Tetrahedron, 1966, Vol. 22, pp. 965 to 973. Pergamon Press Ltd. Printed in Northern Ireland

THE PREPARATION OF MONOCHLORO-, MONOBROMO- AND MONOIODODIACETYLENE

ELSE KLOSTER-JENSEN
Department of Chemistry, University of Oslo, Blindern, Oslo 3, Norway

(*Received* 13 *October* 1965)

Abstract—Monolithium diacetylide was prepared in ether solution and reacted with molecular halogen to give the unstable monochloro- (I), monobromo- (II) and monoiodo- (III) diacetylene. Pure I, II and III were isolated (I and II by GLC) and characterized by their IR absorption spectra. Experimental evidence of the general applicability of the procedure in preparing 1-bromoalk-1-ynes is given.

LIKE diacetylene, halogenodiacetylenes should be linear molecules. By extrapolation from the low-boiling diacetylene (b.p. 9°[1]) a considerable volatility of monohalogenodiacetylenes could be predicted, which would enhance their attraction at least from a spectroscopic point of view. The synthesis of monochloro- (I), monobromo- (II) and monoiodo- (III) diacetylene is the subject of the present paper. Essential IR absorption data of the compounds are given. The complete IR spectra and a thorough interpretation will be presented in a separate paper.[2] The procedure employed is of general use in the preparation of 1-bromoalk-1-ynes,[3] in spite of the reports in the literature[4] of unsuccessful attempts in the synthesis of 1-bromoalk-1-ynes by direct bromination of alkali acetylides. By this route 1-bromo derivatives of aryl- and alkylacetylenes in yields of 57% (Experimental) were prepared.

Earlier work

Halogen alkynes of the type Hal—C≡C—R can be prepared either by treatment of the alkyne with an alkaline hypohalite solution,[5] or by conversion of an appropriate organometallic derivative (alkali-, heavy metal-, Grignard-) with halogen or halogen-containing reagents.[6] Acetylene and diacetylene have been halogenated by the former procedure, which chiefly gives the *di*halogenoacetylenes.[5] For the preparation of *mono*halogenoacetylenes elimination reactions of halogeno hydrocarbons and related

---

[1] Lespieau and Ch. Prévost, *C.R. Acad. Sci., Paris* **180**, 678 (1925).

[2] D. Christensen, E. Kloster-Jensen and P. Klaeboe, *in preparation.*

[3] 1-Bromoalk-1-ynes are important intermediates in the Chadiot-Chodkiewics coupling reaction of acetylenes (*inter al.* W. Chodkiewics, *Ann. Chim.* **2**, 819 (1957); W. Chodkiewics and P. Cadiot, *C.R. Acad. Sci., Paris* **248**, 146 (1959).

[4a] P. A. McCuster and R. R. Vogt, *J. Amer. Chem. Soc.* **59**, 1307 (1937); [b] G. Eglinton and W. McCrae, *J. Chem. Soc.* 2295 (1963); 1-bromoacetylenes from alkali acetylides, p. 2296.

[5a] I. G. Farbenind., D.R.P. 495787; [b] H. Biltz and E. Küppers, *Ber. Dtsch. Chem. Ges.* **37**, 4415 (1904); [c] F. Straus, L. Kollek and W. Heyn, *Ibid.* **63**, 1868 (1930); [d] F. Straus, L. Kollek and H. Hauptmann, *Ibid.* **63**, 1886 (1930).

[6] For a survey see for example: [a] R. A. Raphael: *Acetylenic Compounds in Organic Synthesis*, p. 56. Butterworths, London (1955); [b] V. Migridichian: *Organic Synthesis* Vol. **2**, 977; [c] Houben-Weyl: *Methoden der organischen Chemie* Vol. **5/3**, 592; Vol. **5/4**, 218, 554.

compounds are employed. Thus, chloro- and bromoacetylene are formed from the requisite 1,2-dihalogenoethylenes by the action of alkali,[7] and fluoroacetylene by pyrolysis of fluoromaleic anhydride.[8] Only monoiodoacetylene has been prepared by the hypohalite procedure as a by-product in minor amounts.[9,10] No direct method for the preparation of monohalogenodiacetylenes (1-halogenobutadiynes) has so far been available.

Earlier work on the preparation of this group of diacetylenes has been limited to monoiododiacetylene. Grignard and Tschéoufaki[10] reported the isolation of this compound (together with some monoiodoacetylene) from the reaction of equimolar amounts of acetylenedimagnesium bromide and iodine. The product, for which a b.p. of 71° was given, was described as being rather unstable to light, but undergoing no change in the dark during several months. Later, Schlubach and Franzen[11] were unsuccessful in their attempts to repeat this synthesis of monoiododiacetylene. Neither monoiododiacetylene nor monoiodoacetylene could be isolated under the conditions cited. In the hands of these authors the main reaction products were di-iodoacetylene, unsubstituted diacetylene and minor amounts of tetraiodoethylene.

However, Schlubach and Franzen[11] were able to prepare the true monoiododiacetylene by an indirect route, based on the observation in the monoacetylene series, that iodoacetylenemagnesium bromide, prepared as an intermediate of low stability, disproportionates extensively into acetylenedimagnesium bromide and di-iodoacetylene. As this reaction leads in fact to an equilibrium, the authors suggested that a similar equilibrium might be established from the corresponding *di*acetylene couple, as shown in the following reaction scheme:

$$2\,\mathrm{BrMgC{\equiv}C{-}I} \rightleftarrows \mathrm{BrMgC{\equiv}CMgBr} + \mathrm{I{-}C{\equiv}C{-}I}$$

$$\mathrm{BrMgC{\equiv}C{-}C{\equiv}CMgBr} + \mathrm{I{-}C{\equiv}C{-}C{\equiv}C{-}I} \rightleftarrows 2\,\mathrm{BrMgC{\equiv}C{-}C{\equiv}C{-}I}$$

Indeed, by hydrolysis of a reaction mixture from iododiacetylenemagnesium bromide the monoiododiacetylene (III) was isolated (in yields not quoted) together with large amounts of free diacetylene and some unreacted di-iododiacetylene. Compound III was identified by hydrogenation to n-butyl iodide. The authors described monoiododiacetylene as an extremely sensitive compound, which had to be handled with the greatest care. It melted at about −40° and exploded vigorously, when brought to a temperature of 40°. In the presence of light the compound discolourized rapidly, and polymerized immediately to a brown tar at room temperature. Its vapour pressure was negligible below 30°.

Although the chance of obtaining and handling further members of the monohalogenodiacetylene series was meagre, work, however, under carefully controlled conditions was undertaken and the products were manipulated only under vacuum, as elaborated earlier.[12]

---

[7] L. A. Bashford, H. J. Emeleus and H. Y. Briscoe, *J. Chem. Soc.* **1938,** 1358; K. A. Hofmann and H. Kirmreuther, *Ber. Dtsch. Chem. Ges.* **42,** 4232 (1909); V. Sawitsch, *Liebigs Ann.* **119,** 182 (1861).

[8] W. J. Middelton and W. H. Sharkley, *J. Amer. Chem. Soc.* **81,** 803 (1959).

[9] J. K. Brown and J. K. Tyler, *Proc. Chem. Soc.* 13 (1961).

[10] V. Grignard and Tschéoufaki, *C.R. Acad. Sci., Paris* **188,** 357 (1929).

[11] H. H. Schlubach and V. Franzen, *Liebigs Ann.* **573,** 115 (1951). For complex of di-iodoacetylene with ether, see p. 119.

[12] E. Kloster-Jensen, *Acta Chem. Scand.* **18,** 1629 (1964).

Choice of methods

The instability of the products and the ease with which rearrangements might take place during the preparation, precluded the use of elimation reactions.[13] Instead, a general procedure was sought, which allowed the introduction of one halogen substituent into the unsubstituted and relatively readily available diacetylene in an inert reaction medium. In the synthesis of chlorocyanoacetylene[12] from cyanoacetylene the intermediate lithium cyanoacetylide prepared in ethereal solution was reacted with molecular chlorine to give chlorocyanoacetylene in satisfactory yields. Thus, if monolithium diacetylide could be obtained in a *neutral*[14] reaction medium, interaction of this intermediate with chlorine might afford the monochlorodiacetylene (I); alternatively, by the action of bromine and iodine monobromo- (II) and monoiodo- (III) diacetylene would be expected:

$$H{-}C{\equiv}C{-}C{\equiv}C{-}H \xrightarrow{BuLi} Li{-}C{\equiv}C{-}C{\equiv}C{-}H \xrightarrow[(Hal\,=\,Cl,Br,I)]{Hal_2} Hal{-}C{\equiv}C{-}C{\equiv}C{-}H$$

I: Hal = Cl
II: Hal = Br
III: Hal = I

It is well known[15,4a] that sodium acetylides react smoothly with molecular iodine in liquid ammonia to yield 1-iodoalkynes.

The advantages of such a procedure are obvious. The reaction steps are few, and the reactions rapid and readily controlled. The starting material, diacetylene, can be prepared[16] relatively easily in the laboratory and the halogenation agents are the simplest at hand. The pronounced difference in volatility between the reaction products on the one hand and reagents and solvents on the other, would allow direct extraction of the desired product from the crude reaction mixture by a low temperature–vacuum distillation, which would be by far the gentlest method of isolation.

Monolithium diacetylide was prepared by addition of one equivalent of butyllithium to a cooled (−80°) ether solution of diacetylene under an atmosphere of nitrogen. By this sequence of addition the formation of undesired dilithium diacetylide was largely suppressed. Subsequently a solution of one mole of halogen was added at −55°. Trichlorofluoromethane ("Freon 11") was used as an inert, highly volatile and non-solidifying solvent for chlorine and bromine, while iodine was added in ether solution. The halogen reagent was instantaneously decolourized. Decoloration was slower towards the end of reaction and ceased before addition was complete. The reaction mixture was fractionally distilled at −40°/8 mm Hg. Unreacted halogen (chlorine and bromine) was in this way conveniently removed from the reaction mixture. The fractions were collected at −80° and analysed by GLC. The first fractions contained some unreacted diacetylene and residual butane (b.p. 0°), and the much less volatile *di*halogenodiacetylenes remained chiefly in the residue, as shown by

---

[13] The less sensitive methyldiacetylene (1,3-pentadiyne) when first prepared from 1,2,3,4-tetrabromopentane by the action of alkali, could be isolated in very poor yield only (Ch. Prévost, *Ann. Chim.* **10**, 356 (1928)).

[14] J. B. Armitage, E. R. H. Jones and M. C. Whiting, *J. Chem. Soc.* 44 (1951); *Ibid.* 1993 (1952).

[15] T. H. Vaughn and J. A. Niewland, *J. Amer. Chem. Soc.* **55**, 2150 (1933).

[16] The procedure involving treatment of 1,4-dichlorobut-2-yne with aqueous alkali was used, see Ref. 14.

examination of non-volatiles from the reaction with bromine. After further concentration *in vacuo* the last fractions were finally submitted to preparative GLC from which analytically pure portions of I and II could be isolated. The iodo derivative proved much less volatile, but by a lengthy vacuum distillation at moderately low temperature a reaction product (III) very nearly free from ether was obtained.[17]

Properties

The halogenodiacetylenes (I, II and III) were isolated as snow-white crystalline compounds, which deposited as long, coarse needles in a moderately cooled trap (CO_2– ice), or at lower temperatures as a compact mass. The physical characteristics of the compounds are summarized in Table 1.

TABLE 1. PHYSICAL CHARACTERISTICS OF MONOHALOGENODIACETYLENES

Substituted diacetylene	M.p.	Vapour pressure measured at 20° mm Hg	Isolated pure react. prod. calc. from diacetylene %
I Monochloro-[a]	−41°	ca. 120	25–30
II Monobromo-[b]	−18°	ca. 40	15–18
III Monoiodo-	−30°	ca. 4	59
Dichloro-	1[5d]		
Dibromo-	52[5d]		
Diiodo-	ca. 100[5d]		

[a] Isolated by prep. GLC at 49°,
[b] Isolated by prep. GLC at 89°.

As one might expect, these compounds are low-melting. Pure samples of I melted at −41°, of II at −18°. A considerably higher m.p. for III was expected. However, after careful removal of residual ether, a sample liquified at −30– −29°. The presence of minute amounts of ether, which was the sole impurity indicated by the IR spectrum of the compound (in CCl_4), cannot explain the very low observed m.p. A still lower m.p. of ca. −40° was given by Schlubach and Franzen.[11] No m.ps of the corresponding monohalogenomonoacetylenes have been reported, that might be compared with the diacetylene series.

Vapour pressures of ca. 120, 40 and 4 mm Hg for I, II and III, respectively, were measured at room temperature; these are within the range to be expected by comparison with other halogenoacetylenes. The much higher m.ps and lower volatility of the structurally closely related Hal—C≡C—C≡N (Hal = Cl[12], Br[18], I[19]) melting at

---

[17] In preliminary experiments an inverse addition of diacetylene to BuLi was first employed, also at higher temps (up to 0°). A white, fluffy precipitate soon appeared, which disappeared gradually by the addition of halogen (Cl_2). Far less amounts of chlorodiacetylene (I) could be isolated in this case. On the other hand, large amounts of non-volatiles resulted from the reaction mixture examined from the reaction with Br_2; the properties were in good accordance with those described for dibromodiacetylene.[5d] Evidently, by this sequence of addition, in which the base was temporarily in an excess of the actual amount of diacetylene, the formation of dilithium diacetylide was predominant. A similar experience has been reported for acetylene (Ref. 6*a*, p. 12).

[18] E. Kloster-Jensen, *Acta Chem. Scand.* **17**, 1859 (1963).

[19] E. Kloster-Jensen, *Acta Chem. Scand.* **17**, 1862 (1963).

42, 96 and 152°, respectively, can be explained as due to charge-transfer. Surprisingly, I and II proved sufficiently stable to be isolated by GLC. In an atmosphere of helium at a temperature of ca. 50° and 90°, respectively, I, and II were chromatographed in portions of 500 μl of 10–20% ethereal solutions on a stationary phase of Apiezon L. An analytically pure product of I was obtained by a second GLC treatment; 90% of a half-gram portion was hereby recollected, which demonstrates the surprising stability of the compound; 0·5–0·7 g of pure I and II were isolated in this way. By a careful choice of temperature during the primary fractionation of the crude reaction mixture the amounts of additional di- or polyhalogenated products (eluted later in the chromatogram) were kept at a minimum. Purification of III was limited to a repeated vacuum treatment at temperatures between -30 and 20°. Removal of the last traces of ether proved very difficult, as verified by the IR spectrum. The low vapour pressure of III (4 mmHg/20°) excluded, however, the presence of *free* ether in the sample. Complex formation of III with ether may be the explanation, in accord with the observation of Schlubach and Franzen[11] that di-iodoacetylene in ether solution deposited an addition compound with ether at low temperatures.

The yields in this 2-step reaction from diacetylene were satisfactory, and highest for the iodo compound. By continued sublimation from the residue (LiI, after fractionation) for 15 hr at 0·1 mm Hg/20° into a trap cooled in dry ice, III was isolated in nearly 60% yield, in contrast to ca. 25–30 and 15–18% for I and II. These latter yields are comparable with the yield of 27% for $Cl{-}C{\equiv}C{-}C{\equiv}N$.[12] The higher temperature necessary for the chromatographic separation of the rather unstable compound II is presumed to be responsible for the relatively low amounts of pure product isolated. As already mentioned, much higher yields of brominated product were obtained when more stable acetylenic compounds were brominated (Experimental). The remarkable ease of iodonation of acetylenes by iodine has been reported by Vaughn and Niewland,[15] who observed iodination in liquid ammonia to take place even on the free alkyne. The rate of interaction of alkali acetylides with primary aliphatic halides also is faster with the iodide.[20] Running the reaction in an *excess* of diacetylene should favour the formation of the monohalogeno over the dihalogeno derivative; however, the reactions were steadily carried out on a too small scale (1·2–1·5 g of diacetylene) to allow quantitative studies.

The halogenodiacetylenes I, II and III polymerized readily when the temperature was allowed to rise to room temperature, even in the absence of light. By subsequent sublimation unchanged material was recovered, leaving a reddish, glass-like film of a polymer, insoluble in organic solvents. The iodo compound III detonated under illumination by scratching a small sample. Vapours of all three compounds attacked vacuum grease[21] readily. Kept at -80° in vacuum the compounds can be stored for months. The syntheses of I, II and III have been repeated several times, proceeding ordinarily without accidents of any kind.

Aiming at extensive spectroscopic investigations of these compounds, the quantities synthesized were reserved for this purpose and additional chemical proofs of their identity were not undertaken.

IR absorption data. IR spectroscopic investigations of I, II and III allowed identification of the products as chloro- (I), bromo- (II) and iodo- (III) diacetylene.

---

[20] See Ref. 6*a*, p. 2.

[21] Apiezon M, Dow Corning Silicone high vac. grease.

Spectra of the compounds in solution as well as in the gaseous phase have been recorded from 4000–400 cm^{-1}. Characteristic absorption frequencies are given in Table 2, including tentative assignments of some vibrational modes.

As will be seen from the Table, the close relationship between these compounds is evident. The $\mathrm{H{-}C{\equiv}}$ stretching and bending modes of the chloro-, bromo- and iodo-compound are situated at nearly the same frequencies. The symmetric and asymmetric $\mathrm{C{\equiv}C}$ stretching vibrations are but little displaced along the series. The assignments of these bands are beyond doubt, whereas the $\mathrm{C{-}C}$ stretching mode may be less sure. Essential to the identification of I, II and III by their IR spectra is of course the presence of the $\mathrm{Hal{-}C{\equiv}}$ vibration modes. Not much information is available in the literature[22] concerning the position and intensity of these vibrations. A normal coordinate analysis of the spectral data of the three compounds is now being undertaken,[23] from which it is hoped that decisive assignments of the $\mathrm{Hal{-}C{\equiv}}$ vibration modes will be possible. Characteristic contours of parallel and perpendicular vibrational bands in the gas phase spectra confirm the linear structure of the halogenodiacetylenes. The PR separation of these bands agree well with the expected values.[24]

TABLE 2. ESSENTIAL IR ABSORPTION FREQUENCIES AND TENTATIVE VIBRATIONAL ASSIGNMENTS OF $\mathrm{Hal{-}C{\equiv}C{-}C{\equiv}C{-}H}$ (in cm^{-1})

$\mathrm{Hal{-}(C{\equiv}C)_2{-}H}$	$\mathrm{H{-}C{\equiv}}$ stretch	asym $\mathrm{C{\equiv}C}$ stretch	sym $\mathrm{C{\equiv}C}$ stretch	$\mathrm{C{-}C}$ stretch	$\mathrm{H{-}C{\equiv}}$ bend
I Chloro-	3327 vs	2252 vs	2071 m	1093 s	621 vs
II Bromo-	3335 vs	2237 s	2095 w	1046 m	623 vs
III Iodo-	3332 vs	2211 s	2060 vw	1025 vw	623 vs

The spectral region is now being extended down to 50 cm^{-1}. The compounds are also being investigated in the micro-wave region in this department.

Scope of the reaction

As the only *low*-temperature reaction for the preparation of 1-bromoalk-1-ynes,[3] the synthetic route employed above may be preferred where the instability of the alkyne is not compatible with higher reaction temperatures or strongly basic media. A convenient simplification is to carry out the reactions without change of solvent.

Carrying an intact acidic hydrogen in the diacetylene chain, the halogenodiacetylenes I, II and III are expected to undergo further ethynylic reactions. For example, by repeated action of an organolithium reagent on these substances one might expect the formation of $\mathrm{Hal{-}C{\equiv}C{-}C{\equiv}C{-}Li}$, which would afford the acetylenic homologue of $\mathrm{Cl{-}C{\equiv}C{-}Me}$ (Me = Na, Li), successfully prepared by Viehe.[25] The latter synthesized this organometallic compound by an opposite route involving exchange of one halogen from dichloroacetylene by means of organolithium reagents. A second conversion with molecular halogen may lead to the formation of

---

[22a] S. J. Cyvin, E Kloster-Jensen and P. Klaeboe, *Acta Chem. Scand.* **19**, 903 (1965); [b] B. Wöjtkowiak, *Ann. Chim.* **9**, 10 (1964).

[23] S. J. Cyvin, *in progress.*

[24] G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules*, p. 391. van Nostrand, New York (1945).

[25] H. G. Viehe, *Chem. Ber.* **92**, 1270, 1950 (1959).

heterohalogenated diacetylenes Hal—C≡C—C≡C—Hal′ (Hal ≠ Hal′). Investigations on this matter are in progress.

Finally, it should be mentioned that reaction of monolithium diacetylide in an inert solvent with various sensitive organic reactants might provide an alternative route to the preparation of monosubstituted diacetylenes R—C≡C—C≡C—H previously elegantly developed[14] by reaction of the alkali intermediate *in situ* in liquid ammonia (R = alkyl, alkoxy, etc.), or *via* the monogrignard derivative[26] of diacetylene.

EXPERIMENTAL

Preparation of monohalogenodiacetylenes

General procedure. In all experiments diacetylene, freshly prepared, was used in portions of 1·2–1·5 g from 1,4-dichlorobut-2-yne[27] by the action of aqueous alkali.[14] The experiments were run in an atmosphere of N_2 and protected from light.

Absolute ether (ca. 20 ml) was evaporated into the cooled, evacuated trap containing dried diacetylene, and the solution was brought into a reactor swept with N_2 and cooled to −80° in a spaceous alcohol–CO_2 ice bath. To the weighed amounts of diacetylene was added 1 equiv of BuLi in ether (N = 1·22; 20–25 ml) from a storage flask in a dropwise manner over a period of 10 min under vigorous stirring. A strongly exothermic reaction took place. After the reaction was complete, the clear, slightly viscous solution was stirred for another 10–15 min. A solution of slightly more than 2 equivs of molecular halogen (Cl_2, Br_2, I_2) was added dropwise at −55° over a 15-min period. The addition of halogen was discontinued when samples of the reaction mixture were no longer alkaline after addition of water. At the point of neutralization the quantity of halogen added was slightly in excess of the 1 equiv of the BuLi reacted. With Cl_2 or Br_2 the cooled reaction mixture remained clear, although slightly coloured. In the reaction with I_2 a white heavy precipitate appeared after reaction of about half the amount of reagent. Stirring was continued for another 2 hr as the temp was gradually raised to −25°, after which time a fractional distillation *in vacuo* was undertaken at an initial temp of −40°. The fractions (about 5, ca. 10 ml each) were collected in traps cooled in dry ice and subsequently analysed by GLC. The bulk of the product concentrated in the last fraction. Additional quantities of product were removed from the dry, colourless powdered residue (LiHal) by redistillation with 10 ml ether which had been condensed into the residue. After further concentration of the fractions *in vacuo* the product was separated by preparative GLC (I and II) or solely by repeated vacuum treatment (III). The gas chromatographic fractions were collected in a spiral condenser cooled in liquid N_2 and sublimed into vacuum tubes.

Chlorodiacetylene (I). The diacetylene to be reacted was first resublimed *in vacuo*, leaving the last fifth of the portion. A contaminating component otherwise overlapping the reaction product in the gas chromatogram was hereby excluded. The Cl_2-reagent was prepared by collecting Cl_2 gas from a flask in fluorotrichloromethane ("Freon 11", b.p. 23°, m.p. −111°, Du Pont de Nemours & Co., distilled over P_2O_5), cooled in a trap at −80°. The increase of weight during uptake of Cl_2 corresponded to a concentration of about 12% of dissolved Cl_2. From this storage solution an appropriate amount of reagent cooled in a dropping funnel at −70° was added to the solution of lithium diacetylide. At the end of addition (the point of neutralization) samples of the clear reaction mixture deposited fine, heavy crystalline solids when removed from the cooling bath.[18] After continued stirring the reaction mixture was fractionated at −40°/8 mm Hg. Minor amounts of unreacted Cl_2 first collected were in this way readily removed from the solution. The next fractions contained some unreacted diacetylene and butane, as shown by GLC. The reaction product (and some BuCl) mainly concentrated in the last fraction as the temp was allowed to rise to −10°. At higher temps additional amounts of less volatile by-products followed the reaction product as shown from the appearance of broad peaks much later in the chromatogram. The main fraction was further concentrated *in vacuo* to about 4 ml, which in portions of 400–500 μl were gas chromatographed at a temp of 49° (for details see below). The main fraction gave 0·450 g of I from a portion of 1·25 g diacetylene. The preceding fractions contained additional ca. 0·30 g of I, as calculated from the gas chromatograms.

---

[26] L. Skatteböl, E. R. H. Jones and M. C. Whiting, *J. Chem. Soc.* 4767 (1956).

[27] A. W. Johnson, *J. Chem. Soc.* 1011 (1946).

Total yield ca. 35%. A second purification of the 0·450 g of I was accomplished by subliming the product *in vacuo* into 1·5 ml of CCl_4 cooled at −80°. The contents were rechromatographed in 4 portions. The stock solution was kept frozen in CO_2-ice between each portion injected. After sublimation from the collector into a vacuum tube 0·405 g (90%) of very pure I was recollected. The IR spectral features were consistent with the structure $Cl{-}C{\equiv}C{-}C{\equiv}C{-}H$ (I), see Table 2, m.p. −41°. A vapour press at room temp of ca. 120 mm Hg was measured.

The solid, almost colourless residue (LiCl) from the fractional distillation remained practically unchanged when stored over a longer period of time. On the contrary, when diacetylene was added to BuLi,[17] residual material discolourized already during the fractionation and turned brown within a few hr, indicating the presence of considerable amounts of metastable material formed by this sequence of addition.

Bromodiacetylene (II). A cooled solution of Br_2 in Freon 11 (see chlorodiacetylene) was added to a solution of lithium diacetylide as above. At the end of addition (the point of neutralization) the reaction mixture was slightly coloured by Br_2. Fractionation was undertaken as previously described (Br_2 being removed in the first fraction). Separation of the reaction product by GLC was performed at a temp of 89° in portions of 400–500 μl of the ca. 10% concentrate. A completely pure reaction product was isolated after one chromatographic operation, as checked by the IR spectra. The IR absorption data (Table 2) were in accordance with the structure $Br{-}C{\equiv}C{-}C{\equiv}C{-}H$ (II), m.p. −18°. A vapour press of ca. 40 mm Hg at room temp was measured.

The out-put of the reaction was somewhat lower than for the chloro analogue, usually ca. 15–18%.

From the clear reaction mixture of II (and also of I) no precipitation occurred until the temp was raised to about −45°. Once precipitated, it remained irrespective of change of temp. The same phenomenon was always observed during the preparation of chlorocyanoacetylene.[18] Initial participation of the halide in complex formation at low temps may perhaps be an explanation.

The almost colourless residue from the low-temperature fractionation was once analysed for non-volatile components. To the residue 40 ml of ether was condensed *in vacuo* and the contents poured over pieces of ice. The aqueous phase was extracted with ether, the ether phase dried with Na_2SO_4 and the solvent removed *in vacuo*. A yellow, crystalline residue, including minor amounts of oil exhibited the characteristic properties of dibromodiacetylene.[5d] In contact with air it developed white vapours (acid chloride and ozone[5d]) and became gradually converted to a brown oil.

In a preliminary experiment[17] the reagents were added in an inverse order. The yield of pure bromodiacetylene isolated was then 12% (0·290 g). Rapid discolouration of the residue occurred, as by a similar inverse addition by preparation of the chloro compound (I).

Iododiacetylene (III). A saturated solution of I_2 in ether was added to a solution of lithium diacetylide. After about $\frac{2}{3}$ of the reagent had reacted, decolouration occurred more slowly, and ceased before addition was complete. A very heavy precipitate (LiI) appeared in increasing amounts during the reaction. Fractionation of the reaction mixture gave first colourless distillates, which soon turned yellow by standing exposed to daylight, depositing a brown solid. At a press of 0·1 mm Hg the last fractions 4 (10 ml) and 5 (3 ml, during 15 hr) were collected in traps cooled in liquid N_2 as the temp of the flask was raised gradually to room temp. Qualitative GLC at 90° revealed no reaction product present although rich amounts of snowwhite crystalline material deposited when the distillates were cooled in dry ice. Evidently, the reaction product (III) was too unstable and insufficiently volatile to enable isolation by GLC. Separation was therefore restricted to refractionation of fr. 4 and 5 *in vacuo* at −40°. The last fractions herefrom, *viz*. fr. $\frac{4}{4}$ and $\frac{5}{3}$, were distilled *in vacuo* at −20° into vacuum tubes. For short intervals of time the temp was raised to room temp, as volatiles were allowed to expand into a greater, evacuated flask connected on a vacuum line. The vapour press of the residue thereby decreased gradually, and the evaporation of solvent and residual volatiles was repeated invariably until a zero vapour press was observed at −20° (Hg manometer; ether exhibits a vapour press of 67 mm Hg/−20°[28]). By this treatment fr. $\frac{4}{4}$ yielded 1·400 g and fr. $\frac{5}{3}$ 1·21 g of slightly coloured III. From fr. $\frac{5}{2}$ an additional 0·077 g of material were isolated, a solution of which (in CCl_4) gave a very pure IR spectrum. The total amount of reaction product isolated was thus 2·69 g from a portion of 1·30 g of diacetylene reacted, or 59% yield. Even after this tedious vacuum treatment the IR absorption spectrum revealed the presence of minute amounts of ether (complex formation see above) which, however, was nearly completely removed by continued evaporation

---

[28] R. S. Taylor and L. B. Smith, *J. Amer. Chem. Soc.* **44**, 2450 (1922).

under vacuum. The IR spectra (Table 2) identified the product as iododiacetylene I—C≡C—C≡C—H (III). During removal of the last amounts of ether the m.p. rose gradually from −40 to −30° (reported[11] m.p. ca. −40°). A vapour press of ca. 4 mm Hg at room temp was measured. The dry residue from fractionation (LiI) remained only slightly coloured.

Preparation of bromophenylacetylene from lithium phenylacetylide. The reactions were effected under conditions as described under General procedure.

To a solution of freshly distilled phenylacetylene (3·06 g, 0·03 mole) in ether (ca. 25 ml) was added an ethereal solution of BuLi (N = ca. 1·20, 26 ml). A solution of Br_2 (5·0 g, 0·031 mole) in Freon 11 (see above) was added and was decolourized immediately. The point of neutralization was reached by additional, minor amounts of Br_2, at which point the reaction mixture remained coloured. No precipitation of heavy solids (LiBr) were observed as the temp was raised; however, this reaction was performed in greater amount of solvents than in the case of diacetylene.

After continued stirring for 2 hr, water (20 ml) was added with cooling. The ether phase was shaken once with lime, dried over Na_2SO_4 and the solvents removed under red. press. The residue, a yellow liquid, was fractionated *in vacuo*. A colourless liquid (2·8 g, 56·5%) was collected, b.p. 95°C/15 mm Hg, n_D^{23} = 1·6000 (reported b.p. 96°C/15 mm Hg[29], n_D^{25} = 1·6057[30]). Residual brown viscous oil ca. 1 ml (Polymerization takes place during distillation[29]).

Preparation of 1-*bromobutylacetylene* (1-*bromohex*-1-*yne*) *from lithium butylacetylide.* The reaction conditions described under General procedure were followed unless otherwise stated.

To a solution of butylacetylene (5·0 g, 0·061 mole) in ether (25 ml) was added an ethereal solution of BuLi (N = ca. 1·20, 51 ml). During continuous stirring for another 15 min the temp was raised to −20°. Yellowish fluffy solids had then precipitated, which disappeared gradually by the successive addition of liquid Br_2 (9·8 g, 0·061 mole). The instantaneous decolouration ceased at the point of neutralization, then ca. 0·6 g of Br_2 was left. The solution soon deposited a heavy, fine solid (LiBr). Then water (20 ml) was added with cooling, and the ethereal phase was washed 3 times with 7 ml lime, dried over Na_2SO_4 and the solvent distilled off through a short vigreux column on a water bath. The residue, a yellow oil, was fractionated under red. press. A colourless liquid (5·6 g, 57%) was collected between 72–75°C/75 mm Hg. Constant b.p. was 75°/75 mm Hg, $n_D^{20°}$ = 1·4631 (reported b.p. 74°C/72 mm Hg[31], n_D^{25} = 1·4630[32]). Residual red oil ca. 0·7 ml.

The *IR spectra* were recorded on a Beckman IR-9 spectrophotometer (grating) and Perkin–Elmer model 21 (CsBr) in solutions of CCl_4 (NaCl, KBr, KRS-5 windows) and in the gas phase (8 cm cell and 1 meter Multi-Reflector gas cell with KRS-5 windows).

The *gas liquid chromatograms* were performed on a Beckman GC-2 Gas Chromatograph, using a column of 3 m length and ¼″ inner diam with 25% Apiezon L on Chromosorb W. With a flow-rate of He of 60 ml/min the retention time for chlorodiacetylene at 49° was 16 min, for bromodiacetylene at 89° 16·5 min. At this temp no iododiacetylene was eluted during a period of 40 min.

The *m.ps* (uncorrected) were measured on ca. 50 mg samples in a 20 ml vacuum tube immersed in an alcohol bath pre-cooled with CO_2-ice. The samples melted within 1°.

Acknowledgements—Thanks are due to Dr. P. Klaeboe for recording and discussion of the IR spectra. The author is grateful to *Veterinaerinstituttet* for use of the Beckman IR-9 spectrophotometer. Financial aid from *Norges Almenvitenskapelige Forskningsraad* is gratefully acknowledged.

[29] J. Nef, *Liebigs Ann.* **308,** 311 (1899).

[30] L. Field, *J. Amer. Chem. Soc.* **74,** 398 (1952).

[31] M. J. Murry and F. F. Cleveland, *J. Chem. Phys.* **12,** 157 (1944).

[32] D. J. Pflaum and H. H. Wenzke, *J. Amer. Chem. Soc.* **56,** 1106 (1934).