3 H, OMe), 5.35 (s, 2 H, CH_2Ph), 6.32 [s, 1 H, $CH(S_2)$], 7.3–7.5 (m, 5 H, CH_2**Ph**), 9.58 (br s, 1 H, NH); MS, *m/e* 376 (39), 344 (100), 316 (80), 253 (88), 208 (28), 178 (30), 91 (100). Anal. Calcd for $C_{15}H_{15}NO_4$: C, 57.27; H, 5.07; N, 3.71. Found: C, 56.98; H, 5.05; N, 3.57.

Benzyl 3-Methyl-4-oxocyclopenta[*b*]pyrrole-2-carboxylate (23). A solution of sodium nitrite (1.5 g) in water (5 mL) was slowly added to a well-stirred solution of benzyl acetoacetate (4 g) in acetic acid (6 mL) while the temperature was kept below 10 °C. After standing in the refrigerator for 2 h, the solution was added slowly to a solution of 1,3-cyclopentanedione (Aldrich) (2 g) in acetic acid (4 mL). Simultaneously, a mixture of zinc dust (3.7 g) and anhydrous sodium acetate (3.7 g) was added, and after addition was complete the mixture was refluxed for 1 h and then poured onto ice water. The solid precipitate was filtered off and then chromatographed on thick-layer silica plates (elution with 30% ethyl acetate in hexane). The product was recovered from the silica with 50% ethyl acetate in hexane and gave 546 mg (10 %), mp 182–182.5 °C, after recrystallization from methanol: NMR δ 2.50 (s, 3 H, Me), 2.88 (s, 4 H, CH_2CH_2), 5.34 (s, 2 H, CH_2Ph), 7.40 (s, 5 H, Ph), 9.32 (br s, 1 H, NH); MS, *m/e* 269 (92), 178 (38), 161 (83), 135 (70), 108 (30), 91 (100). Anal. Calcd for $C_{16}H_{15}NO_3$: C, 71.36; H, 5.61; N, 5.20. Found: C, 71.32; H, 5.74; N, 5.40.

Benzyl 2-Acetyl-3,4-dimethylpyrrole-5-carboxylate (12). Benzyl 3,4-dimethylpyrrole-2-carboxylate[8] (1.03 g) was added to a solution of acetyl chloride (0.47 mL) in dichloromethane (10 mL) at 0 °C (ice bath); next, stannic chloride (0.77 mL) was added and the mixture was stirred and heated under reflux for 10 min. Analytical TLC indicated all starting material to be consumed at this stage, so the mixture was poured carefully into water, extracted with dichloromethane (50 mL), and dried (anhydrous Na_2SO_4). Evaporation to dryness gave a residue, which was chromatographed on alumina (Brockmann Grade III, elution with dichloromethane), and the appropriate eluates were evaporated to give a solid, which was crystallized from dichloromethane/ether to give white crystals (231 mg; 20%) with mp 103 °C: NMR δ, 2.28, 2.47 (each s, 6 H, 3 H, Me), 5.32 (s, 2 H, CH_2Ph), 7.40 (s, 5 H, Ph), 9.52 (br s, 1 H, NH). Anal. Calcd for $C_{16}H_{17}NO_3$: C, 70.83; H, 6.32; N, 5.16. Found: C, 70.55; H, 6.29; N, 5.16.

Ketal 13 from Benzyl 2-Acetyl-3,4-dimethylpyrrole-5-carboxylate (12): mp 93–94 °C; NMR δ 1.67, 2.04, 2.28 (each s, 3 H, Me), 3.91 (m, 4 H, OCH_2CH_2O), 5.32 (s, 2 H, CH_2Ph), 7.40 (m, 5 H, Ph), 8.93 (br s, 1 H, NH). Anal. Calcd for $C_{18}H_{21}NO_4$: C, 68.55; H, 6.71; N, 4.44. Found: C, 68.48; H, 6.65; N, 4.42.

Acetal 17 from Benzyl 2-Formyl-3-[2-(methoxycarbonyl)ethyl]-4-methylpyrrole-5-carboxylate (14): isolated as an oil; NMR δ 2.24 (s, 3 H, Me), 2.3–2.9 (m, 4 H, CH_2CH_2CO), 3.63 (s, 3 H, OMe), 3.8–4.0 (m, 4 H, OCH_2CH_2O), 5.25 (s, 2 H, CH_2Ph), 5.84 [s, 1 H, $CH(O_2)$], 7.30 (s, 5 H, Ph), 9.10 (br s, 1 H, NH).

Acetal 18 from Benzyl 3-Ethyl-2-formyl-4-methylpyrrole-5-carboxylate (15): isolated as an oil; NMR δ 1.02 (t, 3 H, CH_2CH_3), 2.21 (s, 3 H, Me), 2.24 (q, 2 H, CH_2CH_3), 3.9–4.1 (m, 4 H, OCH_2CH_2O), 5.28 (s, 2 H, CH_2Ph), 6.82 [s, 1 H, $CH(O_2)$], 7.34 (s, 5 H, Ph), 8.90 (br s, 1 H, NH).

Acetal 19 from Benzyl 2-Formyl-3-(methoxycarbonyl)-4-methylpyrrole-5-carboxylate (16): isolated as an oil; NMR δ 2.61 (s, 3 H, Me), 3.84 (s, 3 H, OMe), 4.0–4.2 (m, 4 H, OCH_2CH_2O), 5.35 (s, 2 H, CH_2Ph), 6.33 [s, 1 H, $CH(O_2)$], 7.41 (s, 5 H, Ph), 9.80 (br s, 1 H, NH).

Benzyl 2-[2-((3-Hydroxy-2,2-dimethylpropoxy)carbonyl)ethyl]-4-methylpyrrole-5-carboxylate (24): mp 88–89 °C; 12% yield, NMR δ 0.89 (s, 6 H, $C(Me)_2$), 2.30 (s, 3 H, Me), 2.66, 2.88 (each t, 2 H, CH_2CH_2CO), 3.28 (d, 2 H, CH_2OH), 3.94 (s, 2 H, CO_2CH_2), 5.32 (s, 2 H, CH_2Ph), 5.83 (d, $J = 3$ Hz, 1 H, 3-H), 7.3–7.5 (m, 5 H, Ph), 9.14 (br s, 1 H, NH). Anal. Calcd for $C_{21}H_{27}NO_5$: C, 67.54; H, 7.27; N, 3.75. Found: C, 67.69; N, 7.32; N, 4.06.

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Registry No. **1**, 2386-27-8; **2**, 87462-14-4; **3**, 2199-64-6; **4**, 52459-21-9; **5**, 40236-19-9; **6**, 87462-15-5; **7**, 2199-44-2; **8**, 87462-16-6; **10**, 6122-77-6; **11**, 53700-88-2; **12**, 53700-94-0; **13**, 87462-17-7; **14**, 16258-78-9; **15**, 965-20-8; **16**, 52459-21-9; **17**, 87462-18-8; **18**, 87462-19-9; **19**, 87462-20-2; **23**, 87462-21-3; **24**, 87462-22-4; benzyl 3,4-dimethylpyrrole-2-carboxylate, 954-92-7; benzyl acetoacetate, 5396-89-4; 1,3-cyclopentanedione, 3859-41-4; acetyl chloride, 75-36-5.

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A Facile and Selective Methylation of 5-En-3-yn-1-ols with Titanium Tetrachloride–Trimethylaluminum Yielding (3*Z*)-4-Methylalka-3,5-dien-1-ols

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There is current interest in the nonrepetitive carbometalation of unsaturated carbon–carbon bonds using Ziegler-type titanium- or zirconium–organoalane reagents.[1-7] Negishi and co-workers[2] have had noteworthy success with Cp_2ZrCl_2–$AlMe_3$ in the selective methylmetalation of terminal alkynes. Methylmetal addition occurs in a syn fashion with the methyl group adding to the internal carbon. A variety of functionalized products can be derived from the carbometalated intermediates. Related to our interests is the further reaction of the zircomethylated products with ethylene oxide, leading to the isolation of (*E*)-4-methyl-3-alken-1-ols;[8] we have developed the complementary synthesis of (*Z*)-4-methyl-3-alken-1-ols by reaction of homopropargyl alcohols with $TiCl_4$–$AlMe_3$.[1]

In this paper we report a method to prepare (3*Z*)-4-methylalka-3,5-dien-1-ols (I) via the selective carbometalation of the yne group in 5-en-3-yn-1-ols with $TiCl_4$–$AlMe_3$. Our synthesis of I along with the Cp_2ZrCl_2–$AlMe_3$ routes to the 3*E* isomers (from 1-en-3-ynes and ethylene oxide) and (3*Z*)-3-methylalka-3,5-dien-1-ol (from 5-en-3-yn-1-ols) provide compounds that can be used as intermediates in the synthesis of sinensals, which have applications as orange flavorants.[9]

Experimental Section

Materials. 5-Methylhex-5-en-3-yn-1-ol and 7-methyloct-7-en-5-yn-3-ol were purchased from Farchan. The enynols have a tendency to polymerize and, therefore, were distilled under

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reduced pressure and placed over 3-Å molecular sieves prior to use. Hex-5-en-3-yn-1-ol is not available commercially; however, it was readily synthesized by the method of Rossi et al.[10] Titanium tetrachloride was purchased from Aldrich and used without further purification. Trimethylaluminum was obtained from the Ethyl Corp. as a neat liquid and used as received. Methylene chloride was redistilled over phosphorus pentoxide under nitrogen before use. All liquids were transferred under anhydrous conditions with use of syringe and drybox techniques.

Procedures for Enynol Methylations. In a typical reaction, 36 mmol of $Al(CH_3)_3$ was transferred by syringe into 50 mL of CH_2Cl_2 contained in a 250-mL three-necked round-bottom flask equipped with a gas inlet, rubber septa, and a magnetic stirring bar. Titanium tetrachloride (18 mmol) was transferred by syringe into 50 mL of CH_2Cl contained in a 120-mL "pop-bottle", which was then fitted with an appropriate septum and crown-capped. The above transfers were made in a Vacuum Atmospheres Dri-Lab; subsequent chemistry was done at the bench under a nitrogen atmosphere.

The $Al(CH_3)_3$ solution was cooled to 0 °C and 15 mmol of the enynol was added slowly by syringe through a septum. The liberated methane was vented through the gas inlet and safety bubbler attached to a nitrogen manifold. Both solutions were cooled to -23 °C by using carbon tetrachloride slush baths. With use of a 16-gauge stainless steel needle, the $TiCl_4$ solution was transferred in ca. 1 min under nitrogen pressure into the stirred organoaluminum solution. The reaction mixture was stirred 15 s after $TiCl_4$ addition and then quenched via syringe addition of 10 mL of methanol precooled to 0 °C as rapidly as gas evolution could be controlled (ca. 1 min). An aqueous 3 N HCl solution saturated with NaCl (60 mL) was then added. The reaction mixture was allowed to warm to room temperature and stirred for 30 min.

The product dienols were isolated by separation of the organic layer from the reaction mixture followed by extraction of the aqueous layer with diethyl ether. The organic layers were then combined, dried over $MgSO_4$, and filtered, and the solvents were removed under reduced pressure. The product dienols cannot be isolated in pure form by simple distillation because of the similar boiling points of the starting enynols, e.g., in one reaction (3*Z*)-4,5-dimethylhexa-3,5-dien-1-ol was distilled at 102–104 °C (42 mm) but contained ca. 6% enynol. Samples of the dienols were readily isolated by preparative GLC.

Product Characterization Data. (1) **(3*Z*)-4-Methylhexa-3,5-dien-1-ol**: yield 70% (unreacted enynol, 13%); ^{13}C NMR ($CDCl_3$) δ 19.9 (q, 4-CH_3), 30.9 (t, C_2), 62.3 (t, C_1), 114.2 (t, C_6), 126.5 (d, C_3), 133.6 (d, C_5), 134.9 (s, C_4); ^1H **NMR** ($CDCl_3$) δ 1.80 (m, $J \approx 1$ Hz, 4-CH_3), 2.45 (m, 2-CH_2), 2.72 (br s, OH), 3.59 (t, $J = 7$ Hz, OCH_2), ~5.30 (m, $=CH_2$ and 3-CH=), 6.76 (d of d, $J = 11$ and 18 Hz).[11]

(2) **(3*Z*)-4,5-Dimethylhexa-3,5-dien-1-ol**: yield 76% (unreacted enynol, 5%); ^{13}C NMR ($CDCl_3$) δ 22.1 and 23.2 (both q, 4- and 5-CH_3), 32.6 (t, C_2), 62.8 (t, C_1), 112.8 (t, C_6), 121.3 (d, C_3), 141.5 and 145.1 (both s, C_4 and C_5); ^1H NMR ($CDCl_3$) δ 1.80 (m, $J \approx 1$ Hz, 4- and 5-CH_3), 2.27 (m, 2-CH_2), 2.37 (br s, OH), 3.58 (t, $J = 7$ Hz, OCH_2), 4.67 and 4.90 (both m, $=CH_2$), 5.17 (t, $J = 7$ Hz, CH=).

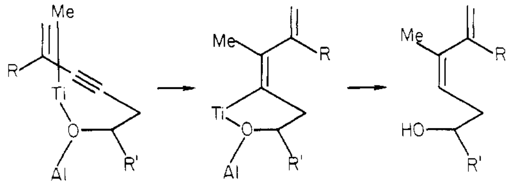
(3) **(3*Z*)-6,7-Dimethylocta-5,7-dien-3-ol**: yield 82% (unreacted enynol, 13%); ^{13}C NMR ($CDCl_3$) δ 10.0 (q, C_1), 22.2 and 23.4 (both q, 6- and 7-CH_3), 29.8 (t, C_4), 36.6 (t, C_2), 73.4 (d, C_3), 112.9 (t, C_8), 121.6 (d, C_5), 141.3 and 145.2 (both s, C_6 and C_7); ^1H NMR ($CDCl_3$) δ 0.95 (t, $J = 7$ Hz, CH_3CH_2), 1.45 (m, CH_3CH_2), 1.78 (m, $J \approx 1$ Hz, 6- and 7-CH_3), 2.21 (t, $J = 7$ Hz, $CH_2CH=$), 3.46 (quint, $J = 6$ Hz, CHO), 4.65 and 4.88 (both m, $=CH_2$), 5.18 (t, $J = 7$ Hz, CH=).

Gas Chromatography. Yields were determined by GLC (HP 5711A FID-HP3380S integrator) via the internal standard technique, using a 3.0 m × 0.32 cm 10% Carbowax 20M column; the yields are corrected for response factors. Samples were isolated for characterization by preparative GLC (HP 5750 TCD), using a 3.0 m × 0.64 cm 20% Carbowax 20M column. Products were also checked for isomeric purity with a 25 m × 0.31 mm Carbowax 20M capillary column (HP 5793 FID).

Spectra. ^1H and ^{13}C NMR spectra were obtained with a Varian FT80A spectrometer. Carbon spectra for all reported compounds were recorded both fully decoupled and with off-resonance decoupling to confirm assignments.

Results and Discussion

The methylation of the enynols proceeds rapidly under mild conditions to give good yields of I. The facility of the reaction is not surprising since $TiCl_4$–$AlMe_3$ and other titanium–organoaluminum reagents are extremely active multiple carbometalation agents in the polymerization of alkenes, dienes, and acetylenes.[12,13] It is interesting to note that there is little, if any, polymerization of the reactive conjugated enyne substrate. We suggest, for reasons previously outlined,[1] that coordination of the substrate via oxygen to the active carbometalation center favors an intramolecular monomethylmetalation over intermolecular oligmerization. Quenching the reaction with $MeOD/D_2O$ leads to >98% deuterium incorporation into I at the 3-carbon. This verifies the presence of an intermediate metal–dienyl species that may be capable of further functionalization; however, to this point we have not been successful in obtaining satisfactory yields of bromides or iodides by quenching carbometalated intermediates with bromine or iodine. The workup of the product dienols is straightforward. Most of the hydrolyzed titanium and aluminum species remain soluble in the acidic aqueous phase from which the product can be extracted readily. Smaller quantities of the products can be isolated by preparative GLC.



R = H, CH_3; R′ = H, C_2H_5

It seemed likely to us that in the enynols the ene group in the 5-position would not undergo a carbometalation since we previously were unable to obtain a carbometalated product with 5-hexen-1-ol under similar conditions.[1] Indeed, the ^{13}C NMR spectra of the three products (I) show no resonances expected for an internal alkyne group (70–90 ppm). As was observed for the $TiCl_4$–$AlMe_3$ mediated methylations of 3-pentyn-1-ol and 3-hexyn-1-ol,[1] no side products arising from subsequent β-hydride elimination or from hydrometalation were observed.

The ^1H NMR spectra show clearly that methylation occurs at the 4-carbon (relative to OH at C_1) in each case since the proton added to the yne functionality occurs as a triplet split by the β-methylene of the OCH_2CH_2 group ($J = 7$ Hz, plus some small long-range coupling to the CH_3 substituent). The NMR and GLC data confirm the presence of a single isomer (≥98%) in each case. As expected, the added H and CH_3 are in the cis configuration. This expected syn addition is confirmed by the position of the ^{13}C substituent-methyl resonances. In all products these methyl groups occur in the range 19.9–23.4 ppm, which shows that the added CH_3 group exists cis to a

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hydrogen in the trisubstituted olefin setting. This correlation seems firm for trisubstituted olefins containing a vicinal methyl and hydrogen.[14]

Good synthetic routes are available for enynols of the type reported in this work: (1) reaction of an enyne with ethylene oxide in liquid ammonia[15] and (2) the palladium-catalyzed coupling of an alkenyl bromide with a terminal homopropargyl alcohol.[10] Thus, the group IV transition-metal–organoalane reagents provide promise for the selective synthesis of substituted dienols that may be useful in the synthesis of selected natural products and as components of Diels–Alder reactions.

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Registry No. $Al(CH_3)_3$, 75-24-1; $TiCl_4$, 7550-45-0; (3*Z*)-4-methylhexa-3,5-dien-1-ol, 925-53-1; (3*Z*)-4,5-dimethylhexa-3,5-dien-1-ol, 87351-54-0; (3*Z*)-6,7-dimethylocta-5,7-dien-3-ol, 87351-55-1; hex-5-en-3-yn-1-ol, 28916-38-3; 5-methylhex-5-en-3-yn-1-ol, 1559-16-6; 7-methyloct-7-en-5-yn-3-ol, 87371-34-4.

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Communications

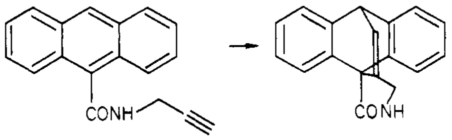
Vibrational Activation. 3. Effect of Solvent Density on the Rate of a Diels–Alder Reaction. Density as an Index of Porosity[1]

Summary: In a set of mixtures of tetraglyme and poly(ethylene glycol) monomethyl ethers, the rates of a Diels–Alder reaction vary linearly with solvent density, which in turn reflects the solvent's porosity because all the solvent molecules are built from the same units. We propose that the reaction goes faster in packed zones than in empty ones because translation of reactant molecules is impeded.

Sir: The vibrational activation theory[2] holds that bond-forming reactions are promoted by vibrational energy in the reactants and that high translational energy is detrimental; i.e., soft collisions are more likely to result in bond formation than are hard ones. High solvent viscosity, then, should promote bond-forming reactions. No conventional theory predicts this effect.[3]

With bimolecular reactions there is a problem in that the reactants cannot find each other if the viscosity is too high. Enzymes solve this problem by providing a microenvironment of high viscosity in which the reaction takes place rapidly, within a bulk medium of low viscosity that permits the reactants and products to come together and separate without hindrance. That is why enzymes need not only the few amino acids required at the active site but also the "ball of wax"—additional long polypeptide chains that are not involved in the chemistry but confer stiffness on the molecule as a whole. This question has aroused much speculation heretofore.[4]

The prediction that viscosity promotes bond-forming reactions was tested for two reactions and verified.[1] Both the Diels–Alder reaction (1) and the Claisen rearrangement of phenyl allyl ether (2) go faster as the solvent viscosity rises. This phenomenon cannot be accounted for by cage, polarity, or polarization effects.



(1)

It was recognized previously that macroscopic viscosity, as measured by the rate of fall of a heavy object, was but a crude measure of the microscopic viscosity experienced by individual molecules. What is needed, according to the theory, is an environment in which, like the cavity of an enzyme, translation is restricted so that collisions between reactants (in our special cases between two reacting sites within a single molecule) are soft rather than hard.

For further investigation, we used as a starting point the observation[1] that adding a small amount of polyethylene to Nujol markedly increased both the viscosity and the rate of reaction 1. It was apparent that there must be (ideally) two rates in this macroscopically homogeneous but microscopically heterogeneous solvent: a normal one for most of the molecules in the Nujol milieu and a high one for those in the polyethylene zones. In the new study, reaction 1 was run at 100 °C in mixtures of tetraglyme and poly(ethylene glycol) monomethyl ethers (PEGE's) of various molecular weights. The compositions of the mixtures were determined by experimentation to find the maximum attainable limits of solubility of the PEGE's of each molecular weight in tetraglyme at 100 °C. The data and results from three separate experiments are presented in Table I.[5]

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[5] The procedure used for the kinetic runs was exactly the same as that used for reaction previously.[1] Tetraglyme was freshly distilled. The PEGE samples, from Aldrich, were used as received. The water content of the PEGE of molecular weight 750, measured by azeotropic distillation with benzene, was <0.3%. Densities and viscosities were measured at 100 °C on pure solvent mixtures, i.e., without reactants or additives. Full-scale NMR spectra of all solvent mixtures, neat, showed no impurities. NMR spectra of product mixtures were spread out at 300 MHz and integrated by planimetry. We thank Dr. Byron Arison and Mr. Herman Flynn For the 300-MHz spectra.

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