

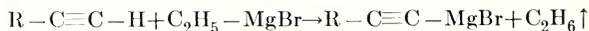
Preparation and Properties of Substituted Acetylenes

G. F. HENNION, University of Notre Dame

Introduction

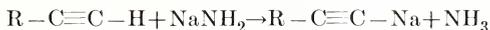
The normal alkyl- and dialkylacetylenes occupy an interesting position among the families of aliphatic hydrocarbons. Beginning with C_3 they are colorless liquids, quite readily prepared and stored. The lower members are gases and, with the exception of acetylene itself, may be condensed by proper refrigeration and (apparently) safely handled. (There is no difficulty in liquefying acetylene, but it is extremely hazardous to do so.) Previous to our investigations very little systematic work had been reported in the literature pertaining to the preparation and reactions of many of these hydrocarbons. Indeed, most of the text and reference works of organic chemistry dismiss these with but a few words or lines at the best. It so happens that many "simple" reactions of the higher acetylenic hydrocarbons remain to be investigated. For example, suitable means for hydration, hydrogenation, oxidation, etc., remain to be reported in many cases. The numerous addition reactions which are possible also promise interesting results. We have reported some of our studies in these connections (1); others are now under active investigation in our laboratory.

If one considers the many homologous series of organic compounds, it is apparent that examples of all of these may be prepared containing a triply bonded pair of carbon atoms, characteristic of acetylene, and containing also various substituents and functional groups. Many such compounds are known, to be sure, but homologous series of these show many vacancies. For such proposed work the monoalkylacetylenes themselves are the logical starting materials. It is evident that two courses of action are possible when one wishes to prepare acetylenic analogs of well-known organic compounds, namely, (a) the desaturation of a suitable paraffinic or olefinic compound to produce a triple linkage where one did not exist previously, and (b) the insertion of a desired alkynyl group into a molecule of fewer carbon atoms. The first method is, in general, not satisfactory. For example, the desaturation of structurally suitable di- and tetrabromides by means of alcoholic alkalies, zinc dust, or other agents, usually gives impure products or low yields or both. The second method is to be preferred whenever possible. It is very fortunate in this connection that acetylenic Grignard reagents are readily prepared. It is only necessary to treat a simple Grignard reagent, such as ethyl magnesium bromide, with an alkylacetylene and warm gently. The ethyl group is replaced by alkynyl as in the following equation.



The resulting acetylenic Grignard reagent may be used to prepare a wide variety of substances—acetylenic alcohols, ketones, acids, and other hydrocarbons, to mention but a few.

Sodium alkyl acetylides also may be prepared from monoalkylacetylenes by interaction of the acetylene with sodamide in liquid ammonia.



Such compounds behave in a manner analogous to the corresponding Grignard reagents and may be used as starting materials for various syntheses.

It is evident then that in the whole field of acetylene chemistry the hydrocarbons themselves occupy a key position. In this sense "acetylene chemistry" includes the study of all organic compounds containing one or more pairs of triply bonded carbon atoms, irrespective of other groups and elements combined in such compounds.

In general the monoalkylacetylenes undergo two fundamental types of reactions:

1. Replacement of acetylenic hydrogen. Typical are reactions in which acetylenic hydrogen is replaced by halogens and by metals. The resulting compounds contain the triple bond intact and may be employed in various syntheses.

2. Addition reactions at the triple bond. These are of two types: catalytic and non-catalytic. Addition of methanol or of carboxylic acids require a catalyst, namely a small amount of the mercuric ion in the presence of a suitable strong acid. On the other hand the halogens and halogen acids add non-catalytically as with the olefins.

The reactions of the dialkylacetylenes are naturally limited to those concerned with the triple bond since acetylenic hydrogen is not contained in these.

It is the purpose of this paper to review the methods now used in our laboratory for the preparation of normal alkyl- and dialkylacetylenes and to cite some of their properties.

Preparation of Monoalkylacetylenes

The best method for preparing monoalkylacetylenes involves the interaction of sodium acetylide and alkyl bromides in liquid ammonia. Well over 500 separate preparations of this general type have been conducted in our laboratory and the results summarized elsewhere (2).

The preparations involve two separate reactions: the preparation of sodium acetylide and its subsequent alkylation. An improvement in the technique of the former reaction has been developed recently whereby 5 to 7 moles of sodium acetylide may be prepared in 2.5 to 3 liters of liquid ammonia in less than 45 minutes. The apparatus used is illustrated in Figure 1 and consists essentially of a special five-liter three-necked flask provided with an efficient stirring mechanism.

In operation this flask is half-filled with anhydrous liquid ammonia and a rapid stream of dry acetylene gas passed in, with rapid agitation. Meanwhile a clean piece of sodium about 4x4x10 cm. is shaved free from oxide coating under dry xylene. The clean sodium is then weighed under dry xylene and a hole punched through one end. A stainless steel wire, about 75 cm. long, is looped through this hole and securely fastened to the sodium. The free end of the wire is led through a piece of

glass tubing, in turn fitted with a rubber stopper suitable for the neck *A*. The assembly is then rapidly transferred to this neck (*A*) and the sodium slowly lowered by means of the wire. In this way the rate of solution of sodium may be controlled readily and an inert atmosphere of ammonia, acetylene, and hydrogen automatically maintained. It is important to maintain a low concentration of dissolved sodium and a

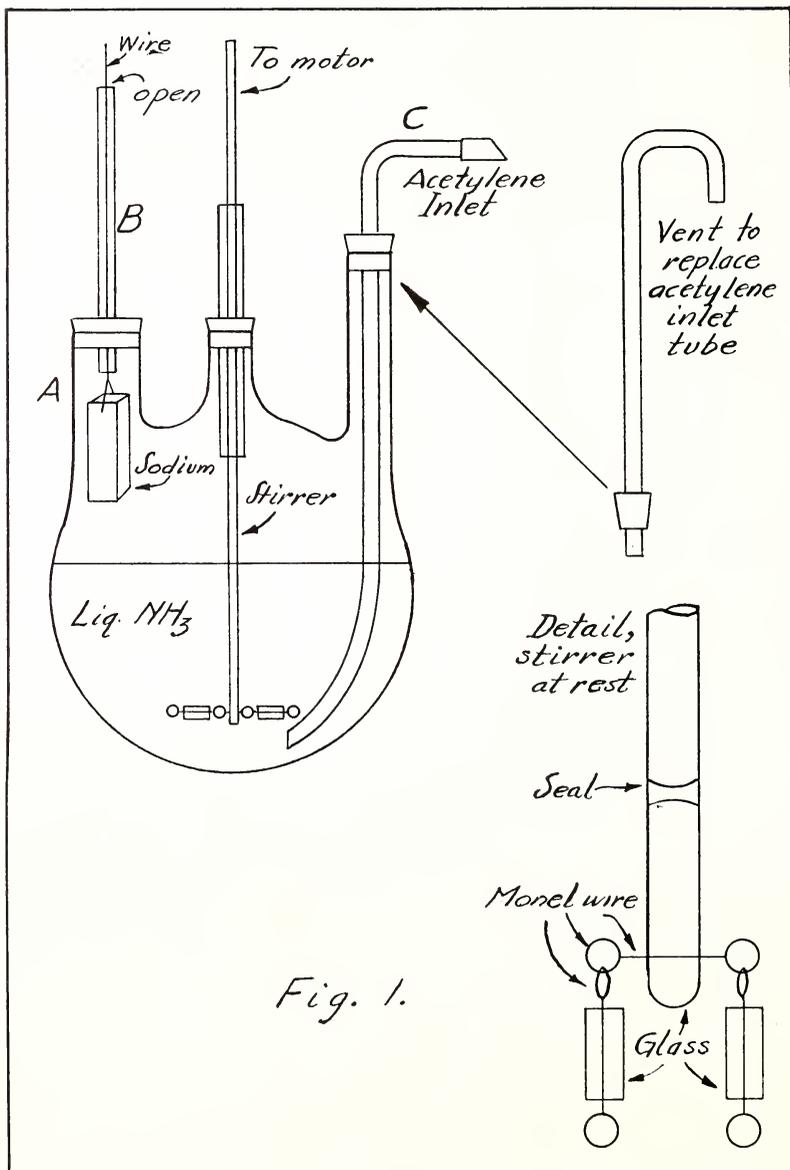


Fig. 1.

high concentration of dissolved acetylene since the latter becomes markedly less soluble as the concentration of sodium increases, consequently slowing tremendously the rate of reaction between sodium and acetylene:

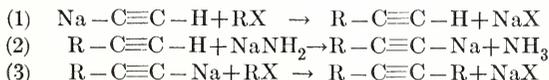


By lowering the sodium into the ammonia at such a rate that only the immediate zone in contact with ammonia is colored blue, as much as 3 gram-atoms of sodium may be converted to acetylide in 15 minutes, providing stirring is effective and acetylene passed in at a rapid rate. Obviously the sodium may be replaced when necessary. Indications are about 2 moles of sodium acetylide may be prepared per liter of liquid ammonia at about -34° , the boiling point of the latter. The acetylide remains substantially in solution and appears to be quite free from sodium hydroxide. Ammonia must be added, of course, from time to time, to maintain the volume of the solution.

When the desired amount of acetylide has been prepared the acetylene inlet tube (*C*) is removed and replaced with a glass tube about 50-75 cm. long, to act as a vent for the ammonia vapor. The tube and wire *B* also are removed and replaced with a dropping funnel containing the desired alkylating agent, e.g., *n*-butyl bromide. The latter is added to the acetylide in a rapid stream of drops and vigorous agitation maintained for 2 to 3 hours after the final addition. The ammonia is then allowed to evaporate until the reaction mixture becomes quite pasty, but not dry. Water or aqueous ammonia (about 300 ml.) is then added with stirring. The product is transferred to a large separatory funnel and the organic layer removed. This is washed with water, 10% hydrochloric acid, water, sodium carbonate solution, and finally with distilled water. Drying over calcium chloride and careful fractional distillation complete the purification. Yields average about 60-70% of the theoretical for butyl and amyl acetylenes and decrease somewhat as the alkyl bromides increase in molecular weight beyond C_5 .

Preparation of Dialkylacetylenes

The most widely used methods for preparing dialkylacetylenes involve the alkylation of sodium alkyl acetylides. Since the latter are prepared from monoalkylacetylenes, the following equations indicate a complete synthesis.



Such reactions are carried out in liquid ammonia with satisfactory results (2), except that the time consumed in conducting these separately is considerable. Recently we have observed that these reactions may be conducted *simultaneously* in liquid ammonia, by simply mixing the three required reagents in suitable proportions (3). Since intermediate products are not isolated or purified in any way, a considerable saving of time is effected.

In a typical synthesis 1.2 moles of sodium acetylide is prepared in one liter of liquid ammonia, as previously described. At the same

time 1.5 moles of sodamide is prepared in a separate container from 1.5 gram-atoms of sodium and 750 ml. of liquid ammonia, using hydrated ferric nitrate as a catalyst (4). The sodium acetylide and sodamide are mixed and 2 moles of n-butyl bromide added with vigorous agitation. After 2 to 3 hours of stirring, water is added and the dialkylacetylene purified in the manner described for monoalkylacetylenes.

These rapid preparations constitute a new technique for obtaining long carbon chains and are therefore of considerable academic interest.

Physical Properties of Substituted Acetylenes

Reliable physical data for the acetylenic hydrocarbons are meager. This is probably due to the fact that few investigators have prepared such compounds in a high degree of purity. It is of interest to note that in the disubstituted acetylenes we have unsaturated compounds in which there are no complications due to cis-trans isomerism.

TABLE I.—Physical Properties of Normal Acetylenic Hydrocarbons

Formulae		Boiling Points			Densities		Refractive Indices	
R—C≡C—R'		Mm. of Hg		Ref.	Densities		Refractive Indices	
R	R'	760	50		d_t	Ref.	n_{D_t}	Ref.
H	H	—83.6		5	0.6208 _{bp}	5		
CH ₃	H	—23.3		5	0.6698 _{bp}	5		
C ₂ H ₅	H	8.6		5	0.6682 _{bp}	5		
CH ₃	CH ₃	27.2		6	0.688 ₂₅	6	1.389 ₂₅	6
C ₃ H ₇	H	39.7		5	0.6718 _{bp}	5	1.388 ₁₇	7
C ₂ H ₅	CH ₃	55.5		8	0.7127 ₁₇	8	1.4045 ₁₇	8
C ₄ H ₉	H	71.0	4.7	9	0.721 ₁₇	7	1.402 ₁₉	7
C ₃ H ₇	CH ₃	83.8		10	0.735 ₂₅	10		
C ₂ H ₅	C ₂ H ₅	82	11.1	9	0.7263 ₂₅	9	1.4112 ₂₅	9
C ₂ H ₁₁	H	99.8	26.5	9	0.7288 ₂₅	11	1.4135 ₁₃	12
C ₄ H ₉	CH ₃	112.0	39.5	9	0.745 ₂₅	9	1.4220 ₂₅	9
C ₃ H ₇	C ₂ H ₅	106–7		7	0.7337 ₂₅	13	1.415 ₂₅	13
C ₆ H ₁₃	H	126.0	50.8	9	0.743 ₂₅	9	1.4140 ₂₅	9
C ₃ H ₁₁	CH ₃	137.2	60.2	9	0.761 ₂₅	9	1.4285 ₂₅	9
C ₃ H ₉	C ₂ H ₅	133	56.7	9	0.7501 ₂₅	9	1.4230 ₂₅	9
C ₃ H ₇	C ₃ H ₇	131	55	9	0.7474 ₂₅	9	1.4225 ₂₅	9

In Table I we present the boiling points, densities, and indices of refraction of the isomeric straight-chain acetylenes to C₆ inclusive, in so far as the data are available. There is sufficient information to permit of certain interesting generalizations. In any group of isomeric straight-chain acetylenes the following are true.

1. The monosubstituted acetylene has the lowest boiling point, density, and index of refraction.

2. The acetylene having a terminal methyl group adjacent to the triple bond has the highest boiling point, density, and index of refraction.

3. Within the disubstituted acetylenes the most symmetrical compound has the lowest boiling point, density, and index of refraction.

These relationships are particularly manifest with the four isomeric octynes where boiling points at two pressures and densities and indices of refraction both at 25°, are available.

Summary

The preparation of some substituted acetylenes from sodium acetylide in liquid ammonia has been described. A new technique for preparing sodium acetylides has been given. The physical properties of a number of alkyl and dialkylacetylenes have been tabulated and certain generalizations established.

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