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Unsymmetrically Substituted Aliphatic Diacetylenes

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Abstract: A general method for the synthesis of pure samples of unsymmetrically disubstituted diacetylenes of the type $CH_3\text{-}(CH_2)_n\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}CH_2\text{-}OH$ (n=2,3,4,5) is described in detail. The materials could be polymerized thermally, in the liquid state. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

Interest in diacetylenes has heightened after Wegner[1] explained the solid-state reactivity of these compounds in terms of a polymerisation reaction and, since then, polydiacetylene chemistry has become an integral part of modern polymer science. In addition to solid-state polymerisations which employ monomeric molecules arranged in a crystal lattice, the reaction has been applied to a range of organised molecular systems including Langmuir-Blodgett films, vesicles, micelles and, more recently, liquid-crystals.[2] The reaction has also been shown to occur in the liquid phase but very little work has been reported in this area.[3]

Unsymmetrically disubstituted diacetylenes are normally synthesised by the Cadiot-Chodkiewicz coupling of 1-halogenoacetylenes with terminal acetylenes. This reaction is particularly efficient for compounds in which the diacetylenic moiety is directly attached to an aromatic ring but the synthesis of aliphatic analogues is often irreproducible and tends to suffer from poor yields.[4] As part of our work on the preparation of new diacetylene monomers we have investigated the coupling behaviour of propargyl alcohol with a series of aliphatic 1-bromo- and 1-iodoacetylenes; the results of our investigation are presented here.

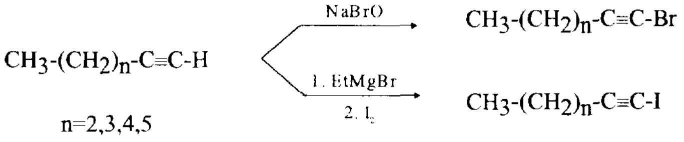
EXPERIMENTAL

The compounds were prepared by the Cadiot-Chodkiewicz coupling[5,6] of 1-halogenoacetylenes with propargyl alcohol according to the scheme below:

$$CH_3\text{-}(CH_2)_n\text{-}C{\equiv}C\text{-}X \;+\; H\text{-}C{\equiv}C\text{-}CH_2\text{-}OH \xrightarrow[NH_2\text{-}OH\cdot HCl]{Cu^+,\ C_2H_5\text{-}NH_2} CH_3\text{-}(CH_2)_n\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}CH_2\text{-}OH$$

n=2,3,4,5 ; X=Br, I

The 1-bromo- and 1-iodoacetylenes were obtained by the Strauss hypobromite method or *via* acetylenic Grignard reagents, respectively,[5] as described below:



General method for the synthesis of 1-bromoacetylenes.[3] Crushed ice (100g), aq. NaOH (60ml; 10M), bromine (10ml) and a solution of the terminal acetylene (0.1 mol) in THF (50ml) were agitated at room temperature for 5 days, after which time saturated aq. NH_4Cl solution (100 ml) was added in order to decompose any excess hypobromite. The reaction mixture was extracted with ether and dried over anhydrous Na_2SO_4. Removal of the solvent gave the crude product which was purified by distillation under vacuum. CAUTION: strong irritant to the respiratory tract.

General method for the synthesis of 1-iodoacetylenes.[7] To an ethereal solution of EtMgBr (40 ml; 3mol/l) in a dry flask equipped with magnetic stirrer and reflux condenser was added, over a period of 1 hr, a solution of terminal acetylene (0.1 mol) in dry ether (50 ml). The mixture was refluxed for 45 min, during which time powdered iodine (26 g; 0.2 mol) was added slowly through the reflux condenser. The contents of the flask were poured into water (300 ml) and acidified with glacial acetic acid. The ether layer was separated, washed successively with a 10% aq. $Na_2S_2O_3$ solution and water and dried over anhydrous Na_2SO_4. After removal of the ether, the yellow residue was purified by distillation under vacuum. CAUTION: strong irritant to the respiratory tract.

General method for the synthesis of diacetylenes. Freshly prepared CuCl (100 mg; 1 mmol), $NH_2OH{\cdot}HCl$ (3 g) and $EtNH_2$ (9 ml, aqueous solution; 70% w/w) were succesively introduced to water (40 ml), under stirring. The resulting solution was warmed to 50 °C (water bath) under a nitrogen atmosphere and propargyl alcohol (3.2 ml; 55 mmol) was added dropwise, followed by the slow addition of a solution of the 1-halogenoacetylene (50 mmol) in EtOH (50 ml); vigorous stirring was applied throughout. When the colour of the solution began to change, a further amount of hydroxylamine hydrochloride (~ 1g) was added and the process repeated until TLC showed no further change in the composition of the reaction mixture (ca. 10 hrs). NaCN (0.5 g) was finally added to destroy any cuprous complexes. Extraction with chloroform (3 x 100 ml), drying over magnesium sulphate and removal of the solvent gave the crude product which was purified by column chromatography on Merck Silicagel 60 using chloroform as the mobile phase (R_f= 0.15 on Merck Kieselgel 60 F_{254} TLC plates).

Instrumental. Infrared spectra (neat liquid) were recorded using a Perkin Elmer Paragon 1000 Fourier Transform spectrophotometer. ^1H and ^{13}C NMR spectra were obtained in $CDCl_3$ on a JEOL GSX FT NMR spectrometer operating at 270.05 MHz and 67.80 MHz, respectively; TMS was used as a standard. Electron impact and chemical ionisation (isobutane) mass spectra were determined on a JEOL JMS-DX 303 mass spectrometer.

RESULTS AND DISCUSSION

Both the Grignard and Strauss methods for the preparation of halogenoacetylenes resulted in the quantitative formation of the desired product. The IR and NMR data for 1-bromo-hept-1-yne and 1-iodo-hept-1-yne are given in Table 1; analogous data were obtained for all the synthesized halogenoacetylenes. In addition to the fragmentation pattern associated with the alkyl chain, the other main products of unimolecular fragmentation observed in the mass spectra were those associated with the cleavage of the propargylic and carbon-halogen bonds ($^+CH_2\text{-}C{\equiv}C\text{-}X$ and $CH_3\text{-}(CH_2)_n\text{-}C{\equiv}C^+$ ions).

The Cadiot-Chodkiewicz reaction was followed by thin layer chromatography. The coupling of 1-iodoalkanes with propargyl alcohol resulted in the formation of the expected pure diacetylenes in yields ranging from 23% to 31%; yields in the order of 35% were achieved when 1-bromoalkynes were employed. Column chromatography yielded the diacetylenic alcohols as colourless liquids. These exhibited high solubility in chloroform but were only partially soluble in water. Some of the spectroscopic data are summarized in Tables 2 and 3.

Table 1. IR and NMR data of 1-Halogeno-hept-1-yne ($X\text{-}C{\equiv}C\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3$).
1 2 3 4 5 6 7

Compound	IR $\nu_{C\equiv C}$ (cm^{-1})	^{1}H (δ ppm)	^{13}C (δ ppm)						
			C1	*C2*	*C3*	*C4*	*C5*	*C6*	*C7*
1-Br-hept-1-yne	2216	2.19(2H,t,$J_{3,4}$=7.0Hz); 1.51(2H,m); 1.34(4H,m); 0.90(3H,t,$J_{7,6}$=8.6Hz)	37.5	80.5	19.7	28.1	31.0	22.2	13.9
1-I-hept-1-yne	2186	2.35(2H,t,$J_{3,4}$=7.0Hz); 1.51(2H,m); 1.33(4H,m); 0.89(3H,t, $J_{7,6}$=7.1Hz)	-7.5	94.8	20.8	28.2	30.9	22.1	13.9

Table 2. IR and ^{1}H-NMR data for $CH_3\text{-}(CH_2)_n\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}CH_2\text{-}OH$ (protons are numbered as in Table 3).

Compound	IR		^{1}H NMR
n	$\nu_{C\equiv C}$ (cm^{-1})	$\nu_{O\text{-}H}$ (cm^{-1})	(δ ppm)
2	2255	3300	**-CH$_2$-O** 4.30(2H,d,$J_{1,0}$=9.7Hz); **-OH** 2.55(1H,broad); **-CH$_2$-C≡** 2.26(2H,t,$J_{6,7}$=7.0Hz); -C**H$_2$**- 1.56(2H,m,$J_{7,6}$=7.0Hz,$J_{7,8}$=7.4Hz); -C**H$_3$** 0.99(3H,t,$J_{8,7}$=7.4Hz)
3	2255	3332	**-CH$_2$-O** 4.30(2H,d,$J_{1,0}$=9.5Hz); **-OH** 2.58(1H,broad); **-CH$_2$-C≡** 2.29(2H,t,$J_{6,7}$=7.0Hz); -(C**H$_2$**)$_2$- 1.45(4H,m); -C**H$_3$** 0.91(3H,t,$J_{9,8}$=7.2Hz)
4	2255	3338	**-CH$_2$-O** 4.31(2H,d,$J_{1,0}$=6.0Hz); -C**H$_2$**-C≡ 2.28(2H,t,$J_{6,7}$=7.0Hz); **-OH** 2.17(1H,t,$J_{0,1}$=6.0Hz); -(C**H$_2$**)$_3$- 1.52(2H,m) and 1.34(4H,m); -C**H$_3$** 0.90(3H,t,$J_{10,9}$=7.0Hz)
5	2255	3330	**-CH$_2$-O** 4.32(2H,d,$J_{1,0}$=5.5Hz); **-OH** 2.31(1H,broad);-C**H$_2$**-C≡ 2.28(2H,t,$J_{6,7}$=7.0Hz); -(C**H$_2$**)$_4$- 1.52(2H,m) and 1.35(6H,m); -C**H$_3$** 0.89(3H,t,$J_{11,10}$=6.8Hz)

Table 3. ^{13}C-NMR data (the corresponding carbon nuclei have been numbered below the formulae)
- for n=2, $HO\text{-}CH_2\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}CH_2\text{-}CH_2\text{-}CH_3$
n=3, $HO\text{-}CH_2\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3$
n=4, $HO\text{-}CH_2\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3$
n=5, $HO\text{-}CH_2\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3$
0 1 2 3 4 5 6 7 8 9 10 11

n	Carbon shifts (δ ppm) for the corresponding numbered carbon atoms										
	C1	*C2*	*C3*	*C4*	*C5*	*C6*	*C7*	*C8*	*C9*	*C10*	*C11*
2	51.4	73.6	70.7	64.5	81.6	21.2	21.8	13.4	-	-	-
3	51.4	73.5	70.8	64.4	81.7	18.9	30.1	21.9	13.5	-	-
4	51.4	73.5	70.8	64.3	81.8	19.2	27.8	30.9	22.1	13.9	-
5	51.4	73.5	70.8	64.3	81.8	19.3	28.5	28.1	31.3	22.6	14.0

DEPT as well as direct and long range HETEROCOSY techniques were employed to assign the ^{13}C shifts (Figure 1). The assignment of the *sp* carbons resonances was in agreement with that previously reported for 2,4-octadiyne-1-ol.[8] The mass spectra were characterised by the presence of species typical of those expected when H_2O and alkyl radicals are lost from the molecular ion.

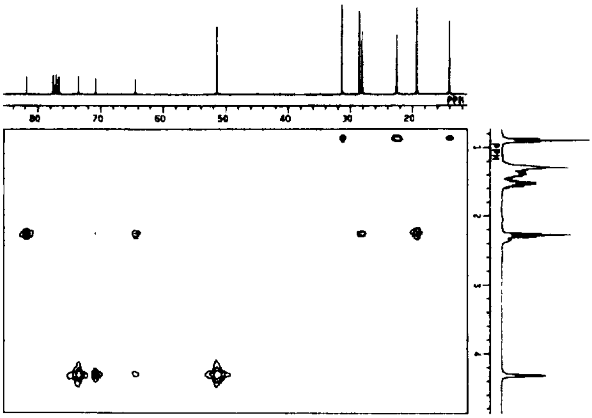


Fig. 1. Long range heteronuclear shift-correlated 2D NMR spectrum of 2,4-undecadiyne-1-ol.

In an effort to account for the low yields associated with these reactions, the byproducts of the coupling reaction were isolated. In addition to symmetrically disubstituted diacetylenes and amine addition products,[5] two types of diiodoalkene (formed by HI addition to the starting materials) were also identified: CH_3-$(CH_2)_n$-CI=CHI[9] (0.2% yield) and 1,2-diiodo-propene-3-ol HO-CH_2-CI=CHI[10] (1% yield).

The synthesised diacetylenes were found to polymerise thermally in the liquid state. Thus, heating of the corresponding monomers at 160° C (nitrogen atmosphere, 20 hrs.) resulted in the formation of black, glassy, brittle polymers, which were only partially soluble in THF, pyridine or diethyl ether. The average molecular masses of the soluble fraction, as determined by gel permeation chromatography (PHENOGEL 5 linear column, 30cm; room temp.; THF, 1 ml min^{-1}; polystyrene standards), were of the order of about 4000. In common with diacetylenes which polymerise in the solid state, the major difference between the IR spectra of the monomer and the polymer is the disappearance of the $\nu_{C\equiv C}$ stretching vibration at 2255 cm^{-1} and its replacement by a new one at 2216 cm^{-1}. In addition, a new broad and intense band appears in the region 1600-1700 cm^{-1}. The results of our detailed investigation into the polymer structure will be reported elsewhere.

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9. eg. for n=3: $\nu_{=C-H}$ = 3068 cm^{-1}; ^1H NMR δ ppm 6.80(1H,s), 2.51(2H,t,$J_{3,4}$=5.5Hz), 1.46(4H,m), 0.95(3H,t,$J_{6,5}$=7.2Hz); ^{13}C NMR δ ppm 104.3(C), 78.9(CH), 44.3, 30.2, 21.3(CH_2), 13.9(CH_3); MS molecular ion 336.
10. $\nu_{=C-H}$ = 3064 cm^{-1}; ν_{O-H} = 3330 cm^{-1}; ^1H NMR δ ppm 7.04(1H,s), 4.29(2H,d,$J_{3,0}$=7.0Hz), 1.96(1H,t, $J_{0,3}$=7.0Hz); ^{13}C NMR δ ppm 104.0(C), 79.8(CH), 70.8(CH_2).

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