Tetrahedron. Vol. 30, pp. 2159 to 2163. Pergamon Press 1974. Printed in Great Britain

THE REACTION OF LITHIUM TRIALKYLALKYNYLBORATE WITH METHANESULPHINYL CHLORIDE

A NOVEL ROUTE TO INTERNAL ACETYLENES

M. NARUSE, K. UTIMOTO and H. NOZAKI
Department of Industrial Chemistry, Kyoto University, Kyoto, Japan

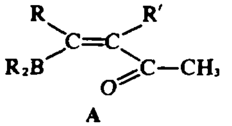
(*Received in Japan* 2 *February, Received in the UK for publication* 12 *February* 1974)

Abstract—Treatment of lithium trialkylalkynylborates (1) with methanesulphinyl chloride gives internal acetylenes (2) in good yields. The reaction proceeds via β-methanesulphinylvinylboranes 3, followed by cis elimination of methanesulphinyl group and dialkylboron groups. The reaction mixture of B-alkyl-9-BBN and 1-lithio-1-heptyne has been treated with methanesulphinyl chloride to provide mainly a cyclooctane derivative 6. This finding is explained in terms of the steric factors in the approach of the methanesulphinyl chloride.

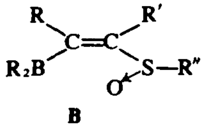
Nucleophilic reactions of lithium trialkylalkynylborates **1** have been reported by Binger and Köster to give substituted vinylboranes.[1] An application of these reactions to organic synthesis recently reported consists of treatment of the borate **1** with acetyl chloride and the subsequent Jones oxidation to afford α,β-unsaturated ketones.[2] The reaction apparently proceeds via β-acetylvinylborane (**A**). The present paper deals with the reaction of **1** with sulphinyl chloride examined in the expectation that the major product could be a β-sulphinylvinylborane (**B**) analogous to **A**. In a favourable case, **B** was actually isolated and characterized, but generally the vinylboranes **B** were apt to be easily transformed into internal acetylenes. A detailed examination of the migratory aptitude of **B**-alkyl groups is also reported.[3]

$$Li^+(R_3B^-{-}C{\equiv}C{-}R')$$

1

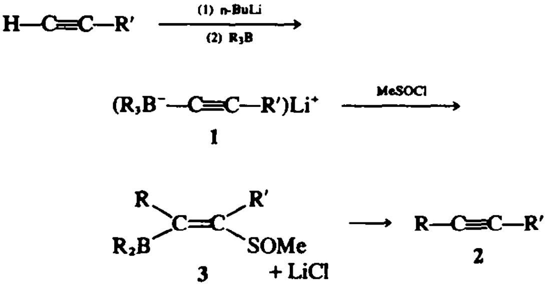


A



B

Successive treatment of phenylacetylene in THF at 0° with an equivalent amount of butyllithium (hexane solution), and then with triisopropylborane gave a hexane–THF solution of lithium triisopropyl-(2-phenylethynyl)borate (**1e**). When methanesulphinyl chloride (1·2 equivalent) was added at room temperature, a vigorous exothermic reaction ensued. GLC analysis of the reaction mixture indicated that the product was 3-methyl-1-phenyl-1-butyne (**2e**; 82%), which was isolated upon distillation and chromatography (silica gel–hexane).

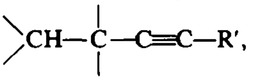


Combination of the substituents (R and R') and disubstituted acetylenes prepared in this way are listed in Table 1. As the R_3B is prepared by hydroboration of an olefin, $>C{=}C<$, the present

Table 1. Disubstituted acetylenes (2)

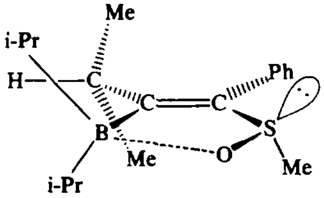
	R	R'	Yield (%)	b.p. °C	(mm)
a	n-Bu	n-Am	55[a]	87–89	(20)
b	sec-Bu	n-Am	72[b]	83–88	(15)
c	cyclohexyl	n-Am	62[b]	117–119	(24)
d	10-pinanyl	n-Am	61[b]	116–120	(7)
e	i-Pr	Ph	82[a]	101–104	(35)
f	n-Bu	Ph	63[a]	92–95	(21)
g	sec-Bu	Ph	62[a]	101–107	(30)

[a] GLC yield. [b] Isolated yield.

sequence of reactions produces an internal acetylene,  $>CH{-}\overset{|}{\underset{|}{C}}{-}C{\equiv}C{-}R'$, thereby making possible the anti-Markovnikov-reductive alkynylation of the olefin.

Although **2g** was also prepared by the reaction of **1g** with methanesulphonyl chloride in THF–hexane (1 : 1) the yield was only 28% even when the mixture was heated at reflux for 10 h.

Supposedly, the interaction of the sulphinyl chloride to the acetylenic π-system of **1** induces alkyl migration from the negatively charged, tetravalent boron atom to afford first the supposed intermediates **3**. Similar pattern of reactions, i.e., electrophilic attack on the β-acetylenic carbon and the simultaneous alkyl migration to the α-acetylenic carbon, has been observed previously with some alkylating reagents,[1,4] acetyl chloride,[2,5] and iodine,[6] in place of the present sulphinyl chloride. Such alkyl migration is also common in reactions of organoboranes with carbon monoxide,[7] or with α-bromo esters.[8] The intermediate **3** was actually isolated in the reaction of **1e** with methanesulphinyl chloride. The crude reaction mixture of **1e** with methanesulphinyl chloride was concentrated under reduced pressure and the residue was subjected to chromatographic separation to afford **3e** as white needles. Structure **3e** was determined on the basis of its chemical behaviour and spectral analyses. When a solution of **3e** was injected with GLC, the corresponding acetylene **2e** was detected in a quantitative yield. Mass spectrometry of **3e** by means of an indirect inlet system at 200° also showed the mass spectrum of a mixture of the cleavage products and nothing else. These results indicated that the sulphinylvinylborane **3e** easily eliminated methanesulphinyl and diisopropylboryl groups in the vapour phase (atmospheric pressure or high vacuum) in the absence of a catalyst, i.e., the acetylene formation was a unimolecular reaction. This type of elimination is reasonably understood when the two leaving groups are situated in cis manner analogously to the reported cases.[9] The NMR spectra of **3e** in CCl_4 (Fig 1) and in benzene (Fig 2) showed two methyl doublets of the C-isopropyl group. The ASIS[10] values of each signal indicate that **3e** forms a single collision complex with benzene, i.e., there exists only one conformer in the solution. Molecular model inspection shows that the nonequivalence of the C-isopropyl Me group should be ascribed to the structure shown:



Attempted treatment of **3e** with NaOH-I_2,[11] NaOH-H_2O_2, AcOH[12] and acetylacetone[1b] resulted in recovery of the starting material. Supposedly, the intramolecular coordination of oxygen to boron stabilizes this highly congested system.

Certain substituents on boron are known to have a negligible migratory aptitude. For example, alky-

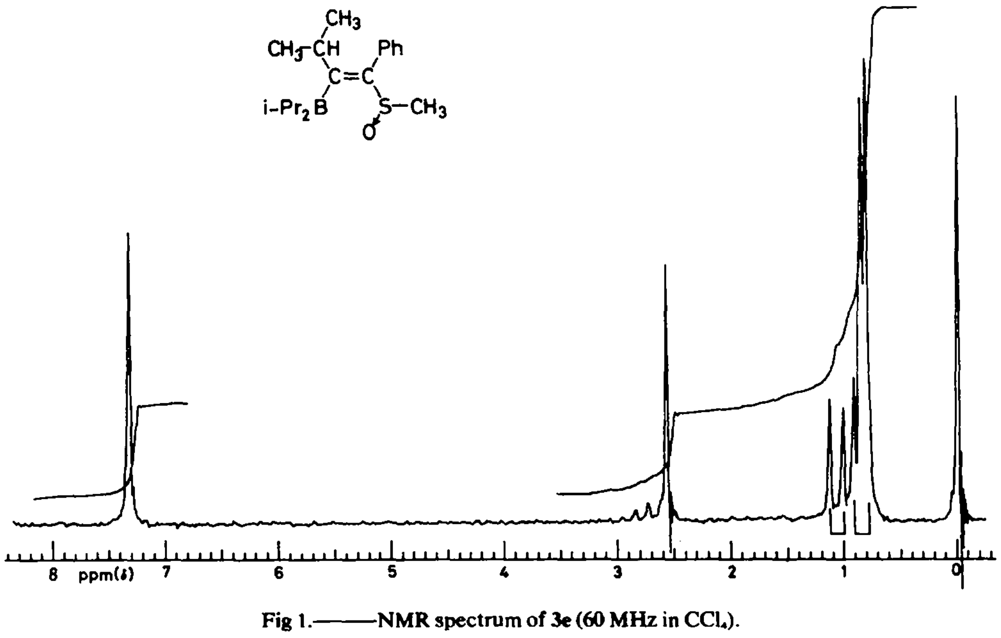


Fig 1.——NMR spectrum of **3e** (60 MHz in CCl_4).

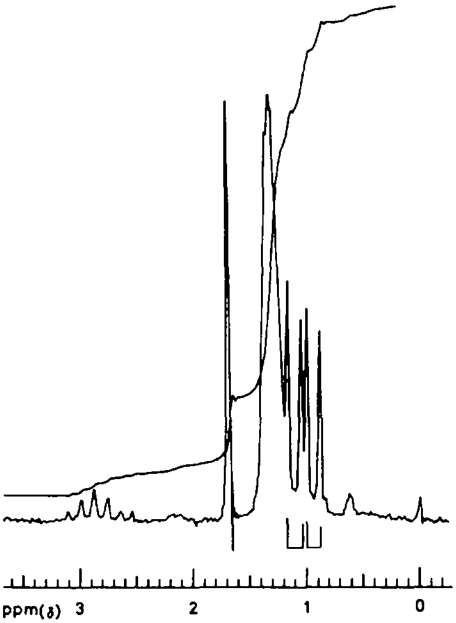
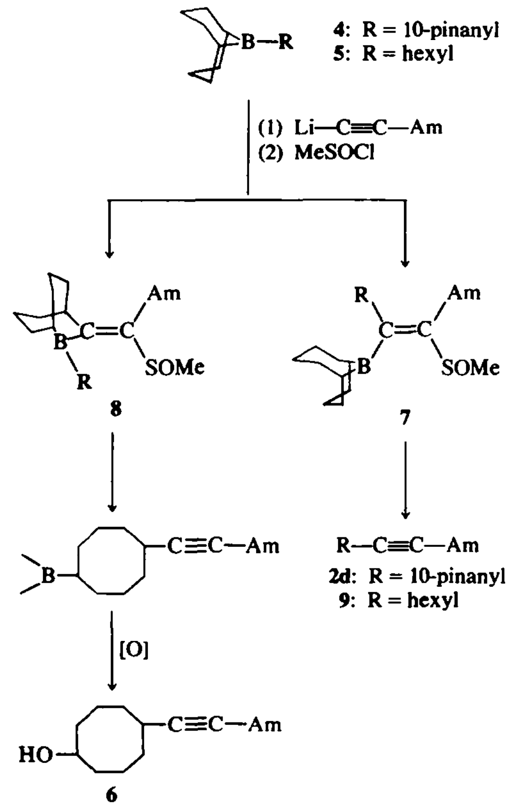


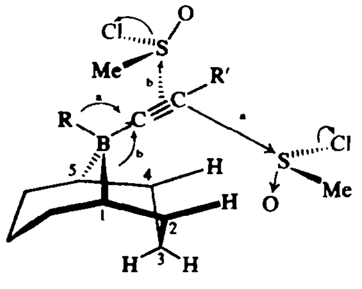
Fig 2.——NMR spectrum of **3e** (60 MHz in C_6H_6).

lation with B-alkyl-9-borabicyclo[3.3.1]nonane (B-alkyl-9-BBN) was shown to be selective, the transfer of the B-alkyl group occurring exclusively.[13] Similar selectivity is apparently exhibited by a thexyldialkylborane as the thexyl group does not migrate.[14,*] We wish to point out that, unexpectedly, neither of these boron reagents exhibited this type of selectivity in the present reaction.

A solution of B-(10-pinanyl)-9-BBN (**4**) in THF was maintained at room temperature and a solution of 1-lithio-1-heptyne in hexane was added. The mixture was stirred for 2 h at room temperature, and then methanesulphinyl chloride was added. After being stirred for an additional 2 h at room temperature, the resulting mixture was treated with alkaline hydrogen peroxide and extracted with hexane. Chromatographic separation (silica gel–hexane, benzene) gave **2d** (4%) and 1-(5-hydroxycyclooctyl)-1-heptyne (**6**) (24%). Similarly, the reaction of B-hexyl-9-BBN (**5**) gave 5-tridecyne (**9**, 2%) and **6** (23%). The predominant migration of the cyclooctyl moiety affording the intermediate **8** is accounted for on the assumption that R migrated to the neighbouring acetylenic carbon while the other acetylenic carbon underwent S_N attack at sulphur. Both reactions are assumed to occur in the trans manner, either concertedly or stepwise as shown in the Scheme 1. Pathway *a* gives rise to R migration under considerable steric inhibition of C(2) and C(4) hydrogens. Pathway *b* is devoid of such nonbonded interactions and apparently results in the preferential migration of the cyclooctyl moiety.



Cyclohexylhexylthexylborane, prepared by the successive addition of equimolar amounts of cyclohexene and 1-hexene to a solution of thexylborane in THF, was treated first with an equivalent amount of 1-lithio-1-heptyne and then with methanesulphinyl chloride. Three isomeric acetylenes (65%) were obtained: 2,3,3-trimethyl-4-decyne (**11**), 1-cyclohexyl-1-heptyne (**2c**) and 5-tridecyne (**9**) in a ratio of 12:50:38. The structures of these new compounds were determined by spectra. The migration of the thexyl group is without precedent, but is probably enforced here by the heavy congestion around the boron atom in the intermediate **10**.



SCHEME 1

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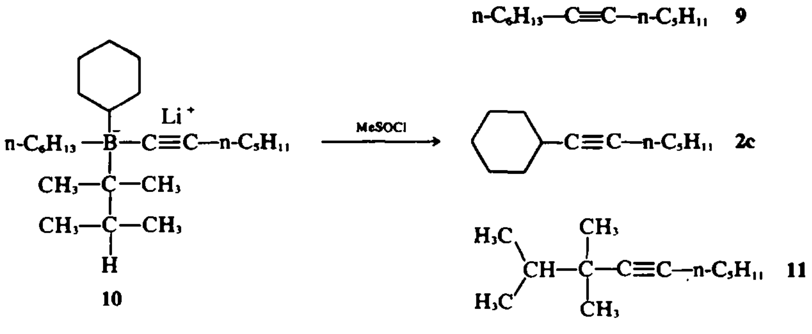
*These selectivities of migration were also observed in the reaction of sodium trialkylcyanoborates.[15,16]



EXPERIMENTAL

All b.ps were uncorrected. Gas chromatography was performed on Shimadzu GC-4BPT with 3 m × 3 mm column packed with 20% polyethyleneglycol and 25% HVSG on Chromosorb W-AW (80–100 mesh). Mass spectra were obtained on a Hitachi RMU-6L with 70 eV ionization potential, NMR with Me_4Si internal standard and CCl_4 solvent on JEOL C-60-H and Varian EM-360, UV on Hitachi EPS-2 and IR on Shimadzu IR-27G spectrometer.

Disubstituted acetylenes (2)

General procedure. To a stirred soln of 1-alkyne (5·0 mmol) in THF (5·0 ml) at 0° maintained under N_2, a hexane soln of n-BuLi (5·0 mmol in 5·0 ml) was added and the resulting mixture was stirred at room temp for 30 min. The mixture was cooled to 0° and trialkylborane (5·0 mmol) was added to the soln, then the resulting mixture was stirred at room temp for 1 h. To the soln, methanesulphinyl chloride (0·59 g, 6·0 mmol) was added. An exothermic reaction took place under precipitation of LiCl. The mixture was stirred for 3 h at room temp. After filtering off the ppt, the mixture was concentrated under reduced pressure. Distillation followed by chromatography on a silica gel column (hexane) gave **2**. Unless otherwise stated, following compounds were prepared in this way.

5-*Undecyne* (**2a**).[17] B.p. 87–89° (20 mm); IR (neat) 1460, 1378 cm^{-1}; MS *m/e* (rel. intensity %) 152 (M$^+$, 4), 95 (54), 81 (79), 67 (99), 54 (100).

3-*Methyl-4-decyne* (**2b**), yield 0·55 g (72%); b.p. 83–88° (15 mm); IR (neat) 1462, 1381, 1338 cm^{-1}; MS *m/e* (rel. intensity %) 152 (M$^+$, 2), 123 (11), 96 (16), 95 (15), 81 (100). (High resolution MS. Found: *m/e* 152·1567. Calcd for $C_{11}H_{20}$: *m/e* 152·1565).

1-*Cyclohexyl*-1-*heptyne* (**2c**), yield, 0·55 g (62%); b.p. 117–119° (24 mm); IR (neat) 2190, 1451 cm^{-1}; MS *m/e* (rel. intensity %) 178 (M$^+$, 8), 122 (33), 107 (41), 93 (55), 81 (77), 67 (100). (High resolution MS. Found: *m/e* 178·1712. Calcd for $C_{13}H_{22}$: *m/e* 178·1722).

1-(10-*Pinanyl*)-1-*heptyne* (**2d**), yield, 0·71 g (61%); b.p. 116–120° (7 mm); IR (neat) 1468, 1387, 1370 cm^{-1}; NMR (CCl_4) δ 1·02 (3H, s), 1·18 (3H, s), 0·8–2·7 (22H, m); MS *m/e* (rel. intensity %) 232 (M$^+$, 1), 161 (28), 123 (68), 81 (67), 69 (92), 67 (93), 41 (100). (High resolution MS. Found: *m/e* 232·2188. Calcd for $C_{17}H_{28}$: *m/e* 232·2191).

3-*Methyl*-1-*phenyl*-1-*butyne* (**2e**). The yield was 82% (GLC); b.p. 101–104° (35 mm); IR (neat) 2245, 1598, 1490, 1386, 1367, 1326, 756, 691 cm^{-1}; NMR (CCl_4) δ 1·26 (6H, d, J = 7 Hz), 2·74 (1H, hept, J = 7 Hz), 7·25 (5H, m); MS *m/e* (rel. intensity %) 144 (M$^+$, 44), 129 (100), 128 (55), 127 (23), 77 (12). (High resolution MS. Found: *m/e* 144·0920. Calcd for $C_{11}H_{12}$: *m/e* 144·0939).

1-*Phenyl*-1-*hexyne* (**2f**).[18] The yield was 63% (GLC); b.p. 92–95° (21 mm); IR (neat) 2245, 1596, 1489, 1380, 756, 691 cm^{-1}; MS *m/e* (rel. intensity %) 158 (M$^+$, 33), 143 (54), 129 (62), 128 (41), 115 (100).

3-*Methyl*-1-*phenyl*-1-*pentyne* (**2g**). The yield was 0·49 g (62%); b.p. 101–107° (30 mm); IR (neat) 2245, 1599, 1490, 1382, 1340, 756, 691 cm^{-1}; NMR (CCl_4) δ 1·07 (3H, t, J = 7 Hz), 1·26 (3H, d, J = 7 Hz), 1·55 (2H, quint, J = 7 Hz), 2·56 (1H, sext, J = 7 Hz), 7·26 (5H, m); MS *m/e* (rel. intensity %) 158 (M$^+$, 46), 143 (72), 129 (100), 128 (88), 127 (32), 77 (19). (High resolution MS. Found: *m/e* 158·1095. Calcd for $C_{12}H_{14}$: *m/e* 158·1096).

Compound **2g** *from* **1g** *and methanesulphonyl chloride.* To a stirred soln of lithium tri-sec-butyl(2-phenylethynyl)borate (**1g**, 5·0 mmol) in THF–hexane (1 : 1, 10 ml), which had been prepared by the general procedure, methanesulphonyl chloride (0·69 g, 6·0 mmol) was added at room temp. The resulting mixture was heated at reflux for 10 h. The yield of **2g** (28%) was obtained by GLC.

2 - *Diisopropylboryl* - 3 - *methyl* - 1 - *phenyl* - 1 - (*E*) - *butenylmethylsulphoxide* (**3e**). Lithium tri-isopropyl(2-phenylethynyl)borate (**1e**; 5 mmol) was prepared by the general procedure. After exchange of the solvent to ether (10 ml), methane–sulphinyl chloride (0·59 g, 6·0 mmol) was added at 0°. The resulting mixture was stirred for 3 h at 20°. Precipitated LiCl was filtered off, and then the solvent was removed under reduced pressure. The residue was chromatographed on a silica gel column with benzene as an eluant to afford 0·90 g (59%) of **3e**: m.p. 61–62·5°; IR (neat) 2945, 2855, 1469, 1373, 943, 912, 788, 737, 701 cm^{-1}; NMR (CCl_4) δ 0·85 (14H, m), 0·87 (3H, d, J = 7 Hz), 1·07 (3H, d, J = 7 Hz), 2·57 (3H, s), 2·74 (1H, hept, J = 7 Hz), 7·33 (5H, m); NMR (benzene) δ 0·96 (3H, d, J = 7 Hz), 1·12 (3H, d, J = 7 Hz), 1·34 (14H, m), 1·71 (3H, s), 2·87 (1H, hept, J = 7 Hz); MS *m/e* (rel intensity %) no parent peak, 261 (2), 167 (7), 160 (11), 144 (42), 129 (100), 128 (57), 127 (23), 117 (14), 89 (21), 77 (13), 71 (17), 47 (30), 41 (39). The two peaks, which *m/e* are 261 and 167, disappeared by heating the sample at 200° for 10 min in a reservoir; UV (EtOH) λ_{max} 254 nm, log ε 3·76. (Anal. Found: C, 71·06; H, 9·85. Calcd for $C_{18}H_{29}BOS$: C, 71·05; H, 9·61%).

Pyrolysis of **3e** *by* GLC. n-Decane (35·5 mg, 0·25 mmol) and **3e** (76·0 mg, 0·25 mmol) were dissolved in hexane (0·5 ml). The solution was injected to GLC (stainless column, 3 m × 3 mm, packed with 25% HVSG on Celite 545, column temp: 150°, injection chamber temp: 250°). The yield of **2e** (quantitative) was calculated by the areas of the two peaks and the relative sensitivity of n-decane and **2e**.

1-(5-*Hydroxycyclooctyl*)-1-*heptyne* (**6**) *and* 1-(10-*pinanyl*)-1-*heptyne* (**2d**). To an ice-cooled soln of BH_3

(10 mmol) in THF (5·9 ml) maintained under N_2, 1,5-cyclooctadiene (1·08 g, 10 mmol) was added. This mixture was then heated at reflux for 2 h. After cooling to room temp, β-pinene (1·36 g, 10 mmol) was added and the resulting mixture was stirred overnight at room temp. A soln of 1-lithio-1-heptyne, which had been prepared from 1-heptyne (0·96 g, 10 mmol) and a hexane solution of n-BuLi (10 mmol in 10 ml), was added to the above described mixture at 0°. The whole was stirred at room temp for 2 h. To the resulting mixture, methanesulphinyl chloride (1·18 g, 12 mmol) was added at room temp. After stirring for 4 h at room temp, the mixture was oxidized with 10 ml of 3N NaOH and 10 ml of 30% H_2O_2. The resulting mixture was extracted with ether, dried (Na_2SO_4), and concentrated. Chromatographic separation of the residue gave **2d** (0·093 g, 4%) and **6** (0·53 g, 24%): b.p. 147–150° (2 mm); IR (neat) 3360, 2930, 2855, 1468, 1381, 1047 cm^{-1}; NMR (CCl_4) δ 0·93 (3H, m), 1·0–2·3 (21H, m), 1·46 (1H, m), 3·77 (1H, m); MS *m/e* (rel. intensity %) 222 (M^+, 1), 165 (30), 81 (76), 79 (79), 67 (93), 55 (100); TMS ether, 294 (M^+, 2), 223 (48), 91 (30), 75 (68), 73 (100). (High resolution MS. Found: *m/e* 222·1984. Calcd for $C_{15}H_{26}O$: *m/e* 222·1984).

5-Tridecyne (**9**) *and* 1-(5-*hydroxycyclooctyl*)-1-*heptyne* (**6**). The same procedure as described above gave **6** (0·51 g, 23%) and **9**: b.p. 104–107° (15 mm); IR (neat) 2940, 2860, 1468, 1382, 1333 cm^{-1}; MS *m/e* (rel. intensity %) 180 (M^+, 1), 109 (30), 95 (69), 81 (83), 67 (100), 55 (67), 54 (79), 41 (78). (High resolution MS. Found: *m/e* 180·1878. Calcd for $C_{13}H_{24}$: *m/e* 180·1878).

5-Tridecyne (**9**), 1-*cyclohexyl*-1-*heptyne* (**2c**) *and* 2,3,3-*trimethyl*-4-*decyne* (**11**) *from* **10**. To a soln of BH_3 (10 mmol) in THF (5·9 ml) maintained under N_2 at 0°, tetramethylethylene (0·84 g, 10 mmol) was added and the stirring was continued for 2 h at the same temp. To the soln, cyclohexene (0·82 g, 10 mmol) was added at 0° and the stirring was continued for 4 h at room temp. To the resulting mixture, 1-hexene (0·84 g, 10 mmol) was added at 0° and the stirring was continued overnight at room temp. To the resulting soln, a hexane soln of 1-lithio-1-heptyne prepared from 1-heptyne (0·96 g, 10 mmol) and a hexane soln of n-BuLi (10 mmol in 10 ml) was added at 0°. To the resulting mixture, methanesulphinyl chloride (1·18 g, 12 mmol) was added at room temp. The resulting mixture was stirred for 4 h at room temp. Precipitated LiCl was filtered off and the soln was concentrated under reduced pressure. Distillation gave a mixture of three isomeric acetylenes, **5b**, **2c**, and 2,3,3-trimethyl-4-decyne (**11**; 1·17 g, 65%). GLC analysis revealed the distribution of three products as 38:50:12 (**5b**:**2c**:**11**). 2,3,3-Trimethyl-4-decyne (**11**): b.p. 95–97° (15 mm); IR (neat) 2970, 2945, 2875, 1467, 1459, 1391, 1380, 1370 cm^{-1}; MS *m/e* (rel. intensity %) 180 (M^+, 1), 109 (18), 95 (33), 71 (48), 43 (100), 41 (47). (High resolution MS. Found: *m/e* 180·1868. Calcd for $C_{13}H_{24}$: *m/e* 180·1878).

Acknowledgement—The authors are grateful to Professor C. Y. Meyers, Southern Illinois University, for helpful discussion.

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