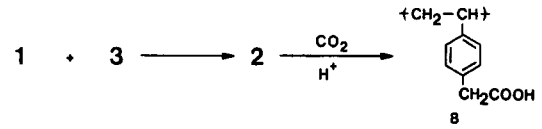


Figure 3.

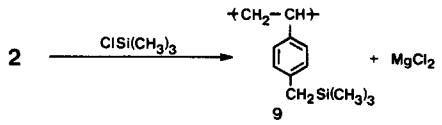
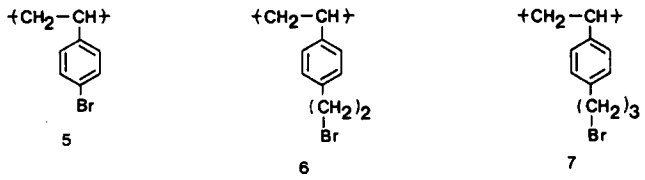


Figure 4.

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 °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 °C, and after the suspension was stirred for another 4 h at room temperature it was cooled to −60 °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 °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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(10) A multistep lithiation procedure involving the para-ethoxymethylated polymer has been descirbed by: Mix, H. *Z. Chem.* **1979**, *19*, 148.

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 solution[2] of **1** at −78 °C and subsequent solvent removal at a temperature below 0 °C produced 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-

(1) For an excellent review, see: Morrison, H. A. In *The Chemistry of Nitro and Nitroso Groups*; Feuer, H., Ed.; Wiley-Interscience: New York, 1969; Vol. 1, pp 165–213.

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

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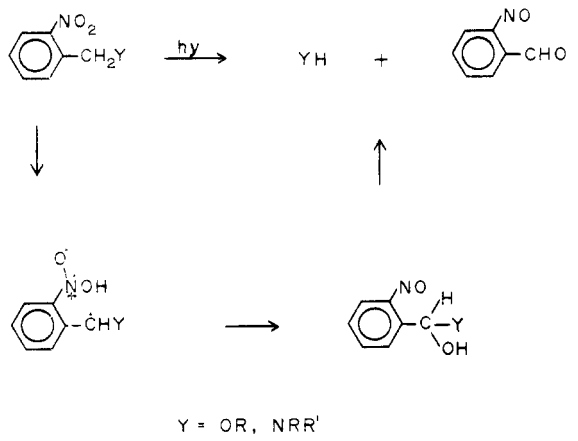
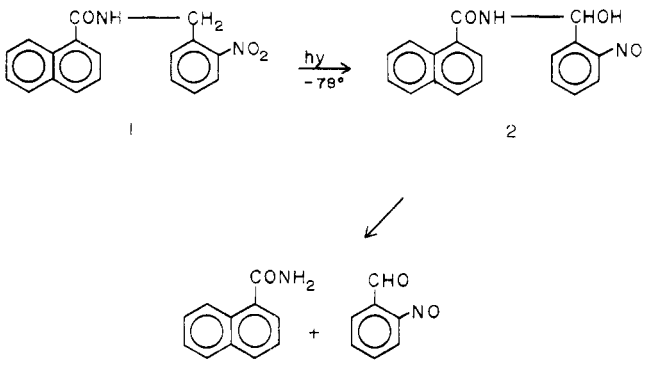
Scheme I



anol, ether, benzene, and acetonitrile, was readily soluble in dimethyl sulfoxide. It produced lime-green iridescent solutions that reversibly became yellow on cooling below 0 °C and gave a single spot upon thin layer chromatography (TLC) on silica gel. Its structure was shown to be that of *N*-(α-hydroxy-2-nitrosobenzyl)-1-naphthamide (**2**)



by the following evidence: elemental analysis[4] indicated that the compound was isomeric with starting material. The ^{1}H NMR spectrum displayed a doublet at δ 6.21 consistent with an aromatic-ring hydrogen ortho to a nitroso substituent which is ortho to an alkyl group,[5] a doublet at δ 7.02 consistent with a hydroxyl hydrogen, and a doublet of doublets at δ 8.52 consistent with the presence of the benzylic hydrogen. The addition of deuterium oxide caused the disappearance of the doublet at δ 7.02 and the collapse of the resonance centered at δ 8.52 to a doublet.[6] In the ^{13}C NMR spectrum the benzylic carbon absorbed at δ 70.05, the nitroso ipso carbon at δ 162.50,[7] and the hydrogen-substituted aromatic ring carbon ortho to the nitroso substituent at δ 105.27.[8] The remaining reasonances and the off-resonance spectrum were consistent with the assigned structure.[9]

The infrared spectrum of **2** displayed a strong O–H stretch at 3320 cm^{-1}, a carbonyl absorption at 1630 cm^{-1}, and a strong nitroso absorption at 1500 cm^{-1}.[10] The ultraviolet spectrum of **2** showed a shoulder at 310 nm (typical of the phenylnitroso chromophore) and maxima at 285 and 222 nm (consistent with the 1-naphthamide chromophore).[11] Compound **2** decomposed slowly at room temperature to produce 1-naphthamide which was identified by mixture melting point with an authentic sample. Gas chromatography/mass spectrometry (GC/MS) indicated two compounds identified as 2-nitrosobenzaldehyde and 1-naphthamide.[12]

It has been shown[13] that the photolysis of *o*-nitrobenzyl derivatives containing a heteroatom bonded to the benzylic carbon yields cleavage products, Scheme I.[1,13]

Our work shows that the irradiation of **1** produces the same types of cleavage products, providing evidence for Scheme I.

The acid- or base-catalyzed condensation of aldehydes with amides to yield *N*-(α-hydroxyalkyl) amides has been reported.[14] These syntheses are limited by the fact that the use of aldehydes other than formaldehyde produces products of further reaction unless the aldehyde is extensively halogenated.[14] Our photochemical pathway to *N*-(α-hydroxyalkyl) amides provides a means for the preparation of compounds unavailable by any other reported method.

Acknowledgment. We thank the College of Graduate Studies for partial support of this work.

(3) This product was a methanol solvate. The calculated yield of solvent-free photoproduct was 60% in four runs and essentially quantitative on the basis of consumption of starting material as determined by TLC of the crude reaction mixture.

(4) The solvent-free photoproduct is unstable at room temperature and was wetted with dichloromethane. Quantitation of the solvent content was based on the integration of the ^{1}H NMR spectrum and confirmed by elemental chlorine analysis. These corrections yielded values for C, H, and N within 0.3% of the theoretical values.

(5) The similar hydrogen in *o*-nitrosotoluene absorbs as a doublet at δ 6.22 (Pouchert, C. J.; Campbell, J. R. *The Aldrich Library of NMR Spectra*; Aldrich Chemical Company, Inc.: Milwaukee, WI, 1974; Vol. V, # 141 B.

(6) The complete ^{1}H NMR spectrum: δ 9.70 (1 H, d, J = 8.3 Hz), 8.52 (1 H, dd, J = 8.3, 4.8 Hz), 8.29–7.33 (10 H, m), 7.02 (1 H, d, J = 4.8 Hz), 6.21 (1 H, d, J = 8.0 Hz).

(7) The analogous carbon in nitrosobenzene absorbs at δ 166.0 (*The Sadtler Standard Spectra, 13-C NMR Spectra*; Sadtler Research: Philadelphia, PA; no. 12723C).

(8) The analogous carbon in a sample of 2-nitrosobenzoic acid (McMahon, R. *Tetrahedron Lett.* **1966**, 2307) was found to absorb at δ 112.8.

(9) The complete ^{13}C NMR spectrum: δ 167.71 (s), 162.50 (s), 144.00 (s), 137.03 (*), 134.44 (s), 133.09 (s), 129.79 (**), 129.79 (**), 128.64 (**), 128.17 (**), 128.09 (**), 126.60 (**), 126.21 (**), 125.33 (**), 125.21 (**), 124.94 (**), 105.27 (d), 70.05 (d). The multiplicities of absorbances marked (**) were unobtainable because of overlap. The absorbance marked (*) is assigned to the carbon para to the nitroso group. The analogous carbon in nitrosobenzene absorbs at δ 135.6 (ref 7).

(10) A similar absorption in nitrosobenzene is found at 1410 cm^{-1} (*The Sadtler Standard Spectra, IR Spectra*; Sadtler Research: Philadelphia, PA, 1963; no. 21426).

(11) Pentamethylnitrosobenzene has an absorption maximum at 318 nm and 1-naphthamide has maxima at 222 and 281 nm (*The Sadtler Standard Spectra, Ultraviolet Spectra*; spectra no. 28446 and 5512 UV, respectively).

(12) Identification of 1-naphthamide was by comparison of mass spectral data with that of an authentic sample. Identification of 2-nitrosobenzaldehyde was by comparison of the spectrum with a published spectrum (*EPA/NIH Mass Spectral Data Base*; National Bureau of Standards, Washington, DC, 1978; p 303).

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