Pergamon

Tetrahedron Letters, Vol. 35, No. 46, pp. 8533-8536, 1994
Elsevier Science Ltd
Printed in Great Britain
0040-4039/94 $7.00+0.00

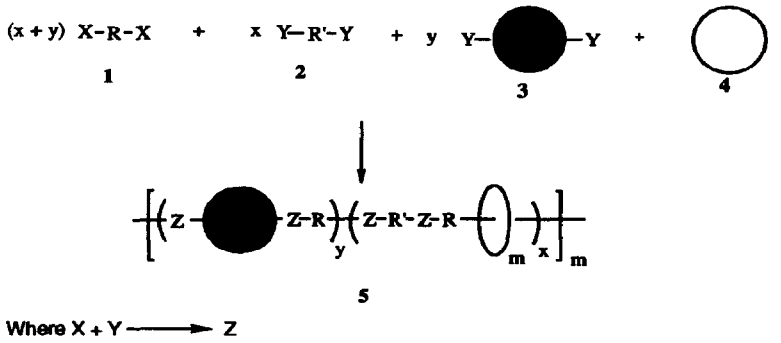
0040-4039(94)01889-8

Difunctional Blocking Groups for Rotaxanes and Polyrotaxanes

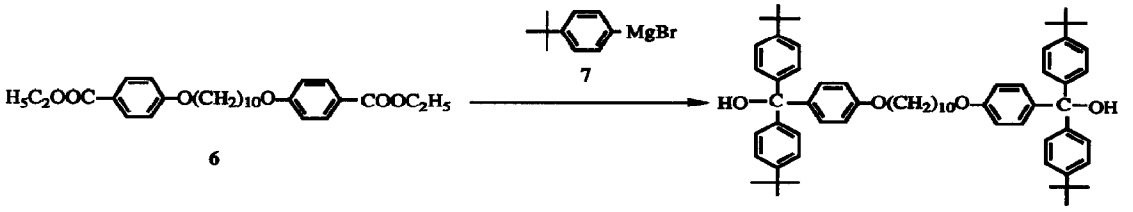
Shu Liu and Harry W. Gibson*
Department of Chemistry, Virginia Polytechnic Institute and State University
Blacksburg, VA 24061

Abstract: Several bulky monomers for polyrotaxanes, including α,α,ω,ω-tetraarylmethyl bisphenol **9**, diethyl di(*p*-*t*-butylbenzyl)malonate (**10**), and 1,1-di(*p*-*t*-butylphenyl)ethene (**12**), were synthesized. All the intermediates (**8**, **11**) and final products (**9**, **10**, and **12**) are new compounds.

Polyrotaxanes are comprised of linear polymeric molecules threaded through macrocycles, typically with bulky groups connected to the polymer chain ends to prevent the macrocycles from dethreading [1]. Triarylmethyl derivatives are a family of the monofunctional blocking groups [2] used in rotaxane and polyrotaxane syntheses. However, the end capping of polymer chains by monofunctional blocking groups is often not complete [3]. Morever, use of excess monofunctional blocking groups reduces the molecular weights of the polymer backbones and unreacted monofunctional blocking groups are difficult to remove from polyrotaxanes. These problems can be solved by involving difunctional blocking groups **3** in the polymerization of monomers **1** and **2** in the presence of macrocycles **4** to give a polyrotaxanes **5**. Furthermore, it has been found that polyrotaxanes show interesting independent crystallization behavior due to the movement of macrocycles along polymer backbones [1]. This phenomenon could be suppressed by the incorporation of bulky spacers along the polymer chains. This paper describes our work to this end, synthesizing a family of difunctional blocking groups of generic structure **3**.

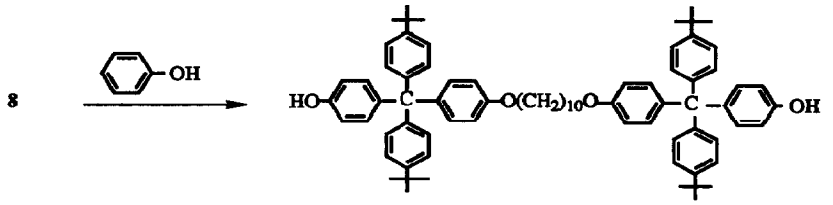


Similar to the syntheses of monofunctional triarylmethyl derivatives [2] our syntheses started from the reaction of the diester **6** with the Grignard reagent **7** derived from *p*-bromo-*t*-butylbenzene in refluxing tetrahydrofuran (THF). The product **8** [4] (56%) was purified by recrystallizations in a mixture of hexane and ethyl acetate (2:1). The starting material **6** was prepared in 74% yield by the reaction of ethyl *p*-hydroxybenzoate with 1,10-dibromodecane in absolute ethanol under reflux, using sodium to deprotonate the phenol [5].



6 8

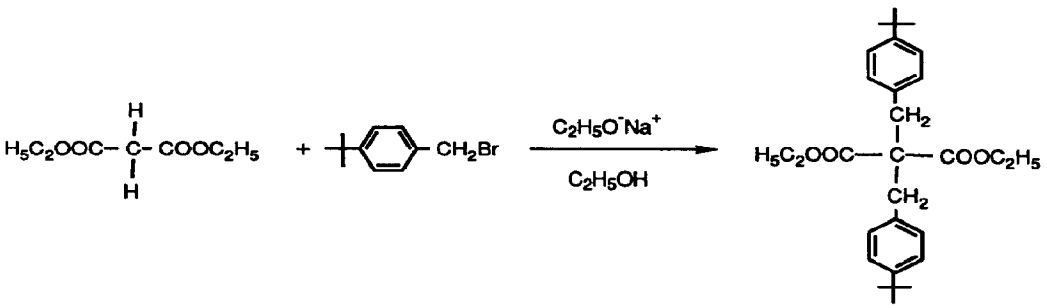
1,10-Bis{*p*-[di(*p*-*t*-butylphenyl)hydroxymethyl]phenoxy}decane (**8**) can not be used directly in the polyrotaxane syntheses because the steric hindrance reduces the reactivity and also the resultant bis(trityl ether) type compounds are hydrolytically unstable. Therefore, it is necessary to have the functional groups remote from the region of steric hindrance. This was achieved by the incorporation of phenol via a carbocationic process by refluxing **8** in phenol, using HCl as a catalyst. 1,10-Bis{*p*-[di(*p*-*t*-butylphenyl)-4-hydroxyphenylmethyl]phenoxy} decane (**9**, 96%) [6] was recrystallized in a mixture of hexane and ethyl acetate (1:1). This compound, similar to tris(*p*-*t*-butylphenyl)methyl monofunctional blocking groups, is capable of constraining rings comprised of up to 42 C, N, O, or S atoms and has been successfully applied in polymerizations to synthesize polyester rotaxanes, which will be reported shortly [3].



9

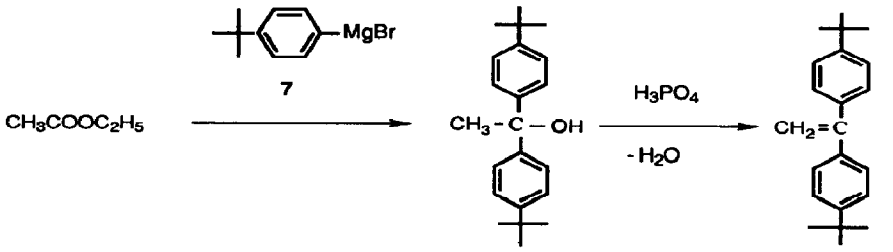
The Grignard approach for synthesis of difunctional blocking groups involves several steps and the final products are huge. A new one step approach starting from diethyl malonate was proposed as depicted in following scheme. Diethyl malonate is an ideal starting material for difunctional blocking group syntheses, because it has two pairs of reactive sites: two methylene protons and two ester groups. The two pairs have different reactivity. Therefore, one can be used for the incorporation of bulky *t*-butylphenyl groups while the other can participate in

polymerization reactions. *t*-Butylbenzyl bromide was chosen because of its bulky size and its high reactivity toward nucleophiles. The reaction was carried out in absolute ethanol under reflux using sodium as a base. Pure product **10** [7] was obtained (55%) by recrystallizations in ethanol. The byproducts generated by the monoalkylation and oxygen alkylation were easily removed by the recrystallization due to their low symmetry. The blocking ability of the product **10** is reduced by the free rotation of its methylene groups. It is only able to constrain rings comprised of up to 30 atoms, according to a CPK model study.



10

While the difunctional blocking groups **9** and **10** and their derivatives can be used in step growth (condensation) polymerizations, we also wished to have difunctional blocking groups suitable for polyrotaxane syntheses via chain growth (addition) polymerizations. Compound **12** was synthesized for this purpose. The reaction of ethyl acetate with the Grignard reagent **7** gave 1,1-di(*p*-*t*-butylphenyl)ethanol (**11**, 67%). The reaction condition was similar to the reaction of **6** with **7**. The product **11** [8] was purified by recrystallizations in a mixture of toluene and hexane (1:2). Elimination of water (Dean-Stark trap) from **11** in refluxing toluene in the presence of phosphoric acid generated the desired product, 1,1-di(*p*-*t*-butylphenyl)ethene (**12**) [9], in 82% yield. **12** was purified by recrystallizations in ethanol. The blocking capacity of **12** for macrocycles depends on the rigidity of polymer chains into which it is copolymerized. In relatively rigid chains such as polystyrene, **12** can constrain rings up to 42 atoms.



11 **12**

Acknowledgement The authors are grateful for support from the National Science Foundation (DMR-90-15729).

References

1. Gibson, H. W.; Marand, H. *Adv. Mater.*, **1993**, *5*, 11. Gibson, H, W.; Bheda, M. C.; Engen, P. T. *Prog. Polym. Sci.*, in press. Shen, Y. X.; Xie, D.; Gibson, H. W. *J. Am. Chem. Soc.*, **1994**, *116*, 537.
2. Gibson, H. W.; Lee, S.-H.; Engen, P. T.; Lecavalier, P.; Sze, J.; Shen, Y. X.; Bheda, M. *J. Org. Chem.*, **1993**, *58*, 3748.
3. Liu, S.; Gibson, H. W. Unpublished results.
4. **8**: mp 130.5-132.0 °C. IR (υ/max, cm^{-1}): 3560, 2950, 2850, 1610, 1500, 1470, 1250, 1180, 1020, 830, 580. ^1H NMR (chloroform-d/TMS, ppm): 1.30-1.48 (m, 48 H, *t*-butyl, -(CH_2)$_3$(CH_2)$_2$O-), 1.76 (p, J = 7.5, 4 H, -CH_2CH_2O-), 2.69 (s, 2 H, -OH), 3.93 (t, J = 6.5, 4 H, -CH_2O-), 6.80-7.32 (m, 24 H, arom.). ^{13}C NMR (chloroform-d/TMS, ppm): 26.0, 29.2, 29.3, 29.4, 31.3, 34.3, 67.8, 81.3, 113.5, 124.6, 127.4, 129.0, 139.2, 144.2, 149.7, 158.0 (16 signals as required). Anal. calculated for $C_{64}H_{82}O_4$: C, 83.98; H, 9.03; found: C, 83.71; H, 9.04.
5. Bonahoe, H. B.; Benjamin, L. E.; Fennoy, L. V.; Greiff, D. *J. Org. Chem.*, **1961**, 26, 474.
6. **9**: mp 162.5-165.7 °C. IR (υ/max, cm^{-1}): 3400, 2940, 2840, 1600, 1490, 1240, 1170, 1010, 830, 590. ^1H NMR (chloroform-d/TMS, ppm): 1.29-1.47 (m, 48 H, *t*-butyl, -(CH_2)$_3$(CH_2)$_2$O-), 1.76 (p, J = 7.6, 4 H, -CH_2CH_2O), 3.92 (t, J = 6.5, 4 H, -CH_2O-), 4.66 (s, 2 H, -OH), 6.68-7.24 (m, 32 H, arom.). ^{13}C NMR (chloroform-d/TMS, ppm): 26.0, 29.2, 29.3, 29.4, 31.3, 34.2, 62.7, 67.8, 112.9, 113.9, 124.0, 130.5, 132.0, 132.3, 139.3, 139.8, 144.1, 148.2, 153.2, 156.8 (20 signals as required). Anal. calculated for $C_{76}H_{90}O_4$: C, 85.51; H, 8.50; found: C, 85.26; H, 8.43.
7. **10**: mp 84.9-86.6 °C. IR (υ/max, cm^{-1}): 2850, 2760, 1725, 1510, 1360, 1265, 1190, 1170, 1650, 860, 810, 570. ^1H NMR (chloroform-d/TMS, ppm): 1.13 (t, J = 7.1, 6 H, CH_3CH_2-), 1.29, (s, 18 H, *t*-butyl), 3.18 (s, 4H, -C_6H_4-CH_2-), 4.08 (q, J = 7.1, 4 H, CH_3CH_2-), 7.09-7.29 (m, 8 H, arom.). ^{13}C NMR (chloroform-d/TMS, ppm): 13.8, 31.3, 34.3, 38.4, 60.2, 61.1, 125.0, 129.8, 133.2, 149.5, 171.1 (11 signals as required). Anal. calculated for $C_{29}H_{40}O_4$: C, 76.95; H, 8.91; found: C, 77.21, H, 8.90.
8. **11**: mp 138.7-139.9 °C. IR (υ/max, cm^{-1}): 3560, 2960, 2860, 1400, 1270, 1170, 1090, 1020, 910, 840, 810, 690, 580. ^1H NMR (chloroform-d/TMS, ppm): 1.30 (s, 18 H, *t*-butyl), 1.94 (s, 3 H, methyl), 2.13 (s, 1 H, -OH), 7.33-7.34 (m, 8 H, arom.). ^{13}C NMR (chloroform-d/TMS, ppm): 30.9, 31.3, 34.4, 75.9, 124.9, 125.4, 145.1, 149.6 (8 signals as required). Anal. calculated for $C_{22}H_{30}O$: C, 85.11; H, 9.74; found: C, 85.12; H, 9.78.
9. **12**: mp 100.8-101.6 °C. IR (υ/max, cm^{-1}): 3080, 2960, 2870, 1840, 1685, 1605, 1470, 1370, 1275, 1120, 920, 845, 620, 580. ^1H NMR (chloroform-d/TMS, ppm): 1.34 (s, 18 H, *t*-butyl), 5.40 (s, 2 H, vinyl), 7.27-7.37(m, 8 H, arom.). ^{13}C NMR (chloroform-d/TMS, ppm): 31.3, 34.5, 113.1, 124.9, 127.9, 138.6, 149.5, 150.6 (8 signals as required). Anal. calculated for $C_{22}H_{28}$: C, 90.35; H, 9.65; found: C, 90.32; H, 9.62.

(*Received in USA* 16 *August* 1994; *accepted* 21 *September* 1994)