

The Reaction of Trialkylvinylborate with Carbon Dioxide. A New Method for the Preparation of β -Hydroxycarboxylic Acids from Alkenes

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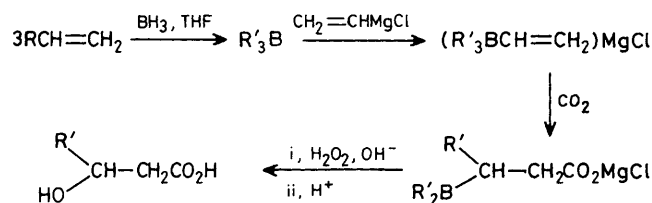
Chloromagnesium trialkylvinylborate, $(R_3BCH=CH_2)MgCl$, on reaction with carbon dioxide under pressure, followed by oxidation with alkaline hydrogen peroxide, gives a β -hydroxycarboxylic acid.

It has been shown that trialkylvinylborate can react with electrophiles such as iodine,¹ epoxide,² and aldehyde in a similar manner to trialkylalkynylborate.³ Recently, we have carried out the carboxylation of trialkylalkynylborate yielding a stereospecific α,β -unsaturated acid in high yield.⁴ Here, we report the result of the reaction between trialkylvinylborate and carbon dioxide.

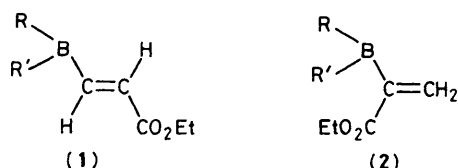
Under pressure, chloromagnesium trialkylvinylborate re-

acted with carbon dioxide to give an intermediate which on oxidation with hydrogen peroxide under alkaline conditions gave a β -hydroxycarboxylic acid with three extra carbon atoms from that of the starting alkene. The reaction sequence is summarised in Scheme 1.

Negishi⁵ has reported a novel method for the preparation of β -hydroxycarboxylic acids from alkenes *via* the dialkyl(2-ethoxycarbonyl-ethenyl)borane (**1**). However, when ethyl



Scheme 1



propiolate is hydroborated with dialkylborane, in addition to the desired intermediate (1), the compound (2), a product of boron attack on the carbon adjacent to the carboxylic group, is also formed. So the yield of the expected β -hydroxycarboxylic acid is notably affected. However, by treating carbon dioxide with trialkylvinylborate, in which any simple alkene may be used, highly regiospecific products can be obtained. Thus, this method permits the maximum conversion of a wider range of alkenes into β -hydroxycarboxylic acids.[†]

The reaction products of various chloromagnesium trialkylvinylborates with carbon dioxide are listed in Table 1.

Apparently, in this carboxylation reaction, the shift of the alkyl group from the boron to the α -carbon atom is an

[†] The preparation of β -hydroxynonanoic acid is representative of the general procedure. To a 2 M solution of BH_3 in tetrahydrofuran (THF), 7.6 g (90 mmol) of hex-1-ene in THF (10 ml) was added at 0 °C and stirred for 30 min at room temp. 2 M Vinylmagnesium chloride⁷ in THF (16.5 ml, 33 mmol) was added at 0 °C and stirred for 2 h at room temp. The mixture was treated with dry CO_2 at 0 °C for 1 h in an autoclave at 25 kg cm^{-2} . After transferring back to glass apparatus, 5 M NaOH (15 ml) was added, then 30% H_2O_2 (10 ml), and the mixture stirred for 4 h at 40 °C. This was neutralized to pH 6 with 6 M HCl. Recrystallisation from Et_2O -hexane gave 4.3 g, 82% yield, m.p. 59–59.5 °C. I.r. (KBr) 3450, 2750–3200, 1690 cm^{-1} ; 1H n.m.r. (CCl_4) δ 0.99 (3H, t, J 6 Hz), 1.17–1.8 (10H, m), 2.41 (2H, d, J 6 Hz), 3.8–4.2 (1H, m), 8.0 (2H, s).

Table 1. The reaction products of $(R_3BCH=CH_2)MgCl$ with CO_2 .^a

R	Product	Yield/%	M.p./°C	M.p./°C ^b
$C_6H_{13}^n$	$C_6H_{13}CH(OH)CH_2CO_2H$	82	59–59.5	58.8–59 ⁶
$C_7H_{15}^n$	$C_7H_{15}CH(OH)CH_2CO_2H$	81	56.5–57	56.4–56.6 ⁶
$C_8H_{17}^n$	$C_8H_{17}CH(OH)CH_2CO_2H$	85	72	71.2–71.4 ⁶
$C_{10}H_{21}^n$	$C_{10}H_{21}CH(OH)CH_2CO_2H$	78	80.5	80.4–80.6 ⁶
$C_{12}H_{25}^n$	$C_{12}H_{25}CH(OH)CH_2CO_2H$	83	87	86.7–87 ⁶
cyh ^c	cyhCH(OH)CH ₂ CO ₂ H	74	79.5–80	79.5–80 ⁵
Mecyp ^d	MecypCH(OH)CH ₂ CO ₂ H	80	70	69.5–70 ⁵

^a Isolated yields. All of the reaction products were completely characterised by spectroscopic methods. Elemental analyses of all products were satisfactory. ^b Literature values. ^c cyh = Cyclohexyl. ^d Mecyp = *trans*-2-Methylcyclopentyl.

intramolecular 1,2-migration. The fact that β -hydroxy- β -*trans*-2-methylcyclopentylpropionic acid is obtained from tris(*trans*-2-methylcyclopentyl)vinylborate indicates that the migration of the alkyl group from the boron to the α -carbon atom proceeds with retention of configuration, which is similar to the Negishi reaction.⁵

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