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A SIMPLE SYNTHESIS OF DIALKYLKETONES FROM ALKENES VIA HYDROBORATION-CARBENOIDATION

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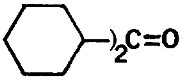
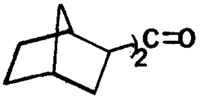
Abstract: Hydroboration of alkenes with sodium acetoxyborohydride($NaBH_3OAc$) followed by carbenoidation using $NaOCH_3/CHCl_3$ system and oxidation with $H_2O_2/NaOH$ give dialkylketones.

We have recently reported that the hydroboration of alkenes with sodium acetoxyborohydride ($NaBH_3OAc$), prepared in situ by the addition of acetic acid (1 mole) to sodium borohydride (1 mole) in THF, is relatively slow and only one equivalent of olefin (eg.1-decene) reacts in 12h at room temperature.[1] Methanolysis of the resulting organoboron species followed by carbenoidation using $NaOCH_3/CHCl_3$ system at 50°C and oxidation with $H_2O_2/NaOH$ gave di-1-decylketone (48%) and 1-decanol (44%) and no tridecylcarbinol was present.[1] This is an interesting observation as it indicates that the acetoxyborohydride species does not have the tendency to form trialkylborane species even in the case of terminal alkenes.[2] Presumably, complexation of the borane species with acetate anion makes the further reaction difficult. Similar behaviour has been noted previously with chloroborane ($ClBH_2$).[3] For example, the hydroboration of 1-butene with $ClBH_2$ in diethyl ether gives dialkylchloroborane (R_2BCl). On the other hand, in the presence of 1 to 2 equivalents of THF, the reagent gives the monoalkylchloroborane (RBHCl).[3] It has been suggested that the stronger complexation of the organoboron species by THF prevents dihydroboration.[3]

It appeared that the acetoxyborohydride species would provide a simple alternate method for the synthesis of mono- and dialkylboron species. These species have enormous synthetic potential.[2] We now wish to report that the hydroboration of alkenes (20 mmol) with sodium acetoxyborohydride (10 mmol) in THF (80 ml) at 50°C followed by carbenoidation using $NaOCH_3/CHCl_3$ at 50°C and oxidation with H_2O_2/ NaOH constitute a simple method for the synthesis of dialkylketones from alkenes. The following is the representative procedure.

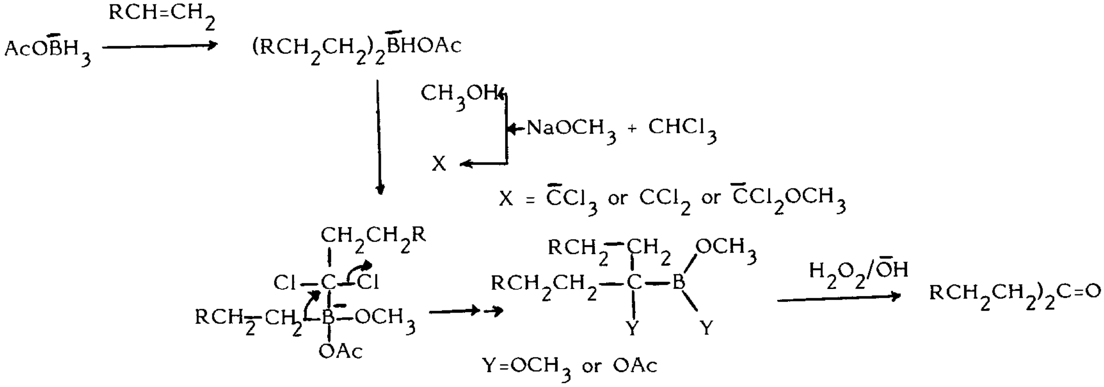
Acetic acid (10 mmol) in anhydrous THF (5 ml) was added dropwise during 30 minutes to sodium borohydride (10 mmol) suspension in THF (75 ml) with stirring at 0°C under nitrogen atmosphere. The contents were brought to room temperature and 1-decene (20 mmol) was added and stirred for 1h. The reaction mixture was further stirred for 2h at 50°C. Chloroform (10 ml) was added and sodium methoxide (40 mmol) was added in portions during 30 minutes at 50°C under nitrogen atmosphere using a solid addition flask. The mixture was further stirred for 2h at 50°C. The flask was brought to room temperature and water (2 ml) was added. The reaction mixture was oxidised using $H_2O_2/NaOH$ following the procedure reported for the oxidation of organoboranes.[2] After workup, di-1-decylketone was isolated in 80% yield by crystallization of the residue using hexane (see Table 1 for other examples).

Table 1: Conversion of alkenes to dialkylketones[a]

Substrate	Product	Yield [%][b]	m.p/b.p. [°C or °C/mm][c]
$C_8H_{17}CH{=}CH_2$	$C_8H_{17}CH_2CH_2)_2C{=}O$	80	64(62[4])
$C_4H_9CH{=}CH_2$	$C_4H_9CH_2CH_2)_2C{=}O$	63[d]	125/10(261/760[5])
		67[d]	64/0.4(96/1.2[6])
		59[e,f]	53(53-54[6])
$H_3COOC(CH_2)_8CH{=}CH_2$	$H_3COOC(CH_2)_8CH_2CH_2]_2C{=}O$	78[e]	72[g]

(a) The reactions were carried out using 20 mmol of alkenes, 10 mmol of $NaBH_4$, 10 mmol of CH_3COOH, 10 ml of $CHCl_3$ and 40 mmol of $NaOCH_3$. The reaction time and temperature for all the substrates for hydroboration and carbenoidation are the same as the time and temperature given in the representative procedure. (b) Yields are of isolated products based on the stoichiometry given in Scheme 1. (c) Literature m.p./b.p. are given in parentheses along with the corresponding literature reference. The spectral data (i.r., ^{1}H-NMR and ^{13}C-NMR] are in accordance with the assigned structures. Additional signals corresponding to the isomeric or epimeric alkyl moieties (if any) are not found in the ^{13}C-NMR spectra. (d) Products isolated by distillation. (e) Products isolated by chromatography on silica gel column using chloroform/hexane (1:9) as eluent. (f) Ethylene glycol (10 mmol) was added before oxidation as mentioned in the text. (g) ^{13}C-NMR (in $CDCl_3$, ppm) 211.5, 174.2, 51.3, 42.8, 34.1, 29.4, 29.2, 25.0, 24.9, 24.0. Mass (m/e, %) M^+H 427(100%), $(M-OCH_3)^+$ or $(M^+H-CH_3OH)^+$ 395(40%).

Scheme 1



Several features of this transformation deserve comments. The yields of the dialkylketones are comparable to the yields of the isolated products in the 'DCME' reaction using pure methyldialkylborinates (R_2BOCH_3) and the relatively expensive dichloromethylmethyl ether and lithium triethylcarboxide.[2,6,7] In the present method 5-10% of alcohols derived from the original organoboranes are also isolated. However the dialkylketones can be readily isolated free of alcohols utilizing simple techniques (see Table 1).

The trialkylcarbinol was not present in any run. Further, when the sodium acetoxyborohydride and 1-decene were used in the 1:3 ratio one equivalent of 1-decene remained unreacted. This indicates that the acetoxyborohydride has difficulty in forming trialkylboranes even with terminal alkenes. This is an important observation as it is not possible to stop the reaction at the dialkylborane stage using borane-tetrahydrofuran (BH_3.THF) complex and terminal alkenes in the 1:2 ratio.[2,7]

In the case of the transformation with norbornene, ethylene glycol (10 mmol) was added at 50°C after carbenoidation and stirred further for 30 minutes at 50°C before oxidation. Otherwise, the yield of the bis-exo-norbornylketone is less (40%) and a product mixture containing boron is also obtained. Presumably, ethylene glycol facilitates the oxidation of the organoboron intermediate by forming the corresponding cyclic boronate.[2]

The species formed by the addition of acetic acid (1 mole) to $NaBH_4$(1 mole) in THF is assumed to be $NaBH_3OAc$ on the basis of literature reports:[8,9] (i) C_2H_5COOH and $NaBH_4$ give $NaBH_3OOCC_2H_5$ which is also obtained by the reaction of C_2H_5COONa and B_2H_6. (ii) $NaBH_3OAc$ crystallizes out from THF/$NaBH_4$ mixture in good yields upon reaction with acetic acid.[9] (iii) $NaBH_3OAc$ species gives $(RO)_3PBH_3$ adducts upon reaction with trialkylphosphites.[9]

In several experiments, assuming the formation of $R_2\bar{B}HOAc$ species we methanolysed the reaction mixture before carbenoidation. Later, we have observed that the methanolysis is not necessary (see the representative procedure and Scheme 1). In an attempt to find out the fate of the remaining hydride, we carried out the hydroboration of cyclohexene (2 equivalents) at 50°C using 1-decanoic acid instead of acetic acid for the preparation of the acyloxyborohydride. Oxidation of the reaction mixture with H_2O_2/NaOH and acidification with 2N HCl gave 1-decanol (10%) besides 1-decanoic acid (90%) and cyclohexanol (85%). Consequently, at least 20% of the hydride has been utilized for the reduction of the carboxylic group.

The transformation reported here may be visualized by the mechanism outlined in Scheme 1.

In the 'DCME' reaction, the sterically hindered lithium triethylcarboxide has been used as the base in order to keep the methyldialkylborinate (R_2BOCH_3) 'free' from complexation with the base.[2,6] The $\bar{C}Cl_2OCH_3$ species, generated from dichloromethylmethyl ether and triethylcarboxide, would from an 'ate' complex with the dialkylborinate and the migration of the alkyl groups from boron to carbon would follow.[2,6] However, in the present case the base is not a hindered one and hence the reaction would most probably proceed by insertion of the electrophilic dichlorocarbene into the boron-carbon bond of the borate complex. It may be of interest to note that the intermediacy of dichlorocarbene has been also considered for the 'DCME' reaction.[2,7]

Although the mechanism is yet to be worked out, the present method has some advantages over the methods available in the literature for the synthesis of dialkylketones from alkenes via hydroboration. For example, whereas the Brown's 'DCME' reaction[2,6] of R_2BOCH_3 requires the dichloromethylmethyl ether and lithium triethylcarboxide, the present procedure utilizes the simple and less expensive $NaOCH_3$/$CHCl_3$ system. Apart from the 'DCME' reaction, the dialkylketones can be prepared from organoboranes by the carbonylation of trialkylboranes (R_3B) in the presence of water[2,7] or by the Pelter's cyanidation of $R'R_2B$ (R'=Thexyl group) followed by treatment with trifluoroacetic anhydride or acid chlorides.[5,10] The present procedure provides a simple alternate method for this purpose.

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