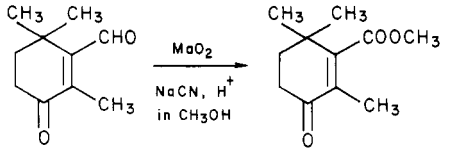
under similar conditions proceeded with 17% and 22% yields, respectively, even after extended reaction times.

The fifth method of oxidation was one developed by Corey[15] for use in natural products synthesis. It worked quite well on a small scale for conversion of 4 to the keto ester 5. Of the methods studied, this procedure gave the



4 5

best conversion of aldehyde to the carboxylic group (80%) and also combined two steps into one, since conversion of the acid to its methyl ester is the next step in the strigol sequence. However, the method has two distinct disadvantages in that a large excess (tenfold by weight) of freshly prepared manganese dioxide is required and hydrogen cyanide is one of the reagents. For these reasons it was considered impracticable to scale-up this oxidation.

The last method of oxidation involved reoxidizing the isolated keto aldehyde with more Jones reagent and gave surprisingly good yields of crude acid, better than those obtained in the initial oxidation of the hydroxy aldehyde. However, this product was not as clean as the Ag_2O product, as evidenced by NMR spectra. The overall crude yield of acid from the double oxidation with the Jones reagent was 50–60% based on hydroxy aldehyde 2, while the two-step oxidation using Jones reagent in the first step and silver(I) oxide in the second step gave 70–85% yields.

Of the several methods studied for oxidation of the keto aldehyde 4, the one which best combined efficiency, practicability, and purity of crude product was the alkaline silver(I) oxide procedure. The one disadvantage of this method is the expense of the reagent. However, this is not as serious a drawback as it first appears, since the colloidal silver recovered from the oxidation can be recycled by dissolving in nitric acid and using this silver nitrate solution in the preparation of fresh silver(I) oxide. The relative purity of the crude product was expected since Ag_2O does not attack carbon–carbon double bonds.

In summary, the one-step literature oxidation procedure for preparation of the keto acid, 3, from the hydroxy aldehyde, 2, consistently gave poor yields and significantly retarded the effort to prepare strigol on a practical scale. A two-step procedure was developed which requires initial oxidation of the allylic alcohol by the Jones reagent followed by alkaline silver oxide oxidation of the conjugated aldehyde. This procedure was successful on a large scale, giving yields of 70–85% of crude acid 3, thus clearing the way for preparation of gram quantities of the important compound, strigol, for additional biological studies.

Experimental Section

General Procedures. Melting points are uncorrected and were determined with a Thomas-Hoover capillary apparatus;[17] IR spectra were measured on a Perkin-Elmer 137 spectrometer; ^1H NMR spectra were recorded on a Varian EM 360L spectrometer.

The first step of the oxidation followed Sih's procedure except that shorter reaction times were used. The hydroxy aldehyde 2 (0.55 mol) was dissolved in 600 mL of acetone and the mixture cooled to 0–5 °C with an ice–salt bath. Dropwise addition of 150 mL of freshly prepared Jones reagent was carried out over a 4-h period, maintaining the temperature below 5 °C. After the mixture was stirred in the cold for an additional 1 h, excess oxidant was destroyed by adding 2-propanol. Water (500 mL) was added with stirring to dissolve the chromium salts and most of the acetone was removed under vacuum. Another 500 mL of water was added and the mixture extracted with four 150-mL portions of ether. The combined ether extracts were washed once with water and twice with 10% aqueous $NaHCO_3$ solution. The aqueous basic extract was acidified with 6 N HCl and extracted with ether. The ether layer was washed with water, saturated NaCl, and dried over Na_2SO_4. Removal of ether under vacuum gave 18.9 g (19% yield) of acid 3.

The nonacidic organic material was recovered from ether layers that had been extracted with $NaHCO_3$. This ether layer was washed with water, saturated NaCl, and dried over Na_2SO_4. Concentration under reduced pressure gave 62.0 g of yellow oil that was identified as the keto aldehyde 4 by NMR and IR spectra and elemental analysis. Distillation to remove impurities afforded the analytical sample: bp 108 °C (1 mm); IR (neat) ν 2960, 2940, 2880 (CH), 1725 (CH=O), 1690 (>C=O); ^1H NMR ($CDCl_3$, Me_4Si) δ 1.35 (s, 6 H, $(CH_3)_2C$), 1.56–2.02 (m, 2 H, $CH_2C(CH_3)_2$), 2.07 (s, 3 H, CH_3C=C), 2.3–2.8 (m, 2 H, CH_2C=O), 10.34 (s, 1 H, CH=O). Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49; mol wt, 166.2. Found: C, 72.04; H, 8.66; mol wt, 156.

Silver Oxide Oxidation. A suspension of silver oxide (0.36 mol) and 10% NaOH (180 mL) in 300 mL of water was vigorously stirred by magnetic stirrer. To this was added the keto aldehyde 4 (0.36 mol) in small portions over a 30-min period, keeping the temperature below 30 °C. The mixture was stirred for 1 h more. The colloidal silver was filtered and washed with water. The filtrate was acidified with concentrated HCl and the precipitate was collected and washed with water to give 56.5 g of crude acid 3, an 86% yield based on keto aldehyde and a 56% yield based on hydroxy aldehyde, giving a total yield of crude acid of 75%.

Acknowledgment. I acknowledge the technical assistance of Jacequeline M. Simoneaux and Margaret M. Soltis.

Registry No. (±)-2, 60078-92-4; 3, 51823-74-6; 4, 18378-66-0; (±)-strigol, 51820-11-2.

(17) Names of companies or commercial products are given solely for the purpose of providing specific information; their mention does not imply recommendation or endorsement by the U.S. Department of Agriculture over others not mentioned.

Highly Selective and Convenient Method for the Synthesis of 1,5-Enynes and 1,5-Dienes by the Reaction of 1,3-Dilithiopropargyl Phenyl Sulfide with Allylic Halides[1]

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Received June 15, 1981

We describe a selective and efficient propargyl–allyl coupling reaction between 1,3-dilithiopropargyl phenyl sulfide (1) and allylic halides to produce lithiated, 1,5-enynes 2, which can be directly treated with Li in liquid ammonia in the presence of $NaNH_2$ (~1 equiv) to produce cleanly 1,5-enynes in 70–80% overall yields (eq 1).

Stereo- and regioselective synthesis of 1,5-dienes of terpenoid origin via cross-coupling has been achieved most commonly by the procedure of Biellmann and related allyl–allyl couplings.[2] While these methods are satisfac-

(1) Selective Carbon–Carbon Bond Formation via Transition Metal Catalysis. 23. Part 22: Negishi, E.; Chatterjee, S.; Matsushita, J. *Tetrahedron Lett.*, **1981**, *22*, 3737.

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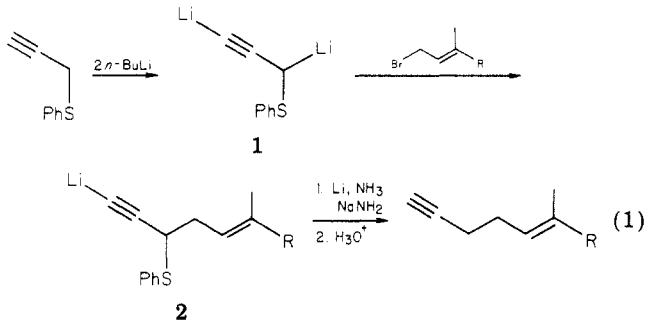


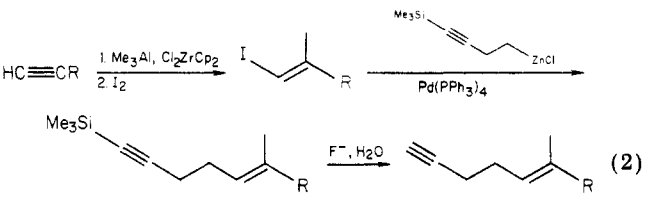
1 2 (1)

tory for the synthesis of the head-to-head 1,5-dienes **3**, their

3 4

application to the synthesis of the head-to-tail 1,5-dienes **4** has met with difficulties such as regio- and stereochemical scrambling.[3] Although an alternate approach involving propargyl–allyl coupling[4] is conceptually attractive, it has not been developed into a satisfactory methodology due to low coupling yields (≤50–60%), propargyl–allenyl rearrangement, and the lack of convenient procedures for converting 1,5-enynes into stereo- and regiodefined 1,5-dienes.

Recent developments of a few carbometalation reactions of alkynes, especially the carbocupraton of Normant[5] and our own Zr-catalyzed carboalumination,[6] have prompted us to develop more satisfactory 1,5-enyne routes to 1,5-dienes, and we have indeed recently developed an efficient and selective homopropargyl–alkenyl coupling route to 1,5-enynes[7] (eq 2). Our study of the Si-directed polyene cyclization, however, required a satisfactory route to 1,5-dienes not involving desilylation.



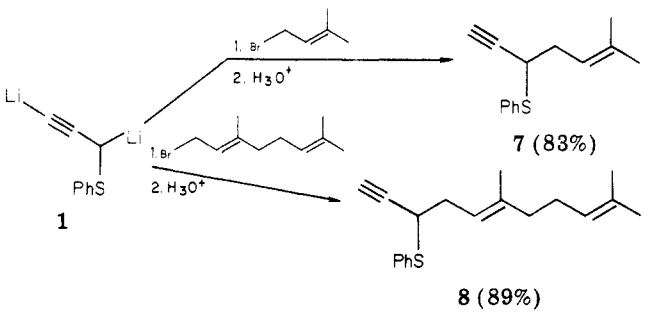
(2)

We initially felt that the difficulty associated with the regioscrambling in the propargyl–allyl coupling might be avoided by using propargyl dianion derivatives such as 1,3-dilithiopropyne[8] or its magnesium analogue, since the allenyl dianion (**5**) must be strongly destabilized relative to the propargyl dianion (**6**). Unfortunately, however, we

$$\underset{\mathbf{5}}{{}^{2-}C{=}C{=}CH_2} \leftrightarrow \underset{\mathbf{6}}{{}^{-}C{\equiv}C{-}{}^{-}CH_2}$$

have been unsuccessful in achieving a clean propargyl–allyl coupling using these reagents.

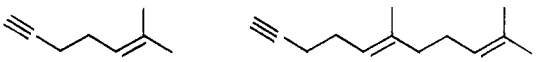
On the other hand, we have found that the phenylthio derivative **1**[9] reacts very cleanly with allyl bromides to produce, after protonolysis, 1,5-enynes in high yields, as exemplified by eq 3.



1 7 (83%) 8 (89%) (3)

Unlike the dilithio derivative of propargyl phenyl sulfide, i.e., **1**, the corresponding sulfoxide and sulfone do not react with allylic halides, e.g., isoprenyl bromide, to give the desired cross-coupled products in significant yields, as judged by ^1H NMR examination of the reaction mixtures. However, oxidation of sulfidic products, e.g., **7**, with 1 equiv of *m*-chloroperbenzoic acid readily provides the corresponding sulfoxides in high yields.[10]

The phenylthio-substituted 1,5-enynes **7** and **8** can be readily reduced to the corresponding 1,5-enynes **9** and **10**



9 10

by using Li in liquid NH_3. The overall procedure is ≥99% stereospecific, as judged by ^1H and ^{13}C NMR. It is, of course, essential to convert first **7** and **8** into terminally metalated derivatives to prevent the undesired reduction of the alkynyl group. As is evident, the direct use of the lithio derivatives of **7** and **8** is satisfactory. Since nonmetalated terminal alkynes are competitively reduced to alkenes, it is recommended to add an appropriate base, e.g., $NaNH_2$, to the lithioalkyne intermediates **2** and use thoroughly dried NH_3 to prevent the unwanted protonolysis of **2**. As described previously, **9** and **10** can readily be converted into geraniol and farnesol, respectively, in a completely stereoselective manner.[7,11]

As an alternate route from **2** to 1,5-dienes, we examined the Zr-catalyzed carboalumination of **7**. For example, the reaction of **7** with 2 equiv of Me_3Al and 1 equiv of Cl_2ZrCp_2[6] (Cp = η^5-C_5H_5) for 1 h at room temperature produced, after hydrolysis, the expected diene **11** in 62% yield with ca. 20% of **7** remaining unreacted. Treatment of an ate complex derived form the carbometalation product with paraformaldehyde[10] in THF (−30 °C to room temperature) gave a phenylthio-substituted geraniol **12** of ≥99% stereoisomeric purity in 56% yield (eq 4).

Applications of the 1,5-enyne synthesis to the preparation of Si-substituted terpenoids is underway in our laboratories.

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(4) (a) Corey, E. J.; Kirst, H. A. *Tetrahedron Lett.* **1968**, 5041. (b) Ireland, R. F.; Dawson, M. I.; Lipinski, C. A. *Ibid.* **1970**, 2247.
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(9) (a) Kreiser, W.; Wurziger, H. *Tetrahedron Lett.* **1975**, 1669. (b) for an example of alkylation of methyl propargyl sulfide, see: Reich, H. J.; Shah, S. K.; Gold, P. M.; Olson, R. E. *J. Am. Chem. Soc.* **1981**, *103*, 3112.
(10) When the quenched reaction mixture was allowed to stand overnight in the presence of aqueous $NaHCO_3$, 6-methyl-2,5-heptadienal was obtained as a byproduct in 20–30% yield. No serious attempts at improving the yield of the dienal have been made. For a recent paper describing a related rearrangement reaction of the corresponding selenium compounds, see ref 9b.
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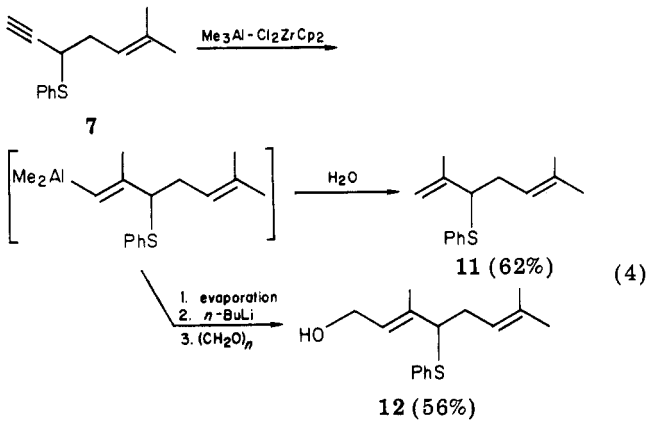

(4)

Experimental Section

Phenyl propargyl sulfide[12] (~80%), phenyl propargyl sulfoxide[13] (~80%), phenyl propargyl sulfone[14] (87%), and geranyl bromide[15] (83%) were prepared by the literature procedures in the yields shown in parentheses.

2-Methyl-5-(phenylthio)-2-hepten-6-yne (7). To phenyl propargyl sulfide (7.41 g, 50 mmol) dissolved in THF (100 mL) were added sequentially tetramethylethylenediamine (TMEDA; 15.1 mL, 100 mmol) and *n*-butyllithium (2.1 M, 47.6 mL, 100 mmol) at −60 to −50 °C. After the mixture was stirred for 1 h, freshly distilled isoprenyl bromide (7.45 g, 50 mmol) in 50 mL of THF was added dropwise at −50 °C. The reaction temperature was raised to 25 °C over a few hours. The reaction mixture was quenched with aqueous NH_4Cl and extracted with pentane. The organic layer was washed with water and dried over $MgSO_4$. Examination of an aliquot by GLC indicated that the desired compound was formed in 94% yield along with two very minor lower boiling byproducts. After evaporation of the volatile substances, distillation gave 8.99 g (83%) of the title compound: bp 102–106 °C (0.3 mmHg); n^{25}_D 1.5580; ^1H NMR ($CDCl_3$, Me_4Si) δ 1.60 (s, 3 H), 1.73 (s, 3 H), 2.32 (d, J = 3 Hz, 1 H), 2.50 (t, J = 7 Hz, 2 H), 3.78 (dt, J = 3, 7 Hz, 1 H), 5.30 (t, J = 7 Hz, 1 H), 7.2–7.7 (m, 5 H); IR (neat) 3300, 1680, 1580, 1480, 1430, 1380, 1030, 850, 750 cm^{-1}.

2-Methyl-2-hepten-6-yne (9). In an oven-dried, 500-ml, three-necked flask were introduced lithium wire (2.08 g, 300 mmol), $NaNH_2$ (1.96 g, 50 mmol), and 200 mL of liquid ammonia, which was dried by passing it through 4A molecular sieves at −78 °C. To this was added at −78 °C via a double-ended needle a reaction mixture containing **2** prepared on a 50-mmol scale as described above. The resultant mixture was warmed to room temperature over 2–4 hours. After evaporation of ammonia, 30 mL of isoprene and 100 mL of methanol were added sequentially to destroy the residual lithium. The pentane extract was washed with water and dried over $MgSO_4$. Examination by GLC indicated the formation of the title compound in 80–90% yield based on the starting phenyl propargyl sulfide and isoprenyl bromide. After evaporation of the volatile substances, the concentrated mixture was passed through a short-path column (silica gel, 60–120 mesh, pentane) mainly to separate *n*-octane introduced as a contaminant in *n*-butyllithium. Evaporation of pentane gave 4.21 g (78%) of essentially 100% pure 2-methyl-2-hepten-6-yne: n^{24}_D 1.4415; ^1H NMR ($CDCl_3$, Me_4Si) δ 1.63 (s, 3 H), 1.70 (s, 3 H), 1.93 (t, J = 2 Hz, 1 H), 2.15–2.3 (m, 4 H), 5.05–5.3 (m, 1 H); IR (neat) 3300, 2120, 1680 cm^{-1}; High-resolution mass spectrum calcd m/e 108.094, found m/e 108.093.

2,6-Dimethyl-9-(phenylthio)-2,6-undecadien-10-yne (8). This compound was prepared in essentially the same manner as described above for the preparation of **7** except that geranyl bromide was used in place of isoprenyl bromide. The yield of **8** on a 20-mmol scale was 5.04 g (89%): bp 150–154 °C (0.6 mmHg); n^{21}_D 1.4777; ^1H NMR ($CDCl_3$, Me_4Si) δ 1.56 (br s, 6 H), 1.65 (s, 3 H), 1.8–2.15 (m with a peak at δ 2.02, 4 H), 2.27 (d, J = 3 Hz, 1 H), 2.46 (t, J = 8 Hz, 2 H), 3.73 (dt, J = 3, and 8 Hz, 1 H), 4.95–5.2 (m, 1 H), 5.27 (t, J = 8 Hz, 1 H), 7.2–7.6 (m, 5 H); IR (neat) 3300, 1670, 1580, 1480, 1430, 1380, 1030, 750 cm^{-1}.

2,6-Dimethyl-2,6-undecadien-10-yne (10). The following procedure is representative of the two-step preparation of 1,5-enynes. The title compound has also been prepared in 75% yield in a manner similar to that described above for the preparation of 2-methyl-2-hepten-6-yne, which did not involve the isolation of **8**. Although the overall yields were comparable in the two experiments, the separation of minor unidentified byproducts was more readily achieved before the removal of the phenylthio group. Thus, the following two-step procedure may be preferable in this particular case.

To 1.42 g (5 mmol) of **8** dissolved in 20 mL of THF was added 2.08 mL (5 mmol) of 2.4 *N* *n*-butyllithium in hexane at −50 °C. After warming to room temperature over 30 min, the resultant mixture was added via a double-ended needle to a flask containing lithium wire (0.208 g, 30 mequiv), sodium amide (0.195 g, 5 mmol), and dry ammonia (20 mL), and the reaction temperature was allowed to rise to room temperature over a few to several hours. The workup procedure is the same as that described above for the preparation of 2-methyl-2-hepten-6-yne. The GLC yield of 2,6-dimethyl-2,6-undecadien-10-yne was ~100%, and the compound was isolated in 87% yield (0.765 g): bp 53–55 °C (0.65 mmHg); n^{21}_D 1.4777; ^1H NMR ($CDCl_3$, Me_4Si) δ 1.60 (br s, 6 H), 1.68 (s, 3 H), 1.91 (t, J = 2.5 Hz, 1 H), 2.0–2.15 (m, 4 H), 2.15–2.3 (m, 4 H), 4.95–5.3 (m, 2 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 16.11, 17.68, 19.04, 25.69, 26.84, 27.40, 39.83, 68.29, 84.28, 122.80, 124.48, 131.16, 136.59; IR (neat) 3300, 2130, 1680 cm^{-1}.

(*E*)-3,7-Dimethyl-4-(phenylthio)-2,6-octadien-1-ol (12). To a slurry of zirconocene dichloride (4.67 g, 15.8 mmol) in 30 mL of 1,2-dichloroethane was added, under nitrogen, trimethylalane (3.04 mL, 32 mmol). The resultant yellow solution was cooled to 0 °C, and 2-methyl-5-(phenylthio)-2-hepten-6-yne (**7**; 3.42 g, 15.8 mmol) in 10 mL of 1,2-dichloroethane was added.[6] After stirring the reaction mixture for 1 h at room temperature, examination by GLC of a quenched aliquot indicated that 2,6-dimethyl-3-(phenylthio)-1,5-heptadiene (**11**) was formed in 62% yield, with 20% of the starting alkyne remaining unreacted. Although the reaction was complete after 3 h, the yield of **11** slightly decreased. The carbometalated mixture was evaporated in vacuo to remove 1,2-dichloroethane and trimethylalane. The residue was extracted with hexane, and the extract was transferred to another flask via double-ended needle. To this were added sequentially 6.6 mL (15.8 mmol) of 2.4 *N* *n*-butyllithium at −30 °C, 30 mL of THF, and 1.42 g (47.4 mmol) of solid paraformaldehyde at 0 °C. After the reaction mixture was stirred overnight at room temperature, it was treated with ice-cold water, 3 *N* HCl, and ether (3 × 20 mL). The ether extract was washed with saturated aqueous $NaHCO_3$, dried over $MgSO_4$, evaporated, and flash chromatographed (silica gel 60, 230–400 mesh, 70:30 hexane–ethyl acetate) to give 2.28 g (56% yield) of **12**: n^{23}_D 1.5603; ^1H NMR ($CDCl_3$, Me_4Si) δ 1.59 (s, 3 H), 1.67 (s, 6 H), 1.80 (s, 1 H), 2.38 (t, J = 7 Hz, 2 H), 3.61 (t, J = 7 Hz, 1 H), 3.96 (d, J = 7 Hz, 2 H), 5.0–5.35 (m, 2 H), 7.1–7.5 (m, 5 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 12.29, 18.16, 25.73, 31.33, 58.32, 58.97, 121.08., 127.24, 127.32, 128.60, 133.19, 133.52, 135.29, 137.04; IR (neat) 3350 (s), 1730 (w), 1670 (w), 1580 (m), 1480 (s), 1440 (s), 1370 (s), 1010 (s), 745 (s), 692 (s) cm^{-1}.

2-Methyl-5-(phenylsulfinyl)-2-hepten-6-yne. To 1.08 g (5 mmol) of **7** in methylene chloride was added 90% pure *m*-chloroperbenzoic acid (1.0 g, ca. 5 mmol) at −78 °C. After 1 h dimethyl sulfide (0.31 g, 5 mmol) was added at −78 °C. The reaction mixture was warmed to 0 °C and treated thoroughly with saturated aqueous $NaHCO_3$ to completely remove any acid, and the organic layer was dried over $MgSO_4$. Evaporation of volatile substances at or below room temperature at reduced pressure (15–20 mmHg) gave 1.16 g of a yellow oil: ^1H NMR ($CDCl_3$, Me_4Si) δ 1.67 (s, 3 H), 1.73 (s, 3 H), 2.39 (d, J = 3 Hz, 1 H), 2.64 (t, J = 7 Hz, 2 H), 3.42 (td, J = 7, 3 Hz, 1 H), 5.30 (6, J = 7 Hz, 1 H), 7.2–7.8 (m, 5 H).

6-Methyl-2,5-heptadienal. In the above oxidation of **7** with *m*-chloroperbenzoic acid, prolonged (overnight) exposure of the

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oxidation product to saturated K_2CO_3 at room temperature led to a 70:30 mixture of the expected sulfoxide and the title compound. The latter was isolated in 23% yield by flash chromatography (silica gel 60, 80:20 hexane–ether): ^1H NMR ($CDCl_3$, Me_4Si) δ 1.61 (s, 3 H), 1.72 (s, 3 H), 2.97 (t, J = 7 Hz, 2 H), 5.16 (tt, J = 7, 1.5 Hz, 1 H), 6.06 (ddt, J = 16, 8, 1.5 Hz, 1 H), 6.82 (dt, J = 16, 7 Hz, 1 H), 9.53 (d, J = 8 Hz, 1 H).

Acknowledgment is made to the National Institutes of Health and the National Science Foundation for support of this research. We thank Professor Hans J. Reich of University of Wisconsin for useful information.

Registry No. 1, 79499-64-2; 7, 79499-65-3; 8, 79499-66-4; 9, 22842-10-0; 10, 22850-55-1; 11, 79499-67-5; 12, 79499-68-6; isoprenyl bromide, 870-63-3; geranyl bromide, 6138-90-5; 2-methyl-5-(phenylsulfinyl)-2-hepten-6-yne, 79499-69-7; 6-methyl-2,5-heptadienal, 79499-70-0.

Polymer-Catalyzed Protection of Alcohols

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Received July 20, 1981

Alcohols can be protected by reaction with dihydropyran to form tetrahydropyranyl ethers under acid catalysis (hydrochloric acid,[1,2] phosphorus oxychloride,[3] boron trifluoride etherate,[4] or *p*-toluenesulfonic acid[5,6,7]). These THP ethers have found wide use in organic synthesis because they are stable to alkali, Grignards, lithium aluminum hydride, chromium trioxide, and many other common reagents. THP ethers are easily converted back into the alcohols by dilute acid. In general, THP ether formation works better for primary and secondary alcohols than for tertiary alcohols. For example, Auterhoff and Egle[8] prepared the THP ether of cholesterol in 89% yield (*p*-toluenesulfonic acid catalyst) compared to only 32% for 2-methyl-2-pentanol. Perhaps steric hindrance and dehydration side reactions adversely affect the yields with tertiary alcohols.

Miyashita, Yoshikoshi, and Grieco[9] recently reported a new and efficient catalyst for tetrahydropyranylation: pyridinium *p*-toluenesulfonate. This work prompted us to test a variety of related polymeric salts for catalytic activity in alcohol protection. Easy reaction workup, in which a recyclable catalyst can be separated by filtration, was one desired goal. The other goal was to secure reasonable isolated yields (>80%) with tertiary alcohols under conditions where conventional catalysts are unsatisfactory.[10,11]

Table I. Tetrahydropyranylation of Alcohols in Benzene with Poly(4-vinylpyridinium *p*-toluenesulfonate) and Poly(2-vinylpyridinium *p*-toluenesulfonate) at 24 °C

	P-4VPTS		P-2VPTS	
alcohol	rctn time, h	isolated yield,[a] %	rctn time, h	isolated yield,[a] %
1-dodecanol	4	95	6	93
cyclohexanol	4.5	87	6	97
nopol[b]	5	90	7	90
geraniol	6	86	8	87
3-acetyl-1-propanol	6	75	4	72
cholesterol	7	95	8	90
benzhydrol	5	92	7	91
2-phenyl-2-propanol	4	81[c]	4	76[c]
1-methylcyclohexanol	3	85[c]	3	84[c]

[a] All products showed satisfactory spectral data and chromatographic purity. [b] 6,6-Dimethylbicyclo[3.1.1]-hept-2-ene-2-ethanol. [c] The molar ratio of dihydropyran to alcohol was 1.5 except with the two tertiary alcohols for which the ratio was 3. The tertiary alcohols gave over twice the yields achieved with pyridinium *p*-toluenesulfonate[9] under comparable conditions.

Three types of polymeric analogues to pyridinium *p*-toluenesulfonate proved useless in the tetrahydropyranylation of alcohols at 25 °C and 3–6 h reaction time: (1) the pyridinium salt of a sulfonated cation exchange resin, Dowex 50X8-50, (2) the *p*-toluenesulfonate salt of an anion-exchange resin, Amberlite IRA-400, and (3) the trifluoromethanesulfonate salt of poly(4-vinylpyridine). On the other hand, synthetically exploitable catalytic activity was observed for the *p*-toluenesulfonate salts of commercially-available poly(4-vinylpyridine) and poly(2-vinylpyridine). Isolated yields at the 0.5–2.0-g scale (room temperature, 3–8 h) exceeded 80% for most alcohols (Table I). As seen from the Experimental Section, reaction workup was simple. Two of the nine alcohols examined were tertiary but, nonetheless, gave good yields of tetrahydropyranyl ethers. Thus, both major objectives of the project were achieved.

Heterogeneous polymer-catalyzed protection of alcohols in roughly 3 times faster with a benzene solvent than with ether. Benzene swells the polymer and increases the rate. Catalysis apparently takes place on the polymer surface since stirring the polymer for several hours with benzene gave no detectable acid in the solvent phase. Polymer recovered after a reaction can be washed with solvent and used again with no impaired yield.

Experimental Section

Preparation of Catalyst. Poly(2-vinylpyridine) (Aldrich) or poly(4-vinylpyridine) (Polysciences) was added to methanol (1.05 g/25 mL) and the mixture was stirred at room temperature until dissolution. *p*-Toluenesulfonic acid monohydrate (1.90 g) was then added to the methanol followed, after a few minutes of stirring, by 9.00 g of Celite. The mixture was stirred well until the polymer derivative uniformly coated the inert support. Solvent removal with the aid of a rotary evaporator produced the catalysts, which was ground to a fine powder and dried under reduced pressure (25 °C, 3 mm) overnight. The product (11.1 g) was stored in a desiccator. The poly(4-vinylpyridinium *p*-toluenesulfonate) seemed to give the faster tetrahydropyranylation reactions es-

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