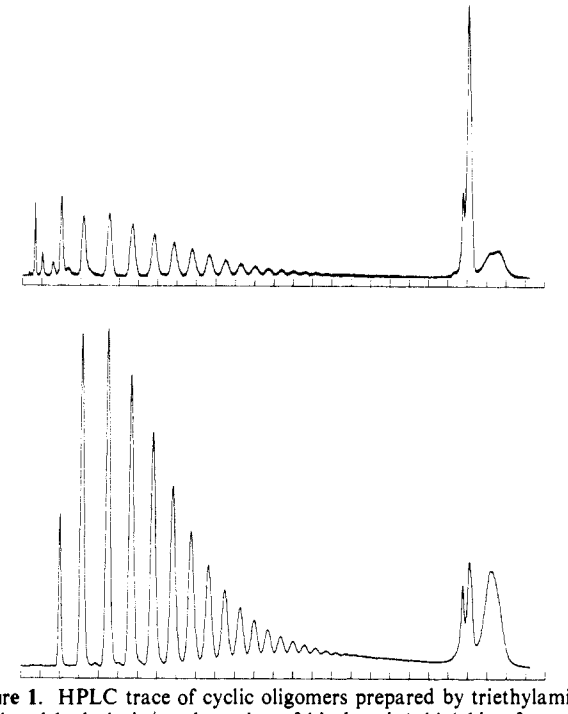


Figure 1. HPLC trace of cyclic oligomers prepared by triethylamine-catalyzed hydrolysis/condensation of bisphenol A bis(chloroformate). Top trace = detection at 285 nm, 0.02 AU full scale; bottom trace = detection at 254 nm, 0.20 AU full scale.

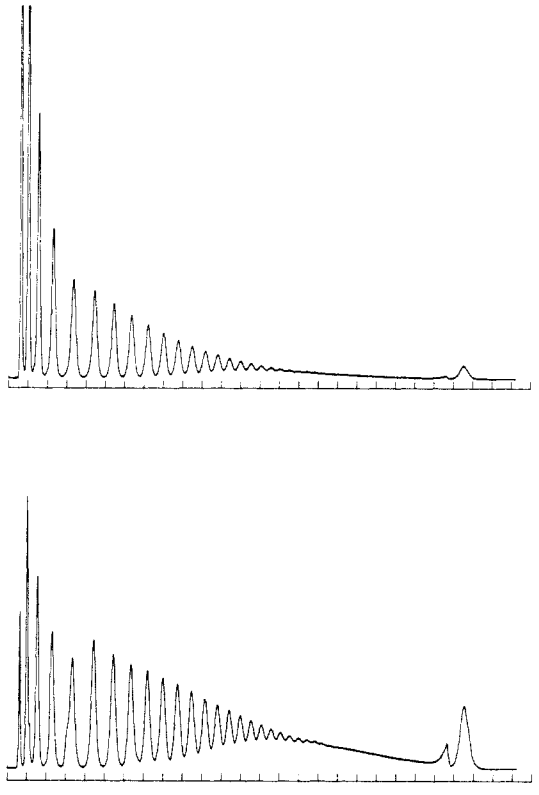


Figure 2. HPLC trace of linear oligomers prepared by pyridine-catalyzed hydrolysis/condensation of bisphenol A bis(chloroformate). Top trace = detection at 285 nm, 0.20 AU full scale; bottom trace = detection at 254 nm, 0.20 AU full scale.

and hexamer) to unambiguously prepared material, and via X-ray crystal structures of cyclic dimer and tetramer. Several linear oligomers were also prepared unambiguously for comparative purposes (dimer, trimer, and tetramer). Higher oligomers from the cyclization reaction were identified as cyclic by analogy of their UV, HPLC, and IR characteristics. UV spectroscopy is particularly useful, in that all of the cyclic oligomers (except the strained cyclic dimer) have 254/285 nm absorbance ratios of ca.

Table I. Interfacial Hydrolysis/Condensation Reactions of Bisphenol A Bis(chloroformate) Using Various Catalysts[a]

catalyst	catalyst concn	% cyclics	products
Et_3N	0.1[b]	85	cyclics and polymer
	0.005	<5	polymer and cyclics
pyridine	0.1	0	linears
	0.5	0	bisphenol A
ethylpiperidine	0.1	58	cyclics and polymer
	0.05[b]	75	cyclics and polymer
n-Pr_3N	0.1	68	cyclics and polymer
	0.25[b]	84	cyclics and polymer
quinuclidine	0.1	<1	36% linears + polymer
	0.005[b]	34	polymer, cyclics, <1% linear
Et_2NMe	0.1	27	linears, cyclics, polymer
	0.005[b]	64	cyclics, polymer, <1% linears
$EtNMe_2$, Me_3N, DABCO[c]	0.1	<1	linears
Proton Sponge,[d] *i*-Bu_3N, Et_4NOH	0.1	0	no reaction
n-Bu_4NBr, PEG 600[e]	0.1	0	no reaction
4-(dimethylamino)-pyridine	0.1	80	cyclics and polymer

[a] Cyclization according to procedure in footnote 6, with final product concentration = 0.5 M. [b] Optimum concentration for cyclic formation. [c] 1,4-Diazabicyclo[2.2.2]octane. [d] 1,8-Bis(dimethylamino)naphthalene. [e] Polyethylene glycol, av MW = 600.

50, whereas the linear oligomers have 254/285 absorbance ratios of 0.2–2.0. Comparison of the HPLC traces in Figures 1 and 2 show that the 285 absorptions are about 20–50 times more intense for the linear oligomers.

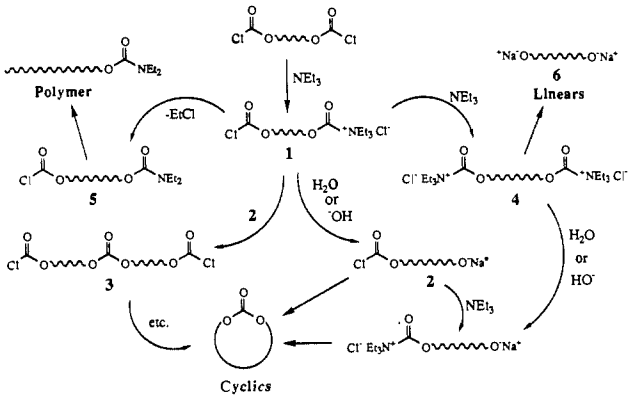
The formation of cyclic vs linear oligomers or polymer is principally controlled by the amine catalyst. We have optimized the reaction both for selectivity of cyclic vs linear *oligomer* formation and for cyclic oligomer vs high molecular weight *polymer* formation. The choice of triethylamine as the reaction catalyst was crucial. A number of catalysts were examined in an attempt to elucidate the mechanism for formation of cyclic carbonates. Surprisingly, substitution of pyridine for triethylamine in an otherwise identical reaction led to selective formation of *linear* oligomers (Figure 2). A variety of products, including cyclic or linear oligomers, high molecular weight polymer, or hydrolysis to bisphenol A can be obtained, merely by changing the catalyst (Table I). The fact that no reaction occurs with use of phase-transfer catalysts, strong, nonnucleophilic organic bases, or hindered amines indicates that a nucleophilic amine with certain key structural features is essential for the purpose at hand.

We believe that the selectivity of the reaction is controlled by the nature of the acylammonium salt **1** formed from initial substitution of tertiary amine on the chloroformate. Acylammonium salt **1** has four possible reaction pathways: hydrolysis to a chloroformate–phenoxide **2**, condensation with a phenoxide to form a new bis(chloroformate) **3**, reaction with amine to form a bis(acylammonium salt) **4**, or decomposition to a carbamate **5**.[10] Since *both* hydrolysis and condensation reactions *must* occur in order to form products, cyclics formation necessitates that condensation reactions occur significantly faster than hydrolysis reactions, to prevent formation of linear (phenoxide terminated) oligomers (Scheme I).

The amine catalyst has two critical roles in controlling the formation of *cyclics* over other products. First, pseudo-high dilution conditions can only be maintained if the amine is sufficiently nucleophilic and present in sufficient concentration to interdict a large increase in chloroformate concentration. Second, the

(10) Formation of carbamates, which are stable to the reaction conditions, leads to undesired products, usually high molecular weight, carbamate-capped polymer. Fortunately, carbamate formation is the slowest of the possible reactions. (a) Hobson, J. D.; McClusky, J. G. *J. Chem. Soc., C* **1967**, 2015. (b) Kosky, P. G.; Boden, E. P. Manuscript submitted.

Scheme I. Mechanism for Et_3N-Catalyzed Interfacial Hydrolysis/Condensation Reactions of Oligomeric Bis(chloroformates)



acylammonium salt formed must react much faster by condensation (by reaction with phenols or phenoxides) than by hydrolysis (by reaction with either hydroxide or water). *The success of triethylamine arises from its ability to optimize these needs.* Although the literature suggests that hydroxide is a better nucleophile than phenoxide, previous studies have been carried out in homogeneous media.[11] The unexpected difference in reaction rates we observe may be because carbonate-forming reactions occur in the organic phase as the acylammonium salt forms, whereas hydrolysis reactions require the salt to migrate to the aqueous phase, or to undergo a slower hydrolysis reaction in the organic phase via reaction with dissolved water. Phase transfer of hydroxide ion into the organic phase is unlikely in our system.[12]

Preliminary molecular modeling studies[13] suggest that the carbonyl group of the acylammonium salt derived from pyridine is very accessible to nucleophiles. Thus, the abundance of water in the system leads to excessive hydrolysis, producing only low MW linear oligomers. Substitution of even a single methyl group on a tertiary amine (e.g., diethylmethylamine) seems to similarly expose the carbonyl carbon, and high levels of linear oligomers are seen when using amine concentrations which are optimal for triethylamine (see Table I). An alternative explanation that may account for these results is that the partition behavior of acylammonium salts derived from pyridine, DABCO, or methylamines may be very different from that of the acylammonium salt obtained from triethylamine. It seems unlikely, however, that this effect would account for the extreme differences seen in reactions using triethylamine and diethylmethylamine. Less sterically hindered amines such as quinuclidine and diethylmethylamine produce high yields of cyclic carbonates with low levels of linear oligomers at very low catalyst concentrations (see Table I). Acylammonium salt formation for these amines may produce higher concentrations of bis(acylammonium salts) (**4**), which may partition more favorably into the aqueous phase than do mono(acylammonium) salts. Although phase-transfer reactions may play a role in the selectivity of the reaction, their importance seems less clear: reactions utilizing phase-transfer agents (n-Bu_4Br or PEG 600) *in the absence of amines* afford no reaction. We are currently attempting to establish kinetic models for the reactions in Scheme I that will allow quantification of the relative rates of acylammonium salt formation, hydrolysis, and condensation for several types of amines.

The macrocyclization reaction is general for a variety of bisphenols, or mixtures of bisphenols, including oxydiphenol, bis(p-hydroxyphenyl)methane, thiodiphenol, hydroquinone, resorcinol, and many others. We were delighted to find that polymerization of the macrocyclic oligomers (at 250 °C for 30 min, using 0.1% LiOPh as catalyst) is unique in that it is driven nearly to completion almost entirely by entropy; the reaction is nearly thermoneutral, with an enthalpy of less than −1.25 kJ/mol.[14] At equilibrium, less than 0.1% cyclic oligomers can be detected.[15] Thus the free energy of reaction is about −30.0 kJ/mol at 250 °C, and the entropy change calculates to about 55.0 J/(deg·mol). Details on this novel polymerization chemistry will be published separately.

We continue to explore the mechanistic subtleties of the macrocyclization reaction, and polymerization fundamentals of this unique route to very high molecular weight polymers.

Experimental Section

Materials and Instruments. Reagent-grade solvents and chemicals were used without furthur purification. Dow Parabis was used as a source of bisphenol A. Purified, crystalline bisphenol A bis(chloroformate), prepared via a modification of the Wingfoot procedure,[16] was used for early studies, and a slightly oligomeric mixture of bis(chloroformates), prepared according to Brunelle et al.,[17] was used for process optimization. Proton NMR spectra were recorded on a Varian EM-390 NMR or a GE QE-300 spectrometer; ^{13}C NMR spectra were recorded on a Varian XL-200 spectrometer, all in $CDCl_3$, and reported in ppm vs TMS. FTIR were measured on a Nicolet 5DXC spectrophotometer. Melting points were measured on a Thomas-Hoover melting point apparatus or on a Mel-Temp hot stage. HPLC analyses were performed on a DuPont Model 850 liquid chromatograph with detection at 254 and 285 nm, or on a Perkin-Elmer HPLC System comprising of a Model 410 pump, ISS-100 autoinjector, and LC-235 diode array detector. The diode array detector was used for generation of UV spectra. THF/water gradients were used for elution of products on C-8 reverse-phase columns. Both instruments were interfaced with a Nelson Analytical Model 2600 Chromatography Data System. Authentic bisphenol A cyclic trimer and cyclic tetramer carbonates were prepared according to literature procedures,[5] as well as by an unambiguous route.[18] Additionally, linear dimer, trimer, tetramer, and pentamer were prepared unambiguously, as well as cyclic pentamer and hexamer.[18]

General Procedure for Preparation of Macrocyclic Aromatic Carbonates. A 1.0-L Morton flask equipped with a mechanical stirrer and condenser was charged with 200 mL of CH_2Cl_2, 7.0 mL of water, 3.0 mL of 9.75 M NaOH (29 mmol), and 2.4 mL of Et_3N (17.25 mmol). The mixture was heated to reflux and vigorously stirred, and a solution of bisphenol A bis(chloroformate) (200 mL of 1.0 M in CH_2Cl_2) was added subsurface over the tip of the impeller at 6.7 mL/min, by use of a peristaltic pump. Concurrently, 59 mL of 9.75 M NaOH (575 mmol) was delivered over 25 min by use of a dropping funnel, and 2.4 mL of Et_3N was added over 28 min via a syringe pump. Within 10 min after complete bis(chloroformate) addition, the phases were separated and washed with 1.0 M HCl and then with water three times. Concentration of the product in vacuo afforded a nearly quantitative yield of product containing 85% cyclics by HPLC analysis (Figure 1). Alternatively, the cyclics and polymer can be isolated by spraying the product/CH_2Cl_2 solution into rapidly stirred water at 85–95 °C. A typical distribution of cyclic oligomers was 5% dimer, 18% trimer, 16% tetramer, 12% pentamer, 9% hexamer, and 25% higher oligomeric cylics. The level of linear oligomers was approximated by doping a known quantity of authentic linear trimer into the crude product, noting the increase in size of the trimer peak, which determined the level of linear trimer. The total level of linear oligomeric impurities could be calculated to about 0.01–0.05% by using the known relative response factors for bisphenol A, linear dimer, trimer, and tetramer.

(11) (a) Hudson, R. F.; Green, M. *J. Chem. Soc.* **1962**, 1055. For similar examples in reactions with esters, see: Jencks, W. P.; Gilchrist, M. *J. Am. Chem. Soc.* **1968**, *90*, 2622. (b) Bender, M. L.; Glasson, W. A. *J. Am. Chem. Soc.* **1959**, *81*, 1590.

(12) True phase transfer of hydroxide ion with n-Bu_4NBr is very difficult. See, for example: (a) Halpern, M.; Cohen, Y.; Sasson, Y.; Rabinovitz, M. *Nouv. J. Chim.* **1984**, *8*, 443. (b) Halpern, M.; Sasson, Y.; Rabinovitz, M. *Tetrahedron* **1982**, *38*, 183. (c) Halpern, M.; Sasson, Y.; Willner, I.; Rabinovitz, M. *Tetrahedron Lett.* **1981**, *22*, 1719. It seems very unlikely that either an acylammonium salt or $HNEt_3^+$ would phase transfer hydroxide ion.

(13) The molecular modeling software used, Biograf, is available from Biodesign, Inc., Pasadena, CA.

(14) Shultz, A. G. Personal communication. The enthalpy is lower and the entropy significantly higher than in typical ring-opening polymerizations; see: McGrath, chapter 1 in ref 1a.

(15) Polymerization at 250 °C for 30 min; analysis by HPLC.

(16) Brit. Pat. 613,280, 1948 (Wingfott Corp.). Use of diethylaniline instead of dimethylaniline allows reaction at 0 °C and provides purer product.

(17) Brunelle, D. J.; Shannon, T. G. U.S. Patent 4,638,077, 1987.

(18) Linear dimer, trimer, tetramer, and pentamer were prepared via reactions of monoprotected bisphenol A with phosgene or various oligomeric bischloroformates. Discrete cyclic oligomers were prepared via traditional high dilution reactions of these linear oligomers with bisphenol A bis(chloroformate): Brunelle, D. J.; Shannon, T. G. Manuscript in preparation.

Washing the crude cyclics/polymer product with 5 volumes of acetone provided a solution of pure cyclics in about 75% yield (the high molecular weight polymer and macrocyclic carbonates with more than ca. 15 repeat units are insoluble in acetone). The mixed macrocyclic oligomers have mp = 200-210 °C. FTIR shows no phenolic O—H and a strong C=O at 1770.6 cm^{-1}. ^{13}C NMR: absorptions at 28.3, 30.27, and 30.87 (methyls), 42.29 and 42.53 (quaternary carbons), 120.2-120.4 and 127.7-127.9 (unsubstituted aromatics), 148.2-149.05 (substituted aromatics), and 152.1-152.2 (carbonyls). 300 MHz ^1H NMR: Major resonances associated with bisphenol A carbonates: 7.26 (d, J = 8.8, 4 H), 7.17 (d, J = 8.8, 4 H), 1.69 (s, 6 H); minor resonances associated with cyclic dimer and trimer are also observed (vide infra). Field desorption shows parent ions at m/e 508, 762, 1016, 1270, 1524, and 1778. HPLC elution using a THF/water gradient on a C-8 reverse-phase column showed the following pattern:

component	t_R (min)	254/285 nm ratio
cyclic dimer	3.10	17.5
cyclic trimer	4.29	46.6
cyclic tetramer	5.68	49.65
cyclic pentamer	6.91	52.65
cyclic hexamer	8.07	56.26
cyclic heptamer	9.125	51.5
cyclic octamer	10.10	50.7
cyclic nonamer	11.02	50.2

Anal. Calcd for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55. Found: C, 75.36; H, 5.21.

Isolation and Identification of Discrete Oligomers: Bisphenol A Cyclic Tetramer Carbonate. One hundred grams of polymer-free macrocyclic carbonates were dissolved in 500 mL of hot 70:29:1 acetone/CH_2Cl_2/2-propanol. Upon standing, 95% pure cyclic tetramer crystallized. Recrystallization from benzene afforded 15.0 g of pure cyclic tetramer with mp = 368-372 °C. FTIR shows no O—H and a strong C=O at 1770.3 cm^{-1}. ^1H NMR has a slightly broadened singlet at 1.66 ppm and a collapsed A_2B_2 pattern at 7.20 and 7.24 ppm. ^{13}C NMR: 30.849 (methyls), 42.481 (quaternary carbon), 120.231 and 127.837 (unsubstituted aromatic), 148.843 and 148.196 (substituted aromatic), and 151.999 (carbonyl carbons). A single-crystal X-ray structure has been solved.[19] High-resolution mass spectrum has a parent at 1016.3772; calcd = 1016.3708. Anal. Calcd for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55. Found: C, 75.58; H, 5.21.

Bisphenol A Cyclic Trimer. The tetramer-poor filtrate from above was evaporated and the residue dissolved in hot toluene. Cooling caused cyclic dimer and trimer to crystallize. Trimer was removed by washing with 60:40 acetone/hexane, which when recrystallized from benzene gave 13.4 g of white solid with mp = 345-350 °C. The transparent plates obtained from benzene occluded benzene, and a crystal structure could not be solved. FTIR shows no O—H and a strong C=O at 1771 cm^{-1}. ^1H NMR has a slightly broadened singlet at 1.66 ppm and a collapsed A_2B_2 pattern at 7.09 and 7.14. ^{13}C NMR: 30.293 (methyls), 42.300 (quaternary carbon), 120.461, 127.717 (unsubstituted aromatics), 148.400, 149.078 (substituted aromatic), and 152.256 (carbonyl). High-resolution mass spectrum has a parent at 762.2829; calcd = 762.2825. Anal. Calcd for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55. Found: C, 75.62; H, 5.76.

Bisphenol A Cyclic Dimer. The residue from above, after removal of cyclic trimer was 98% pure cyclic dimer. Recrystallization from toluene afforded 5.8 g of pure dimer with mp = 330-335 °C. FTIR had no O—H and a strong C=O at 1780.9 cm^{-1}. ^1H NMR had a singlet at 1.73 and an A_2B_2 pattern at 6.81 and 7.02 ppm (J = 9 Hz). ^{13}C NMR: 28.199 (methyls), 42.029 (quaternary carbon), 119.325 and 127.364 (unsubstituted aromatic), 148.645 and 149.485 (substituted aromatic); the carbonyl carbon was shifted upfield, and revealed by integration to be accidentally equivalent to the 148.645 absorption. A single-crystal X-ray structure has been solved and reveals significant ring strain and transannular coplanarity of the aromatic rings, explaining the shifted C=O stretch, and the NMR data. High-resolution MS: calcd for $C_{32}H_{28}O_6$ 508.1886, found 508.1897. Anal. Calcd: C, 75.57; H, 5.55. Found: C, 75.61; H, 5.86.

Preparation of Linear Oligomers. A reaction was carried out identical with that described above for preparation of macrocyclic carbonates, except that pyridine was used as the amine catalyst rather than triethylamine. Identical reaction workup provided a white solid with mp = 140-145 °C. HPLC analysis (Figure 2) indicated selective formation of linear oligomers, by comparison of retention times and 254/285 nm values to bisphenol A and to authentic linear dimer, trimer, and tetramer. HPLC elution using the same THF/water gradient as for cyclics analysis showed the following pattern:

component	t_R (min)	254/285 nm ratio
Bisphenol A	1.69	0.187
linear dimer	2.077	0.408
linear trimer	2.626	0.679
linear tetramer	3.417	0.879
linear pentamer	4.496	1.39
linear hexamer	5.635	1.47
linear heptamer	6.673	1.61
linear octamer	7.618	1.69
linear nonamer	8.496	2.16
linear decamer	9.326	2.05

FTIR showed an O—H absorption at 3597 and a C=O absorption at 1770.2 cm^{-1}. 300-MHz ^1H NMR, major resonances associated with carbonate linkages: 7.26 (d, J = 8.9, 4 H), 7.18 (d, J = 8.9, 4 H), 1.69 (s, 6 H). 300-MHz ^1H NMR, minor resonances associated with phenolic end groups (about 10%): 7.08 (m), 6.70 (m), and 4.91 (s). ^{13}C NMR: 30.892 (methyls), 42.05 and 42.54 (quaternary carbons), 114.65, 114.78 (phenolic carbon), 119.90-120.75 and 127.52-128.21 (unsubstituted aromatics), 142.20, 148.28-149.03 (substituted aromatics), 152.214 and 153.635 (carbonyls). Field-desorption mass spectrum showed parent peaks at m/e 272, 482, 736, and 990. Anal. Calcd for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55. Found: C, 75.80; H, 5.42.

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(19) Brunelle, D. J.; Garbauskas, M. F. Manuscript in preparation.

Allene/Haloolefin Electrocyclic Reactions: A New Route to Stable Triarylmethyl Radicals

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Abstract: Electrocyclization of allene 1,1-diphenyl-3-[2-(2-bromoethenyl)phenyl]propadiene (**5**), followed by one-electron reduction with elemental mercury, gives β-naphthyldiphenylmethyl radical **6** in good yield. In the absence of mercury, the only product isolated is the corresponding triarylmethyl halide. Although both reactions presumably involve an intermediate *o*-quinodimethane species, no evidence for this intermediate was found by ^1H NMR or UV spectroscopy. Allene **5** was formed by isomerization of the corresponding alkyne **7** with activated basic alumina. Palladium-catalyzed coupling of iodo chloride **9** and 3,3-diphenylpropyne gave alkyne **7** in 89% yield.

Recent interest in the chemistry of stable triarylmethyl radicals has been stimulated by the suggestion that polyradicals, linked by appropriate groups, might be possible organic ferromagnets.[1] Thus, compounds having multiple carbene or radical functionality

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