The Chemistry of Organoborates. Part 5.[1] Alkylation of Alkynyltrialkylborate Salts

By Andrew Pelter,* T. William Bentley,* Colin R. Harrison, Chitti Subrahmanyam, and Richard J. Laub, Department of Chemistry, University College of Swansea, Singleton Park, Swansea SA2 8PP

Alkynyltrialkylborates undergo β-alkylation with alkyl migration from boron to the α-carbon atom under mild conditions to give dialkylvinylboranes which were previously unobtainable. Oxidation of these intermediates provides a versatile route to regiospecifically α-substituted ketones. Hydrolysis yields alkenes in high yields as E–Z mixtures. The reaction is more stereoselective with borates derived from phenylethyne and with alkynyldialkyl(thexyl)borates. Formation of the major products appears to be kinetically controlled and, in all cases, the the major product has alkylating agent and the migrating group on the same side of the double bond. Whilst the rate of reaction is dependent on the alkylating agent, the rearrangement appears to have much less polar character than expected from reactions of carbocations, as the isomer ratio (E : Z) is essentially independent of the alkylating agent and solvent. MINDO/3 calculations are used to support a two-stage mechanism (Scheme 4) in which rate-determining electrophilic attack produces a bent vinyl cation-like intermediate; this then undergoes rapid, exothermic rearrangement with preferential retention of stereochemistry at the migration terminus.

WE have extended our earlier investigations of reaction (i), one of the general reactions previously discussed in connection with the chemistry of organoborates,[1–4] by studying the reactions of alkynylborates ($X\equiv Y$ is $C\equiv CR'$).[2] When these studies began, alkynylborates[5] were known to react with electrophiles,[6,7] and in general, there was competition between the synthetically useful β-attack [equation (i)] and the much less useful α-attack [equation

We have now found reaction conditions under which β-attack occurs almost exclusively, and oxidation of the mixtures of E- and Z-intermediates leads to ketones in high yield (Scheme 1). As R^1, R^2, and R^3 all originate from simple and independent units, they can be varied at will to give a novel, highly flexible ketone synthesis, and the problem of the regiospecific substitution of a ketone, $R^1CO\cdot CH_2R^2$, by R^3 to yield $R^1COCHR^2R^3$ is

SCHEME 1

(ii)]. It was reported that, for alkylations, β-attack is non-stereospecific, the intermediates giving rise to mixtures of E- and Z-olefins on hydrolysis [equation (iii)].

† Thexyl = 1,1,2-trimethylpropyl.

automatically solved.[8a] Furthermore, when alkynyldialkyl(thexyl)borates † are used the reaction is far more stereoselective and represents a useful trisubstituted olefin synthesis.[8b]

[1] Part 4, A. Pelter, M. G. Hutchings, K. Smith, and D. J. Williams, J.C.S. Perkin I, 1975, 145.

[2] A. Pelter, K. Smith, M. G. Hutchings, and K. Rowe, J.C.S. Perkin I, 1975, 129.

[3] A. Pelter, M. G. Hutchings, K. Rowe, and K. Smith, J.C.S. Perkin I, 1975, 138.

[4] A. Pelter, M. G. Hutchings, and K. Smith, J.C.S. Perkin I, 1975, 142.

[5] P. Binger and R. Köster, Tetrahedron Letters, 1965, 1901.

[6] P. Binger, Angew. Chem. Internat. Edn., 1967, 6, 84.

[7] P. Binger, G. Benedikt, G. W. Rotermund, and R. Köster, Annalen, 1968, 717, 21.

[8] Preliminary communications: (a) A. Pelter, C. R. Harrison, and D. Kirkpatrick, J.C.S. Chem. Comm., 1973, 544; (b) A. Pelter, C. Subrahmanyam, R. J. Laub, K. J. Gould, and C. R. Harrison, Tetrahedron Letters, 1975, 1633.

RESULTS AND DISCUSSION

Synthesis of Ketones.—Trialkylboranes and alkynyl-lithium derivatives readily reacted at 0 °C in a mainly ethereal solvent to form lithium alkynyltrialkylborate salts; all these salts are freely soluble in tetrahydrofuran (THF), glyme (2,5-dioxahexane), or diglyme (2,5,8-trioxanonane; DG). In our first experiments, lithium trihexyloctynylborate was produced in THF, the solvent was then removed, and toluene was added. The reaction with methyl fluorosulphate was followed by i.r. spectroscopy (a standard procedure in this work), which indicated, in accord with previous results, that both α- and β-attack were taking place. However,

methyl tosylate was complete in 1 h at 40 °C, reaction of the same salts with cyclopentyl tosylate took 2.5 h at 65 °C. The reaction with cyclohexyl tosylate was even slower, taking 9 h at 85 °C, and the compounds derived from protonation (presumably from acid produced by decomposition of the alkylating agent) became major products. These results point to this reaction being an S_N2 displacement on the alkylating agent, and provide one limitation in terms of the suitability of alkylating agents.

Contrary to our expectations, the reaction of lithium hexynyltriphenylborate with methyl tosylate was very slow: after alkylation for 24 h at 20—25 °C, followed by

TABLE 1

Ketone synthesis via alkylation of $R_3{}^1\overline{B}C{\equiv}CR^2$ Li^+ in diglyme (Scheme 1)

Electrophile R³X	No.[a]	Ketone R¹CO·CHR²R³			Yield (%)[b]
		R¹	R²	R³	
Me₂SO₄	(1)	n-Octyl	Buⁿ	Me	85[c]
Me₂SO₄	(2)	n-Hexyl	n-Hexyl	Me	84[c]
Me₂SO₄	(3)	Cyclopentyl	n-Hexyl	Me	81[e]
MeOTs	(2)	n-Hexyl	n-Hexyl	Me	98[d]
MeOTs	(3)	Cyclopentyl	n-Hexyl	Me	88[d]
Et₃O⁺BF₄⁻	(4)	n-Octyl	Buⁿ	Et	93[c]
Et₃O⁺BF₄⁻	(5)	n-Hexyl	n-Hexyl	Et	95[c]
Et₃O⁺BF₄⁻	(6)	Cyclohexyl	Buⁿ	Et	83[c]
CH₂:CH·CH₂Br	(7)	n-Hexyl	n-Hexyl	CH₂:CH·CH₂	88[d]
CH₂:CH·CH₂Br	(8)	n-Octyl	Buⁿ	CH₂:CH·CH₂	80[d]
CH₂:CH·CH₂Br	(9)	Cyclopentyl	Buⁿ	CH₂:CH·CH₂	86[d]
PhCH₂Br	(10)	Cyclopentyl	Buⁿ	PhCH₂	81[d]
PhCH₂Br	(11)	n-Octyl	Buⁿ	PhCH₂	79[d]
PhCH₂Br	(12)	n-Hexyl	n-Hexyl	PhCH₂	78[d]
Me₃SO₄	(13)	Phenyl	Buⁿ	Me	79[e]

[a] See Experimental section for characterisation. [b] Yields of isolated purified product after correction for traces of impurity shown by g.l.c. [c] Alkylation occurred rapidly (<10 min at −78 °C). [d] Alkylation for 2 h at 40 °C. [e] Alkylation for 6 h at 20—25° with THF as solvent.

when an ether was substituted for toluene as the reaction medium, α-attack became minimal.

Experiments with methyl tosylate showed that product yields were consistently higher in DG than in THF by about 5—10%. However, THF also gives satisfactory yields and may be more convenient, whilst high yields are also obtained with glyme.

Oxidation was carried out by standard procedures,[9a] except that 50% hydrogen peroxide rather than 30% was used. The products were isolated by column chromatography to give ketones of 95—97% purity (Table 1). This process (Scheme 1; Table 1) is a major new route to ketones (V), and proceeds in high yield under conditions which would not affect many sensitive groups. Some of these have been dealt with in separate communications.[10-12] Migration of either secondary or primary groups occurs readily. Since the terminal carbon atom of an alkyne is both alkylated and converted into a carbonyl group, while the neighbouring carbon atom is alkylated, the process (Scheme 1) is an important extension of alkyne chemistry.

Whereas reaction of alkynyltrialkylborates with

19 h at 90 °C, the product yield (after oxidation) was 30%. Even reaction with dimethyl sulphate required 6 h at 20—25° to give a 79% yield of ketone (Table 1), and only methyl fluorosulphate reacted at low temperatures. This suggests that the negative charge is delocalised over the three phenyl rings in the parent salt, which in turn leads to a lowering of the negative charge upon the β-alkyne carbon atom and thence to a slower attack by the electrophile.

Synthesis of Olefins.—The above synthesis of ketones proves that, if ether solvents are used, the β-alkylation-migration reaction (Scheme 1) of alkynyltrialkylborates to give substituted dialkylvinylboranes (III) and (IV) is an efficient process. This is the first time that such vinylboranes have become available and they could be used for a variety of purposes.

The use of iodine in the presence of base to induce further migration, previously used for dialkylvinyl-boranes produced by the hydroboration of terminal alkynes,[13] was only partly successful with our highly substituted vinylboranes (III) and (IV). In every case the desired double migration product (from β-attack)

[9] H. C. Brown, ' Organic Syntheses *via* Boranes,' Wiley, New York, 1975, (a) p. 16; (b) p. 81; (c) pp. 47—50; (d) pp. 15—35; (e) p. 21.
[10] A. Pelter, C. R. Harrison, and D. Kirkpatrick, *Tetrahedron Letters*, 1973, 4491.

[11] A. Pelter and K. J. Gould, *J.C.S. Chem. Comm.*, 1974, 347.
[12] A. Pelter, K. J. Gould, and C. R. Harrison, *Tetrahedron Letters*, 1975, 3327.
[13] G. Zweifel, H. Arzoumanian, and C. C. Whitney, *J. Amer. Chem. Soc.*, 1967, **89**, 3652.

was accompanied by the trialkylvinyl iodide from α-attack.*

Thus attention was turned to the hydrolytic work-up (acetic or isobutyric acid) [9b] of the vinylborane intermediates to yield trisubstituted olefins, which were isolated by column chromatography in the yields given in Table 2. On the basis of these data, it was apparent that an efficient, new synthesis of olefins was to hand. Unfortunately, the products were mixtures of E- and Z-isomers in the ratio of about $65 : 35$.

ratio of isomers appears to be insensitive to the solvent over a wide range. A similar result was obtained with alkynyldialkyl(thexyl)borates: $E : Z$ ratios varying from $87 : 13$: to $84 : 16$ were obtained over the same range of solvents (see later). Also the substitution of potassium (with or without 18-crown-6) for lithium as the cation did not affect the isomer ratio.† These results are unusual for reactions involving salts, and will be discussed later.

As we could not influence the isomer ratio by changing

TABLE 2

Alkylation of $R_3{}^1BC{\equiv}CR^2$ Li$^+$ with R^3X to give $R^1CH{=}CR^2R^3$ [equation (iii)]

Solvent	Electrophile	R^1	R^2	R^3	$E : Z$	Yield $(E + Z)$ (%) [a]
THF	Me$_2$SO$_4$	Bu^n	Bu^n	Me	$61 : 39$	83 [e]
THF	Me$_2$SO$_4$	Bu^n	Pentyl	Me	$69 : 31$	80 [e]
DG	MeOTs	n-Hexyl	n-Hexyl	Me	$68 : 32$	85 [d]
DG	Et$_3$O$^+$BF$_4{}^-$	n-Hexyl	Bu^n	Et	$60 : 40$	96 [e]
DG	Et$_3$O$^+$BF$_4{}^-$	n-Octyl	Bu^n	Et	$63 : 37$	93 [e]
DG	Et$_3$O$^+$BF$_4{}^-$	Cyclopentyl	n-Hexyl	Et	$67 : 33$	96 [e]
THF	Pr^{n}I	Bu^n	Bu^n	Pr^n	[b]	82 [e]
Glyme	Pr^{n}I	n-Hexyl	n-Hexyl	Pr^n	$71 : 29$	69 [e]
Glyme	Me[CH$_2$]$_5$I	n-Hexyl	Pr^n	n-Hexyl	$29 : 71$	68 [e]
DG	CH$_2{:}$CH·CH$_2$Br	n-Hexyl	n-Hexyl	CH$_2{:}$CH·CH$_2$	$32 : 68$	72 [d]
DG	CH$_2{:}$CH·CH$_2$Br	n-Hexyl	Bu^n	CH$_2{:}$CH·CH$_2$	$34 : 66$ [f]	80 [d]
DG	CH$_2{:}$CH·CH$_2$Br	n-Octyl	Bu^n	CH$_2{:}$CH·CH$_2$	$31 : 69$ [f]	81 [d]
DG	CH$_2{:}$CH·CH$_2$Br	Cyclopentyl	Bu^n	CH$_2{:}$CH·CH$_2$	$34 : 66$ [f]	77 [d]
DG	PhCH$_2$Br	n-Hexyl	n-Hexyl	PhCH$_2$	$40 : 60$ [f]	74 [d]
DG	PhCH$_2$Br	Cyclopentyl	Bu^n	PhCH$_2$	$45 : 55$ [f]	76 [d]
DG	MeOTs	n-Hexyl	Ph	Me	$82 : 18$	85 [d]

[a] All yields are of isolated, purified products. [b] Isomers not separable. [c,d] See Table 1. [e] Alkylation for 24 h at 40 °C. This apparent inversion is simply due to the stereochemical priority rules.

TABLE 3

Alkylation of $(Me_2CH·CMe_2)R_2{}^1BC{\equiv}CR^2Li^+$ with R^3X in glyme to give $R^1CH{=}CR^2R^3$

Electrophile	R^1	R^2	R^3	$E : Z$	Yield (%)
Me$_2$SO$_4$	Bu^n	Bu^n	Me	$83 : 17$	74 [a]
Me$_2$SO$_4$	n-Hexyl	n-Hexyl	Me	$85 : 15$	84 [a]
FSO$_2$·OMe	n-Hexyl	n-Hexyl	Me	$86 : 14$	55 [a]
Et$_3$O$^+$BF$_4{}^-$	n-Hexyl	n-Hexyl	Et	$91 : 9$	88 [a]
Et$_3$O$^+$BF$_4{}^-$	Bu^n	Bu^n	Et	$88 : 12$	82 [a]
CH$_2{:}$CH·CH$_2$Br	n-Hexyl	n-Hexyl	CH$_2{:}$CH·CH$_2$	$16 : 84$ [d]	70 [b]
PhCH$_2$Br	n-Hexyl	n-Hexyl	PhCH$_2$	$8 : 92$ [d]	70 [b]
Pr^{n}I	n-Hexyl	n-Hexyl	Pr^n	$89 : 11$	69 [c]
Me[CH$_2$]$_5$I	n-Hexyl	Pr^n	n-Hexyl	$17 : 83$ [d]	68 [c]

[a] Alkylation for 1 h at 20 °C. [b] Alkylation for 120 h at 20 °C. [c] Alkylation for 180 h at 40 °C. [d] See Table 2, footnote f.

Our studies uncovered two remarkable features of the reaction. The first was the insensitivity of the isomer ratio to the alkylating agents used. Methylations carried out in DG with methyl iodide, methyl tosylate, dimethyl sulphate, and methyl fluorosulphate, all gave approximately the same ($65 : 35$) ratio, though the rate varied greatly. Even when reagents differing as greatly as propyl iodide and allyl bromide are used, similar proportions are obtained (Table 2). This insensitivity in a formally polar reaction was unexpected.

The second noteworthy feature became apparent when we examined solvent effects. Dimethyl sulphate reacted with lithium tri-n-hexylhexynylborate in DG to give, on hydrolytic work-up, 5-methyldodec-5-ene as a mixture of E- and Z-isomers in the ratio $67 : 33$. In THF this ratio was $64 : 36$, in methylene chloride, $70 : 30$, in benzene, $66 : 34$, and in pentane $67 : 33$. Thus, the

either the solvent or the alkylating agent, we investigated another approach. Dialkyl(thexyl)boranes [9c] reacted as usual with alkynyl-lithium derivatives to give the corresponding alkynyldialkyl(thexyl)borate salts, which were then alkylated. The thexyl group did not migrate and the reaction was considerably more stereoselective (Table 3). Again the $E : Z$ ratio of olefins hardly varied with alkylating agent or with solvent. Mechanistically, the last two entries in Table 3 are of interest. If product formation was thermodynamically controlled, n-propylation of the octynyl salt (R^2 = n-hexyl) and n-hexylation of the pentynyl salt (R^2 = n-propyl) should lead to the same mixture of products, whereas the results (Scheme 2) show a marked difference in composition of the product mixtures. In addition, when lithium tri-n-hexyloctynylborate was alkylated with propyl iodide, an $E : Z$ ratio of $71 : 29$ was obtained for 7-propyltetradec-7-ene. When lithium tri-n-hexylpentynylborate was treated with hexyl iodide, the same olefins were obtained

* Some of these experiments were carried out by Dr. M. Shawe.
† We thank Mr. W. Paget for these results.

in a ratio of 29 : 71. All these reactions were carried out in the same solvent (THF) at the same concentrations and temperature. In each case, an n-hexyl group migrates, a primary alkyl group is attached to the alkyne group and the electrophile is a primary alkyl iodide. This clearly establishes that the alkylation of lithium alkynyldialkyl(thexyl)borates and lithium alkynyltri-alkylborates is mainly (if not completely) kinetically controlled, and cannot proceed by equilibration via a linear vinyl cation, as has been postulated by Suzuki [14] for the protonation of trialkyl(phenylethynyl)borates (our own protonation results are presented separately [15]).

Alkylation of lithium alkynyldialkyl(thexyl)borates followed by protonolysis is thus a new, flexible stereo-selective synthesis for trisubstituted olefins.

products of ethylation (R^3 = Et), propylation (R^3 = Pr^n), etc. but, as with R^3 = Me, the major product was always the one with the longer retention time on an Apiezon g.l.c. column. Plots of log [relative retention time (α)] for each isomer vs. carbon number fit pairs of straight lines, intersecting at the predicted integral carbon number (Table 4; Figures 1 and 2). As the linear relationship between log α and carbon number is well established for other homologous series, e.g. cis- and trans-disubstituted or trisubstituted alkenes, run on 'boiling point' columns,[18] we conclude that each pair of lines (Figures 1 and 2) represents a homologous series of E- and Z-isomers. Furthermore, since isomers with R^3 = Me have been identified unambiguously, and the E-isomer has the longer retention time, it follows that

SCHEME 2

Assignment of Stereochemistry.—It has been reported that protonation of dialkyl(phenylethynyl)(thexyl)-borates gives exclusively the olefin with the migrating group and incoming proton on opposite sides of the double bond.[14] In contrast, our preliminary results [8b] indicate that our major olefinic products had the in-coming alkyl group and the migrating group on the same side of the double bond, and this was verified as follows. We synthesised mixtures of the E- and Z-olefins (I) and (II) by alkylation of either the alkynyltrialkyl- or the alkynyldialkyl(thexyl)-borates (Tables 2 and 3). The major products from methylation (R^3 = Me, R^1 = R^2 = alkyl) showed vinylic methyl signals in the ^{1}H n.m.r. spectra at τ 8.45 ($J_{allylic}$ 0.5 Hz), and the minor products showed the corresponding signals at τ 8.37 (J 1.1 Hz). An authentic sample of (II; R^1 = Bu^n, R^2 = pentyl, R^3 = Me), prepared * by an unambigous method,[16] gave the same values for the vinylic methyl group as our minor component, which also had the same retention time as the authentic sample in serveral g.l.c. systems. As these g.l.c. and n.m.r. data are in accord with other literature data,[17,18] it is clear that the major products of methyl-ation have the longer g.l.c. retention times, and are E-isomers (I).

N.m.r. criteria were less helpful for identifying the

the isomer of each pair (R^3 = Et etc.) with the longer retention time is the E-isomer (Table 4). To support these assignments further, we had available a sample of (I; R^1 = R^2 = Bu^n, R^3 = Et) made by the method of

TABLE 4

Retention times (α) of Z and E isomers of 5-substituted dec-5-enes (R^1 = R^2 = Bu^n) and 7-substituted tetra-dec-7-enes (R^1 = R^2 = n-hexyl) relative to n-dodecane [a]

Alkene ($R^1CH=CR^2R^3$) R^3	R^1 = R^2 = Bu^n [b]	R^1 = R^2 = n-hexyl [c]
Me	0.39, 0.43 [d]	3.29, 3.74 [d]
Et	0.62, 0.67	4.70, 5.22
Pr^n	[e]	7.06, 7.55
Bu^n	1.73 [f]	

[a] Relative adjusted retention time (α) = $[t_R(alkene) - t_A(CH_4)]/[t_R(dodecane) - t_A(CH_4)]$. [b] Apiezon N at 125 °C. [c] Apiezon M at 160 °C. [d] It is well established that this corresponds to the E-isomer—see text for discussion. [e] The two isomers could not be separated. [f] Only one isomer.

Normant † [19] which was identical in n.m.r. and g.l.c. characteristics with our corresponding major component.

In every case, our major isomer had the longer reten-tion time. There can therefore be no doubt that the

* We thank Professor Yamamoto for kindly supplying this sample.

† We thank Professor Normant for supplying us with this compound.

[14] N. Miyaura, T. Yoshinari, M. Itoh, and A. Suzuki, *Tetra-hedron Letters*, 1974, 2961.

[15] Part 7, A. Pelter, C. R. Harrison, C. Subrahmanyam, and D. Kirkpatrick, *J.C.S. Perkin I*, 1976, 2435.

[16] K. B. Sharpless, R. C. Michaelson, J. D. Cutting, S. Tanaka, H. Yamamoto, and H. Nozaki, *J. Amer. Chem. Soc.*, 1974, **96**, 5254.

[17] D. J. Faulkner, *Synthesis*, 1971, 175; U. T. Bhalerao and H. Rapoport, *J. Amer. Chem. Soc.*, 1971, **93**, 4835.

[18] A. Matukuma in 'Gas Chromatography 1968,' ed. C. L. A. Harbourn, Institute of Petroleum, London, 1969, p. 55; J. J. Walraven and A. W. Ladon, 'Gas Chromatography 1970,' ed. R. Stock, Institute of Petroleum, London, 1971, p. 358.

[19] J. F. Normant, G. Cahiez, C. Chuit, and J. Villeras, *J. Organometallic Chem.*, 1974, **77**, 269.

major olefinic products from all the simple alkylations of alkynyltrialkyl- or alkynyldialkyl(thexyl)-borates are those in which the migration group (R^1) and the alkylating group (R^3) are on the same side of the double bond.

FIGURE 1   Plot of log α vs. carbon number for 5-substituted dec-5-enes

FIGURE 2   Plot of log α vs. carbon number for 7-substituted tetradec-7-enes

Since hydrolysis proceeds with retention,[20] the stereochemistry of the intermediate vinylboranes follows.

Allylation products cannot be correlated by g.l.c., and assignments based on allylic coupling alone are suspect.

* It would not be appropriate to use MINDO/3 to study the processes of electrophilic attack, either β [equation (i)] or α [equation (ii)], because these polar processes are markedly dependent on solvent, which cannot be adequately taken into account by our calculations.

Therefore, the mixture of olefins (I) and (II) ($R^1 = R^2 = $ n-hexyl, $R^3 = $ allyl) was hydroborated by 1 equiv. of bis(di-2-methylcyclohexyl)borane, and the product hydrolysed by isobutyric acid. The product was a mixture of two components in the same proportion as the original diene. The major component had the longer retention time and both components ran concurrently with authentic (I) and (II) ($R^1 = R^2 = $ n-hexyl, $R^3 = Pr^n$). Therefore allylation proceeds in the same sense as alkylation.

Benzylation gave product mixtures similar to those obtained with alkylation, but no direct correlation was possible. However, the major component of the mixture [(I) and (II) $R^1 = R^2 = $ n-hexyl, $R^3 = PhCH_2$)] gave the benzylic-allylic methylene signal at τ 6.68, the minor isomer showing this signal at τ 6.76. The corresponding peaks for the very similar allyl compounds ($R^3 = $ allyl) are at τ 7.30 and 7.47, respectively. The shift in τ value from the major to the minor component is in the same direction in both cases, and we therefore conclude tentatively that benzylation proceeds in the same sense as other alkylations.

Reaction of lithium (tri-n-hexyl)phenylethynylborate with methyl tosylate gave an 85% yield of a mixture of (E)- and (Z)-2-phenylnon-2-ene. The mixture was easily resolved by g.l.c. into two components in the ratio 82 : 18, the reactions being rather more stereoselective than others (Table 2). The major component (retention time on 12 ft Apiezon N at 200 °C, 35 min) gave the vinyl proton signal at τ 4.24 and the minor (retention time 31.5 min) the corresponding signal at τ 4.60. The calculated value for the E-isomer [21] is τ 4.2, and for the Z-isomer τ 4.64. There is no doubt that this alkylation proceeds in the same way as the other reactions, in contrast to protonation of phenylethynylborates.[15]

Mechanistic Aspects.—This section deals with the mechanism of rearrangement including MINDO/3 calculations of the stereochemistry of rearrangements after β-attack by the electrophile [equation (i)].*

The available experimental evidence suggests that attack by the alkylating agent occurs in the rate-determining step and also enables us to rule out two mechanistic possibilities for β-attack [equation (i)]. If attack by the electrophile and rearrangement from boron to carbon were concerted and anchimerically assisted by the migrating group, a stereospecific reaction should occur, and the predicted product would be (IV), the vinylborane with the migrating group (R^1) and the incoming electrophile (R^3) *trans*. Since the reaction is not stereospecific and the predominant product is the opposite isomer, we rule out a concerted mechanism, but this argument leads us to conclude that the reaction probably proceeds *via* a reactive intermediate (or at least *via* a two-stage mechanism in which electrophilic attack is followed by rearrangement). The absence of anchimeric assistance

[20] H. C. Brown and G. Zweifel, *J. Amer. Chem. Soc.*, 1961, **83**, 3834.
[21] C. von Pasual, J. Meier, and W. Simon, *Helv. Chim. Acta*, 1966, **49**, 164.

is also apparent from the low reactivity of the alkynyl-triphenylborate (discussed above).

A plausible intermediate, the linear vinyl cation (VI), has been proposed by Suzuki et al.[14] for the protonation of alkynylborates, but we show later [15] that this mechanism (Scheme 3) for protonation is based on insufficient

distinguished by comparing the preferred modes of rearrangement for each of the two bent structures (VII) and (VIII) with the observed product. Suzuki,[14] followed by others,[23] postulated that rearrangement occurred with complete retention of stereochemistry at the carbon atom of the migration terminus (Scheme 3).
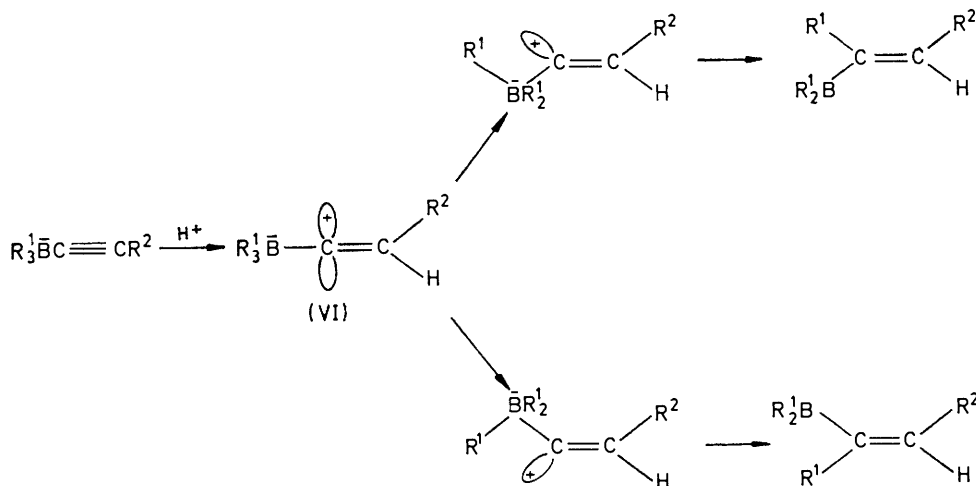
SCHEME 3

data. Unfortunately, for alkylation, the analogous mechanism is incompatible with our evidence that the reaction is predominantly or exclusively kinetically controlled (Scheme 2). We now propose that the probable cause of kinetic control is a change in the BCC bond angle (from 180°) during electrophilic attack. This can be envisaged to occur in one of two possible ways. If the boron atom moved towards the incoming electrophile, there might be a favourable interaction between the counterions (Li$^+$ from the alkynylborate and X$^-$ from the electrophile) to give (VII). Alternatively, if the

In contrast, we expected that inversion of configuration would occur by analogy with the inversion of configuration noted during rearrangement of the chloride (IX)[24] and with the independent studies of vinyl cations.[25] Since the two qualitative interpretations led

to opposite predictions for any one mode of bonding of (VI), and the discrepancy could not be resolved by any experimental method currently available, we investigated the mechanism of rearrangement by the semi-empirical SCF MO theory, MINDO/3.[26,27] Of particular importance is that the MINDO/3 computer program allows changes of geometric co-ordinates of the molecule to find the structure of minimum energy, so that the most favourable conformations can also be calculated.

The calculated charge distributions for the linear intermediate (X) and its pentamethyl derivative (XI) are as shown. Although these intermediates formally appear to be ylides (VI), even in the simplest system (X) the positive charge on the carbon atom adjacent to boron is calculated to be less than 0.5 whereas its formal charge is +1. In the pentamethyl derivative (XI), this carbon atom is calculated to have a partial charge of only +0.28. Thus, for highly alkylated

boron atom moved away from the incoming electrophile [to give (VIII)], this would be consistent with our recent interpretation of the stereochemistry of electrophilic addition to alkynes.[22] Bending away from the incoming electrophile may be due to R^3 bridging both C$_\alpha$ and C$_\beta$ during the initial electrophilic attack or to electrostatic repulsions between the negatively charged boron and the solvated X$^-$ group and/or between the incoming electrophile and the metal counterion, Li$^+$.

In principle, the two possible modes of bending can be

[22] T. W. Bentley, Ann. Reports, 1974, 71B, pp. 125—128.
[23] K. Utimoto, T. Furabayashi, and H. Nozaki, Chem. Letters, 1975, 397.
[24] G. Köbrich and H. R. Merkle, Angew. Chem. Internat. Edn., 1967, 6, 74.

[25] R. H. Summerville and P. von R. Schleyer, J. Amer. Chem. Soc., 1974, 96, 1110.
[26] R. C. Bingham, M. J. S. Dewar, and D. H. Lo, J. Amer. Chem. Soc., 1975, 97, 1285, and following papers.
[27] T. W. Bentley, ' M.T.P. International Review of Science,' ed. D. Ginsburg, ser. 2, vol. 5, Butterworths, London, 1976, ch. 6.

systems, the carbon atom may be only slightly positively charged, and rearrangement may occur in a species which behaves more like a neutral molecule than like a carbocation. This would explain the lack of dependence of product stereochemistry on both the solvent and the

mol^{-1} is required to bend the boron atom 10° out of line of the carbon–carbon double bond (Table 5, column A), our proposal that bending is the likely source of kinetic control appears to be energetically feasible. By comparing the results in columns B and C, it appears
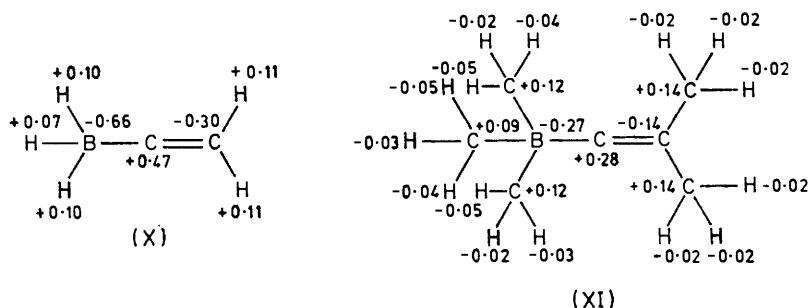
nature of the counterion in the electrophile (see above), and would also support our application of a ' gas phase ' calculation to a problem in solution chemistry.

We studied the simplest system [equation (v)] as a model reaction of this general type. It was calculated
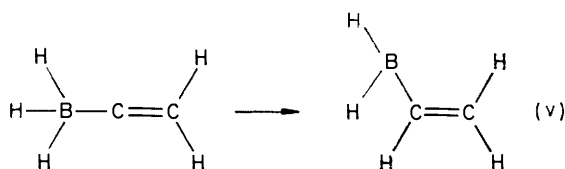
that the rearrangement was exothermic by 33.5 kcal mol^{-1} and that the activation energy to rearrangement was zero; indeed, rearrangement during the geometry optimisation could only be prevented by assuming that the three B–H bonds were identical and the minimum energy of the unrearranged dimethyl derivative (XII) could not be found without fixing certain bond angles to prevent rearrangement. Therefore, in solution, we expect that the barrier to rearrangement of these proposed reactive intermediates will be very small, even allowing for the possibility that the migrating group would have to displace solvent molecules in its path.

In contrast to the highly exothermic rearrangement of alkynylborates [equation (v)] the first rearrangement of cyanoborates [equation (i), X≡Y = C≡N [1–4]] is calculated to be endothermic. However, the second rearrangement of the intermediate from acylation of cyanoborates is calculated to be exothermic by 40 kcal mol^{-1}, whereas the second rearrangement of alkynylborates is calculated to be slightly endothermic. These results are consistent with the experimental observations that a second rearrangement during simple alkylation of alkynylborates does not occur, whereas for the acylation of cyanoborates, the second rearrangement cannot be prevented.*

Possible reaction co-ordinates for rearrangement of (X) are shown in Tables 5 and 6. As less than 0.5 kcal

that the retention mechanism becomes increasingly more favourable as the angle of bending (θ_1) increases. However, because the heats of formation of all the rearranged structures in Table 5 are less than those of the corresponding unrearranged structures, it seems likely that both rearrangement processes will occur, in agreement with the experimental results.

As might be expected, rearrangement was most favourable when the migrating hydrogen was in the plane of the boron and the two carbon atoms. However, rearrangement with retention is exothermic even when the migrating group is 60° out of the most favourable plane, i.e. for $\theta_1 = 95°$, the heat of formation (50.56 kcal mol^{-1}, Table 6) is less than that of the corresponding unrearranged structure (57.98 kcal mol^{-1}, Table 5). Thus, many conformations of the unrearranged structure (X) are capable of rearranging exothermically. We also calculated possible reaction co-ordinates for rearrangement of the dimethyl derivative (XII) (see Tables 7 and 8). Whilst the effects on changes in torsion angles are similar (cf. Tables 6 and 8), rearrangement with retention of configuration is much more favourable than rearrangement with inversion, even with angles of bending of only 10° (Table 7). These results imply that our simplest model system (X) underestimates the stereoselectivity of the reaction, and the results are consistent with the observation that stereoselectivity increases with bulky substituents (e.g. thexyl).

Although these calculations do not lead to quantitative predictions of product stereochemistry, it seems clear that rearrangement with retention of stereochemistry at the migration terminus is preferred and that, potentially, there is some stereoselectivity even when the intermediate is bent by only 2°. Also the more bent the intermediate, the more stereoselective the reaction should be. If rearrangement with retention is preferred, the source of kinetic control would have to cause a bending of the boron atom away from the incoming electrophile, so that the predominant product would be an alkene with a cis-arrangement of the rearranged group (R^1) and the incoming electrophile (R^3). Consequently, the bent intermediate (VIII) is implicated as the source of kinetic

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* Details of these and other calculations will be reported elsewhere.

control. Also, in contrast to published interpretations, it appears that rearrangements with both retention and inversion of stereochemistry at the migration terminus
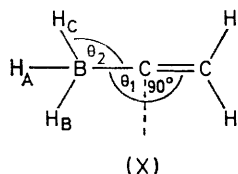
of the alkynylborate is rate-determining and gives the bent, neutral intermediate (VIII). This accounts for the marked dependence of reaction rate on the alkylating
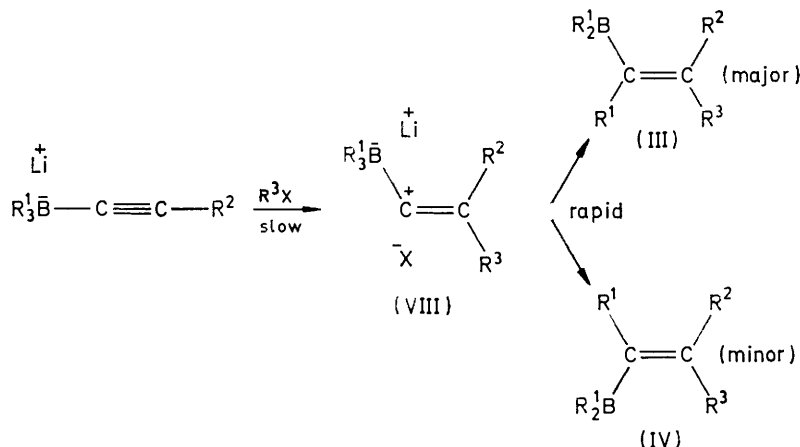
SCHEME 4

TABLE 5

Possible reaction co-ordinates for rearrangement of alkynylborates as a function of angle of bending (θ_1)

A 'Rigid' bending without rearrangement, $\theta_2 = 105.7°$
B Bending with rearrangement (retention, $\theta, > 90°$ H_B shifts)
C Bending with rearrangement (inversion, $\theta, > 90°$ H_C shifts)

Bond angle (θ_1) (°)	Angle of bending $(\theta_1 - 90)$ (°)	Heat of formation (kcal mol^{-1}) †			
		A		B	C
		a	b	'retention'	'inversion'
90	0	57.88	57.88	31.02	31.02
92	2			30.66	31.46
95	5	57.98	57.99	30.24	32.21
100	10	58.34	58.37	29.85	33.82
110	20	59.76	59.87	30.20^c	38.33^c
120	30	62.20	62.46	31.90	44.64
130	40	65.71	66.26	34.61	52.84

^{a} H_B held in BCC plane. ^{b} H_C held in BCC plane. ^{c} STO-3G ab $initio$ calculations, using the optimum geometry calculated by MINDO/3, predict a preference of 16.7 kcal mol^{-1} favouring 'retention' over 'inversion.'

TABLE 6

Dependence of rearrangement on torsion angle ϕ^a with $\theta_1 = 95°$

Torsion angle (ϕ) (°)	0	10.0	20.0	30.0	45.0	60.0
Heat of formation (kcal mol^{-1})†	30.24^b	30.84	32.64	35.59	42.03	50.56

^{a} ϕ is the angle between the H–B bond and the BCC plane. ^{b} Table 5 column B, $\phi_1 = 95°$, $\phi = 95°$, $\phi = 0°$, $i.e.$ rearrangement in the BCC plane.

can occur. The illustrated mechanism (Scheme 4) for alkylation of alkynylborates is consistent with all available evidence. According to this mechanism, alkylation

28 K. Krogh-Jespersen, Universität Erlangen-Nürnberg, unpublished results.
29 J. E. Williams, jun., and A. Streitwieser, $Tetrahedron$ $Letters$, 1973, 5041.
30 N. L. Allinger and J. H. Siefert, $J.$ $Amer.$ $Chem.$ $Soc.$, 1975, **97**, 752.

TABLE 7

Possible reaction co-ordinates for rearrangement of alkynylborates as a function of angle bending (θ_1)
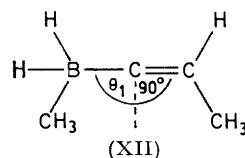
B Bending with rearrangement (retention, $\theta_1 > 90°$, CH_3 rearranges)
C Bending with rearrangement (inversion $\theta_1 < 90°$, CH_3 rearranges)

θ_1 (°)		Angle of bending (°)	Heat of formation (kcal mol^{-1}) †	
B	C		B 'retention'	C 'inversion'
90	90	0	3.38	3.38
92	88	2	1.78	4.89
95	85	5	−0.31	7.45
100	80	10	−3.34	12.16
110	70	20	−7.79	22.86

TABLE 8

Dependence of rearrangement on torsion angle ϕ^a with with $\theta_1 = 95°$

Torsion angle (ϕ) (°)	0	10	20	30	45
Heat of formation (kcal mol^{-1}) †	−0.31^b	+0.32	+2.23	+5.42	+12.6^c

^{a} ϕ is the angle between the CH_3–B bond and the BCC plane. ^{b} Table 7 column B, $\theta_1 = 95°$. ^{c} Not fully optimised.

† Whilst MINDO/3 is parameterised to calculate the heats of formation of particular arrangements of atoms in space, the mechanistic conclusions from calculations in this paper are based on energy differences and trends in energy differences. Absolute values for heats of formation are probably unreliable as bridging in boranes is frequently overemphasised by MINDO/3:[28] $e.g.$ surprisingly, the preferred conformation of vinylborane [equation (v)] is calculated to be perpendicular (rather than planar) with the angle BCC = 77°. However if the angle BCC in vinylborane is fixed at 120°, MINDO/3 predicts that the planar conformation is favoured, in agreement with ab $initio$ calculations.[28—30] In our calculations, the angle BCC is fixed at values >120°, so this defect of MINDO/3 should not affect our results. The preference for rearrangement with retention was verified further by two ab $initio$ calculations (Table 5, footnote c).

agent. The observed kinetic control of product form-ation, as well as the lack of product stereospecificity with the preferred migration towards the incoming electro-phile, are explained by formation of an intermediate in which the boron is bent away from the incoming electro-phile. Although the intermediate (VIII) is formally a zwitterion, the charges on boron and carbon appear to be small. Consequently, (VIII) behaves more like a neutral molecule and the stereochemistry of the rapid rearrange-ment is almost independent of solvent and leaving group (X). As protonation of simple alkenes and alkynes is known to occur by several complex mechanisms,[22] it is not surprising that the stereochemistry and mechanism of protonation of alkynylborates, discussed in a following paper,[15] are more difficult to interpret.

EXPERIMENTAL

Ether solvents were distilled under nitrogen from calcium hydride or lithium aluminium hydride prior to use. Other solvents and liquid reagents were purified by standard procedures.[31] Diborane was kept as a boron trifluoride-free solution in THF and was standardised before use. I.r. spectra were recorded on a Perkin-Elmer 257, n.m.r. spectra on a Varian HA-100 instrument, and mass spectra on an A.E.I. MS9 spectrometer. Commercially available n-butyl-lithium in hexane was standardised and used directly.

All manipulations prior to work-up were carried out in dry glassware under nitrogen; dry syringes being used to trans-fer liquids. Hydroborations were accomplished according to published procedures.[9d]

The reaction vessel was a 100 ml three-necked flask fitted with a magnetic stirrer. One neck was connected *via* a three-way tap to a source of oxygen-free nitrogen (with pressure release bubbler) and to a rotary pump. Another was sealed with a tap capped with a silicone rubber septum used for direct introduction of reagents or for sampling. The centre neck was fitted with a pressure-equalised dropping funnel sealed with a serum cap which was used for the preparation and addition of trialkylboranes. The apparatus was assembled hot, evacuated, flushed with nitrogen several times, and allowed to cool.

General Alkylation Procedure.—A solution of trialkyl-borane (5 mmol) in THF was prepared under nitrogen in the dropping funnel. To a stirred solution of the alkyne (5 mmol) in light petroleum (b.p. 40—60 °C; 5 ml), in the ice-cooled round-bottomed flask, n-butyl-lithium (5 mmol) in hexane was added dropwise. The alkynyl-lithium pre-cipitated as a white solid and butane was evolved. The ice-bath was removed and the mixture stirred thoroughly for 30 min. The flask was re-cooled to 0 °C and the solution of trialkylborane was added dropwise. Diglyme (5 ml) was added and the residual trialkylborane solution was washed into the flask with diglyme. After 2—3 min the precipitate had completely dissolved, and volatile materials were pumped off. Stirring was continued for a further 15 min at ambient temperature to complete formation of the salt. The solution was then cooled to −78 °C and the alkylating agent added. After treatment for the appro-priate length of time at specified temperatures (see Tables 1—3), the mixture was either hydrolysed or oxidised.

For the investigation of solvent effects, a variation of the above procedure was adopted: the trialkylborane was

prepared in THF and the solution added to the alkynyl-lithium stirred in light petroleum–hexane. After 45 min stirring at room temperature, the solvent was removed on a rotary pump and the solvent (5 ml) added.

To avoid protonation products in the allylation and benzylation reactions, the bromides were distilled and passed down a short alumina column immediately before use.

Oxidative work-up. Hydrogen peroxide (50%; 1.5 ml) was placed in the funnel, the serum caps being removed. The reaction flask was cooled in ice and aqueous sodium hydroxide (5M; 1.5 ml) added to the reaction mixture. Hydrogen peroxide (1 ml) was then added dropwise (care! —the reaction may be vigorous). The remainder of the oxidising reagent was then carefully added, the ice-bath removed, and the mixture left for at least 3 h. The product was extracted into ether and the extract was washed with water, dried (MgSO₄), filtered, and evaporated to give a syrupy residue from which the pure ketone was obtained by column chromatography as before.[2]

Hydrolytic work-up. Dry degassed isobutyric acid (2 ml) was added to the reaction mixture under nitrogen and the resultant solution stirred for 3 h at room temperature (hydrolysis is normally fast, but we have used up to 18 h at 25 °C, without lowering of yield). The apparatus was then opened to the air and the products were extracted into ether. The extract was washed with aqueous sodium hydrogen carbonate solution and water, dried (MgSO₄), filtered, and evaporated. The residue was applied as a solution in the minimum quantity of light petroleum (b.p. 40—60 °C) to a dry silica gel column (*ca.* 40 g), and the olefin fraction was obtained from the first 150 mol of light petrol-eum eluate.

It may be convenient, after hydrolysis, to oxidise the reaction mixture with NaOH–H₂O₂ to convert borinic acids into boric acid. This is particularly useful for borates derived from higher olefins.

All the olefins were obtained as mixtures of *E*- and *Z*-isomers, and gave correct carbon and hydrogen analyses and/or correct molecular weight. As the products were in fact mixtures, the physical constants (b.p., n_D) are not recorded here.

Reduction of 7-Allyltetradec-7-ene to 7-Propyltetradec-7-ene.—Bis-2-methylcyclohexylborane (4.37 mmol) was pre-pared in the usual way as white crystals from THF (3.35 ml).[9e] A solution of 7-allyltetradec-7-ene (1.03 g, 4.37 mmol) (*Z* : *E* 68 : 32) in THF (8 ml) was added to the suspension and the mixture stirred for 1 h at 23 °C; the precipitate had then all dissolved. Stirring was continued for another 30 min and the mixture then warmed for 17 h at 55 °C with isobutyric acid (1 ml). The mixture was cooled to 0 °C, and the olefin was isolated as described above. The product was 7-propyltetradec-7-ene [50% yield; *E* : *Z* (68 : 32)].

Ketonic Products (see also Table 1).—5-*Methyltetradecan*-6-*one* (1), n_D^{22} 1.433 8; b.p. 87—90° at 1.5 mmHg; (Found: C, 79.4; H, 13.2%; *M*⁺, 226.230.* C₁₅H₃₀O requires C, 79.55; H, 13.35%; *M*, 226.229 6); 8-*methyltetradecan*-7-*one* (2), n_D^{20} 1.435 3; b.p. 83—86° at 1.0 mmHg; (Found: C, 79.7; H, 13.2%; *M*⁺, 226.230. C₁₅H₃₀O requires C, 79.55%; H, 13.35%; *M*, 226.229 6); *cyclopentyl* 1-*methylheptyl ketone* (3) n_D^{20} 1.453 2; b.p. 95—97° at 2.5

* All high resolution data accurate to ±0.000 7 a.m.u.

[31] D. D. Perrin, W. L. F. Armarego, and D. W. Perrin, 'Purification of Laboratory Chemicals,' Pergamon, London, 1966.

mmHg; (Found: C, 79.7; H, 12.5%; M^+, 210.198. $C_{14}H_{26}O$ requires C, 79.95; H, 12.45%; M, 210.198 3); 5-*ethyltetradecan-6-one* (4), n_D^{20} 1.435 8; b.p. 90—93° at 0.8 mmHg; (Found: C, 80.2%; H, 13.4%; M^+, 240.245. $C_{16}H_{32}O$ requires C, 79.95; H, 13.4%; M, 240.245 3); 8-*ethyltetradecan-7-one* (5), n_D^{20} 1.439 7; b.p. 91—93° at 0.8 mmHg; (Found: C, 79.8; H, 13.2%; M^+, 240.245. $C_{16}H_{32}O$ requires C, 79.95; H, 13.4%; M, 240.245 3), *cyclohexyl* 1-*ethylpentyl ketone* (6), n_D^{20} 1.433 0; b.p. 88—90° at 1.2 mmHg; (Found: C, 79.85; H, 12.65%; M, 210.198. $C_{14}H_{26}O$ requires C, 79.95; H, 12.45%; M, 210.198 3); 8-*allyltetradecan-7-one* (7) n_D^{20} 1.439 7; b.p. 96—90° at 0.8 mmHg; (Found: C, 80.65; H, 12.6%; M^+, 252.245. $C_{17}H_{32}O$ requires C, 80.9; H, 12.8%; M, 252.245 3); 5-*allyltetradecan-6-one* (8), n_D^{20} 1.444 9; b.p. 100—102° at 0.9 mmHg; (Found: C, 80.9; H, 12.6%; M^+, 252.245. $C_{17}H_{32}O$ requires C, 80.9; H, 12.8%; M, 252.245 3); *cyclopentyl* 1-*propylbut-3-enyl ketone* (9), n_D^{20} 1.459 0; b.p. 89—92° at 1.0 mmHg (Found: C, 80.5; H, 11.7%; M^+, 208.183. $C_{14}H_{24}O$ requires C, 80.7; H, 11.6%; M, 208.182 7); *cyclopentyl* 1-*benzylpentyl ketone* (10), n_D^{22} 1.492 0; b.p. 120—122° at 1.0 mmHg (Found: C, 83.5; H, 10.2%; M^+, 258.198. $C_{18}H_{26}O$ requires C, 83.65; H, 10.15%; M, 258.198 46); 5-*benzyltetradecan-6-one* (11), n_D^{20} 1.479 2; b.p. 129—131° at 0.8 mmHg; (Found: C, 83.2; H, 11.3%; M^+, 302.261. $C_{21}H_{34}O$ requires C, 83.4; H, 11.35%; M, 302.260 9); 8-*benzyltetradecan-7-one* (12), n_D^{20} 1.484 8; b.p. 125—129° at 0.9 mmHg; (Found: C, 83.55; H, 11.3%; M^+, 302.261. $C_{21}H_{34}O$ requires C, 83.4; H, 11.35%; M, 302.260 9); *phenyl* 1-*methylpentyl ketone* (13), n_D^{23} 1.505 4 (Found: C, 82.4; H, 9.85%; M^+, 190.136. $C_{13}H_{18}O$ requires C, 82.05; H, 9.55%; M, 190.135 8).

Gas Chromatography.—A Perkin-Elmer F11 instrument with columns of silanized glass [6 mm o.d., 4 mm i.d., length 12 ft; Chromosorb G (AW-DMCS), (60—80 mesh)] was used. Apiezon M (15% w/w) was employed for the homologous hexyl series, and Apiezon N (8% w/w) for the butyl series. The packing was prepared by dissolving the required amount of stationary phase in redistilled toluene, adding the solid support, and removing the solvent by rotary evaporation. The columns were packed by suction and vibration, and conditioned by programming at 30 lb in^{-2} from 50 to 275 °C at 10° min^{-1}, the final temperature being held for 18 h.

For the homologous hexyl series, the column inlet pressure was varied between 10 and 20 lb in^{-2}, the injector temperature was 175 °C, and column temperature 160 ± 1 °C. For the butyl series, the inlet pressure was 13 lb in^{-2}, the injector temperature 150 °C, and the column temperature 125 ± 1 °C. Nitrogen was used as the carrier gas and all injections were of 0.5 µl from a 1.0 µl syringe.

' Purissimus ' dodecane was routinely used as the internal standard, and methane was used to measure the air time. Each *E*- and *Z*-pair was analysed separately.

Calculations.—The calculations were carried out by using Dewar's MINDO/3 programme,[26] available through the quantum chemistry program exchange (Indiana University), and the Swansea link to the University of Manchester Regional Computer Centre. Unless otherwise stated, all bond lengths and bond angles were optimised to find the structure and conformation of minimum energy. The *ab initio* calculations were carried out by Dr. D. Poppinger (Universität Erlangen-Nürnberg) using the Gaussian 70 program.[32]

[32] W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, 1969, **51**, 2657.