[lower-boiling form; ^{1}H NMR δ 7.20 (s, 5, C_6H_5), 5.40 (t, 1, =CH), 0.6–2.7 (m, 20, CH_2CH_3)].

Preparation of 6-Phenyl-6-undecanol. The alcohol was obtained (51%) from the reaction of phenylmagnesium bromide with 6-undecanone; bp 107–108 °C (0.15 mm); n^{25}_D 1.4950; ^{1}H NMR (CCl_4) δ 7.27 (s, 5, C_6H_5), 1.5–2.0 (s, 4, CH_2), 0.6–1.4 (m, 19, CH_2CH_3). Anal. Calcd for $C_{17}H_{28}O$: C, 82.20; H, 11.36. Found: C, 82.10; H, 11.20.

Reaction of 6-Phenyl-6-undecanol with Acid. (a) H_2SO_4. A mixture of 4.00 g (0.015 mol) of 6-phenyl-6-undecanol and 50 mL of concentrated H_2SO_4 was stirred until homogeneous, poured into 500 mL of ice water, and extracted with four 25-mL portions of petroleum ether (bp 60–65 °C). The combined extracts were dried (Na_2SO_4) and distilled through a spinning-band column. There was obtained 1.46 g (42%) of 6-phenylundecane; bp 88–89 °C (0.20 mm); n^{25}_D 1.4812; ^{1}H NMR (CCl_4) δ 7.11 (s, 5, C_6H_5), 2.2–2.6 (s, 1, CH), 0.6–1.9 (m, 23, CH_2CH_3). Anal. Calcd for $C_{17}H_{28}$: C, 87.86; H, 12.14. Found: C, 88.00; H, 12.14.

(b) $KHSO_4$. A mixture of 1.0 g (4.0 mmol) of 6-phenyl-6-undecanol and 0.27 g of fused $KHSO_4$ was heated at 160 ± 5 °C for 4 h. The product was distilled to afford 0.87 g (94%) of mixed 6-phenyl-5-undecenes; bp 93–94 °C (0.15 mm); n^{25}_D 1.5040. A sample, 0.46 g (2.0 mmol) of the latter was hydrogenated over 4 mg of PtO_2 catalyst to give 0.42 g (100%) of unpurified 6-phenylundecane; n^{25}_D 1.4798.

Saponification of Methyl 2-Pentyl-2-phenylheptanoate. A solution of 2.9 g (0.1 mol) of the ester and 2.9 g (0.05 mol) of 85% KOH in 265 mL of 95% C_2H_5OH, containing 1.5 mL of H_2O, was refluxed for 120 h. The reaction mixture was poured into 500 mL of 10% HCl, extracted with four 100-mL of ether, dried (Na_2SO_4), and concentrated. There was obtained 1.18 g (55%) of 2-pentyl-2-phenylheptanoic acid; mp 81–82 °C (petroleum ether, bp 60–65 °C); IR 3350–2300 (m), 1790 (s), 1290 (s), 950 (s) cm^{-1}; ^{1}H NMR (CCl_4) δ 11.91 (s, 1, CO_2H), 7.28 (s, 5, C_6H_5), 1.7–2.2 (s, 4, CH_2), 0.6–1.4 (m, 18, CH_2CH_3). Anal. Calcd for $C_{18}H_{28}O_2$: C, 78.21; H, 10.21. Found: C, 78.45; H, 10.43.

Electrolysis of 2-Pentyl-2-phenylheptanoic Acid. A solution of 0.25 g (0.91 mmol) of 2-pentyl-2-phenylheptanoic acid and 0.20 g (0.91 mmol) of 25 wt % CH_3ONa in 400 mL of CH_3OH was electrolyzed in the previously described apparatus at an initial 91 V and 1.0 A. The reaction was discontinued after 1 h when a steady state of 93 V and 0.25 A had been reached. The reaction mixture was acidified and worked up to afford a residue that was purified by evaporative distillation (Kugelsrohr) to give 0.215 g (91%) of 6-methoxy-6-phenylundecane; n^{25}_D 1.4851. It was identified by comparison of its IR and ^{1}H NMR spectra with those of an authentic sample.

Oxidation of 2-Pentyl-2-phenylheptanal. The aldehyde was obtained by the titanium(III) cleavage of the corresponding (2,4-dinitrophenyl)hydrazone by the method of McMurry and Silvestri.[21] The product resulted in 44% yield and distilled at 114–115 °C (0.15 mm); n^{25}_D 1.4912.

To a solution of Ag_2O, prepared from 1.75 mL (0.56 mmol) of 5% $AgNO_3$, and 0.5 g (1.11 mmol) of NaOH in 5.0 mL of H_2O, was added 70 mg (0.27 mmol) of the aldehyde. The mixture was stirred at 0 °C for 30 min, filtered, acidified with 10% HCl, and extracted with petroleum ether (bp 60–65 °C). The solvent was removed to leave 62 mg (83%) of crude 2-pentyl-2-phenylheptanoic acid, which was identified by comparison of its IR and ^{1}H NMR spectra with those of an authentic sample.

Registry No. 1 (acid), 815-17-8; 2 (acid), 26269-42-1; 3 (acid), 89579-45-3; 3 (ethyl ester), 89579-54-4; 4 (acid), 26269-44-3; 4 (ethyl ester), 89579-55-5; 5 ($R_1 = R_2 = R_3 = CH_3$), 598-98-1; 5 ($R_1 = R_2 = R_3 = C_5H_{11}$), 89579-46-4; 5 ($R_1 = C_4H_9$, $R_2 = C_6H_{13}$, $R_3 = C_{12}H_{25}$), 89579-47-5; 5 ($R_1 = C_4H_9$, $R_2 = C_6H_{13}$, $R_3 = C_{12}H_{25}$; acid), 89579-56-6; 5 ($R_1 = R_2 = C_5H_{11}$, $R_3 = C_6H_5$), 89579-48-6; 5 ($R_1 = R_2 = C_5H_{11}$, $R_3 = C_6H_5$; acid), 89579-57-7; 6 ($R_1 = R_2 = R_3 = CH_3$), 630-19-3; 6 ($R_1 = R_2 = R_3 = C_5H_{11}$), 26269-54-5; 6 ($R_1 = R_2 = C_5H_{11}$, $R_3 = C_6H_5$), 89579-49-7; 6 ($R_1 = R_2 = C_5H_{11}$, $R_3 = C_6H_5$; (2,4-dinitrophenyl)hydrazone), 89579-50-0; 7 ($R_1 = R_2 = R_3 = CH_3$), 4026-20-4; 7 ($R_1 = R_2 = R_3 = C_5H_{11}$), 85613-93-0; 8 ($R_1 = R_2 = C_5H_{11}$, $R = C_4H_9$), 51677-36-2; 8 ($R_1 = C_5H_{11}$, $R_2 = C_6H_5$, $R = C_4H_9$), 89579-51-1; 9 ($R_1 = R_2 = C_5H_{11}$, $R_3 = C_6H_5$), 89579-52-2; 10, 942-92-7; dodecyl bromide, 143-15-7; ethyl 3-butyl-2-cyano-2-nonenoate, 25594-05-2; ethyl 3-butyl-2-cyano-3-hexylpentadecanoate, 89579-53-3; 6-undecanone, 927-49-1; 6-phenyl-6-undecanol, 67267-86-1; 6-phenylundecane, 4537-14-8.

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Transition-Metal-Promoted Alkylations of Unsaturated Alcohols: The Ethylation of 3-Butyn-1-ol and 3-Buten-1-ol via Titanium Tetrachloride-Organoaluminum Ziegler-Natta Catalyst Systems

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Reaction of 3-butyn-1-ol with diethylaluminum chloride followed by treatment with titanium tetrachloride under a variety of conditions gave selectively up to 70% yields of (*E*)-3-hexen-1-ol, the product expected from a syn ethylmetalation of the multiple bond. No complications arising from in situ β-hydride elimination were observed. Similarly, 4-pentyn-2-ol was ethylated to give (*E*)-4-hepten-1-ol; however, 3-pentyn-1-ol did not give an ethylated product. Additionally, the effect of "third components", i.e., Lewis bases, on the ethylation of 3-butyn-1-ol and 3-buten-1-ol was studied.

Several groups have made progress in adapting Ziegler–Natta polymerization catalyst chemistry to effect the monomethylmetalation of alkene and alkyne functionalities with potential usefulness in organic synthesis.[1-5] Notable in this regard is the work of Negishi and coworkers who found that $(\eta^5\text{-}C_5H_5)_2ZrCl_2$–$AlMe_3$ smoothly

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Table I. Ethylation of Homopropargyl Alcohols via Titanium Tetrachloride-Diethylaluminum Chloride Reagent Systems

reagents[a]	T, °C	reaction time, min	products	product yield, %	starting alkynol recovered, %	mass balance, %
			R = 3-Butyn-1-yl			
$[Al_2Et_4Cl_2$ + ROH] + $TiCl_4$	0	1	(E)-3-hexen-1-ol (I)	13	2	15
	−23	1	I	70	13	83
	−29	1	I	68	0	68
	−45	1	I	56	31	87
	−65	1	I	43	41	84
	−78	1	I	10	76	86
$[Al_2Et_4Cl_2$ + ROH] + $TiCl_4$	−100	120	I	23	63	86
	−78	120	I	30	24	54
	−45	120	I	12	4	16
	0	120	I	3	0	3
			R = 4-Pentyn-2-yl			
$[Al_2Et_4Cl_2$ + ROH] + $TiCl_4$	−45	1	(E)-4-hepten-1-ol (III)	30	61	91
	−29	1	(III)	58	34	92
	−23	1	(III)	51	36	87

[a] The stoichiometries are those indicated by the formulae for each reaction.

effects the stereo- and regioselective methylzirconation of a variety of alkynes that upon functionalization leads to selectively substituted olefins. However, with higher trialkylaluminums regioselectively is lost and hydrometalation occurs.[6,7] Recently, we found that $TiCl_4$–$AlMe_3$ gives a high-yield, selective carbometalation of 3-hexyn-1-ol and similar homopropargyllic alcohols leading to (Z)-4-methyl-3-alken-1-ols.[2] Thus, with a need for selective carbometalations with alkyl groups containing β-hydrogens, we chose to study the $TiCl_4$-promoted ethylation of alkynols.

Experimental Section

Materials. The alkynols and 3-buten-1-ol were purchased from Albany International (Farchan Labs) and Wiley Organics (Chemical Samples Co.), respectively, and were used without further purification except for storage over Linde 3-A molecular sieves. Triphenyl phosphite and triethyl phosphite were obtained from Aldrich; triphenylphosphine was from Eastman. The phosphorus bases were used without further purification. Pyridine and triethylamine were obtained from Fischer and distilled prior to use. The organoalanes (Ethyl Corp) were obtained as neat liquids and were transferred to reaction vessels in a nitrogen-filled Vacuum Atmospheres Dri-Lab. Titanium tetrachloride and bis(η^5-cyclopentadienyl)titanium dichloride were used as obtained from Aldrich and Alfa-Ventron, respectively.

Methylene chloride was redistilled under nitrogen over P_2O_5 and stored over nitrogen. All liquids were transferred by using syringe and/or drybox techniques.

Representative Alkylation Procedure. In a typical reaction, 30 mmol of an organoalane was transferred in a drybox with a syringe into 75 mL of CH_2Cl_2 contained in a 250-mL round-bottomed three-necked flask equipped with a gas inlet, magnetic stirring bar, and two tight-fitting rubber septa. $TiCl_4$ (15 mmol) was transferred in the drybox into 25 mL of CH_2Cl_2 contained in a 120-mL crown-cap pressure bottle (Lab Glass, Inc.); the bottle was then capped with a two-hole crown fitted with a Teflon or neoprene liner. Both the 250-mL flask and the pressure bottle were removed from the drybox to the bench and attached to a dry, oxygen-free nitrogen line. The organoalane solution was cooled to 0 °C, and the alkynol was added dropwise via a gas-tight syringe (weighed before and after transfer). The alkynoxy–organoalane solution was stirred for 15 min. (In third component studies the Lewis base was added to the 250-mL flask at this point.) Both solutions were cooled to the reaction temperature

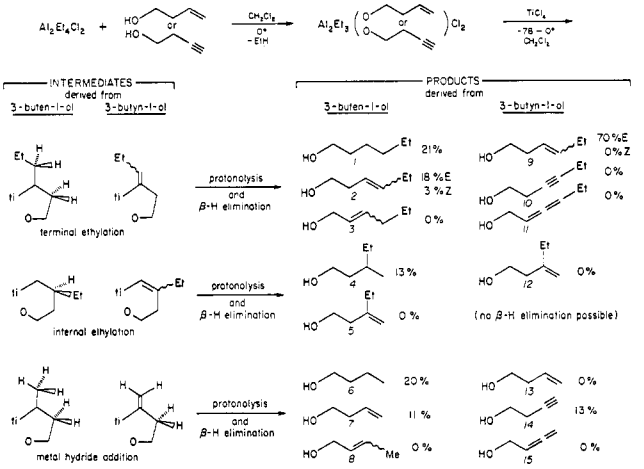

Figure 1. Product possibilities from the ethylation of 3-buten-1-ol and 3-butyn-1-ol via $TiCl_4$–$AlEt_2Cl$ (yields for 3-buten-1-ol from ref 1a; for 3-butyn-1-ol from Table I herein).

after which the $TiCl_4$ solution was rapidly transferred under nitrogen pressure through large-gauge stainless steel tubing to the well-stirred organoaluminum solution. The reactions were quenched rapidly by adding cold methanol (10 mL at −23 °C) followed by 50 mL of 5% aqueous H_2SO_4 saturated with NaCl. After stirring for ca. 0.5 h at room temperature, the appropriate internal standard was added for quantitative GLC analysis. The organic layer was separated off, and the aqueous layer was extracted with several portions of diethyl ether. The organic portions were combined, dried over $MgSO_4$, and analyzed by GLC. When appropriate, pure samples were isolated by preparative GLC. Products reported in this study have been previously characterized.[3,4]

Gas Chromatography. Yields were determined by GLC (HP 5711 FID-3380S integrator/HP 5793 FID-3390A integrator) with the internal standard technique using 3.0 m × 0.32 cm Carbowax 20M and 25 m (0.31 mm) i.d. capillary columns. For all 3-buten-1-ol and 3-butyn-1-ol alkylations, 1-heptanol was used as the internal standard. All yields reflect corrections for response factors determined from authentic samples.

Results and Discussion

We chose to study first the $TiCl_4$-promoted ethylation of 3-butyn-1-ol incorporated as $[Al_2Et_3Cl_2(OCH_2CH_2C{\equiv}CH]$ in a manner similar to previous studies[1] with 3-buten-1-ol to establish trends in the reaction characteristics of ethylaluminum–$TiCl_4$ reagent systems particularly with regard to the facility of carbometalation, regio- and stereoselectivity, β-hydride elimination, and hydrometalation.

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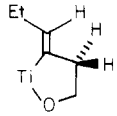
Figure 1 summarizes the varied chemistry involved in the 3-buten-1-ol ethylations and the corresponding chemistry in the ethylation of 3-butyn-1-ol. Selected results of the 3-butyn-1-ol ethylation study are tabulated in Table I.

Relative to our earlier work[1a] with the analogous $TiCl_4$–$Al_2Et_4Cl_2$–$HOCH_2CH_2CH{=}CH_2$ system, the striking feature of the 3-butyn-1-ol ethylation reactions is that virtually only a single monoethylated product (after hydrolysis) arising from cis metal–ethyl addition, (*E*)-3-hexen-1-ol, is observed. Thus the $TiCl_4$-promoted ethylation reaction is stereo- and regioselective. We found no evidence for more than very small quantities (~1% or less by GLC) of other ethylated products; 3-buten-1-ol, a hydrometalation product, was only a minor constituent (<-3%) in a few reactions, and no 1-butanol was observed. This selectivity in the $TiCl_4$–$Al_2Et_4Cl_2$ reactions giving moderate yields of (*E*)-3-hexen-1-ol as the sole product is rather surprising when compared with the reaction of the olefinic alcohol 3-buten-1-ol under similar conditions. Reference to Table II and Figure 1 shows that the ethylation of 3-buten-1-ol proceeds to an extent of 55% (**1**, **2**, **4**) with terminal ethylation predominating (terminal/internal = 3.2). While there is 42% terminal addition, only 21% 1-hexanol (**1**) is isolated because half of the terminally ethylated intermediate eliminates a 4-β-hydrogen to give mostly (*E*)-3-hexen-1-ol (**2**). No β-hydride elimination product (**5**) is observed arising from the ethylated intermediate from which 3-methyl-1-pentanol (**4**) is derived. Thus, under conditions similar to the 3-buten-1-ol reaction the $TiCl_4$–$Al_2Et_4Cl_2$ reagent system with 3-butyn-1-ol gives a stereo- and regioselective product with yields of (*E*)-3-hexen-1-ol at various reactions temperatures for 2 h in the range 10–30%.

The absence of β-hydride elimination products, namely, 3-hexyn-1-ol (**10**) and 2,3-hexadien-1-ol (**11**), is consistent with the carbometalation of homopropargyl alcohols being an intramolecular process generating a metallocyclic intermediate such as below.



In this intermediate there are only a trans vinylic β-hydrogen and endocyclic β-hydrogens. Both of these structural types have unfavorable dihedral angles for hydride elimination, and both structural types have been found to be relatively stable to elimination.[8,9] Consistent with a crucial role for the oxygen atom of the 3-butyn-1-oxy group and with an intramolecular alkylation of alkynols is the fact that we have observed that the $TiCl_4$–$AlMe_3$-based methylation of 1-octyne (an intermolecular reaction) gives greater than 95% methylated dimers and higher oligomers.[10]

Since reactions with $TiCl_4$–$Al_2Et_4Cl_2$ for 2 h from 0 to −78 °C consume 3-butyn-1-ol but give low yields of the single carbometallated product, the initial carbometalated intermediate must react further to give perhaps oligomers or other higher molecular weight species that we have not been able to identify. In an attempt to curtail those side reactions which limit isolation of the monocarbometalated product, we decided to look at the $TiCl_4$–$Al_2Et_4Cl_2$–3-butyn-1-ol system, which gave a maximum of ca. 30% of

Table II. Reaction of 3-Buten-1-ol in the $TiCl_4$–$AlEt_2Cl$ Reagent with Added Base[a]

added base	T(°C)/time (min)	molar ratios Ti/Al/ROH/B	products (% yield)						
			1-butanol	3-buten-1-ol	3-methyl-1-pentanol	1-hexanol	(*E*)-3-hexen-1-ol	(*Z*)-3-hexen-1-ol	total mass
none	−45/120	1/2/1/1	20	11	13	21	18	3	86
$P(OPh)_3$	−45/120	1/2/1/1	3	43	0	27	3	0	76
$P(OEt)_3$	−45/120	1/2/1/1	2	57	0	24	2	0	85
PPh_3	−45/120	1/2/1/1	2	74	0	15	1	0	92
C_5H_5N	−45/120	1/2/1/1	1	89	0	4	1	0	95
Et_3N	−45/120	1/2/1/1	0	85	0	0	0	0	85

[a] These reactions were run in methylene chloride in the same manner as described for 3-butyn-1-ol alkylations in the Experimental Section.

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(*E*)-3-hexen-1-ol with a 2-h reaction time, under conditions where the reaction time was on the order of 1 min before protonolysis. Indeed, as reference to Table I shows, the carbometalation is remarkably facile with the brief reaction time very effective at improving the yields and percent conversions.

The effect of adding a "third-component" to the basic $TiCl_4$–$Al_2Et_4Cl_2$–$HOCH_2CH_2C{\equiv}CH$ systems was also studied. The addition of organic bases (third-components) to Ziegler–Natta polymerization systems has been extensively studied with beneficial effects on poly-α-olefin formation.[11] We examined methoxide (added as CH_3OH to the organoalane) and triphenyl phosphite. Methoxide addition inhibits the primary carbometalation and subsequent secondary reactions, e.g., oligomerization. At corresponding temperatures the yields of (*E*)-3-hexen-1-ol are low (<5%) but the mass balance is improved. With the addition of triphenyl phosphite percent conversions are better at corresponding temperatures, but the overall yield of (*E*)-3-hexen-1-ol is still low (<25%). (Specific reaction data for the base effects as well as reaction data for several other similar systems is available as supplementary data—see paragraph at the end of the paper.)

The third component data above compares well with the effects of several Lewis base components added to the $TiCl_4$–$Al_2Et_4Cl_2$–$HOCH_2CH{=}CH_2$ system. The data for this system (Table II) indicate clearly that as the σ Lewis base strength increases from phosphites through amines the overall amount of 3-buten-1-ol which reacts decreases with the strongest bases, pyridine and triethylamine essentially stopping the carbometalation process. Note also that the phosphorus-containing bases enhance ethylation at the terminal carbon of 3-buten-1-ol and that they inhibit β-hydride elimination so that very little (*E* or *Z*)-3-hexen-1-ol is formed and little of the hydrogenation product, 1-butanol, is seen. Thus, the base effect is one that enhances significantly the selectivity of the carbometalation reaction; however, it is unfortunate that the factors which curtail unwanted side reactions and improve selectively also apparently are those which decrease the facility of the primary carbometalation reaction.

The ethylation of two substituted homopropargyl alcohols, 4-pentyn-2-ol and 3-pentyn-1-ol, was studied. The terminal alkynol was selectively ethylated, giving (*E*)-4-hepten-1-ol in moderate yields. Surprisingly, the internal alkynol gave none of the expected monoethylated products.

In conclusion, the titanium tetrachloride–diethylaluminum chloride system does hold promise for the ethylation of terminal homopropargyllic alcohols. At this point, however, the addition of Lewis bases to Z–N systems appears to have the major effect of curtailing the primary carbometalation of the unsaturated carbon–carbon linkage and thus does not look promising for improving the synthetic usefulness of group 4B organolane reagents.

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Registry No. 1, 111-27-3; (*E*)-2, 928-97-2; 7, 627-27-0; 14, 927-74-2; III, 24469-79-2; $AlEt_2Cl$, 96-10-6; $TiCl_4$, 7550-45-0; 4-pentyn-2-ol, 2117-11-5; 3-pentyn-1-ol, 10229-10-4.

Supplementary Material Available: Extended reaction data for attempted ethylations of 3-butyn-1-ol and 3-pentyn-1-ol (2 pages). Ordering information is given on any current masthead page.

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Organocuprate Reactions with Cyclopropanes. Evidence for Three Types of Mechanism[1]

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Cyclopropane ring openings by organocuprates can be classified into three distinct classes. Mechanistically, the simplest openings are the direct nucleophilic displacements with enolate leaving groups. In order to be synthetically useful, these reactions usually require activation by two groups. Substrates that contain vicinal olefin and activating groups generally are opened by S_N2'-like displacements. Finally, β-cyclopropyl-α,β-unsaturated ketones react by a mechanism intimately related to the conjugate addition reaction of α,β-unsaturated ketones.

Introduction

House and his co-workers have reported the results of a number of experiments supporting an electron-transfer mechanism for the conjugate addition reaction of lithium diorganocuprates to α,β-unsaturated ketones;[2-6] however, alternative explanations also have been advanced. For example, Casey and Cesa[7] have pointed out that the cis-

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