Chemistry of Organoborates. Part IV.[1] Stereochemistry and Relative Migratory Aptitudes of Alkyl Groups in the Cyanoborate Process [1-4]

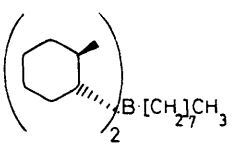
By **Andrew Pelter,* Michael G. Hutchings, Keith Smith,** and **David J. Williams,** Departments of Chemistry, University College of Swansea, Singleton Park, Swansea SA2 8PP, and The University of Manchester, Manchester M13 9PL

All three possible migrations from boron to carbon in the cyanoborate process involve retention of configuration at the migrating centre. For each of the three migrations the relative migratory aptitudes of alkyl groups are in the order n- > s- > t-, a result rationalised in terms of the charge density at carbon in the transition state. Products derived from certain di- and tri-substituted olefins should theoretically be mixtures of diastereoisomers and in one instance this has been verified.

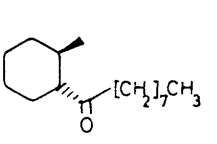
THE value of the cyanoborate process[1-3] for the production of ketones and trialkylmethanols would be considerably enhanced if the stereochemistry of the migrating centre were clearly defined and if the order of ease of migration of alkyl groups were readily predictable for each migration. We have therefore studied the reaction with a number of organoboranes in order to clarify the position.

Migratory Aptitudes.—The reaction of bis-(*trans*-2-methylcyclohexyl)-n-octylborane (I) with sodium cyanide followed by trifluoroacetic anhydride (TFAA) under the standard conditions used for ketone production[2] gave *trans*-2-methylcyclohexyl n-octylketone (II) (84%) on oxidation as the only identifiable ketone. In a similar way dicyclohexyl(ethyl)borane gave the corresponding unsymmetrical ketone contaminated by only traces of dicyclohexyl ketone. Two explanations would fit these observations. The first is that the primary group migrates faster than the secondary group in the first migration step. The second supposes that the secondary alkyl group migrates faster than the primary alkyl group in the first migration step and then this order is reversed for the second step. Although the second explanation may be considered less probable it should be stressed that each of the three migrations in the cyanoborate process is quite distinct from any other, that each will have differing electronic and steric requirements, and no valid pre-judgements can be made.

Careful examination by g.l.c. of the ketonic product of the reaction of potassium cyanocyclohexyldiethylborate with TFAA showed that it was diethyl ketone



(I)



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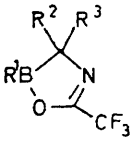


(III)

and that no cyclohexyl ethyl or dicyclohexyl ketone had been formed. Clearly the first explanation is correct and also the order n- > s- is established for the second migration of the groups studied.

Previous studies[2] have shown that both n- and s-alkyl groups migrate in preference to the t-alkyl group 'thexyl' (1,1,2-trimethylpropyl) for the first two migrations, and this has allowed us to use this group as an 'anchor' group for ketone synthesis. The order n- > s- > t- is clear for the first two migrations in the cases studied.

It is not possible to carry out intramolecular comparisons for the third migration, and intermolecular comparative experiments are necessary in this case.

[1] Part III, A. Pelter, M. G. Hutchings, and K. Smith, preceding paper.

[2] Part I, A. Pelter, K. Smith, M. G. Hutchings, and K. Rowe, *J.C.S. Perkin I*, 1974, 129.

[3] Part II, A. Pelter, M. G. Hutchings, K. Rowe, and K. Smith, *J.C.S. Perkin I*, 1974, 138.

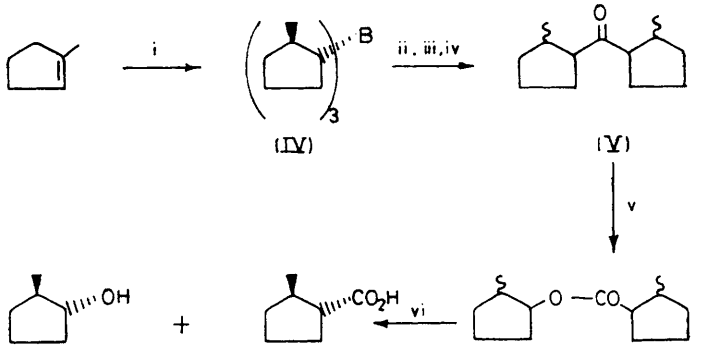
[4] A. Pelter, M. G. Hutchings, and K. Smith, *J.C.S. Chem. Comm.*, 1973, 186.

Our previous experience of the difficulties involved in inducing the third migration of bulky groups [3] strongly suggested the same relative ease of migration, but in order to eliminate any effects due to variations at the migration terminus in the intermediate (III) [2] we studied a series of boranes in which R^2 and R^3 were not varied. Using identical conditions in each case [addition of KCN (16·5 mmol) to the trialkylborane (15 mmol) followed by addition of TFAA (45 mmol) at 20° to the reaction mixture in diglyme, 3 h reaction, then oxidation with alkaline hydrogen peroxide], tri-n-hexylborane gave only products of three migrations (tri-n-hexylmethanol and the olefin derived from its dehydration), cyclohexyl-di-n-hexylborane gave cyclohexyl-di-n-hexylmethanol and di-n-hexyl ketone (7·3 : 1), and di-n-hexylthexylborane gave di-n-hexylthexylmethanol (and its dehydration product) and di-n-hexyl ketone (1 : 1).

being available for comparison (see Experimental section).

To check whether the ketone obtained from the intermediate (III; $R^1 = R^2 = R^3 =$ *trans*-2-methylcyclopentyl) by buffered oxidation was enolised at any time, the oxidation was carried out in D_2O. The ketone (V) did not contain any deuterium and enolisation at this stage was excluded. A degradation of the ketone (II) gave only *trans*-2-methylcyclohexanol. These results prove that each of the first two migrations is stereospecific and proceeds with retention of configuration.

The third migration was investigated by dehydrating the trialkylmethanol derived from (IV). Reductive ozonolysis of the olefin so obtained gave 2-methylcyclopentanone and a ketone identical in all respects, including the results of degradation as in Scheme 1, with bis-(*trans*-2-methylcyclopentyl) ketone (V). The third



SCHEME 1 Reagents: i, BH_3–THF; ii, NaCN; iii, TFAA; iv, H_2O_2, pH 9; v, *m*-$ClC_6H_4CO_3H$; vi, OH^-

The migratory aptitude for the third migration of the groups studied is thus n- > s- > t-, as for the first two migrations.

Although we have studied only a few groups, the consistency is such that it is reasonable to assume that this order is general.

Stereochemistry at the Migrating Centre.—The stereochemistry associated with the *cis*-addition of borane to double bonds was utilised to solve this problem. Hydroboration of 1-methylcyclopentene gives tris-(*trans*-2-methylcyclopentyl)borane [5] (IV). A comparison of the stereochemistry of the products of the cyanoborate process involving this borane with its known stereochemistry may be used to decide whether the migrations have proceeded with retention, inversion, or scrambling of configuration.

The ketone (V) derived from (IV) was subjected to Baeyer–Villiger oxidation with *m*-chloroperbenzoic acid in conditions such that migration from carbon to oxygen proceeds with retention.[6a,7,8] This reaction gave only *trans*-2-methylcyclopentanol and *trans*-2-methylcyclopentanecarboxylic acid (Scheme 1), authentic samples of the *cis*- and *trans*-isomers of these compounds

[5] H. C. Brown, M. M. Rogic, M. W. Rathke, and G. W. Kabalka, *J. Amer. Chem. Soc.*, 1969, **91**, 2150.

[6] 'Molecular Rearrangements,' part I, ed. P. de Mayo, Interscience, New York, 1963; (*a*) p. 579, (*b*) pp. 15—25.

[7] R. B. Turner, *J. Amer. Chem. Soc.*, 1950, **72**, 878.

migration therefore also proceeds with retention of configuration at the migrating centre.

Mechanism.—The stereospecificity of each step indicates that it is unlikely that migration involves a free carbanion but rather that bond making and breaking processes are concerted, with the migrating groups bonded at all times to the rest of the molecule. The migrations should thus be subject to the usual rules for pericyclic reactions.[9] Scheme 2 shows the formal nature of the migrations and their isoelectronic carbon analogues.

The first and third migrations are analogues of Wagner–Meerwein migrations and are formally allowed suprafacial shifts with retention of configuration.[9] The second migration is analogous to a 1,5-sigmatropic shift in a cyclopentadiene system, also allowed with retention of configuration in a suprafacial fashion. The stereospecificity found is thus in accord with predictions based on concerted mechanisms for all three reactions.

In the Wagner–Meerwein shift, however, the relative ease of migration is t- > s- > n-, a result rationalised [6b,10] in terms of the development of a degree of positive

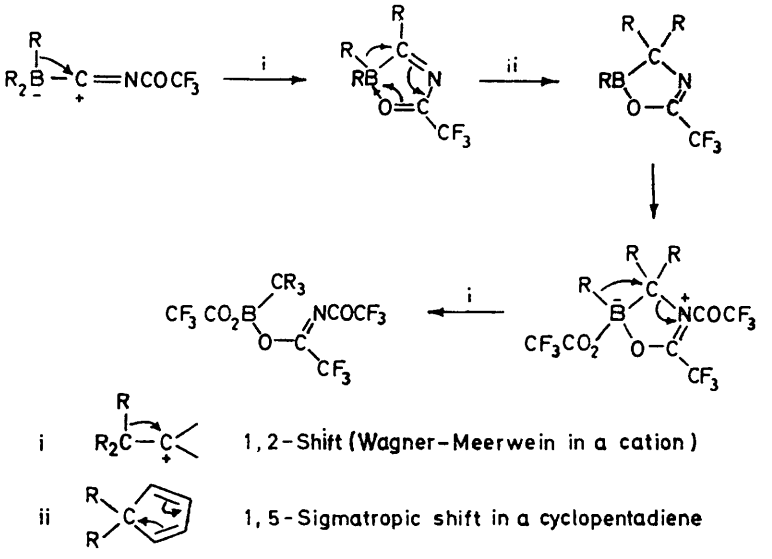
[8] K. Mislow and J. Brenner, *J. Amer. Chem. Soc.*, 1953, **75**, 2318.

[9] R. B. Woodward and R. Hoffmann, 'The Conservation of Orbital Symmetry,' Verlag Chemie, Weinkeim, 1970.

[10] M. Stiles and R. P. Mayer, *J. Amer. Chem. Soc.*, 1959, **81**, 1497; *cf.* W. M. Schubert and P. H. Lefevre, *ibid.*, 1972, **94**, 1639.

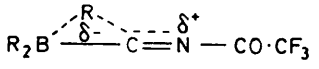
charge at the migratory centre in the transition state. This would be most stabilised by tertiary alkyl groups and least by primary groups.

In the reactions under consideration, however, the overall charge of the species undergoing migration is zero and it would seem likely that the migrating group bears some negative charge in the transition state,



SCHEME 2

e.g. (VI), particularly if the transition state occurs early in the reaction. This would lead to a reversal of the



(VI)

order of stabilisation of the charge in the transition state and an ease of migration in the order n- > s- > t- would thus not be unreasonable on electronic grounds.[11]

The relative importance of steric and electronic factors varies with each migration. For the first migration the two influences will oppose each other. The migration terminus is unsubstituted and hence the predominant steric factor will be relief of steric strain around the boron atom. The bulkier the group that migrates the greater the relief of strain and the relative ease of migration based on this factor alone would be t- > s- > n-. As the opposite order is found, it is clear that electronic considerations are paramount. For the electronically similar third migration, steric and electronic factors may be in accord as relief of steric strain around the boron atom will be of little importance compared with the increase in steric crowding around the heavily substituted migration terminus. For the second migration the steric influences at the boron atom and the carbon atom which is the terminus of the migration will tend to cancel out leaving the electronic factor decisive.

Diastereoisomerism of Trialkylboranes and Derived Products.—When hydroboration produces a chiral centre, then for an individual olefin molecule either an *R*- or an *S*-centre will be introduced. Three such reactions will give rise to a mixture of diastereoisomeric trialkylboranes which may be designated as ($[R]_3B + [S]_3B$) and ($[R][S]_2B + [R]_2[S]B$) where $[R]$ and $[S]$ represent alkyl groups of a particular absolute configuration. If the second and third additions were completely random then the ratio of ($[R]_3B + [S]_3B$) : ($[R][S]_2B + [R]_2[S]B$) would be 1 : 3 but such an assumption may of course be invalid and deviations from this ratio may well be expected.

In the cyanoborate process to give ketones (two migrations) the product should consist of a mixture of ($[R]_2CO + [S]_2CO$) and $[R][S]CO$, in a ratio of 1 : 1 for a completely random set of reactions. The hydroboration of 1-methylcyclopentene introduces two chiral centres rigidly related to each other due to the *cis*-nature of the addition. Hence an examination in the ^1H n.m.r. spectrum of the readily discernible methyl signal of bis-(*trans*-2-methylcyclopentyl) ketone (V), prepared in 80% yield by the cyanoborate reaction, should serve as a test of this reasoning.

In the 60 MHz spectrum the methyl group was observed as a doublet at τ 9·05 (J 6·5 Hz) on which was superimposed a minor splitting of 0·75 Hz. At 100 MHz the major coupling was little changed (6·3 Hz) but the minor splitting was now 1·2 Hz. At 220 MHz the relevant constants were 6·6 and 2·6 Hz showing that the major splitting was a true coupling but the minor one was due to the presence of a mixture which we suggest consists of the diastereoisomeric ketones ($[R]_2CO + [S]_2CO$) and $[R][S]CO$. The ratio of the signals was *ca.* 1·2 : 1, a small deviation from the statistical expectation for this product. Attempts to separate the

[11] D. E. Applequist and D. F. O'Brien, *J. Amer. Chem. Soc.*, 1963, **85**, 743.

diastereoisomers on a number of g.l.c. systems were not successful.

EXPERIMENTAL

Apparatus and reagents are as described previously.[2] Except where otherwise stated, all g.l.c. analyses were carried out at 10 lb in^{-2} N_2 pressure.

Stereochemistry of Migrations.—trans-2-*Methylcyclohexyl n-octyl ketone.* 1-Methylcyclohexene (2·84 g, 3·48 ml, 30 mmol) was treated with diborane dissolved in tetrahydrofuran (THF) (1·2M in BH_3; 12·5 ml, 15 mmol). The dialkylborane separated as white crystals which slowly dissolved on addition of oct-1-ene [12-14] (1·62 g, 2·25 ml, 15 mmol) and THF (30 ml) followed by gentle warming with a hair-dryer. Sodium cyanide (0·93 g; *ca.* 20% excess) was added and the mixture stirred at 23° for 18 h. TFAA (2·8 ml; 33% excess) was added at −78° and the mixture allowed to warm to room temperature. Oxidation was accomplished by addition of a solution of *m*-chloroperbenzoic acid [15] (MCPBA) (90% pure; 5·8 g, 30 mmol) in CH_2Cl_2 (20 ml) to the mixture at 10°. After 4 h the normal work-up [with addition of a washing with aqueous copper(I) chloride solution] gave the *ketone* (3·01 g, 84·5%; eluted with benzene), b.p. 90° at 0·1 mmHg; $n_D^{19·5}$ 1·4607 (Found: C, 80·8; H, 12·5%; M^+, 238·2298. $C_{16}H_{30}O$ requires C, 80·7; H, 12·6%; *M*, 238·2297). Analysis by g.l.c. showed a single peak, t_R 10·5 min (1 m column, 8% PEGA on 60—80 Chromosorb A, 150°).

Baeyer–Villiger oxidation of trans-2-*methylcyclohexyl n-octyl ketone.*[7,8] The ketone (1·02 g) in purified chloroform (10 ml) was treated in the dark with MCPBA (1·00 g; *ca.* 20% excess) at 25° until titration showed the reaction was 58% complete. The neutral product was isolated by washing with saturated sodium hydrogen sulphite solution until an iodide test was negative, then with ice-cold saturated sodium hydrogen carbonate (2 × 10 ml) and water (2 × 10 ml). The neutral product was saponified [8] by refluxing with 50% aqueous ethanol (20 ml) containing KOH (3·0 g) for 35 min. The neutral fraction from the saponification (0·817 g) was put on a silica column using pentane. Unchanged ketone (0·61 g) was isolated from the benzene eluate and *trans*-2-methylcyclohexanol (0·21 g) from the ether eluate. The alcohol was pure by g.l.c. (2 m column, 8% PEGA, 115°), t_R 6 min. Co-injection with authentic *trans*-2-methylcyclohexanol (see below) showed the identity of the two samples; their i.r. spectra were also identical.

Bis-(trans-2-*methylcyclopentyl*) *ketone.* Sodium cyanotris-(*trans*-2-methylcyclopentyl)borate (12·7 mmol) in bis-(2-methoxyethyl) ether (diglyme) (10 ml) was prepared as usual [2] from 1-methylcyclopentene (4·2 ml, 3·27 g, 40 mmol), diborane (12·7 mmol of BH_3), and NaCN (0·7 g, 14 mmol). TFAA (2·0 ml, 15 mmol) was added at −78° and the reaction stirred and allowed to warm to 20° over 1 h. A 1 ml aliquot portion was transferred to a dry, nitrogen-filled flask. The bulk of the reaction mixture was oxidised by the addition of $NaHCO_3$ (4 g) and 50% H_2O_2 (7 ml) at 0°, the mixture having pH 8 at that point. After stirring for 30 min (pH rose to 9), the mixture was allowed to warm to 20° and stirring continued for 15 h, at the end of which time the pH was unchanged. Extraction as usual [2] gave crude, neutral product (3·55 g). A sample (2·07 g) was chromatographed as usual to give the *ketone* (1·11 g); b.p. 74° at 0·5 mmHg; $n_D^{19·5}$ 1·4607. Allowing for the portion extracted the yield is 82% (Found: M^+, 194·1672. $C_{13}H_{22}O$ requires *M*, 194·1671); dinitrophenylhydrazone, m.p. 117·5—118·5° (from 95% EtOH) (Found: C, 60·5; H, 6·9; N, 15·0. $C_{19}H_{26}N_4O_4$ requires C, 60·9; H, 7·0; N, 15·0%).

The 1 ml aliquot portion was oxidised as above but using $NaHCO_3$ dissolved in D_2O (overall D : H ratio 2 : 1). The ketone (0·138 g) was shown by mass spectrometry to be free of deuterium. The dinitrophenylhydrazone also did not contain deuterium.

Baeyer–Villiger oxidation of bis-(trans-2-*methylcyclopentyl*) *ketone.* The ketone (190·7 mg, 1 mmol) was stirred with MCPBA (346·6 mg; 90% pure; 2 mol. equiv.) in purified chloroform (10 ml) at 20° in the dark for 11 days. Work-up as above was followed by reflux in methanol (5 ml) and 5N-NaOH (20 ml) for 4 h. The reaction was cooled, saturated with NaCl, and extracted with ether (2 × 20 ml). The ether extract was washed with 3N-NaOH (10 ml) and saturated NaCl solution (2 × 10 ml), dried ($MgSO_4$), and evaporated. Chromatography as usual gave unchanged ketone (40·2 mg, 21%; eluted with benzene) and *trans*-2-methylcyclopentanol (55·9 mg, 75%; eluted with ether). This was identical with an authentic sample [12] (see below) by i.r., n.m.r. [τ 9·07 (3H, d, *J* 6 Hz)], and g.l.c. (15% PEGA column, 50°).

The basic washings were combined, acidified, and extracted with ether. From the ether extract crude product (90·3 mg, 91%) was isolated which on distillation gave *trans*-2-methylcyclopentanecarboxylic acid (71·7 mg, 72%) identical with an authentic sample [16-18] (see below), τ ($CDCl_3$) 8·93 (3H, d, *J* 6 Hz).

Methylation (CH_2N_2) of the acid gave an ester, identical by co-injection on a 1 m column of 8% PEGA, 75° (t_R 4 min) with methyl *trans*-2-methylcyclopentanecarboxylate made from authentic acid.

The acid (55·1 mg) was reduced with an excess of lithium aluminium hydride in ether (5 ml) for 20 min at 20°. Excess of reducing agent was destroyed by addition of ethyl acetate, and the usual work-up gave crude *trans*-2-methylcyclopentylmethanol (44·6 mg, 91%) which was identical with an authentic synthetic sample [18] by g.l.c. on a 1 m column of 8% PEGA at 80° (t_R 6·5 min) and by i.r. spectroscopy.

Preparation of Authentic Samples.—trans-2-*Methylcyclopentanol.* This was made by the hydroboration–oxidation procedure of Brown,[13] and had b.p. 59—60° at 15 mmHg; $\nu_{max.}$ (film) 3300 cm^{-1}; τ ($CDCl_3$) 9·06 (3H, d, *J* 6 Hz); g.l.c. (1 m column, 15% PEGA at 50°) essentially one peak, t_R 24 min.

cis- *and* trans-2-*Methylcyclopentanol.* 2-Methylcyclopentanone ($\nu_{max.}$ 1740 cm^{-1}; t_R 7 min on a 3 ft 8% PEGA column at 75°) produced by Jones oxidation of *trans*-2-methylcyclopentanol (t_R 12 min, same column and conditions) was reduced with an excess of $NaBH_4$ in aqueous

[12] H. C. Brown and G. Zweifel, *J. Amer. Chem. Soc.*, 1961, **83**, 2544.
[13] H. C. Brown and A. W. Moerikofer, *J. Amer. Chem. Soc.*, 1962, **84**, 1478.
[14] H. C. Brown, N. R. Ayyangar, and G. Zweifel, *J. Amer. Chem. Soc.*, 1964, **86**, 397.
[15] J. R. Johnson and M. G. van Campen, *J. Amer. Chem. Soc.*, 1938, **60**, 121.
[16] F. Rouessac, P. Le Perchec, and J. M. Conia, *Bull. Soc. chim. France*, 1967, 818.
[17] L. Otvos, H. Tudos, and L. Radics, *Chem. and Ind.*, 1970, 597.
[18] H. Pines and N. E. Hoffman, *J. Amer. Chem. Soc.*, 1954, **76**, 4417.

ethanol for 90 min. The solution was saturated with NaCl and the alcohols were taken into ether. An i.r. spectrum showed that no ketone was left. The product was a mixture (*ca.* 3 : 1) of the *trans*- and *cis*-2-methylcyclopentanols which were well separated on a 1 m column of 15% PEGA at 50° (t_R; *trans*-alcohol 24 min, *cis*-alcohol 20 min). The mixture was used for comparison purposes.

trans-2-*Methylcyclopentanecarboxylic acid.* *trans*-1-Acetyl-2-methylcyclopentane, b.p. 80° at 13 mmHg; M^+ 126; $\nu_{max.}$ (film) 1700 cm^{-1}; τ 8·97 (3H, d, J 6 Hz) and 7·90 (3H, s), was prepared by acetylation of cyclohexane [16–18] (Found: C, 76·2; H, 11·1. Calc. for $C_8H_{14}O$: C, 76·2; H, 11·1%). It was contaminated by *ca.* 15% of the *cis*-isomer, τ 9·18 (3H, d, J 7 Hz). Oxidation by means of the iodoform reaction gave a product consisting almost entirely of the *trans*-acid [16–18] which was purified by bulb to bulb distillation, M^+ 128; $\nu_{max.}$ (film) 3500—2400 (OH) and 1710 cm^{-1} (CO); τ 8·95 (3H, d, J 6·5 Hz).

trans-2-*Methylcyclopentylmethanol.* Reduction of the *trans*-acid by a method of Pines and Hoffman [18] gave the pure *trans*-alcohol, n_D^{23} 1·4531 (lit., n_D^{20} 1·4533) running as one peak on g.l.c., t_R 6·5 min (1 m column, 4% PEGA, 80°).

trans-2-*Methylcyclohexanol.* This was prepared following the method of Brown,[13] b.p. 64—66° at 15 mmHg; n_D^{23} 1·4623 (lit.,[13] n_D^{20} 1·4611). G.l.c. analysis showed that 97% of the product ran as one peak, t_R 6 min (1 m column, 8% PEGA, 115°).

Dehydration of tris-(trans-2-*methylcyclopentyl*)*methanol to* 1-*methyl*-2-*bis*-(trans-2-*methylcyclopentyl*)*methylenecyclopentane.* The tertiary alcohol [3] (80 mg) in dry benzene (30 ml) containing some crystals of toluene-*p*-sulphonic acid was heated so that 20 ml of benzene distilled off in 1 h. The remaining benzene was removed and the residue taken into light petroleum (b.p. 40—60°) (10 ml) which was washed with saturated sodium hydrogen carbonate solution (10 ml), water (2 × 10 ml), dried ($MgSO_4$), filtered, and evaporated. The material was chromatographed on a dry silica column from which the required *alkene* (71 mg, 96%) was eluted with pentane, b.p. 196—199° at 768 mmHg; n_D^{23} 1·4814; one peak on g.l.c., t_R 3·5 min (1 m column, 8% PEGA, 172°) (Found: C, 87·4; H, 12·1%; M^+, 260·2504. $C_{19}H_{32}$ requires C, 87·7; H, 12·3%; M, 260·2504).

Ozonolysis of 1-*methyl*-2-*bis*-(trans-2-*methylcyclopentyl*)-*methylenecyclopentane.* Ozone was passed into a solution of the foregoing alkene (151 mg) in ethyl acetate (10 ml) at −78° until a pale blue colour persisted. The reaction was allowed to warm to room temperature and stirred whilst acetic acid and zinc dust were added in small portions. After 1 h acidified KI solution gave no iodine with a sample and the mixture was poured into water (20 ml) and extracted twice with ether. The organic extract was washed with 2N-NaOH (2 × 10 ml), H_2O (10 ml), dried ($MgSO_4$), and evaporated. The material was chromatographed as usual, the benzene eluate containing mainly bis-(*trans*-2-methylcyclopentyl) ketone [2] plus a little 2-methylcyclopentanone, as shown by mass spectra and by co-injection on g.l.c. with authentic samples on a 1 m column of 4% PEGA.

Baeyer–Villiger oxidation of the product was carried out at 55° for 4 days in purified chloroform using MCPBA. Work-up as for Baeyer–Villiger oxidation of the ketone (see above) gave *trans*-2-methylcyclopentanecarboxylic acid and *trans*-2-methylcyclopentanol identified by direct comparison with authentic samples.

Order of Migrations.—Preparation of cyclohexyldiethylborane.[19] Triethylborane (10 mmol) was placed in a three-necked flask under dry N_2. The flask was connected *via* a drying tube to a manometer and was equipped with a tap and septum cap. n-Butanethiol (100 mmol) was added *via* a syringe at 0° over 4 min. Ethane was evolved and estimated throughout the reaction which continued for 3 h at room temperature, during which time 1 ml of air was injected every 20 min. When evolution of ethane ceased, the mixture was fractionally distilled to give butylthiodiethylborane (95%); b.p. 39—42° at 1·5 mmHg (lit.,[20] 78—79° at 14 mmHg).

The product (1·58 g, 10 mmol) was taken into a three-necked flask and cyclohexene (0·90 g, 11 mmol) was added. The flask was cooled to −78° and $LiAlH_4$ (2·5 mmol) in THF added dropwise by syringe. The reaction was allowed to warm to 23° and stirred for 1 h. The solvent and excess of cyclohexene were evaporated off under nitrogen at room temperature and distillation afforded cyclohexyldiethylborane (1·08 g, 70%), b.p. 33—34° at 1·5 mmHg; g.l.c. (2 m column, 1·5% silicone gum rubber, 80°) showed only one peak, t_R 2 min, with a small peak (*ca.* 5% of product, t_R <30 s) shown by co-injection to be THF. No peaks corresponding to dismuted boranes were seen.

The borane (45 mg) was oxidised as usual with 50% NaOH–5N-NaOH and the neutral product isolated in the normal manner (ensuring that all aqueous solutions were saturated in order to obtain quantitative recoveries). G.l.c. (1 m column, 4% PEGA, octanol as internal standard) showed that 96% of the theoretical amount of cyclohexanol was present.

Cyanoborate reaction of cyclohexyldiethylborane. A standard ketone-forming cyanoborate reaction [2,3] in THF (10 ml) was performed on cyclohexyldiethylborane (0·8 g, 5·27 mmol). The solution after oxidation was saturated with salt and the organic products were extracted into pentane. G.l.c. (1 m column, 4% PEGA, 85°) showed three peaks, (i) t_R 2·25 min, shown by co-injection to be diethyl ketone, (ii) t_R 4·5 min, shown by co-injection to be cyclohexanol, and (iii) t_R 19 min, unidentified, shown by co-injection not to be dicyclohexyl ketone (t_R 17 min) or cyclohexyl ethyl ketone (t_R 7 min). The yield by g.l.c. of diethyl ketone was *ca.* 55% and peak (iii) had an area about 30% of this. Distillation gave diethyl ketone (0·22 g, 55%), b.p. 98—106°, identical with an authentic sample.

The i.r. of the residue showed no carbonyl absorption but a strong OH absorption at 3460 cm^{-1}. The third peak was most probably cyclohexyldiethylmethanol formed by three migrations of the alkyl groups from boron to carbon. This is likely [3] as the reaction was carried out in THF with a 20% excess of TFAA.

Preparation of cyclohexyl ethyl ketone by the cyanoborate process. Diborane in THF (4 ml; 1·25M in BH_3; 5 mmol) was added to cyclohexene (1 ml, 10 mmol) at 0° and the mixture stirred for 1 h. Ethylene was then passed over the reaction (still at 0°) until the precipitate of dicyclohexylborane dimer had dissolved (*ca.* 5 min) and the reaction was stirred for a further 1 h at room temperature.

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[20] B. M. Mikhailov and Yu. N. Bubnov, *Zhur. obshchei Khim.*, 1961, **31**, 160.

The usual ketone-forming cyanoborate reaction [2] in diglyme was performed to give the crude, neutral products of oxidation which were examined by g.l.c. (1 m column, 2% PEGA, programmed from 50 to 190° at 12° min^{-1}). No diglyme or cyclohexanol were present and the following peaks (estimated by use of octan-1-ol as an internal standard) were seen; (i) t_R 2·5 min, unknown, (ii) 3·5 min, cyclohexyl ethyl ketone, 76%, (iii) 6 min, unknown (trace), (iv) 8·5 min, dicyclohexyl ketone, 1%, and (v) 10·75 min, dicyclohexyl(ethyl)methanol, 6%.

The CH_2Cl_2 eluate from the usual chromatography [1] did not contain the unknown compounds (i) and (iii) but was a mixture of (ii), (iv), and (v). A sample (500 mg) was refluxed with benzene (50 ml) containing methanesulphonic acid (20 mg) for 10 min, and worked up in the standard way, after which all the trialkylmethanol had disappeared and two new peaks, t_R 5·75 and 6·25 min, appeared. This product was rechromatographed to give a mixture of 1-cyclohexyl-1-cyclohexylidenepropane and 1,1-dicyclohexylprop-1-ene [derived from dehydration of dicyclohexyl(ethyl)methanol] (49 mg, 5%; pentane eluate) (Found: M^+, 206·2034. Calc. for $C_{15}H_{26}$: M, 206·2034). The CH_2Cl_2 eluate contained cyclohexyl ethyl ketone (483 mg, 69%), b.p. 193—195° at 766 mmHg (lit.,[23] 196° at 760 mmHg), n_D^{24} 1·4523 (lit.,[23] n_D^{20} 1·4530) (Found: M^+, 140·1201. Calc. for $C_9H_{16}O$: M, 140·1201); semicarbazone, m.p. 147—149° (lit.,[23] 150—152°). G.l.c. analyses showed that the only contaminant was *ca.* 1% of dicyclohexyl ketone. This sample of cyclohexyl ethyl ketone was used for comparison purposes.

Cyclohexyldi-n-hexylborane. To chlorodi-n-hexylborane (1·08 g, 5 mmol) made from chloroborane,[21] was added dry methanol (0·41 ml, 10 mmol) at 0° and the mixture stirred for 30 min at 23°. Hydrogen chloride and excess of methanol were removed by prolonged pumping.

To the product *in situ* was added cyclohexene (0·5 ml, 5 mmol) and THF (5 ml). A solution of $LiAlH_4$ in THF (1·5 ml; 1·3M; 2 mmol) was added at 0°, and left for 1 h at room temperature.[22] The reaction was acidified with conc. H_2SO_4 and water (10 ml) was added. The organic product was extracted into pentane (all manipulations under N_2) and the resulting solution distilled to give cyclohexyldi-n-hexylborane (1·01 g, 3·7 mmol, 74%), b.p. 80—84° at 3 mmHg, g.l.c., broad, single peak, t_R 18 min (2 m column, 1·5% silicone gum rubber, 120°). The product (0·4 g) was oxidised overnight with 5N-NaOH (5 ml) and 50% H_2O_2 (5 ml). The alcohols were examined by g.l.c. (1 m column, 4% PEGA, using octanol as an internal standard): 97% of the theoretical amount of n-hexanol and 95% of the theoretical cyclohexanol were present, molar ratio 2·04 : 1.

Products from the Cyanoborate Process from Organoboranes which would have the same Groups at the Migration Terminus. —*Tri-n-hexylborane.* To potassium cyanotri-n-hexylborate [2,3] (5 mmol) in diglyme (10 ml) was added TFAA (2 ml, 15 mmol). The reaction was stirred for 3 h at 20°, TFAA was evaporated off, and the mixture was oxidised and worked-up as usual. The product was examined by g.l.c. (1 m column, 2% PEGA on 60—80 Chromosorb programmed from 50 to 190° at 12° min^{-1}, hexadecane as internal standard) and consisted of tri-n-hexylmethanol (65·4%; t_R 11·25 min) and its dehydration product (11·9%; t_R 6·24 min). No trace of di-n-hexyl ketone was seen.

Cyclohexyldi-n-hexylborane. This borane (0·4 g, 1·5 mmol) was subjected to the same conditions and gave cyclohexyldi-n-hexylmethanol (61·7%; t_R 11 min), di-n-hexyl ketone (8·6%; t_R 7·25 min), the alkene from dehydration of the trialkylmethanol (*ca.* 1%; t_R 6·25 min), and the alkene from a double migration [3] (*ca.* 1%; t_R 2·75 min). No other ketone was present.

Di-n-hexylthexylborane.[3] This was submitted to the same process and gave di-n-hexyl ketone (35·1%; t_R 7·25 min), di-n-hexylthexymethanol (32·3%; t_R 11 min), the alkene from dehydration of the triethylmethanol (3·1%; t_R 6·25 min), and the alkene from a double migration [3] (5·2%; t_R 2·75 min).

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