The Formation of the Acetylenic Bond

W. Franke, W. Ziegenbein, and H. Meister

Wissenschaftliches Laboratorium der Chemischen Werke Hüls A. G., Marl

Introduction

The formation, reactions (1,2), and nature of the triple bond (3,4) in acetylenes have already been repeatedly reviewed. Only the newer methods leading to the formation of the triple bond are given here. This can involve either the conversion of a given compound into an acetylene, or the formation of an additional triple bond.

The method predominantly used for the formation of the acetylenic bond is the dehydrohalogenation of the corresponding halogenated compounds. Dichloro or dibromo compounds and chloro- or bromo-olefins are the chief starting materials (I-VII).

\[
\begin{align*}
\text{I} & : \text{XCH}_2\text{CH}-\text{R, XCH}_2\text{CH}-\text{H}_2, \text{CH}_2\text{CXX}_2\text{R}, \text{R}_1\text{CH}-\text{CHR}, \\
\text{II} & : \text{CH}_2=\text{CHR}, \text{CHX}=\text{CHR}, \text{CH}_2\text{CXX}_2\text{R, R}_1\text{CH}-\text{CHR}, \\
\text{III} & : \text{CH}_2=\text{CXR}, \text{CHX}=\text{CHR}, \text{R}_1\text{CXX}_2\text{R}_4,
\end{align*}
\]

The compounds may be obtained from carbonyl compounds and phosphorus pentachloride, or by the addition of halogen to olefins followed by partial dehydrohalogenation.

Alkali hydroxides, amides, and alkoxides are the favorite dehydrohalogenating agents; alkali carbonates, metal hydrides, and organometallic compounds are less frequently used. Other, nondehydrohalogenation methods for the production of the triple bond are also known.

The Dehydrohalogenation of Dihalides or Haloalkenes

The comprehensive review by T. L. Jacobs (2), which also deals with the preparation of acetylenes by the alkylation of metal acetylides, covers the subject to 1949. It is consequently the more recent work which is chiefly considered here.

Using Alkali Hydroxide

Treatment with alkali hydroxide is the oldest method used in the preparation of an acetylene from a halogenated compound. Methylacetylene, which was the first substituted acetylene, was prepared from 1,2-dibromopropane and ethanolic sodium hydroxide (5).

Bromides react in general more rapidly than chlorides with alkali
hydroxides, and when starting materials of formula I to IV are used, the reaction is frequently carried out in stages; this is due to the fact that the elimination of the second molecule of hydrogen halide is more difficult and requires more energetic conditions. Dihalides of general formula I to IV and haloalkenes of formula V to VII can be made to react in this manner. Dihalides in which the halogen atoms are not linked to adjacent carbon atoms also give rise to a triple bond, as long as the intervening carbon chain already contains a double or triple bond. The quantity of hydroxide is always greater than equimolar, and the concentration is generally above 4 normal. The solvents chiefly used are methanol, ethanol, and higher alcohols, as well as alcohol-water mixtures, glycol, glycol ether, glycerol, and even hydrocarbons. Examples are occasionally encountered where solvents are dispensed with; finely powdered or fused alkali hydroxide is then used with vigorous stirring. In the latter case the reaction temperature must be raised to 180–200°C. The normal reaction temperature is the boiling point of the solvent though higher temperatures, under increased or reduced pressures, are not infrequently employed. The reaction time varies from a few minutes to several hours.

Methylacetylene is thus obtained in good yield when 1,2-dichloropropane is treated with at least 2 moles of 14–23% aqueous sodium hydroxide solution at 150–175°C, the pressure being maintained above 17.5 atm. A duration time of 17 to 42 min in the reaction vessel gives good results. Ten per cent allene, a little trans-1-chloro-1-propene, 2-chloro-1-propene, and acetone are obtained as by-products (6). In an improved preparative method for 1-alkynes, 1,2-dihalides or 1- or 2-monohaloalkenes are added continuously to a stirred mixture of alkali hydroxide or alkoxide and inert solvents (e.g., higher alcohols) heated to above 110°C. The 1-alkyne formed distills off. Methylacetylene is thus obtained in 63% yield by the dropwise addition of 1,2-dichloropropane to a mixture of ethoxyethoxyethanol, commercial gas oil, and sodium hydroxide at 160–170°C (7).

Trifluoromethylacetylene has been prepared from dihalotrifluoropropanes or monohalotrifluoropropenes (8, 9). Comparisons with regard to the yields of acetylene and the lability of the different halogens split off as hydrogen halide are obtained from the experimental data. The following classes of compounds have been used in the synthesis of the corresponding acetylenes:

\[
\text{CF}_3\text{CH}(-\text{CHX}_n\text{CF}_3\text{CH}(-\text{CH}_2\text{X}\text{CF}_3\text{CH}(-\text{CH}_2\text{X})\text{CF}_3\text{CH}(-\text{CHX})}
\]

Table 1 shows the results of well-stirred reactions with powdered potassium hydroxide in the absence of solvent and under otherwise similar conditions.
It will be seen that better yields are obtained in a shorter reaction time from the bromo than from the chloro compounds. Fluorine is practically unaffected under these conditions.

<table>
<thead>
<tr>
<th>Starting material</th>
<th>Trifluoromethylacetylene (%)</th>
<th>Yield (X)-Trifluoropropane (%)</th>
<th>Reaction time (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3,3-Dichlorotrifluoropropane</td>
<td>45</td>
<td>(Cl) 10</td>
<td>12</td>
</tr>
<tr>
<td>3-Chloro-3-bromotrifluoropropane</td>
<td>55</td>
<td>(Cl) 8</td>
<td>4</td>
</tr>
<tr>
<td>3-Chloro-3-iodotrifluoropropane</td>
<td>52</td>
<td>(Cl) 10</td>
<td>6</td>
</tr>
<tr>
<td>3-Bromo-3-iodotrifluoropropane</td>
<td>66</td>
<td>(Br) 11</td>
<td>6</td>
</tr>
<tr>
<td>2,3-Dichlorotrifluoropropane</td>
<td>12</td>
<td>(Cl) 50</td>
<td>12</td>
</tr>
<tr>
<td>1-Chlorotrifluoropropane</td>
<td>70</td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>1-Bromotrifluoropropane</td>
<td>72</td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>1-Iodotrifluoropropane</td>
<td>70</td>
<td></td>
<td>6</td>
</tr>
</tbody>
</table>

It is worth noting that cycloheptadecyne, the first cyclic acetylene, was prepared from 1-bromo-1-cycloheptadecene and potassium hydroxide in absolute alcohol in a pressure tube at 180°C (10). Furthermore, in the course of the synthesis of large rings, the ethylene ketal of 9-oxo-17-cycloheptadecyne was obtained in 98% yield from the dibromide and potassium hydroxide in amyl alcohol (11).

A laboratory method for the preparation of vinylacetylene starts from 1,3-dichloro-2-butene, which is allowed to react with potassium hydroxide in glycol and butyl glycol at 165-170°C (yield 50%) (12).

Quaternary ammonium salts containing the 3-chloro-2-butenyl residue can be dehydrochlorinated by aqueous sodium hydroxide at 55°C. Even at room temperature the dehydrochlorination proceeds at an appreciable rate. Dialkylaminobutynes are obtained, and thermal decomposition then affords pure, chloroprene-free vinylacetylene. This reaction is also applied to compounds containing two 3-chloro-2-butenyl residues (13) (VIII), to give dialkylaminobutyne (IX) free from dialkylamino-3-chloro-2-butene:

$$\begin{align*}
\text{CH}_2=\text{CH}-\text{C}l \rightarrow \text{NaOH} & \quad \text{R}_1\text{N}^+\text{CH}_2-\text{C}_2 \equiv \text{C}-\text{CH}_3 \\
\text{CH}_2=\text{CH}-\text{C}l & \quad \text{OH}^- \\
\text{CH}_2=\text{CH}-\text{C}_2 \equiv \text{C}-\text{CH}_3 + \text{CH}_2=\text{CH}-\text{C}_2 \equiv \text{C}
\end{align*}$$
Diacetylene is obtained in varying yields from 1,4-dichloro-2-butyn and sodium hydroxide. Incompleteness of this reaction results in the formation of by-products, namely 2-chlorobut-1-en-3-yne, 1-chlorobut-1-en-3-yne, and 4-chlorobut-1-en-3-yne, together with acetylene and methylacetylene. One of the processes described consists in stirring a 40% solution of sodium hydroxide into a 25% solution of the starting material in ethanol at 65–75°C (14,15). Diacetylene has been obtained by other workers in 60% yield from the same starting material, by vigorous stirring with aqueous potassium hydroxide at the reflux temperature (16,17).

Triacetylene may be prepared from an ethereal solution of 1,6-di-chlorohexadiyne and powdered sodium hydroxide, and collected in a receiver cooled in liquid air (18).

Cyclohexylacetylene has been obtained in 47% yield by treatment with alcoholic potassium hydroxide of 1,1-dichloro-2-cyclohexylethane, prepared by condensing cyclohexyl chloride with vinyl chloride (19).

1-Phenyl-2-propyne can be prepared in 84–88% yield by allowing sodium hydroxide to react with a warm alcoholic solution of the mixture of 2-chloro-1-phenylpropene and 2-chloro-3-phenylpropene, obtained from phenylacetone and PCl₅ (20).

Phenylacetylene is most conveniently prepared by the dehydrohalogenation of styrene dibromide; the reaction is carried out by boiling under reflux with methanolic potassium hydroxide. Yields of approximately 65% are obtained (21). Boiling 6-1'-chlorovinyl-1,2,3,4-tetrahydronaphthalene for 5 hr under reflux with ethanolic potassium hydroxide affords 6-ethynyl-1,2,3,4-tetrahydronaphthalene in good yield (22). Several dipyriridylacetylenes have recently been prepared in almost quantitative yield by boiling 1,2-dipryridyl-1,2-dibromoethanes with potassium hydroxide in absolute methanol (23).

1-Hydroxy-2-butyne can be obtained in 80% yield by maintaining 1-hydroxy-3-chloro-2-butene and 20% alcoholic potassium hydroxide at the boiling point for 7 hr (24,25).

5-Hydroxy-1-pentyne has been prepared by a five stage synthesis from tetrahydrofururfuryl alcohol via 1-hydroxy-4,5-dibromopentane (26) [cf. the more advantageous method (27)].

The preparation of ethoxyacetylene from 1,2-dibromoethyl ethyl ether (obtained from vinyl ether) provides an example of stepwise dehydrohalogenation with various alkaline reagents. The removal of the first molecule of hydrogen bromide is effected by diethylaniline, that of the second by potassium hydroxide under vacuum (28,29). Methoxyacetylene and 1-ethoxypropyne can be obtained in like manner (28,29).

It is worth noting in this connection that it has not thus far been found possible to prepare 1,2-dialkoxyacetylenes from the corresponding...
1-halo-1,2-dialkoxyethylenes \((30,31)\). Neither will the halogen atom of such a compound undergo an exchange reaction. 1-Bromo-3-ethoxy- and 1-bromo-3-phenoxypyropene are obtained from 1,1-dibromo-3-ethoxy- and 1,1-dibromo-3-phenoxypyropane, respectively, with potassium hydroxide in glycerol. In accordance with the known fact that bromides are more easily dehydrohalogenated than chlorides, 1,3-dibromo-1-chloropropene and potassium hydroxide in glycerol give 1-chloro-3-hydroxypropyne \((32)\).

Stepwise dehydrohalogenation is used in the preparation of ethynyl ethyl sulfide, just as in the preparation of ethoxyacetylene \((33,34)\). Unlike the case of the 1-halo-1,2-dialkoxyethylenes, the corresponding sulfur compound, 1,2-bisethylmercaptochloroethylene, does form 1,2-bis-alkylmercaptoacetylene in 60\% yield by heating at the boiling point with alcoholic potassium hydroxide \((35)\).

The preparation of 2-ethynylthiophene from 2-\(\beta\)-bromovinylthiophene by the use of fused potassium hydroxide at 200–240°C affords unsatisfactory yields \((36)\), as does that of \(\beta\)-2-thiencylpropionic acid from \(\beta\)-2-thienylbromoacrylic ester.

Aldehyde groups unstable to alkali hydroxide are protected by acetal formation, with the result that even dihalogenated aldehydes can be dehydrohalogenated. Propargyl aldehyde diethyl acetal may be prepared from 2,3-dibromopropionaldehyde diethyl acetal \((37)\).

The usefulness of the alkali hydroxides ends with the presence of groups unstable to alkali. Thus the preparation of acetylene-carboxylic or dicarboxylic acids is only accomplished in isolated cases free from simultaneous decarboxylation or other side reactions: acetylenedicarboxylic acid from dibromosuccinic acid \((38)\), 16-heptadecynoic acid \((39)\), and a few chlorophenyl-, nitrophenyl-, and methoxyphenylpropionic acids \((40,41)\). The decarboxylation of \(\alpha,\beta\)-acetylene-carboxylic acids, which frequently proceeds relatively easily, can be used for the preparation of aryl acetylenes when cinnamic acid or its derivatives are used as starting materials. Acetylene-carboxylic acid is, however, more easily obtained by a different route, e.g. the carboxylation of metal acetylides \((40)\).

A preparation worth noting is that of \(m\)-nitrophenylpropionic acid \((XI)\) from \(3-m\)-nitrophenyl-4,4-dichloro-2-pyrazolin-5-one \((X)\) by dehydrohalogenation accompanied by hydrolysis and loss of nitrogen, using

\[
\begin{align*}
\text{NO}_2 & \quad \text{Cl} & \quad \text{Cl} \\
\text{X} \quad \text{NH} & \quad \text{O} \\
\rightarrow & \quad \text{NaOH} \\
\rightarrow & \quad \text{C}\equiv\text{C}\text{COOH}
\end{align*}
\]
aqueous sodium hydroxide at 5-10°C, and affording a yield of 75% (42). The corresponding alkylpropionic acids, not easily prepared otherwise, can similarly be obtained in this manner.

A further disadvantage of using alkali hydroxide as dehydrohalogenating agent is the possibility of triple bond migration away from the end of the chain, especially at higher alkali concentrations or temperatures, resulting in the formation of disubstituted acetylenes instead of, or together with, the 1-alkyne. Examples have been described by Faworskij (43). The details quoted above for the preparation of methylacetylene show that under the conditions employed for triple bond formation by dehydrohalogenation, allenes can also be produced (6). It has been observed in the preparation of alkynyl ethers from cis- and trans-β-haloalkenyl ethers that whereas the trans compound yields the alkynyl ether exclusively the cis isomer is also partly converted into allenes (29).

The acetylene-allene isomerization resulting from the treatment of 1,4-nonadiyne with alkali has been thoroughly investigated. It was found that isomerization to 1,2-nonadien-4-yne takes place first, followed by that to 2,4-nonadiyne. The rearrangement to the dienyne proceeds at a substantially faster rate than that to 2,4-nonadiyne (44). A further complication occasionally arises in the dehydrohalogenation of α,β-dihalides. It is well known that β-quinolyl-, β-pyridyl-, and β-(benz-2-thiazolyl)-α,β-dibromopropionic acid, when treated with aqueous or alcoholic alkali hydroxides or other basic reagents, yield the acrylic acids and not the corresponding acetylenic compounds as major product (3, 44a). This reaction is by no means confined to heterocyclic compounds; instead of the acetylenes, olefins have also been obtained from α,β-dihalogenated stilbenes (3). A further possible side reaction is the addition of alcohol to the acetylenic linkage in the course of the dehydrohalogenation, especially at higher alkali concentrations and temperatures. Acetylenic compounds in which the triple bond is strongly activated, e.g. by phenyl, vinyl, ethynyl, or other functional groups, are particularly susceptible to this side reaction (3).

**Using Alkali Amide**

The use of sodamide in the formation of the acetylenic bond from dibromoethane and its homologs has been known since the twenties (45, 46). It is especially applicable to the conversion into acetylenes of dihalides in which the halogen atoms are linked to the same or neighboring carbon atoms, or of haloalkenes in which the halogen is attached to the double-bonded carbon atom. Dilution is effected by the addition of inert, high-boiling hydrocarbons, the working range of which extends to at least 100°C and preferably to 130-160°C (47). Liquid ammonia is an
excellent solvent, recently often used in the conversion of the above-mentioned dihalides, haloalkenes, or other starting materials into acetylenic compounds by means of alkali amides. Dehydrohalogenation can be effected under very mild conditions in this manner: in an open container at the boiling point of ammonia, or in a pressure vessel at room temperature. Reaction times are generally shorter with ammonia than with hydrocarbons. This method is particularly well-suited to reactions in which the acetylene is to be converted further via an alkali acetylide; in such a case, sufficient quantities of the alkali (lithium, sodium, or potassium) amide are simply added for simultaneous acetylide formation. Admittedly the use of liquid ammonia in the laboratory requires greater expenditure than that of solvents boiling above room temperature. Also, the quality of the amide must always be tested. Moisture causes a sodium hydroxide coating to be formed on sodamide and, especially in the case of commercial grades, the danger exists that a considerable proportion of the material is present as the hydroxide. The dehydrohalogenation may then partly proceed under the action of the latter, when, as pointed out above, the comparatively high temperature required by the hydrocarbon method may cause migration of the triple bond in the newly formed acetylene. It must be noted, furthermore, that sodamide may contain peroxide; the crushing of such a product can cause violent explosions. In preference to the use of commercial sodamide, therefore, it is recommended that sodium be allowed to react with anhydrous liquid ammonia in the presence of catalytic amounts of ferric chloride or nitrate, or salts of cobalt (48, 49).

By the use of sodamide in light oil at 140°C it is possible to obtain a 62% yield of 3-methyl-1-butyne from 1,1-dichloro-3-methylbutane, 3-methyl-1-pentyne (68%) from 1,1-dichloro-3-methylpentane, 4-methyl-1-pentyne (80%) from 2-chloro-4-methyl-1-pentene, and 3,3-dimethyl-1-butyne (45%) from 1,1-dichloro-3,3-dimethylbutane at 95–100°C (16).

The preparation of a series of 1-, 2-, and 3-alkynes is discussed later in connection with observations concerning triple bond migration due to the presence of alkali amide as dehydrohalogenating agent.

Sodium vinylacetylide required for further transformations is conveniently obtained from 1,4-dichloro-2-butene and 1,2-dichloro-2-butene or a mixture of the two at —35°C (50). 1,5-Hexadiyne can be made in 63% yield from 1,2,5,6-tetrabromohexane (obtained from 1,5-hexadiene) in liquid ammonia at —33°C (16, 51).

5-Hydroxy-1,3-pentadiyne may be prepared in 65% yield by the dehydrochlorination of 1,4-dichloro-2-butyne in liquid ammonia, followed by the action of paraformaldehyde on the diacetylene so obtained (18, 52).
The dehydrochlorination of 1,6-dichloro-2,4-hexadiyne to form 1,3,5-hexatriyne [also obtainable via another route (53)] is accomplished in 10 min by the use of sodamide in liquid ammonia at $-70^\circ$C. Following decomposition with ammonium chloride and warming to $-33^\circ$C, the highly explosive triyne can be extracted with butane. At $-5^\circ$C the semi-solid residue left after evaporation of the solvent can be sublimed at 0.1 mm pressure into a receiver cooled by liquid air. Approximately 300 mg of triyne are obtainable in this manner from 7.4 gm of 1,6-dichloro-2,4-hexadiyne (54). Identical treatment of 1,6-dichloro-2,4-octadiyne affords 1,3,5-octatriyne, which is substantially more stable than the hexatriyne (52). 3-Isopropylphenylethylene dibromide (55).

Phenylacetylene can be obtained in distillable form via 1-phenyl-1,4-dichloro-2-butyne (56) or from phenylbutadiene tetrabromide (57). Diphenylbenzene may be prepared in similar manner from 1,6-dichloro-1,6-diphenyl-2,4-hexadiene (18).

1-Hydroxy-2-butyne can be obtained from 1-hydroxy-3-chloro-2-butene, itself prepared by the action of 10% sodium carbonate solution on 1,3-dichloro-2-butene; yields of the same order are obtained, whether the reagent is sodamide in ammonia (58) or ethanolic potassium hydroxide (24,25).

The use of sodamide in liquid ammonia in the production of 5- and 6-hydroxyacetylenes represents an improvement and simplification of the method previously used. Whereas the older preparation of these compounds, from tetrahydrofurfuryl alcohol, respectively, 2-hydroxymethyltetrahydropyran, requires five steps (26), the single-stage conversion of 2-chloromethyltetrahydrofuran (XII) (accessible by the chlorination of the corresponding alcohol) into 5-hydroxy-1-pentyne (XIII) by sodamide affords yields of 85%.

\[
\begin{align*}
\text{XII} & \xrightarrow{\text{NaNH}_2, \text{NH}_3} \text{XIII} \\
\end{align*}
\]

1-Hydroxy-4,5-dibromopentane, on the other hand, affords yields of only 56% of XIII. Similarly, up to 80% of the theoretical yield of 6-hydroxy-1-hexyne is obtained from 2-chloromethyltetrahydropyran, and 46% of propargyl alcohol from epichlorohydrin.

3-Chloro-2-ethyltetrahydrofuran (XIV) is converted into 1-hydroxy-3-hexyne (XV) in similar manner, albeit in lower yield; 2-ethylidihydrofuran is also formed.

Reaction times of 12 to 20 hr are quoted for dehydrohalogenation and ring-opening accompanied by triple bond formation (27).
The simultaneous elimination of hydrogen halide and alcohol from dialkoxychloroacetals (XVI) caused by the action of sodamide in liquid ammonia constitutes a convenient method for the preparation of alkoxyacetylenes, which are important intermediates in many further syntheses (59). Methoxyacetylene, ethoxyacetylene, and butoxyacetylene can be obtained by this route in 57, 61, and 44% yields, respectively.

\[
\text{ClCH}_2\text{CH(OR)}_2 + 3 \text{NaNH}_2 \rightarrow \text{H-C=C-OR} 
\]

Lithium amide is recommended for the conversion of \(\beta\)-chlorovinyl ethers into alkoxyacetylenes with the concurrent formation of the alkoxyacetylene-lithium compound for immediate further reaction (60).

1-Diethylamino-2-propyne has been obtained in 82.5% yield from 1-diethylamino-2-bromo-2-propene, readily prepared from diethylamine and 2,3-dibromopropene. \(N-n\)-Butyl-di-2-propynylamine was obtained in 76.5% yield under the same conditions (61); liquid ammonia is used as the solvent. In contrast, 1-dimethylamino-2-propyne is obtained in only 25% yield from the corresponding starting material and a suspension of sodamide in mineral oil at 165°C (62).

2-Ethynylthiophene, a comparatively unstable acetylene derivative, can be prepared in 60% yield by allowing sodamide to react with 2-(\(\beta\)-bromovinylthiophene) in absolute ether containing a small amount of aniline. 3-Methyl-2-ethynyl-, 4-methyl-2-ethynyl-, 5-chloro-2-ethynyl-, and 2,5-dimethyl-3-ethynylthiophene can likewise be obtained in 65, 63, 24, and 45% yields (63). In the preparation of these heterocyclic acetylenes, the dehydrohalogenation using sodamide in liquid ammonia is superior to the alkali hydroxide method; the latter has afforded yields of only 20–25% of 2-ethynylthiophene (36). While the presence of alkali hydroxides sometimes causes isomerization of the desired 1-alkynes to 1,2-disubstituted acetylenes, several examples are known where treatment with alkali amides results in the formation of 1-alkynes instead of the expected disubstituted acetylenes. These reports, however, are limited to reactions at elevated temperatures in high-boiling aliphatic or aromatic hydrocarbons (3). No triple bond migration has been observed in the case of ethylamylacetylene with sodamide in liquid ammonia at \(-34^\circ\text{C}\) (49). On the other hand, it is known from other work that under similar conditions, 2-alkynes are formed from \(\text{sym}\)-3-alkenes via their dibromides. Thus chiefly 2- and
very little 3-hexyne are obtained from a predominantly cis-containing mixture of cis- and trans-3-hexene via the corresponding dibromides. The same is true when trans-3-hexene is the starting material. trans-3-Octene, on the other hand, gives predominantly 3-octyne with some 2-octyne. sym-4-Octene affords 4-octyne in 56% yield. If 3-hexyne is treated with sodamide in liquid ammonia, mainly 2-hexyne is obtained, as it is from the dibromides of the isomeric cis- and trans-3-hexenes. 2-Pentyne is formed from cis- and trans-2-pentene (70% trans and 30% cis isomer). No isomerization was observed in the preparation of 4-methyl-1-pentyne from 4-methyl-1-pentene via the dibromide, when a yield of 74% was obtained. 3-Methyl-1-butene and 3,3-dimethyl-1-butene give the expected 1-pentyne and 1-butyne compounds (64).

The fact that opposite directions of isomerization are encountered with alkali hydroxides and alkali amides at higher temperatures can be accounted for by the greater stability of the 2-alkynes. This is in accord with results from measurements of pure 1-pentyne: The equilibrium mixture at 175°C in the presence of potassium hydroxide (with or without ethanol) consists predominantly of 2-pentyne (65), with a little 1-pentyne and 1,2-pentadiene. The opposite isomerization with alkali amide at higher temperatures is due to alkali acetylide formation.

Finally it must be added that even in the earlier literature, mention is made, in connection with the decomposition of 1,2-dihalides with sodamide at higher temperatures, of a side reaction leading to olefin formation, similar to that encountered in isolated cases when alkali hydroxides are used (3).

In cases where special structural conditions obtain, a different type of dehydrochlorination reaction with alkali amides is also known. 1,1-Diaryl-2-haloethylene or 1,1-diaryl-2,2-dihaloethane are converted into 1,2-diarylalkyne in liquid ammonia (66). This transformation has for a long time been known to occur when 1,1-diphenyl-2-chloroethylene and 1-methyl-1-phenyl-2-bromoethylene are treated with sodium ethoxide at 200°C and potassium hydroxide at 180°C, respectively (67–70). Whereas it requires several hours and a high temperature with sodium ethoxide or potassium hydroxide, the reaction is completed in but a few minutes when sodamide in liquid ammonia is used. The investigations into the mechanism of the reaction have been reviewed by Franzen (71).

A more recent example is found in the conversion of 1-p-fluorophenyl-
1-phenyl-2-bromoethylene (XVII) into 1-phenyl-2-\((p\text{-flourophenyl})\)-acetylene (XVIII) in 75% yield, by the action of potassium amide in liquid ammonia (72).

**Using Other Alkaline Reagents**

Alkali alkoxides and, less frequently, alkali carbonates and hydrides are additional alkaline dehydrohalogenating agents mentioned in the preparation of acetylenes. Basic anion exchange materials have also been used.

Sodium ethoxide was the first dehydrohalogenating agent, after sodium hydroxide, used in the preparation of a substituted acetylene, namely methylacetylene, obtained from bromopropene (3, 73).

Potassium butoxide has recently been used in the preparation of methylacetylene from 1,2-dibromopropane, when a yield of 70% was obtained (74). Diarylacetylenes have been synthesized with sodium ethoxide or tert butoxide. \(p\)-Chlorophenylphenylacetylene may be prepared in 60% yield from \(p\)-chlorophenylacetophenone and sodium tert butoxide via the trichloro derivative. Similarly, bis-\(p\)-chlorophenylacetylene has been obtained in good yield by the use of sodium in absolute ethanol (75). Potassium ethoxide has been used to prepare 1,6-diphenylhexatriyne from 1,6-diphenyl-1,6-dichloro-2,4-hexadiyne (76), 1,8-diphenyloctatetrayne from 1,8-diphenyl-3,6-dichloro-1,4,7-octatriyne, and 1,10-diphenyl-decapentayne from 1,10-diphenyl-3,8-dichloro-1,4,6,9-decatetrayne (57).

It is worthy of note that cis- and trans-3,4-dibromo-2-methyl-1,3-butadiene differ markedly in their behavior towards sodium methoxide. Whereas XIX remains unchanged, XX forms isopropenylbromoacetylene (XXI) even at 20°C.

\[
\begin{align*}
\text{CH}_3\text{C}-\text{C}=\text{C}-\text{H} & \quad \text{CH}_3\text{C}-\text{C}=\text{C}-\text{Br} \\
\text{XIX} & \quad \text{XX} & \quad \text{CH}_3\text{C}-\text{C}=\text{CBr} \\
\text{CH}_3 \quad \text{Br} & \quad \text{CH}_3 \quad \text{H} & \quad \text{CH}_3 \quad \text{C}=\text{CBr} \\
\end{align*}
\]

In analogous manner 1-(1'-cyclohexenyl)-1,2-cis-dibromoethylene produces 1-cyclohexenyl-2-bromoacetylene (77). Phenylpropionic acids containing substituents in the benzene ring can often be prepared in good yield when sodium ethoxide is used as the dehydrohalogenating agent (41).

It has been observed that in the dehydrobromination of bromocrotonaldehyde diethyl acetal (XXII) by aqueous potassium carbonate solution, some 1-butynal-4-acetal (XXIV) and probably a small amount
of 1,2-buta dienal-4-acetal (XXV) are produced together with the major product, 2-butynal-1-acetal (XXIII) (78).

\[
\text{CH}_3\text{CBr} = \text{CH} - \text{CH(OCH}_3\text{H}_2) + \rightarrow \text{CH}_3\text{C} = \text{C} - \text{CH(OCH}_3\text{H}_2) + \quad \text{XXIII}
\]

\[
\text{CH} = \text{C} = \text{CH} - \text{CH(OCH}_2\text{B})_2 + \quad \text{XXIV}
\]

A benzene solution of sodium hydride in the presence of a little absolute alcohol has proved useful in the conversion of phenyl-substituted \(a,\beta\)-dibromopropionic esters into the phenylpropiolic esters. The sodium alkoxide formed is thought to be the actual dehydrohalogenating agent:

\[
\text{C}_8\text{H}_5\text{OCH}_2\text{H} + \text{NaH} \rightarrow \text{C}_8\text{H}_5\text{ONa} + \text{H}_2
\]

The alkoxide is neutralized by the eliminated hydrogen bromide and the alcohol is regenerated; the molar quantity of sodium hydride used can thus once again form sodium alkoxide. Very small amounts of alcohol therefore suffice; this results in the suppression or elimination of side reactions, e.g. ether formation, which occur at higher alkali, alkoxide, or hydroxide concentrations in reactions where alcohol is the solvent.

The preparation of phenylpropiolic ester from \(\beta\)-phenyl-\(\alpha,\beta\)-dibromopropionic ester by the method indicated above proceeds with relatively little \(\beta\)-ethoxycinnamic ester formation; if, on the other hand, sodium ethoxide is used under normal conditions, \(\beta\)-ethoxycinnamic ester constitutes practically the whole of the product. \(\alpha\)-Chlorophenylpropiolic ester is obtainable in 89.5% yield from the corresponding dibromide, and \(p\)-chlorophenylpropiolic ester can be prepared in similar manner (41).

It has been pointed out that the use of alkali alkoxides may give rise to alkoxy compounds as by-products. This undesirable effect is also generally enhanced at elevated temperatures and higher alkoxide concentrations.

In the first preparation of triacetylene from 1,6-dichloro-2,4-hexadiyne, the solution of the complex formed by silver salts, aqueous alkali, and concentrated ammonium hydroxide solution was used. Acidification of the precipitated triacetylene silver with dilute aqueous acid is followed by the removal of the silver as the sulfide, and 1,3,5-hexatriyne can then be isolated in a cold-trap (53). A yield of 10% is obtained; the use of sodamide afforded no better result (54).

Weakly basic anion exchange materials have also been used in the dehydrohalogenation of a number of 1,2-dibromides; 1-hexyne, 1-heptyne, and 1-octyne were obtained in approximately 40% yield by this method. The reaction is carried out in high-boiling hydrocarbons, e.g. tetralin; the solution is heated for several hours at 160°C with the anion
exchanger, the acetylene being distilled as it is formed. Phenylacetylenes could not be obtained (79).

**Using Organometallic Compounds**

A number of organometallic compounds, e.g. butyllithium, butylsodium, and phenyllithium have in recent years been used for the dehydrohalogenation in the preparation of acetylenes. It was discovered quite a long time ago in connection with the action of phenyllithium on ω-chlorostyrene (or ω-bromostyrene) in ether that the hydrogen of the vinyl group becomes acidic under the influence of the halogen, and is replaced by lithium. Loss of lithium halide results in the formation of phenylacetylene in yields exceeding 70% (80). Thus, in the reaction between butyllithium and ω-bromostyrene in ether at —35°C in the presence of powdered solid carbon dioxide, acetylene formation, and carboxylation give rise to a 45% yield of phenylpropionic acid after a few minutes.

\[
C_6H_6CH=CHBr + C_4H_9Li \xrightarrow{CO_2} C_6H_5C≡C-COOH
\]

α-Bromostyrene, on the other hand, gives α-phenylaacrylic acid (81). 2,3-Dehydro-3-bromopyran and butylsodium in the presence of a small amount of butanol at 0°C afford 5-hydroxypentyne in 87% yield (82).

\[
\text{HOCH}_2-(\text{CH}_2)_4-\text{C≡CH}
\]

The formation of dehydrobenzene (XXVI) as intermediate in the reaction between fluorobenzene and phenyllithium in ether or tetrahydrofuran is worthy of notice (83). Although the “dienyne” cannot be isolated as such, it can be detected by its secondary products, e.g. the furan adduct (84,85,85a).

**Dehalogenation and Reductive Dehalogenation Using Metals**

Metals, usually finely divided, are relatively little used as dehalogenating, or, in the presence of alcohols as reductive dehalogenating, agents in the preparation of acetylenes. 1,2-Dihaloalkenes, as well as polyhalogen compounds in the case of reductive dehalogenation, are the
usual starting materials. Repeated attempts to prepare cyclic acetylenes used sodium in the removal of chlorine or bromine from 1,2-dihalocyclo-olefins. 1,2-Dibromocyclopentene was treated in this manner, as were the corresponding halogen compounds of the six- and seven-membered rings; the results were unsatisfactory, however (86). Cyclooctyne was subsequently prepared by the action of sodium on 1-chloro-2-bromocyclo-octene (87, 97). The synthesis of cyclodecyne was attempted in a similar manner; this merely produced a mixture, which was shown by oxidative degradation to consist mostly of 1,2-cyclodecadiene and only a little cyclodecyne (88). Zinc dust in alcohol gives a 25% yield of diacetylene from polychlorobutadiene (89), and triacetylene from perchlorohexadiene (90).

\[
\begin{align*}
\text{Cl}_2\text{C} & \text{CCl} \text{CCl} \text{CCl} \text{C} \rightarrow \text{HC}\equiv\text{C} \text{C} \equiv \text{CH} \\
\text{Cl}_2\text{C} & \text{CCl} \text{CCl} \text{CCl} \text{C} \rightarrow \text{HC}\equiv\text{C} \text{C} \equiv \text{C} \equiv \text{CH}
\end{align*}
\]

Trifluoromethylacetylene is obtainable in 25% yield from 2,3-dichloro-1,1,1-trifluoropropene, by heating under reflux for 120 hr with zinc dust and absolute ethanol. The 2,3-dibromo compound, on the other hand, gives the same product in 96% yield after only 6 hr (8).

\[
\text{CF}_3\text{C} \equiv \text{CH} \rightarrow \text{CF}_3\text{C} \equiv \text{CH}
\]

A 90% yield of hexafluoro-2-butyn has been obtained by allowing 2,3-dibromo-1,1,4,4,4-hexafluoro-2-butene to react with zinc dust and absolute ethanol under reflux (91). The formation of dehydrobenzene (XXVI) from o-fluorobromobenzene and magnesium in tetrahydrofuran, via the nonisolable o-fluorophenylmagnesium bromide, is worth noting.

Dehydrobenzene required for immediate further use is best prepared by this route (83, 84).

**Decomposition of Nitrogen-Containing Compounds**

**Bisquaternary Ammonium Compounds**

The conversion of quaternary ammonium hydroxides into olefins, known as the Hofmann degradation, can be applied to the preparation of acetylenes from 1,2-diquaternary ammonium hydroxides (XXVII):

\[
[(\text{CH}_2)_2\text{N} \equiv \text{CH} \equiv \text{CH} \equiv \text{CH} \equiv \text{CH}] \rightarrow \text{HC} \equiv \text{CH}
\]
This route was investigated as a laboratory method for the production of acetylene and its homologs (92). Acetylene is obtained in 80\% and 2-hexen-4-yne in 85\% yield. Methylacetylene can also be prepared in good yield by this method.

A yield of 60\% is afforded by the laboratory preparation of diacetylene. The 1,4-diquaternary ammonium hydroxides of 2-chloro-2-butene or of the corresponding 2-butyne compound, obtained from their quaternary salts, may be used as starting materials; warming with aqueous alkali converts them into diacetylene (93).

\[
\text{[CH}_3\text{N-CH}_2\text{-CH=CCI-CH}_2\text{-N(CH}_3\text{)}_3\text{]Br}_2 \text{ or}
\]
\[
\text{[(CH}_3\text{)}_3\text{N-CH}_2\text{-C≡C-CH}_2\text{N(CH}_3\text{)}_3\text{]Br}_2 \xrightarrow{\text{NaOH}} \text{HC=C-C≡CCH}
\]

A noteworthy reaction occurs between trimethyl-2,2,3,3-tetrachlorobutylammonium iodide (XXVIII) and aqueous alkali hydroxide, whereby tetrolic acid is formed (94).

\[
[\text{CH}_3\text{-C}(\text{Cl})_2\text{-C}(\text{Cl})_2\text{-CH}_2\text{-N(CH}_3\text{)}_3\text{]}\text{I} \rightarrow \text{CH}_2\text{-C≡C-COOH}
\]

XXVIII

Bishydrazones

Tolan (diphenylacetylene) can be obtained in a pure state and almost quantitative yield by the oxidation of benzil dihydrazone, effected by boiling under reflux with excess yellow mercuric oxide in benzene solution (75). More recently a number of substituted tolanes were synthesized by this method, with silver benzoate or trifluoroacetate as the oxidizing agent. N-Methylpyrrolidone, triethylamine, acetonitrile, etc., are suitable solvents. The reaction is complete after approximately 4 hr, and, e.g., o-chlorophenolphenylnacetylene is obtained in good yield with silver benzoate. When silver trifluoroacetate is used as the oxidizing agent, m-chlorophenolphenylnacetylene is obtainable in 80\%, and diphenylacetylene and di-p-methoxyphenylacetylene in 85\% yield (95).

The method starting from diketones can sometimes be used with advantage in the preparation of cyclic acetylenes. Attempts to synthesize these compounds by other routes either met with no success, or yielded also cyclic allenes (sometimes exclusively) (86, 96); the products are almost invariably obtained in poor yields and an impure state (10, 88, 97; but see ref. 11). Cyclodecyne can be obtained from sebacil in 36\% yield with yellow mercuric oxide in benzene in the presence of ethanolic potassium hydroxide and anhydrous sodium sulfate (88). Sebacic acid can be used as the starting material; this is converted first into sebacoin, and then into sebacil with chromium trioxide. Cyclocdecyne results in similar manner from the dihydrazone of the corresponding 1,2-diketone (96).
W. FRANKE, W. ZIEGENBEIN, AND H. MEISTER

\[
\begin{align*}
\text{N-NH,} & + \text{N}_2 + 2 \text{Hg} + 2 \text{H}_2\text{O} \\
\text{S} & \\
\end{align*}
\]

\[
\begin{align*}
\beta\text{-Substituted Nitrosoacylamines}
\end{align*}
\]

It is well known that the action of dilute alkali on N-nitroso-0,N-
phthalylaminoethanol (XXIX) produces acetylene with elimination of
nitrogen (97a).

\[
\text{NO} \quad \text{XXIX} \quad \text{HC} = \text{CH} + \text{N}_2
\]

Phenyl-substituted acetylenes, e.g. tolan, may be obtained from 3-nitroso-
2-oxazolidones under similar conditions (97b). More recently, 1-alkynes
have become accessible in good yield via \(\beta\)-substituted nitrosoacylamines
(XXX) (97c). Even under very mild conditions, namely with dilute alco-
holic alkali hydroxide solutions, acetylenes possessing a terminal triple
bond are obtained; this is particularly the case when nitrosoacylamines
with \(\beta\)-hydroxyl or acetoxy groups (X) are used.

\[
\text{NO} \quad \text{XXX} \quad \text{HC} = \text{CR}_2 + \text{N}_2
\]

**Miscellaneous Methods**

Acetylenes may be synthesized by a number of other methods which
cannot be assigned to any of the groups mentioned hitherto.

Loss of carbon monoxide at 130–140°C gives a 20% yield of tolan
from diphenylecyclopropenone (98), obtainable from phenyldichloro-
methane and 1-phenyl-2,2-dimethoxyethylene (phenylketene acetal).

\[
\text{C}_6\text{H}_5 - \text{C} = \text{C} - \text{C}_6\text{H}_5 \rightarrow \text{C}_6\text{H}_5 - \text{C} = \text{C} - \text{C}_6\text{H}_5
\]

Ethylmercaptoacetylene can be prepared by allowing 1,2-bis(ethyl-
mercapto)ethylene to react with 2 moles of butyllithium in ether. Lithium
ethyl mercaptide and the lithium derivative of ethylmercaptoacetylene
are formed; water decomposition of these affords a 47% yield of ethylmercaptopoacetylene and ethylmercaptan (99).

\[ \text{C}_4\text{H}_8\text{S}-\text{CH}=\text{CH}-\text{S}-\text{C}_2\text{H}_5 \rightarrow \text{C}_4\text{H}_8\text{S}-\text{C}≡\text{CH} + \text{C}_2\text{H}_5\text{SH} \]

Phenylmercaptoacetylene is obtained in analogous manner in 60-80% yield from cis- and trans-1,2-bis(phenylmercapto)ethylene in ether after a reaction time of 2 hr, followed by water decomposition (100).

The transformation of coumarone—formally to be regarded as an isomerization—by the action of sodium metal in the presence of pyridine produces o-hydroxyphenylacetylene (101). The sulfur analog, thionaphthene, on the other hand, affords phenylacetylene in 30–40% yield on treatment with sodium at 150–180°C in the absence of oxygen (102). Thionaphthenes with substituents in the phenyl ring can also be used. Iodine in ethanol converts 1,2,3-butatriene into 1,4-diiodo-2-butyne, which can be isomerized to 2,3-diiodo-1,3-butadiene by potassium iodide in acetone (103).

By the Pyrolysis of Hydrocarbons and Other Compounds

The use of pyrolysis as a means of obtaining acetylenic compounds is restricted to the lower members of the series. Large-scale technical processes are known, and the essentials only are mentioned here.

The production of the triple bond is thermodynamically based on the fact that whereas the free energy of the formation of acetylene from its elements decreases with increasing temperature, most of the paraffins and olefins under consideration show a free energy curve rising with temperature (104, 105). At higher temperatures, in other words, the stability relationship is reversed. Thus, methane is thermodynamically less stable than acetylene above 1600°C; the temperature functions of the free energy of ethane and acetylene cross around 1300°C, and those of propane and acetylene around 1220°C. The large-scale processes for the manufacture of acetylene by high-temperature cracking are differentiated mainly in their method of producing the required temperature and in their choice of starting material.

If methane, ethane, propane, and other hydrocarbons are sparked by an electric arc (104, 106) (using direct current, between two electrodes at 8000–10,000 volts and 800 amps), the major products are acetylene, ethylene, propylene, and hydrogen. In a modified process, hydrogen is introduced into the arc, giving activated hydrogen atoms; these react with
the hydrocarbon to form acetylene in particularly high yield (up to 85%) (107). In the Sachsse process (108, 109), part of the hydrocarbon is burned to carbon monoxide with oxygen (1100° to 1500°C), thus providing the energy for the conversion of the remainder. Similarly, the heat required in Hoechster pyrolysis is supplied by the combustion with oxygen of the residual gases accumulating in the reaction (110). One method of cracking liquid hydrocarbons at low pressures involves the use of small carbon rods as auxiliary electrodes, connected to an alternating current source. Arcs of shorter length and burning time are thus obtained. The cooling required in other pyrolytic alkyne syntheses is unnecessary in this case, and soot formation is slight (111). A process for the thermal decomposition of liquid hydrocarbons (e.g. Diesel oil) has also been patented, in which the heat required is produced by the surface combustion of part of the hydrocarbon with oxygen or oxygen-containing gases (112). Here too, auxiliary cooling to lower temperatures is unnecessary, as this already occurs at the surface of the liquid.

In another process, methane, propane, and liquid hydrocarbons, diluted with steam, are converted into acetylene in a cracking oven at 1300°C under vacuum (113). A similar cracking process (114) converts petroleum in the presence of catalysts into a mixture of olefins in the first step; these, diluted with an inert gas, are then decomposed at 1000° to 1200°C to acetylene in the second step.

A more recent technique involving partial combustion resembles that of Sachsse, though lower pressures and smaller quantities of oxygen are used (115). Relatively high yields of acetylene (45-50%) are obtained. The use of catalysts is found to be advantageous when methane is used as the starting material. The high temperature required can be obtained by the combustion of hydrogen and oxygen (116). A modified process utilizes petroleum as the fuel; this is burned with air or oxygen in the presence of steam in a reaction chamber. The hot gases are then led into a pipe, where they mingle with the gas to be decomposed, providing it with the heat required (117). There is further a patented process which makes use of molten iron at 1650–1930°C and finds favorable application in the conversion of methane; this is accomplished by passing the hydrocarbon into or over the molten metal (118).

In all these pyrolytic processes, it is to be expected that much hydrogen, ethylene, and higher acetylenes will be produced. Thus, in the electric arc method of the Chem. Werke Hüls A.G., methylacetylene, allene, vinylacetylene, diacetylene, trisacetylene, and phenylacetylene are obtained, together with other thermodynamically favored products, e.g. benzene, styrene, naphthalene, and other aromatic compounds (53, 106). These by-products are separated by oil washing or intense cooling.
The formation of the acetylenic bond

Methylacetylene can be obtained together with allene from isobutylene and \textit{tert} butyl alcohol at 800–1050°C \cite{119,120}, with a maximum yield of approximately 30%. Steam, in quantities of 50 to 90 mole %, is used. Another patent describes the production of methylacetylene and allene from propylene and steam at 800–1100°C \cite{121}. Dichloropropane or chloropropene can be converted thermally into methylacetylene at 920–1050°C; it is best to dilute with inert gases, such as nitrogen, carbon dioxide, methane, or water vapor. A yield of up to 58% of methylacetylene, and 12.7% of allene, is obtained \cite{122}. Methylacetylene and much allene are produced in the decomposition of itaconic anhydride at 900°C and 3–4 mm pressure \cite{123}. Methylacetylene is also obtained by the thermal decomposition of citraconic anhydride at 750°C and 50 mm pressure \cite{123}.

Recent investigations into the position of the equilibrium between propyne and allene in the temperature range of 100° to 370°C have shown that in the presence of all the catalysts used, an isomerization equilibrium dependent on temperature alone is set up. The equilibrium constant $K_p$ has a value of 0.172 at 400°K and 0.242 at 600°K \cite{124}.

2-Butyne is a by-product in the large-scale dehydrogenation of butane to 1,3-butadiene at 600°C (Houdry process). It may be isolated from the residues of the butadiene distillation \cite{125}.

Fluoroacetylene is obtained in almost quantitative yield in the pyrolysis of monofluoromaleic anhydride at 650°C and 5–7 mm pressure \cite{125a}.

In the temperature range of the pyrolyses mentioned above, the free elements carbon and hydrogen are thermodynamically still substantially more stable than acetylene and its homologs. The preparation of acetylenic hydrocarbons therefore necessitates short reaction times and rapid cooling \cite{126} of the reaction mixture to under 200°C. Thus, the duration time in the electric arc preparation of acetylene must not exceed 0.001 second, nor that of propyne from isobutylene or \textit{tert} butanol 0.01 to a maximum of 10 sec.

**Experimental**

\textit{Diacetylene} \cite{15}. Sodium hydroxide (570 gm of a 40% aqueous solution) is added dropwise to a mixture of 1,4-dichloro-2-butyne (123 gm) and ethanol (100 to 500 gm) maintained at 75°C. The gaseous diacetylene formed is collected. It is then washed with dilute sodium hydroxide and dried with calcium chloride. Yield, 79.3%.

\textit{Phenylacetylene} \cite{127}. Bromine (410 gm) is added dropwise over a period of 2 hr to a cooled and stirred mixture of chloroform (200 ml) and
styrene (312 gm). Stirring at 30°C is continued for a further half-hour. The chloroform is distilled off, and drying in air affords pure white styrene dibromide. Yield, 653 gm; m.p. 73°C.

Styrene dibromide (264 gm) is added in small portions over a period of 1.5 hr to a stirred mixture of potassium hydroxide (240 gm) and methanol (240 ml) under reflux. The reaction mixture is boiled for a further half-hour and cooled. Water (400 ml) is added, the oily layer formed is separated, dried over potassium carbonate, and distilled under vacuum. At 10 mm and below 100°C an oil (75 gm) is obtained which, on redistillation at atmospheric pressure, gives phenylacetylene (67 gm, 66%) b.p. 141–143°C.

5-Hydroxy-1-pentyne (27). Tetrahydrofurfuryl chloride (242 gm) is added dropwise over 25 min to a stirred suspension of sodamide (made from 161 gm of sodium) in liquid ammonia (3500 ml). After 16 hr stirring, anhydrous ammonium chloride (350 gm) is gradually added, the greater part of the ammonia allowed to evaporate, and the reaction product extracted with ether. The ether is evaporated and the product distilled under vacuum. 5-Hydroxy-1-pentyne (142 gm, 85%) is obtained. B.p. 64–65°C/16 mm, $n_D^{10} = 1.4451$. After purification via the silver salt: B.p. 77°C/37 mm, $n_D^{25} = 1.4464$.

o-Chlorophenylpropiolic acid (41). Bromine (305 gm) is added dropwise to a solution of o-chlorocinnamic ester (400 gm) in methylene dichloride (500 ml). After an initial period of induction the reaction becomes violent and cooling is necessary. The solvent and unreacted bromine are evaporated under reduced pressure, benzene is added and the mixture distilled for 5 min to remove any water present. Sodium hydride (22 gm) is added to the stirred, dry ester (163 gm) in benzene (200 ml), followed by ethanol (3 ml). The reaction mixture becomes warm, and requires initial cooling. After standing for 1 hr, the mixture is boiled under reflux for an hour, after which time there is practically no further evolution of hydrogen. The reaction mixture is stirred into water, and an acidic and neutral fraction are separated. The acidic fraction yields o-chlorophenylpropionic acid (6.4 gm, 8%). Distillation of the neutral fraction affords crude o-chlorophenylpropionic ester (82.2 gm, 89.5%), b.p. 110–117°C/1–2 mm, $n_p^{20} = 1.5590–1.5580$. The dry ester is saponified with a slight excess of a 20% aqueous solution of sodium hydroxide to which a little alcohol has been added. The alkaline solution is extracted with ether to remove neutral material and slowly acidified with hydrochloric acid. A small amount of o-chlorocinnamic acid is first precipitated and is removed. o-Chlorophenylpropionic acid is then precipitated, and is purified via its potassium salt (obtained by the addition of a hot 3% alcoholic solution of potassium hydroxide and precipitation
by cooling the solution). The free acid may be recrystallized from benzene; m.p. 132.7–133.8°C. Total yield 54% (calculated with respect to o-chlorocinnamic ester).

**Phenylacetylene (80).** A mixture of ω-chlorostyrene (0.05 mole, 6.9 gm), b.p. 79–81°C, and phenyllithium (0.1 mole) in ether (total volume 100 ml) is allowed to warm up to the boiling point of the solvent; at this temperature the lithium chloride is precipitated. After cooling, the mixture is allowed to stand for 15 min, and the solution hydrolyzed (52% LiOH is recovered). Fractionation of the ether layer yields phenylacetylene (3.6 gm, 70%), b.p. 141–143°C, and chlorostyrene (0.6 gm).

**Trifluoromethylacetylene (8).** 1,2-Dibromo-3,3,3-trifluoropropene (12.7 gm) is treated for 6 hr with zinc dust (20 gm) and absolute alcohol (200 ml) in a flask fitted with a reflux condenser maintained at —40°C; after this period the reaction is complete. Trifluoromethylacetylene (4.5 gm, 96%) is obtained, b.p. —48 to —46°C (9).

**Polyfluoro-2-butyne (91).** 1,2-Dibromo-1,1,1,4,4,4-hexafluoro-2-butene (1.98 gm) is vigorously stirred for 4 hr under reflux with zinc dust (20 gm) and absolute alcohol (60 ml). 1,1,1,4,4,4-Hexafluoro-2-butyne (0.90 gm, 90%) is obtained, b.p. —24°C.

**Cyclododecyne (96).** 1,2-Cyclododecanedione bishydrazone (21.25 gm) is added portionwise to a mixture of mercuric oxide (41.1 gm), sodium sulfate (50 gm), potassium hydroxide (2.1 gm), and toluene (220 ml) in a three-necked flask fitted with a stirrer and separator; the addition is carried out with vigorous stirring, at a bath temperature of 140°C. After heating for 2 hr, the solid is filtered off and the filtrate is put on an alumina column (200 gm, activity I–II). Cyclododecyne, b.p. 106–109°C/11 mm, is eluted with pentane.

**Phenylmercaptoacetylene (100).** A solution of cis-1,2-bis(phenylmercapto)ethylene (129) (ca. 2 gm) in ether (5 ml) is added dropwise to a solution of n-butyllithium (prepared from lithium turnings, 1.65 gm) and n-butyl bromide (14.1 gm) according to the method of Gilman and Morton (128) in ether (55 ml). After the reaction mixture has been cooled to —10 to —15°C, the remainder of the cis-1,2-bis(phenylmercapto)ethylene (total quantity, 14.03 gm) is added dropwise with stirring; the reaction mixture thus obtained is stirred for a further 2 hr at —10°C, allowed to warm up to 0°C, and decomposed by the dropwise addition of water (40 ml). The mixture is allowed to warm up to room temperature, stirred for 2 hr and refluxed for 30 min. After cooling, the two layers are separated. The ether layer is dried over sodium sulfate, concentrated, and the orange-yellow residue (9.37 gm) distilled. Phenylmercaptoacetylene (4.63 gm, 60%) is obtained, b.p. 78–79°C/7 mm, \( n_0^{25} = 1.5938 \).
REFERENCES


(3) F. Bohlmann, Angew. Chem. 69, 82 (1957).


(6) D. A. Bagett, German Patent 1029364 (1956-1958); Dow Chemical Co., U. S. Patent 2755319.


THE FORMATION OF THE ACETYLENIC BOND

(70) P. Lipp, Ber. deut. chem. Ges. 56, 567 (1923).
(71) V. Franzen, Chemiker-Ztg 82, 220 (1958).
(73) V. Sawitsch, Compt. rend. acad. sci. 52, 399 (1861); Ann. Chem. Liebigs 119, 185 (1861).
(80) G. Wittig and H. Witt, Ber. deut. chem. Ges. 74, 1474 (1941).
(81) D. Y. Curtin and E. E. Harris, J. Am. Chem. Soc. 73, 4519 (1951).
(83) G. Wittig and L. Pohmer, Angew. Chem. 67, 348 (1955); G. Wittig, ibid. 66, 10 (1954); 69, 245 (1957); cf. also R. Huisgen and H. Rist, Naturwissenschaften 41, 358 (1954).
(85a) Editor’s note: cf. the review which has meanwhile appeared, entitled “Nucleophile aromatische Substitution über Arine” by R. Huisgen and J. Sauer, Angew. Chem. 72, 91 (1960).
(97a) S. Gabriel, Ber. deut. chem. Ges. 38, 2405 (1905).
(110) K. Winnacker, Kunststoffe 47, 402 (1957).


(113) G. H. Bixter and C. W. Coberly, Ind. Eng. Chem. 45, 2596 (1953); also references to the patent literature.


(123) F. O. Rice and M. T. Murphy, J. Am. Chem. Soc. 64, 896 (1942).


(125) Unpublished, Buna-Werke Hüls GmbH.


