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The Chemistry of Organoborates. 9.[1] A Regiospecific and Highly Stereoselective Construction of Trisubstituted αβ-Unsaturated Ketones, Tetrasubstituted αβ-Unsaturated Ketones and Specifically Protected 1,3-Diketones from Alkynyltrialkylborates

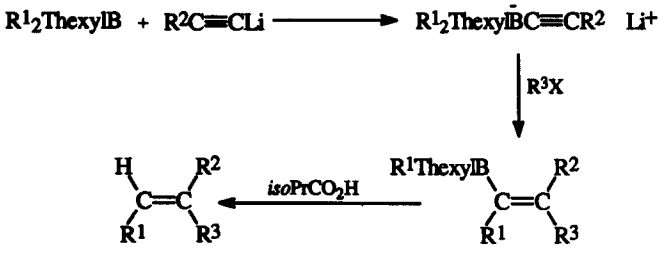
Andrew Pelter* and M. Eamon Colclough

Department of Chemistry, University of Wales, Swansea, Singleton Park, Swansea SA2 8PP, UK.

Abstract. Lithium alkynyltrialkylborates react with dioxolanium fluorosulphonates in a highly stereoselective fashion such that the dioxolanium group and the migrating group are on the same side of the new alkene intermediate. Hydrolysis of the intermediate yields Z-trisubstituted αβ-unsaturated ketones in which all three substituents have different origins and can be independently varied. Oxidation of the intermediates gives β-ketoacetals, which are regiospecifically protected 1,3-diketones. If the initial intermediates are allowed to stand, then another migration occurs and tetra-substituted αβ-unsaturated ketones result.

1. INTRODUCTION

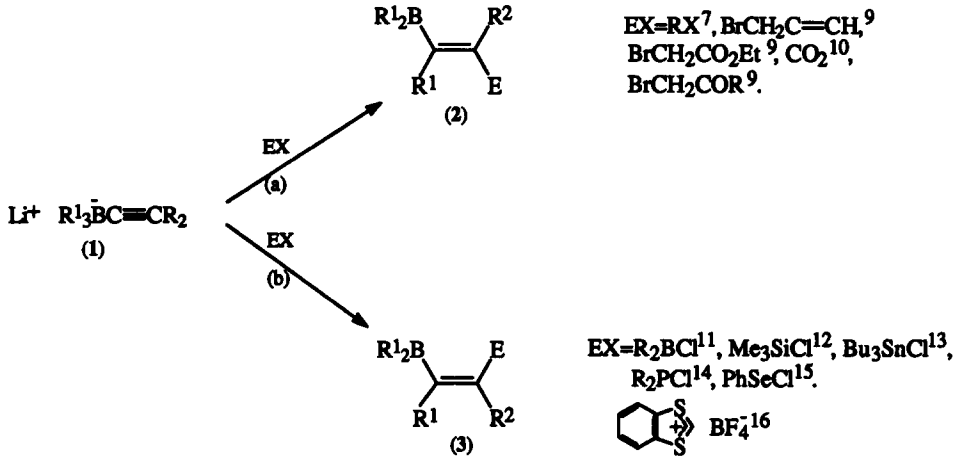
The stereoselective production of simple trisubstituted alkenes has been a major synthetic challenge which has been met in a variety of ways.[2] These can be divided into controlled elimination reactions on a preformed carbon skeleton, an example being the reaction due to Cornforth,[3] and those which involve stereocontrolled assemblage of the constituent parts of the alkene. The latter can be exemplified by carbocupration of an alkyne followed by alkylation[4] or by the reaction of a sterospecifically substituted haloalkene[5,6] with an organocuprate. In this context we introduced[7] the sequence shown in Scheme 1.



Scheme 1

In this process, an intramolecular version of which has been used in syntheses of *Z*-[8a] and *E*-γ -bisabolene[8b], the product trisubstituted alkene is assembled in a regiospecific and stereoselective fashion from three separate units; a triorganylborane, an alkyne and an alkylating agent. When the alkylating agent is propargyl bromide, an α-bromoketone or an α-bromoester, the reaction is stereospecific.[9]

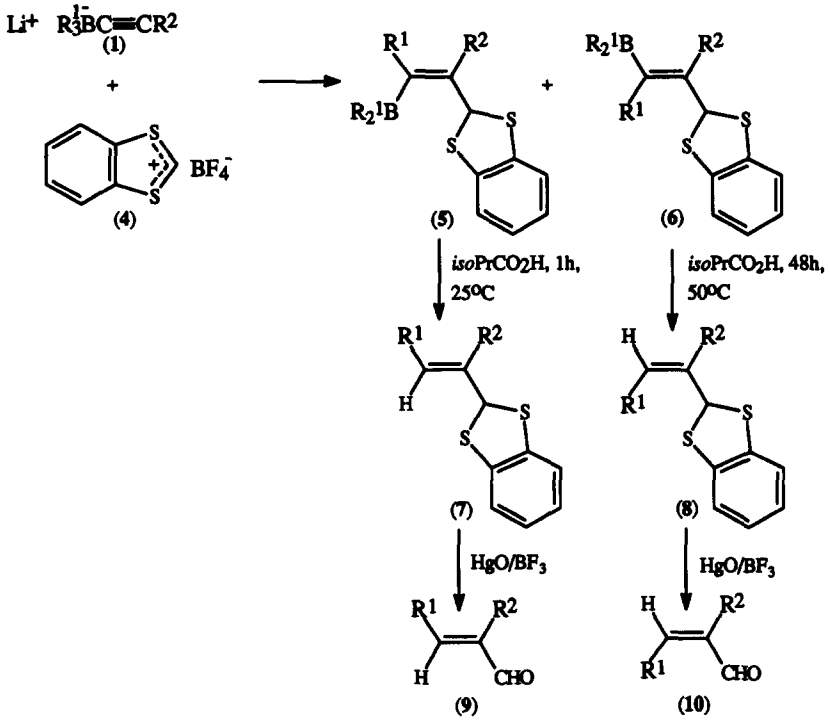
The 1,2-migration reactions of alkynyltrialkylborates (1) fall into two stereochemical categories. In the first, the migrating group and the electrophile finish on the *same* side of the double bond to give (2) (Scheme 2, path a). The second category refers to those reactions in which the migrating group finishes on the opposite side to the electrophile, as in (3) (Scheme 2, path b).



Scheme 2

The situation with regard to the stereoselective synthesis of trisubstituted αβ-unsaturated ketones is far less defined, despite the importance of such compounds. One general method is the Friedel-Crafts acylation of stereochemically defined alkenylsilanes, from which the major product is drawn from reaction with retention of configuration.[17,18] We have made available[16] a method, shown in Scheme 3, in which the whole carbon framework is produced in a stereoselective fashion.

The readily available[19] salt (4) reacts with (1) in good yields to give mixtures of (5) and (6) in ratios varying from 100:0 (R^1 = Ph) to, at the lowest, 83:17 R^1 = *n*-hexyl, (R^2 = *n*-pentyl). The mixtures are readily handled due to the great difference in the ease of hydroloysis of (5) and (6), so that pure (7) and (8) are readily available, and from them the corresponding pure trisubstituted αβ-unsaturated aldehydes (9) and (10). The reaction is surprising as salt (4) behaves more like a metal halide than like a carbon electrophile (Scheme 2) in that the major isomer is always that one in which the migrating group and the electrophile are on *opposite* sides of the double bond. For the production of αβ-unsaturated ketones, Scheme 3 has the disadvantages that the required 2-alkylbenzo-1,3-dithiolium salts are not readily available, in contrast to the corresponding anions,[20] and that deprotection of the highly substituted dithioacetals could present difficulties.



Scheme 3

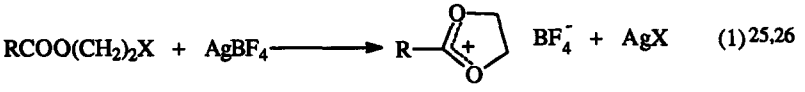
Direct acylation of alkynyltrialkylborates gives mixtures of stereoisomers. The one with the boron and acyl group on the same side of the double bond undergoes a rapid second migration.[21] In the presence of pyridine, it is the pyridine ring that is attacked, specifically at C4.[22]

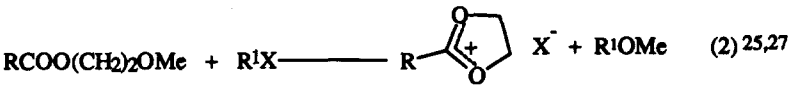
We considered that an alternative would be the reactions of 2-alkyl-1,3-dioxolanium salts (**11**) with alkynylborates (**1**). The salts are readily available by a variety of processes and the product acetals would be readily deprotected. Hence we undertook to investigate this approach to αβ-unsaturated trisubstituted ketones.[23]

2. REACTIONS OF 2-ALKYL-1,3-DIOXOLANIUM SALTS WITH ALKYNYLTRIALKYLBORATES

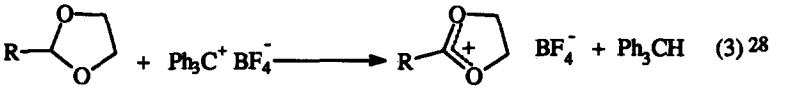
2.1. The preparation of 2-alkyl-1,3-dioxolanium salts (11).

Three general methods for the preparation of (**11**) are summarised in equations (1) to (3).



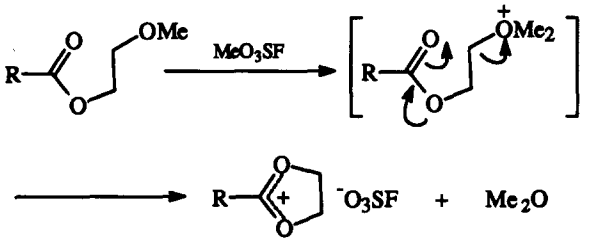


(2)[25,27]



(3)[28]

Process (2), with $R^1X = MeO_3S.F^*$ represented a cheap, efficient reaction, which proceeds in greater than 90% yields.[27] We therefore decided to use this reaction, shown in more detail in Scheme 4 to prepare (11)



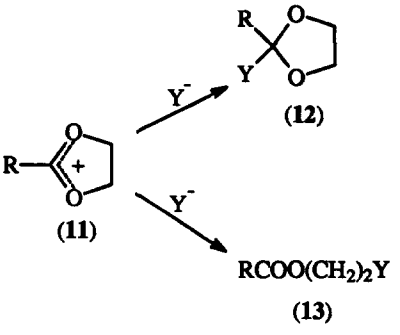
(11)

Scheme 4

To make (11), neat reagents are used in a 1:1 ratio. The by-product dimethyl ether is released to leave essentially pure (11). Salts (11) are readily soluble in dichloromethane and glyme and may be further purified by recrystallisation at -78°C from the former solvent.

2.2. The reactions of dioxolanium salts with electrophiles.

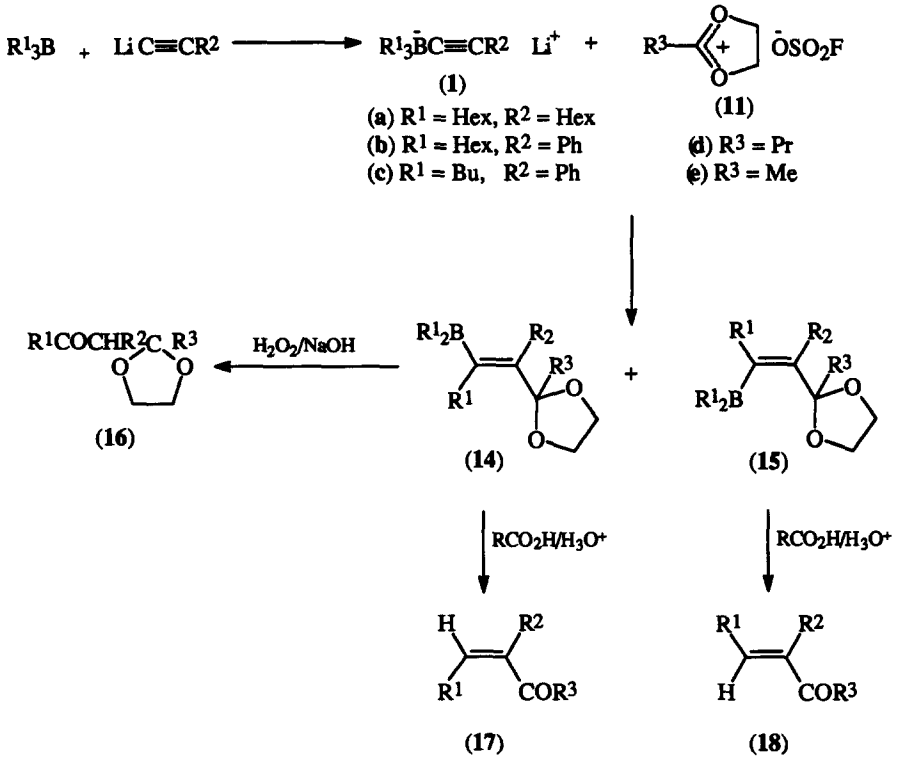
Salts (11) are ambidentate cations[24] which may react at C-2 or C-4 to give (12) or (13) respectively (Scheme 5).[28,29]



Scheme 5

* $MeO_3S.F$ is no longer commercially available, but $Me_3O^+BF_4^-$ or $Et_3O^+BF_4^-$ are excellent alternatives.[25]

Under kinetic control a nucleophile would be expected to react at C-2, the atom of greatest electron deficiency, to give (12). In general this is true for negatively charged nucleophiles since ion combination generally has a low activation energy.[30] Therefore it appeared that there was a good chance of successfully carrying out the reactions shown in Scheme 6, and particularly to test the stereoselectivity of the reaction leading to (14) and (15).



(1)
(a) R^1 = Hex, R^2 = Hex
(b) R^1 = Hex, R^2 = Ph
(c) R^1 = Bu, R^2 = Ph

(11)
(d) R^3 = Pr
(e) R^3 = Me

Scheme 6

If the anticipated attack by (1) on C-2 of (11) occurs, then the products would be (14) and/or (15), both of which, on oxidation in basic conditions, should yield the β-ketodioxolanes (16). Complete hydrolysis of (14) and (15) should proceed to remove both the dialkylboron and dioxolane moieties to give ketones (17) and/or (18) in a very direct fashion.

2.3. Results and discussion.

The lithium alkynyltrialkylborates (1a-c) were made by published procedures[7,31] as solutions in glyme, which were added to a glyme solution of either (11d) or (11e) at -78°C. The reaction mixtures were then subjected to one of three different work-up procedures.

2.3.1 Protonolysis. Dry, degassed *iso*butyric acid was used to hydrolyse (14) and/or (15), after which the reaction mixture was stirred with aqueous hydrochloric acid to produce (17) and/or (18). For simpler isolation, the reaction mixture was oxidised[6] so that all organoboranes were converted to boric acid.

Following this procedure, *Z*-αβ-unsaturated ketones (**17**) were isolated in fair to reasonable yields (Table 1). In only one case was any *E*-alkene (**18cd**) isolated, and that in a yield of only 2.8%. Thus *the carbon skeleton assemblage is either stereospecific or overwhelmingly stereoselective.* Of great interest is that the stereoselectivity fits in with almost all other carbon electrophiles (Scheme 2) and *is opposite to that of the corresponding reaction with benzodithiolium tetrafluoroborate (4).*

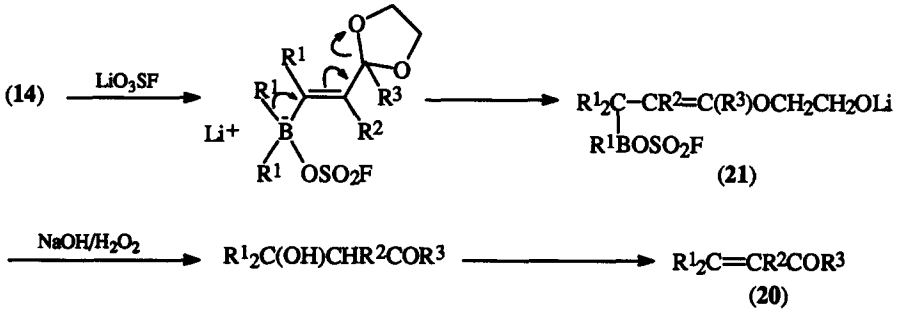
In addition to (**17**), the reaction always gave some (**19**) and (**20**).

$$R^1CH=CHR^2 \qquad (19) \qquad\qquad R^1{}_2C=CR^2COR^3 \qquad (20)$$

The protonation of alkynyltrialkylborates (**1**) is a fast and efficient process[31] from which (**19**) arises (equation 4) despite careful washing of (**11**). However, (**19**) is very readily separated from the product ketone (**17**).

$$(1) \xrightarrow{HX} R^1{}_2BCR^1=CHR^2 \xrightarrow{RCO_2H} \underset{(19)}{R^1CH=CHR^2} \qquad (4)$$

Compounds (**20**) are double migration products arising from (**14**) by attack by the weakly nucleophilic lithium fluorosulphonate, as in Scheme 7, to give (**21**), which on oxidation and elimination yields (**20**).



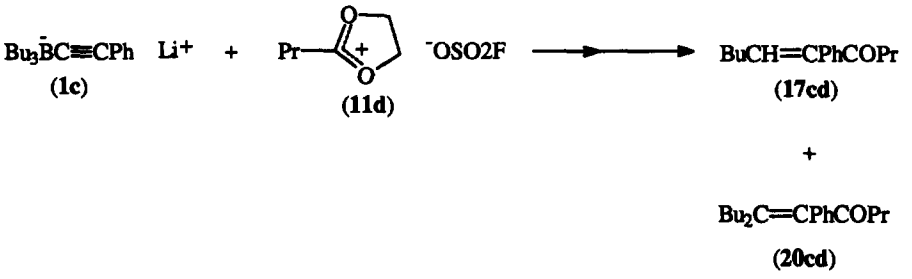
Scheme 7

Table 1. Products from the reactions of (**1**) and (**11**) followed by protonolysis.

Experiment	R^1	R^2	R^3	Yields (%)[a] (17)	(19)	(20)
1	Hex	Hex	Pr	60	10	8
2	Hex	Hex	Me	57	14	10
3	Hex	Ph	Me	50	13	16
4	Bu	Ph	Pr	70	7	18

[a] Yields are of isolated, characterised products except for experiment 4, which is a g.c. yield. All yields are based on starting alkyne (Scheme 6).

The standard conditions for experiments 1-3 consisted of mixing (**1**) and (**11**) at -78°C followed by stirring at -78°C for 3h., after which *iso*butyric acid was added at the same temperature. However, when these conditions were used in experiment 4, the yields of (**17cd**)* and (**29cd**) were 42% and 33% respectively (equation 5), a ratio of only 1.27:1.



(5)

Therefore, the production of (**17cd**) and (**20cd**) was monitored as a function of time, with the results shown in Table 2.

Table 2. Yields and ratios of (**17cd**) and (**20cd**) as a function of time.

Time	Yields (%)[a]		Ratios
	(17cd)	(20cd)	(17cd) : (20cd)
45	67	24	2.79
168	40	30	1.33
288	47	41	1.15
540	42	39	1.08
1080[b]	30	44	0.68

[a] G.c. yield based on initial alkyne. [b] The last 540 min. were at 25°C.

Therefore, the reaction of (**11c**) and (**11d**) was carried out for a 30 min. period to give the result reported in Table 1, experiment 4, which gave a ratio of (**17cd**) : (**20cd**) of 3.88. It seems likely that yields of (**17**) in all these reactions would benefit from as brief a reaction time as possible.

The initial reaction mixtures were examined and the presence of dioxolanes (**14**) was shown by the presence in the ^{1}H nmr of triplets at δ5.41 and 5.80 (**14cd**) and δ5.45 and 5.14(**14ad**) together with broad peaks at δ3.8 in each case. When the reaction mixture was stirred with hydrochloric acid in ethanol the higher field signals disappeared and the ^{1}H nmr spectra of isomerically pure (**17cd**) and (**17ad**) were left.

The stereochemistry of our products was established by a mixture of i.r. and nmr data, which are given in Table 3.

* Products are denoted as a combination of the letters of the reactants as in equation 5.

Table 3. Spectral data for trisubstituted αβ-unsaturated ketones.

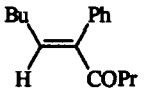
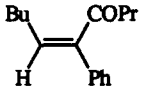
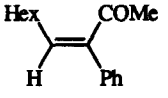
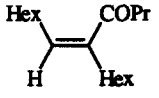
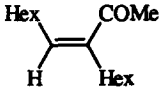
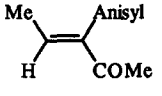
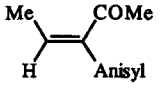
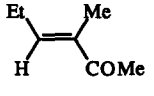
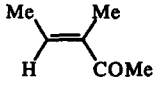
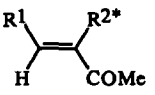
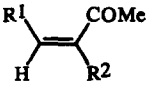
Entry	Compound	Stereochem.	ν_{max}(C=O)cm^{-1}	δ_H H-C=C	δ_C C=C	Ref.
1.	 (18cd)	*E*	1670	6.91	148.07 139.46	-
2.	 (17cd)	*Z*	1690	5.86	143.42 135.14	-
3.	 (17be)	*Z*	1695	5.89	143.29 136.28	-
4.	 (17ad)	*Z*	1695	5.48	141.82 134.27	-
5.	 (17ae)	*Z*	1695	5.52	141.55 135.85	-
6.		*E*	1665	7.0	- -	32
7.		*Z*	1685	5.97	- -	32
8.		*E*	1670	6.46	- -	33
9.		*E*	1655	6.46	- -	33

Table 3. (continued).

Entry	Compound	Stereochem.	ν_{max}(C=O)cm^{-1}	δ_H H-C=C	δ_C C=C	Ref.
10.		*E*	1655	6.2	- -	18
11.		*Z*	1690	5.2	- -	18

* R^1=*c*-C_6H_{11}, R^2=Et; R^1=Pr^i, R^2=*c*-C_5H_9; R^1=$C_{10}H_{21}$, R^2=*c*-C_5H_9.

Our major isomers had ν_{max} (C=O) ≥ 1690cm^{-1} (entries 2-5) in line with the quoted values of 1685cm^{-1} (entries 7, 11) for the Z-isomers. Our minor isomer, (**18cd**) had ν_{max} (C=O) 1670cm^{-1} corresponding to quoted values for the *E*-isomers which range from 1655cm^{-1} to 1670cm^{-1}.

Equally convincing are the δ_H values for *H*-C=C. *Z*-Alkenes (**17cd**) and (**17ce**) (entries 2,3) which have a phenyl group on the double bond had δ_H of 5.86 and 5.89. The value for a corresponding compound (entry 7) is 5.97. The *E*-alkene, (**18cd**) (entry 1) had δ_H 6.91 and the corresponding compound (entry 6) had δ_H 7.0. The purely aliphatic *Z*-αβ-unsaturated ketones (**17ad**) (δ_H 5.48) and (**17ae**) (δ_H 5.52) compare well with the *Z*-alkenes of entry 11 (δ_H 5.2) and contrast with the *E*-alkenes (entries 8, 9, 10) at δ_H 6.2-6.46.

The ^{13}C nmr emphasises the similarity of the products in entries 2-5 as compared with entry 1, but more examples are required for structure assignment.

2.3.2 Low temperature oxidations. To obtain compounds (**16**), the reaction mixtures were oxidised at -78°C by the addition of 5M NaOH followed by 60% w.v. hydrogen peroxide, after which the reactions were allowed to warm to room temperature. Compounds (**16**) were readily isolated in the yields shown in Table 4.

Table 4. The synthesis of β-oxodioxolanes (**16**) according to Scheme 6.

Product	R^1	R^2	R^3	Yield (%)[a]
(**16ae**)	Hex	Hex	Me	50
(**16be**)	Hex	Ph	Me	49
(**16cd**)	Bu	Ph	Pr	46

[a] Yields are of isolated, characterised products based on starting alkyne.

In addition to (**16**) there was always *ca.* 10% of (**20**) from which (**16**) were readily separated by chromatography on alumina.

Although the yields are modest, they are the result of four reactions. The sequence has value in that the products (**16**) are 1,3-diketone derivatives specifically protected on a designated ketone group. Moreover, each of the organyl groups of (**16**) has been incorporated regiospecifically and can be independently varied.

2.3.3 Further rearrangement of intermediates (14) to give (21). As we always isolated some product arising from two 1,2-rearrangements from boron to carbon, it seemed worthwhile to leave the reaction to stand at room temperature to encourage the production of interrmediates (**21**), which we intended to protonolyse to the saturated ketones (**22**) (equation 6).

$$(14) \longrightarrow (21) \longrightarrow \underset{(22)}{R^1_2CHCHR^2COR^3} \qquad (6)$$

In practice, all our efforts to convert (**21**) to (**22**) were unsuccessful and, in the subsequent oxidation step in the work-up, tetrasubstituted αβ-unsaturated ketones (**20**) were produced as before (Scheme 7). The results are given in Table 5, from which (entry 2) it can be seen that the yield of (**20**) was improved by omission of the protonolysis step. Yields are modest, but in line with other double migration reactions of alkynylborates.[34,35]

Table 5. The synthesis of tetrasubstituted αβ-unsaturated ketones (**20**).

Experiment	R^1	R^2	R^3	Yield (%)[a]
1	Hex	Ph	Me	40
2	Bu	Ph	Me	45 (60[b])
3	Hex	Hex	Me	48
4	Hex	Hex	Prop	43

[a] Yields are of isolated, characterised products. [b] G.c. yield with protonolysis step omitted.

3. SUMMARY

The reaction of alkytrialkynylborates (**1**) with dioxolanium salts (**11**) followed by protonolysis is a unique, one-pot method for assembling three separate units to yield Z-trisubstituted unsaturated ketones (**17**) in a regiospecific and highly stereoselective fashion. Isolated yields for the six-step process, based on starting alkyne range from 50-70%.

From the same components, an oxidative work-up gives specifically protected 1,3-diketone derivatives (**16**). Allowing the reaction to stand for 16h prior to protonolysis allows a further migration to occur, so that oxidative work-up gives tetrasubstituted αβ-unsaturated ketones (**20**).

The initial units and products are summarised in Figure 1.

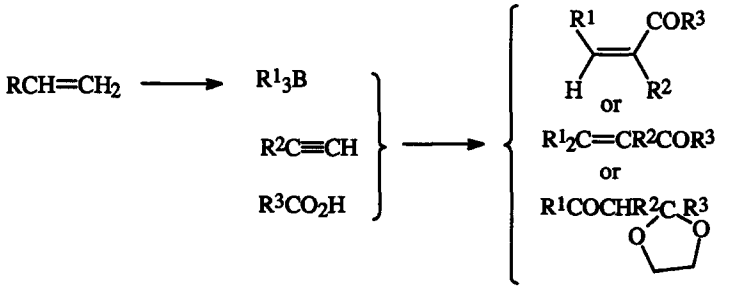


Figure 1

4. EXPERIMENTAL

4.1. Instrumentation

Infra-red spectra were recorded on a Unicam SP1050 infra-red spectrometer using the polystyrene absorbances at 1603 cm^{-1} and 1495 cm^{-1} as references. Proton (^1H) nmr spectra were recorded on a Hitachi Perkin-Elmer R-24B spectrometer at 60 MHz and on a Varian HA-100 spectrometer at 100 MHz using deuterochloroform as solvent and tetramethylsilane as reference, except where stated. Boron (^{11}B) and carbon (^{13}C) nmr spectra were recorded on a Varian XL-100 Fourier transform nmr spectrometer using boron trifluoride etherate as external standard and tetramethylsilane as internal standard, respectively, except where stated. Low resolution mass spectra were recorded on an AEI MS9 mass spectrometer or a VG12-253 mass spectrometer. High resolution mass spectra were recorded on an AEI MS9 mass spectrometer or a VG ZAB-E mass spectrometer. Melting points were recorded on a Gallenkamp Hot Stage apparatus and were uncorrected. Boiling points were determined by Kugelrohr distillation and the temperature given is that of the Kugelrohr oven. Boiling points of alkenes were determined on *E-/Z*-mixtures.

Gas liquid chromatography was performed on a Varian Vista Series 6000 chromatograph with a Varian CDS-401 data system as integrator and plotter. The various temperature programs and columns used for each analysis will be given in the appropriate place. Glc estimations of reaction yields were made by adding a known weight of a standard to the reaction mixture and determining the detector response factor for each component to be examined. Typical internal standards were straight chain hydrocarbons such as dodecane and tridecane. Where possible products were identified by co-injection of an authentic sample.

Thin layer chromatography was performed on either silica gel (Merck) or alumina (Fluka) plastic or aluminium backed plates, with fluorescent indicator (254 nm).

Preparative chromatographic separations were achieved using silica or alumina as adsorbents either on a Chromatotron plate or in a glass column, using uv detection.

Finally, microanalyses where given were determined using a Carlo Erba Strumentazione Elemental Analyser. Some liquid products proved difficult to analyse and in these cases the molecular formula was determined by high resolution mass spectrometry on a sample which was pure by glc and tlc.

4.2 Reagents

All reactions were carried out using purified anhydrous reagents, unless otherwise stated. Reactions involving the use or production of air and water sensitive compounds were carried out under argon used directly from the cylinder through a glass line directly connected *via* a three-way tap to a vacuum pump. The preparation and purification of reagents for use in reactions of organoboron compounds have been reviewed.[36] THF and glyme were purified by passage through a column of dry alumina (neutral) under nitrogen or argon, stirring with LAH for thirty minutes and distillation from LAH; diethyl ether and light petroleum were passed through an alumina column, stirred for 16 hours with calcium hydride and distilled from calcium hydride under nitrogen or argon. (Light petroleum refers to the fraction boiling between 30° and 40°C except where otherwise stated). Chloroform was purified by distillation from phosphorus pentoxide[37] before use.Hex-1-ene was dried over LAH, distilled and stored under argon. But-1-ene was used directly from the cylinder supplied

by B.D.H. Chemicals. Oct-1-yne and phenylethyne were dried with, and distilled from LAH under reduced pressure and stored under argon. Borane was used as its THF complex supplied by Aldrich. The hydride molarity was estimated before use by hydrolysis using a glycerol-water mixture and determination of the amount of hydrogen released by means of a gas burette.[37]

Methyl fluorosulphate supplied by Aldrich was stirred with anhydrous sodium carbonate and distilled under argon. Otherwise it was made as described in 4.6.1. Acetic and butanoic acids were distilled under argon and 2-methoxyethanol (methyl cellosolve) was used as supplied by B.D.H. Chemicals.

Purified solvents and reagents were stored under standard conditions for use in reactions involving air-sensitive compounds.[36]

4.3. Preparation of trialkylboranes

4.3.1 Preparation of tri-n-hexylborane. A solution of hex-1-ene (0.76g, 9mmol) in THF (15ml) was made up in a dry, argon flushed round-bottomed flask (50ml) equipped with a magnetic follower and a septum inlet. To this solution was added, by means of a dry syringe, borane-THF solution (3ml of 1M, 3mmol) at 25°C and the reaction was stirred for 1 hour. The solution of trihexylborane in THF was then ready for further reaction.

4.3.2 Preparation of tri-n-butylborane. A dry, argon flushed round-bottomed flask (50ml) was equipped with a magnetic follower and septum inlet. The flask was charged with THF (15ml) and borane-THF solution(3ml of 1M, 3mmol) and the solution cooled to -5°C by means of a salt-ice bath.

A cylinder of but-1-ene was placed on a balance adjacent to the reaction flask. A piece of PVC tube fitted to a syringe needle was attached to the cylinder and the tube and needle flushed with but-1-ene. The weight of the cylinder and contents was noted. The needle was inserted into the reaction flask to a point just above the stirred solution of borane in THF and a slow stream of gas was passed into the flask. The needle was then submerged into the reaction mixture and the amount of but-1-ene added monitored by the weight loss of the cylinder. A slight excess over the 0.504g (9mmol) required was added to compensate for any uncertainties in the weighing procedure. After the addition was completed, the needle was removed and the cylinder valve closed. The reaction mixture was stirred for 30 minutes to ensure complete hydroboration and the solution was then ready for further use.

4.4 General procedure for the reactions of trialkylboranes with alkynyllithium compounds

n-Butyllithium (3mmol) in hexane was added dropwise under argon to a stirred solution of alkyne (3mmol) in light petroleum (b.p. 40-60°C, 3ml) in an ice cooled round-bottomed flask (100ml). The alkynyllithium precipitated as a white solid and butane was evolved. The ice bath was removed and the mixture stirred thoroughly for 30 minutes. The flask was then recooled to 0°C and the solution of trialkylborane added slowly by means of a double-ended needle. Glyme (5ml) was added and the residual trialkylborane was washed into the flask with glyme (5ml). After 2-3 minutes, the precipitate had completely dissolved, and volatile materials were pumped off. Stirring was continued for a further 15 minutes at ambient temperature to complete formation of the alkynyltrialkylborate salt and the flask was then cooled to -78°C ready for further reaction.

4.5 General procedure for the preparation of 2-methoxyethyl carboxylates

A quickfit conical flask (250ml) was equipped with a magnetic follower and a guard tube containing self-indicating silica gel. The flask was charged with the appropriate carboxylic acid (0.3mol) and 2-methoxyethanol (34.4g, 0.45mol), and cooled to 0°C with stirring. Concentrated sulphuric acid (1.7ml, 0.03mol) was then added dropwise, and the reaction stirred at 25°C for three days. The mixture was extracted with diethyl ether (3 x 50ml) and the ether layers combined. The ether solution was washed with water (2 x 30ml), and potassium carbonate solution (10% w/v) until no acid remained. After a final washing with water (30ml), the ether solution was dried over magnesium sulphate, filtered and evaporated to dryness to give a clear liquid which had the distinctive odour of an ester.

The crude product was purified by fractional distillation to give the pure 2-methoxyethyl ester.

2-Methoxyethyl butanoate (27.1g, 69%), b.p. 64°C/13 mmHg (lit.[38], 177°C/768 mmHg). υ_{max}, (cm^1), 1748, 1185, 1139, 1103; δ_H, 0.94(3H, t, CH_3-CH_2), 1.66(2H, m, CH_3-CH_2-), 2.30(2H, t, CH_2-CO-), 3.32(3H, s, -O-CH_3), 3.53(2H, m, CH_2-OCH_3), 4.17(2H, m, CH_2-OCH_3).

2-Methoxyethyl acetate, b.p. 143-144°C (lit.[39], 144.5°C). υ_{max}, (cm^{-1}), 2980, 2930, 2880, 2820, 1745, 1370, 1245, 1125, 1050; δ_H, 2.03(3H, s, CH_3-CO-), 3.36(3H, s, -OCH_3), 3.56(2H, m, -CH_2-OCH_3), 4.18(2H, m, CO-OCH_2-).

4.6. Preparation of dioxolanium salts

4.6.1 Preparation of methyl fluorosulphate. A two-necked round-bottomed flask (100ml) was charged with a magnetic follower, dimethyl sulphate (52.92g, 40ml, 0.42mol) and fluorosulphonic acid (35g, 21ml, 0.35mol). One neck of the flask was then equipped with a tap adaptor and the other with a normal distillation apparatus. The flask was heated by means of an oil bath to a temperature of 120°C and a liquid distilled at 92°C. The distillate was dried over sodium carbonate for 30 minutes and then redistilled from sodium carbonate to give methyl fluorosulphate (31.95g, 80%), b.p. 92°C, (lit.[40], 92°C); ^{1}H nmr (neat) δ 4.12(s).

4.6.2 Reactions of methyl fluorosulphate with 2-methoxyethyl butanoate and 2-methoxyethyl acetate. A dry, round-bottomed flask (100ml) was charged with the appropriate 2-methoxyethyl-carboxylate (4.2mmol) and a magnetic follower. Methyl fluorosulphate (0.479g, 4.2mmol) was added and the reaction flask was sealed with a rubber septum and flushed with argon. The reaction mixture was left standing for 16 hours with an outlet leading to an oil bubbler allowing the escape of dimethyl ether. After this time, the reaction mixture was a white solid, although occasionally it did have a yellow colour. Dry distilled dichloromethane (20ml) was added and the flask slightly warmed until all the solid had dissolved to give a pale yellow solution. The flask was then cooled to -78°C at which temperature a solid came down from the solution. The dichloromethane solution was decanted under argon pressure using a double-ended needle of very narrow bore. The solid was further recrystallised from dichloromethane (3 x 20ml) using the same procedure, and finally any residual solvent was removed by suction pressure at 1 mmHg to give the products, which were analysed by ^{1}H nmr spectroscopy.

2-Propyl-1,3-dioxolan-2-ylium fluorosulphate (11d). (0.77g, 86%); δ_H ($CDCl_3$), 1.03(3H, t, CH_3), 1.89(2H, m, CH_3CH_2), 2.96(2H, t, CH_2-$C(OR)_2$, 5.22(4H, s, OCH_2CH_2O).

2-Methyl-1,3-dioxolan-2-ylium fluorosulphate (11e). (0.67g, 87%); δ_H ($CDCl_3$), 2.71(3H, s, CH_3), 5.25(4H, s, OCH_2CH_2O).

4.7. General procedures for the reactions of alkynyltrialkylborates with dioxolanium salt.

A solution of the appropriate alkynyltrialkylborate (3mmol) in glyme, prepared as above, was added to a mixture of the appropriate 1,3-dioxolanium salt (3.6mmol, Section 4.6.2) and glyme (15ml), at -78°C, and stirred for 3 hours. From this point, three different work-up procedures were employed.

4.7.1. Low temperature hydrolysis: synthesis of Z-trisubstituted α,β-unsaturated ketones. To the reaction mixture at -78°C was added dry degassed 2-methylpropanoic acid (isobutyric acid, 2ml) and the mixture stirred at room temperature for 16 hours. Hydrochloric acid (3ml of 3M) and water (10ml) were then added and the mixture stirred for 8 hours. The reaction mixture was then poured into diethyl ether (25ml) and the layers separated. The ether layer was washed with potassium carbonate solution (10% w/v; 2 x 15ml) and water (15ml). The ether solution was transferred to a round-bottomed flask (100ml) and sodium hydroxide solution (1.5ml of 5M) and hydrogen peroxide solution (60% w/v, 1.5ml) were added. The mixture was stirred at room temperature for 16 hours and then the layers were separated. The ether layer was washed with water (3 x 15ml), dried over magnesium sulphate, filtered and the solvent evaporated to leave a crude product which was separated by column chromatography or by use of the Chromatotron. The reaction was carried out on four sets of reactants and the data for the products of each reaction will be given separately. The products were all liquids for which the molecular formulae were determined by high resolution mass spectrometry on samples which were pure by glc and tlc.

4.7.1.1 Preparation of Z-3-hexyldec-3-en-2-one(17ae). Chromatography of the crude product gave *tetradec-2-ene* (0.082g, 14%) eluted with petrol and identified by comparison with an authentic sample.[31] Elution with 80:20 petrol/dichlomethane gave *Z-3-hexyldec-3-en-2-one* (**17ae**) (0.407g, 57%, b.p. 83°C (1.5mm Hg). Calc. for $C_{16}H_{13}O$ is 238.2297. Observed mass = 238.2296. υ_{max} (cm^{-1}), 2960, 2940, 2860, 1695, 1470.

δ_H, 0.84(6H, t, H-10, H-6'), 1.22[16H, m, 2 x $(CH_2)_4$], 2.10(4H, m, H-5, H-1'), 2.20(3H, s, H-1), 5.52(1H, t, H-4).

δ_C, ppm, 14.05, 22.66, 28.61, 29.02, 29.13, 29.26, 29.34, 29.52, 29.72, 31.68, 31.76, 33.52 (2-hexyl groups and $COCH_3$), 135.88(C-4), 141.55(C-3), 207.15(C-2). m/z 238(6), 223(2), 113(49), 85(11), 71(21), 57(36), 43(100). Glc retention time = 12.3 min. (70-190°C, 10°C/min., 6' x 0.25" glass column of 5% SE30 on Chrom.W. AW/DMCS (100-120 mesh).

3,4-Dihexyldec-3-en-2-one (20ae) (0.097g, 10%), b.p. 140%/1mm Hg also eluted with 80:20 petrol/dichloromethane. Calculated for $C_{22}H_{42}O$ is 322.3235. Observed mass = 322.3235. υ_{max} (cm^{-1}), 2970, 2940, 2680, 1695, 1630, 1470. δ_H, 0.95(9H, m. 3 x CH_3CH_2), (24H, m, 3 x $(CH_2)_4$), 2.00(6H, m 3 x CH_2-C=C-), 2.18(3H, s, H-1).

δ_C, ppm, 14.07, 22.68, 28.63, 29.16, 29.28, 29.33, 29.54, 29.59, 29.71, 30.49, 31.64, 31.70, 31.79, 33.54 (hexyl groups and C-1), 138.10, 141.80 (C-3, C-4), 206.98 (C-2). m/z, 322(9), 307(17), 237(25), 113(21), 85(11), 71(27), 57(39), 43(100). Glc retention time = 15.4 min. (70-250°C, 10°C/min., on a 6' x ¼" glass column of 5% SE30 on Chrom.W. AW/DMCS 100-200 mesh).

4.7.1.2 Preparation of Z-5-Hexyldodec-5-en-4-one (17ad). Chromatography of crude product gave tetradec-7-ene (0.059g, 10%) identical with an authentic sample,[31] eluted with petrol. Elution with 80:20 petrol/dichloromethane gave (**17ad**) (0.479g, 60%) and (**20ad**) (0.084g, 10%).

Z-5-Hexyldodec-5-ene-4-one (17ad), b.p. 85°C/1mm Hg had M^+ = 266.2610. $C_{18}H_{34}O$ requires 266.2610. υ_{max} (cm^{-1}), 2960, 2940, 2860, 1695, 1620, 1470. δ_H, 0.90(9H, m, H-1, H-12, H-6'), 1.60 (18H, m, H-2, 8, 9, 10, 11, 2', 3', 4', 5'), 2.05(4H, m, H-7, H-1'), 2.46(2H, t, H-3) 5.48(1H, t, H-6).

δ_C, 14.07, 17.39 (C-12, C-6'), 22.68(C-1), 28.63, 28.95, 29.25, 29.33, 29.42, 29.60, 29.68, 31.23, 31.70, 31.79, 33.48(C-7, 8, 9, 10, 11, 1', 2', 3', 4', 5', 2), 44.74(C-3), 134.27(C-6), 141.82(C-5), 209.79(C-4). m/z, 266(0.6), 223(2.6), 113(3), 85(5), 71(6), 57(11), 43(100). Glc retention time = 15.1 min. on a programme rising from 70°-250°C at 10°C/min. on a 6' x 0.25" glass column of 5% SE30 on Chrom. W. AW/DMCS (100-200 mesh).

5,6-Dihexyldodec-5-en-4-one (20ad). b.p. 132°C/0.5mm Hg, had M^+ = 350.3548. $C_{24}H_{46}O$ requires 350.3549. υ_{max} (cm^{-1}), 2970, 2940, 2860, 1695, 1470, 1380. δ_H, 0.90(12H. m. 4 x CH_3), [26H, m, 3 x -$(CH_2)_4$- and CH_2CH_2CO], 1.80-2.20(6H, m, 3 x CH_2-C=C), 2.42 (2H, t, H-3).
δ_C, 14.07, 17.43, 22.71, 28.67, 29.23, 29.28, 29.37, 29.51, 29.64, 29.72, 31.30, 31.74, 31.85, 33.54 (3-hexyl groups and C-1, C-2), 44.78 (C-3), 138.22, 140.76 (C-5, C-6), 209.61 (C-4). m/z 350(5), 307(40), 265(14), 113(18), 85(41), 71(100), 57(94), 43(100). Glc retention time = 17.5 min. (70-250°C, 10°C/min., on a 6' x 0.25" glass column of 5% SE30 on Chrom. W. AW/DMCS 100-200 mesh).

4.7.1.3. Preparation of Z-3-phenyldec-3-en-2-one, (17be). Chromatography of the crude reaction mixture gave *1-phenyloct-1-ene* (0.073g, 13%) eluted with petrol, and identified by direct comparison with an authentic sample.[31] Elution with 80:20 petrol:dichloromethane gave (**17be**) (0.345g, 50%) and (**20be**) (0.151g, 16%).

Z-3-Phenyldec-3-en-2-one (17be), b.p. 76°C/1.1 mmHg, had M^+ = 230.1671; $C_{16}H_{22}O$ requires 230.1671. υ_{max} (cm^{-1}), 3070, 3030, 2980, 2937, 2865, 1695, 1620, 1600, 1470, 1180, 710, 700; δ_H 0.86 (3H, m, H-10), 1.26(8H, m, H-6 to H-9), 2.16(3H, s, H-1), 2.20(2H, m, H-5), 5.89(1H, t H-4), 7.30(5H, m, C_6H_5). δ_C, 14.04(C-10), 22.53, 28.80, 29.00, 29.50, 29.65, 31.69 (C-5 to C-9, C-1), 127.15, 127.67, 128.65, 138.20 (C_6H_5), 136.28(C-4), 143.29(C-3), 204.02(C-2). m/z 230(7), 215(1), 105(100), 91(17), 77(29), 43(63). Glc retention time = 12.2 min. (70-190°C, 10°C/min., on a 6' x 0.25" glass column of 5% SE30 on Chrom. W. AW/DMCS 100-200 mesh).

3-Phenyl-4-hexyldec-3-en-2-one (20be), b.p. 121°C/0.8mm Hg had M^+ = 314.2609. $C_{22}H_{34}O$ requires 314.2609. υ_{max} (cm^{-1}) 2970, 2940, 2870, 1690, 1600, 1470, 1155. δ_H, 0.85(6H, m, H-10, H-6'). 1.40(16H, m, H-6 to 9, H-2' to 5'), 1.90(2H, m, H-1'), 1.95(3H, s, H-1), 2.36(2H, m, H-5), 7.20(5H, m, C_6H_5). δ_C, 14.00, 14.09(C-10, C-6'), 22.47, 22.70, 28.76, 29.07, 29.36, 29.67, 30.94, 31.46, 31.77. 32.56, 33.36 (C-1,C-5 to C-9, C-1'-C-5'), 127.23, 128.57, 129.67, 138.97(C_6H_5), 139.14(C-4), 150.01(C-3), 202.69(C-2). m/z, 314(43), 299(50), 229(55), 105(31), 91(59), 77(12), 43(100). Glc retention time = 16.0 min. (70-250°C) 10°C/min., on 6' x 0.25" glass column of 5% SE30 on Chrom. W AW/DMCS 100-200 mesh.

4.7.1.4 Preparation of Z- and E-5-phenyldec-5-en-4-one, (17cd) and (18cd). Chromatography of the crude reaction product using petrol, gave 1-phenylhex-1-ene (0.034g, 7%), identical with an authentic sample.[31] Further chromatography using 80:20 petrol/dichloromethane gave (**17cd**) (0.483g, 70%), (**18cd**) (0.020g, 2.8%) and (**20cd**) (0.154g, 18%).

Z-5-Phenyldec-5-en-4-one (17cd), b.p. 73°C/1mm Hg, had M^+ = 230.1671, $C_{16}H_{22}O$ requires 230.1671. υ_{max} (cm^{-1}) 3060, 2985, 2930, 2880, 1690, 1595, 1460, 1435, 750, 695. δ_H, 0.86(6H, m, H-1, H-10), 1.41(6H, m, H-2, H-8, H-9), 2.24(2H, q, H-7), 2.40(2H, t, H-3), 5.86(1H, t, H-6). 7.24(5H, m, C_6H_5). δ_C

13.74, 13.92(C-1, C-10), 17.25, 22.42, 29.35, 31.84 (C-2, C-7, C-8, C-9), 45.11(C-3), 126.98, 127.61, 128.63, 138.11(C_6H_5), 135.14(C-6), 143.42(C-5), 206.85(C-4). m/z 230(27), 187(15), 105(100), 91(72), 77(40), 43(73). Glc retention time = 14.3 min. (70-250°C, 10°C/min., on a 12' x 0.25" stainless steel column of 5% SE30 on Chrom. W AW/DMCS 100-200 mesh).

E-*5-Phenyldec-5-en-4-one (18cd)* had M^+ = 230.1670. $C_{16}H_{22}O$ requires 230.1671. υ_{max} (cm^{-1}) 3050, 2980, 2930, 2880, 1670, 1600, 1470, 750, 695. δ_H, 0.90(6H, m, H-1, H-10), 1.40(6H, m, H-2, H-8, H-9), 2.06(2H, q, H-7), 2.56(2H, t, H-3), 6.91(1H, t, H-6), 7.20, 7.40(5H, m, C_6H_5).

5-Phenyl-6-butyldec-5-en-4-one (20cd), b.p. 110°C/0.8mm Hg had M^+ = 286.2284. $C_{20}H_{30}O$ requires 286.2296. υ_{max} (cm^{-1}) 2970, 2940, 2880, 1690, 1600, 1470, 700. δ_H, 0.82(9H), m, H-1, H-10, H-4') 1.1-1.7(10H, br, H-8, H-9, H-2', H-3', H-2), 1.90(2H, m, H-1'), 2.21(4H, m, H-3, H-7), 7.20(5H, m, C_6H_5). δ_C, 13.72, 13.78, 14.04(C-1, C-10, C-4'), 17.35, 22.79, 23.06, 30.47, 31.29, 32.23, 32.51(C-7 to 9, C-1' to 3', C-2), 44.71(C-3), 127.15, 128.46, 129.65, 138.52(C_6H_5), 139.46(C-6), 148.07(C-5), 205.74(C-4). m/z 286(27), 243(52), 229(16), 105(45), 91(100), 77(15), 57(30), 43(87). Glc retention time = 16.7 min. (70-250°C, 10°C/min., on a 12' x 0.25" stainless steel column of 5% SE30 on Chrom.W AW/DMCS 100-200 mesh). Yields were calculated by glc using dodecane as internal standard. The programme used was 70°C (5 min.) - 250°C (10 min. at 10°C/min.).

4.7.2. General procedure for the low temperature oxidation of intermediate (14). To the well-stirred reaction mixture from the interaction of (**1**) and (**11**) (Section 4.7) on a 3mmol scale at -78°C was added 5M NaOH (1.5ml) and 60% w/v H_2O_2 (1.5ml). The reaction flask was allowed to warm to room temperature and then the stirred reaction mixture was held at this temperature for 16h. It was then extracted with ether (30ml) and the ether layer washed with water (3 x 15ml). The aqueous layers were combined, dried with magnesium sulphate, filtered and evaporated to dryness. The crude product was dissolved in light petroleum and applied to a silica or preferably an alumina (Brockmann activity III) column made up in light petroleum. The column was eluted by gradient elution using petrol and dichloromethane to give the pure β-oxo-1,3-dioxolanes. In this way the following compounds were made, isolated and purified.

4.7.2.1. 2-(1',3'-Dioxolan-2'-yl)-3-phenyldecan-4-one, (16be). (0.426g, 49%), b.p. 130°C/0.2mm Hg, had C, 74.14%; H, 9.00%. $C_{18}H_{26}O_3$ requires C, 74.48%, H, 8.97%. υ_{max} (cm^{-1}), 3080, 3040, 2970, 2940, 2880, 1723, 1603, 1500, 1458, 1380, 1210, 1155, 1048, 950, 700. δ_H, 0.82(3H, m, CH_3CH_2-), 1.18(8H, m, $(CH_2)_4$, 1.32(3H, s, $CH_3C(OR)_2$), 2.43(2H, t, CH_2CO), 3.81(4H, m, 2 x CH_2O), 4.07(1H, s, H-3), 7.30(5H, m, C_6H_5). δ_C, 13.99, 22.46, 23.23, 23.56, 28.66, 31.57(C_5H_{11}, C-1), 44.44(CH_2CO), 64.86, 64.94(OCH_2CH_2O), 65.28(C-3), 110.21(C-2), 127.52, 128.26, 130.15, 134.70(C_6H_5), 207.85(CO). m/z 87(100), 43(12). Very small molecular ion at 290.1882. $C_{18}H_{26}O_3$ requires 290.1882.

2-(1',3'-Dioxolan-2'-yl)-3-hexyldecan-4-one (16 ae). (0.447g, 50%), b.p. 125°C/0.3mm Hg, had C, 72.64%; H, 11.09%. $C_{18}H_{34}O_3$ requires C, 72.48%; H, 11.41%. M-15 = 283.2273. $C_{17}H_{31}O_2$ requires 283.2273. υ_{max} (cm^{-1}), 2975, 2940, 2800, 1726, 1470, 1375, 1067, 724. δ_H, 0.86(6H, m, 2 x CH_3CH_2), 1.24(21H, br., $(CH_2)_5$, $(CH_2)_4$, $CH_3C(OR)_2$), 2.41(2H, t, H-5), 2.75(1H, t, H-3), 3.91(4H, m, O-CH_2-CH_2-O). δ_C, 14.04(2C), 21.28, 22.62(2C), 23.17, 28.23(2C), 28.91, 29.48, 31.70(2C), (C-6 to C-10, C_6H_{11}, C-1), 45.65(C-5), 60.07(C-3), 64.46, 64.68(O-CH_2-CH_2-O), 110.37(C-2), 211.83(C-4). m/z, 87(100), 43(20).

4-(1',3'-Dioxolan-2'-yl)-5-phenyldecan-6-one (16cd), (0.400g, 46%), b.p. 118°C/0.5mm Hg, had C, 72.60%; H, 11.23%. $C_{18}H_{26}O_3$ requires 72.48%, H, 11.41%. υ_{max} (cm^{-1}), 3080, 3040, 2970, 2940, 2880,

1720, 1600, 1495, 1463, 1380, 1245, 1160, 1180, 695. δ_H, 0.84(6H, m, H-1, H-10), 1.20(8H, br., H-2, H-3, H-8, H-9), 2.4(2H, t, H-7), 3.85(4H, m, H-4', H-5'), 4.10(1H, s, H-5), 7.25(5H, m, C_6H_5). δ_C, 13.78, 14.07(C-1, C-10), 22.26, 25.89, 29.39(C-2, C-8, C-9), 41.71(C-3), 50.16(C-7), 108.90(C-4), 126.94, 128.69, 129.42, 134.49 (C_6H_5), 208.38(C-6). m/z 115(100), 71(20).

4.7.3. General procedure for synthesis of tetrasubstituted αβ-unsaturated ketones (**20**). The reaction mixture from the reaction of (**1**) and (**11**) was stirred at room temperature for 16h. 5M NaOH (1.5ml) and H_2O_2 (1.5ml, 60% w/v) were added and the reaction stirred for a further 24h. The mixture was poured into ether (30ml) and the layers separated. The ether layer was washed with water (3 x 15ml) and the aqueous layers combined and further extracted with ether (30ml). The combined ether layers were dried ($MgSO_4$), filtered, and evaporated to give crude product. The crude product was purified by chromatography either on a silica column or on a 4mm Chromatotron plate, using gradient elution from petrol to dichloromethane. Products (**20**) were eluted with a 70:30 petrol/dichloromethane mix, to give the following ketones.

*3,4-Dihexyldec-3-en-4-one (**20ae**)* (0.452g, 45%). See Section 4.7.1.1. for physical data.

*5,6-Dihexyldodec-5-en-4-one (**20ad**)* (0.377g, 40%). See Section 4.7.1. for physical data.

*3-Phenyl-4-butyloct-3-en-2-one (**20ce**)* (0.463g, 60%), b.p. 105°C/1mm Hg., had M^+ = 258.1983. $C_{18}H_{26}O$ requires 258.1984. υ_{max} (cm^{-1}), 2970, 2940, 2860, 1690, 1600, 1470, 1350, 700. δ_H, 0.85(6H, m, H-8, H-4'), 1.30(8H, m, H-6, H-7, H-2', H-3'), 1.90(2H, m, H-5), 1.95(3H, s, H-1), 2.36(2H, m, H-1'), 7.14(5H, m, C_6H_5). δ_C, 13.77, 14.01(C-8, C-4'), 22.79, 23.06, 30.44, 30.94, 31.28, 32.35, 33.04(C-5, C-6, C-7, C-1', C-2', C-3', C-1, 127.23, 128.57, 129.66, 138.93(C_6H_5), 139.17(C-4), 149.85(C-3), 202.69(C-2). m/z 258(59), 243(43), 201(67), 105(78), 91(60), 77(25), 57(20), 43(100). G.C. retention time was 12.5 min. using a programme rising from 70°-250°C at 10°C/min. on a 6' x 0.25" glass column of 5% SE 30 on Chrom.W. AW/DMCS 100-200 mesh.

*3-Phenyl-4-hexyldec-3-en-2-one (**20be**).* (0.377g, 40%). See Section 4.7.1.3. for physical data.

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