New Triarylmethyl Derivatives: "Blocking Groups" for Rotaxanes and Polyrotaxanes

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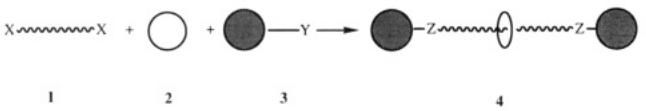
Received February 23, 1993

Five triarylcarbinols (**8**, three new compounds) were synthesized. Using carbanion chemistry the triarylmethanes (**13**, five new compounds) made by formic acid reduction of **8** were converted to the ω,ω,ω–triarylalkanols (**15**, three new compounds) and thence to the chloro (**17**) and iodo (**18**) derivatives (five new compounds). Via carbocation chemistry *p*-(triarylmethyl)phenols (**20**, two new compounds) and aniline (**21**, new compound) were produced. Alkylation of **20** yielded alcohol (**22**), benzylic bromide (**23**), and carboxy (**25**) functionalized derivatives. The alcohol, halide, phenol, aniline, and carboxylic acid functionalized triarylmethane compounds are suitable end blocking groups for rotaxanes and polyrotaxanes.

Introduction

Rotaxanes (**4**) are made from difunctional linear molecules (**1**), cyclic species (**2**), and 2 equiv of monofunctional bulky end "blocking groups" (**3**) by functional group conversion X + Y → Z, e.g., X = –OH, Y = –COCl, Z, = –OOC–. Although such ensembles have been known since



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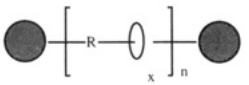

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1967,[1] recently there has been increased interest in these types of structures[2–6] and their polymeric analogs **5**.[7–14] As new types of rotaxanes are prepared there is a need for new blocking groups. This paper describes our work to this end using triarylmethyl derivatives.

The most important parameter to be considered in the design of blocking groups is their sizes, which, of course, have to be bigger than the cavities of the macrocycles to be blocked. The size of a blocking group required to block a specific macrocycle can be theoretically calculated and demonstrated with a CPK molecular model or computer simulation. However, few experimental demonstrations have been reported.

In 1967, Harrison reported preparing a rotaxane consisting of a 30-membered macrocycle threaded by 1,10-decanediol and end-capped with triphenylmethyl chloride.[1] The trityl group served as a blocking group. Harrison next investigated how large a macrocycle could be constrained by various blocking groups. His investigation involved reacting cyclohexylacetyl chloride, triphenylmethyl chloride, or tris(*tert*-butylphenyl)methanol with 1,10-decanediol in the presence of a cyclic species.[15] With the cyclohexylacetate group only macrocycles of less than 28 methylene units could be constrained on the linear component. The trityl and tris(*tert*-butylphenyl)methyl groups, on the other hand, blocked macrocycles with up to 29 and 42 methylene groups, respectively. Although Harrison was able to prepare rotaxanes using the above-mentioned blocking groups, a major drawback with the latter two is that the trityl ether linkage can be easily hydrolyzed.

Schill et al. circumvented the problem of trityl ether hydrolysis by reaction of the anion of triphenylmethane (formed when n-butyllithium was added to the triphenylmethane) with a suitable electrophile.[2] They found that by reaction of this anion with 1,10-dibromodecane in the presence of a cyclic species hydrolytically stable rotaxanes could be prepared.

Another factor to consider is functionality. In order to introduce a blocking group into a rotaxane or polyrotaxane molecule, the functionality Y of **3** is required to be compatible with the reaction system. For example, the functional group of a blocking group has to be highly reactive toward the end groups of the linear species (X of **1**) under the same conditions as those for the other reactions, such as polymerization, in the system. Halo,

(1) (a) Schill, G.; Zollenkopf, H. *Nachr. Chem. Techn.* **1967**, *79*, 149; *Ann. Chem.* **1969**, 721, 53. (b) Harrison, I. T.; Harrison, S. *J. Am. Chem. Soc.* **1967**, *89*, 5723.

(2) Schill, G.; Beckmann, W.; Schweikert, N.; Fritz, H. *Chem. Ber.* **1986**, *199*, 2647.

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(14) Gibson, H. W., Marand, H. *Adv. Mater*, **1993**, *5*, 11.

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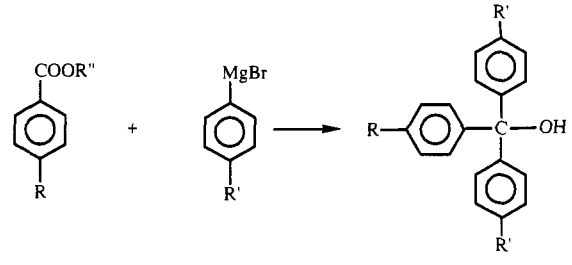
phenolic, carboxylic, alcohol, and amino functional groups (Y of **3**) would enable end capping of a wide variety of rotaxanes (**4**) and polyrotaxanes (**5**).

The solubility of the blocking group should also be compatible with the reaction system. In other words, blocking groups have to be soluble in the reaction solvent, which may be either a melted macrocycle (**2**) or a mixture of macrocycle and another solvent. For this reason, we focused on triarylmethyl compounds with *tert*-butyl substituents which confer solubility while also exerting a large steric influence, capable of constraining rings comprised of up to 42 C, N, O, or S atoms.

Results and Discussion

I. Grignard Reactions. Our syntheses were generally initiated by reaction of a benzoate ester (**6**) with the Grignard reagents **7** derived from *p*-bromo-*tert*-butylbenzene or *p*-bromobiphenyl in refluxing tetrahydrofuran (THF). The triarylmethanols **8** were produced in good to excellent yields. **8a** and **8b** are known compounds. **8c** is



6

a. R=H, R"=CH_3
b. R=t-Bu, R"=CH_3
c. R=OCH_3, R"=C_2H_5

7

a. R'=t-Bu
b. R'=C_6H_5

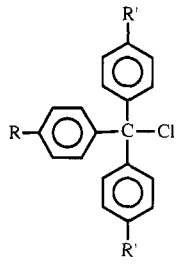
8

a. R=H, R'=t-Bu
b. R=R'=t-Bu
c. R=OCH_3, R'=t-Bu
d. R=H, R'=C_6H_5
e. R=OCH_3, R'=C_6H_5

a new compound. **8d** and **8e** were not purified but used directly in the next step (see section III below). The tris(*tert*-butyl) compound **8b** melts considerably higher (215–6 °C) than **8a** (111–2 °C) and **8c** (150–1 °C), presumably because of its higher symmetry. Stoddart et al. reported the synthesis of **8b** from **7** and diethyl carbonate in 77% yield without any details.[16]

In the case of **8b** a byproduct was a fluorescent compound. Marvel and co-workers reported the synthesis of **8b** in about 45% yield[17] but did not comment on the byproduct. Initially, it was thought that it could be 4,4'-di-*tert*-butylbiphenyl formed by the coupling of (*p*-*tert*-butylphenyl)magnesium bromide. However, the melting point (129–130 °C) and proton NMR spectrum of 4,4'-di-*tert*-butylbiphenyl do not match those of the byproduct (mp 199.1–200.0 °C), which showed sharp peaks for hydroxyl groups and peaks corresponding to C–O stretching vibrations. Further, in the proton NMR spectrum a singlet at 2.97 ppm corresponding to one proton (OH) per three *tert*-butyl groups (from integral values) was observed; it was exchangeable with D_2O. These results indicated that the side product was 1,1,2,2-tetrakis(*p*-*tert*-butylphenyl)-1,2-dihydroxyethane arising via a Gomberg–Bachmann reaction;[18] mass spectral and elemental analyses were consistent with this compound. Use of the attached proton test (APT) in ^{13}C NMR supported this structure also. Reaction of *p,p'*-di-*tert*-butylbenzophenone (**12**) with Mg and I_2 produced this compound in 70% yield, confirming the structure

II. Alternatives to the Grignard Approach. One of the disadvantages of this chemistry is the high cost of 4-bromo-*tert*-butylbenzene. Attempts to make **9a** using a Friedel–Crafts reaction of *tert*-butylbenzene and carbon tetrachloride, both inexpensive, have been made. This

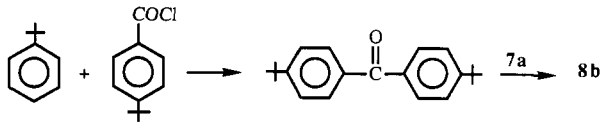


9

a. R=R'=t-Bu

could decrease the costs considerably. However, loss of *tert*-butyl groups by a retro-Friedel–Crafts process was observed, resulting in a very low (5–6%) yield of tris(*p*-*tert*-butylphenyl)methyl chloride (**9a**).

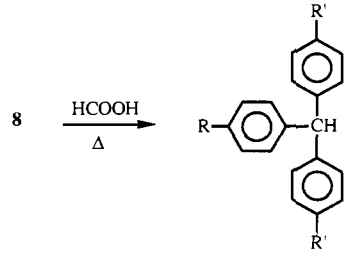
An alternative synthesis of **8b** utilized the Friedel–Crafts reaction of *tert*-butylbenzene (**10**) and the chloride (**11**) of *p*-*tert*-butylbenzoic acid, both cheap starting materials, to form 4,4'-di-*tert*-butylbenzophenone (**12**, 60%). Reaction of 1 equiv of **7a** and **12** produced **8b** in 82% yield.



10 **11** **12**

III. Modification Method 1. The triarylmethanols **8** cannot be directly used as blocking groups because the steric hindrance reduces the reactivities and also the resultant trityl ether type compounds are hydrolytically unstable. Therefore, it is necessary to have the functional group remote from the region of steric hindrance. This can be achieved by adding a spacer between the triarylmethyl moiety and the functional group.

a. Reduction. In order to generate carbanions for nucleophilic substitution reactions, the triarylmethanols **8** were reduced to triarylmethanes **13** by formic acid in toluene. This is essentially a quantitative reaction, and the products were easily separated and purified. **13a-e** are all new compounds. Again, the tris(*tert*-butyl) derivative **13b** is the highest metling (180–1 °C) compared to 99–100, 112–3, 168–9, and 83–5 °C for **13a**, **13c**, **13d**, and **13e**, respectively; again, this probably reflects its higher symmetry.



13

a. R=H, R'=t-Bu
b. R=R'=t-Bu
c. R=OCH_3, R'=t-Bu
d. R=H, R'=C_6H_5
e. R=OCH_3, R'=C_6H_5

(16) Ashton, P. R.; Philp, D.; Spencer, N.; Stoddart, J. F. *J. Chem. Soc. Chem. Commun.* **1992**, 1124.
(17) Marvel, C. S.; Kaplan, J. F.; Himel, C. M. *J. Am. Chem. Soc.* **1941**, *63*, 1892.
(18) Bachmann, W. E.; Shankland, R. V. *J. Am. Chem. Soc.* **1929**, *51*, 306. Gomberg, M.; Van Natta, F. J. *J. Am. Chem. Soc.* **1929**, *51*, 2238.

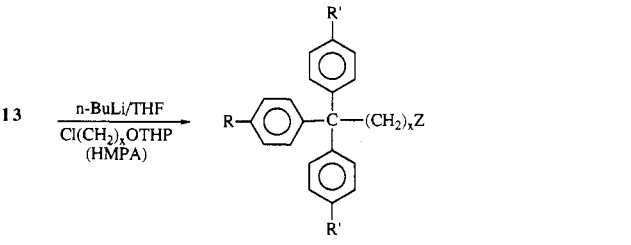
b. Addition of a Linear Chain by Nucleophilic Substitution. The triarylmethanes **13** were allowed to react in THF at 0 °C with n-BuLi as base with tetrahydropyran-protected (THP-protected) 3-chloropropanol, 4-chlorobutanol, or 6-chlorohexanol to form chain-extended THP-protected alcohols **14**. The appearance and disappearance of a deep red or blue color during the reaction indicated the formation and consumption of the triarylmethyl carbanion. Ethers **14** without purification were subjected to deprotection with HCl to produce hydroxyl-terminated blocking groups **15**. The yields of these reactions were 5–10% (**15c**), up to 47% (**15b**). All are new compounds. Again, the tris(*tert*-butyl) compounds **15c** and **15d** display higher melting points (210–211 and 189.6–190.4 °C, respectively) than the bis(*tert*-butyl) compounds **15a** (77–79 °C) and **15b** (oil); this dramatic difference again probably reflects the higher symmetry of the tris derivatives but also may reveal more severe conformational constraints.

It was surprising to see such a difference in the reactivity of bis(*p-tert*-butylphenyl)phenylmethane (**13a**) and tris-(*p-tert*-butylphenyl)methane (**13b**) with n-butyllithium to form **15a** and **15c**, respectively. In the case of tris(*p-tert*-butylphenyl)methane (**13b**), the increased steric bulk of three *p-tert*-butylphenyl groups could make the proton less accessible and the resulting anion could be less nucleophilic compared to that for bis(*p-tert*-butylphenyl)-phenylmethane (**13a**). The low yields may in part be due to the anionic ring opening of tetrahydrofuran. There is some precedence in the literature that supports this idea. Assarson reported that in attempts to prepare *tert*-butylmagnesium bromide in tetrahydrofuran he obtained a white precipitate which he assumed to be a product of the cleavage of tetrahydrofuran by the Grignard reagent.[19] However, in a reinvestigation of this reaction, Normant was able to prepare *tert*-butylmagnesium bromide in normal fashion in tetrahydrofuran.[20] But, Wittig and coworkers found that, in the presence of triphenylaluminum and triphenylboron, (triphenylmethyl)sodium reacted with tetrahydrofuran at room temperature to produce 5,5,5-triphenylpentan-1-ol in good yield;[21] (triphenylmethyl)-sodium alone, however, was ineffective. Jensen and Bedard found that (triphenylmethyl)magnesium bromide also cleaves tetrahydrofuran to produce 5,5,5-triphenylpentan-1-ol in good yield (~63–95%).[22]

In such S_N2 reactions use of an aprotic, highly polar solvent such as hexamethylphosphoramide (HMPA) can often considerably improve the nucleophilicity of the anion and increase the yield of the product.[23] Indeed, when THF/HMPA (75:25) was used as the reaction medium and a low temperature (−78 °C) was employed to minimize THF ring opening, the reaction mixture after hydrolysis yielded **15c** in 66% yield.

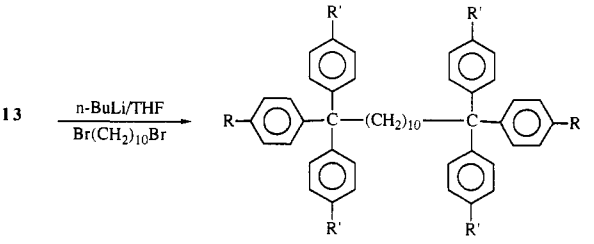
As a prelude to a rotaxane synthesis, **13c** was treated with n-butyllithium at −78 °C; a dark red color developed. After the solution was stirred for 1 h at room temperature, the intense color persisting, 1,10-dibromodecane was added and stirring was continued overnight. Unfortunately, analysis of the reaction indicated that neither the desired di- (**16a**) nor the mono-end-capped product had been prepared. Reaction of **13e** under similar conditions did yield the expected new compound **16b**, but in only 50% yield.

We propose that the *p*-methoxy groups of **13c** and **13e** are responsible for the low yields. ^{1}H-NMR analysis of the reaction of the anion of **13a** under similar conditions with 1,10-dibromodecane indicated that the dicapped compound **16c** was formed in 65% yield. Schill et al. showed that the trityl anion, when reacted with 1,10-dibromodecane, produced the diblocked compound **16d** in 84% yield;[2] we verified this by forming **16d** in 85% yield. Furthermore, we found that quenching of the anion of **13d** (from n-BuLi) with D_2O led to 95% deuteration, while **13e** upon n-BuLi and D_2O treatment afforded only 40% deuteration and unknown byproducts, perhaps the result of nucleophilic attack by n-BuLi on THF. Clearly, the methoxy group has an adverse effect on the anionic chemistry of the triarylmethanes, at least under these conditions, probably as a result of decreased acidity.



14, Z=OTHP → **15**, Z=OH → **17**, Z=Cl → **18**, Z=I

a. R=H, R'=t-Bu, x=3
b. R=H,R'=t-Bu, x=6
c. R=R'=t-Bu, x=4
d. R=R'=t-Bu, x=6



16

a. R=OCH_3, R'=t-Bu
b. R=OCH_3, R'=C_6H_5
c. R=H, R'=t-Bu
d. R=R'=H

c. Conversion of Functional Groups. Alcohol-functionalized blocking groups **15** can be used in rotaxane (**4**) and polyrotaxane (**5**) syntheses. However, to apply the blocking groups more widely, hydroxyl groups were converted to halides. First, the alcohols **15** were was converted into the chlorides **17** by reaction with thionyl chloride in benzene and pyridine.[24] **17a** was made in 85% yield, **17b** in 100% yield, and **17c** in 60% yield. Second, the chlorides were converted into the iodides **18** by reaction with sodium iodide in acetone.[25] **18a** and **18b** were produced in 83 and 92% yields, respectively. All these halides are new compounds.

The functional group conversions were clearly seen from ^{1}H-NMR spectra. When the functional group was changed from −OH to −Cl to −I, the α-methylene protons shifted upfield from 3.63 to 3.47 to 3.12 ppm for **15a**, **17a**, **18a**,

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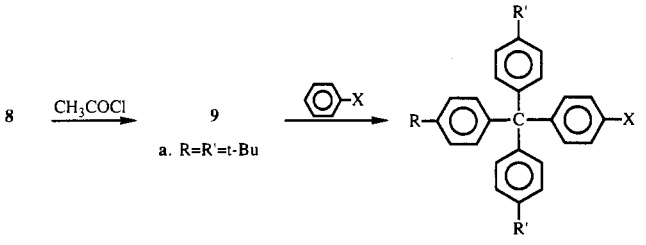
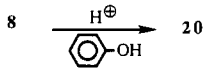
(25) Schroder, C.; Wolf, S.; Agosta, W. C. *J. Am. Chem. Soc.* **1987**, *109*, 5491.

3.65 to 3.55 to 3.19 for **15b**, **17b**, **18b**, and 3.55 to 3.44 for **15c**, **17c**. These upfield shifts are consistent with the order of decrease in electronegativities of the functional groups from –OH to –Cl to –I.

IV. Modification Method 2. a. Addition of Aryl Ring by Aromatic Electrophilic Substitutions. Since the reactions of the triarylmethyl carbanions and THP-protected alcohols were not high yielding except in the presence of toxic HMPA, we studied carbocationic processes to incorporate the spacer and functional group. This method was based on literature report by Mikroyannidis who used a similar reaction to prepare bis-(4-hydroxphenyl)diphenylmethane (**20**, X = R = H, R′ = OH).[26]

The formation of tris(*p-tert*-butylphenyl)methyl chloride (**9a**) was accomplished in 94% yield by reaction of **8b** with acetyl chloride using the procedure suggested by Marvel et al.[17] The synthesis of **9a** from **8b** using thionyl chloride reportedly proceeds in 69% yield;[16] however, the reported melting point is different from ours and Marvel's. Tris(*p-tert*-butylphenyl)methyl chloride (**9a**) thus prepared was allowed to react at 100 °C with excess neat phenol to obtain the new phenolic functional blocking group **20a** in very high, ca. 97%, yield. This reaction was very recently reported to proceed in 95% yield.[16] The reaction of **9a** with phenol is a Friedel–Crafts-type reaction without the use of a catalyst. This reaction also takes place with aniline to give the new amino functional blocking group **21a**. However, the yield of **21a** was considerably lower (71%) than that of **20a**.





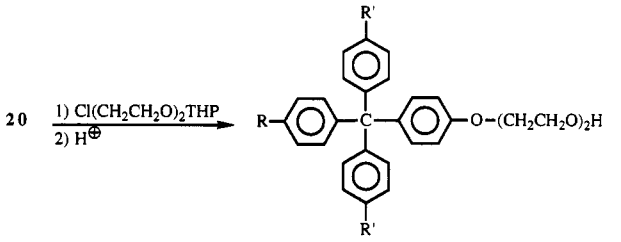
Alternatively, direct reactions of the triarylcarbinols **8** were carried out in phenol with HCl as the catalyst to produce phenol-type blocking groups **20a** and **20b**. These are also aromatic electrophilic substitution reactions. The carbocations formed by the acid catalyzed ionization of the triarylmethanols attack the para-position of phenol to form the desired products in 85 and 80% yields, respectively. Compounds **20** and **21** were easily purified by recrystallizations since the crystallizabilities were largely increased by introduction of a fourth phenyl ring.

Furthermore, direct reactions of the triarylmethanols offered much higher yields and also shortened the synthetic route to functional blocking groups.

b. Further Chain Extension by Williamson Reactions. The phenolic and amino blocking groups **20** and **21** made cationically are themselves useful, but we also wished to have a diverse series of functional blocking groups available. This was done by elaboration of the phenols **20**.

(26) Mikroyannidis, J. A. *Eur. Poly. J.* **1985**, *21*, 895.

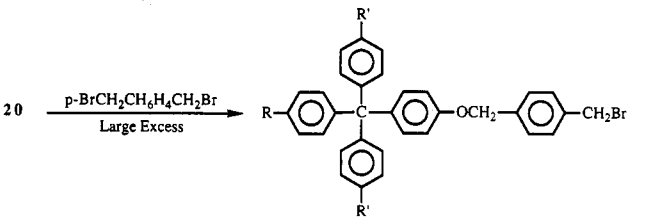
20a was allowed to react with an excess of THP-protected di(ethylene glycol) monochloride in a KOH/1-butanol system followed by deprotection with HCl; hydroxyl-terminated blocking group **22a** was obtained in 95% yield. Stoddart et al. recently stated in a paper that reaction of **20** with chloroethoxyethanol produced **22a** in 92% yield, but no melting point or spectroscopic data were given.[16] The melting point (218.3–218.6 °C) of **22a** is 80 °C lower than that of starting material **20a** because a flexible ethylene oxide chain was added. However, because of the additional aromatic ring **22a** melts 75 °C higher than alcohol **15c**. Therefore, it is possible to adjust the melting point (as well as solubility) of a hydroxyl terminated blocking group by proper choice of chain length of the ethyleneoxy segment. This adjustment may be necessary when the blocking group is subjected to different reaction conditions.



22

a. R=R'=t-Bu
b. R=H,R'=t-Bu

On the other hand, **20a** was allowed to react with large excess of α,α'-dibromo-*p*-xylene to form the benzyl bromide terminated blocking group **23a**. This blocking group can be used in Menschutkin reactions to prepare paraquat dication-containing rotaxanes and polyrotaxanes[27] and other reactions in which the bromide serves as a leaving group. The benzylic ether bond in the blocking group can be cleaved by treatment with acid or by catalytic hydrogenolysis. This property is important in the verification of rotaxane formation and study of dethreading processes. After removal of the blocking group from a rotaxane or polyrotaxane, dethreading can be followed by analytical methods either qualitatively or quantitatively.



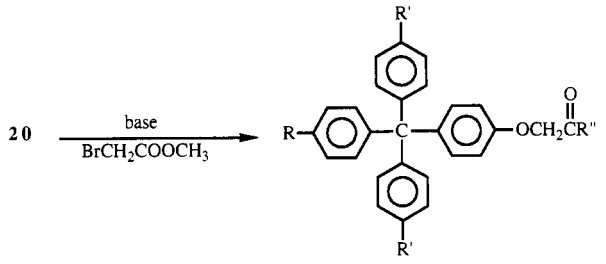
23

a. R=R'=t-Bu

Synthesis of the acid functional blocking group **24a** was accomplished using two different procedures. Phenol functional blocking group **20a** was treated with a base followed by reaction with 2.6 equiv of methyl bromoacetate. When excess KOH (in dioxane/ethanol (2:1) was used, the resulting crude product had multiple peaks from 3.8 to 4.8 ppm in the proton NMR spectrum due to ester hydrolysis and polymerization. This was confirmed by adding KOH to methyl bromoacetate in THF and heating the mixture at reflux for 24 h. The resulting product had similar

(27) Shen, Y. X. Ph.D. Dissertation, Virginia Polytechnic Institute and State University, 1992. Bheda, M. C.; Gibson, H. W., unpublished results.

multiple peaks from 3.8 to 4.8 ppm. These multiple peaks are due to oligomeric glycolides.[28] The ester linkages in the oligomers can be easily hydrolyzed with base, allowing the desired acid **25a** to be isolated in 90% yield. With NaH/DMF the intermediate ester **24a** was cleanly formed in 93% yield. The new acid chloride **26a** also was made from **25a**.



24. R"=OCH_3
25. R"-OH
26. R"=Cl

a. R=R'=t-Bu

Conclusions

A series of five triarylcarbinols (**8**), three of them new compounds, were synthesized, via Grignard reactions in very good yields. Two distinct approaches were employed to attach functionalized spacers to the triarylmethyl moiety. In the first approach via triaryl carbanions, the triarylcarbinols (**8**) were reduced with formic acid to the triarylmethanes (**13**) (five new compounds) essentially quantitatively. The triarylcarbanions formed with n-butyllithium were alkylated with protected chloro alcohols, which after deprotection afforded three new ω,ω,ω-triarylalkanols (**15**); however, the carbanions react sluggishly, unless HMPA is used in significant amounts. The presence of a methoxy substituent on an aryl ring retards anion formation as shown by deuteration studies. The triarylalkanols (**15**) were converted to the chlorides (**17**) (three new compounds) and thence to the iodides (**18**) (two new compounds) in very good yields. In the second approach triarylcarbocations derived from the triarylcarbinols (**8**) or the triarylmethyl chlorides (**9**) were utilized in aromatic electrophilic substitution reactions on phenol and aniline, producing *p*-(triarylmethyl)phenols (**20**) and *p*-(triarylmethyl)anilines (**21**) in good yields. Williamson ether syntheses were applied to the *p*-triarylmethylphenol **20a** to form hydroxy (**22**), benzylic bromide (**23**), and carboxylic acid (**25**) functionalized compounds.

These functionalized triarylmethyl derivatives are suitable for service as end blocking units (**3**) in rotaxanes (**4**) and polyrotaxanes (**5**), in which the macrocycle (**2**) contains up to 42 ring atoms.

Experimental Section

Measurements. Melting points were taken in capillary tubes and have been corrected. Proton and carbon NMR spectra, reported in ppm, were obtained on 270- or 400-MHz spectrometers using chloroform solutions with tetramethylsilane as an internal standard. The following abbreviations have been used in describing the NMR spectra: s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), and m (mutliplet). FTIR spectra, reported in cm^{-1}, were obtained using KBr pellets unless otherwise noted. Mass spectra (MS) are reported in units of *m/z* (fragmentation, relative abundance). Elemental analyses were performed by Atlantic Microlab of Norcross, GA, or Galbraith Laboratories, Knoxville, TN.

Starting Materials. THF was dried over Na/benzophenone and distilled just before use. The n-butyllithium was titrated as 2.4 M. α,α'-Dibromo-*p*-xylene was recrystallized once from n-hexane. The other compounds were used without purification as obtained from commercial sources.

General Procedure for Grignard Reactions: Bis(*p*-*tert*-butylphenyl)phenylmethanol (8a). In an oven-dried 2-L three-necked flask equipped with a condenser, dropping funnel, mechanical stirrer, and nitrogen system were placed magnesium turnings (12.2 g, 500 mmol) with dry THF (800 mL). *p*-*tert*-Butylbromobenzene (100 g, 469 mmol) in dry THF (200 mL) was added dropwise over 1-h with gentle heating; when the reaction started the heat was removed. The reaction was allowed to go for 2 h. A brown color was observed. Methyl benzoate (**6a**) (30.0 g, 220 mmol) in dry THF (100 mL) was added dropwise over 1 h. The mixture was stirred overnight at reflux under nitrogen. The solution was cooled to room temperature and neutralized with 10% HCl. Product was extracted with n-hexane (2 × 350 mL). The combined organic phase was washed with water (3 × 500 mL) and dried with $MgSO_4$. A yellow solid (80.0 g) was obtained after removal of the solvent by rotary evaporation. The solid was subjected to recrystallization two times in methanol to afford 78.0 g (95%) of white powder, mp 111–112 °C (lit.[29] mp 111–112 °C). IR: 3590, 2950, 2873, 1510, 1499, 1475, 1463, 1395, 1360, 1306, 1259, 1201, 1162, 1123, 1046, 1026, 912, 848, 828, 768, 698. ^{1}H-NMR: 1.27 (s, 18H, CH_3), 2.98 (s, 1H, OH), 7.15–7.35 (m, 13H, arom.). ^{13}C-NMR: 32.32, 35.35, 83.07, 124.18, 126.79, 127.15, 128.24, 128.78, 141.21, 144.56, 149.71.

Tris(*p*-*tert*-butylphenyl)methanol (8b) was prepared from 4-bromo-*tert*-butylbenzene and methyl 4-*tert*-butylbenzoate (**6b**). The product was crystallized from methanol or ethanol, 59.1 g (71%), mp 214.6–215.8 °C (lit.[17] mp 212–213 °C). IR: 3576 (sharp, OH), 3084, 3056, 3029 (arom), 2974, 2903, 2865 (aliph), 1507, 1470, 1463 (arom), 1320, 1306, 1268, 1160 (OH bending), 1008, 1019, 1005, 923, 910 (C–O), 841, 834, 821, 705. ^{1}H-NMR: 1.30 (s, 27H, CH_3), 2.71 (s, 1H, OH), 7.18 (dd, 6H, arom), 7.31 (dd, 6H, arom). ^{13}C-NMR: 31.40, 34.47, 81.55, 124.72, 127.59, 144.26, 149.84. Anal. Calcd for $C_{31}H_{40}O$: C, 86.86; H, 9.41. Found: C, 86.79; H, 9.39.

The more soluble byproduct (30% yield) had mp 199.6-200.4 °C after recrystallization from methanol. IR: 3582, 3564 (OH), 3087, 3033 (arom), 2955, 2948, 2901, 2863 (aliph), 1509, 1476 (arom), 1270, 1107, 1141, 1015, 838, 824, 800, 695. ^{1}H NMR: 1.26 (s, 18H, CH_3), 2.97 (s, 1H, OH, exchangeable with D_2O), 7.14, 7.18 (2 d, 8H, arom). ^{13}C NMR: 31.33, 34.32, 83.08, 123.96, 128.25, 141.32, 149.44; APT experiments indicate that 31.33 corresponds to CH_3, 34.32 to $C(CH_3)_3$, 83.08 to COH, 123.96 and 128.25 to arom CH, and 141.32 and 149.44 to quat arom C. MS (NaCl FAB): 613 $(M + Na - H)^+$, 573 $(M - H_2O)^+$, 556, 541, 515, 383, 329, 307, 296, 295. Anal. Calcd for $C_{42}H_{54}O_2$: C, 85.37; H, 9.21. Found: C, 85.10, H, 9.21. This product was confirmed as 1,2-dihydroxy-1,1,2,2-tetrakis(*p*-*tert*-butylphenyl)ethane by a Gomberg–Bachmann synthesis as follows. Into a 50-mL one-neck flask equipped with a magnetic stirrer, a condenser, and N_2 inlet were put Mg turnings (0.13 g, 5.40 mmol), I_2 (0.12 g, 0.47 mmol) and THF (12 mL, dried with Na/benzophenone) followed by the addition of bis(*p*-*tert*-butylphenyl) ketone (**12**, see below) (0.20 g, 0.68 mmol). The color of the solution changed gradually from purple-blue to brown during 20 min at room temperature. The mixture was heated to reflux temperature. The color of the solution turned to white-greenish. After 3 h the color of the solution was gray. The reaction mixture was filtered, and THF was evaporated. The residual yellow solid was treated with CH_2Cl_2 and ice–water/HCl. The organic layer was separated, and CH_2Cl_2 was removed by rotavap. The yellow solid (0.30 g, 75%) after recrystallization was identical in all respects with the sample from the Grignard reaction.

4-*tert*-Butylbenzoyl Chloride (11). 4-*tert*-Butylbenzoyl chloride was prepared by the treatment of 5.0 g (2.8 mmol) of 4-*tert*-butylbenzoic acid with 6.0 g (50 mmol) of thionyl chloride under reflux conditions for 12 h. Excess thionyl chloride was removed under vacuum leaving a pale yellow solution, which was

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not purified. Fuson et al. report 90% yield, bp 144–146 °C/25 Torr, using the same procedure.[30]

4,4'-Di-*tert*-butylbenzophenone (12). *p*-*tert*-Butylbenzoyl chloride (5.0 g, 25 mmol) was added slowly to dry *tert*-butylbenzene (8.0 g, 6.0 mmol) and anhydrous aluminum chloride (6.4 g, 48 mmol) at room temperature. During the addition of *p*-*tert*-butylbenzoyl chloride, the reaction turned from a yellow suspension to a dark reddish brown solution. After the addition was complete, the reaction was warmed at 80 °C for 2.5 h. Vigorous bubbling was observed along with the evolution of hydrogen chloride. Workup consisted of pouring the hot mixture into 100 g of crushed ice and 35 mL of concentrated hydrochloric acid. This yielded a tarlike substance which metamorphosed to a yellow solid after decomposition was complete. This yellow solid was filtered, dissolved in toluene (50 mL), washed with water (2 × 25 mL), 5% aqueous sodium hydroxide (3 × 20 mL), and again with water (2 × 25 mL), and finally dried over sodium sulfate. Removal of toluene yielded 4.42 g (60%) of a yellow solid, mp 110–124 °C. Recrystallization from toluene produced an off-white solid, mp 135–137 °C. Larner et al. record mp 133–134 °C.[31] Cristol et al. record mp 134–135.5 °C.[32] IR: 2963, 1646, 1606, 1315, 1283, 1187, 934, 688. ^{1}H-NMR: 1.35 (s, 18H, CH_3), 7.45 (d, 4H, arom), 7.75 (d, 4H, arom). ^{13}C-NMR: 31.3, 35.2, 125.3, 130.1, 135.3, 156.0, 196.3.

Tris(*p*-*tert*-butylphenyl)methanol (8b) from 12. A Grignard reagent was prepared from 4-bromo-*tert*-butylbenzene and allowed to react with 4,4'-di-*tert*-butylbenzophenone (12). The crude yellowish crystalline product (82%) was recrystallized from acetone:hexane (65:35), giving pure tris(*p*-*tert*-butylphenyl)-methanol (8b), identical in all respects to that described above.

Bis(*p*-*tert*-butylphenyl)*p*-methoxyphenyl)methanol (8c). Grignard reaction of bromo-*tert*-butylbenzene and methyl *p*-methoxybenzoate (6c) produced a viscous residue which was crystallized from hexane to afford white crystals, mp 150.0–150.8 °C. IR: 3525, 2964, 1609, 1508, 1241, 1024, 828. ^{1}H-NMR: 1.32 (d, 18H, CH_3), 2.70 (s, 3H, OH), 3.80 (s, 3H, OCH_3), 6.85 (d, 2H, arom), 7.20 (m, 5H, arom), 7.32 (m, 5H, arom). ^{13}C-NMR: 31.3, 34,4,, 55.2, 81.4, 113.1, 124.7, 127.5, 129.1, 139.6, 144.3, 149.7, 158.5. Anal. Calcd for $C_{28}H_{34}O_2$: C, 83.54; H 8.51. Found: C, 83.36; H, 8.60.

General Procedure for Formic Acid Reductions: Bis(*p*-*tert*-butylphenyl)phenylmethane (13a). Bis(*p*-*tert*-butylphenyl)phenylmethanol (8c) (80.0 g, 210 mmol) was dissolved in toluene (800 mL) in a 2-L three-necked flask equipped with a condenser and mechanical stirring. The solution was heated to reflux, and formic acid (350 mL) was added. The mixture was allowed to reflux overnight. The system was cooled to room temperature. Two layers were observed. The organic phase was separated, and product was extracted from the formic acid and water phase with toluene (2 × 200 mL). The combined organic phase was washed with water (3 × 500 mL) and dried with $MgSO_4$. An oil (75.5 g) was obtained afer removal of the solvent by rotary evaporation. The first recrystallization was done in n-hexane and the second recrystallization was done in toluene, both by cooling to −20 °C. A white powder (60.0 g, 80%), mp 99–100 °C, was obtained after it was vacuum dried overnight. IR: 2950, 2873, 1510, 1495, 1475, 1468, 1395, 1360, 1259, 1201, 1138, 1123, 1088, 1040, 862, 850, 828, 780, 768, 698. ^{1}H-NMR: 1.30 (s, 18 H, CH_3), 5.49 (s, 1 H, Ar_3CH), 7.03–7.32 (m, 13 H, arom). ^{13}C-NMR: 31.4, 34.4, 56.1, 125.1, 126.1, 128.2, 129.0, 129.5, 144, 149. Anal. Calcd for $C_{27}H_{32}$: C, 90.95; H, 9.05. Found: C, 90.70; H, 9.04.

Tris(*p*-*tert*-butylphenyl)methane (13b). Tris(*p*-*tert*-butylphenyl)methanol (8b) was reduced by formic acid. The crude product was recrystallized from 50:50 methanol/acetone. Pure yield: 97%, mp 179.5–180.6 °C. IR: 3050, 3023 (arom), 2961, 2945, 2862 (aliph), 1507, 1474, 1464, 1405, 1392 (arom), 1267, 1201, 1109, 1019, 956, 840, 819, 729, 695–687. ^{1}H NMR: 1.29 (s, 27H, CH_3), 5.42 (s, 1H, Ar_3CH), 7.04, 7.28 (2 d, 12H, arom). Anal. Calcd for $C_{31}H_{40}$: C, 90.23; H, 9.77. Found: C, 90.28; H, 9.81.

Bis(*p*-*tert*-butylphenyl)*p*-methoxyphenyl)methane (13c). Crude bis(*p*-*tert*-butylphenyl)(*p*-methoxyphenyl)methanol (8c) was reduced with formic acid to produce a yellow solid, which was chromatographed on silica gel with hexane/ethyl acetate (95:5 v/v) as the eluting agent. Crystallization of the column eluate residue from hexane gave a 92% yield (from 6c) of white solid, mp 112.3–112.7 °C. IR: 2959, 1609, 1510, 1249, 822. ^{1}H-NMR: 1.3 (s, 18H, CH_3), 3.79, (s, 3H, OCH_3), 5.42, (s, 1H, Ar_3CH), 6.80 (d, 2H, arom), 7.05 (dd, 6H, arom), 7.28 (d, 4H, arom). ^{13}C-NMR: 31.4, 34.4, 55.2, 113.6, 125.1, 129.0, 130.4, 136.7, 141.4, 148.8, 158.0. Anal. Calcd for $C_{28}H_{34}O$: C, 86.89; H, 8.87. Found: C, 86.82; H, 8.91.

Di-*p*-biphenylylphenylmethane (13d). The crude Grignard reaction product 8d from *p*-bromobiphenyl and methyl benzoate (6a) was reduced with formic acid. Recrystallization from ethyl acetate afforded at 66% overall yield of colorless crystals, mp 168.5–169.2 °C. ^{1}H NMR: 5.63 (s, 1H, CH), 7.2–7.7 (m, 23H, arom). Anal. Calcd for $C_{31}H_{24}$: C, 93.90; H, 6.10. Found: C, 93.90; H, 6.10.

Ethyl *p*-Methoxybenzoate (6c). Ethyl *p*-hydroxybenzoate, 75.15 g (450 mmol), was dissolved in 25 mL of dry acetone. K_2CO_3, 69.10 g (500 mmol), was added followed by 42.0 mL (675 mmol) of CH_3I. The mixture was heated at reflux for 6 h, and 100 mL (160 mmol) of CH_3I was added. After overnight heating at reflux TLC (20/80 EtOAc/hexane) showed some starting material, so 10.0 mL (160 mmol) of CH_3I was added and heating was continued for 4 h. The mixture was filtered and the acetone was evaporated to give 81.15 g of crude material. Distillation (78 °C/0.02 Torr) gave 78.13 g (96%) of the desired product; (lit.[33] bp 104.2–104.4 °C/2 Torr). IR: 1712 (CO), 1607, 1257, 1168, 1031. ^{1}H NMR: 1.43 (t, 3H, CH_3), 3.92 (s, 3H, OCH_3), 4.37 (q, 2H, CH_2), 6.93 (d, 2H, arom), 8.04 (d, 2H, arom).

Dibiphenylyl-*p*-anisylmethane (13e). The crude Grignard reaction product 8e from 4-bromobiphenyl and ethyl *p*-methoxybenzoate (6c) was reduced with formic acid. Recrystallization from ethyl acetate gave 82% of pure material, mp 83–85 °C. IR: 1035, 1177, 1485, 1509. ^{1}H NMR: 3.81 (s, 3H, OCH_3), 5.59 (s, 1H, Ar_3CH), 6.85 (d, 2 H, arom), 7.09 (d, 2H, arom), 7.15–7.63 (m, 18H, arom). Anal. Calcd for $C_{32}H_{26}O$: C, 90.10; H, 6.14. Found: C, 89.94; H, 6.11.

3-Chloropropyl 2-Tetrahydropyranyl Ether. Equimolar amounts of 3-chloropropanol and 3,4-dihydro-2*H*-pyran were placed in a round-bottom flask, and 1 drop of concd hydrochloric acid was added. After 3 h, enough sodium hydroxide was added to neutralize the mixture. The resulting liquid was distilled at 103 °C/15 Torr to give the product in 75% yield. Parham reported 78% yield, bp 103 °C/14 Torr, using similar reaction conditions.[34]

4-Chlorobutyl 2-Tetrahydropyranyl Ether. This reaction was done using a procedure similar to that described above. The product distilled at 77–85 °C/0.5–1 Torr. After two distillations the yield was 79%. The IR spectrum of the product did not show any –OH groups. (lit.[35a] yield 72%, bp 130–130 °C/15 Torr; lit.[35b] yield 91%, bp 118–120 °C/15 Torr).

6-Chlorohexyl 2-Tetrahydropyanyl Ether. This method described above afforded an 86% yield of this compound, bp 94–98 °C/0.5 Torr (lit.[36] yield 98%, bp 90–92 °C/0.05 Torr).

4,4-Bis(*p*-*tert*-butylphenyl)-4-phenylbutanol (15a). In an oven-dried 500-mL, three-necked flask equipped with magnetic stirring and nitrogen inlet was placed bis(*p*-*tert*-butylphenyl)-phenylmethane (13a) (19.4 g, 54.3 mmol) with dry THF (200 mL). The flask was immersed in an ice bath. n-BuLi (2.5 M, 21.8 mL, 54.3 mmol) was syringed into the flask over 15 min. A red color was observed. The reaction was allowed to proceed for 45 min. THP-protected 3-chloropropanol (9.70 g, 54.3 mmol) was syringed into the flask over 15 min. The solution was stirred for 20 h. The red color disappeared. Water (15 mL) was added. The product was extracted with diethyl ether (3 × 200 mL). The combined organic phase was washed with water (3 × 500 mL) and dried with $MgSO_4$. A yellow oil (30.8 g) was obtained after the removal of solvent by rotary evaporation. TLC showed one major spot. This oily product was subjected to the deprotection reaction. The oil (30.0 g) was dissolved in a mixture of methanol and methylene chloride (1:1/v:v, 240 mL) in a 500-mL one-necked flask. HCl (36%, 3.5 mL) was added. The solution was

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magnetically stirred for 2 h at room temperature. Most of the solvent was rotary evaporated. The residue was dissolved in 200 mL of methylene chloride. The solution was washed with water (3 × 300 mL) and dried with $MgSO_4$. A yellow solid (20 g) was obtained after removal of the solvent by rotary evaporation. This solid was subjected to column separation on silica gel with eluting solvent grading from pure n-hexane to a mixture containing 60% n-hexane and 40% ethyl acetate. A white solid (8.00 g, 36%), mp 77.0–79.0 °C, was obtained as the third component eluted. IR: 3440, 3040, 2961, 2840, 1620, 1540, 1516, 1460, 1417, 1376, 1280, 1259, 1221, 1160, 1139, 1088, 1070, 1053, 1025, 970, 955, 925, 874, 843, 818, 763, 742, 707. ^{1}H-NMR: 1.30 (s, 18 H, CH_3), 1.40 (m, 2 H, Ar_3CCCH_2), 2.63 (m, 2 H, Ar_3CCH_2), 3.63 (t, 2 H, CH_2OH), 7.20–7.35 (m, 13 H, aromatic). ^{13}C-NMR: 21.5, 25.7, 31.8, 34.6, 37.5, 65.2, 125.0, 126.0, 128.0, 129.1, 129.8, 144.6, 148, 148.9. Anal. Calcd for $C_{30}H_{38}O$: C, 86.90; H, 9.25. Found: C, 86.78; H, 9.26.

7,7-*Bis*(*p*-*tert*-butylphenyl)-7-phenylheptanol (15b). Application of the above procedure to **13a** and THP-protected 6-chlorohexanol produced **15b** in 47% yield as a light yellow oil. IR: 3380, 3015, 2955, 2841, 1609, 1511, 1471, 1403, 1375, 1330, 1280, 1207, 1128, 1083, 1065, 1038, 1020, 952, 909, 845, 824, 767, 758, 749, 710, 695. ^{1}H-NMR: 1.32 (s, 18 H, CH_3), 1.45 (m, 2 H, CH_2CO), 1.58 (m, 2 H, (Ar_3CCCH_2), 1.78 (m, 2 H, CH_2COH), 2.55 (m, 2 H, Ar_3CCH_2), 3.56 (m, 2 H, Ar_3CCCCH_2), 3.65 (t, 2 H, CH_2O), 7.13–7.25 (m, 13 H, aromatic).

7,7,7-Tris(*tert*-butylphenyl)heptanol (15d). Application of the procedure given for synthesis of **15a** to the reaction of **13b** and 6-chlorohexyl tetrahydropyranyl ether produced **15d** in ca. 40% yield. Recrystallized from methanol it had mp 191.5–192.3 °C. IR: 3329, 3090, 2964, 2864, 1509, 1463, 1397, 1364, 1271, 1204, 1111, 1018, 839, 819. ^{1}H NMR: 1.12 (m, 2 H, $-CH_2-$), 1.20–1.38 (m, 4H, $-CH_2-$), 1.30 (s, 27H, CH_3), 1.48 (m, 2H, Ar_3CCCH_2), 2.50 (m, 2H, Ar_3CCH_2), 3.58 (t, 2H, CH_2O), 7.14, 7.23 (2d, 12H, arom). Anal. Calcd for $C_{37}H_{52}O$: C, 86.66; H, 10.22. Found: C, 86.77; 11, 10.21.

5,5,5-Tris(*p*-*tert*-butylphenyl)pentan-1-ol (15c). Tris(*p*-*tert*-butylphenyl)methane (**13b**) (8.0 g, 19 mmol) was dissolved in 400 mL of dry THF and 100 mL of hexamethylphosphoramide and cooled to −78 °C. To this solution was added 1.3 equiv of n-butyllithium, and the color of the solution turned dark blood red. The solution was stirred for 1 h followed by addition of 5.5 g (28 mmol) of THP-protected chlorobutanol using a syringe. The reaction was allowed to warm overnight for 12 h. The dark red color had disappeared. To this solution was added 20 mL of concd HCl, and the resulting solution was stirred for 30 min, after which organic and aqueous layers were separated. The organic layer was rotary evaporated to obtain solid crude product, which was crystallized from hexanes: 6.25 g (66%), mp 209.8–210.6 °C. IR: 3295 (OH), 3050, 3023 (arom), 2955–2868 (aliph), 1066–1046 (COH). ^{1}H NMR: 1.29 (s, 27H, CH_3), 1.17 (p, 2H, CH_2CO), 1.56 (p, 2H, Ar_3CCCH_2), 2.54 (t, 2H, Ar_3CCH_2), 3.55 (t, 2H, CH_2O), 7.14, 7.23 (2d, 12 H, arom). Anal. Calcd for $C_{35}H_{48}O$: C, 86.72; H, 9.98. Found: C, 86.46; H, 10.00.

1,12-Bis(*p*-methoxyphenyl)-1,1,12,12-tetra-*p*-biphenylyldodecane (16b). To a stirred solution of 15.00 g (35.2 mmol) of di-*p*-biphenylyl(*p*-methoxyphenyl)methane (**13d**) in 50 mL of dry THF at −78 °C under nitrogen was added 14.1 mL of 2.5 M n-BuLi (35.2 mmol). The solution was allowed to warm to 25 °C and stirred for 1 h. 1,10-Dibromodecane, 5.28 h (17.6 mmol), in 10 mL of dry THF was added dropwise. After being stirred overnight the reaction was quenched with water (20 mL) and extracted with CH_2Cl_2 (3 × 25 mL), which was washed with water (1 × 20 mL). Evaporation of the solvent left 19.4 g of solid. The solid was subjected to chromatography on silica gel with 5/95 ethyl acetate/hexanes to afford 7.86 (45%) of colorless crystals, mp 81.0–83.0 °C. IR: 1038, 1183 (COC), 1251 (COC), 1485, 1509 (arom C=C). ^{1}H NMR: 1.18 (broad m, 16 H internal CH_2's), 2.54 (m, 4H, terminal CH_2's), 3.77 (s, 6H, OCH_3), 6.82 (d, 4H, H's meta to OCH_3), 7.15–7.66 (m, 40 H, arom). Anal. Calcd for $C_{74}H_{70}O_2$: C, 89.65; H, 7.12. Found: C, 89.44; H, 7.12.

1,1,1,12,12,12-Hexaphenyldodecane (16d). Application of the above procedure to 1,10-dibromodecane and triphenylmethane produced an 85% yield of **16d** as a colorless crystalline solid, mp 126–128 °C (lit.[2] yield 84%, mp 126.5–127.0 °C).

Deuteration of Di-*p*-biphenylylphenylmethane (13d). To a solution of 0.21 g (0.53 mmol) of **13d** in 15 mL of dry THF was added 0.25 mL (0.62 mmol) of 2.5 M n-BuLi at room temperature. A blue color formed immediately. After 10 min 1.0 mL of D_2O was added. The mixture was extracted with CH_2Cl_2 and dried over $MgSO_4$. The product was isolated by removal of the solvent. ^{1}H NMR: the methine proton which appeared at 5.63 ppm in **13d** had been replaced with deuterium to the extent of ~95%.

Attempted Deuteration of Di-*p*-biphenyl(*p*-methoxyphenyl)methane (13e). The procedure above for **13d** was applied to **13e**. ^{1}H NMR indicated ca. 40% D exchange of the proton at 5.59 ppm and a series of aliphatic signals suggestive of ring opening of THF by n-BuLi. No attempt was made to purify this mixture of products.

4,4-Bis(*p*-*tert*-butylphenyl)-4-phenyl-1-iodobutane (18a). Hydroxyl-terminated blocking group **15a** (2.00 g, 4.82 mmol) was placed in an oven-dried 250-mL three-necked flask equipped with a condenser, dropping funnel, and nitrogen inlet. Benzene (50 mL) and pyridine (15 mL) were added. Thionyl chloride (4.89 g, 41.1 mmol) in benzene (10 mL) was added dropwise over 45 min at room temperature. The mixture was stirred for 1 h at room temperature and then heated at reflux overnight. The system was cooled to room temperature, and product was extracted with benzene (3 × 75 mL). The combined organic phase was washed with water (3 × 200 mL) and dried with $MgSO_4$. A dark brown oil (2.34 g) was obtained after the removal of solvent by rotary evaporation. Some dark colored impurities were removed by filtration through silica gel. A brown viscous oil (**17a**, 2.00 g, 85%) was obtained, and TLC showed one spot. ^{1}H-NMR: 1.30 ppm (s, 18 H, CH_3), 1.58 (m, 2H, CH_2CCl), 2.68 (m, 2 H, Ar_3CCH_2), 3.47 (t, 2 H, CH_2Cl), 7.15–7.30 (m, 13 H, arom).

This crude product was subjected to the next reaction without further purification. NaI (3.50 g, 23.1 mmol) was dissolved in acetone (75 mL) in a 250-mL one-necked flask. The crude **17a** (2.00 g, 4.62 mmol) in acetone (25 mL) was added. The mixture was stirred at reflux for 72 h. The system was cooled to room temperature, and the solvent was removed by rotary evaporation. The product was extracted with methylene chloride (3 × 75 mL). The combined organic phase was washed with water (3 × 200 mL) and dried with $MgSO_4$. A brown sticky solid (**18c**, 2.00 g, 83%) was obtained. ^{1}H-NMR: 1.30 (s, 18 H, CH_3), 1.60 (m, 2 H, CH_2CI), 2.65 (m, 2 H, Ar_3CCH_2), 3.12 (t, 2 H, CH_2I), 7.15–7.30 (m, 13 H, aromatic). No further purification was attempted.

7,7-Bis(*p*-*tert*-butylphenyl)-7-phenyl-1-iodoheptane (18b). Hydroxyl-terminated blocking group **15b** (8.06 g, 17.7 mmol) was placed in an oven-dried 500-mL three-necked flask equipped with a condenser, dropping funnel, and nitrogen system. Toluene (300 mL) and pyridine (60 mL) were added. Thionyl chloride (20.0 g, 168 mmol) in toluene (20 mL) was added dropwise over 1 h at room temperature. The mixture was stirred for 1 h at room temperature and then heated at reflux overnight. The system was cooled to room temperature, and product was extracted with toluene (3 × 100 mL). The combined organic phase was washed with water (3 × 300 mL) and dried with $MgSO_4$. A yellow oil (**17b**) (8.50 g, 100%) was obtained after decolorizing with activated carbon and removal of solvent by rotary evaporation. TLC showed one spot. ^{1}H-NMR: 1.30 (s, 18 H, CH_3), 1.46 (m, 2 H, CH_2CCl), 1.69 (m, 2 H, Ar_3CCCH_2), 1.80 (m, 2 H, CH_2CCl), 2.54 (m, 2 H, Ar_3CCH_2), 3.47 (t, 2 H, Ar_3CCCCH_2), 3.55 (t, 2 H, CH_2Cl), 7.15–7.27 (m, 13 H, arom).

This crude product was subjected to the next reaction without further purification. NaI (10.0 g, 66.7 mmol) was dissolved in acetone (150 mL) in a 500-mL one-necked flask. The crude **17b** (8.20 g, 17.3 mmol) in acetone (50 mL) was added. The mixture was stirred at reflux for 72 h. The system was cooled to room temperature, and the solvent was removed by rotary evaporation. The product was extracted with methylene chloride (3 × 150 mL). The combined organic phase was washed with water (3 × 300 mL) and dried with $MgSO_4$. A brown oil (**18b**) (9.02g, 92%) was obtained. No purification was attempted. IR: 3011, 2890, 1602, 1529, 1506, 1465, 1400, 1370, 1300, 1237, 1215, 1198, 1135, 1122, 1040, 1019, 970, 908, 845, 830, 761, 697. ^{1}H-NMR: 1.32 (s, 18 H, CH_3), 1.45 (m, 2 H, (CH_2CI), 1.75 (m, 2 H, Ar_3CCH_2, 1.85 (m, 2 H, CH_2CI), 2.53 (m, 2 H, Ar_3CH_2), 3.14 (t, 2 H, Ar_3CCCCH_2), 3.19 (t, 2 H, CH_2I). MS (EI): 566 (M^+, 4), 565 ($M^+ - H$, 9), 551 ($M^+ - CH_3$, 10), 489 ($M^+ - C_6H_5$, 28), 433 [$M^+ - C_6H_4C(CH_3)_3$, 50], 355 [$M^+ - (CH_2)_6I$, 100], 307 (40), 223 (30), 143 (20), 129 (30);

isotopic peaks at 567, 568 and 552, 553 are in agreement with calculated abundances.

1-Chloro-5,5,5-tris(*p-tert*-butylphenyl)pentane (17c). 5,5,5-Tris(*p-tert*-butylphenyl)pentan-1-ol (**15c**) (5.0 g, 10 mmol) was dissolved in 40 mL of thionyl chloride. To this solution was added 2.0 mL of pyridine. The solution was heated at reflux for 24 h and cooled, and excess thionyl chloride was distilled under aspirator vacuum. The remaining semisolid was poured into cold water and filtered. The solid was dried, and product was extracted with hexanes, crude yield 3.11 g (60%). The product was purified by passing it through a 10-cm-long silica gel column using hexanes and then recrystallization from 75:25 methanol/acetone, mp 138.4–139.2 °C. IR: 3050, 3023 (arom), 2961–2868 (aliph), 727 (CH_2Cl). ^1H NMR: 1.29 (s, 27H, $-CH_3$), 1.15 (buried under CH_3 peak, p, 2H, CH_2CCl), 1.75 (p, 2H, Ar_3CCCH_2), 2.52 (t, 2H, Ar_3CCH_2), 3.44 (t, 2H, CH_2Cl), 7.14, 7.25 (2 d, 12H, arom). Anal. Calcd for $C_{35}H_{47}Cl$: C, 83.54; H, 9.41. Found: C, 83.42; H, 9.42.

Tris(*p-tert*-butylphenyl)methyl chloride (9a). Tris(*p-tert*-butylphenyl)methanol (**8b**), 4.50 g (10.5 mmol), was added to 40 mL of acetyl chloride, and the reaction was refluxed for 48 h. The excess acetyl chloride was removed by distillation. The product was vacuum dried at room temperature, 4.20 g (94%), mp 274.1-276.6 °C. The reported yields/mp's were 17%, 259–260 °C[9] and 69%, 211–213 °C.[16] TLC (hexane/ethyl acetate (8:2, v/v)): one spot. IR: 705, 800, 830, 850, 910, 1040, 1100, 1200, 1250, 1370, 1410, 1475, 1500, 2800, 2820. ^1H NMR: 1.30 (s, 27H, CH_3), 7.2 (d, 6H, arom), 7.33 (d, 6H, arom).

Tris(*p-tert*-butylphenyl)(4-hydroxyphenyl)methane (20a).
a. Directly from 8b. Tris(*p-tert*-butylphenyl)methanol (**8b**) (13.0 g, 30.3 mmol) was dissolved in phenol (50 g) by warming in a 250-mL one-necked flask equipped with a condenser and nitrogen system. HCl (36%, 1 mL) was added as a catalyst. A deep reddish-blue color was observed immediately. The mixture was heated at reflux for 24 h. The system was cooled to room temperature. The product was extracted with toluene (3 × 150 mL). The combined organic phase was washed with aqueous NaOH solution (3 × 250 mL) and with water (20 g/L, 3 × 250 mL) and dried with Na_2SO_4. A white solid (13.7 g) was obtained after it was decolorized with activated carbon and the solvent was rotary evaporated. The solid was boiled in n-hexane for 30 min, filtered, dried under vacuum and weighed (11.5 g, 85%), mp 301.0–301.8 °C. Recrystallized from a toluene/hexane mixture, **20a** had mp 304.0–305.8 °C (lit.[16] mp 235–237 °C). IR: 3605, 3425, 2960, 2920, 1611, 1510, 1505, 1445, 1425, 1400, 1373, 1285, 1250, 1221, 1188, 1109, 1021, 847, 821, 703, 700. ^1H NMR: 1.30 (s, 27H, CH_3), 6.72 (d, 2H, arom), 7.02 (d, 2H, arom), 7.08, 7.22 (2 d, 12H, arom). Anal. Calcd for $C_{37}H_{44}O$: C, 88.03; H, 8.79. Found: C, 88.02; H, 8.71.

b. Via Triarylmethyl Chloride 9a. Tris(*p-tert*-butylphenyl)methanol (**8b**), 20.0 g (46.6 mmol), was dissolved in 80.0 mL (21 equiv) of acetyl chloride, and the reaction mixture was heated at reflux for 24 h. The reaction mixture was then cooled; excess acetyl chloride was removed using aspirator vacuum. A light cream yellow solid was left in the flask. This crude **9a** was converted to (*p*-hydroxyphenyl)tris(*p-tert*-butylphenyl)methane (**20a**) by adding 44.0 g of phenol (11 equiv) and letting it react for 20 h at 100 °C. Upon addition of phenol the solution was a dark blood red color, which disappeared in about 2–3 h, and the dirty dark yellow viscous liquid solidified. The reaction mixture was cooled, and the solid was washed with hot and cold (3 × 100 mL each) water to remove phenol. The solid was then treated with 1% sodium hydroxide solution and warmed to remove traces of phenol, filtered, washed with water (2 × 50 mL), and acidified, again washed with water, and recrystallized from ethanol. The yield was 22.9 g (97%) of a colorless solid, identical in all respects to the compound made by method a.

Bis(*p-tert*-butylphenyl)phenyl(4-hydroxyphenyl)methane (20b). Application of procedure a above to **8a** produced **20b** in 80% crude yield. Recrystallization from toluene–hexane produced colorless crystals, mp 210.0–210.9 °C. FTIR: 3320, 2958, 2920, 1705, 1611, 1510, 1525, 145, 1400, 1373, 1283, 1245, 1221, 1188, 1109, 1021, 881, 847, 821, 754, 712, 705, 700. ^1H-NMR: 1.29 (s, 18H, *tert*-butyl), 4.89 (s, 1H, OH), 6.72 (d, 2H, arom ortho to OH), 7.05–7.28 (m, 15H, arom).

(*p*-Aminophenyl)tris(*p-tert*-butylphenyl)methane (21a).
a. Directly from 8b. Tris(*p-tert*-butylphenyl)methanol, 10.0 g (23.3 mmol), was dissolved in 40 mL of acetyl chloride, and the reaction mixture was heated at reflux for 24 h. The reaction mixture was then cooled; excess acetyl chloride was removed using aspirator vacuum. A light cream-yellow solid **9a** was left in the flask. The crude product was converted directly to (*p*-aminophenyl)tris(*p-tert*-butylphenyl)methane (**21a**) by adding 30 mL of dry aniline (14 equiv) and letting it react for 36 h at 100 °C. Upon addition of aniline the color of the solution changed to dark red-purple and with time became purple. After the reaction was over, the product was precipitated in 800 mL of water containing 20 mL of concd HCl, stirred for 30 min, filtered, and washed with water. The product was purified by extraction of starting materials with hot methanol, pure yield 5.9 g (50%), mp 285.8–287.9 °C dec. IR: 3443, 3362 ($-NH_2$, sharp peaks), 3088, 3026 (arom), 2984, 2898, 2866 (aliph), 1621, 1507, 1460 (arom), 1269, 1187, 1019, 840, 823, 706, 595–577 cm^{-1}. ^1H NMR: 1.30 (s, 27H, $-CH_3$), 3.56 (s, 2H, $-NH_2$), 6.56 (d, 2H, arom), 6.96 (d, 2H, arom), 7.10, 7.22 (2 d, 12H, arom). Anal. Calcd for $C_{37}H_{45}N$: C, 88.22; H, 9.00; N, 2.78. Found: C, 87.82; H, 8.93; N, 2.98.

b. Via Triarylmethyl chloride (9a). Tris(*p-tert*-butylphenyl)methyl chloride, 4.20 g (9.39 mmol), was added to 40 mL of distilled aniline. The reaction was refluxed for 24 h. The reaction mixture was precipitated in 300 mL of 10% HCl solution. The crude product was a purple solid which was washed with potassium carbonate solution. The purple solid was dissolved in methylene chloride and filtered through a silica gel filled funnel. The purple-colored impurity remained in the silica gel. The reddish filtrate was precipitated in hexane. A white solid product was obtained. The product was recrystallized from a mixture of toluene/hexane (3:7, v/v). The product weighed 3.34 g, 71% yield, mp 288.8–291.2 °C. It was identical to the product prepared by method a.

2-(2′-Chloroethoxy)ethyl Tetrahydropyranyl Ether. To 150 g (1.2 mol) of 2-(2′-chloroethoxy)ethanol in 151.97 g (1.8 mol) of 3,4-dihydro-2*H*-pyran was added 1 drop of concd HCl. After 2 h of stirring at room temperature the pH was raised to 6.5 by the addition of tribenzylamine. Distillation provided 239 g (95%) of colorless liquid, bp 82–85 °C/0.7 Torr (lit.[37] bp 87–89 °C/0.5 Torr).

Mono-*p*-[tris(*p-tert*-butylphenyl)methyl]phenyl Ether of Di(ethylene glycol) (22a). The phenolic blocking group **20a** (5.00 g, 9.90 mmol) was dissolved in 1-butanol (100 mL) by heating in a 250-mL one-necked flask equipped with a condenser and magnetic stirring bar. KOH (1.00 g, 17.8 mmol) in H_2O (5 mL) was added, and the mixture was refluxed for 30 min. THP-protected di(ethylene glycol) monochloride (4.00 g, 19.2 mmol) in 1-butanol (20 mL) was added. The solution was refluxed for 36 h. A white precipitate was observed after 5 h. Methylene chloride (100 mL) was added. The precipitate was removed by filtration and discarded. The filtrate was rotary evaporated down to a solid (8.30 g). The solid was dissolved in a mixture of methylene chloride and methanol (2:1/v:v, 150 mL) in a 250-mL one-necked flask. HCl (35%, 2.00 mL) was added, and the solution was magnetically stirred for 2.5 h at room temperature. Solvents were rotary evaporated, and a white solid was obtained (6.88 g). The solid was dissolved in methylene chloride (200 mL). The solution was washed with water (3 × 200 mL) and dried with Na_2SO_4. A white solid (5.92 g) was obtained after the removal of solvent. This solid was subjected to recrystallization in acetone two times to give white fine crystals that weighed 5.58 g (95%), mp 218.3–218.6 °C. IR: 3425, 2910, 2860, 1603, 1505, 1470, 1445, 1400, 1375, 1273, 1240, 1205, 1195, 1133, 1109, 1070, 1021, 939, 915, 847, 821, 703. ^1H-NMR: 1.30 (s, 27 H, CH_3), 3.69 (m, 2 H, CH_2COH), 3.76 (m, 2 H, CH_2OH), 3.87 (m, 2 H, CH_2CH_2-OCH_2CH_2OH), 4.11 (m, 2 H, $ArOCH_2$), 6.79 (d, 2 H, arom closest to OH), 7.08 (m, 6 H, arom), 7.23 (m, 6H, arom). Anal. Calcd for $C_{41}H_{52}O_3$: C, 83.06; H, 8.84. Found: C, 83.14, H, 8.76.

Mono-*p*-[*bis*(*p-tert*-butyphenyl)phenylmethyl]phenyl Ether of Di(ethylene glycol) (22b). Application of the above procedure to phenol **20b** afforded 95% of pure **22b**, mp 129.8–130.8 °C, after recrystallization from methanol. IR: 3425, 2957, 2864, 1609, 1503, 1457, 1443, 1397, 1364, 1271, 1244, 1184, 1131, 1065, 1018, 826, 759, 706. ^1H NMR: 1.30 (s, 18H, CH_3), 3.69 (m,

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2H, CH_2COH), 3.76 (m, 2H, CH_2OH), 3.85 (m, 2H, $CH_2CH_2OCH_2CH_2OH$), 4.11 (m, 2H, $ArOCH_2$), 6.79 (d, 2H, arom ortho to O), 7.0–7.3 (m, 15H, arom). Anal. Calcd for $C_{37}H_{44}O_3$: C, 82.80; H, 8.26. Found: C, 82.71; H, 8.31.

α-[p-[Tris(p-*tert*-butylphenyl)methyl]phenoxy]-α′-bromo-p-xylene (23a). The phenolic blocking group **20a** (6.00 g, 11.9 mmol) was dissolved in dry THF (50 mL) in a 250-mL one-necked flask equipped with nitrogen system and magnetic stirring. NaH (60%, 0.83 g, 20.8 mmol) was added, and the mixture was stirred for 20 min. α,α′-Dibromo-p-xylene (10.6 g, 40.2 mmol) in dry THF (25 mL) was added. The solution was stirred for 20 h at room temperature. A few drops of water were added to destroy the excess NaH. Bubbles were observed. The product was extracted with methylene chloride (3 × 75 mL). The combined organic phase was washed with water (3 × 100 mL) and dried with Na_2SO_4. The solution was passed through a silica gel filtration column. The white solid (9.50 g) obtained after the removal of solvent was dissolved in methylene chloride (70 mL), and acetone (100 mL) was added during heating. The precipitate was filtered, and the above procedure was repeated three times. A white powder (4.20 g, 51%), mp 236.0–236.7 °C, was obtained after vacuum drying. ^{1}H-NMR: 1.29 (s, 27 H, CH_3), 4.52 (s, 2 H, CH_2Br), 5.02 (s, 2 H, $ArOCH_2Ar$), 6.86 (d, 2 H, arom closest to OCH_2–), 7.05–7.26 (m, 15 H, arom), 7.43 (s, 4 H, arom of xylene unit). MS (EI): 688 ($M^{81}Br^+$, 13), 686 ($M^{79}Br^+$, 12), 6.07 (M^+ – Br, 35), 555 [$M^{81}Br^+$ – $C_6H_4C(CH_3)_3$, 10] 553 [$M^{79}Br^+$ – $C_6H_4C(CH_3)_3$, 10], 479 (50), 475 (40), 411 [$M^{81}Br^+$ – $C_6H_4OCH_2C_6H_4Br$, 80], 370 [$M^+ - C_6H_4C(CH_3)_3CH_2C_6H_4CH_2Br$, 100], 354 [$M^+$ – $C_6H_4C(CH_3)_3OCH_2C_6H_4CH_2Br$, 20], 315 (10), 277 ($C_6H_4OCH_2C_6H_4CH_2{}^{81}Br^+$, 30), 105 ($C_7H_5O$, 100); isotopic peaks at 687, 689 correspond to calculated abundances.

Methyl p-[tris(p-*tert*-butylphenyl)methyl]phenoxyacetate (24a). (p-Hydroxyphenyl)tris(p-*tert*-butylphenyl)methane (**20a**), 2.0 g (4 mmol), was dissolved in 25 mL of dry DMF followed by addition of 0.13 g of 80% NaH (4.3 mmol). The reaction mixture was warmed for 30 min and cooled to room temperature. To this solution was added 1.626 g (10.5 mmol) of methyl bromoacetate, and the reaction mixture was heated at 90–100 °C for 12–13 h. The reaction mixture was cooled and diluted with 50 mL of water to precipitate the product. The product was filtered and washed with 5 × 100 mL of hot water and dried. The product was recrystallized from hot ethanol, yield 2.14 g (93%), mp 212–213 °C. IR: 3084, 3029 (arom), 2960, 2906, 2865 (aliph), 1764, 1744 (C=O), 1607, 1500, 1504, 1463 (arom), 1273, 1204, 1183 (broad, OH bending), 1108, 1087, 1019, 841, 821, 705. ^{1}H-NMR: 1.30 (s, 27H, CH_3), 3.80 (s, 3H, OCH_3), 4.60 (s, 2H, CH_2), 6.76 (d, 2H, arom), 7.11 (d, 2H, arom), 7.06, 7.23 (2 d, 12H, arom). Anal. Calcd for $C_{40}H_{48}O_3 \cdot 1/3C_2H_5OH$: C, 82.48; H, 8.51. Found: C, 82.53; H, 8.37. Hydrolysis of the ester afforded the acid with the same melting point reported below.

p-[Tris(p-*tert*-butylphenyl)methyl]phenoxyacetic Acid (25a). (p-Hydroxyphenyl)tris(p-*tert*-butylphenyl)methane (**20a**), 15.0 g (30 mmol), was dissolved in 240 mL of dioxane, and 140 mL of ethanol was added. To this was added 2.85 g of 87% KOH (1.7 equiv), and the mixture was allowed to stir at reflux for 14 h. To this solution was added 5.7 mL (2.0 equiv) of methyl bromoacetate, and the solution was refluxed for 72 h. The solution was cooled and acidified with concd HCl, and 500 mL of water was added slowly to precipitate the product. It was filtered and washed with warm water (5 × 500 mL) and allowed to air dry, and then it was suspended in methanol, stirred for 4 h, filtered, washed with methanol (4 × 100 mL), and air dried. The ^{1}H NMR spectrum showed multiple peaks from 3.8 to 4.8 ppm. The product was dissolved in 500 mL of hot ethanol and 10 mL water, and to this was added 4.0 g of 87% KOH with stirring. Immediately, precipitate began to form, and it became difficult to stir. Hence, 400 mL of water was added to the mixture, and it was stirred overnight. It was filtered and washed with water (4 × 500 mL). The precipitate was then placed in 600 mL of water, acidified using concd HCl, stirred for 2 h, filtered, washed with 2 × 500 mL of water, and dried under vacuum for 24 hours, 14.8 g (89%), mp 297.5–299 °C dec. IR: 3418 (OH, broad), 3084, 3036 (arom), 2960, 2906, 2872 (aliph), 1737 (C=O), 1607, 1586, 1504, 1463 (arom), 1265, 1169 (broad, OH bending), 1087, 1019, 841, 824, 705. ^{1}H-NMR 1.30 (s, 27H, CH_3), 4.52 (s, 2H, CH_2), 6.78 (d, 2H, arom), 7.18 (d, 2H, arom), 7.06, 7.22 (2 d, 12H, arom). Anal. Calcd for $C_{39}H_{46}O_3$: C, 83.23; H, 8.24. Found: C, 83.33; H, 8.25.

p-[Tris(p-*tert*-butylphenyl)methyl]phenoxyacetyl chloride (26a). **25a** (7.04 g, 12.5 mmol) was placed in a 250-mL round-bottom flask under nitrogen equipped with a stirring bar, condenser, and nitrogen bubbler. To this was added 28.3 mL (0.36 mmol) of thionyl chloride, and the mixture was refluxed for 13 h to obtain a light yellow orange solution, with the evolution of HCl. It was cooled, and excess thionyl chloride was removed under aspirator vaccum and gentle heat. The light yellow solid was dried under aspirator vacuum for 1 h and then under vacuum of 0.01 Torr overnight, 7.15 g (100%), mp 270–272 °C. ^{1}H-NMR: 1.30 (s, 27 H, CH_3), 4.92 (s, 2 H, CH_2), 6.74 (d, 2 H, arom), 7.12 (d, 2 H, arom), 7.06, 7.24 (2 d, 12 H, arom). The crude product was used without purification.

Acknowledgment. This work has been supported by grants (DMR-87-12428 and DMR-90-15729) from the National Science Foundation (NSF) and by the NSF Science and Technology Center for High Performance Polymeric Adhesives and Composites (DMR-88-09714). P.T.E. acknowledges support from the Plastics Institute of America for a Fellowship during the 1989–90 academic year; we are grateful for that support. We also thank our colleagues at Virginia Tech for their advice and support, both moral and technical: Professor James E. McGrath, Professor Joseph S. Merola, Professor Thomas C. Ward, and Professor Herve Marand.