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PREPARATION OF ALKYNES

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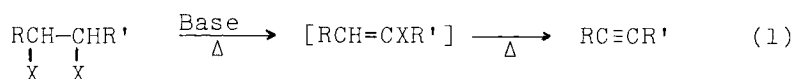
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PREPARATION OF ALKYNES

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For some time we have been interested in the synthesis of alkynes.¹ The desired products essentially dictated that the triple bond be introduced by double elimination reactions (eq. 1) Early experiments gave low yields of alkynes because



approximately half of the olefins formed had cis H-halogen bonds which would not yield the alkynes under conventional conditions such as potassium hydroxide, sodium hydride in mineral oil in diglyme or ethanol and at pot temperatures up to 200°. In order to avoid isolation of the olefins and their dehydrohalogenation in a separate second step (eq. 1) under more vigorous conditions such as with sodamide in liquid ammonia, the use of a stronger base from the start was investigated.

Many substances are much stronger bases in dipolar aprotic solvents and are effective in elimination reactions

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where olefins are formed.² Only one example of the formation of an alkyne albeit in low yield, from a dihalide aprotic solvent had been reported³ at the inception of our work. We have obtained relatively high yields (Table I) in short reaction times at moderate reaction temperatures in dipolar aprotic solvents using moderately to very strong bases without isolation of the intermediate olefins as shown in equation 2. The base can be sodium or potassium hydroxide or an

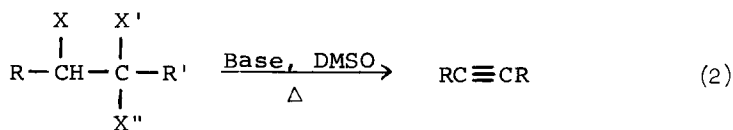
Table I. - Yields of Alkynes from Dihalides (KOH/DMSO)

Dihalides	Alkyne	Yield (%)
Me ₃ CCH ₂ CHBrCl	Me ₃ CC≡CH	91
Me ₂ CHCH ₂ CHBrCl	Me ₂ CHCH≡CH	75
CH ₃ CHBrCHBrCH ₃	CH ₃ C≡CCH ₃	86
C ₆ H ₁₃ CHBrCH ₂ Br	C ₆ H ₁₃ C≡CH	70
PhCHBrCHBrPh	PhC≡CPh ^a	100
Me ₃ CCH ₂ CH ₂ CHBrCl	Me ₃ CCH ₂ C≡CH ^b	64-82
Et ₃ CCH ₂ CHBrCl	Et ₃ CC≡CH	c

- a) See Org. Prep. Proced. Inter., 6, 183 (1974) for procedure.
 b) Characterized by IR and nmr; slightly impure.
 c) Not isolated as pure compound and detected by IR and nmr; its solution thickened on standing and peaks assignable to the acetylene group disappeared.

alkoxide whose alcohol boils preferably higher than the alkyne.

Table II shows the variation substituents (R and R') and



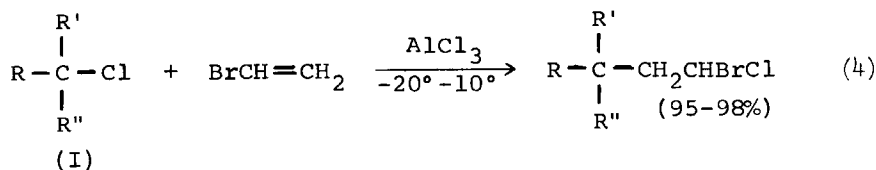
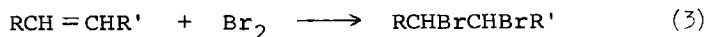
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halides which have been used.

Table II - Alkyl Halides used in Alkyne Synthesis

R	R'	X	X'	X''
C ₈ H ₁₇	H	Br	Br	H
CH ₃	CH ₃	Br	Br	H
(CH ₃) ₃ C	H	H	Br	Cl(Br)
(CH ₃) ₂ CH	H	H	Br	Cl(Br)
H	H	Br	Br	H
(C ₂ H ₅) ₃ CH	H	H	Br	Cl
(CH ₃) ₃ CCH ₂	H	H	Br	Cl

These examples illustrate the bisdehydrohalogenation of vicinal and geminal and of hindered and unhindered dihalides to give alkynes dihalides ranging from quite volatile over to relatively high boiling examples. Dichloro derivatives were also used but were typically slower than the bromo analogues. When alkoxides were used as bases, the reaction proceeded at temperatures lower than with sodium or potassium hydroxide. However as more alcohol was formed, the pot temperatures decreased sufficiently so that the alcohol had to be removed so that reasonable reaction temperatures could be obtained. In many of these cases, the unreacted olefins had to be separated from the recovered alcohol so that they could be returned to the reaction vessel. Although the dihalides can be made by any of the usual procedures, reactions 3⁴ and 4 were found to be most efficient and seemed to be useful for the preparation of a wide variety of dihalides from easily obtainable starting materials. Vinyl chloride has also been utilized⁵ in reaction 4 but temperatures of -30° to -20° must be used while I is



typically a secondary or tertiary halide. The overall advantages of these techniques resides in that a wide variety of secondary and tertiary halides may be used to prepare the dihalides instead of having to first obtain suitable aldehydes or ketones which may sometimes be inaccessible, followed by conversion to the gem-dihalides with phosphorus pentachloride. In addition, the reaction times for the preparation of the dihalide is less than 1 hr. and the yields are quite high. At 10° the yields of the dihalides are usually better than 80% while at -10 to -20° the yields are almost quantitative. The dehydrohalogenation reactions and simultaneous distillation generally require about 4 hrs.

EXPERIMENTAL

Preparation of 1-Bromo-1-Chloroalkanes.— The general procedure is illustrated by the preparation of 1-bromo-1-chloro-3,3-dimethylbutane. Into a 3-necked 500 ml round bottomed flask equipped with a condenser, addition funnel, thermometer and teflon coated magnetic stirring bar was added 148 g (1.6 moles) of t-butyl chloride. The flask was then cooled to about -20° with a Dry Ice-acetone bath and 3 g of anhydrous AlCl₃ added. About 171 g (1.6 moles) of liquid vinyl bromide (II)⁶ (from

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a gas cylinder pre-cooled to below 10°) was added slowly to the reaction mixture over 30 minutes, while temperature of the reaction mixture was kept between -20° to -25° . The reaction is exothermic and the temperature rises rapidly if the addition of the vinyl bromide is too fast.

After the addition of the vinyl bromide was complete, the reaction mixture was maintained between -20° to -25° for 30 min. before decantation into 50 ml of water. The mixture stirred until the two phases became colorless. The lower organic layer was separated, washed with 50 ml of 10% aqueous sodium hydroxide and two 50 ml portions of water. The product was then stored over potassium hydroxide overnight or dried by pouring through anhydrous sodium sulfate and distilled, bp. $60-64^{\circ}/17$ mm to give 3.3 g (98%) of 1-bromo-1-chloro-3,3-dimethylbutane.

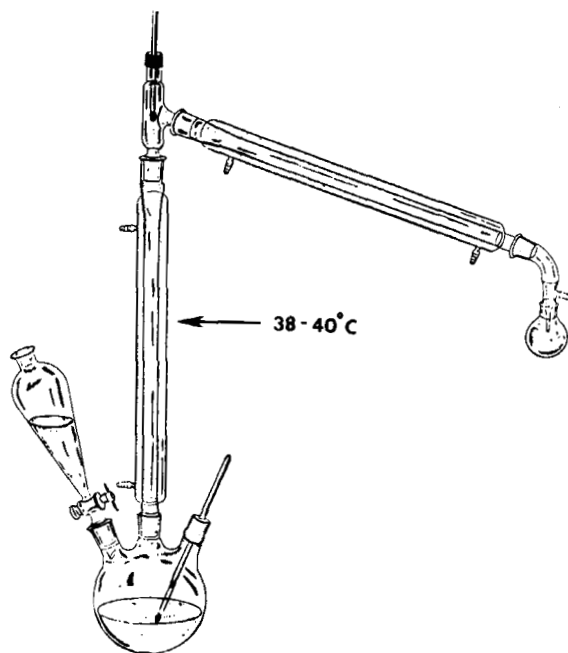
Preparation of Alkynes.-

1. Alkynes with bp. below about 60° . This is illustrated by the preparation of t-Butylacetylene.

Preparation of t-Butylacetylene.- To a 500 ml 3-necked round bottomed flask equipped with an addition funnel, thermometer and reflux condenser (to which has been attached a set up for downward distillation; see diagram) was added 112 g (1.7 mole) of potassium hydroxide and 250 ml of dimethyl sulfoxide. The temperature of the reflux condenser was adjusted to about $38-40^{\circ}$ by attaching it to a water tap. About 3-5 g of the 169 g (.85 moles) of 1-bromo-1-3,3-dimethylbutane was added and the pot temperature raised to about $110-130^{\circ}$. The potassium hydroxide pellets became slightly coated and the

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reaction mixture warmed up slightly. The remainder of the dihalide was then added at such a rate that the pot temperature



remained between 130-160° throughout the reaction and the t-butylacetylene was collected at a rate of about 1 drop every two seconds. The crude t-butylacetylene was fractionally distilled, bp. 37-39°, to yield 62.1 g (89%). Its nmr spectrum was consistent with that expected.⁴

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We have also prepared vinyl bromide by this technique from 1,2-dibromoethane under the same reaction conditions but eliminating the reflux condenser.

2. Preparation of alkynes with bp above about 60°. This is illustrated by the preparation of 1-decyne.

Preparation of 1-Decyne.- To a 500 ml 3-necked round bottomed flask equipped with a reflux condenser, addition funnel and stirrer was added 250 ml of dimethylsulfoxide and 67 g (1.02 mole) of potassium hydroxide. The stirred mixture was heated until all of the potassium hydroxide dissolved (approximately 120°). The heat source was removed and 90 g (0.30 moles) of 1,3-dibromodecane was added over a 20 minute period to the hot reaction mixture. After addition was complete, the addition funnel was replaced by a thermometer, the reaction flask was heated to and maintained at 130-140° for 1.5 hrs. After that time, the mixture was cooled to 50-60° and poured into a 1 liter beaker containing 500 ml of water. The layers were separated and the organic layer washed 3 times with 50 ml portions of water and dried over anhydrous magnesium sulfate. Distillation gave 27.7 g (65.7%), bp. 24.26°/0.5 mm.

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