JOC Notes

Conversion of Propargyl Alcohols to Chloroallenes and Arylalkynes Using the $TiCl_4/R_3N$ Reagent System

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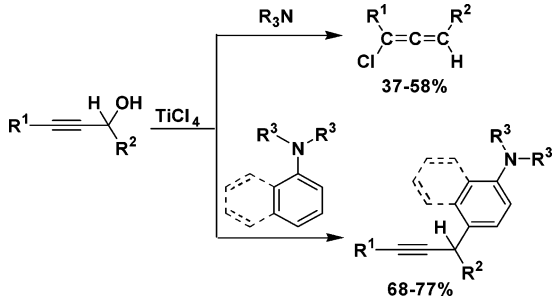
Received March 30, 2006



Whereas the reaction of certain propargyl alcohols with $TiCl_4$ in the presence of tertiary alkylamines gives the corresponding chloroallenes in 37−58% yields, reaction with the tertiary arylamines gives the corresponding arylalkynes in 68−77% yields.

The readily accessible propargyl alcohols[1] have a very rich chemistry.[2,3] These versatile building blocks are useful in the synthesis of many natural and medicinally important products such as prostaglandins, steroids, carotenoids, α-tocopherol (vitamin E) and related isoprenoids, biologically active prostacyclin mimetics,[4] important molecules such as cytostation,[5] 11-α-hydroxyprogesterone,[6] vitamin K,[7] insect sex phermones,[8] fatty acids,[9] enediynes (Taxamycins),[10] (*Z*)-tamoxifen,[11] AB-taxane ring with enone,[12] Taxol and taxotere,[13] vitamin A,[14] *β*-lactones,[15] (+)-parviflorin, and (+)-5*S*-hydroxyparviflorin.[16]

During the investigations on the development of new synthetic methods using the $TiCl_4/R_3N$ reagent system,[17] we have observed that certain propargyl alcohols **1** are readily converted to the corresponding chloroallene derivatives and aryl substituted alkynes. Initially, we have carried out the preparation of the alkynyltitanium reagent in situ for reaction with benzaldehyde (1 equiv) using 1-heptyne (1 equiv), $TiCl_4$ (1 equiv), and Et_3N (1.5 equiv) in dichloromethane. In this experiment, the corresponding chloroallene was isolated in 21% yield (Scheme 1).

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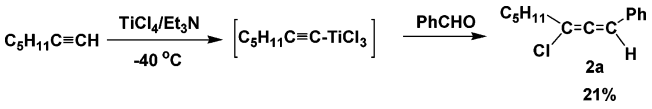
10.1021/jo060683m CCC: $33.50
Published on Web 08/23/2006

SCHEME 1. Formation of Chloroallene 2a in the Reaction of 1-Heptyne with Benzaldehyde



SCHEME 2. Formation of Chloroallenes from Propargyl Alcohols

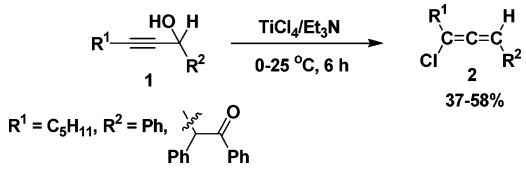
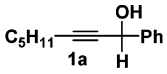
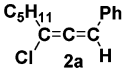
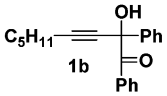
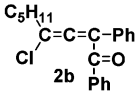
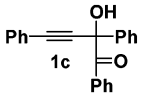
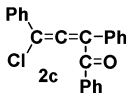


TABLE 1. Conversion of Propargyl Alcohols to Chloroallenes Using the $TiCl_4/R_3N$ Reagent System[a]

Entry	Substrate	Amine	Product[b]	%Yield[c]
1	 1a	Et_3N	 2a	56
2	1a	Bu_3N	2a	45
3	1a	i-Pr_2NEt	2a	37
4	 1b	Et_3N	 2b	54
5	 1c	Et_3N	 2c	58

[a] The reagents were used in the following quantities: propargyl alcohol (1 mmol), $TiCl_4$ (1 mmol), and alkylamines (2 mmol). [b] The products were identified by ^1H NMR, ^{13}C NMR, mass spectral data, and elemental analysis. [c] Yields of isolated products.

Since this transformation would most probably involve the intermediacy of the corresponding propargyl alcohol derivative formed in situ, we have examined the reaction of 1-phenyl-2-octyn-1-ol **1a** with triethylamine and $TiCl_4$. In this case, the corresponding chloroallene was obtained in 56% yield (Scheme 2).

We have examined this reaction using different amines. It was found that the Et_3N gave better yields (Table 1). In the case of Bu_3N and *i*-Pr_2NEt, the chloroallene was isolated in 45% and 37% yields, respectively (Table 1). The chloroallenes were also isolated in reasonable yields from the propargyl alcohols derived from benzil (Table 1). However, the propargyl alcohols derived from aliphatic aldehydes and ketones (e.g., butyraldehyde, acetophenone, and cyclohexanone) led to unclean reactions, and the corresponding chloroallenes were not obtained in these cases. It is of interest to note here that the Ti(III) species, produced in situ by first reacting the $TiCl_4$ with the Et_3N at 0 °C for 1 h, upon subsequent addition of with certain propargyl alcohols including those derived from aliphatic aldehydes, give the corresponding 1,5-diynes through the intermediacy of the corresponding radical species.[17a]

An interesting observation was made in the case of the propargyl alcohol **1d** prepared from benzophenone and phenylacetylene (1,1,3-triphenyl-2-propyn-1-ol). In this case, the corresponding allenyl quaternary salt **3** was isolated in 68% yield

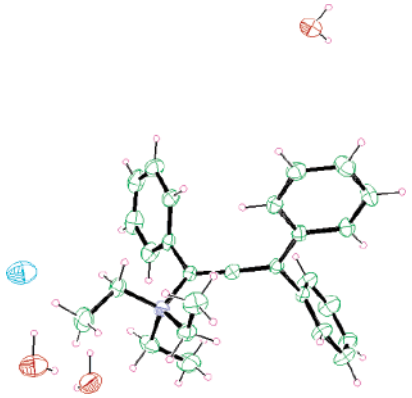
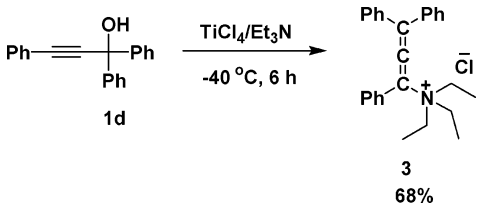
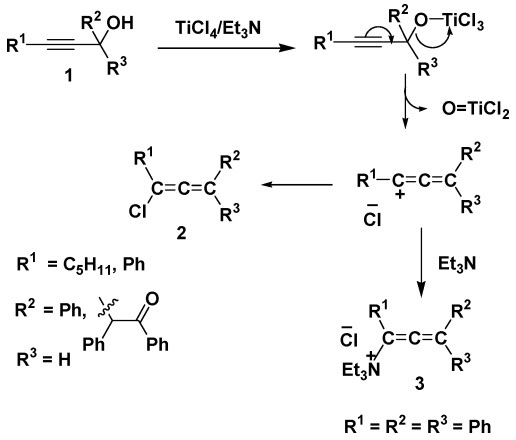


FIGURE 1. ORTEP diagram of the allenyltriethylamine salt **3** (thermal ellipsoids are drawn at 20% probability).

SCHEME 3. Allenyltriethylamine Salt 3 Formation in the Reaction of $TiCl_4/Et_3N$ Reagent System with the Propargyl Alcohol 1d



SCHEME 4. Mechanism for the Formation of Chloroallenes and the Allenylammonium Salt



(Scheme 3). This salt **3** was characterized by single-crystal X-ray analysis (Figure 1).[18]

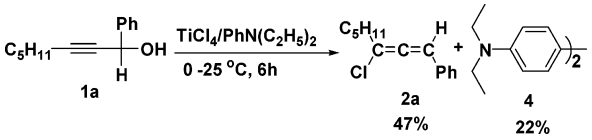
The formation of the chloroallene derivatives may be explained by the tentative mechanism outlined in Scheme 4 involving the intermediacy of the corresponding allenyl cations.

However, as mentioned earlier, the propargyl alcohols react with the Ti(III) species, produced in situ using the $TiCl_4/Et_3N$ reagent system under slightly different conditions, to give the corresponding 1,5-diynes or enynes via the coupling of the corresponding radical intermediates.[17a]

We have observed when the propargyl alcohol **1a** was reacted with *N*,*N*-diethylaniline at 0−25 °C the chloroallene **2a** was

(18) **Crystal data for allenyltriethylamine salt (3):** $C_{27}H_{36}ClNO_3$, MW = 458.03, monoclinic, space group: $P2_1/n$, a = 9.1453(18) Å, b = 9.8672(5) Å, c = 17.0435(9) Å, β = 99.15(3)°, V = 2606.5(2) Å^3, Z = 42, ρ_c = 1.143 Mg m^{-3}, μ = 0.100 mm^{-1}, T = 298 K. Of the 24177 reflections collected, 4574 were unique [R_{int} = 0.0401]. Refinement on all data converged at R1 = 0.0821, wR2 = 0.2610.

SCHEME 5. Formation of Chloroallene 2a from Propargyl Alcohol 1a



SCHEME 6. Arylated Alkynes from Propargyl Alcohols

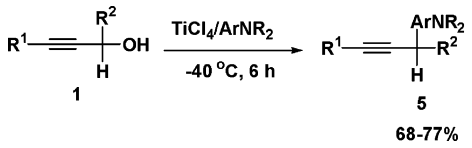
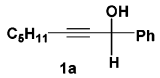
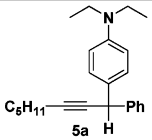
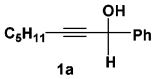
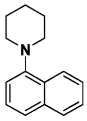
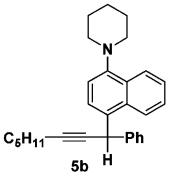
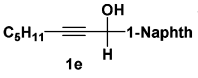
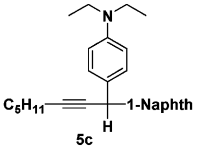
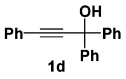
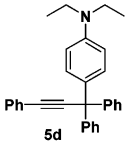
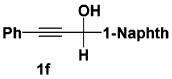
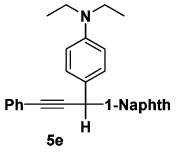


TABLE 2. Arylation of Propargyl Alcohols Using the $TiCl_4/R_2NAr$ Reagent System[a]

Entry	Substrate	Aryl amine	Product[b]	Yield (%)[c,d]
1	 1a		 5a	68
2	 1a		 5b	71
3	 1e		 5c	73
4	 1d		 5d	77
5	 1f		 5e	73

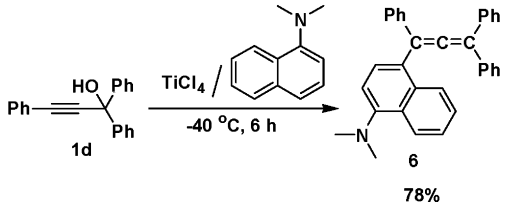
[a] The reagents were used in the following quantities: propargyl alcohol (1 mmol), $TiCl_4$ (1 mmol), and of arylamines (1.5 mmol). [b] The products were identified by ^1H NMR, ^{13}C NMR, mass spectral data, and elemental analysis. [c] Yields of isolated products. [d] The corresponding benzidine was isolated with <12% yield.

isolated in 47% yield, besides the corresponding benzidine **4** (22% yield) (Scheme 5).[19]

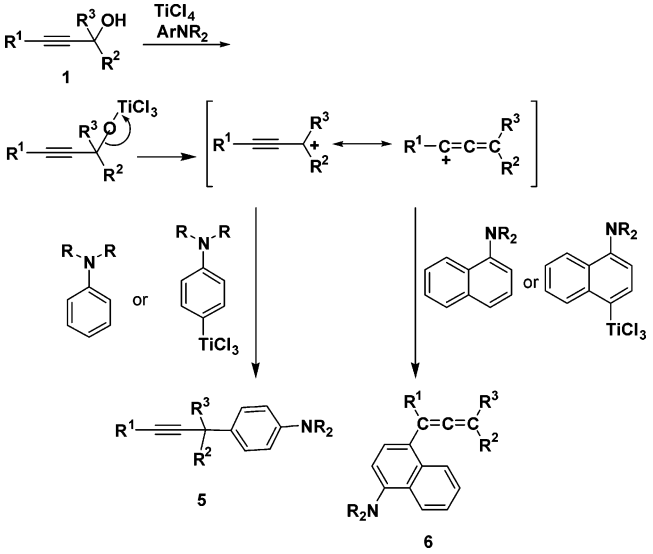
However, when the reaction was carried out −40 °C, the corresponding arylated alkynyl product **5a** was isolated in 68% yield as major product besides the corresponding benzidine (12% yield) (Scheme 6). This transformation was found to be general for other tertiary aromatic amines and the results are summarized in Table 2.

(19) Periasamy, M.; Jayakumar, K. N.; Bharathi, P. *J. Org. Chem.* **2000**, *65*, 3548−3550.

SCHEME 7. Arylamine-Substituted Allenic Product 6 from Propargyl Alcohol 1d



SCHEME 8. Tentative Mechanism for the Arylation of Propargyl Alcohols Using $ArNR_2$



Interestingly, in the case of the propargyl alcohol **1d** prepared from benzophenone, the corresponding allenic product **6** was obtained in 78% yield (Scheme 7). Presumably, in this case the allene is formed as there would be tremendous steric hindrance toward attack of the propargyl cation that would be formed in situ (Scheme 8).

These transformations leading to arylation of the propargyl derivatives may be explained by the mechanism outlined in Scheme 8. Although the transformation can be rationalized by the electrophilic substitution reaction of the allenyl cation formed in situ with the aniline derivatives, the alternative mechanism involving the reaction of aryltitanium species cannot be ruled out as in all these cases the corresponding benzidine derivatives are isolated in <12% yields. Previously, the formation of benzidine from *N*,*N*-dialkylarylamines and $TiCl_4$ was explained by considering the coupling of the radical cations and/or aryltitanium species formed in situ.[19]

To further examine the intermediacy of aryltitanium species in this transformation, we have quenched the reaction (Scheme 6) with D_2O in the case of *N*,*N*-dialkylaniline after 6 h. In this case, the benzidine was isolated in 10% yield and the recovered *N*,*N*-dialkylaniline did not contain deuterium in the 4 position. Presumably, this transformation (Scheme 8) does not go through the corresponding aryltitanium intermediate or the aryltitanium formed in situ is not stable and undergoes coupling to give the corresponding benzidine before quenching with D_2O.

In recent years, several methods have been reported for the preparation of allene derivatives from propargyl alcohol derivatives.[20] The simple method of synthesis of chloroallenes described here is a good addition to this pool of procedures. In addition, the interesting reactivity pattern uncovered for the

$TiCl_4$/tertiary arylamine reagent system should be useful for further synthetic exploitations.

Experimental Section

Typical Experimental Procedure for the Conversion of 1-Heptyne and Benzaldehyde in the Presence of $TiCl_4/Et_3N$ Reagent System. In CH_2Cl_2 (35 mL), 1-heptyne (0.96 g, 1.3 mL, 10 mmol), $TiCl_4$ (1.9 g, 1.1 mL, 10 mmol), Et_3N (1.5 g, 2.1 mL, 15 mmol), and benzaldehyde (1.06 g, 1 mL, 10 mmol) were taken at −40 °C under N_2 and stirred for 2 h at −40 °C. It was stirred further at 25 °C for another 6 h. A saturated NH_4Cl solution (20 mL) was added and the mixture stirred for 30 min. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (2 × 15 mL). The combined organic extract was washed with brine solution (10 mL) and dried over anhydrous Na_2SO_4. The solvent was removed, and the residue was chromatographed on a silica gel column with hexane as eluent to isolate the chloroallene **2a** (0.46 g, 21%). Spectral data for product **2a**: IR (neat) 2957, 1930, 1493 cm^{-1}; ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm) 14.0, 22.3, 26.8, 31.0, 36.5, 101.7, 108.8, 127.7, 128.2, 128.7, 133.3, 200.4; ^1H NMR (400 MHz, $CDCl_3$, δ ppm) 7.5−7.2 (m, 5H), 6.48 (s, 1H), 2.53 (t, 2H, J = 6.8 Hz), 1.67−1.38 (m, 6H), 0.95 (t, 3H, J = 6.8 Hz); MS (EI) m/z 220 (M^+). Anal. Calcd for $C_{14}H_{17}Cl$: C, 76.18; H, 7.76. Found: C, 76.21; H, 7.78.

Typical Experimental Procedure for the Conversion of Proparyl Alcohols to Chloroallenes in the Presence of $TiCl_4$/Et_3N Reagent System. In CH_2Cl_2 (35 mL), propargyl alcohol **1a** (0.20 g, 1 mmol), $TiCl_4$ (0.19 g, 0.11 mL, 1 mmol), and Et_3N (0.2 g, 0.28 mL, 2 mmol) were taken at 0 °C under N_2. The reaction mixture was stirred for 30 min at 0 °C. It was stirred further at 25 °C for 6 h. A saturated NH_4Cl solution (20 mL) was added and stirred for 30 min. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (2 × 15 mL). The combined organic extract was washed with brine solution (10 mL) and dried over anhydrous Na_2SO_4. The solvent was removed, and the residue was chromatographed on a silica gel column using hexane as eluent to isolate chloroallene **2a** (0.14 g, 56%). The same procedure was followed to obtain the compound **2b** (0.17 g, 54%) and **2c** (0.19 g, 58%).

Typical Experimental Procedure for the Conversion of Proparyl Alcohols 1d to Allenyltriethylamine Salt 3 in the Presence of $TiCl_4/Et_3N$ Reagent System. In CH_2Cl_2 (35 mL), propargyl alcohol **1d** (0.284 g, 1 mmol), $TiCl_4$ (0.19 g, 0.11 mL, 1 mmol), and Et_3N (0.3 g, 0.42 mL, 3 mmol) were taken at −40 °C under N_2. The reaction mixture was stirred for 6 h. The reaction mixture was quenched with water (10 mL). The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (2 × 5 mL). The solvent was removed, and the residue was concentrated. The residue was crystallized from ethyl acetate. The allenyl triethylamine salt **3** was isolated in 68% yield (0.27 g). Spectral data for product **3**: IR (neat) 3393, 1946, 1454 cm^{-1};^{13}C NMR (100 MHz, $CDCl_3$, δ ppm) 8.8, 53.1, 115.1, 121.6, 126.1, 127.4, 128.2, 128.6, 129.2, 129.7, 130.1, 131.2, 200.1; ^1H NMR (400 MHz, $CDCl_3$, δ ppm) 7.56−7.29 (m, 15H), 3.75−3.7 (q, 6H, J = 6.8 Hz), 1.48 (t, 9H, J = 6.8 Hz); MS (EI) m/z 403 (M^+). Anal. Calcd for $C_{27}H_{30}ClN$: C, 80.27; H, 7.48; N, 3.47. Found: C, 80.31; H, 7.25; N, 3.56.

Typical Experimental Procedure for the Conversion of Proparyl Alcohols to Arylalkynes in the Presence of $TiCl_4/Et_3N$ Reagent System. In dichloromethane (35 mL), propargyl alcohol **1a** (0.20 g, 1 mmol), $TiCl_4$ (0.19 g, 0.1 mL, 1 mmol), and *N*,*N*-diethylaniline (0.3 g, 0.32 mL, 2 mmol) were taken at −40 °C under N_2. The reaction mixture was stirred for 6 h at −40 °C. A saturated K_2CO_3 solution (20 mL) was added and the mixture stirred for 10 min. The organic layer was separated, and the aqueous layer was extracted with dichloromethane (2 × 15 mL). The combined organic extract was washed with brine solution (10 mL) and dried over anhydrous Na_2SO_4. The solvent was removed, and the residue was chromatographed on a silica gel column using 1% ethyl acetate in hexane to isolate the aryl alkyne **5a** (0.26 g, 68%) and benzidine (0.03 g, 12%). Spectral data for **5a**: IR (neat) 3412, 3067, 2069, 1634 cm^{-1}; ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm) 12.5, 14.0, 18.9, 22.2, 28.7, 30.9, 42.2, 44.3, 84.4, 96.0, 111.8, 123.3, 126.3, 128.0, 128.6, 129.1, 133.2, 143.3, 146.5; ^1H NMR (400 MHz, $CDCl_3$, δ ppm) 7.13−7.39 (m, 9H), 4.48 (s, 1H), 3.12−3.32 (m, 2H), 2.2−2.24 (m, 4H), 1.48−1.56 (6H), 1.41 (t, 6H, J = 7.3 Hz), 0.92 (t, 3H, J = 7.2 Hz); MS (EI) m/z 333 (M^+). Anal. Calcd for $C_{24}H_{31}N$: C, 86.43; H, 9.37; N, 4.27. Found: C, 86.45; H, 9.39; N, 4.23.

Acknowledgment. G.V.K. is thankful to the ILS-UOH for a fellowship and M.P. is thankful to ILS-UOH for a research grant. UGC support under the "University with Potential for Excellence (UPE)" and "Centre for Advance Study (CAS-SAP)" programs is gratefully acknowledged. We are thankful to the DST for 400 MHz NMR spectrometer and National XRD-CCD facilities in the School of Chemistry, University of Hyderabad.

Supporting Information Available: Spectral data for compounds **2b**,**c**, **5b**−**e,** and **6**, ^{13}C NMR spectra of products, crystallographic diagrams and crystallographic information files (CIF) for compound **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO060683M

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