was warmed to room temperature and allowed to stand for 3 hr, then placed directly on a silica column. Elution with CH_2Cl_2 and solvent evaporation afforded a pale yellow crystalline mass (1.33 g, 90%) of about equimolar amounts of the cis and trans isomers of **7**. The presence of the two isomers was evident from nmr analysis ($CDCl_3$), which showed two distinct ethyl triplets centered at *ca.* δ 0.92 and 1.35.[6] A small sample of trans isomer, mp 222–224°, was obtained as colorless crystals from $CHCl_3$–methanol, uv spectrum λ_{max} 329 nm (log ϵ 4.21).

Anal. Calcd for $C_{22}H_{20}NO_7Br$: C, 53.87; H, 4.11; N, 2.86. Found: C, 53.69; H, 4.24; N, 2.62.

***N*-Carbethoxy-6a,7-dehydrocassythidine (8).** A solution of crude **7** (cis-trans mixture, 1.298 g) in benzene (750 ml), *tert*-butyl alcohol (100 ml), and 15% potassium *tert*-butoxide in *tert*-butyl alcohol (9.5 ml) was irradiated (Hanovia 450-W lamp, Corex filter) for 7 hr under N_2; the photolysis was interrupted three times in order to clean the irradiation probe. Dilution with water and evaporation of the washed and dried benzene layer gave a residue which was dissolved in $CHCl_3$ and chromatographed on silica. Elution by $CHCl_3$, followed by crystallization from $CHCl_3$–methanol, gave colorless crystals of **8** (0.345 g, 32%): mp 260–261°; uv spectrum λ_{max} 261 nm (log ϵ 5.33), 301 (4.56), 336 (4.56), 378 (4.16); nmr ($CDCl_3$) δ 8.32 (s, 1 H), 7.33 (s, 1 H), 7.06 (s, 1 H), 6.14 (s, 2 H), 6.01 (s, 2 H), 4.26 (q, J = 8 Hz, 2 H), 4.03 (s, 3 H), 3.98 (t, J = 6 Hz, 2 H), 3.06 (t, J = 6 Hz, 2 H), 1.31 (t, J = 8 Hz, 3 H).

Anal. Calcd for $C_{22}H_{19}NO_7$: C, 64.55; H, 4.68; N, 3.42. Found: C, 64.21; H, 4.63; N, 3.16.

***N*-Methyl-6a,7-dehydrocassythidine (9).** Ester **8** (0.164 g, 0.040 mmol) was added to a slurry of lithium aluminum hydride (0.0456 g, 1.14 mmol) and $AlCl_3$ (0.080 g, 0.60 mmol) in dry ether (5 ml), and the mixture was refluxed with stirring for 90 min. Water was added slowly, followed by ammonium hydroxide, and the product was extracted into $CHCl_3$. Evaporation of the dried organic extract gave crystalline **9** (0.102 g, 87%). Recrystallization from $CHCl_3$–methanol gave pure **9**: mp 198–201°; uv spectrum λ_{max} 262 nm (log ϵ 4.71), 301 (4.33), 336 (4.32).

Anal. Calcd for $C_{20}H_{17}NO_5$: C, 68.37; H, 4.88; N, 3.99. Found: C, 68.13; H, 4.90; N, 4.07.

Cassamedine (1). A solution of peracetic acid (0.254 ml of a 40% acetic acid solution) in acetic acid (20 ml) was added dropwise to a cooled solution of **9** (0.186 g, 0.53 mmol) in acetic acid (40 ml). After warming to room temperature, the solution was allowed to stand for 1 hr, then basified with aqueous ammonia and extracted with $CHCl_3$. Evaporation of the dried extract gave a residue which was chromatographed ($CHCl_3$) on grade II neutral alumina. The desired orange band was eluted by 2% methanol in CH_2Cl_2. The chromatographic purification was repeated in exactly the same way using a second alumina column. Crystallization from $CHCl_3$–benzene gave bright orange needles (0.060 g, 28%) of cassamedine: mp 278° (lit.[1] 278°); uv spectrum 251 nm (log ϵ 4.32), 281 (4.43), 323 (3.77), 361 (3.58), 460 (3.28); nmr (CF_3CO_2D) δ 8.83 (m, 2 H), 8.18 (s, 1 H), 7.83 (s, 1 H), 6.61 (s, 2 H), 6.21 (s, 2 H), 4.48 (s, 3 H); *m/e* (M^+ 349); reported uv spectrum[1] 252 nm (log ϵ 4.47), 281 (4.53), 324 (4.12), 364 (3.97), 460 (3.76); reported nmr[1] (CF_3CO_2H) δ 8.85 (2 H), 8.19, 7.83, 6.62 (2 H), 6.23 (2 H), 4.48 (3 H). The infrared spectrum (KBr) of synthetic cassamedine was superimposable upon that of the natural alkaloid.

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Registry No.—**1**, 16408-75-6; **3** oxalate salt, 49689-85-2; **4**, 5470-14-4; **5**, 49689-87-4; **6** HCl, 49844-61-3; *cis*-**7**, 49689-88-5; *trans*-**7**, 49689-89-6; **8**, 49689-90-9; **9**, 49689-91-0.

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Reactions of Organometallic Reagents with Unsaturated Epoxides. II.[1a,b] Control of Product Ratios

Charles B. Rose* and Stephen K. Taylor[1c]

Department of Chemistry, University of Nevada, Reno, Nevada 89507

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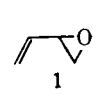
The addition of Grignard reagents to α,β-unsaturated ketones has been commonly recognized as a versatile synthetic tool since an option of two distinct pathways is available: 1,2 addition is generally obtained in the absence of cuprous catalysts, whereas 1,4 addition results in the presence of cuprous catalysts.[2,3] Recently, the analogous regioselectivity was reported for 3,4-epoxy-1-butene[4,5] (**1**) and a cyclic conjugated epoxide, 3,4-epoxycyclohexene[6,7] (**2**).



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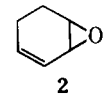

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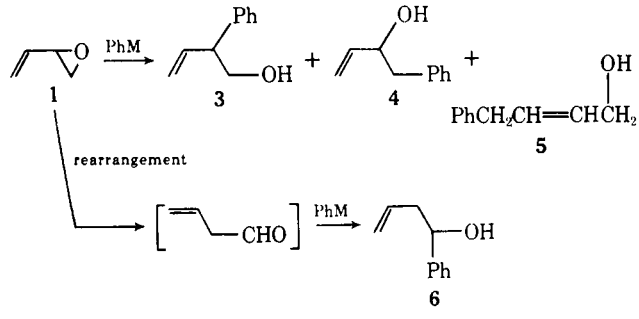
Scheme I illustrates the possible products resulting from the reaction of **1** with metallophenyl reagents.

Scheme I



1 **3** **4** **5** **6**

Although pathways to products **3** and **5** had been regioselectively demonstrated,[1,4-8] pathways to products **4** and **6** had not. Prior related work with amines and methoxides,[8d,e,9] organolithium compounds,[5,10] and bulky Grignard reagents[11] suggested that product **4** could be made to predominate, and Kharasch's studies[12] with styrene oxide seemed to indicate that **5** could be obtained by using appropriate inverse addition conditions. Thus, any one of the four specific sites of alkylation could be chosen by modifying the reagent and/or reaction parameters. To do this would disclose the full but implicit synthetic potential of **1**, a model for the general conjugated epoxide structural unit.

Furthermore, it appeared highly desirable to explore the effect of solvent upon the course of this reaction. Tetrahydrofuran appeared to be an ideal solvent to use inasmuch as current reports suggested that tetrahydrofuran, relative to ether, shifted the Schlenk equilibrium to the right.[13] Since rearrangement products in Grignard reactions with epoxides are known to result from magnesium halide induced rearrangement,[8,14] a shift in the Schlenk equilibrium (and hence the amount of MgX_2) should be reflected in the amount of rearrangement product. A demonstration of this phenomenon corroborating the Schlenk equilibrium studies, product control factors, and metal ion influence is herein described.

$$2RMgX \rightleftharpoons R_2M + MgX_2$$

Results and Discussion

The products formed from the reactions of **1** with metallophenyl reagents are summarized in Table I. Several

Table I
Products from the Reaction of Metallophenyl Reagents with 3,4-Epoxy-1-butene (1)

Reagent	Solvent	Addition mode	Molarity PhM	Molarity 1	Product distribution, % 3	4	5 (trans:cis)	6
PhMgBr	Et_2O	Regular[1a]	0.5	1.4	84.0		7.6 (85:15)	8.4[a]
PhMgBr	Et_2O	Inverse[b]	0.62	1.3	16.7		10 (67:33)	73.3
PhLi(LiBr)	Et_2O	Regular	1.0	4.5	10.7	78.5	10.8 (76:24)	
PhLi(LiBr)	Et_2O	Inverse	1.0	2.3	10.2	79.4	10.4 (60:40)	
PhMgBr[c] $Cu(OAc)_2 \cdot H_2O$	Et_2O/THF	Regular	1.3 (Et_2O)	0.29 (THF)	17.6	Trace	82.4 (86:14)	Trace
PhMgBr[d,e]	THF	Regular	0.5	1.4	31.3	0.0	30.9	37.8
PhMgBr[e,f]	THF	Regular	0.5	1.4	33.6	0.0	15.2 (58:42)	51.2
PhMgBr[e,f]	THF	Inverse	1.4	3.8	26.1	0.0	9.3 (55:45)	64.6

[a] This product was previously identified as 4,[1a] but has been proven by independent synthesis to be 6. [b] Long addition time (0.67 hr) required to obtain results. [c] Reaction temperature 10°; significant amounts of biphenyl present (10–15%). [d] Reaction temperature 45°. [e] Significant amounts of bromohydrin present (15–20%). [f] Reaction temperature 20–31°.

attempts were made to maximize the major product of each reaction by varying reaction parameters.

As previously shown,[1a,4-8] the major Grignard product is derived in high yield from attack at the secondary carbon atom. However, in line with Kharasch's[12] work, inverse addition dramatically affected the products of the reaction. When this reaction mode was used, Table I reveals that the rearrangement pathway predominated. To effect the maximum percentage of 6, however, several attempts were carried out at different reagent concentrations. It was found that a large volume of ether and a long addition time produced the greatest amount of rearrangement product, whereas fast addition and less solvent produced significantly less of this compound. For example, when the Grignard reagent concentration was high (1.6 *M*) and the addition time fast, only 27% of 6 resulted.[15a,b]

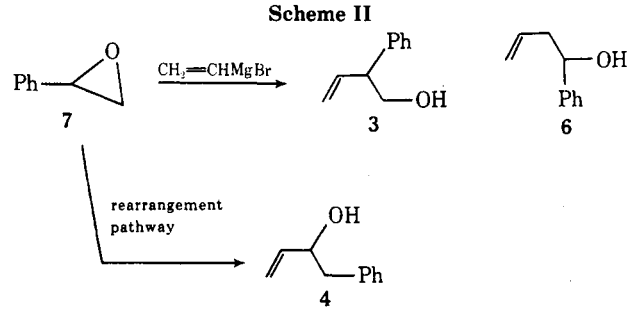
In contrast to the organomagnesium reagent, inverse addition has almost a negligible effect on phenyllithium reactions. However, both addition modes give strikingly different product distributions than the Grignard. In this case, terminal attack, which is sterically favored, predominates to yield mostly 4. The smaller methyllithium produced significant but not preponderant amounts of least hindered attack,[5] but instances involving bulkier groups yield only sterically controlled products.[10] The lesser Lewis acidity of organolithiums has been shown to be significant in these reactions with epoxides,[10] and steric factors consequently play a more important role. Our work, as well as earlier work by Cristol[10] and Kharasch[12] with styrene oxide, dramatizes the importance of this influence. Of interest also is the fact that the organolithium reagent produces no rearrangement product.[5,8b-e,14a]

Although Anderson[4] and Johnson[5] found that conjugate addition predominated in the reaction of 1 with lithium diphenylcuprate and lithium dimethylcuprate, respectively, we felt that it would be instructive to compare results with the less familiar 1,4 catalyst cupric acetate monohydrate. This compound has, on occasion, been reported to be superior to other reagents in promoting conjugate addition.[16-18] Our results with this compound were similar to work with lithium dimethylcuprate,[4] although small quantities of biphenyl accompanied the formation of 5, the major product, and 3.[19]

Having found conditions that would give a predominance of any one of the four isomeric alcohols, our attention shifted to studies in the solvent tetrahydrofuran. As mentioned earlier, more magnesium halide should be present in tetrahydrofuran than in ether. This increased amount of Lewis acid, which presumably catalyzes the rearrangement, should lead to more of 6. Although the reaction in THF did give more of 6 for normal addition, the inverse mode did not. The key to this apparent anomaly lies in the fact that up to 20% of the product mixture was 1-bromo-3-buten-2-ol. It is entirely possible that this bromohydrin is formed in small amounts along with the expected bromohydrin 2-bromo-3-buten-1-ol.[20] The latter compound, being more labile, isomerizes and eventually leads to 6, whereas the less labile halohydrin is stable enough to be recovered. Therefore, since no halohydrin is recovered from reactions in ether, it appears that all isomerization leads to rearrangement product 6, whereas in THF a portion of the rearrangement pathway is short circuited prior to forming 6. This would explain why less 1-phenyl-3-butenol results than is expected in THF.

To extend these studies, we decided to switch to the simpler and more readily available styrene oxide. Since fewer products would be formed with this compound, a more direct comparison would be made between direct addition and rearrangement pathways. This epoxide was combined with vinylmagnesium bromide. The products of the reaction and their origin are illustrated in Scheme II.

Scheme II



Product distributions are summarized in Table II.

Reaction in THF yielded the rearrangement product 4 almost exclusively when the Grignard was added to the epoxide. Normal addition reactions produced slightly more of this product than expected owing to residual THF coordinated to the Grignard;[21] it definitely conforms, however, to expectations based on Schlenk equilibrium findings.[13] The percentage of 4 formed in these reactions increases in direct proportion to the increase in mole fraction of THF used; a plot of the data in Table II dramatically illustrates this shift in product distribution to the Schlenk equilibrium.

All of the isomeric phenylbutenols were independently synthesized and confirmed by nmr, ir, and vpc data. 1-Phenyl-3-buten-1-ol was prepared by the method of Klimenko;[22] isomer 4 was synthesized by adding phenylacetaldehyde to vinylmagnesium bromide, and Table II shows the synthesis of 3.

Some difficulty was encountered in the synthesis of *cis*- and *trans*-4-phenyl-2-butenol. Colonge and Poilane[23] reported that the cis isomer could be prepared by treating

Table II
Solvent Studies. Products from the Reaction of Vinylmagnesium Bromide with Styrene Oxide[a]

Addition mode	Molarity: RM	Molarity: Epoxide	Mole fraction[b] THF (vs. Et_2O)	Product distribution, %: 3	4	6
Regular	1.8	1.5	0.00	80.2	19.3	0.5
Regular	1.8	1.5	0.12	74.0	25.0	1.0
Regular	1.8	1.5	0.25	62.3	36.7	1.0
Regular	1.8	1.5	0.48	60.0	37.5	3.0
Regular	1.8	1.5	0.68	52.5	46.5	1.0
Regular	1.8	1.5	1.00	42.0	54.5	3.5
Inverse	1.8	1.5	1.00	18.5	80.5	1.0
Inverse	1.8	0.5	1.00	39.0	59.0	2.0
Inverse	1.8	2.6	1.00	9.5	90.5	0.0

[a] Tetrahydrofuran, where necessary, was removed from the Grignard reagent by vacuum evaporation with N_2 bleed. It was then replaced by the solvent system of proper proportion. Some solvent undoubtedly remained coordinated to the Grignard reagent. [b] Calculated from the number of moles of solvent only.

cis-4-chloro-2-butenol with 2 mol of phenylmagnesium bromide. However, repeating this procedure gave up to a 50:50 mixture of the alcohols *cis*-4-phenyl-2-butenol and 2-phenyl-3-butenol (apparently arising from an S_N2'-type reaction on the chloro alcohol). We therefore prepared the analogous 4-chloro-2-butynol and treated it with phenyl Grignard. Subsequent reduction of the product with sodium and liquid ammonia and a modified palladium catalyst gave the trans and cis isomers, respectively (see Experimental Section). A minor chemical shift difference between the geometric isomers allowed determination of trans–cis ratios (methylene doublets centered at δ 4.0 and 4.2, respectively).

Experimental Section

Infrared spectra were obtained with Perkin-Elmer Infracord and Beckman IR-8 spectrophotometers. Gas chromatographic analyses were performed on a Wilkens Aerograph A-90-P equipped with a 10 ft × 0.25 in. column packed with 5% QF-1 on Chromosorb G, a 6 ft × 0.25 in. column packed with 10% FFAP on Chromosorb W, and a 15 ft × 0.25 in. 20% Carbowax 20M on firebrick column. Nmr spectra were recorded on a Varian Associates A-60 spectrometer, using tetramethylsilane as an internal standard, and elemental analyses were determined by Chemalytics, Inc., Tempe, Ariz. Melting points and boiling points are uncorrected. All reagents used were obtained commercially in high purity unless noted otherwise.

Preparation. A. 4-Phenyl-2-butenols (5). Using the method of Dupont,[24] 4-phenyl-2-butynol was prepared.[25] The phenylbutynol was reduced to the *trans*-4-phenyl-2-butenol with sodium in liquid ammonia, according to Campbell and Eby's method,[26,27] to give 8.0 g (57%) of isolated alcohol product: bp 86–87° (0.5 mm); $n^{25}D$ 1.5411; nmr (CCl_4) δ 7.18 (s, 5, aromatic H), 5.68 (m, 2 H, vinyl), 4.02 (d, 2, J = 4 Hz), 3.64 (s, 5, hydroxyl H), 3.30 (d, 2, J = 4 Hz). Small amounts of fully reduced phenylbutanol and 4-phenyl-3-buten-1-ol were present, but were removed by distillation or preparative gc (FFAP column) for analysis.

Anal. Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 81.03; H, 8.08.

The cis isomer was prepared from the phenylbutanol using a modified Lindlar catalyst.[28] A quantitative transformation resulted, but 10% of 4-phenylbutanol contaminated the *cis*-4-phenyl-2-buten-1-ol. Preparative vpc (10% FFAP column) was used for purification of the material: bp 82.5–83.5° (0.4 mm) [lit.[23,29] bp 125–126° (11 mm)]; $n^{25}D$ 1.5432; nmr same as that of trans isomer except that allylic protons were at δ 4.22.

Anal. Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 80.91; H, 8.08.

B. 1-Phenyl-3-buten-2-ol. Approximately 0.135 mol of vinylmagnesium bromide was prepared in 40 ml of $LiAlH_4$-dried THF. Freshly distilled Aldrich reagent phenylacetaldehyde (15.0 g) in 25 ml of dry ether was added dropwise to the Grignard solution. Standard work-up procedures gave 16.0 g of the alcohol (86%): bp 98–99° (6 mm); $n^{25}D$ 1.5313 (lit.[30] $n^{20}D$ 1.5333).

Anal. Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 80.79; H, 8.41.

General Procedure for Regular Addition, PhMgBr + 1. Approximately 12 mmol of phenylmagnesium bromide was prepared in 22 ml of ether. To this was added 0.701 g (10 mmol) of freshly distilled 3,4-epoxy-1-butene in 7 ml of ether to maintain gentle reflux. After 0.5-hr reflux, the cooled solution was worked up with 10% HCl, and the ether layer was washed with $NaHCO_3$ and H_2O, dried ($MgSO_4$), and concentrated. A 90% yield of the phenylbutenols was obtained.

General Procedure for Inverse Grignard Addition. Phenylmagnesium bromide (25 mmol) was prepared in 40 ml of ether and was added to a solution of 1 (1.4 g, 20 mmol) in 15 ml of ether over a 40-min interval. After a 30-min reflux, normal work-up yielded 2.34 g (79% of the isomeric alcohols).

General Procedure for Phenyllithium Reactions. After the method of Walter, 0.05 mol of phenyllithium was prepared in 50 ml of ether.[31] Freshly distilled butadiene monoxide (3.15 g, 45 mmol) was dissolved in 10 ml of ether and added to maintain gentle reflux. Typical work-up resulted in 70–80% yields. Inverse addition, using 20 ml of ether to dissolve the epoxide, produced similar yields.

Copper Catalyst Reactions.[16-19] Approximately 50 mmol of phenylmagnesium bromide was prepared in 40 ml of ether. Under a N_2 blanket, and at a temperature of −10°, 1.4 g (20 mmol) of **1** and 1.00 g of cupric acetate monohydrate dissolved in 70 ml of dry tetrahydrofuran were added dropwise to the Grignard over a 40-min period. The resulting solution was allowed to warm up to room temperature after 1 hr, and was then refluxed for 15 min. Normal work-up with 10% HCl, sodium bicarbonate, and brine washes, and drying with $MgSO_4$, produced an 84% yield of the alcohol products. Two unidentified products totaling 2–4% of the product distribution were recovered along with 12–15% of biphenyl and small amounts of phenol.

Vinyl Grignard + Styrene Oxide Reactions. Vinylmagnesium bromide (20 mmol in 11 ml of tetrahydrofuran) was prepared according to the method of Seyferth.[32] Freshly distilled styrene oxide (2.16 g, 18 mmol) in 10 ml of tetrahydrofuran was added dropwise to the Grignard solution. For mixed solvent reactions, the tetrahydrofuran was removed from the Grignard reagent by rotary evaporation under nitrogen bleed. It was then replaced by the solvent or solvent mixture listed in Table II. In each case, 11 ml of the appropriate solvent mixture was added to the organometallic reagent, and 10 ml of the same solvent mixture was used to dilute the epoxide. Both inverse and regular addition reactions were carried out. Typical yields were 85%.

Registry No. **1**, 930-22-3; **4**, 6052-66-0; *cis*-**5**, 22910-59-4; *trans*-**5**, 49676-93-9; **7**, 96-09-3; phenyl bromide, 108-86-1; phenyllithium, 591-51-5; vinyl bromide, 593-60-2.

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(15) (a) We had difficulty repeating precise product ratios for this method of combination, whereas for regular addition results were highly reproducible. (b) At this time, we have no conclusive evidence to explain why dilution and increased addition time maximize the rearrangement pathway. However, it seems reasonable that inverse addition, as well as the slow addition time for this mode, allows greater contact time between the Grignard's Lewis acid component and the epoxide. Thus, when the Grignard reagent is added to the epoxide it reacts, but the Lewis acid component persists in the presence of the oxirane to perpetuate isomerization. In this manner, the concentration of the rearrangement intermediate builds up prior to the addition of more nucleophile. For the regular combination mode, however, the epoxide is consumed immediately upon addition, and no accumulation of rearrangement intermediate is possible. This explanation would also account for the sensitivity of product distribution to slight changes in reaction conditions with the inverse mode.
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(20) House[13b] gives evidence that in the presence of $MgBr_2$ epoxides are converted to bromohydrins prior to rearrangement. See H. O. House in "Modern Synthetic Reactions," W. A. Benjamin, New York, N. Y., 1965, p 123. Often this possibility is not implicated[8,13a] in the rearrangement, but it does afford an explanation of our data.
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Vinyl Triflates in Synthesis. I. *tert*-Butylacetylene

Robert J. Hargrove[1] and Peter J. Stang*

Department of Chemistry, University of Utah, Salt Lake City, Utah 84112

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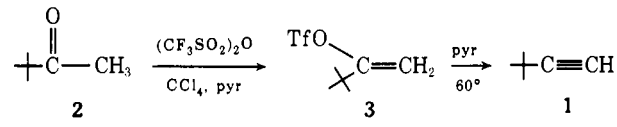
The recent paper by Collier and Macomber[2] on an improved synthesis of *tert*-butylacetylene (**1**) and the relative importance of this substance[3] prompts us to report a new synthesis in two steps of this material, in moderate yield under mild conditions, starting from the readily available pinacolone (**2**).

In this preparation pinacolone (**2**) is readily converted by methods previously developed[4] into 3,3-dimethyl-1-buten-2-yl triflate (**3**), which in turn easily eliminates CF_3SO_3H in the presence of pyridine to give **1** of >99% purity.



2 **3** **1**

Although a variety of conditions[4] were tried for the conversion of **2** into **3** and gc was used to follow the extent of reaction, on the scale employed (20.0 mmol), **3** could only be isolated in yields of 35–45%. It was evident from the results of gc monitoring that the best results on larger scale preparation would be obtained by not permitting the reactions to go to completion but rather allowing the reaction to proceed to only ~60% conversion and reisolation and recycling of the unreacted pinacolone. In this manner, overall conversions of 60–70% could be readily achieved.

A number of different bases such as Et_3N and *t*-BuOK and solvents such as THF, dioxane, and CCl_4 were tried for the elimination of CF_3SO_3H from **3** and formation of **1**. However, the best results and yields (90%) were obtained when pyridine was used as both solvent and base. Interestingly, *in situ* elimination, *i.e.*, preparation and elimination of **3** in the same reaction, resulted in lower or only comparable yields of **1** (based on **2**) than the two-step process.

Triflate **3** is presumably formed through base-catalyzed enolization of the ketone and subsequent acylation of the enol with triflic anhydride. There is little doubt[5] that the elimination of HOTf to form acetylene is an E-2 process under the reaction conditions employed.

This procedure then represents an alternative and simple preparation of *tert*-butylacetylene (**1**) in very high purity, albeit in only moderate yield, from a readily available precursor, pinacolone. Furthermore, preliminary results indicate[6] that this may represent a general procedure for the conversion of certain ketones, such as ring-substituted acetophenones, and simple dialkyl ketones and aldehydes, as exemplified by valeraldehyde, into acetylenes in moderate yields.

Experimental Section

Boiling points are uncorrected. The nmr spectra were recorded on a Varian A-60 spectrometer using TMS as an internal standard; infrared spectra were obtained on a Beckman IR-5 spectrophotometer. Gas–liquid chromatography was performed on a Varian Aerograph Model 90-P unit using a 15 ft × 0.25 in. column with 15% SF-96 on Chromosorb W.

3,3-Dimethyl-1-buten-2-yl Triflate (3). A solution of 2.0 g (0.020 mol) of pinacolone (**2**) and 1.74 g (0.022 mol) of pyridine in 25 ml of anhydrous CCl_4 was cooled to −22° by means of a Dry Ice–CCl_4 slush bath. Over a period of 10 min 6.20 g (0.022 mol) of triflic anhydride was added with continuous swirling to the above cold solution, whereupon a white solid precipitate formed. The mixture was allowed to slowly warm to about 15° and maintained at that temperature for 60 hr, during which time the solution turned dark black. Gc monitoring showed that at this point the mixture consisted of ~60% product and ~40% unreacted ketone.

Prior to work-up an additional 20 ml of anhydrous CCl_4 was added to the mixture, which was then quickly washed with two 10-ml portions of ice-water. The water layer in turn was back extracted with three 10-ml portions of CCl_4. The combined organic layer was dried over anhydrous $MgSO_4$ and the solvent was distilled under reduced pressure. Distillation of the residue yielded 1.85 g (40% yield, 66% conversion) of colorless product: bp 42–45° (17 mm) [lit.[7] bp 45–50° (15 mm)]; ir 1650 (C=C), 1410 (S=O), 1210 cm^{-1} (CF); nmr (CCl_4) δ 1.18 (s, 9 H), 4.97 (d, 1 H, J = 4.1 Hz), 5.04 (d, 1 H, J = 4.1 Hz). The unreacted ketone may be re-