Identification of 2,2,4-Trimethyl-2,3-dihydrofuran (8). Forerun from the pyrolysis of 3 at above the optimum temperture was fractionated to yield a small amount of unidentified yellow distillate, bp 35-44 °C (2 Torr), and a fraction, bp 43-44 °C (2.0 Torr), which contained a 70/30 mol ratio of 8 and 5 by NMR analysis: 200-MHz ^{1}H NMR ($CDCl_3$) δ 1.11 (s, 6, CCH_3), 2.12 (m, J = 1 Hz, 3, $C{=}CCH)_3$, 2.44 (m, J = 1 Hz, 2, CH_2), 5.86 (m, J small, $C{=}CH$); GC-M, m/e calcd for $C_7H_{12}O$ 112.0888, found, 112.062 (±0.015).

Acknowledgment. We thank the National Institutes of Health for support (Grant GM33801) and the Boeing Corporation for partial support of purchase of the departmental Nicolet NT-200 NMR instrument.

Registry No. 1, 37031-29-1; (4*R*,5*R*)-**2**, 81706-69-6; (4*R*,5*R*)-**3**, 110373-86-9; (4*R*,5*R*)-**3** (monoacetate), 110373-88-1; **4**, 110373-87-0; (4*S*,5*S*)-**5**, 110454-08-5; (4*S*,5*S*)-**6**, 110454-09-6; (3*S*,4*S*)-**7**, 109785-53-7; **8**, 102548-10-7.

Vinyl Triflate Syntheses Using Polymer-Bound 2,6-Di-*tert*-butylpyridine

Michael E. Wright* and Shon R. Pulley

Department of Chemistry and Biochemistry, Utah State University, Logan, Utah 84322-0300

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Polymer-bound organic reagents often provide advantages over their homogeneous counterparts.[1] For instance, ease of workup, higher yields, and sometimes enhanced product selectivity have largely contributed to their popularity. In the case of expensive reagents, recovery of the reagent is important from an economical viewpoint.

Nonnucleophilic organic bases represent an important class of reagents which have been utilized in a variety of applications.[2] Surprisingly, only two examples have been reported where a sterically hindered nonnucleophilic base has been incorporated into a polymer.[3,4] In the most recent case, we presented a new and improved synthesis of 4-vinyl-2,6-di-*tert*-butylpyridine (4) and its suspension copolymerization with styrene and divinylbenzene.[4]

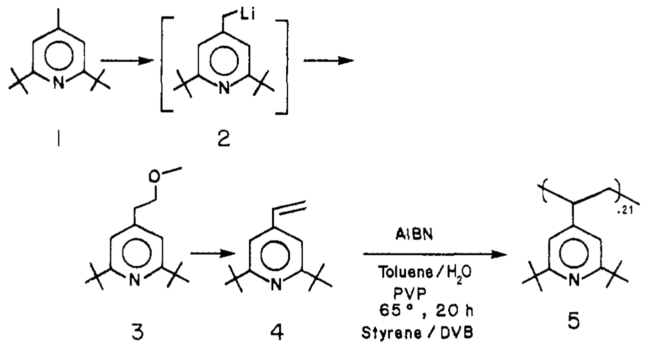
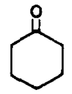
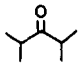
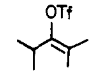
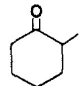
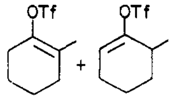


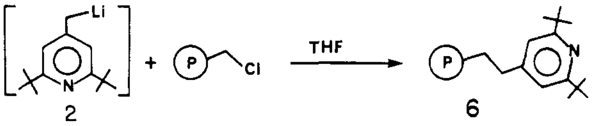
Table I. Vinyl Triflate Synthesis Using 6

ketone	solvent	time, h	temp, °C	products (% yield)
 ref 5	CH_2Cl_2	24	25	7 (57), 8 (18)
	pentane	24	25	7 (40), 8 (14)
	CCl_4	24	25	7 (86)
 ref 10	CCl_4	48	40	 (58)
 ref 11	CCl_4	24	25	 (90) (10)[a]

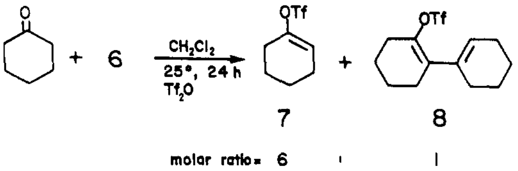
[a] Isolated yield of both isomers, 83%.

In this paper we wish to report a two-step, quantitative, incorporation of 2,6-di-*tert*-butylpyridine into polystyrene (1% cross-linked) beads and the unique reactivity pattern which we have observed from the polymer-bound base.

Treatment of porous chloromethylated polystyrene beads (1% cross-linked) with 2 gave a quantitative conversion to the copolymer 6. The copolymer beads are clear and colorless, and retain excellent swelling properties in benzene, tetrahydrofuran (THF), and methylene chloride. It is noteworthy to mention that copolymer 6 is quite different from copolymer 5 in that the pyridine moiety in the former is located considerably farther from the polymer backbone.



Since 1 has been shown to be the base of choice in vinyl triflate syntheses when using Tf_2O,[5-7] we decided to explore the use of the polymer-bound version. Not only did the reaction of cyclohexanone with triflic anhydride and 6 in methylene chloride produce the expected vinyl triflate 7 but a new product was isolated, which we have assigned the structure of 8.[8] Compound 8 would appear to be formed from a sequence of reactions, first of which is an aldol condensation of cyclohexanone, then a "dehydration step", and finally reaction of the unsaturated ketone with Tf_2O to form the diene triflate. Diluting the reaction one-fold caused the ratio of 7/8 to increase to 12. In addition, if the ratio of base to ketone was increased we also observed an increase in the ratio of 7/8. In examining the formation of 7 using 1, we do find minor (≤5%) amounts of 8 are present in the crude product. However,



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(2) For selected examples related to this work, see: Kanner B. *Heterocycles* **1982**, *18*, 411. Stang, P. J.; Hanack, M.; Subramanian, L. R. *Synthesis* **1982**, 85.

(3) Okamoto, Y.; Khojasteh, M.; Hou, C. J.; Rice, J. *Polym. Prep. Am. Chem. Soc., Div. Polym. Chem.* **1980**, *21*, 99. Okamoto, Y.; Khojasten, M.; Hou, C. J. *Polym. Sci. Tech* **1982**, *16* 111.

(4) Wright, M. E.; Pulley, S. R. *J. Org. Chem.* **1987**, *52*, 1623.

(5) Stang, P. J.; Treptow, W. *Synthesis*, **1980**, 283.

(6) The pyridine base **I** can be recovered using a slightly modified procedure: Stang, P. J.; Fisk, T. E. *Synthesis* **1979**, 438.

(7) Vinyl triflates can also be prepared in high yield, however, under strongly basic conditions, from the reaction of metal–enolates and $PhNTf_2$: McMurry, J. E.; Scott, W. J. *Tetrahedron Lett.* **1983**, *24*, 979. Crisp, G. T.; Scott, W. J. *Synthesis* **1985**, 335.

(8) Spectroscopic data for **8**: ^{1}H NMR ($CDCl_3$) 5.63 (m, 1 H), 2.32 (m, 2 H), 2.18 (m, 2 H), 2.03 (m, 4 H), 1.75 (m, 2 H), 1.60 (m, 6 H); ^{13}C NMR ($CDCl_3$) 141.9, 133.6, 133.5, 127.3, 118.3 (CF_3, q, J = 319 Hz), 29.0, 27.7, 26.9, 25.1, 23.0, 22.6, 21.83, 21.80.

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pure **7** is easily obtained by distillation away from the higher boiling aldol-derived product, **8**. Compound **8** has been prepared independently by the reaction of Tf_2O, **1**, and dehydrated aldol product of cyclohexanone.[9]

By changing the solvent to carbon tetrachloride we have been able to nearly eliminate formation of **8** and increase the isolated yield of **7** to 86%, a modest improvement over the reaction using **1**[5] (Table I). A solvent change to pentane gives similar results as methylene chloride, indicating the change in solvent polarity for carbon tetrachloride is not the key to nearly eliminating the diene triflate **8**.

The polymer-bound base **6** is easily regenerated using diisopropylamine/benzene in combination with other organic washes. The beads do become slightly discolored after several uses, but elemental analysis verifies they are unchanged in their chemical makeup. This latter statement is also supported by the fact that through five regeneration cycles, **6** produces consistent yields of vinyl triflate. Mechanical damage to the beads does occur through stirring, but this fact does not seem to effect the efficiency of the polymer-bound base.

The polymer-bound base also works on more sterically hindered ketones (Table I, entries 2 and 3), only requiring somewhat more forcing reaction conditions relative to cyclohexanone, but improved yields are obtained. However, it should be pointed out that given a common substrate, the polymer-bound base appears to react ever bit as fast as **1** in vinyl triflate syntheses. When a ketone, in which a kinetic and thermodynamic vinyl triflate are possible (entry 3) is used, *both* **1** and **6** give predominately the thermodynamic vinyl triflate (90%) and only minor amounts of the kinetic vinyl triflate.

Use of aldehydes in the synthesis of vinyl triflates has been carried out quite successfully with **1** as the base with Tf_2O.[5] We find that when the polymer-bound base is utilized with identical reaction conditions (heptanal, Tf_2O, refluxing 1,2-dichloroethane, 2 h) almost 25% of the product is the diene triflate and the remainder is the expected (*Z*)- and (*E*)-vinyl triflate. Lower reaction temperatures, changes in solvent (CCl_4, CH_2Cl_2), and variation of concentrations (both heptanal and equivalents of **6**) have no beneficial effect; in fact, the yield of vinyl triflate decreases.

In summary, an expensive and very useful base, 2,6-di-*tert*-butylpyridine, has been quantitatively incorporated into polymer beads and then shown to be 100% reusable through several cycles of use. In addition, the polymer-bound base **6** gives improved yields of vinyl triflates from ketones when compared to **1** and has the distinct advantage of easy removal at the completion of the reaction. Current efforts are directed at understanding the role of **6** in catalyzing the aldol reaction and surveying the polymer-bound base's full synthetic utility.

Experimental Section

General. All manipulations of compounds and solvents were carried out by using standard Schlenk techniques. Solvents were degassed and purified by distillation under nitrogen from standard drying agents.[12] Spectroscopic measurements utilized the following instrumentation: ^1H NMR, Varian XL 300; ^{13}C NMR, Varian XL 300 (at 75.4 MHz). NMR chemical shifts are reported in δ vs Me_4Si, assigning the $CDCl_3$ resonance in ^{13}C spectra to be at 77.00 ppm. The chloromethylated polystyrene beads (S-X1) were purchased from Bio-Rad Laboratories and used as received. Elemental analyses were performed by Atlantic Microlab, Atlanta, GA.

Preparation of Polymer-Bound 2,6-Di-*tert*-butylpyridine 6. To a chilled (−78 °C) tetrahydrofuran (THF) (40 mL) solution containing **1**[13] (3.70 g, 18 mmol) was added *sec*-BuLi (17.0 mL, 1.1 M in cyclohexane) dropwise via syringe. The mixture was stirred at −78 °C for 10 min and then removed from the cold bath. After the mixture became homogeneous, it was cannulated into a chilled (−78 °C) THF slurry containing the chloromethylated polystyrene beads (3.00 g, 3.90 mequiv/g, Bio-Beads S-X1, Bio-Rad Laboratories). Stirring was continued for 30 min at −78 °C, then the cooling was removed, and the mixture was allowed to warm to ambient temperature over a 2-h time period. Methanol (35 mL) was added to the mixture and stirred for 30 min. The solvents were decanted away from the beads and washed with a benzene/methanol (150 mL, 1/1, v/v) solution for 15 min. This solution was decanted off, and the beads were washed with methanol (100 mL) and then dried under reduced pressure at 65 °C for 24 h to yield 4.9 g (100%) of **6**. Nitrogen Anal. Calcd: 3.29%. Found: 3.27%.

Vinyl Triflate Preparations. A Schlenk flask was charged with carbon tetrachloride (8 mL), **6** (3.0 mmol, 1.30 g), the appropriate ketone (3.0 mmol), and Tf_2O (3.0 mmol, 0.50 mL), in that order. The mixture was allowed to react for the specified temperature and time given in Table I. After the reaction was complete, the mixture was diluted with pentanes (30 mL), and the organic solvents were decanted away from the beads. The product mixture was washed with water (50 mL) and then brine (25 mL). The organic layer was filtered through basic alumina with a final elution of pentanes/ethyl acetate (50 mL; 9/1, v/v). The solvents were removed, and the vinyl triflate was purified by a bulb-to-bulb transfer at reduced pressure (see Table I for yields and product distributions).

Regeneration of 6. The protonated polymer was treated with a diisopropylamine/benzene solution (15 mL; 1/4, v/v) for 15 min with stirring. The diisopropylamine/benzene solution was removed by cannulation and then the beads were treated with an additional diisopropylamine/THF solution (15 mL; 1/9, v/v) for 15 min with stirring. The solution was removed by cannulation, and the beads were treated with THF (15 mL) for 10 min with stirring, then transferred to a glass-frit (medium porosity), washed with dichloromethane (100 mL) and methanol (100 mL), and finally dried under reduced pressure at 65 °C for 12 h.

Acknowledgment. M.E.W. is grateful to the Office of the Vice President for Research at Utah State University for generously funding this work.

Registry No. **6**, 38222-83-2; **7**, 28075-50-5; **8**, 110315-54-3; $(H_3C)_2CHC(OTf){=}C(CH_3)_2$, 52149-35-6; $(H_3C)_2CHCOCH(CH_3)_2$, 565-80-0; cyclohexanone, 108-94-1; 2-methylcyclohexanone, 583-60-8; 2-methyl-1-cyclohexenyl triflate, 32363-21-6; 6-methyl-2-cyclohexenyl triflate, 76605-82-8.

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Hexacyclo[6.6.1.$0^{2,7}$.$0^{3,12}$.$0^{6,11}$.$0^{9,14}$]pentadecane and Pentacyclo[8.4.0.$0^{3,8}$.$0^{4,14}$.$0^{7,11}$]tetradecane Systems from Decahydro[1,4;5,8]dimethanoanthracene-11,12-dione

A. Srikrishna* and G. Sunderbabu

Department of Organic Chemistry, Indian Institute of Science, Bangalore 560 012, India

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The 2:1 Diels–Alder adduct of 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene and 1,4-cyclohexadiene[1,2] is a

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