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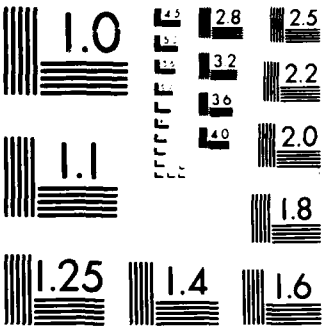

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FACILE SYNTHESIS OF α-DEUTERATED ACRYLICS AND ACTIVATED VINYLS

by

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A simple, direct exchange reaction has been discovered for vinyl groups in which the exchangable deuterium of alcohols (e.g. CH_3OD) or water (D_2O) replaces only the α-hydrogen of activated vinyls under catalysis by DABCO (1,4-diazabicylo-[2.2.2]octane). Acrylate esters, acrylonitrile, acrylamides and methyl vinyl ketone were found to go rapid exchange at room temperature to give easily isolated, pure and readily polymerizable α-deuterated compounds. This procedure is the most general efficient and cost-effective one available for obtaining such isotopically labeled materials.

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FACILE SYNTHESIS OF α-DEUTERATED ACRYLATES AND ACTIVATED VINYLS

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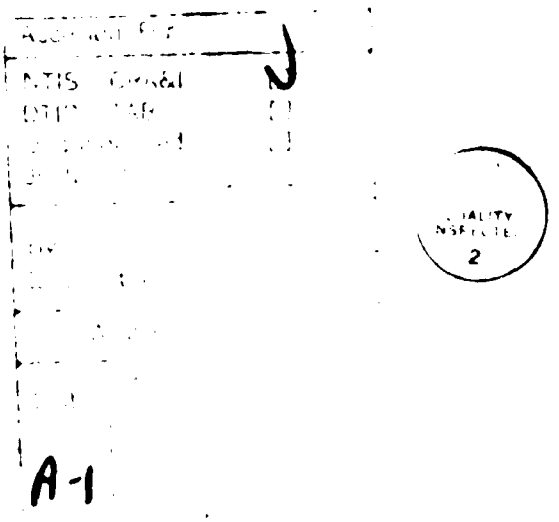
Abstract

A simple, direct exchange reaction has been discovered for vinyl groups in which the exchangeable deuterium of alcohols (e.g. CH_3OD) or water (D_2O) replaces only the α-hydrogen of activated vinyls under catalysis by DABCO (1,4-diazabicylo-[2.2.2]octane). Acrylate esters, acrylonitrile, and methyl vinyl ketone were found to undergo rapid exchange at room temperature to give easily isolated, pure and readily polymerizable α-deuterated compounds. This procedure is the most general, efficient and cost-effective one available for obtaining such isotopically labeled materials.



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Introduction

Enormous capability exists for studying reaction mechanisms, and the solution and solid state behavior of small molecules and polymers by ^2H NMR. In polymer characterization, for example, the molecular relaxation times available using variable temperature wide-line techniques spans the range of characteristic frequencies from ca. 10 MHz to 1 Hz[1]. New methods of deuterium incorporation at pivotal positions are vital for expanded use of these techniques.

An additional advantage in using deuterated reactants in synthesis is that ^2H NMR can be used directly to follow conversion, monitor intermediate formation and disappearance, and examine side-reactions and by-products. The present discovery stems from the combined use of ^2H, ^1H and ^{13}C solution spectroscopy to monitor the synthesis of a deuterated monomer needed for another study[2]. The specific reaction under investigation involved functionalization of acrylate esters by reaction with aldehydes in the presence of DABCO[3]. In the absence of acceptor aldehydes, and in the presence of a suitable exchangeable deuterium donor, rapid incorporation of deuterium at the α position was observed for a number of activated vinyl species (1 - 2). The Table summarizes our initial results.

TABLE

compound	reaction conditions	% deuterium*
methyl acrylate	30 min / CH_3OD	93.7
butyl acrylate	30 min / CH_3OD	81.8
acrylonitrile	30 min / CH_3OD	90.5
"	10 min / D_2O	82.0

* determined by integration of the vinyl region of the ^1H NMR spectra.

We propose a DABCO-catalyzed equilibration (Figure 1) in which deuterium incorporation can be driven to high levels by use of a large excess of the deuterium donor. Levels of incorporation greater than 80% were obtained in minutes with a single exchange process. This procedure is straightforward in contrast to previously reported multistep methods of α-deuteration of acrylates[4,5,6].

While either CH_3OD or D_2O served in the exchange for acrylonitrile, hydrolysis of the intermediate species formed from acrylate esters occurred in D_2O. In addition, higher alkyl esters underwent transesterification to methyl acrylate if the exchange reaction was extended. Exhange of methyl vinyl ketone was complete in a matter of minutes, although prolonged reaction led to Michael addition and aldol condensation products[7].

The general procedure involves simply mixing together excess deuterium donor with the activated substrate, adding DABCO, and monitoring the reaction with ^1H or ^2H NMR. Figure 2 gives

representative spectra for methyl acrylate. The vinylic region of the ^1H spectrum displays a typical ABX pattern with coupling constants J_{AB} = 1.5, J_{AX} = 17.3, and J_{BX} = 10.2 Hz. The deuterium spectrum displayed splitting of the α-^2H by the cis and trans hydrogens with J_{D-H_a} = 4.18 and J_{D-H_b} = 2.52 Hz. Complete ^1H-^2H equilibration was observed; *eg*, for methyl acrylate, 94% found vs. 92% theoretical.

These labeled materials, in addition to their value in forming specifically labeled polymers, should be useful in probing mechanisms in organic and natural product syntheses involving a variety of Grignard, Michael and Diels-Alder reactions.

ACKNOWLEDGEMENT

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LIST OF FIGURES

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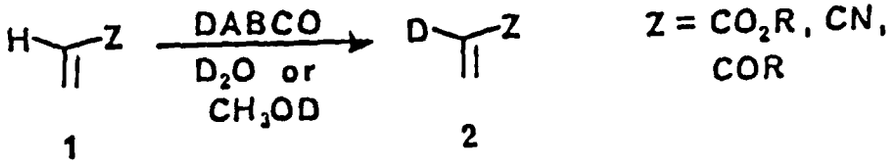
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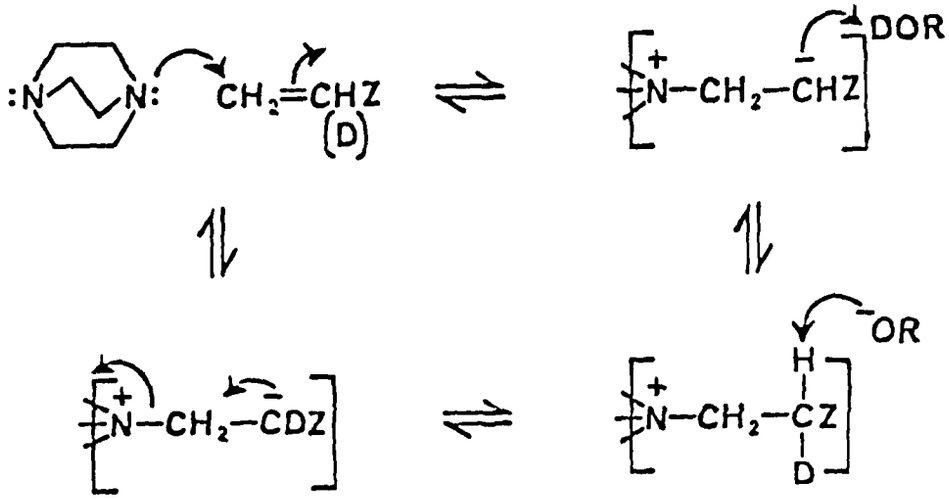
Figure 1.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N–CH2–CDZ
OR
H
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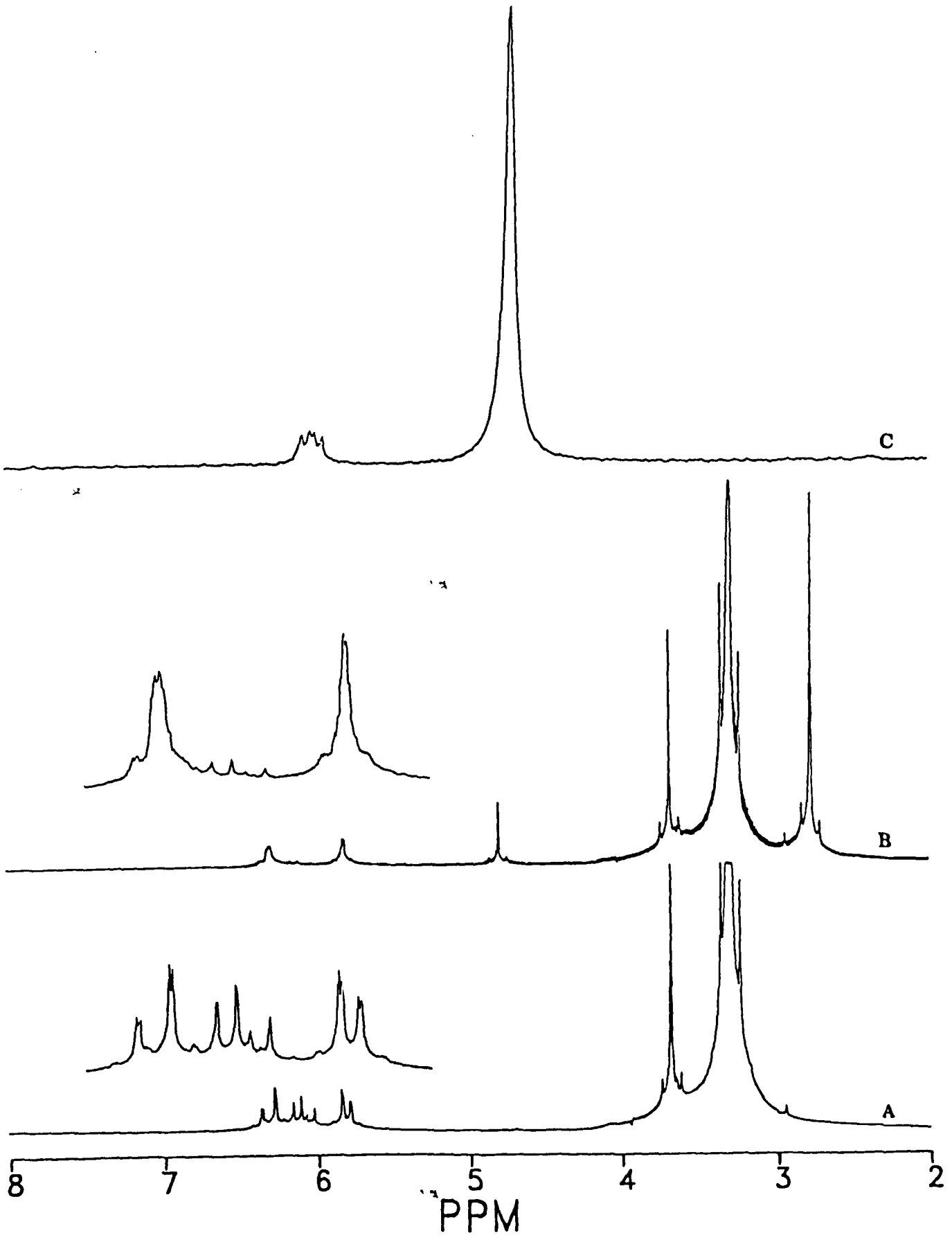
D

Figure 2.



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