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REACTION OF CARBON DIOXIDE WITH TRIALKYLALKYNYL BORATES —— A NOVEL METHOD FOR THE SYNTHESIS OF STEREOSPECIFIC α,β-UNSATURATED ACIDS[*]

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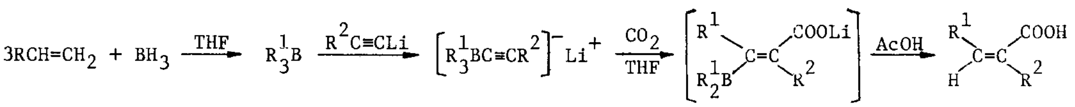
Abstract: Carboxylation of lithium trialkylalkynylborate can take place under favourable conditions. Protonation of the reaction product yields (Z)-α,β-unsaturated acid.

Quite a variety of electrophiles have been used in reaction with alkynylborates. Among these are carboxylic acids, iodine[1], simple alkylating agents, such as alkyl halides or tosylates[2], metal stablized cations[3], acid pyridinium salts[4], epoxides[5], and metal halides[6], which all gave non-stereospecific mixtures of addition products. Only in one case, however, Pelter et al. succeeded in preparing stereospecific trisubstituted alkenes by using more complexed alkylating agents[7]. We now wish to report a reaction between carbon dioxide and trialkylalkynylborates, the products of which on further treatment with carboxylic acids gave stereospecific α,β-unsaturated acids in rather good yields. The reaction is shown as follows:



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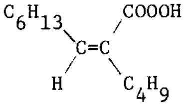
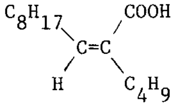
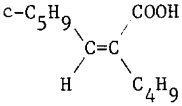
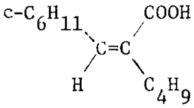
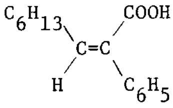
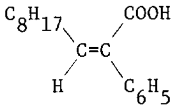
[*] This work was reported in the Second China-Japan-USA Symposium on Organometallic and Inorganic Chemistry in June 1982, Shanghai.

The lithium trialkylalkynylborates listed in the accompanying table were prepared by literature procedures[2]. Carboxylation of the alkynyl borates could not occur unless suitable conditions were employed. Thus, on passing carbon dioxide into the THF solution of the lithium trihexylhexynylborate, which was prepared from trihexyl borane (obtained by the hydroboration of hexene) and alkynyl lithium, no reaction took place under ambient conditions. There was no carboxylated product generated even by raising the temperature of the carboxylation reaction to 100-110°C. However, when the reaction was carried out under a carbon dioxide pressure of 25 kg/cm^2, a 56% yield of 2-butylnonenoic acid was obtained from the protonated product. The yield can be further improved to 82.3% by lowering the reaction temperature to about 20°C. Successful demonstration of the generality of the reaction was shown by using various alkenes and alkynes as starting materials, and all reactions took place smoothly giving the corresponding α,β-unsaturated acids after protonation with good yields as shown in table 1.

All the products listed in table 1 gave correct elemental analyses. Infra red spectra showed the presence of carboxyl group (2700-3100 cm^{-1}, 1680 cm^{-1}, 950 cm^{-1}) and double bond (1640 cm^{-1}) in each of these products. Mass spectra gave the correct m/e$^+$ and rational fragment peaks as expected. GLC of the ozonization products of compound (I) and (II) showed them to be n-heptyl aldehyde and n-nonyl aldehyde, respectively (in comparison with that of the standard aldehydes). All these results supported the structure as depicted. ^{1}H NMR of all the products in table 1 showed only single vinyl signal, which indicated that all the products are single isomers. In addition, the methyl esters of the products proved to be single isomers by GLC with various columns. Furthermore, the chemical shifts and coupling constants of vinyl hydrogens of the products (e.g. the chemical shift of vinyl hydrogen of compound (I) is 6.10 ppm and the coupling constant is 6.0 Hz) were in well agreement with those shown by similar compounds of Z-form as reported in the literature[8]. Likewise, calculation by Matter's empirical formula[9] gave results denoted them to be of Z- configuration. Thus, on the basis of spectroscopic as well as chemical evidences, all the α,β-unsaturated acids shown above have the Z-form.

Table 1: Yields of Products from Reaction of $[R^1_3BC\equiv CR^2]^- Li^+$ and CO_2

Starting	Material	Product		Yield*(%)
R^1	R^2			
n-Hexyl	n-Butyl		(I)	82.3
n-Octyl	n-Butyl		(II)	81.4
cyclo-Pentyl	n-Butyl		(III)	83.7
cyclo-Hexyl	n-Butyl		(IV)	80.5
n-Hexyl	Phenyl		(V)	71.4
n-Octyl	Phenyl		(VI)	75.6

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[*] Isolated yield.

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