PREPARATION AND PHYSICAL CHARACTERIZATION OF PURE HETERO AND HOMO DIHALOACETYLENES

ELSE KLOSTER-JENSON*

Department of Chemistry, University of Oslo, Blindern, Oslo 3, Norway

Abstract—Bromochloro- (I) and chloroiodoacetylene (II) have been prepared from 1,2-dichloroethylene by the action of phenyl-lithium and bromine or iodine. Treatment of 1,2-dibromoethylene with alkali amide and iodine yielded bromoiodoacetylene (III), while diiodoacetylene (VI) was produced when phenyl-lithium was used as base. Dichloro- (IV) and dibromoacetylene (V) were alternatively prepared by halogenation of dilithium acetylide. Spectroscopically pure I–VI were characterized by their IR and Raman spectra. All fundamental absorption bands were localized and assignments to their normal modes of vibration were made. General physical properties are summarized.

IN CONTINUATION of our earlier work on small linear molecules[1, 2] we wished to prepare the structurally very simple, but rather explosive and poisonous dihaloacetylenes, X—C≡C—Y. The unsymmetrical (X≠Y, $C_{\infty v}$) as well as the symmetrical (X=Y, $D_{\infty h}$) dihaloacetylenes[3] were desired. We have reported[4, 5] synthetic pathways to the hitherto unknown† bromochloroacetylene, chloroiodoacetylene and bromoiodoacetylene, and also a new synthesis of dichloro-, dibromo- and diiodoacetylene,‡ which allows the isolation of the products in a spectroscopically pure state. We now wish to present the experimental procedure and the preparative technique required for the safe handling of these critical¶ substances. Some general properties of the compounds are given and fundamental features of their simple IR spectra are compiled. Comprehensive spectroscopical investigations are presented in separate papers. Finally, synthetic attempts at two fluorohaloacetylenes‖ are summarized.

PREPARATION

By extrapolation from known properties of the symmetrical dihaloacetylenes one would expect the unsymmetrical haloacetylenes to exist under standard conditions as volatile liquids or low melting solids, which are highly sensitive to air, but capable of being isolated in an inert atmosphere at moderate temperatures. For the preparation of these compounds, low temperature reaction paths on a small scale and handling of the dangerous products exclusively under vacuum were imperative to avoid hazardous work. Since products of highest purity were required, effective methods of purification

---

* Present address: Physikalisch-Chemisches Institut der Universität, Klingelbergstrasse 80, CH-4056 Basel, Switzerland.

† The English edition of [3a] is erroneously translated regarding this statement.

‡ Earlier syntheses are given in Ref. 3.

¶ Diiodoacetylene is the only comparatively stable dihaloacetylene.

‖ Chlorofluoroacetylene, *Proceedings of the Third International Symposium on Fluorine Chemistry* Munich, Aug. 1965; Ref. 3*b*, p 660.

were of particular importance These requirements were fulfilled in the present work.

Special precautions were taken with all glassware, and only high vacuum stop cocks were used. Even the choice of vacuum grease was critical (see Properties). The synthesis of the six compounds were repeated several times over the course of two years without accident.

Generally, the reactions were performed at low temperatures (0–50°) in ether solution and under an atmosphere of nitrogen. The reaction mixtures were directly subjected to low-temperature fractional distillation under vacuum, followed by preparative GLC. The syntheses were run on a 20–50 mmole scale, yielding ca 20–50 % of isolated product.

Bromochloroacetylene and chloroiodoacetylene

As shown by Viehe,[6] 1,2-dichloroethylene produces alkali chloroacetylide $M{-}C{\equiv}C{-}Cl$ (M = alkalimetal) under the influence of an organolithium base in ether or alkaliamide in liquid ammonia. The existence of this intermediate, which is explosive in a dry state, but stable in solution, was proved by reacting ketones to form chloroethynylcarbinols.

Alternatively, reaction of alkali chloroacetylide with molecular halogen under strictly controlled conditions was expected to produce chlorohaloacetylenes.

Lithium chloroacetylide was prepared in ether solution from cis 1,2-dichloroethylene by the action of 2 equivs of phenyl-lithium at 0°. Molar amounts of molecular bromine or iodine were then added to the reaction mixture at $-50°$. A strongly exothermic reaction took place during formation of bromochloroacetylene (I) and chloroiodoacetylene (II); the reaction scheme is shown below:

<div align="center">Scheme 1</div>
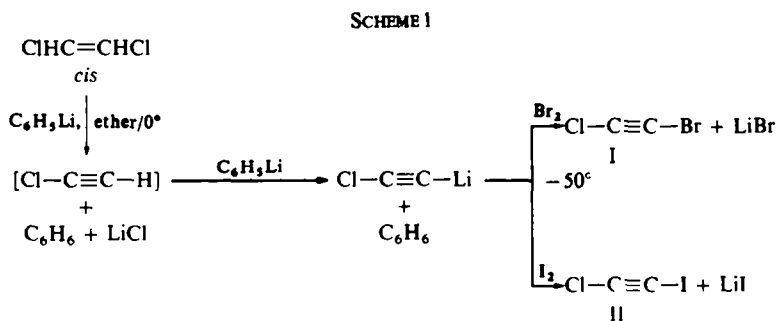
Concentrates from the fractional distillation of the reaction mixture were subjected to GLC at ca 50° (I) and 90° (II), yielding colourless crystalline products (collected at $-80°$). Residual impurities* were removed by a second GLC treatment which furnished highly pure I and II. A considerable loss of product occurred during GLC (at least ca 30 %), as shown by the rechromatography of known quantities of sample. The m.ps, however, did not increase significantly, $-54- -52°$ (I) and $-37- -35°$ (II), an increase of approx 2° for each. The yields were 40 % (I) and 35·5 % (II) (after GLC collection.

The slightly greyish and dry-looking residual lithium halides contained minor amounts of yellow oil, which was extracted with ether.

* Impurities critical to separation were benzene generated from the phenyl-lithium base, phenyl halide and ether.
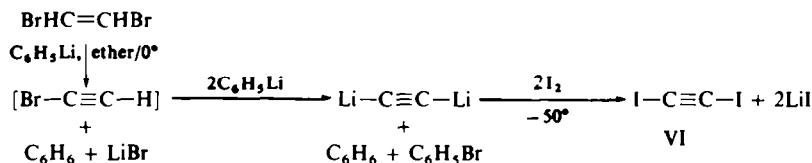
When the phenyl-lithium base was exchanged for the stronger n-butyl-lithium, the reaction changed critically, so that no volatiles could be isolated from the reaction mixture.* Changing the sequence of addition of dihaloethylene and base (phenyl-lithium was now added to dichloroethylene), reduced the yield of dihaloacetylene to about one third.

Bromoiodoacetylene

In analogy with the preparation of chloroiodoacetylene from 1,2-dichloroethylene one might expect bromoiodoacetylene to be produced from 1,2-dibromoethylene by phenyl-lithium and iodine under similar conditions. However, the reaction product which was isolated, possessed a m.p. and chemical properties which were incompatible with expectations. The highly pure product was identified as diiodoacetylene (VI; yield 18%) by its m.p.76° (m.ps between 74–82° are reported[3a]) and by its IR spectrum, which showed the highest frequency absorption at 720 cm^{-1} (718 cm^{-1} [7]).

Obviously the monobromoacetylene primarily formed by the action of phenyl-lithium on dibromoethylene had been subjected to a double attack by the strong base. The dilithium acetylide thus formed in a subsequent reaction with iodine yielded diiodoacetylene (VI), as shown in the following reaction:

<div align="center">SCHEME 2</div>

$$BrHC=CHBr$$
$$\downarrow C_6H_5Li, \ ether/0°$$
$$[Br-C\equiv C-H] \xrightarrow{2C_6H_5Li} Li-C\equiv C-Li \xrightarrow[-50°]{2I_2} I-C\equiv C-I + 2LiI$$
$$+ \qquad\qquad\qquad + \qquad\qquad\qquad VI$$
$$C_6H_6 + LiBr \qquad\qquad C_6H_6 + C_6H_5Br$$

Exhaustive analysis of the reaction mixture revealed no other acetylenic products.

A proof that bromine exchange occurred in the intermediately formed bromo-acetylene was obtained by reacting dibromoethylene with a phenyl-lithium reagent which was free of bromobenzene. If, in this case, bromobenzene was also present in the reaction mixture, its formation could only be explained by the action of phenyl-lithium on the bromoacetylide (Scheme 2). In fact, the reaction with phenyl-lithium prepared from chlorobenzene produced bromobenzene in quantities similar to those of diiodoacetylene.

By changing the sequence of addition, so that the base was added to the dibromo-ethylene, we hoped to suppress the destruction of the bromoacetylide intermediate. However, in this case no volatiles could be isolated from the final reaction mixture. Instead, tetraiodoethylene was produced.†

Replacement of phenyl-lithium with a less strong base, like lithium amide, was more likely to leave the sensitive intermediate intact during the reaction. A single experiment has been described[10] in which the bromoacetylide was prepared from 1,2-dibromoethylene by the action of sodium amide in liquid ammonia. Reactions with cyclohexanone yielded 1-bromoethynyl-1-cyclohexanol. The free ethynyl-

---

* Viehe[6] by reacting dichloroethylene with a base and cyclohexanol isolated much less amounts of condensation product when n-butyl-lithium (31%) was used than when phenyl-lithium (80%) was reacted.
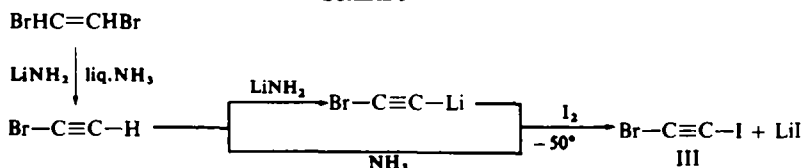
† From the residue ca 2 g (10%) of higher melting solids were extracted with benzene, which after sublimation was identified as tetraiodoethylene, m.p. 189·5–190·0 (187°[8]). The IR spectrum showed weak bands at 675, 635 and 525 cm^{-1} (676, 639 and 525 cm^{-1} [9]).

carbinol was also isolated, in quantities which were not reported. This indicates that even sodium amide is capable of producing halogen-metal interconversion with the bromoacetylide.

Consequently, by reacting lithium bromoacetylide with iodine in liquid ammonia, we hoped to produce bromoiodoacetylene.

1,2-Dibromoethylene was added to 2 equivs of lithium amide in liquid ammonia at −55°. One equivalent of molecular iodine was then added, in portions, to the dark contents under vigorous stirring. However, a dry-way isolation of the product directly from this medium was not attempted, because the possibility of admixture of highly explosive iodonitrides[11] in the dry residues could hardly be excluded. Inorganic materials were removed from the concentrated ammonia/ether solution by the addition of water. Fractional distillation of the ether extracts was performed under vacuum at low temperatures and the concentrates were subjected to preparative GLC at 90°. A colourless, crystalline bromoiodoacetylene (III) was isolated, which contained minute amounts of monobromoacetylene, as shown by its mass spectrum. A second GLC treatment yielded the pure compound, m.p. 15·3–16·5°, isolated in ca 21 % yield. Extensive destruction of III occurred during GLC, as only one third of the amount injected could be collected. This was clearly demonstrated by the presence of rich deposits of carbonized dry powder in the GLC inlet system. The actual formation of bromoiodoacetylene, therefore, was at least 60%. *† (Experimental). The synthesis of bromoiodoacetylene can be formulated as the following:

<div align="center">SCHEME 3</div>

BrHC=CHBr

$$LiNH_2 \downarrow liq.NH_3$$

$$Br-C\equiv C-H \longrightarrow \boxed{ \begin{array}{c} LiNH_2 \to Br-C\equiv C-Li \\ \\ NH_3 \end{array} } \xrightarrow[-50°]{I_2} Br-C\equiv C-I + LiI$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad III$$

The intermediate monobromoacetylene might also iodinate in the absence of base, in analogy to the preparation of diiodoacetylene[12] from acetylene, and 1-iodopenta-1,3-diyne[13] from penta-1,3-diyne in liquid ammonia.

Since dichloroacetylene exchanges one chlorine for lithium in the presence of one equiv of an organolithium base, [6c] we checked whether III could be prepared from the readily available diiodoacetylene by a base and bromine. The reaction was performed with butyl-lithium and bromine, but only non-volatile, probably polyhalogenated solids (m.p. 90–105°) were obtained with no starting material being recovered.

Dichloroacetylene and dibromoacetylene

Previous syntheses[3] of these compounds were mainly concerned with treatment of acetylene with hypohalite[14] or dehydrohalogenation of trihaloethylene by alkali at 130°.[15] In the course of the latter, explosions frequently occurred. Only diiodoacetylene has been prepared via dialkali acetylide in liquid ammonia, as iodination is readily effected in this medium.[16]

---

* The ether concentrates from the fractionation soon turned brown even at dry ice temp., and the amount of products gradually decreased, as shown by GLC.
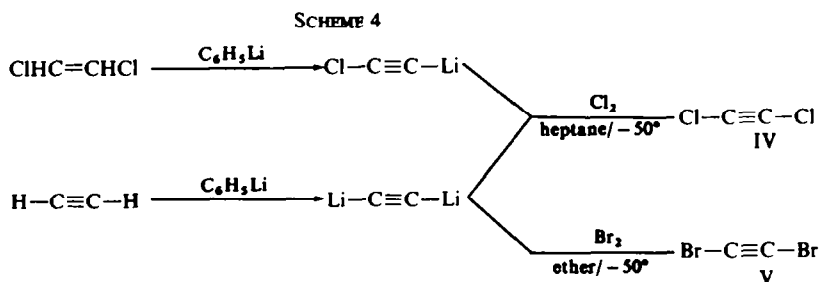
† The synthesis was also run with reduced amounts (1 equiv) of LiNH₂. This furnished a far less discoloured reaction mixture and somewhat reduced yield of product.

Since alkali diacetylide can also be prepared in a polar organic medium,[17] an appropriate choice of solvent, base and reaction temperature was expected to produce a smooth reaction of dialkali acetylide with bromine or chlorine to yield dibromo-acetylene and dichloroacetylene, respectively. The products could be worked up directly from the reaction medium under exclusion of air.

Thus, dry acetylene was bubbled through an etherial solution of phenyl-lithium at room temp and the dilithium acetylide produced was reacted with chlorine (in a solution of Freon 11) or bromine (undissolved) at a temp of $-50°$ until the reaction was no more alkaline.

Reacting chlorine with dilithium acetylide in a preliminary experiment yielded dibromoacetylene (V) as the only product. Obviously chlorine had preferentially oxidized the bromide ions which were present as lithium bromide in the ethereal phenyl-lithium reagent. The molecular bromine thus formed reacted with dilithium acetylide to form dibromoacetylene (V). Accordingly, addition of bromine to dilithium acetylide yielded an identical product V.

Phenyl-lithium was instead prepared from chlorobenzene, in smaller yields (less than 50%). When acetylene was reacted with this phenyl-lithium, the subsequent introduction of chlorine into the reaction mixture yielded dichloroacetylene (IV):

SCHEME 4

$$CIHC=CHCl \xrightarrow{C_6H_5Li} Cl-C{\equiv}C-Li$$

$$\xrightarrow[\text{heptane}/-50°]{Cl_2} Cl-C{\equiv}C-Cl \quad IV$$

$$H-C{\equiv}C-H \xrightarrow{C_6H_5Li} Li-C{\equiv}C-Li$$

$$\xrightarrow[\text{ether}/-50°]{Br_2} Br-C{\equiv}C-Br \quad V$$

Complications arose, however, during isolation of the highly volatile dichloro-acetylene (b.p. $32°$[14]) from the ether solution. By the fractional distillation of the reaction mixture at $-50°/8$ torr, IV concentrated mainly in the first two fractions, which were trapped in liquid nitrogen. The first fraction contained substantial quantities of unreacted chlorine and was discarded. During GLC of the second concentrate the reaction product was eluted simultaneously with ether. The characteristic odour as well as the fumes from the exit. indicated the presence of dichloroacetylene.

To isolate IV from solvent, ether, whose presence was necessary to provide a polar medium for the acetylide formation, had to be exchanged for a less volatile solvent before the final reaction with chlorine could be run. By removal of the ether under vacuum during successive introduction of n-heptane* to the concentrated ethereal suspension of the dilithium acetylide, almost completely ether-free IV was obtained. Two preparative GLC treatments at *ca* 70° yielded a very pure IV, yield 27%. The isolation of ether-free IV is remarkable, since dichloroacetylene is known to form a strong 1:1 complex with diethyl ether and also an azeotrope with this solvent.[15] The m.p. was approximately -68– $-65°$ (-66– $-64.2°$[14]).

The much less volatile dibromoacetylene (V) was abundant in the last distillation fractions. Its isolation from by-products was no problem. However, the high reactivity

* Attempts to prepare phenyl-lithium from chlorobenzene in n-heptane as a solvent were unsuccessful.

of this compound towards vacuum grease* called for special precautions in handling the product. Two preparative GLC treatments at *ca* 90° yielded a very pure V, m.p. −17− −16° (−25− −23° [14]), yield 41·3%.

Monochloro- and monobromoacetylene were also produced in the synthesis of IV and V, from acetylene. Their much higher volatility (b.p.[18] −30 and +5°, resp) permitted complete separation from the dihalo compounds.

Analogous to the preparation of I and II, IV could also be obtained from *cis*-1,2-dichloroethylene, but in much lower yield, from a reaction mixture which was rather contaminated with byproducts.

As experienced in the isolation of I-III, GLC of IV-V seriously reduced the amounts of product, whereas only a modest increase in m.ps was observed (Experimental). The most seriously attacked was V, which was reduced by about 50% by weight, owing to its disastrous reactivity towards Apiezon L as the stationary phase. Vacuum equipment first greased with Apiezon soon turned brown. The efficient separatory power of this stationary phase, however, greatly made up for this loss.

Non-volatile slightly discoloured residues obtained from the fractionation of IV contained large amounts of a crystalline compound, whose IR spectrum and m.p. 69° (69–71° [8]) were identical with biphenyl (cf the modified PhLi reagent used). The residues from V contained essentially no byproducts.

Diiodoacetylene

Among the several methods of preparing diiodoacetylene (VI), [3a] the one in which acetylene was reacted directly with iodine in liquid ammonia,[12] proved far the simplest, and this method was used in further preparations of VI. Highly pure samples of VI were obtained (m.p. see above). In addition to a *ca* 50% yield of the diiodoacetylene, a small percentage of the otherwise hard-to-obtain monoiodoacetylene[19] was also isolated.[5] Similar treatment of diacetylene produced diiododiacetylene[20] in high yields, together with some monoiododiacetylene.[21,2] These compounds were desired for extended spectroscopical studies on haloacetylenes.[22]

From the large scale synthesis of VI very small quantities of highly pure tetra-iodoethylene[9] were isolated.

The sample of diiodoacetylene unexpectedly obtained in the intended preparation of bromoiodoacetylene (III) furnished a high-quality product (VI), which was used in the following IR and Raman spectroscopic investigations.

PROPERTIES

The close similarity of the six hetero and homo dihaloacetylenes was clearly reflected in the general physico-chemical properties of the two series. Essential features are summarized in Table 1.

Compounds I-II and IV-V are water-clear, fairly stable liquids which can be handled in light and under vacuum for a short period of time, without discoloration. III is nearly solid at room temperature (m.p. 15°), very sensitive to light, and decolorizes upon melting† VI, which is moderately insensitive to air, but soon turns violet in the

---

* Apiezon M: Silicone high vacuum grease was moderately resistant.
† Discolored samples of I-V yielded pure products after resublimation *in vacuo*.

TABLE 1. PHYSICAL CHARACTERISTICS AND GLC ISOLATION OF DIHALOACETYLENES

Compound	M.p.[a] °C	Vap. pr[a] torr/°C	Elec. dipole moment debye	Prep. GLC[a] °C/elution time	Overall yield %[b]
I Cl—C≡C—Br	−54- −52[c]	52/−1[c]	0·15 ± 0·10[d]	52°/31 min	40[e]
II Cl—C≡C—I	−37- −35[c]	6/−1	0·30 ± 0·15[d]	92°/37 min	35·5
III Br—C≡C—I	15·3–16·5	8·5/17·5	<0·15[d]	90°/42 min	20·8
IV Cl—C≡C—Cl	−68- −65[f]	748/32[f]		72°/7 min	27·0[e]
V Br—C≡C—Br	−17- −16[h]	13/−1		91°/20 min	41·3[g]
VI I—C≡C—I	76·0–76·5[i]				{ ca. 50[k] ⎰ 18[l]

[a] See Experimental.
[b] once GLC product I–V.
[c] reproduced from different syntheses.
[d] ref. 23.
[e] calculated from 1,2-dichloroethylene on a single 60 mmole scale.
[f] m.p. −66- −64·2° [14].
[g] from PhLi (on acetylene).
[h] m.p. −25- −23 [14].
[i] sublimed until constant m.p.
[k] from iodine (on acetylene).
[l] from 1,2-dibromoethylene.

light, is the only relatively stable dihaloacetylene. VI appears in different crystal forms, and in a pure form it melts without decomposition.

A particularly remarkable characteristic of the dihaloacetylenes, which allows isolation and purification of I–V (GLC at temps between 50–90°), is their stability in an atmosphere of helium. III was the least thermally stable, while VI was not eluted during the GLC treatment. Obviously VI was completely destroyed in the column which was at a temp of 100°. The later-prepared monoiodoacetylene can be isolated at a lower temp by GLC.[5] Collected at liquid nitrogen temp, I–V deposit as a snow-white, fine powder, which after storing at −70° is transformed to long, thin, transparent needles, up to 35 mm in length (I–II).

As is seen in the Table, all the dihaloacetylenes containing different halogens solidify at temps between those of the respective acetylenes with equivalent halogens. Their m.ps, however, are closer to the lower-melting of the two. The m.p. of V of −17° was found to be higher than that reported (−25° [14]). It is of interest to note that the electric dipole moments of the heterohaloacetylenes I–III are very low. From micro-wave studies,[23] approximate values of 0·30 ± 0·15 for II, and 0·15 ± 0·10 debye for I were found, and an even lower value was estimated for III. In comparison, monoiodo-acetylene exhibits practically no electric dipole moment (<0·05 debye[19c]).

As shown by a check on the vapour pressures of the dihaloacetylenes, the volatility of the unsymmetrical dihaloacetylenes (I–III) varies within the range of those of the respective pairs of symmetrical dihaloacetylenes (IV–VI).

An indication of the relative thermal stability and chemical reactivity of I–VI was given during the gas chromatographic separation and the spectroscopic work on the compounds. Traces of the vapours of I–V in a stream of helium, or in solutions, had

very disagreeable odours, characteristically sticky or sweetish, which produced fumes when in contact with air. The heavy white fumes from V smelled strongly of ozone. Dibromodiacetylene is reported to produce ozone with air.[20] I–V are highly lachrimatory compounds, VI is less so and has a somewhat iodoform-like odour.

Dichloroacetylene is by far the most inflammable of the compounds and even traces of its vapour are known to explode violently in the presence of air.[3] The other chloroacetylenes, along with dibromoacetylene, are explosive in character and readily ignite upon contact with air. These facts became evident from work on milligram samples of the compounds. Pure diiodoacetylene is reported to explode at temps above 84°.[12] In dilute cooled solutions of ether or heptane, I–V could be handled in air without danger. The stability of the complex of IV with ether was particularly studied by Wotiz.[15d] A 1:1 complex of IV with diethyl ether is reported[24] not to be spontaneously inflammable at low temperatures. The dihaloacetylenes attack vacuum grease,* causing leakages in the vacuum system, especially when Apiezon was used primarily in work on I. Silicone grease proved moderate resistance and was utilized in small quantities in all subsequent work on the haloacetylenes.

The reactivity of the dihaloacetylenes towards Apiezon was responsible in part for the very reduced amount of isolated product in gas chromatographic work on I–V, as already mentioned. The most extreme loss, $\frac{2}{3}$ of the amount of III, was due to a great extent to its thermal instability at 90°, as shown by large deposits of carbonized material in the injector, and column, which sometimes caused stoppage of gas flow.†

Under vacuum at low temp (– 70°), I–V proved to be quite stable. A 150 mg sample of II remained unchanged after being stored in a dry ice case for 14 months during which time the sample was frequently removed for use in micro-wave investigations.[23] Under vacuum and protected from light, VI was quite stable at room temp.

IR, far IR and Raman spectral data. The dihaloacetylenes were satisfactorily identified by their IR absorption spectra. The spectral region was extended to the far IR, where the lowest frequencies were located. Complementary bands were observed in their Raman spectra. The linear[25] configuration of the molecules permitted us to predict 3 N-5 (N = 4 atoms) fundamental modes of vibration, 3 stretching and 2 doubly degenerate bending modes, all of which were identified in the spectra.‡¶ In Fig 1 the fundamental vibrational frequencies of I–VI are compiled and assigned to the appropriate normal modes of vibration.∥

The large frequency difference between the two lowest stretching modes is peculiar of the stiff, linear vibrating system. The two modes are both outside the frequency range given for the C—X stretching frequencies.[27] Their average, however, is in the midst of this range. Raman depolarization measurements, force constant calculations,

---

* See footnote* on page 38.

† After replacement of the contents in the first 10 cm of the column with fresh material, the GLC could be satisfactorily accomplished.

‡ After this work was completed, we became aware of research by A. F. Flannery, *Diss. Abstr.* B **28**, 132 (1967); *Chem. Abstr.* **68**, 17217c (1968), who reported some of the vibrational bands in dichloro-, dibromo- and diiodoacetylene.

¶ In a contaminated sample of dichloroacetylene one infrared and one Raman band were observed, Ref. 26.

∥ G. Herzberg: *Molecular Spectra and Molecular Structure,*II. *Infrared and Raman Spectra of Polyatomic Molecules* p. 181, D. van Nostrand (1968); N. Sheppard and D. M. Simpson, *Quart. Rev.* **6**, (1952).
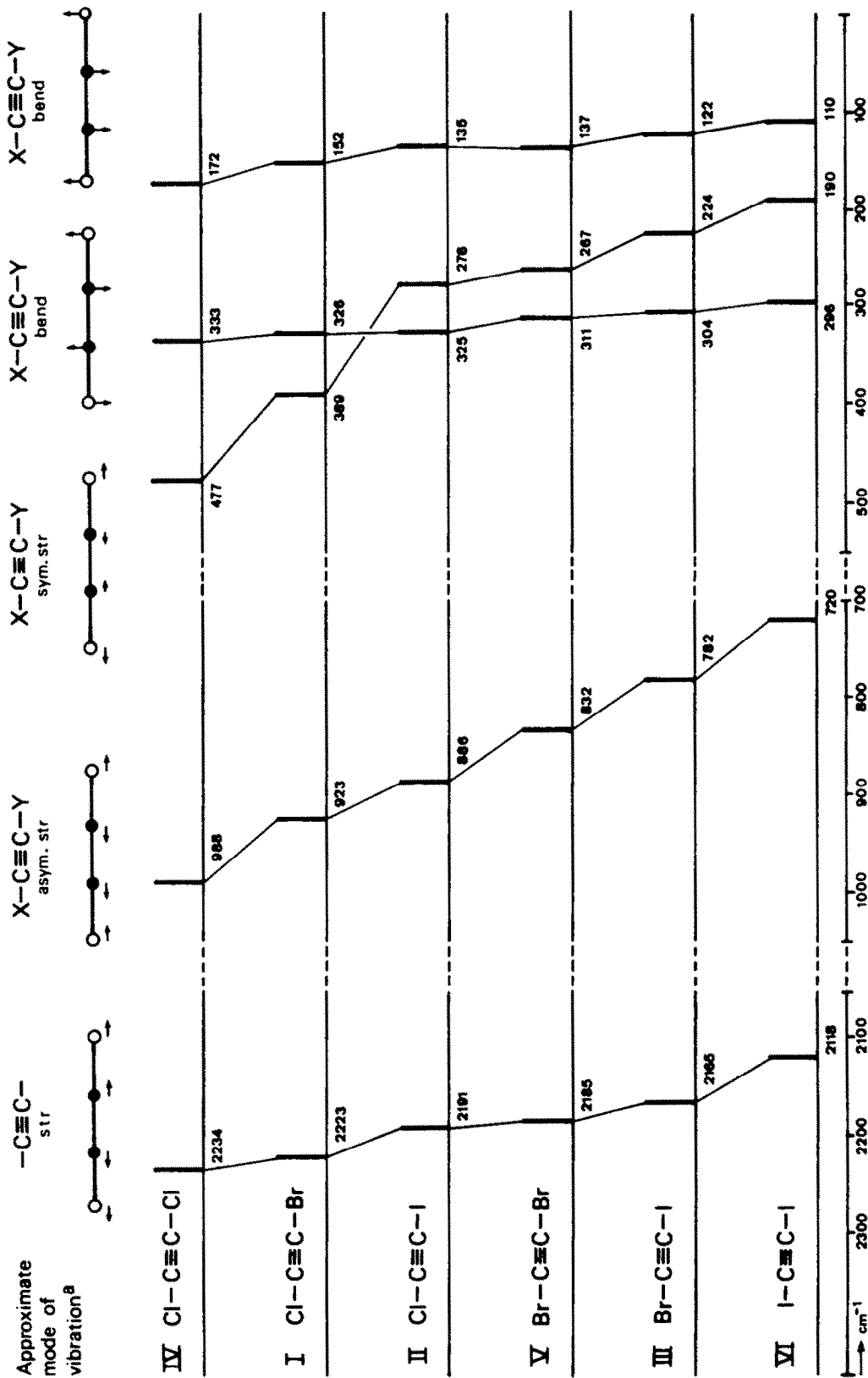
Fig 1. Observed fundamental frequencies (cm⁻¹) and vibrational assignments of dihalo-acetylenes.[28,29] See footnote ‖ on page 40.

as well as micro-wave studies,[23] revealed that the assignments for the lowest stretching modes were correct. The sequence of the latter thus crosses that of the highest bending mode (Fig 1).

Arranged according to increasing weight of the halogen substituent, the spectra visibly demonstrate the expected displacement of the stretching frequencies towards lower wave-numbers with increasing mass of the vibrating system. Least influenced is the highest frequency stretching mode, located within a range of *ca* 100 cm^{-1} (2234–2118 cm^{-1}), indicating that this vibrational mode is mainly concerned with the —C≡C— stretching. Much more displaced are the assymmetric and symmetric stretching modes, which move down through a *ca* 300 cm^{-1} range.

In contrast, the two degenerate bending modes remain fairly constant throughout the series. The shifts to lower wave-numbers are very small and these bands are situated within 40 and 60 cm^{-1} for the highest and lowest bending vibration, respectively. Undoubtedly, with heavier halogens these modes involve predominantly a displacement of the carbons with the halogens nearly at rest.

The spectral findings on VI were in good accordance with those of Meister and Cleveland,[7] who measured all but the lowest band. A complete vibrational analysis of I–V is being published separately.[28, 29] A discussion of the vibrational and electronic spectra of acetylenes was recently given by Dale.[30]

Micro-wave spectral studies of unsymmetrical I and II have been undertaken and are published elsewhere.[23] From the suprisingly low electric dipole moments of these acetylenes already mentioned, a still lower dipole moment of III could be predicted which excluded III from micro-wave investigations with the equipment available.

Mass spectra. In subsequent work on the dihaloacetylenes, mass spectra were run on the samples to test their purity. Spectra, showing the absence of impurities for all six compounds, were obtained. The mass spectra will be published elsewhere.[31]

Photoelectron spectra. Investigations of the 6 dihaloacetylenes by means of photo-electron spectroscopy have been undertaken and recently published.[32]

The electronic spectra of I–VI have been recorded down to 115 nm.[33]

Nuclear quadropole resonance measurements of chlorobromo- and chloroiodo-acetylene, in addition to other linear chloroacetylenes, have been carried out.[34]

Electron diffraction studies are being undertaken presently.[35]

A synthetic approach to fluorobromo- and fluoroiodoacetylene

Attempts were made to prepare these compounds from 1-fluoro-2-bromoethylene by the methods used to prepare I and II, from 1,2-dichloroethylene (see above). At the time of these studies, chlorofluoroacetylene was briefly reported* to have been obtained by dehydrohalogenation of 1,1-dichloro-2-fluoroethylene at 120° in vacuum.†

Reacting (Scheme 5) the fluorobromoethylene, prepared according to Viehe,[36] with phenyl-lithium and bromine, yielded a colourless insoluble non-volatile solid (m.p. > 330°) whose IR spectrum showed aromatic characteristics. When iodine was used, minor amounts of tetraiodoethylene‡ were formed, and reaction with cyclohexanone

---

* See footnote ‖ on page 33.

† After these studies were finished the extremely unstable chlorofluoroacetylene was reviewed in a survey of fluoroacetylenes by S. A. Delavarenne and H. G. Viehe, Ref. 3*b*, p. 660, and in *Chem. Ber.* 103, 1198 (1970).
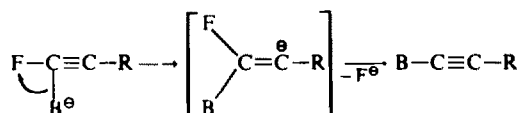
‡ See footnote† on page 35.

yielded very pure bis(1-hydroxycyclohexyl)acetylene[8] (yield 30%) as the only product. Obviously, both halogens had been attacked by the base, leaving a diacetylide intermediate. Under the same conditions, 1,2-dibromoethylene gave 40% of the same bis(1-hydroxy-cyclohexyl)acetylene. In reaction with iodine, the intermediate from dibromoethylene gave diiodoacetylene, as described above in synthetic attempts on III. 1,2-Dichloroethylene, on the other hand, produced the *mono* condensate 1-chloroethynyl-1-cyclohexanol[14] (yield 68%) in good agreement with the formation of chlorobromo-(I) and chloroiodoacetylene (II) from this dihaloethylene with bromine and iodine, as shown above.

When a less strong base like lithium amide in liquid ammonia was used on 1-bromo-2-fluoroethylene in accomplishing the condensation with cyclohexanone, a very vigorous carbonization occurred at − 55°. 1,2-dichloro- and 1,2-dibromoethylene produced 1-chloroethynyl- (86%) and 1-bromoethynyl-1-cyclohexanol (42%), respectively,[10] and dibromoethylene further yielded bromoiodoacetylene (III) (~ 60%) with iodine (see above). The action of a stronger base like methyl-lithium on 1-chloro-2-fluoroethylene yielded 1-chloroethynyl-1-cyclohexanol (27%).[37] The reactions are summarized in Scheme 5.

SCHEME 5
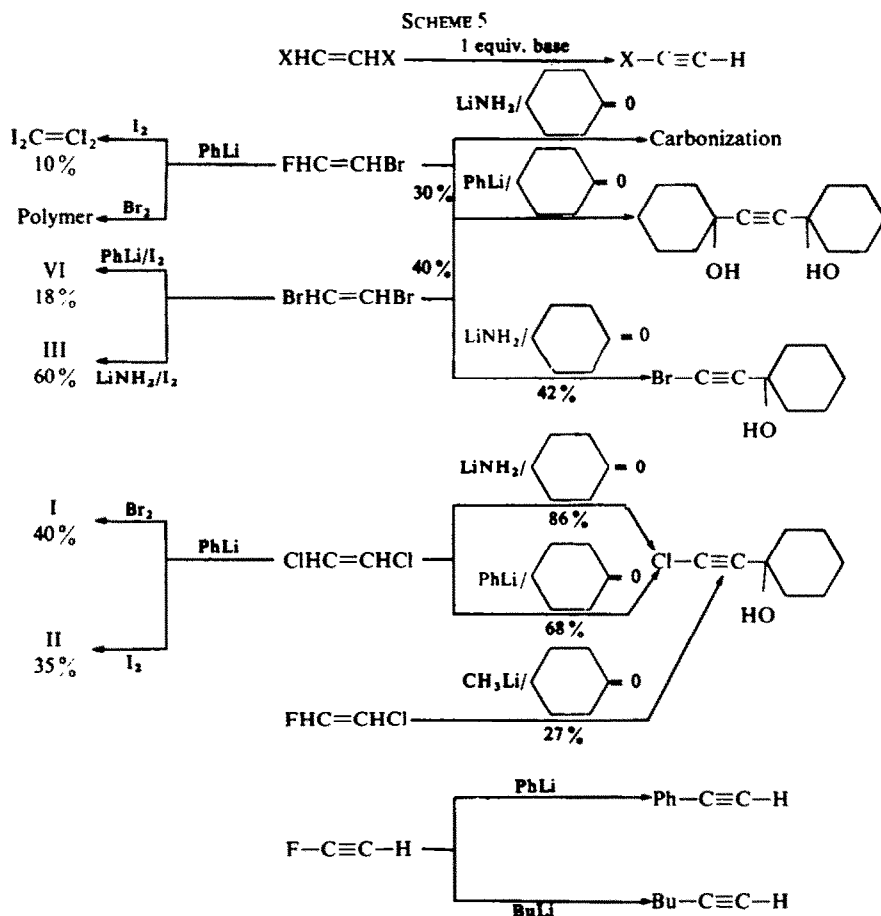
Obviously, the strength of the base influences the reaction course. The relative acidity of the dihaloethylene,[38] as well as the electronegativity of the halogen, must also be taken into account in determining the reacting course. In the examples cited, if one considers the monohaloacetylene $X—C\equiv C—H$ as the primary product formed by the action of the base on the dihaloethylene, only acetylenic chlorine resisted further attack by the base. Acetylenic bromine proved moderately resistant in the presence of a less strong base. Also with a less strong base, fluorine (linked to sp^2- or sp^3-hybridized carbon) was completely eliminated. The fact that acetylenic fluorine is removed in a nucleophilic attack by PhLi or BuLi was shown in mono-fluoroacetylene, which yielded $Ph—C\equiv C—H$ and $Bu—C\equiv C—H$, respectively.[37]

The extremely high electronegativity of fluorine is thought to be responsible for the preferred attack of the base at the α-carbon in fluoroacetylene. The α-addition of base is followed by a β-elimination of halogen:

$$F—C\equiv C—R \longrightarrow \left[\begin{array}{c} F \\ \diagdown \\ \diagup \\ B \end{array} C=\overset{\ominus}{C}—R \right] \xrightarrow{-F^{\ominus}} B—C\equiv C—R$$

The sp-carbon–chlorine linkage constitutes a much less polar bond, which remains fairly unaffected by the base. As opposed to chlorine, the acetylenic bromine is thought to be partially positively charged and hence more readily exposed to nucleophilic attack. Experimental evidence of these considerations was given by the isolation of bromobenzene in the reaction of 1,2-dibromoethylene with phenyl-lithium, as mentioned under III.

A directiospecific[39] elimination of hydrogen halide by a base attack was shown to occur in chlorofluoroethylene, as only one direction of H-X elimination was effected (minus H-F). Obviously, to preserve the fluorine substituent in the fluorohaloethylene, no β-hydrogen should be present. Thus 1,1-dichloro-2-fluoroethylene afforded chloro-fluoroacetylene by the action of solid potassium hydroxide in the gas phase.*

EXPERIMENTAL

The IR spectra were recorded on a Perkin–Elmer 225 spectrometer from 4000–200 cm^{-1} in the gas phase (10 cm and 1 m cells with KRS5 windows) and in solns of CS_2 and CCl_4. The Raman spectra were recorded on a Cary 81 Raman spectrometer equipped with a Spectra Physics Model 125 Helium-Neon Laser, in solns of CCl_4, C_6H_6, CS_2 and acetonitrile, or in liquid state. The Far IR spectra were accomplished on a RIIC Interferometer at Kemisk Laboratorium 5 at the University of Kopenhagen, in a range from 300–50 cm^{-1}. The mass spectra were performed on a Hitachi Perkin–Elmer RMU-7 Mass spectrometer. The GLC separations were performed on a Beckman GC-2a and an Aerograph A-90-P gas chromatograph with He as a carrier gas. Columns of ca 3 m length and $\frac{3}{16}$ in. outer diam were prepared with Apiezon L 20% on Chromosorb W HMDS. 40–60 or 60–80 mesh. The choice of Chromosorb W proved critical in achieving an effective separation. For chromatography on a preparative scale about 10% concentrates were injected in portions of 400–500 µl by a gas-tight syringe. The haloacetylene was collected in spiral condenser cooled in an EtOH-dry ice bath or in liquid N_2. The condenser was fitted with high vacuum stop cocks and connected to the exit of the gas chromatograph by a stainless steel/glass joint. From the condenser solid product in portions of $\frac{1}{2}$–1.g was sublimed (10^{-2} torr) into vacuum tubes cooled in liquid N_2. These products were 95–98% pure. A second GLC was accomplished by subliming solvent (ether, n-heptane) in vacuum into

portions of product in the cooled vacuum tube. The contents were allowed to melt and N_2 was let in. The 10–20 °$_0$ solns were removed in portions by a Pasteur pipette throught the cock of the tube into a cooled glass tube and injected in portions of 200–500 μl by a cooled syringe. The stock soln was kept frozen between each injection. The same column was used in hundreds of injections on a preparative scale. The same stationary phase was used in all separations. The m.ps (uncorrected) of I–V were measured on ca 50 mg samples in a ca 20 ml vacuum tube immersed in an alcohol bath pre-cooled with dry ice. Two thermometers were used for control. Otherwise the m.ps were measured on a Büchi m.p. apparatus. The vapour pressures (approximate) were measured on a 760 mm capillary column of mercury.

General procedure. The reactions were run on a 20–40 mmole scale under N_2 and protected from light. The glass equipment was greased with silicon high vacuum grease and fitted with 1st-quality high-vacuum stop cocks. Freshly prepared solns of PhLi were used and the solvents were distilled over colloidal Na.

The appropriate dihaloethylene in ether soln or dry acetylene was introduced into the ethereal soln of base at 0° under mechanical stirring. After stirring for another 15 min molecular halogen (Cl_2 in trichloro-fluoromethane, "Freon-11", distilled over P_2O_5, Br_2 undissolved, or I_2 in ether soln) was added at $-50°$ over a 15 min period. A strongly exothermic reaction took place. Decoloration of the halogen, which occurred immediately, proceeded more slowly towards the end of the reaction. A colourless fine ppt appeared in increasing amounts, and previous discoloration disappeared. The addition of halogen was discontinued when samples of the reaction mixture were no longer alkaline after addition of water. Almost equivalent amounts of halogen were consumed.

Fractional distillation of the reaction mixture was subsequently undertaken at an initial temp of $-45°/8$ torr. Fractions of ca 10 ml were trapped in a spiral condenser cooled in dry ice or liquid N_2 (1), and the contents were analyzed by GLC. Except for I, the reaction product concentrated mainly in the last two fractions. A slightly coloured dry-looking powdered residue contained no further acetylenic product. Only the poorly volatile VI was isolated from the residue by sublimation at 10^{-2} torr.

After refractionation of the last fractions, the ca 10% concentrates were submitted to preparative GLC (isothermal, for details see above). The dihaloacetylene was trapped at dry ice or liquid N_2 temps and sublimed *in vacuo* into a vacuum tube. GLC once gave products of more than 95% purity. A second GLC yielded products of highest quality, although in rather reduced quantities.

In vacuum tubes in a dry ice case, the dihaloacetylenes could be stored over months.

Bromochloroacetylene (I)

After several preparations of this compound on a 40 mmole scale, a single run on a 60 mmole scale, which is described below, furnished considerably higher yields.

A. *cis* 1,-2-Dichloroethylene (5·8 g) in ether (10 ml) was dropped slowly into a solution of PhLi from bromobenzene (18·9 g) and Li (1·85 g) in ether (80 ml) at 0°. The reaction mixture soon became blackish in colour, but remained clear. Br_2 (9·6 g) was added dropwise at $-50°$. At the point of neutralization the consumption of Br_2 was nearly complete, and the dark colour had disappeared. After fractional distillation at $-45°/8$ torr, the concentrates were gas chromatographed at 52°. From fractions 3 and 4, a crystalline product of I (2·40 g) was isolated, which contained a little benzene. Rechromatography furnished very pure I, 90% of I was thereby recovered. Fractions 5 and 6 contained another 1·0 g, as estimated by GLC, total yield 40%.

To the dry powdered residue under N_2 was introduced 40 ml ether and ca 25 ml water at 0° under stirring. Repeated extraction of the clear water phase, drying and removal of the ether gave an oily, yellowish residue in minor amounts which contained essentially no products.

I had m.p. $-54–-52°$ and a vapour pressure of 52 torr/$-1°$.

B. PhLi from bromobenzene (12·56 g, 80 mmole) and Li (1·20 g, 17 mmole) in ether, was added to *cis*-1,2-dichloroethylene (3·88 g, 40 mmole) in ether (10 ml) at $-80°$. The reaction mixture darkened quickly and was almost black, but was transparent at the end of the reaction. Subsequently Br_2 (6·40 g, 40 mmole) was added at $-50°$. The reaction mixture was neutral after addition of the last drops of Br_2. Fractionation was performed at an initial temp of $-50°/8$ torr. GLC at 52° of the 8 fractions collected, showed that fractions 1–4 ($-50–-23°$) contained very little product, but increasing amounts of dichloroethylene and benzene. The product mainly concentrated in the fractions 5–7 ($-23–-20°$), which also contained dichloroethylene and benzene. Fraction 8 ($-20–-10°$) contained very little product, starting material, and benzene. No bromobenzene was eluted at the GLC temp.

After further concentrations of fractions 5-7 at $-45°$, GLC at 47° of fractions 5 and 6 yielded 624 mg of I. Fractions 3 and 4 contained another 150 mg, and fraction 7 320 mg, as estimated by GLC, total yield 20%.

Chloroiodoacetylene (II)

A. *cis* 1,2-Dichloroethylene (4·85 g, 50 mmole) in ether (5 ml) was added to an ethereal soln of PhLi from bromobenzene (15·7 g, 100 mmole) and Li (1·4 g, 200 mmole) at 0°. To the dark, clear soln was added a soln of I_2 (13·7 g, 50 mmole) in ether at −50°. The point of neutralization was reached when 95 % of the I_2 had reacted. By the fractional distillation the first 7 fractions were void of product. Fraction 8 (−40–16°, 12 ml) after refractionation at −40° and GLC at 92° yielded 1·32 g of II; fraction 9 (20°, 10 ml) gave another 2·0 g of II, yield 35·5 %. Traces of benzene were removed by a second GLC. From a sample of 358 mg of II 242 mg (68 %) of very pure II was thereby recovered. The m.p. rose thereby *ca* 2°, m.p. −37– −35°, vapour pressure 6 torr/−1°.

B. To *cis*-dichloroethylene (3·88 g, 40 mmole) in ether was added ethereal PhLi from bromobenzene (12·56 g, 80 mmole) and Li (1·26 g, 180 mmole) at −40°. At the end of the reaction (40 min) the bath temp was −20°. Stirring was continued for another 30 min and I_2 (10·16 g, 40 mmole) in ether was added at −40°. The reaction mixture was neutral when 85 % of the I_2 had reacted. Fractionation was undertaken at −40°, but no reaction product was collected up to −10°. The last fraction (25 ml) was collected overnight by leaving the residual amounts of reaction mixture under vacuum at room temp. This fraction contained rich amounts of product together with some unreacted dichloroethylene and small amounts of benzene and bromobenzene. After refractionation at −42° residual 2·5 ml of concentrate was submitted to GLC at 93° in portions of 200 µl. 826 mg of 11 (yield 11·1 %) was isolated which yielded a very pure product after rechromatography.

C. On a 30 mmole scale the preparation was carried out with BuLi instead of PhLi. GLC of the fractions showed no peak related to II. Minute amounts of unpure material isolated from the last fractions by GLC were alkyl compounds, as shown by their IR spectra. The powdered residue from the fractionation was brown and wet in contrast to the almost colourless dry residue from the synthesis with PhLi.

Bromoiodoacetylene (III)

A. Dibromoethylene (5·0.g, 27 mmole) was added slowly to lithium amide (from 0·38 g Li, 54 mmole) in liquid ammonia (80 ml) at −40°. After stirring for another 15 min I_2 (6·85 g· 27 mmole) was added in portions under vigorous stirring. The brownish reaction mixture was concentrated by evaporation of the ammonia through a cellophane membrane. Ether (25 ml) was added, and after further evaporation of ammonia, additional ether (25 ml) was added and then water (50 ml), under vigorous stirring at 0°. The ether layer was removed from the reactor and extraction was repeated with ether (4 times 25 ml) under stirring in the reactor. The extracts were dried over $MgSO_4$ overnight and fractional distillation was undertaken at −45°/8 torr. In the slightly coloured residue (7 ml) yellowish crystalline solids deposited in the cold. GLC of the concentrate at 90° (injector 100°, exit 105°) gave a colorless crystalline product (1·30 g) which was identified as III by its mass spectrum. By rechromatography of III (discoloured in ether soln), only one third of the quantities injected were recollected (f.i. from a sample of 500 mg only 168 mg, or from 162 mg 54 mg of III were trapped). Extremely pure III (MS) then showed m.p. 15·3–16·5° (discoloration). Vapour pressure 8·5 torr/17·5°, yield 20·8 % (once GLC product). Solns of III soon turned brownish and the quantities of product decreased when kept at −80° during GLC. Hence III should be worked up as quickly as possible.

Dichloroacetylene (IV)

A. Purified* acetylene from a gas flask was conducted in a stream of N_2 through a stirred soln of PhLi prepared from chlorobenzene and Li (95 ml, 0·48 N) at room temp. A white voluminous ppt appeared in increasing amounts. After 1 hr the gas stream was discontinued, and the contents were concentrated under vacuum (8 torr) to *ca* 20 ml. To the ethereal suspension was added 50 ml n-heptane, and the contents were again concentrated. This procedure was repeated twice with 30 ml heptane. The concentrate was diluted to 100 ml with heptane, and Cl_2 gas in a stream of N_2 or a cooled soln of Cl_2 in trichlorofluoromethane (Freon-11, distilled over P_2O_5), was introduced at a temp of −50°. The light solids were slowly replaced by a fine, crystalline, heavy ppt.

Fractional distillation of the yellowish reaction mixture was performed at −50°/torr. For each of the first two fractions, 5 ml heptane was first introduced into the empty trap (now cooled in liquid N_2) to trap critical volatiles, which were expected to concentrate readily in the first fractions. Fraction 1 (−50– −30°, 7 ml) contained minute amounts of ether, some Cl_2, and a very volatile component, presumed to be mono-

---

* Acetylene was purified by bubbling through conc. sulphuric acid and passing a trap cooled in dry ice.

chloroacetylene, from its ready elution by GLC and its particular odour. The presence of small quantities of IV was indicated by a separate peak shortly after that of ether whose eluate produced white fumes at the exit. Fraction 2 ($-30- -15°$, 7 ml) contained considerable amounts of III and minor amounts of more readily eluted components in addition to benzene and chlorobenzene. After refractionation of fraction 2, the first 2·5 ml were submitted to preparative GLC at 72°. 580 mg of snow-white solid IV were isolated from this fraction. Practical yield 27·0 %. By a second GLC treatment the amount of IV was reduced to 330 mg. The m.p., however, remained fairly constant. A highly pure IV was obtained, m.p. $-68- -65°$. Minor amounts of product in later fractions were not isolated.

When the second reaction step was first performed in ether, the latter appeared on the chromatogram as a very large unsymmetric peak (on a preparative scale) which completely covered IV. However, the fumes as well as the characteristic odour from the exit left no doubt about the simultaneous elution of IV with ether.

The dry yellow residue from the fractional distillation contained considerable amounts of solids which were identified as biphenyl.[8]

B. Starting from cis-1,2-dichloroethylene the procedure described under A was repeated. Less of IV was thereby obtained, and several new peaks in the gaschromatogram indicated a more contaminated reaction mixture.

Dibromoacetylene (V)

A. Purified acetylene gas was reacted with a stirred soln of PhLi prepared from bromobenzene (9·42 g, 60 mmole) and Li (0·91 g, 130 mmole) in ether (100 ml) at room temp over a period of $1\frac{1}{2}$ hr. At a bath temp of $-42°$ Br$_2$ (9·6 g, 60 mmole) was added during 30 min. As the last drops of Br$_2$ were added the mixture was no longer alkaline. In contact with air the latter developed white fumes with a strong smell of ozone.

In fractional distillation at $-50°/8$ torr the product concentrated in the last fraction, collected overnight at room temp (26 ml). After further concentration in vacuum at $-50°$, residual 12·5 ml of yellowish concentrate was submitted to GLC at 91°. A total amount of 2·28 g of snow-white V was isolated, yield 41·3 %.

In the second GLC treatment a serious loss of substance was observed. From a portion of 586 mg of V 266 mg (45 %) of highly pure dibromoacetylene was isolated, m.p. $-17- 16°$, vapour pressure 13 torr/$-1°$.

B. Aiming at the preparation of dichloroacetylene, the procedure under V A was first performed by reacting the diacetylide with molecular Cl$_2$. GLC of the fractions showed that after ether and benzene a product was eluted whose m.p. and vapour pressure were rather different from those of dichloroacetylene. From its mass spectrum the product was identified as dibromoacetylene. By preparative GLC considerable amounts of product were isolated.

Running the reaction in ether soln prevented the appearance of dichloroacetylene as separate peak. However, a characteristic odour of haloacetylene during the elution of ether indicated that dichloroacetylene had been present under the broad ether peak.

Diiodoacetylene (VI)

A. Diiodoacetylene was prepared on a 10 g scale by bubbling acetylene through a soln of I$_2$ in liquid ammonia.[12] The white solids isolated were recrystallized from pentane and sublimed twice over P$_2$O$_5$ at 50°/10^{-2} torr, yield ca 50 %. Small quantities of very pure tetraiodoethylene, m.p. 191° (dec; 187°[8]) were further isolated.

B. 1,2-Dibromoethylene (7·44 g, 40 mmole) in ether (5 ml) was added dropwise to a soln of PhLi from bromobenzene (12·56 g, 80 mmole) under stirring at $-45°$. To the opaque soln was added I$_2$ in ether until the soln remained coloured, although still slightly alkaline (11·4 g, 45 mmole). Fractional distillation from $-45°/8$ torr to $20°/10^{-2}$ torr gave fractions devoid of product. At $45°/10^{-2}$ torr the last 5 ml of distillate were collected, in which crystalline solids partly deposited in the cooled trap. By removal of the solvent in vacuum at low temp ca 2 g (18 %) of crystalline product were isolated. Recrystallization from light petroleum and repeated sublimation at $49°/10^{-2}$ torr yielded colourless, transparent needles of high quality. From its m.p. 76–76·5° and IR spectrum the compound was identified as diiodoacetylene VI (see above).

C. In a second run PhLi (80 mmole) was added to dibromoethylene (40 mmole) and subsequently I$_2$ (40 mmole). After fractionation nonvolatile solids (ca 2 g) were extracted from powdered residue with benzene. Recrystallization from hexane and sublimation yielded yellowish crystals, which from their m.p. 189·5–190° and an IR spectrum were identified as tetraiodoethylene.*

* See footnote† on page 35.

Reaction of 1,2-dibromoethylene with phenyl-lithium and cyclohexanone

To PhLi from bromobenzene (6·3 g, 40 mmole) and Li (0·63 g, 90 mmole) in ether (80 ml) was added 1-fluoro-2-bromoethylene[37] (2·5 g, 20 mmole) during 20 min at $-43°$. Cyclohexanone (2·0 g, 20 mmole) in ether (10 ml) at $-50°$ was added to the opaque soln. Stirring was continued at room temp for another 4 hrs. The mixture was acidified with H_2SO_4 and extracted with ether. After washing with water saturated with NaCl, drying with Na_2SO_4 and removal of the solvent in vacuum, 4 g of yellow oil were isolated in which white solids readily separated. Additional amounts were precipitated by light petroleum. 0·75 g of snow-white crystals of m.p. 106–107° were identified by a mass spectrum as bis(1-hydroxycyclohexyl)acetylene. Recrystallization from light petroleum gave m.p. 107·0–107·2°,[8] yield 30% (calc. from fluorobromo-ethylene). Fractionated oily residues contained no acetylenic product.

Reaction of 1,2-dibromoethylene with phenyl-lithium and cyclohexanone

Following the procedure above 1,2-dibromoethylene (9·7 g) furnished bis(1-hydroxycyclohexyl)acetylene (2·55 g, 40%) as the only reaction product.

REFERENCES

[1] X—C≡C—C≡N, X=Cl, Br, I: E. Kloster-Jensen, *Acta. Chem. Scand.* 17, 1859 (1963); *Ibid.* 17, 1862 (1963); *Ibid.* 18, 1629 (1964) ·

[2] X—C≡C—C≡C—H, X=Cl, Br, I: E. Kloster-Jensen, *Tetrahedron* 22, 965 (1966)

[3] [a] K. M. Smirnov, A. P. Tomilov and A. I. Shchenekotikhin, *Uspekti Khimii* 36, 777 (1967); *Russ. Chem. Rev.* 36, 326–339 (1967);
     [b] S. Y. Delavarenne and H. G. Viehe; 1-*Halogenoacetylenes* Chap 10 in *Chemistry of Acetylenes* (Edited by H. G. Viehe). Marcel Dekker, New York (1969);
     [c] T. F. Rutledge, *Acetylenic Compounds*. Reinhold, New York, Amsterdam, London (1968)

[4] E. Kloster-Jensen, *J. Am. Chem. Soc.* 91, 5673 (1969)

[5] E. Kloster-Jensen, *Tetrahedron Letters* 5323 (1969)

[6] [a] H. G. Viehe, *Chem. Ber.* 92, 1270 (1959);
     [b] *Ibid.* 92, 1950 (1959);
     [c] Preparation from dichloroacetylene, *Ibid.* 92, 3064 (1959)

[7] A. G. Meister and F. F. Cleveland, *J. Chem. Phys.* 17, 212 (1949); *J. Chim. Phys.* 46, 108 (1949)

[8] C. D. Hodgman, *Handbook of Chemistry and Physics*

[9] E. J. Flourie and W. D. Jones, *Spectrochim. Acta* 25A, 653 (1969)

[10] H. G. Viehe, Ger. Pat. 1 126 390, 4. Oct (1962)

[11] A. F. Holleman and E. Wiberg, *Anorganische Chemie* p. 225, Walter de Gruyter, Berlin (1945)

[12] T. H. Vaughn and J. A. Nieuwland, *J. Am. Chem. Soc.* 54, 787 (1932)

[13] J. B. Armitage, E. R. H. Jones and M. C. Whiting, *J. Chem. Soc.* 1993 (1952)

[14] F. Straus, L. Kollek and W. Heyn, *Chem. Ber.* 63, 1868 (1930)

[15] [a] E. Ott, W. Ottenmeyer and K. Packendorff, *Ibid.* 63, 1941 (1930)
     [b] E. Ott and K. Packendorff, *Ibid.* 64, 1324 (1931);
     [c] E. Ott, *Ibid.* 75, 1517 (1942);
     [d] J. H. Wotiz, F. Huba and R. Vendley, *J. Org. Chem.* 26, 1626 (1961);
     [e] R. Riemschneider and U. Brendel, *Liebigs Ann.* 640, 5, (1961)

[16] Ref. 12, p. 789

[17] H. H. Inhoffen, H. Pommer and E. G. Meth, *Liebigs Ann.* 565, 454 (1949); R. A. Raphael: *Acetylenic compounds in Organic Synthesis* p. 12. Butterworths, London (1955)

[18] L. A. Bashford, H. J. Emeléus and H. V. A. Briscoe, *J. Chem. Soc.* 1358 (1938)

[19] [a] G. R. Hunt and M. K. Wilson, *J. Chem. Phys.* 34, 1301 (1961);
     [b] J. K. Brown and J. K. Tyler, *Proc. Chem. Soc.* 13 (1961);
     [c] W. J. Jones, B. P. Stoicheff and J. K. Tyler, *Canad. J. Phys.* 41, 2098 (1963)

[20] F. Straus, L. Kollek and H. Hauptmann, *Chem. Ber.* 63, 1886 (1930)

[21] E. Kloster-Jensen, unpublished work

[22] To be published
[23] A. Björseth, E. Kloster-Jensen, K.-M. Marstokk and H. Möllendal, *J. Mol. Struct.* **16**, 181 (1970)
[24] Ref. 3c, p. 134
[25] O. Hassel and T. Taarland. *Tidsskr. Kjem. Bergv. Met.* **1**, 172 (1941)
[26] M. Schmeisser, H. Schröter, H. Schilder, J. Masonne and F. Rosskopf, *Chem. Ber.* **95**, 1648 (1962)
[27] B. N. Colthup, L. H. Daly and S. Wiberley, *Introduction to Infrared and Raman Spectroscopy.* Academic Press. New York (1964)
[28] P. Klaboe. E. Kloster-Jensen. D. H. Christensen and I. Johnsen. *Spectrochim Acta* **26A**. 1576 (1970)
[29] P. Klaboe. E. Kloster-Jensen. D. H. Christensen. to be submitted
[30] J. Dale. *Structure and Physical Properties of the Acetylenic Bond; The Nature of the Triple Bond* Chap 1 in ref. 3b
[31] E. Kloster-Jensen. C. Pascual and J. Vogt. *Helv. Chim. Acta.* (1971)
[32] E. Heilbronner. V. Hornung and E. Kloster-Jensen. *Ibid.* **53**. 331 (1970)
[33] Physikalisch-Chemisches Institut der Universität Basel, unpublished work
[34] H. Labhardt, P. Gerber (Physikalisch-Chemisches Institut der Universität Zürich) and E. Kloster-Jensen. *J. Mol. Struct.* (1971)
[35] Department of Chemistry, University of Oslo
[36] H. G. Viehe, *Chem. Ber.* **93**, 1697-1709 (1960)
[37] H. G. Viehe and E. Frachimont, *Ibid.* **95**, 319 (1962)
[38] D. Daloze, H. G. Viehe and G. Chiurdoglu, *Tetrahedron Letters* 3925 (1969)
[39] H. G. Viehe, *Angew. Chem.* **79**, 744 (1967); Int. Ed. 767 (1967)