

erization. Scarcity of material at this stage precluded further investigation of conditions for improved decarbonylation.¹⁸

Conclusion. Pentalenene sesquiterpenes have been synthesized in a stereocontrolled manner. The selectivity in the epi series was better than 95:5 as a consequence of the reduction of the cyclopentenecarboxylate from a less hindered face. The base-catalyzed epimerizations then gave equilibrium mixtures in which the isomers possessing the natural configuration at C-9 predominated and could yield, after one recycling, stereoselectivity of 86:14, in analogy with our previous experience in the isocomene series. The alkylation/decarbonylation approach gave 9:1 stereoselectivity in favor of the natural series. In addition to the controlled access to pentalenenes, pentalenic acids and desoxypentalenic acids may be prepared by starting the synthetic route with aldehyde 8 and using [4 + 1] annulation.¹² We are currently completing the synthesis of pentalenic acid (2), epipentalenic acid, and the corresponding deoxypentalenic acids.¹² Thus most members of the pentalenene family of sesquiterpenes are available by the unified design described here.

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The First Direct Formation of a Grignard Reagent on an Insoluble Polymer

Summary: Reaction of the normally mutually unreactive magnesium and solid halogenated polymers has been accomplished by using a magnesium-anthracene/THF complex to afford a high yield of the reactive Grignard polymers.

Sir: The design of specialized polymers that can be used as reagents, catalysts, or supports requires that new methods be developed for the chemical modification of cross-linked resins. In particular, it is important to be able to modify preformed polymers by grafting of reactive functionalities through C-C bonds as these are less likely to create interferences in the use of the finished polymers.¹ In spite of numerous previous attempts, the direct oxidative addition of insoluble polymeric halides to magnesium metal to form the corresponding supported Grignard

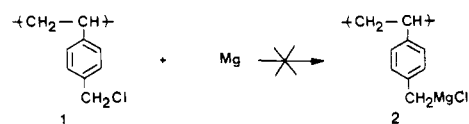


Figure 1.

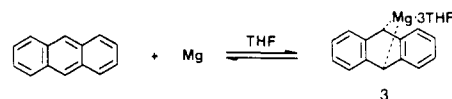


Figure 2.

Table I. Reaction of Chloromethylated Polystyrene 1 with Activated Magnesium

run	Mg transfer agent	temp, °C	time, h	loss of Cl ^d after quenching
1 ^a	Mg activated by dibromoethane	r.t. ^e	75	0
2 ^b	Rieke's Mg	r.t.	50	0
3 ^c	Mg-anthracene/THF	-30	1	40
4 ^c	Mg-anthracene/THF	r.t.	0.7	93
5 ^c	Mg-anthracene/THF	r.t.	3.5	100
6 ^c	Mg-anthracene/THF	60	4	100

^a [Mg]/[Cl] = 2.5:1. ^b [Mg]/[Cl] = 2:1. ^c [Mg]/[Cl] = 5:3. ^d Determined by Cl analysis. ^e r.t. = room temperature.

reagents on insoluble polymers had not been previously achieved² as both the polymeric halide and the magnesium metal are insoluble solids which cannot come into intimate contact with one another (Figure 1). Even when Rieke's magnesium,³ which is considered to be the most highly activated magnesium metal, was used, no chlorine of cross-linked (chloromethyl)polystyrene (1) was lost upon hydrolytic quenching of the reaction mixture (Table I). Although exchange of halogen for metal between organolithium reagents and organic halides has been a successful method for the preparation of cross-linked lithiopolystyrene resins,⁴ the related exchange reaction for magnesium is complicated by the possible concurrent occurrence of Wurz-type coupling and the fact that, being an equilibrium process, complete conversion may not be achieved.⁵ The reaction of organolithium compound with 1 equiv of magnesium halide, MgBr₂ or MgI₂, is an alternate route to Grignard reagents that are difficult to prepare directly,⁶ and indeed this indirect procedure has been used for the preparation of one insoluble Grignard from lithiopolystyrene.⁷ In the case of (chloromethyl)polystyrene, this indirect route is less available as its lithiated derivative has never been prepared successfully¹⁰ from the halogenated precursor.

Recently, some new and difficult to prepare Grignard reagents have successfully been synthesized by using a

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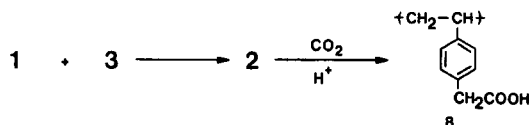


Figure 3.

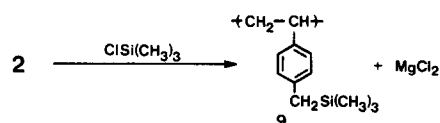
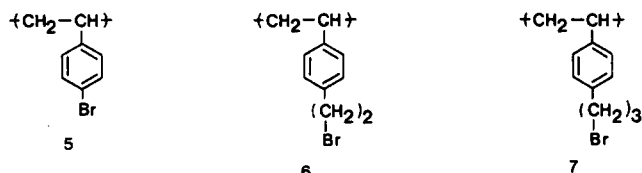


Figure 4.

magnesium-anthracene/THF complex,⁸ 3, which was also found to reduce dramatically the undesirable coupling reaction. By using 3 as an alternative to magnesium metal in the high yield synthesis of Grignard reagents, we have worked out, for the first time, a simple preparative route to insoluble polymeric Grignard reagent 2 (Figure 2). As shown in Table I the transformation is complete within 3.5 h at room temperature, as evidenced by chlorine and FT-IR analyses of the polymer 4, which is obtained after aqueous quenching. The reaction of 3 with insoluble polymeric bromide resins such as 5-7 also proceeds satisfactorily although in yields (<70%) lower than for chloride 1 (90%). The driving force in these reactions



which produce insoluble polymeric Grignard reagents is that intimate contact between the polymer and the metalating agent is possible as the latter (3) is a soluble form of magnesium, even if its solubility in THF is very low.

Polymeric Grignard reagents such as 2 are potentially very versatile intermediates in the preparation of numerous new functional polymers. For example, quenching of 2 with carbon dioxide (dry ice) followed by hydrolysis affords the product 8, containing a carboxyl group (Figure 3). The IR spectrum of 8 confirmed the absence of the CH_2Cl peak at 1266 cm^{-1} for the chloride precursor and the presence of a strong peak at 1711 cm^{-1} for the carboxyl group, while the reaction can also be quantitated by direct titration.⁴ NMR analysis of the silylated product 9 obtained by reaction of 2 with trimethylchlorosilane (Figure 4) provides interesting insight in the overall process while helping to quantify it. Line broadening of the ^{13}C NMR signals is observed after the transformation, indicating that it is accompanied by additional cross-linking. Calibration experiments with polymers of known degrees of cross-linking correlate well with the data of Errede et al.⁹ and indicate up to 3% additional cross-linking. While this limits our ability to use NMR of the swollen gels to quantify the transformation of 1 into 8, no such limitation exists for silylated polymer 9. The trimethylsilyl group appears as a sharp signal at -1.73 ppm while the CH_2Si signal shows

as a broader but isolated peak centered at 28 ppm. A quantitative NMR analysis using inverse gated decoupling indicates a degree of functionalization (DF) of 0.15 ± 0.02 , in good agreement with that calculated from Si analysis (DF = 0.14) and that of the original chloromethylated polymer (DF = 0.15).

A typical reaction procedure is as follows. Magnesium turnings (0.122 g, 5 mmol) and 1,2-dibromoethane (3 drops) in 50 mL of THF (purified over benzophenone sodium) were heated at $40\text{ }^\circ\text{C}$ for 1 h. Anthracene (1.34 g, 7.5 mmol) was added, and the mixture was stirred at room temperature for 2 days. Resin 1 (1.35 mequiv of Cl/g, 2.22 g; 1% cross-linked chloromethylated Bio-beads SX-1, from Bio-Rad Laboratories) was added at $0\text{ }^\circ\text{C}$, and after the suspension was stirred for another 4 h at room temperature it was cooled to $-60\text{ }^\circ\text{C}$ prior to portionwise addition of powdered dry ice. The polymer was filtered, washed with 1 N HCl, THF, and methanol, and dried under vacuum at $40\text{ }^\circ\text{C}$ for 20 h, yielding 2.23 g of 8. Acid-base titration indicated a 90% functional yield based on starting polymeric chloride.

We are continuing our investigation of this interesting new approach to metalated solid polymers and its application to several previously inaccessible structures which may be particularly well suited for use in polymer-assisted processes such as asymmetric syntheses.

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N-(α -Hydroxy-2-nitrosobenzyl)-1-naphthamide: A Photochemical Intermediate

Summary: *N*-(α -Hydroxy-2-nitrosobenzyl)-1-naphthamide has been isolated from the ultraviolet-light irradiation of *N*-(2-nitrobenzyl)-1-naphthamide.

Sir: The photochemistry of nitro compounds has been studied since the 1800s.¹ The irradiation of ortho-substituted aromatic nitro compounds has been reported to yield rearrangement products. We report here the isolation of an unstable intermediate resulting from the irradiation of *N*-(2-nitrobenzyl)-1-naphthamide (1).

Irradiation of a millimolar solution² of 1 at $-78\text{ }^\circ\text{C}$ and subsequent solvent removal at a temperature below $0\text{ }^\circ\text{C}$ producing a lime-green slurry which, when filtered and the resulting solid rinsed thoroughly with methanol, afforded a white powder.³ This powder, slightly soluble in meth-

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(2) Solvents used include benzene, methanol, and diethyl ether, the solvent of choice.