Pergamon

Tetrahedron Vol. 51, No. 47, pp. 12939-12954, 1995

0040-4020/95 $9.50+0.00

0040-4020(95)00816-0

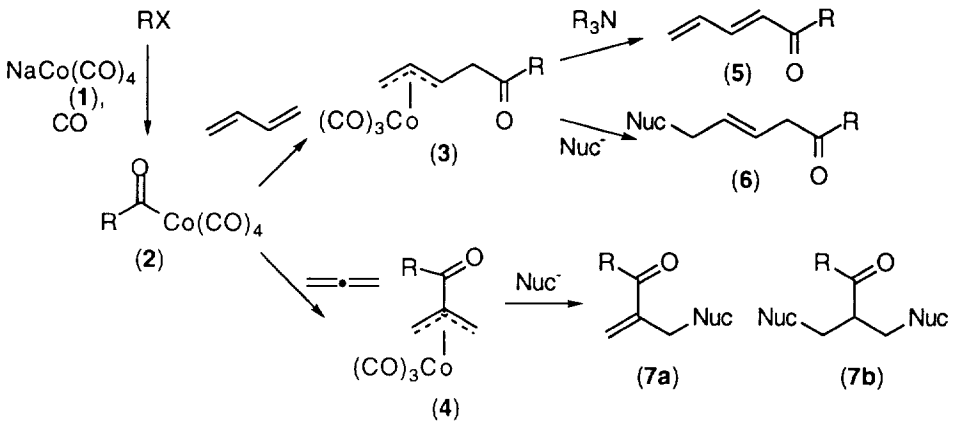
Acylation-Cyclization Of Allenes

Roderick W. Bates* , Thota Rama-Devi and Huei-Huei Ko

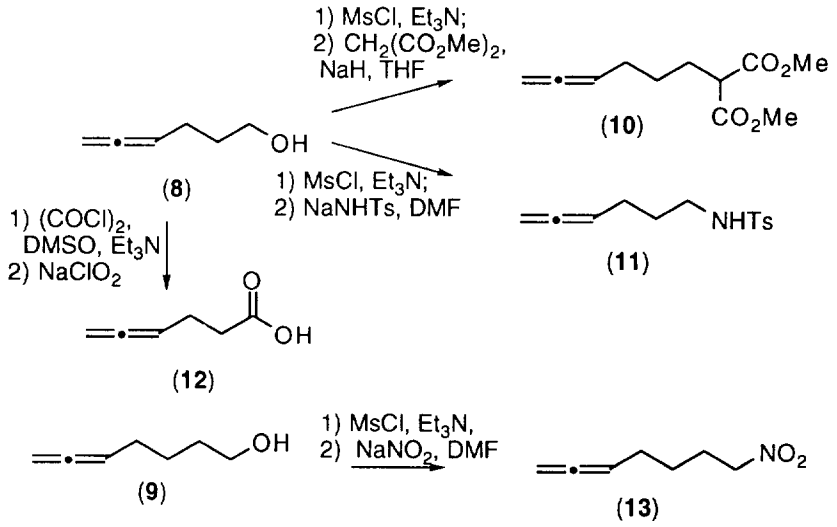
Department of Chemistry, University of North Texas, Denton, TX 76205, USA

Abstract: Allenes bearing a nucleophilic group cyclize on treatment with acyltetracarbonyl cobalt complexes in the presence of mild bases. Various nucleophilic groups and cobalt complexes can be used to give highly functionalized pyrrolidines, cyclopentanes and tetrahydrofurans. Disubstituted allenes may be used in the reaction. 1,3-disubstituted allenes give products with high stereoselectivity.

It has been known for some time that sodium tetracarbonylcobaltate (**1**) could be alkylated by reactive alkyl halides, especially methyl iodide.[1] The resulting alkyl cobalt complexes were unstable, but would undergo facile carbon monoxide insertion to give the corresponding acyl tetracarbonylcobalt complexes (**2**). Such complexes have been shown to react with either alcohols or amines to give esters and amides respectively.[2] The insertion of both 1,3-dienes and 1,2-dienes giving η^3-allylcomplexes, (**3**) and (**4**), has been demonstrated. Heck has shown that the η^3-allyl complexes are converted to 1,3-dienes (**5**) on treatment with mild bases.[3] Hegedus has shown that carbanions stabilized by either two carbonyl[4] or one nitro group[5] will attack the allyl complex to give alkylation products, (**6**) and (**7**), usually in reasonable to good yield considering the number of bonds that are formed in the one pot operation. η^3-Allyl complexes from allenes were found to give the products of both monoalkylation (**7a**) and dialkylation (**7b**).



An intramolecular reaction offers a number of potential advantages over the intermolecular process.[6] To examine this, a number of monosubstituted allenes bearing various tethered potential nucleophiles were synthesized. Malonates and nitro compounds were selected as examples of carbon nucleophiles as their use was well precedented. The use of heteroatom nucleophiles is less well precedented.[7] The use of an alcohol, carboxylate and sulfonamide were examined. All of the required compounds were prepared from an appropriate allenol, (**8**) or (**9**), which were in turn available by the use of the copper modified Mannich conditions developed by Searles and Crabbé.[8]



All of the allenes on treatment with acetyltetracarbonylcobalt and base underwent cyclization to give the expected five-membered rings (**14a-k**). The most efficient were those involving malonate and sulfonamide nucleophiles. Other nucleophilic groups gave distinctly more modest yields. The yield was sensitive to the base employed. For the malonate derivative, a substantial improvement was observed on going from our initial choice, sodium hydride, to milder bases such as potassium carbonate and especially tertiary amines. In no cases were we able to detect any dienes arising from (formal) elimination of $HCo(CO)_3$ or any products arising from direct acylation of the nucleophilic group.

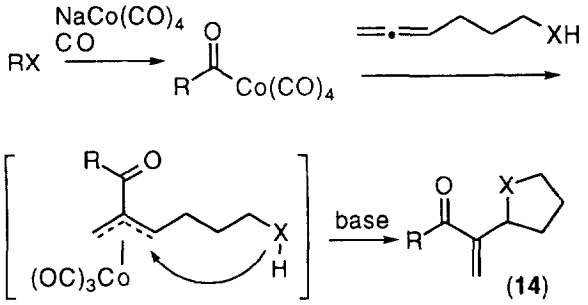
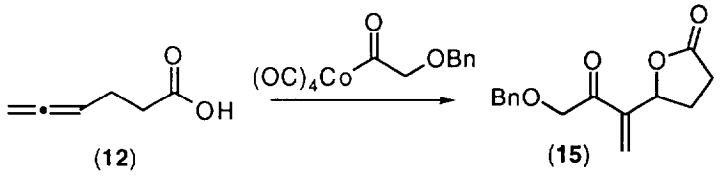


Table 1. Acylation-Cyclization of Monosubstituted Allenes

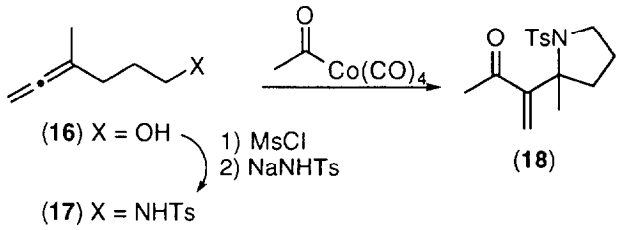
Allene	Product	Nucleophile	alkyl halide	base	yield (%)
(**10**)	(**14a**)	$CH(CO_2Me)_2$	MeI	NaH	49
(**10**)	(**14a**)	$CH(CO_2Me)_2$	MeI	K_2CO_3	78
(**10**)	(**14a**)	$CH(CO_2Me)_2$	MeI	i-Pr_2NEt	92
(**10**)	(**14a**)	$CH(CO_2Me)_2$	MeI	Et_3N	92
(**13**)	(**14b**)	$CHNO_2$	MeI	i-Pr_2NEt	24
(**9**)	(**14c**)	OH	MeI	NaH	30
(**9**)	(**14d**)	OH	$BnOCH_2Cl$	i-Pr_2NEt	25
(**11**)	(**14e**)	NHTs	MeI	NaH	69
(**11**)	(**14f**)	NHTs	$BnOCH_2Cl$	NaH	80
(**11**)	(**14g**)	NHTs	EtO_2CCH_2Br	i-Pr_2NEt	23
(**11**)	(**14h**)	NHTs	$PhCH_2Br$	i-Pr_2NEt	41
(**11**)	(**14i**)	NHTs	$PhthCH_2Br$	i-Pr_2NEt	76
(**11**)	(**14j**)	NHTs	$H_2C{=}CHCH_2Br$	i-Pr_2NEt	27

We found that the reaction is not limited to the use of acetylcobalt complexes. The acyl complexes generated from benzyl chloromethyl ether and bromomethylphthalimide gave comparable results. The use of benzyl bromide, ethyl bromoacetate and allyl bromide gave lower yields. This may be due to the lower reactivity of the halide or, in the case of allyl bromide, preferential formation of an η^3-allyl complex rather than an acyl complex. Similarly, carboxylic acid (**12**) cyclized to give lactone (**15**) in 41% yield.



(**12**) (**15**)

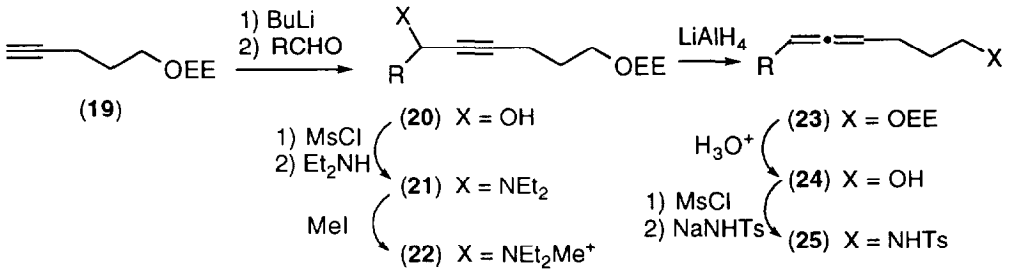
The acylation-cyclization is not limited to monosubstituted allenes. Both kinds of disubstituted allenes, *gem*-disubstituted and 1,3-disubstituted, are reactive towards the acyl cobalt complexes, although trisubstituted allenes give very low yields of acylated products. The *gem*-disubstituted allenol (**16**) was prepared following the procedure of Bertrand[9] and converted into the corresponding sulfonamide (**17**) in the usual way. This underwent smooth and clean cyclization to give the pyrrolidine (**18**) in 70% yield. It should be noted that this cyclization involves the formation of a quaternary center; the cyclization is not therefore sensitive to steric hindrance.



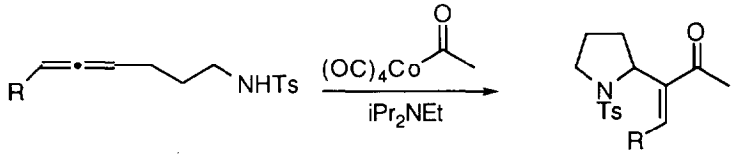
(**16**) X = OH (**18**)

(**17**) X = NHTs

1,3-Disubstituted allenes were prepared following the procedure of Claesson and Olsson.[10,11] EE protected pentynol (**19**) was deprotonated and treated with an aldehyde to give the secondary alcohols (**20a**) and (**20b**). The secondary hydroxyl group was mesylated and treated with diethylamine to give the tertiary amines (**21**). Quaternization with methyl iodide gave the salts (**22**) which underwent clean reduction with lithium aluminum hydride to give the 1,3-disubstituted allenes (**23**), uncontaminated with isomeric alkynes. The protected alcohols were converted, using routine chemistry, into the sulfonamides (**25**).



These sulfonamides (**25**) underwent smooth cyclization on treatment with acetyl tetracarbonylcobalt to give the pyrrolidines (**26**).



(**25a**) R = Me
(**25b**) R = Ph

(**26a**) R = Me
(**26b**) R = Ph

In each case a single isomer of the product was observed. These were determined to be E by nOe difference spectroscopy.[12] It is pertinent to note that the corresponding palladium catalyzed arylation-cyclization results in modest E/Z selectivity.[13] Among the various difference nOe experiments carried out on both (**26a**) and (**26b**), the most striking involves irradiation of the acetyl protons of compound (**26b**), causing enhancement of only the vinyl proton (16%) and virtual disappearance of all other protons (figure).

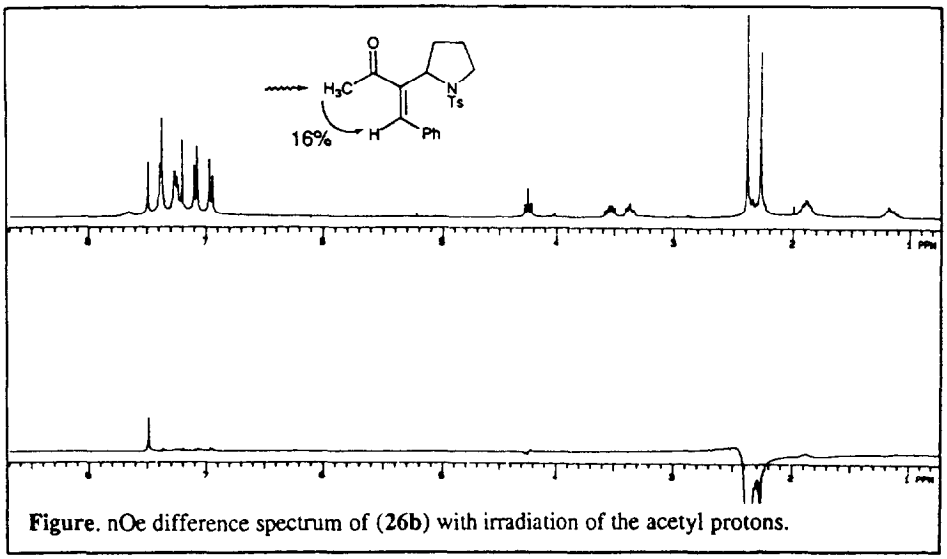
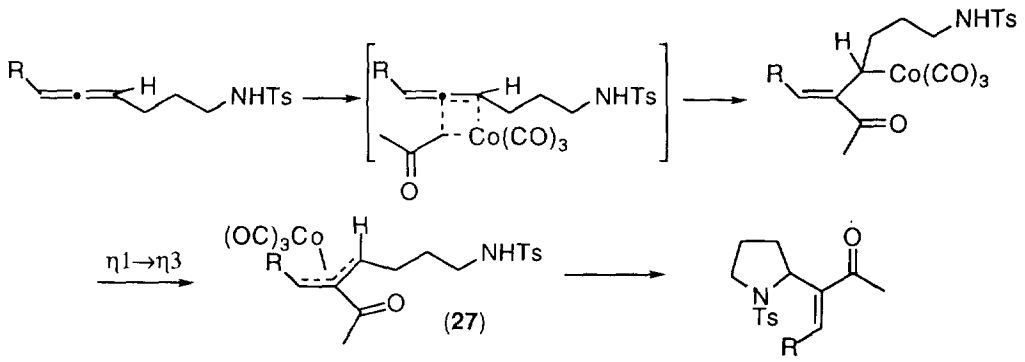


Figure. nOe difference spectrum of (**26b**) with irradiation of the acetyl protons.

The chemical shifts of the vinyl and methyl protons of (**26a**) are consistent with the nOe results. The chemical shift of the methyl protns in E-(**26a**) is 2.25 ppm, upfield of those in Z-(**26a**) which are cis to the carbonyl group. As expected the opposite trend is observable with vinyl protons: E-(**26a**) at 6.8 ppm; Z-(**26a**) upfield at 6.25 ppm.

The accepted mechanism[3,4] for this kind of reaction involves formation of an η^3-allyl cobalt complex. followed by nucleophilic attack (after base addition). As isomerization of the double bond results in a mixture,[12] it is reasonable to suppose that the double bond geometry originates in the geometry of the η^3-allyl complex. The observed E products should therefore arise from the *endo*-complex (**27**). At this stage it is not clear whether this is due to the greater stability of the *endo*-complex over the *exo*-comples, although this is not usually the case. Alternatively, preferential insertion of the double bond proximal to the heteroatoms into the carbon-cobalt bond followed by η^3-allyl complex formation may occur. Heteroatom direction of complexation has been noted in other cases[14]. If this were the case, then the acyl cobalt complex would be expected to approach from the face opposite the terminal substituent, R, leading directly to the *endo*-complex (**27**). Further experiments are in progress to determine the true stereochemical course of the reaction.



Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the ACS, for partial support of this work. We also thank the Robert A. Welch Foundation for financial support.

EXPERIMENTAL

General. All melting points are uncorrected. NMR spectra were obtained on Varian Gemini-200 NMR spectrometer in $CDCl_3$ at 200 MHz (^1H) or 50 MHz (^{13}C). nOe Experiments were obtained at 300 MHz on a Varian Gemini-300. Infrared spectra were obtained on a MIDAC FTIR spectrometer, neat or as nujol mulls. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ. Flash chromatography was carried

out on silica gel: 60 Å, 230-400 Mesh. Dichloromethane was distilled from calcium hydride; ether and tetrahydrofuran was distilled from sodium/ benzophenone; toluene was distilled from sodium. Triethylamine and N-ethyldiisopropylamine were distilled from potassium hydroxide and stored over activated molecular sieves (3Å). Sodium tetracarbonylcobaltate was prepared according to the published procedures[15], titrated gasimetrically[16] and stored as a solution in THF over molecular sieves (3Å) under CO at 0°C.

General procedure: monosubstituted allenes: A mixture of the alkynol (15 mmol), paraformaldehyde (37.5 mmol), anhydrous cuprous iodide (7.5 mmol) and diisopropylethylamine (30 mmol) in anhydrous 1,4 dioxane (30 mL) was heated at reflux for 18 hr under nitrogen. The reaction mixture was cooled and filtered through celite, washing throughly with ether. The ether was evaporated and the 1,4-dioxane was removed by short path distillation (25°C, 5 mmHg).The residue was acidified and extracted thoroughly with ether. The organic layer was washed with brine, dried and concentrated. The allene was purified by distillation undr reduced pressure.

4,5-Hexadienol (9): Yield 35%; ^{1}H NMR δ 5.12 (quin., J = 6.5 Hz, 1H, =CH), 4.67 (dt, J = 6.5, 3.3 Hz, 2H, H_2C=), 3.67 (t, J = 6.8 Hz, 2H, CH_2OH), 2.01-2.18 (m, 2H, $CHCH_2$), 1.65-1.81 (m, 2H, CH_2); ^{13}C NMR δ 208.9 (=C=), 89.9, 75.6, 62.7, 32.3, 24.9; ir (neat) 3354 (OH), 2940, 1958 (=C=), 1651, 1551, 1508, 1437, 1053, 831 cm^{-1}.

5,6-Heptadienol : Yield 60 %; ^{1}H NMR δ 5.06 (quin., J = 6.7 Hz, 1H, =CH), 4.63 (dt, J = 6.5, 3.3 Hz, 2H, H_2C=), 3.60 (t, J = 6.2 Hz, 2H, CH_2OH), 2.22 (brs, 1H, OH), 1.91-2.08 (m, 2H, =CHC<u>H</u>2), 1.38-1.65 (m, 4H, CH_2); ^{13}C NMR δ 209.0 (=C=), 90.2, 75.2, 63.0, 32.6, 28.4, 25.9; ir (neat) 3362 (OH), 1956 (=C=), 1698, 1454, 1269, 1123, 1067, 843 cm^{-1}.

General Procedure for the Preparation of Mesylates: Triethylamine (6.5 mmol) and mesyl chloride (6.5 mmol) were added to a solution of the allenol (5 mmol) in dichloromethane (25 mL) at 0°C. The mixture was stirred for 2 h, diluted with dichloromethane,then washed with saturated sodium bicarbonate solution and brine. The organic layer was dried and concentrated. The mesylate was used without further purification.

General procedure for the Preparation of Malonates: Sodium hydride (6.5 mmol) was added to a solution of dimethyl malonate (13 mmol) in THF (30 mL). The mixture was stirred under nitrogen for 30 min, then added via cannula to a solution of the mesylate (5 mmol) in THF (10mL). The mixture was heated at reflux for 18 h, allowed to cool, quenched with saturated ammonium chloride and extracted with ether. The organic

layer was washed with brine, dried, concentrated and purified by flash chromatography (silica gel/ 20% ether-hexane).

Methyl 2-methoxycarbonyl-6,7-octadienoate (10): Yield 80 %; ^{1}H NMR δ 5.04 (p., J = 7.1 Hz, 1H, =CH), 4.63 (dt, J = 7.1, 3.5 Hz, 2H, CH_2=), 3.71 (s, 6H, OCH_3), 3.34 (t, J = 7.8 Hz, 1H, C<u>H</u>$(CO_2CH_3)_2$), 1.97 (m, 4H, =CHC<u>H</u>$_2$, C<u>H</u>$_2$CH), 1.41 (p., J = 7.2 Hz, 2H, CH_2); ^{13}C NMR δ 208.9 (=C=), 170.2 (C=O), 89.6, 75.5 (C=), 52.9, 51.9, 28.7, 28.2, 27.1, ir (neat) 2959, 2874, 1956 (=C=), 1738 (C=O), 1443, 1346, 1152, 1069, 851 cm^{-1}; *m/z* 181 (M^+ - OCH_3), 153 (M^+ - CO_2CH_3), 145 ($CH_2CH(CO_2CH_3)_2^+$): calc. anal. for $C_{11}H_{16}O_4$: C 62.25, H 7.6, found: C 62.34, H 7.44.

General procedure for the preparation of sulfonamides: Sodium hydride (6.5 mmole of a 60% suspension) was added to a solution of p-toluenesulfonamide (5 mmol) in DMF (10 mL) at 0°C. After stirring at room temperature for 30 min, a solution of the mesylate (5 mmol) in DMF (10 mL) was added at room temperature. The mixture was heated at 130°C under nitrogen for 18 h. The reaction mixture was cooled and quenched with saturated ammonium chloride solution. The DMF was removed by distillation. The residue was taken up in ether, washed with brine, dried, concentrated, and purified by flash chromatography (silica gel/ 30 % ether-hexane) to give the sulfonamide.

N-5,6-hexadienyl-p-toluene sulfonamide (11): 80 % yield; ^{1}H NMR δ 7.75 (d, J = 8.3 Hz, 2H, Ar), 5.02 (m, 2H, =CH, NH), 4.99 (dt, J = 6.5, 3.3 Hz 2H, CH_2=), 4.61 (q, J = 3.3 Hz, 2H, $CHCH_2$), 2.42 (s, 3H, CH_3), 1.98 (m, 2H, CH_2N), 1.57 (p., J = 7.3 Hz, 2H, CH_2); ^{13}C NMR δ 208.9 (=C=), 143.8, 137.4, 130.2, 127, 89.3, 75.8, 43.0, 29.2, 25.5, 22.0; ir (neat) 3289 (NH), 2940, 2876, 1958 (=C=), 1605, 1443, 1327, 1155, 1086, 823 cm^{-1}; *m/z* 250 (M^+ - H), 155 (Ts^+), 96 (M^+ - Ts), 91 ($C_7H_7^+$);

4,5-hexadienoic acid. (12) Oxalyl chloride (2.23 mL, 25.5 mmol) was added dropwise to a solution of dimethyl sulfoxide (3.62 mL, 51.0 mmol) in dichloromethane (50 mL) at -78°C under nitrogen. The mixture was stirred at -78°C for 15 min. and a solution of the alcohol (**8**) (1.0 g, 10.2 mmol) in dichloromethane (20 mL) was added dropwise. After stirring for 30 min, triethylamine (14.2 mL, 102 mmol) was added and the mixture was allowed it to come to room temperature over a period of 1 h. The reaction mixture was diluted with dichloromethane, washed with water, 10% HCl, and brine, dried and concentrated. The crude 4,5-hexadienal[17] was used directly in the next step.

A solution of sodium chlorite (674 mg, 5.97 mmol) and potassium dihydrogen phosphate (811 mg, 5.97 mmol) in water (5 mL) was added to a solution of 4,5 hexadienal (441 mg, 4.59 mmol) and 2-methyl-2-butene (3.25 mL, 30.7 mmol) in t-butanol (6 mL) at 0°C. The yellow mixture was stirred overnight. The

volatiles were removed under aspirator pressure and the residue was diluted with water. The aqueous solution was washed with hexane, then acidified and extracted with ethyl acetate. The organic layer was dried and concentrated to give the acid (360 mg, 70%).[18] ^{1}H NMR δ 8.82 (brs, 1H, COOH), 5.14 (p., J = 6.5 Hz, 1H, = CH), 4.69 (dt, J = 6.5, 3.3 Hz, 2H, =CH_2), 2.44 (t, J = 7.0 Hz, 2H, CH_2COOH), 2.28 (m, 2H, CH_2); ir (neat) 3516 (br, COOH), 1958 (=C=), 1705 (CO), 1410, 1261, 843 cm^{-1}.

1-Nitro-5,6-heptadiene (13): A solution of sodium nitrite (3.6 mmol) and the mesylate (3 mmol) in dry dimethylformamide (10 mL) was stirred at 0°C to RT for 1 h. The solvent was removed by distillation under reduced pressure. The residue was taken up in ether, washed with brine, dried and concentrated. The oily residue was purified by flash chromatography (silica gel, 5 % ether-hexane) to give the nitro allene. Yield 59 %; ^{1}H NMR δ 5.08 (p., J = 6.0 Hz, 1H, =CH), 4.69 (dt, J = 7, 3.5 Hz, 2H, =CH_2), 4.39 (t, J = 6.9 Hz, 2H, CH_2NO_2), 2.07 (m, 4H, =CH$\underline{CH_2}$, $\underline{CH_2}CH_2NO_2$), 1.53 (p., J = 8.2 Hz, 2H); ^{13}C NMR δ 209 (=C=), 89.3, 75.9, 75.8, 27.7, 27.2, 25.9; ir (neat) 2945, 1962 (=C=), 1553 (NO_2), 1440, 1383, 1099, 856 cm^{-1}; *m/z*: 67 ($CH_2CCHCH_2CH_2^+$); calc. anal. for $C_7H_{11}NO_2$: C 59.56, H 7.85, found: C 59.52, H 8.03.

Generation and cyclization of acyl cobalt complexes: The alkyl halide (1 eq) was added to a stirred solution of sodium tetracarbonylcobaltate (1eq) in THF (ca 0.1M) at 0°C under an atmosphere of carbon monoxide.The mixture was stirred at room temperature for 30 min (methyl iodide) or for 60 min (other halides). The allene (1 eq) in THF (0.1 M) was added via cannula at 0°C, under an atmosphere of nitrogen. Stirring was continued for 5 h. The base (1 eq) was added and the reaction mixture was stirred under carbon monoxide for 18 h (if the base is diisopropylethylamine) or for 1 h (sodium hydride). Residual cobalt carbonyl complexes were decomposed by addition of ethereal iodine until the color of iodine became permanent and no further gas evolution was observed. The reaction mixture was diluted with ether, washed with aqueous ammonium chloride, aqueous sodium thiosulfate solution and brine. The organic layer was dried and concentrated. The residue was purified by flash chromatography (silica gel, 20 - 30% ether-hexane) to afford the cyclized products.

Cyclopentane (14a): ^{1}H NMR δ 6.05 (s, 1H, =CH_2), 5.75 (s, 1H, =CH_2), 3.95 (t, J = 8.9 Hz, 1H, CH), 3.55 (s, 3H, OCH_3), 3.72 (s, 3H, OCH_3), 2.51 (m, 1H, $\underline{CH_2}$CH), 2.31 (s, 3H, $COCH_3$), 2.14 (m, 1H, $\underline{CH_2}$CH), 1.58-2.01 (m, 4H, CH_2); ^{13}C NMR δ 199.8, 172.9, 171.5, 149.9 (CH_2=$\underline{C}$CO), 125.2 (CH_2=), 64.6 ($\underline{C}(CO_2CH_3)_2$), 53.1, 52.5 (C-O), 45.3 (CO$\underline{C}H_3$), 35.5, 32.1, 26.7, 23.7 ; ir (neat) 2959, 2888, 1726 (C=O),

1680 (C=O), 1597 (C=C), 1443, 1371, 1271, 1159, 935 cm^{-1}; *m/z*: 254 (M^+), 211 (M^+ - Ac), 59 ($CO_2CH_3^+$); calc. anal. for $C_{13}H_{18}O_5$: C 61.41, H 6.92, found: C 61.23, H 7.13.

Cyclopentane (14b): ^1H NMR δ 6.13 (d, *J* = 0.5 Hz, 1H, $=CH_2$), 5.81 (d, *J* = 1.6 Hz, 1H, $=CH_2$), 5.18 (dt, J = 2.1, 6.5 Hz, 1H, $CHNO_2$), 3.37 (br dt., *J* = 12.5, 6.5 Hz, 1H, CHC=), 2.37 (s, 3H, $COCH_3$), 1.68-2.28 (m, 4H, CH_2); ^{13}C NMR δ 199.6 (C=O), 145.9, 126.7 (C=C), 90.5 (CN), 46.6, 30.4, 27.1, 26.3, 23.1; ir (neat) 2959, 2878, 1676, 1632, 1545, 1449, 1369, 1307, 1267, 1159, 972, 875 cm^{-1}; *m/z*: 168 (M^+ - CH_3), 137 (M^+ - NO_2); calc. anal. for $C_9H_{13}NO_3$: C 59.00, H 7.15 found: C 59.05, H 6.96.

Tetrahydrofuran (14c): ^1H NMR δ 6.09 (d, *J* = 1.8 Hz, 1H, $=CH_2$), 6.08 (d, *J* = 1.8 Hz, 1H, $=CH_2$), 4.72 (t, *J* = 7.6 Hz, 1H, HCO), 3.97 (q, *J* = 6.9 Hz, 1H, CH_2O), 3.82 (q, *J* = 6.9 Hz,1H, CH_2O), 2.35 (s, 3H, CH_3CO), 2.28 (m, 1H, $C\underline{H}_2CHO$), 1.89 (m, 2H, CH_2CH_2O), 1.51 (m, 1H, CH_2CHO); ^{13}C NMR δ 199.7 (C=O), 150.8 , 124.0 (C=C), 68.8, 33.0, 26.8, 26.1; ir (neat) 3229, 2957, 2880, 1667 (C=O), 1580 (C=C), 1381, 1281, 1076, 941 cm^{-1}; *m/z*: 140 (M^+), 125 (M^+ - CH_3), 111(M^+ - HCHO), 97 (M^+ - Ac), 71 (M^+ - CCH_2Ac).; calc. anal. for $C_8H_{12}O_2$: C 68.55, H 8.63, found C 68.29, H 8.43.

Tetrahydrofuran (14d): ^1H NMR δ 7.33 (m, 5H, Ph), 6.06 (d, *J* = 1.6 Hz, 1H, =CH2), 5.96 (s, 1H, $=CH_2$), 4.71 (t, *J* = 7.1 Hz, 1H, CHO), 4.59 (s, 2H, $COCH_2$), 4.46 (s, 2H, CH_2Ph), 3.93 (dt, *J* = 6.6, 7.9 Hz, 1H, CH_2O), 3.80 (dt, *J* = 7.9, 7.0 Hz, 1H, CH_2O), 2.29 (dq, *J* = 12.1, 7.2 Hz, 1H, CH_2CHO), 1.85 (m, 2H, $C\underline{H}_2CH_2O$), 1.51 (dq, *J* = 12.2, 7.2 Hz, 1H, CH_2CHO); ^{13}C NMR δ 197.7 (C=O), 148.0, 137.8, 128.9, 128.5, 127.9, 127.3, 123.1, 76.9, 73.8, 72.6, 68.8, 32.8, 26.0 ; ir (neat) 2976, 2883, 1692, 1454, 1391, 1265, 1134, 1026 cm^{-1}; *m/z*: 155 (M^+- Bn), 140 (M^+ - PhCHO), 107 (OBn^+), 97 (M^+ - $BnOCH_2CO$), 91 ($C_7H_7^+$), 77 (Ph^+); calc. anal. for $C_{15}H_{18}O_3$: C 73.15, H 7.37, found: C 72.90, H 7.35.

Pyrrolidine (14e): ^1H NMR δ 7.69 (d, *J* = 8.2 Hz, 2H, Ar), 7.31 (d, *J* = 8.2 Hz, 2H, Ar), 6.27 (d, *J* = 1.5 Hz, 1H, =CH2), 6.24 (s, 1H, $=CH_2$), 4.60 (dd, *J* = 5.0, 3.3 Hz, 1H, CHN), 3.55 (m, 1H, CH_2N), 3.13 (m, 1H, CH_2N), 2.42 (s, 3H, $COCH_3$), 2.36 (s, 3H, $ArCH_3$), 1.42-1.78 (m, 4H, CH_2); ^{13}C NMR δ 199.4 (CO), 149.7 144.0, 134.5, 130.2, 128.1, 127.1, 59.5, 49.8, 33.3, 26.8, 23.9, 21.9; ir (neat) 2932, 2859, 1670 (C=O), 1630 (C=C), 1561, 1454, 1369, 1342,1155, 1084, 1003, 839 cm^{-1}; *m/z*: 224 ($C_4H_7NTs^+$), 155 (Ts^+), 138 (M^+ -Ts), 95 (M^+ - Ac-Ts), 91 ($C_7H_7^+$); calc anal. for $C_{15}H_{19}NO_3S$: C 61.41, H 6.53, found C 61.28, H 6.68.

Pyrrolidine (14f): ^1H NMR δ 7.70 (d, J = 9.2 Hz, 2H, Ar), 7.35 (m, 7H, Ar), 6.26 (d, *J* = 1.2 Hz, 1H, $=CH_2$), 6.16 (s, 1H, $=CH_2$), 4.61 (m, 2H, OCH_2), 4.53 (s, 2H, CH_2Ph), 3.55 (m, 1H, CH_2N), 3.15 (m, 1H, CH_2N), 2.42 (s, 3H, $ArCH_3$), 1.50-1.90 (m, 4H, CH_2); ^{13}C NMR δ 197.4 (C=O), 147.4, 144.1, 137.8, 134.5, 130.3,

128.9, 128.5, 128.1, 126.0, 73.9, 72.6, 59.6, 49.8, 33.4, 23.9, 22.0; ir (neat) 2962, 2881, 1687, 1597, 1501, 1444, 1156, 1006, 911, 732, 650 cm^{-1}; *m/z* 278 (M^+ - CH_2OBn), 224 ($C_4H_7NTs^+$), 155 (Ts+), 91 ($C_7H_7^+$).

Pyrrolidine (14g): ^1H NMR δ 7.71 (d, *J* = 8.2 Hz, 2H, Ar), 7.32 (d, *J* = 8.1 Hz, 2H, Ar), 6.36 (s, 1H, $=CH_2$), 6.21 (s, 1H, $=CH_2$), 4.62 (brd, *J* = 6.9 Hz, 1H, NCH), 4.19 (q, *J* = 7.0 Hz, 2H, OCH_2), 3.86 (d, *J* = 16 Hz, 1H, $COCH_2CO$), 3.67 (d, *J* = 16 Hz, 1H, $COCH_2CO$), 3.55 (m, 1H, CH_2N), 3.15 (m, 1H, CH_2N), 2.43 (s, 3H, $PhCH_3$), 1.5-1.8 (m, 4H, CH_2), 1.26 (t, *J* = 7.2 Hz, 3H, $CH_2C\underline{H}_3$); ^{13}C NMR δ 199.9 (CO), 167.7 (CO_2CH_3), 149.1, 144.1, 134.4, 130.3, 128.9, 127.9, 127.8 (Ph, vinyl), 61.9, 59.5, 49.8, 46.1, 33.0, 23.9, 22.0, 14.5; ir (neat) 2980, 2974, 1742 (COO), 1678 (C=O), 1634, 1597 (C=C), 1493, 1449, 1346, 1157, 1093, 951 cm^{-1}; *m/z*: 292 (M^+ - TsH), 224 ($C_4H_7NTs^+$) 155 (Ts^+), 138 (M^+ - Ts - CO_2Et), 91 ($C_7H_7^+$); calc anal. for $C_{18}H_{23}NO_5S$: C 59.16, H 6.34, found C 59.42, H 6.47.

Pyrrolidine (14h): ^1H NMR δ 7.70 (d, *J* = 7.3Hz, 2H, Ar), 7.35 (m, 7H, Ar), 6.35 (s, 1H, $=CH_2$), 6.31 (s, 1H, $=CH_2$), 4.63 (m, 1H, NHTs), 3.99 (d, *J* = 15.8 Hz, 1H, CH_2Ph), 4.09 (d, *J* = 15.8 Hz, 1H, CH_2Ph), 3.52 (m, 1H, CH_2NTs), 3.51 (dt, *J* = 9.4, 7.6 Hz, 1H, CH_2NTs), 2.41 (s, 3H, $ArCH_3$), 1.36 - 1.75 (m, 4H, CH_2CH_2); ^{13}C NMR δ 198.4 , 148.6, 143.5, 134.3, 133.9, 129.6, 129.3, 128.5, 127.5, 126.8, 126.2 , 59.2, 49.2, 45.1, 32.6, 23.3, 21.4: ir (neat) 3028, 2978, 2874, 1672 (CO), 1632, 1597 (C=C), 1495, 1452, 1400, 1159, 1094, 1036, 816, 734, 665 cm^{-1}; *m/z*: 369 (M^+), 224 ($C_4H_7NTs^+$). 214 (M^+ - Ts), 155 (Ts^+), 91 ($C_7H_7^+$); calc. anal for $C_{21}H_{23}NO_3S$: C 68.27 H 6.27 N 3.79; found: C 68.21 H 6.07 N 3.56.

Pyrrolidine (14i): ^1H NMR δ 7.85 (m, 2H, Ar), 7.72 (m, 4H, Ar), 7.31 (d, *J* = 8.1Hz, 2H, Ar), 6.45 (s, 1H, $=CH_2$), 6.39 (s, 1H, $=CH_2$), 4.96 (d, *J* = 17.5 Hz, 1H, $COCH_2$), 4.82 (d, *J* = 17.5 Hz, 1H, $COCH_2$), 4.55 (m, 1H, CHNTs), 3.58 (m, 1H, CH_2NTs), 3.17 (m, 1H, CH_2NTs), 2.39 (s, 3H, $ArCH_3$), 1.48 - 1.77 (m, 4H, CH_2CH_2); ^{13}C NMR δ 191.8 , 167.7 , 146.8, 143.6, 134.0, 132.0, 129.7, 127.6, 126.6, 123.4, 59.1, 49.3, 43.8, 32.6, 23.4, 21.4; ir (neat) 2926, 2849, 1715 (NCO), 1689 (CCO), 1620, 1595, 1190,1157, 1090, 1043, 947, 715, 657 cm^{-1}; *m/z*: 439 (M^+ + H), 283 (M^+ - Ts), 224 ($C_4H_7NTs^+$) ; calc. anal for $C_{23}H_{22}O_5N_2S$: C 63.00 H 5.06 N 6.39; found: C 62.83, H 4.94 N 6.27.

Pyrrolidine (14j): ^1H NMR δ 7.71 (d, *J* = 8.2 Hz, 2H, Ph), 7.31 (d, *J* = 9.0 Hz, 2H, Ph), 5.80 (m, 1H, =CH), 5.14 (m, 2H, $CH=C\underline{H}_2$), 5.06 (s, 1H, $=CH_2$), 4.91 (s, 1H, $=CH_2$), 4.10 (t, *J* = 5.9 Hz, 1H, CHN), 3.21-3.52 (m, 2H, CH_2N), 2.87 (dd, *J* = 16, 6.1 Hz, 1H, $COCH_2$), 2.73 (dd, *J* = 16, 7.2 Hz, 1H, COCH2), 2.43 (s, 3H, CH_3), 1.55-1.91 (m, 4H, CH_2); ^{13}C NMR δ 198.7, 143.7, 136.4, 135.5, 130.0, 129.0, 117.1, 112.2, 64.5, 49.6, 37.4, 32.0, 24.3, 21.9 ; ir (neat) 3081, 2988, 1647, 1603, 1445, 1354, 1167, 1096, 1015, 907, 824, 654 cm^{-1}; *m/z*:

250 (M^+ - COAllyl), 224 ($C_4H_7NTs^+$), 155 (Ts^+), 91 ($C_7H_7^+$), calc anal. for $C_{17}H_{21}NO_3S$: C 63.92, H 6.63, found: C 64.14, H 7.00.

Lactone (15): ^1H NMR δ 7.35 (s, 5H, Ph), 6.14 (s, 2H, = CH_2), 5.29 (t, *J* = 7.1 Hz, 1H, CHO), 4.62 (s, 2H, $COCH_2O$), 4.49 (s, 2H, $PhCH_2$), 2.62 (m, 3H, CH_2CO_2,C<u>H</u>$_2$CH), 1.89 (m, 1H, C<u>H</u>$_2$CH); ^{13}C NMR δ 196.6 , 177.1, 144.9, 137.4, 129.0, 128.6, 124.9, 77.8, 73.9, 72.4, 29.2, 28.5; ir (neat) 2957, 2932, 2859, 1779 (C=O), 1695(C=O), 1454 (C=C), 1178, 1148, 1025, 996, 913, 739, 670 cm^{-1}; *m/z*: 168 (M^+ - Bn), 139 (M^+ - $BnOCH_2$), 91 ($C_7H_7^+$); calc. anal. for $C_{15}H_{16}O_4$: C 69.22, H 6.2, found: C 69.29, H 5.94.

N-4-methyl-4,5-hexadienyl toluenesulfonamide (17) was prepared from 4-methyl-4,5-hexadienol according to the previous procedure: Yield 40%. ^1H NMR δ 7.76 (d, *J* = 8.2 Hz, 2H, Ar), 7.31 (d, *J* =8.2 Hz, 2H, Ar), 4.56 (m, 3H, H_2C=, NH), 2.96 (q, *J* = 6.8 Hz, 2H, CH_2NH), 2.42 (s, 3H, $ArCH_3$), 1.82-1.98 (m, 2H, =CCH_2), 1.50 - 1.68 (m, 5H, =CCH_3, CH_2); ^{13}C NMR δ 206, 144, 137.6, 130.1, 127.6, 97.8, 75.1, 43.2, 30.6, 27.7, 21.9, 19.1; ir (neat) 3283 (NH), 2924, 1960 (=C=), 1656, 1599, 1323, 1157, 1094, 814, 660 cm^{-1}; *m/z* 251 (M^+ - O), 155 (Ts^+), 91 ($C_7H_7^+$); calc. anal. for $C_{15}H_{16}O_4$: C 63.37, H 7.22, found: C 63.12, H 7.22.

Pyrrolidine (18): ^1H NMR δ 7.61 (d, *J* = 8.2 Hz, 2H, Ar), 7.21 (d, *J* = 8.2 Hz, 2H, Ar), 6.14 (s, 2H, CH_2=), 6.08 (s, 2H, CH_2=), 3.57 (dt, *J* = 6.0 , 2.8 Hz, 1H, CH_2N), 3.26 (dt, *J* = 7.1, 1.8 Hz, CH_2N), 2.85 (q, *J* = 6.8 Hz, 1H C<u>H</u>$_2$CHN), 2.32 (s, 3H, $ArCH_3$), 2.28 (s, 3H, $COCH_3$), 1.91 (q, *J* = 6.8 Hz, 1H, C<u>H</u>$_2$CHN), 1.55 (s, 3H, CCH_3), 1.59 - 1.67 (m, 2H, C<u>H</u>$_2$$CH_2N$); ^{13}C NMR δ 200 (C=O), 152.7, 143.3, 139.0, 129.8, 127.5, 126.7, 69.7, 49.9, 35.1, 29.0, 25.3, 23.0, 21.9 ; ir (neat) 2951, 2874, 1680, 1589, 1451, 1333, 1155, 1094, 816, 670 cm^{-1}; *m/z*: 292 (M^+ - Me), 238 (M^+ - CCH_2Ac). 155 (Ts^+), 152 (M^+ - Ts), 91 $C_7H_7^+$); calc. anal. for $C_{16}H_{21}NSO_3$: C 62.52, H 6.89, found C 62.52, H 7.00.

General Procedure:1,3 disubstituted allenes: *n*-Butyllithium (22 mmole, of a *ca* 2.4 M solution in hexane) was added under nitrogen at -78°C, to a solution of the EE-protected alkynol (20 mmol) in THF (80 mL) .The temperature was allowed to rise to -20°C over 1 h. A solution of the aldehyde (30 mmol) in THF (30 mL) was added and stirring was continued for 1 h at -20°C. The mixture was allowed to come to 0°C. Saturated ammmonium chloride solution was added and the mixture was extracted with ether. The organic layer was washed with brine, dried and concentrated. The residue was purified by flash chromatography (silica gel/ 35 % ether-hexane) to give the alcohol.

1-(2-ethoxyethyl)-4-heptyn-6-ol (20a): 93% yield. ^1H NMR δ 4.66 (q, *J* = 5.6 Hz, 1H, OCHO), 4.32-4.45 (m, 1H, CHC≡C), 3.31-3.64 (m, 4H, CH_2O), 2.98 (brs, 1H, OH), 2.27 (dt , *J* = 1.8, 6.6 Hz, 2H, C≡CCH_2),

1.72 (p., J = 6.6 Hz, 2H, CH_2), 1.38 (d, J = 6.8 Hz, 3H, $CHCH_3$), 1.24 (d, J = 5.6 Hz, 3H, CH_3CHC), 1.15 (t, J = 7.5 Hz, 3H, OCH_2CH_3); ^{13}C NMR δ 99.9 , 83.8, 83.3 , 63.8, 61.1, 58.6 , 29.2, 25.1, 20.2, 15.9, 15.7 ; ir (neat) 3418 (OH), 2984, 2942, 2882, 1655, 1452, 1381, 1331, 947 cm^{-1}; *m/z* 185 (M^+ - CH_3), 111 (M^+ - OEE), 73 (EE); calc. anal. for $C_{11}H_{20}O_3$: C 65.97, H 10.07, found: C 66.04, H 9.89.

1-(2-ethoxyethyl)-6-phenyl-4-hexyn-6-ol (20b): Yield 56%; ^1H NMR δ 7.52 (dd, J = 2.0, 8.0 Hz, 2H, Ph), 7.34 (m, 3H, Ph), 5.42 (s, 1H, PhCH), 4.66 (q, J = 5.4 Hz, 1H, $OCHOCH_3$), 3.35-3.71 (m, 4H, CH_2O), 2.99 (brs, 1H, OH) 2.37 (dt, J = 2.0, 7.1 Hz, 2H, $C{\equiv}CCH_2$), 1.78 (p., J = 6.5 Hz, 2H, $CH_2CH_2CH_2$), 1.27 (d, J = 6.0 Hz, 3H, $CHCH_3$), 1.16 (t, J = 7.0 Hz, 3H, CH_2CH_3); ^{13}C NMR δ 141.9 (PhC),123.9, 128.6, 127.1 (Ph), 100.0 (OCO), 87.0, 81.1 (C≡C), 65.1, 64.0 (CO), 61.3 (C≡CC), 29.3, 20.3, 16.2, 15.7; ir (neat) 3426 (OH), 2986, 2940, 1497, 1452, 1381, 1339, 1127 cm^{-1}; *m/z* 216 (M^+ - C_2H_5OH), 172 (M^+ - OH - EE), 131 (M^+ - $(CH_2)_3OEE$), 103 (CH_2OEE), 73 (EE^+); calc. anal. for $C_{16}H_{22}O_3$: C 73.25, H 8.45, found: C 73.46, H 8.37.

General procedure for the preparation of tertiary amines: A solution of diethylamine (20 mmol) and the mesylate (10 mmole, prepared according to the general procedure) in dichloromethane (30 mL) was stirred under nitrogen at room temperature for 24 h. The volatiles were removed under reduced pressure. The residue was purified by flash chromatography (silica gel/ 10 % ether-hexane) to give the tertiary amine.

N,N-diethyl-1-(2-ethoxyethyl)-4-heptyl-6-amine (21a): Yield 80%; ^1H NMR δ 4.60 (q, J = 5.6 Hz, 1H, $OCHCH_3$), 3.35-3.65 (m, 5H, CH_2O, CHN), 2.55 (dq, J = 7.3, 12.8 Hz, 2H, NCH_2), 2.33 (dq, J = 6.9, 14.5 Hz, 2H, NCH_2), 2.22 (dt, J = 6.8, 12.4 Hz, 2H, $C{\equiv}CCH_2$), 1.66 (p., J = 6.8 Hz, 2H, CH_2CH_2CH2), 1.22 (d, J = 5.3 Hz, 3H, $OCHCH_3$), 1.19 (d, J = 6.4 Hz, 3H, $CHCH_3$), 1.11 (t, J = 6.8 Hz, 3H, OCH_2CH_3), 0.96 (t, J = 7.5 Hz, 6H, NCH_2CH_3); ^{13}C NMR δ 100.3 (OCO), 83.4, 80.3 (C≡C), 64.0, 61.2, 48.2, 44.9, 29.8, 20.8, 20.2, 15.8, 15.7, 14.1 ; ir (neat) 2984, 1451, 1383, 1341, 1310, 1182, 1130, 951, 868, 735 cm^{-1}

N,N-diethyl-1-(2-ethoxyethyl)-6-phenyl-4-hexyl-6-amine (21b): Yield 75 %; ^1H NMR δ 7.61 (d, J = 7.61 Hz, 2H, Ph), 7.30 (m, 3H, Ph), 4.80 (s, 1H, PhCH), 4.69 (q, J = 5.3 Hz, 1H, $CHCH_3$), 4.68 (q, J = 5.3 Hz, 1H, $CHCH_3$), 3.41-3.82 (m, 4H, CH_2O), 2.31-2.62 (m, 6H, NCH_2, $C{\equiv}CCH_2$), 1.84 (p., J = 6.9 Hz, 2H, $CH_2CH_2CH_2$), 1.31 (d, J = 5.3 Hz, 3H, $CHCH_3$), 1.31 (d, J = 5.4 Hz, 3H, $CHCH_3$), 1.19 (t, J = 6.9 Hz, 3H, OCH_2CH_3), 1.19 (t, J = 7.03, 3H, OCH_2CH_3), 1.03 (t, J = 7.2 Hz, 3H, NCH_2CH_3), 1.02 (t, J = 7.2 Hz, 3H, NCH_2CH_3); ^{13}C NMR δ 140.9, 128.8, 128.7, 128.3, 127.5 (Ph), 100.2, 87.2, 76.9 (C≡C), 64.2, 61.4, 57.0, 44.9 , 30.0, 20.4, 16.2, 15.8, 14.1; ir (neat) 2969, 2884, 1961 (C≡C), 1607, 1499, 1457, 1388, 1340, 1195, 1133, 1052, 952, 867, 779 cm^{-1}.

General Procedure For The Synthesis Of 1,3-Disubstituted Allenes: Methyl iodide (14 mmol) was added at 0°C to a solution of the amine (7 mmol) in acetone (14 mL). The mixture was stirred at room temperature for 24 h under nitrogen. The volatiles were removed under reduced pressure. The residue was washed twice with ether to remove the non polar impurities. The crude quaternary salt was suspended in THF (35 mL). Lithium aluminium hydride (8.4 mmol) was added to the mixture under nitrogen at 0°C.The mixture was heated at reflux for 3 h, then cooled and quenched by the addition of water. The solid was removed by filtration, washing thoroughly with ether. The filtrate was evaporated and the residue was purified by flash chromatography (silica gel/ 10 % ether-hexane) to give the allene.

1-(2-ethoxyethyl)-4,5-heptadiene (23a): Yield 70%; ^{1}H NMR δ 5.02 (m, 2H, =CH), 4.63 (q, J = 5.4 Hz, 1H, C<u>H</u>CH$_3$), 3.33-3.68 (m, 4H, CH$_2$O), 1.92-2.08 (m, 2H, =CHC<u>H</u>$_2$), 1.60 (m, 5H, CH$_2$, C<u>H</u>$_3$CH=), 1.25 (d, J = 5.4 Hz, 3H, CHC<u>H</u>$_3$), 1.16 (t, J = 7.1 Hz, 3H, CH$_2$C<u>H</u>$_3$); ^{13}C NMR δ 205.2 (=C=), 99.9 (OCO), 90.1, 86.3 (C=), 64.8, 61.1 , 29.7, 25.8, 20.3, 15.7, 14.9 ; ir (neat) 2984, 2861, 1977 (=C=), 1452, 1373, 1331, 1142, 1055, 959, 870 cm^{-1}; m/z 169 (M$^+$ - CH$_3$), 139 (M$^+$ - OC$_2$H$_5$), 111 (M$^+$ - EE,) 95 (M$^+$ - OEE), 67 (CH$_3$CH=C=C=CHCH$_2^+$).

1-(2-ethoxyethyl)-6-phenyl-4,5-hexadiene (23b): 60% yield; ^{1}H NMR δ 7.2 (m, 5H, Ph), 6.14 (dt., J = 6.4, 3.2 Hz, 1H, PhC<u>H</u>), 5.60 (q, J = 6.4 Hz, 1H, =CH), 4.66 (q, J = 5.3 Hz, 1H, C<u>H</u>CH$_3$), 3.41-3.72 (m, 4H, CH$_2$O), 2.22 (dq, J = 3.2, 7.3 Hz, 2H, =CHC<u>H</u>$_2$), 1.76 (p., J = 6.5 Hz, 2H, CH$_2$), 1.29 (d, J = 5.4 Hz, 3H, CHC<u>H</u>$_3$), 1.19 (t, J = 7.1 Hz, 3H, CH$_2$C<u>H</u>$_3$), 1.18 (t, J = 1.18 Hz, 3H, CH$_2$C<u>H</u>$_3$); ^{13}C NMR δ 205.7 (=C=), 135.4, 129.0, 128.9, 128.8, 127.1, 100.1, 95.5, 95.0, 65.0, 64.9, 61.3, 61.2 , 29.7, 25.9, 20.4, 15.8 ; ir (neat) 2974, 2932, 1952 (=C=), 1601, 1503, 1458, 1373, 956, 889, 777, 704 cm^{-1}; *m/z* 246 (M$^+$), 173 (M$^+$ - EE), 157 (M$^+$ - OEE), 129 (M$^+$ - CH$_2$CH$_2$OEE), 89 (OEE$^+$), 77 (Ph$^+$), 73 (EE$^+$); calc. anal. for C$_{16}$H$_{22}$O$_2$: C 78.01, H 9.00, found: C 78.09, H 8.88.

Hydrolysis of ethoxyethyl ethers: 10% aqueous HCl (1 mL) was added to a solution of the EE-protected allenol (4 mmol) in methanol (20 mL) at O°C. The mixture was stirred for 1 h at room temperature, then neutralized with triethylamine. The volatiles were removed on under reduced pressure and the residue was purified by flash chromatography (silica gel/ 25 % ether-hexane) to give the pure alcohol.

4,5-heptadienol (24a): Yield 81 %; ^{1}H NMR δ 5.06 (m, 2H, =CH), 3.66 (t, J = 6.7 Hz, 2H, CH$_2$OH), 1.98-2.23 (m, 2H, =CHC<u>H</u>$_2$), 1.89 (brs, 1H, OH), 1.67 (m, 5H, CH$_2$, C<u>H</u>$_3$CH=); ^{13}C NMR δ 205.2, 90.1, 86.4 , 62.7 (CO), 32.4, 25.5, 14.9; ir (neat) 3337 (OH), 2940, 1956 (=C=), 1682, 1433, 1061, 870 cm^{-1}; *m/z* 81 (M$^+$ -

CH_2OH), 68 (M^+ - CH_3CHO), 67 (EE^+), 66 (M^+ - C_2H_5OH), calc. anal. for $C_7H_{12}O$: C 74.95, H 10.78, found: C 74.75, H 10.57.

6-Phenyl-4,5-hexadienol (24b): Yield 72 %; ^1H NMR δ 7.33 (m, 4H, Ph), 7.22 (m, 1H, Ph), 6.19 (dt, *J* = 6.5, 3.0 Hz, 1H, PhC<u>H</u>), 5.63 (p., *J* = 6.5, 12.9 Hz, 1H, =CH), 3.69 (t, *J* = 6.6 Hz, 2H, C<u>H</u>$_2$OH), 2.38 (brs, 1H, OH), 2.24 (ddt, *J* = 3.0, 7.0, 7.1 Hz, 2H, =CHC<u>H</u>$_2$), 1.77 (p., *J* = 6.5 Hz, 2H, $CH_2C\underline{H}_2CH_2$); ^{13}C NMR δ 205.6, 135.4, 129.1, 127.2, 127.1 , 95.6, 95.0, 62.6, 32.4, 25.5; ir (neat) 3348 (OH), 2931, 1944 (=C=), 1600, 1495, 1453, 1057, 876, 780 cm^{-1}.

N-5,6-heptadienyl-p-toluene sulfonamide (25a): Yield 80 %; ^1H NMR δ 7.75 (d, *J* = 8.3 Hz, 2H, Ar), 7.29 (d, *J* = 8.1 Hz, 2H, Ar), 5.02 (m, 2H, CH =, NH), 2.94 (q, *J* = 6.8 Hz, 2H, CH_2N), 2.41 (s, 3H, ArC<u>H</u>$_3$), 1.94 (m, 2H, =CHC<u>H</u>$_2$), 1.58 (m, 5H, CH_3, CH_2); ^{13}C NMR δ 205.2, 143.8, 137.5, 130.1, 127.6, 89.5, 86.7 (C=), 43.0, 29.2, 26.1, 21.9, 14.9; ir (neat) 3288 (NH), 2921, 1977 (=C=), 1595, 1449, 1314, 1152, 1096, 826 cm^{-1}; *m/z* 155 (Ts^+), 110 (M^+ - Ts), 106 ($CH_2CH_2NHTs^+$), 91 ($C_7H_7^+$); calc. anal. for $C_{14}H_{19}NO_2S$: C 63.37, H 7.22, found: C 63.51, H 6.94.

N-6-phenyl-4,5-hexadienyl-p-toluene sulfonamide (25b): Yield 80 %; ^1H NMR δ 7.72 (d, *J* = 8.3 Hz, 2H, Ph), 7.25 (m, 7H, Ph), 6.09 (dt., *J* = 6.3, 3.0 Hz, 1H, PhCH), 5.48 (q, *J* = 6.3 Hz, 1H, =CH), 4.93 (t, *J* = 6.2 Hz, 1H, NH), 2.97 (q, *J* = 7 Hz, 2H, CH_2N), 2.38 (s, 3H, $PhCH_3$), 2.10 (m, 2H, =CHC<u>H</u>$_2$), 1.63 (p., *J* = 7.2 Hz, 2H, $CH_2C\underline{H}_2CH_2$); ^{13}C NMR δ 205.6, 143.8, 137.5, 135.1, 130.2, 129.1, 127.6, 127.3, 127.1, 95.8, 94.3, 43.1, 29.3, 26.1, 21.9; ir (neat) 3286 (NH), 2939, 1964 (=C=), 1594, 1498, 1318, 1158, 1090 cm^{-1}.

Pyrrolidine (26a): Yield 59%; M.p. 84-86°C; ^1H NMR δ 7.67 (d, *J* = 8.3 Hz, 2H, Ar), 7.30 (d, *J* = 8.3 Hz, 2H, Ar), 6.80 (q, *J* = 7.2 Hz, 1H, HC=), 4.63 (t, *J* = 7.9 Hz, NCH), 3.54 (m, 2H, CH_2N), 2.42 (s, 3H, $ArCH_3$), 2.25 (s, 3H, $COCH_3$), 2.06 (d, *J* = 7.2 Hz, 3H, $=CHCH_3$), 1.62-2.01 (m, 4H, CH_2), ^{13}C NMR δ 199.3, 143.7, 142.9, 141.0, 135.3, 130.1, 130.0, 128.0 , 56.8, 50.2, 32.9, 26.9, 25.7, 21.9, 15.0; ir (neat) 2953, 2924, 2254, 1664 (C=O), 1606 (C=C), 1348, 1255, 1158, 1091, 993, 820, 721, 652 cm^{-1};*m/z*: 224 (M^+ - $C(CHCH_3)Ac$), 152 (M^+ - Ts), 91 ($C_7H_7^+$), 43 (Ac^+); calc. anal. for $C_{16}H_{21}NO_3S$: C 62.52, H 6.89, found: C 62.30, H 6.66.

Pyrrolidine (26b): Yield 35%; M.p. 108-110°C; ^1H NMR δ 7.55 (s, 1H, =CH), 7.0-7.5 (m, 9H, Ar), 4.32 (t, *J* = 8.5 Hz, 1H, CHN), 3.61 (dt, *J* = 5.9, 10.5 Hz, 1H, CH<u>H</u>N), 3.43 (ddd, *J* = 3.4, 7.8, 10.5 Hz, 1H, CH<u>H</u>N), 2.45 (s, 3H, Ar<u>C</u>H$_3$), 2.25 (s, 3H, $COCH_3$), 1.87-2.48 (m, 3H), 1.23 (m, 1H); ^{13}C NMR δ 200.2, 143.4, 142.8, 140.6, 135.7, 134.7, 129.8, 129.3, 128.9, 128.8, 127.8 , 57.4, 50.9, 33.5, 29.4, 28.2, 25.6, 21.9, ir (neat) 2885, 1676, 1466, 1377, 1345, 1237, 1155, 990, 821, 790 cm^{-1}; *m/z*: 214 (M^+ - Ts), 185 ($TsNCH_2^+$), 155 (Ts^+), 91 ($C_7H_7^+$); calc. anal. for $C_{21}H_{23}NO_3S$: C 68.27, H 6.27, found: C 68.02, H 6.06.

Footnotes

* Present address: 853 Taksin 21, Taksin Road, Thonburi, Bangkok 10600, Thailand.

[1] Kemmitt, R.D.W., Russel, D.R., in Comprehensive Organometallic Chemistry , Vol 5, Wilkinson, G., Stone, F.G.A., Eds, Pergamon, Oxford, 1982, page 48; Heck, R.F., Adv. Organometallic Chem., 1966, 4, 243.

[2] Heck, R.F., Breslow, D.S., *J.Am.Chem.Soc.*, **1963**, *85*, 2779.

[3] Heck, R.F., *J.Am.Chem.Soc.*, **1963**, *85*, 3381, 3383.

[4] Hegedus, L.S., Inoue, Y., *J.Am.Chem.Soc.*, **1982**, *104*, 4917.

[5] Hegedus, L.S., Perry, R.J., *J.Org.Chem.*, **1984**, *49*, 2570.

[6] For a preliminary report of this work, see Bates. R.W., Rama Devi, T., *Tetrahedron Lett.*, **1995**, *36*, 509.

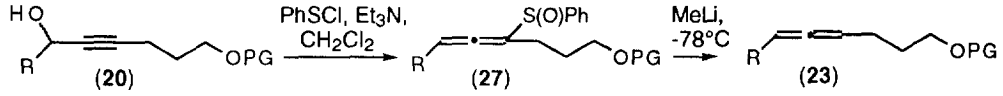
[7] Gambarotta, S., Alper, H., *J.Org.Chem.*, **1981**, *46*, 2142.

[8] Searles, S., Li, Y., Nassim, B., Lopes, M.-T.R., Tran, P.T., Crabbé, P., *JCS Perkin I*, **1984**, 747.

[9] Ragonnet, B., Santelli, M., Bertrand, M., *Bull.Soc.Chim.France*, **1973**, 3119.

[10] Claesson, A., Olsson, L.-I., *J.Am.Chem.Soc.*, **1979**, *101*, 7302.

[11] The 1,3-disubstituted allenes can also be prepared by the method of Neef, G., Eder, U., Seeger, A., *Tetrahedron Lett.*, **1980**, *21*, 903. The propargylic alcohol (**20**) is treated with PhSCl (1.1 eq) and triethylamine (1.2eq) in dichloromethane at -78°C and allowed to warm slowly to room temperature to give the sulfoxide (**27**) as a mixture of diastereomers (62%). The sulfoxide is taken up in THF and treated with methyl lithium (4eq) at -78°C for 20 minutes, then quenched with ammonium chloride and purified in the usual way to give the allene (**23**) (72%).



(**20**) (**27**) (**23**)

[12] If the iodine work-up is left for too long, mixtures of the E and Z isomers are obtained.

[13] Davies, I.W., Scopes, D.I.C., Gallagher, T., *Synlett*, **1993**, 85.

[14] Whitesides, T.H., Slaven, R.W., Calabrese, J.C., *Inorg. Chem.*, **1974**, *13*, 1895; Koot, W.-J., Hiemstra, H., Speckamp, W.N., *J.Chem.Soc.Chem.Comm.*, **1993**, 156.

[15] Edgell, W.F., Lyford, John, IV, *Inorg. Chem.*, **1970**, *9*, 1932.

[16] Sternberg, H.W., Wender, I., Orchin, M., *Anal. Chem.*, **1952**, *24*, 175.

[17] Walkup, R.D., Kim, S.W., *J. Org. Chem.*, **1994**, *59*, 3433

[18] Walkup, R.D., Guan, L., Mosher, M.D., Kim, S.W., Kim, Y.S., *Synlett.*, **1993**, 88

(*Received in USA* 30 *April* 1995; *revised* 20 *September* 1995; *accepted* 21 *September* 1995)